THE CHEMISTRY OF SOME

EXCITED STATE

CHARGE-TRANSFER COMPLEXES

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by

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STATEMENT.

The experimental work in this thesis has been carried

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The Formation of Intramolecular Exciplexes by Derivatives

of 1-methylnaphthalene,

G.S. Beddard, R.S. Davidson and A. Lewis,

J. Photochem., 1, 491 (1972/3).

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phthalimides,

R.S. Davidson and A. Lewis,

Tet. Letts., No. 7, 611 (1974).

CONTENTS.

SECTION THREE: EXPERIMENTAL.

SECTION ONE : INTRODUCTION.

The formation of an excited state complex is generally brought about by absorption of light. The introduction to this thesis will constitute a discussion of this process and of the complexes that can be formed by quenching of the initially excited species.

1:1 ABSORPTION OF LIGHT AND POPULATION OF EXCITED STATES.

The ground electronic states of organic molecules are, for the most part, singlet states i.e. a configuration in which the spins of the electrons in the ground state orbitals are all paired. At room temperature most molecules will be in the lowest vibrational level of this ground electronic state.[1] Rotational levels are usually ignored for work in solution since they are very closely spaced (typical separations are in the region of 0.1 kcal/mole) and cannot be distinguished by spectroscopic means.

. The electronically excited state can then be produced from the zeroth vibrational level of the electronic ground state by absorption of light of the appropriate wavelength. In solution photochemistry, wavelengths between 200 - 700 NM are generally used.

The most probable electronic transitions are those in which spin inversion does not occur, hence the initial states formed on excitation are singlet states.[2] The excited state of the molecule will have vibrational levels associated with it, and as a consequence of the Franck-Condon Principle

the excited state initially produced will be in a high
vibrational level. The excess vibrational energy will
be rapidly lost by collision with surrounding molecules,
the resultant state being the lowest vibrational level of
the first excited state. In a similar manner, production
of an excited state higher than the first leads to the
lowest vibrational level of that state, a rapid process
known as internal conversion then occurs, whereby the
molecule passes into the next lowest excited state. Hence
all molecules on excitation will rapidly revert to the lowest
vibrational level of the first excited state.[1] The lifetime
of this state is typically 10^{-9} sec compared to 10^{-13} -
10^{-11} sec for an upper excited state.

The excited state may then return to the ground state
by a number of routes:-

1. Fluorescence: the molecule returns to any of the
ground state vibrational levels with emission of light,
thus losing its electronic excitation energy.

2. Internal conversion: the electronic energy is dissip-
ated as heat to the surrounding molecules.

3. Energy transfer: the electronic energy is transferred
to another molecule.

4. Chemical reaction: reaction, either inter or intra-
molecularly, to produce a non-excited molecule.

5. Inter-system crossing: a triplet excited state is
produced by spin inversion of an electron.

A diagram of the type first used by Jablonski sums
up the basic processes described above.[1.3]
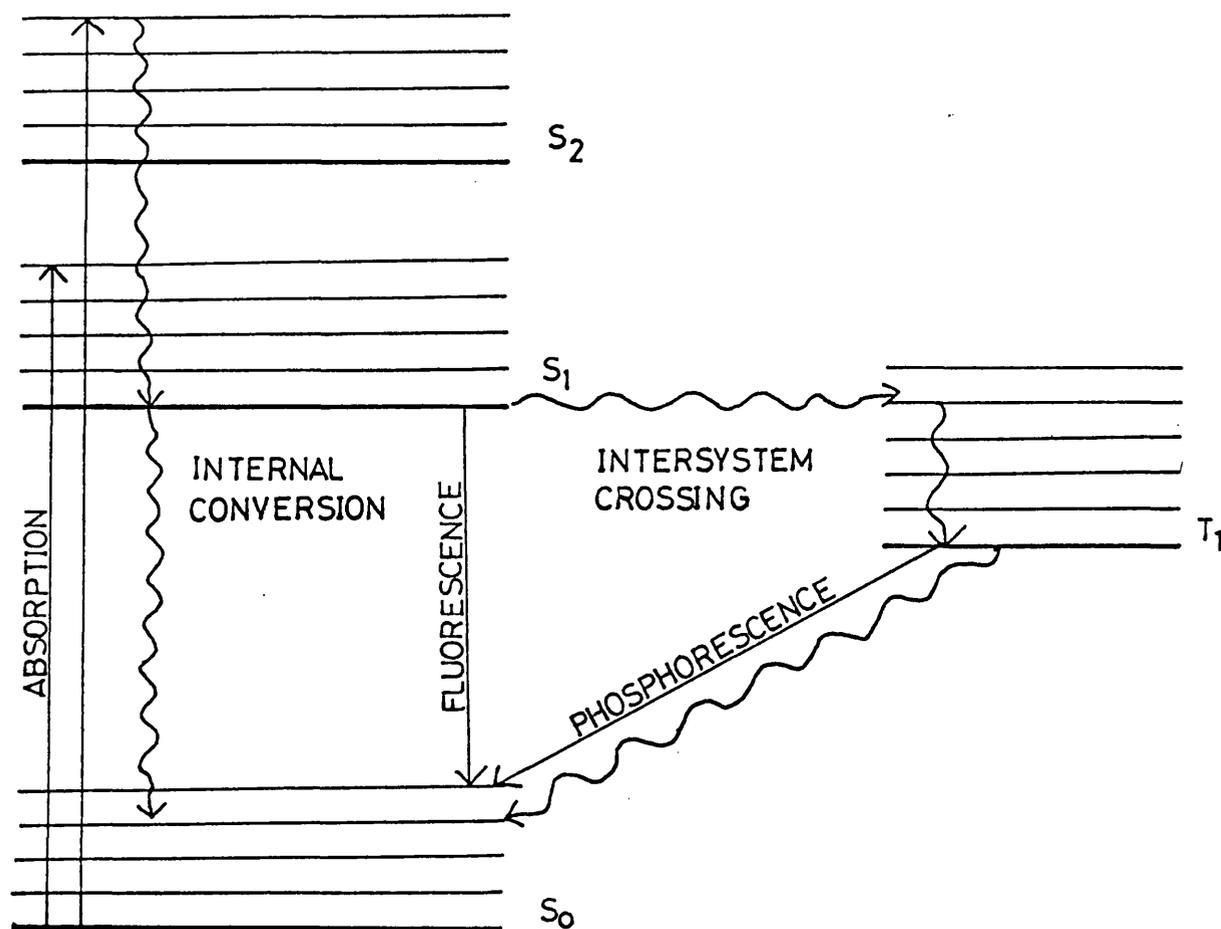
FIGURE 1.

Jablonski Diagram.

The triplet state is invariably of lower energy than the corresponding singlet state since the spins of the electrons are not paired i.e. Hund's rule for atoms applies to the molecules under consideration.[4]

Transitions to the ground state, whether radiative or non-radiative will be spin forbidden and as a consequence the lifetime of a triplet state is relatively long. Emission from T_1 is known as phosphorescence, this is only rarely observed in fluid solution because of the long lifetime (typically 10^{-6} to 1 sec for organic molecules) which

results in energy loss by radiationless processes e.g. collisions with surrounding molecules. There is also a greater possibility of reaction due to the longer lifetime, but in general triplet states decay in the same way as singlet states.

This work has been primarily concerned with complexes formed by aromatic hydrocarbons, in such molecules the electronic transition of lowest energy is $\pi\text{-}\pi^*$ i.e. the electron is promoted from a π bonding molecular orbital to a π^* anti-bonding molecular orbital. The state produced is therefore known as a $\pi\text{-}\pi^*$ state.[5] The energy difference between S_1 and T_1 is large for aromatic hydrocarbons and this lowers the probability of inter-system crossing. Fluorescence can compete with this process and aromatic hydrocarbons generally fluoresce in solution at room temperature.

The other important excited state in organic compounds is the $n\text{-}\pi^*$ state i.e. promotion of a non-bonding electron to a π^* anti-bonding molecular orbital. Examples of this type of transition are found in aromatic ketones where the important feature of the $n\text{-}\pi^*$ singlet state is the smaller energy separation between S_1 and T_1, the rate of inter-system crossing is greatly enhanced and the result is that population of T_1 is very effective.[6] Data for energy separations $E(S_1 \longrightarrow T_1)$, and quantum yields for fluorescence and phosphorescence are shown in Table 1.

TABLE 1.

Singlet-triplet energy separations and quantum yields.[a]

	$E(S_1-T_1)$[b]	ϕ_F	ϕ_T	Excited State.
Benzene.	24.38	0.21	0.19	$\pi-\pi^*$
Naphthalene.	30.12	0.39	0.008	$\pi-\pi^*$
Anthracene.	32.74	0.27	–	$\pi-\pi^*$
Acetophenone.	5.02	Small	1.0	$n-\pi^*$
Benzophenone.	4.78	Small	0.7	$n-\pi^*$

a. from ref. 7.

b. kcal/mole.

1:2 QUENCHING OF FLUORESCENCE.

The fluorescence of aromatic hydrocarbons is an important phenomena and a great deal of study has been devoted to it. Fluorescence may be quenched in a variety of ways and this technique is often used to detect the existence of excited state complexes. In solution work the fluorescence, as well as the other processes mentioned above will compete with bimolecular quenching which can be brought about in one of two ways, either by increasing the concentration of the fluor or by addition of another molecule. The main types of quenching processes are summarised below.

1. Energy transfer.

2. Charge transfer.

3. Self quenching.

4. Heavy atom quenching.

5. Oxygen quenching.

In each case complexes have been identified or post-
ulated as being finite lived intermediates in the quenching
process and each will be dealt with in turn. Although most
of the quenching mechanisms are concerned with singlet states,
reference will be made to the triplet state where appliciable.

1:2:1 QUENCHING OF FLUORESCENCE BY ENERGY TRANSFER.

Internal conversion (Section 1:1) is strictly speaking
an energy transfer process whereby electronic energy is
transferred to the medium as vibrational energy but is not
normally included in discussions on the subject. The most
important type of transfer is where the electronic excitation
energy from an excited molecule appears as excitation energy
in an acceptor molecule.

The general requirement is that the energy of the
acceptor molecule is lower than that of the donor molecule.
The transfer can be simply represented by the following
equation (excited states are indicated by asterisks; D
refers to the donor molecule; A to the acceptor molecule).

$$D^* + A \longrightarrow D + A^*$$
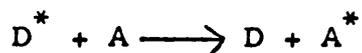
Three processes can now be considered whereby electronic
excitation energy can be transferred in fluid solution.

1. Radiative transfer.

2. Resonance or long range dipole-dipole transfer.

3. Diffusion controlled non-radiative transfer (exchange
or contact transfer).

The first mechanism is often known as a "trivial" process

since it merely involves emission of light by the donor

and reabsorption by the acceptor.

$$D + h\nu \longrightarrow D^*$$

$$D^* \longrightarrow D + h\nu'$$

$$A + h\nu' \longrightarrow A^*$$

$$A^* \longrightarrow A + h\nu''$$
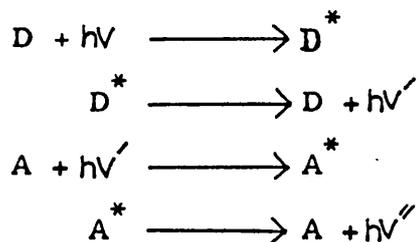
The most important energy transfer mechanisms are

both non-radiative i.e. 2 and 3. The second type does not

require a close approach of donor and acceptor molecules.

Förster[8] has developed a theory of this mode of energy

transfer and has noted that it can operate even when the

two participating molecules are separated by distances of up

to approximately 60Å . Resonance transfer will only occur

when there is an overlap between donor fluorescence and

acceptor absorption bands. Bowen and Livingstone[9] studied

three donor-acceptor pairs, 1-chloroanthracene — perylene,

1-chloroanthracene — rubrene, 9-cyanoanthracene— rubrene.

Rate constants for energy transfer are shown in Table 2 for

one of the pairs in three different solvents.

TABLE 2.

Rate constants for energy transfer between 1-chloroanthracene and perylene.

	$CHCl_3$	C_6H_6	Liquid paraffin.
k_D a. 1 mol^{-1}s^{-1}	1.1×10^{10}	1.0×10^{10}	-
k_{ET} b. 1 mol^{-1}s^{-1}	2.4×10^{11}	1.7×10^{11}	1.4×10^{11}

a. k_D is the diffusion controlled rate constant.

b. k_{ET} is the rate constant for energy transfer.

It can be seen from the table that the rate constant for energy transfer exceeds the diffusion controlled rate limit by a factor of at least ten, and is also apparently independent of solvent. These results do indicate that resonance transfer is not a diffusion controlled process.

Overlap between the fluorescence of the donor and the absorption of the acceptor may be negligible, if this is the case then energy transfer can still take place, but an encounter of the two molecules is necessary. Overlap of the electron clouds occurs and under these circumstances electron exchange may occur; the electron in the high energy orbital of the donor may find itself in a high energy orbital of the acceptor. The efficiency of exchange transfer will be affected by the viscosity of the medium, hence rate constants will be limited by the rate constant for diffusion. An example of this mechanism is furnished by the work of Dubois,[10,11] who obtained rate constants for singlet-singlet energy transfer to biacetyl for a number of donors as shown in Table 3.

TABLE 3.

Rate constants[a] for singlet energy transfer to biacetyl (cyclohexane, 25°).

Donor	k_q[b] 1 mol^{-1}s^{-1}
Diethyl ketone	7.6×10^9
Methyl ethyl ketone	7.4×10^9
Cyclopentanone	7.4×10^9
Phenanthrene	7.5×10^9
Chrysene	7.6×10^9

a. from ref. 10.

b. k_q is the rate constant for energy transfer, the diffusion

controlled rate constant in cyclohexane at 25° is approximately 7.3×10^{9} $1 \text{ mol}^{-1}\text{s}^{-1}$.

The rate constants he obtained are diffusion controlled, unlike the resonance transfer mechanism.

Triplet-triplet energy transfer is also known, and is in itself, particularly useful, e.g. the sensitisation of the triplet state of aromatic hydrocarbons by aromatic aldehydes and ketones is a well documented phenomena.[12] It is possible by this method to obtain triplet states of organic molecules whose triplet levels cannot be populated by direct excitation. The photo-isomerisation of olefins and the stilbenes in particular has received much attention. The mechanism of the isomerisation depends upon the triplet energy of the sensitiser. Three mechanisms have been proposed:

1. The triplet mechanism: this is generally held to be the favoured route when the excitation transfer steps are exothermic i.e. the triplet energy of the sensitiser is greater than that of the olefin. The olefin triplets are then formed by transfer of excitation energy from the sensitiser.[13]

2. The "Schenck" mechanism: this has been used to account for isomerisation where triplet energy of the sensitiser is less than that of the olefin.[14,15] Reaction of the olefin with the triplet sensitiser forms a 1,4-biradical in which rotation about the central bond is rapid relative to bond breaking. The biradical may then cleave to give the triplet

9.

olefin in either the _cis_ or _trans_ forms. It has also been
suggested that the primary interaction involves the formation
of a charge-transfer complex which subsequently collapses
to the biradical.[16]

3. Non-vertical excitation: this is an alternative to the
"Schenck" mechanism. A triplet state intermediate has been
suggested which has an energy below that of either _cis_ or
trans triplet states. It is said to be reached from the
ground state by "non-vertical" excitation i.e. by a process
that does not obey the Franck-Condon Principle.[17] This
state is often called a phantom or twisted triplet.

Intramolecular energy transfer has also been observed,
since both donor and acceptor moieties are within the same
molecule, then the concentration required for observation
of energy transfer will be very much lower than for the
equivalent intermolecular case. An example is that discovered
by Weber and Teale,[18]
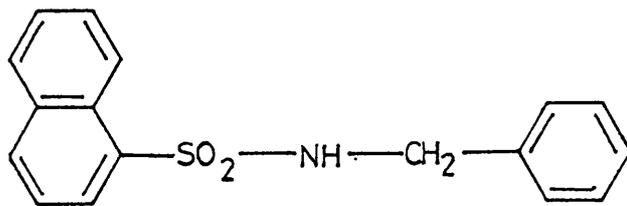
this molecule possesses two independent aromatic chromophores.
Excitation of either the benzene or naphthalene rings gives
rise to fluorescence from the naphthalene; no fluorescence was
observed that could be attributed to the benzene ring. Inter-
molecular energy transfer was discounted since dilute solutions
were used for the fluorescence measurements.

It is possible to obtain quantitative data on the

quenching of excited states, both singlet and triplet, by the use of an expression called the Stern-Volmer equation.[19] Consider the following simple mechanism for the quenching of emission from an excited molecule D^* by the addition of a second molecule or quencher, Q.

<u>Rate.</u>

Excitation $D + h\nu \xrightarrow{\quad I \quad} D^*$ I

Emission $D^* \xrightarrow{\quad\quad} D + h\nu'$ $k_f [D^*]$

External Quenching $D^* + Q \xrightarrow{\quad\quad} D + Q^*$ $k_q [D^*][Q]$

Internal Quenching $D^* \xrightarrow{\quad\quad} D + heat$ $k_d [D^*]$
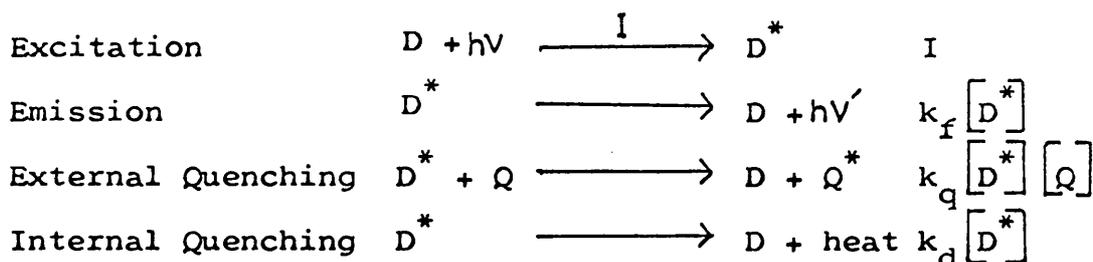
Squared brackets represent concentrations and k_f, k_q, and k_d are, respectively rate constants for emission from D^*, energy transfer to Q and thermal deactivation of D^1. I is the rate of light absorption.

If it is assumed that there is a steady state of D^* under conditions of steady illumination, then

$$\frac{d[D^*]}{dT} = 0.$$

In the absence of quencher we can write,

$$I = k_f [D^*] + k_d [D^*] \qquad\qquad 1.$$

Similarly, when quencher is present,

$$I = k_f [D^*] + k_d [D^*] + k_q [Q][D^*] \qquad\qquad 2.$$

The quantum yield for emission from D^* in the absence of Q is given by,

$$\phi_0 = \frac{k_f [D^*]}{I} \qquad\qquad 3.$$

and in its presence by,

$$\phi = \frac{k_f [D^*]}{I} \qquad 4.$$

substituting for I from equation 1 into equation 3 gives

$$\phi_o = \frac{k_f}{k_f + k_d} \qquad 5.$$

and substituting for I from equation 2 into equation 4 gives

$$\phi = \frac{k_f}{k_f + k_q [Q] + k_d} \qquad 6.$$

Dividing equation 5 by equation 6 we obtain

$$\frac{\phi_o}{\phi} = \frac{k_f + k_d + k_q [Q]}{k_f + k_d} \qquad 7.$$

Now, the mean radiative lifetime of the excited state in the absence of quencher is given by the reciprocal of the sum of the rate constants for unimolecular deactivation processes:

$$\tau = \frac{1}{k_f + k_d}$$

Rewriting equation 7 gives,

$$\frac{\phi_o}{\phi} = 1 + \frac{k_q [Q]}{k_f + k_d}$$

$$\therefore \frac{\phi_o}{\phi} = 1 + k_q \tau [Q]$$

The term $k_q \tau$ is often denoted K_{sv} or K_Q and is called the Stern-Volmer quenching constant. A plot of $\phi_o/\phi - 1$ vs. $[Q]$ will give a straight line of slope K. Hence it is possible to determine the rate of quenching from this equation,

since the lifetime τ can be obtained from independent measurements.

The observation of a Stern-Volmer quenching relationship does not, of necessity, imply that the quenching takes place by a collisional mechanism, the quencher molecule may form a complex, either fluorescent, or non-fluorescent, with the quenchee molecule. There may also be an equilibrium in the excited state, between donor, quencher, and complex,

$$D^* + Q \rightleftharpoons DQ^*$$
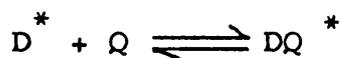
under these conditions the appropriate derivation yields the observed quenching rate constant as K_c, the equilibrium constant of the complex formation.[1] An example of the problem of reversibility is found in triplet-triplet energy transfer. The efficiency depends upon the energy separation of the participating electronic states of the donor-acceptor pair, the greater the separation, the faster the transfer. Two possible situations are shown (Figure 2).

In the first case (1.) the transfer is irreversible because the acceptor molecule rapidly loses excess vibrational energy to reach the lowest vibrational level of the excited state, and there will not be sufficient thermal energy available for the back reaction to occur.[20] This quenching would follow the Stern-Volmer law; i.e.

$$\frac{\phi_p^{\,o}}{\phi_p} = 1 + k_q \left[Q \right]$$

In the second case (2.) the energy separation is much smaller and transfer is possible in both directions,

hence the experimental quenching rate constant will reflect
the fact that transfer is reversible.[21]
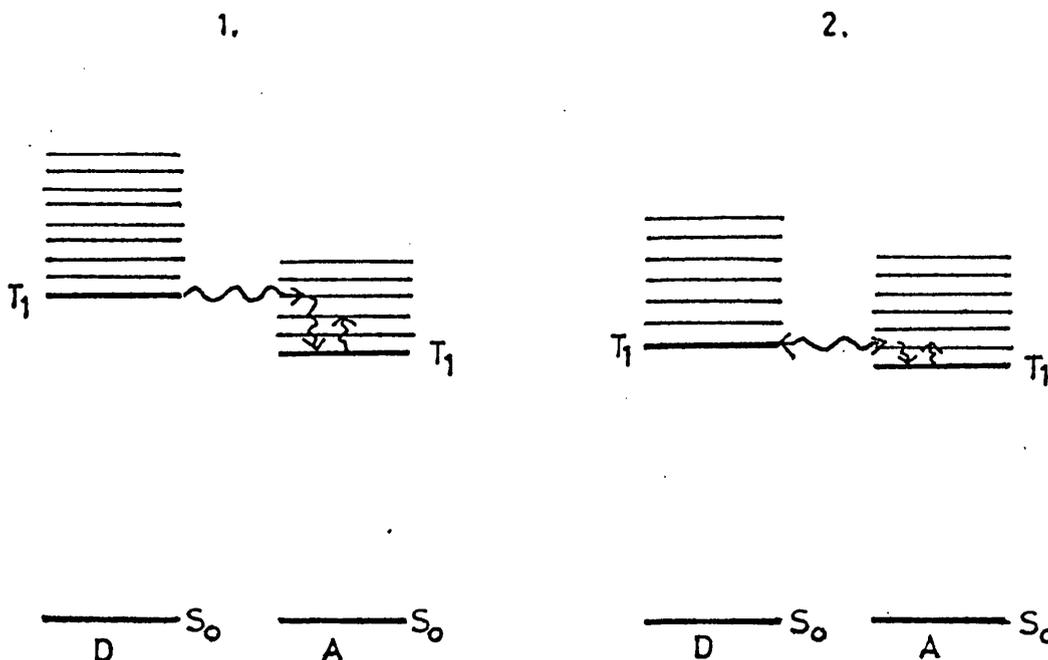
FIGURE 2.

Dependence of energy transfer efficiency upon the separation
of triplet levels.

1:2:2 FLUORESCENCE QUENCHING DUE TO CHARGE-TRANSFER.

The existence of association in the ground state has
been known for a long time and there is abundant evidence
for such a process.[22] In many cases a band appears in the
electronic absorption spectrum which is not present in the
spectra of the separated molecules, this band is frequently
termed a charge-transfer absorption. Mulliken[23] has put
forward a theoretical description of these complexes based
on resonance between "no-bond structures" and charge-
transfer states.

$$AD \longleftrightarrow A^-D^+$$

This however, implies that charge transfer has taken place. In a recent paper Dewar and Thompson[24] have pointed out that molecules may associate for other reasons and that charge-transfer is not a necessary pre-requisite for observation of a charge-transfer absorption band. Nevertheless, ground state complexes can be raised to an excited charge-transfer complex by exciting into the charge-transfer band, and in this case the partners did not have to diffuse together to form the complex.

The possibility of charge-transfer complexes that are stable only in the excited state was put forward some time ago,[25,26] but the experimental evidence has only recently been provided by Leonhardt and Weller.[27] The fluorescence quenching of perylene by amines was studied and several important observations made. Firstly, it was possible to correlate the quenching efficiency, which followed a Stern-Volmer law, with the ionisation potential of the amine. The absorption spectra showed no anomalous bands i.e. there was no evidence for ground state association. Flash photolysis of amine-hydrocarbon mixtures in polar solvents e.g. aceto-nitrile, showed the presence of the perylene radical anion, the amine radical cation and the perylene triplet.[28,29] Further evidence was furnished by the observation of a new fluorescence band in nonpolar solvents, this was of lower energy than the hydrocarbon fluorescence.[28] Increasing the concentration of the amine gave an increase in the intensity

of the new band, and a concomitant decrease in the fluor-

escence intensity from the hydrocarbon. The wavelength of

the band was highly sensitive to the solvent polarity,

shifting to lower energy (i.e. to the red) and decreasing in

intensity as the polarity increased. In polar solvents it

disappeared completely. Dipole moments of approximately

12 Debye[30,31] were calculated from the effect of the solvent

polarity.

From these results the quenching was believed to be

due to transfer of an electron from the amine to the hydrocarbon

and the new fluorescence band was attributed to a charge-

transfer complex being formed in the excited state. Its

formation can be represented by the following equation;

$$A \xrightarrow{\quad h\nu \quad} A^*$$

$$A^* + D \longrightarrow (A^{d-} \ldots D^{d+})^*$$

$$(A^{d-} \ldots D^{d+})^* \longrightarrow AD + h\nu'$$

$$AD \longrightarrow A + D$$
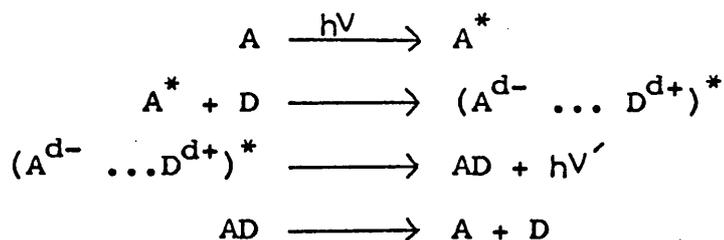
The disappearance of fluorescence from the charge-transfer

complex in acetonitrile was believed to be due to the form-

ation of radical ions, there are two possible routes;

1. Directly from the complex itself.

2. Radical ion formation becomes the quenching mechanism.

$$1. \quad (A^{d-} \ldots D^{+})^* \longrightarrow A^{-\cdot} + D^{+\cdot}$$

$$2. \quad A^* + D \longrightarrow A^{-\cdot} + D^{+\cdot}$$
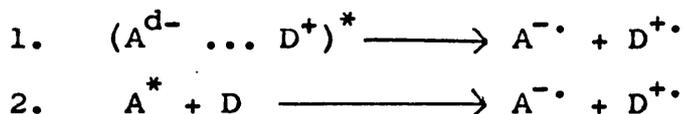
This type of charge-transfer complex, which is only

stable in the excited state, is often termed an exciplex,

Weller[32] has stated that "the exciplex should be treated

as an excited singlet state species of its own in which

the electrons are mutually coupled by exchange. The (part-
ially) solvated ion pair on the other hand, represents a
geometrically quite arbitrary encounter complex of the
solvated radical ions, both of them still being in their
characteristic doublet ground states."

In the above examples the electron acceptor is the
initially excited species, this need not necessarily be the
case and exciplexes are known in which the electron donor
is excited in the first instance. The charge-transfer
process can be represented by a simplified molecular orbital
scheme (Figure 3).

Numerous examples of exciplexes have been discovered
since the early work of Weller and it has become apparent
that their formation is widespread. This is not suprising;
consideration of the π-π^* state, typically found in aromatic
hydrocarbons, shows that the molecule has a half occupied
high energy orbital, i.e. the lowest anti-bonding orbital.
It is therefore likely to act as an electron donor. There
will also be a single electron in an orbital of relatively
low energy (highest bonding orbital) hence reaction as an
electron acceptor will be favourable. Redox reactions in
aromatic hydrocarbons should therefore be more favourable
in the excited state, whether singlet or triplet, than they
are in the ground state and the reaction mode will depend
upon the properties of the other reactant.

Exciplexes have been postulated as being formed
between aromatic hydrocarbons, both substituted and un-
substituted, and aromatic amines, aliphatic amines,[30]

17.
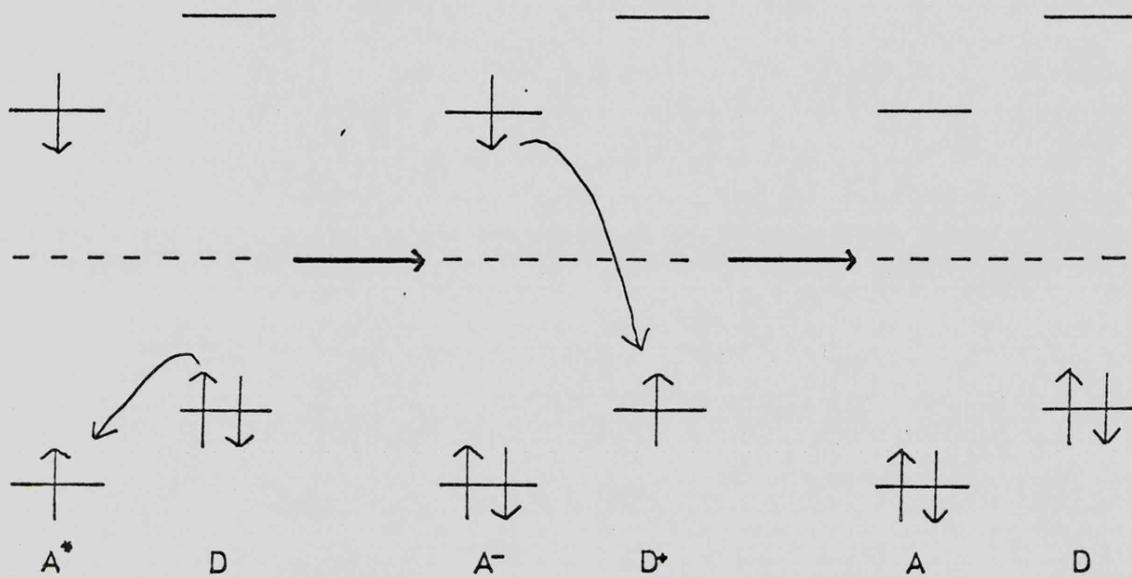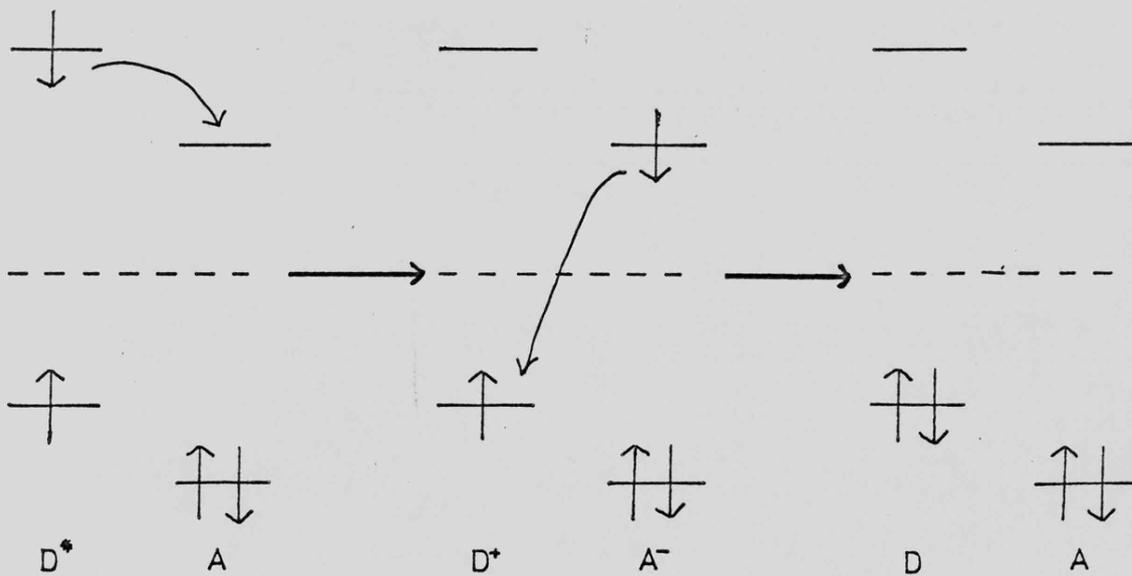
FIGURE 3.

Molecular orbital scheme for interpretation of charge-transfer.

1. Acceptor initially excited.

2. Donor initially excited.

dienes,[33] mono-olefins,[34] strained hydrocarbons,[35] and cyano substituted aromatic compounds.[36]

The energetics of the charge-transfer for systems with similar configuration can be understood by using the following equation which assumes that stabilisation of the complex will be entirely due to charge-transfer interactions.

$$h \nu_{CT}^{max.} = I.P._D - E.A._A + \text{constant}$$

Where $h\nu_{CT}^{max.}$ is the frequency of the exciplex fluorescence maximum, $I.P._D$ is the ionisation potential of the donor, $E.A._A$ is the electron affinity of the acceptor. Hence $h\nu_{CT}^{max.}$ should bear a relationship to $I.P._D$ and $E.A._A$ and this has been found to be true for many exciplexes thus substantiating their charge-transfer character.

Since the early work, detailed investigations have been made of the primary processes involved in electron transfer reactions, including the problems of dissociation of the exciplex into radical ions and the formation of triplet states. Currently, exciplex formation is believed to involve an intermediate, non-fluorescent species. This has been termed the non-relaxed exciplex, the quench complex, and the encounter complex. It is vibrationally relaxed but the solvent has not relaxed around it. Consequent relaxation of the solvent gives the lower energy, relaxed, fluorescent exciplex.

$$A + D \xrightarrow{h\nu} {}^1A^* + D \longrightarrow {}^1(A....D)^* \longrightarrow {}^1(A^{d-}....D^{d+})^*$$

| | | NON-RELAXED | RELAXED |
| | | EXCIPLEX. | EXCIPLEX. |

Mataga et. al.[37] carried out a detailed survey of exciplex

formation between aromatic hydrocarbons and aliphatic amines.

Time resolved fluorescence spectra were obtained for the

exciplex emission in a very viscous environment. It was

found that a part of the exciplex was formed immediately

after excitation, and solvent relaxation about the exciplex

led to a time-dependent red shift of the emission. Hence it

was possible to observe successive stages of solvent relax-

ation about the initially formed exciplex in these cases.

Selinger and McDonald[38] carried out a kinetic study

and rationalised their results by postulating the non-

relaxed exciplex which could then react further. The tech-

nique of laser flash photolysis has been used to determine

the origin of both radical ions and triplet states. The

decay of the exciplex was found to match the growth of the

triplet in non-polar solvents indicating that the triplet

is formed by the decay of the relaxed exciplex.[39,40] The

mechanism of formation of the triplet state in polar solvents

is uncertain, it has been suggested that it is derived from

the non-relaxed exciplex[39,41] and also from the radical ions.[42]

Radical ion formation has been shown to be from the non-

relaxed exciplex.[43,44]

1:2:3 SELF-QUENCHING OF FLUORESCENCE.

Self-quenching or concentration quenching of fluorescence

of aromatic hydrocarbons has been well known for a long time,

but it is only relatively recently that changes in the fluor-

eScence spectrum of organic compounds have been noticed
i.e. new fluorescence bands appear as the concentration is
increased.

The first report of such an emission was by Förster
and Kasper.[45] It was found for pyrene, in benzene solut-
ion, that a new structureless fluorescence appeared to the
red of the monomer emission. The intensity of the broad,
structureless band increased as the concentration of the
pyrene was raised. No corresponding changes could be
observed in the electronic absorption spectrum and con-
sequently the new fluorescent component was believed to arise
from an excited state complex, the formation and decay is
shown by the following equations.

$$A \xrightarrow{h\nu} A^* + A \rightleftharpoons (AA)^* \longrightarrow AA$$
$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$
$$A + h\nu' \qquad AA + h\nu'' \qquad A + A$$
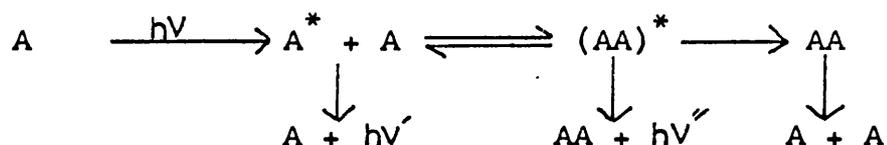
The complex is termed an excimer, and is a dimer that is
stable in the excited state only.

Since this discovery many aromatic compounds have
been shown to form excimers e.g. benzene,[46] naphthalene.[47]

The stability of excimers was first assumed to be due
entirely to exciton resonance,[50] i.e. to a sharing of the
electronic excitation energy between the two partners,

$$A^*A \longleftrightarrow AA^*.$$

A second theory, from Ferguson,[51] was to rewrite the resona-
nce hybrid as a charge-transfer state,

$$A^+A^- \longleftrightarrow A^-A^+.$$
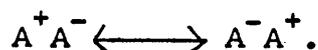
This was supported by the fact that the energy of the
excimer depended upon the difference between the ionisation

potential and the electron affinity of the monomer. Theoretical calculations,[50,52] however, indicated that both of these hybrids had to be taken into account i.e.,

$$A^*A \longleftrightarrow AA^* \longleftrightarrow A^-A^+ \longleftrightarrow A^+A^-$$
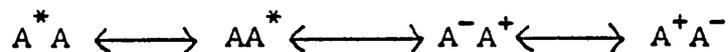
and the predominance of any hybrid would depend upon the particular excimer under consideration.

Evidence for a lack of charge-transfer stabilisation in the excimer state comes from the fact that the wavelength of excimer fluorescence does not depend upon solvent polarity, consequently the dipole moments are zero.

The excimer and the exciplex represent the two possible limits for an excited state complex, but it would not be difficult to imagine complexes that lie between these two extremes i.e. where the stabilisation is due to a mixture of both exciton and charge-transfer resonance.

1:2:4   FLUORESCENCE QUENCHING BY HEAVY ATOMS.

Fluorescence quenching nearly always takes place when a solvent posessing a heavy atom is used,[53] the most common are the simple alkyl halides. Halogens are believed to increase the extent of spin-orbit coupling in aromatic systems, the selection rules for electronic transitions break down and the result is that processes previously "spin-forbidden" become more favourable.[54] The rates of the radiationless processes, $S_1 \longrightarrow T_1$ and $T_1 \longrightarrow S_0$, are both increased. The perturbations caused by the presence of a heavy atom are commonly called "the heavy-atom effect". Apart from lowering

the fluorescence efficiency, heavy atom environments gen-
erally increase phosphorescence efficiencies, as well as
decreasing the radiative lifetime of the triplet state
of the aromatic hydrocarbon.

There is some evidence that complexing occurs in the
ground state. Aromatic hydrocarbons such as benzene,[55]
and anthracene[56] in solvents such as chloroform and carbon-
tetrachloride exhibit charge-transfer absorption bands at
low temperature. Excitation into this band has been post-
ulated as giving rise to an excited complex and this appears
to be preferred to an exciplex mechanism.

The effect has also been studied for various halo-
substituted hydrocarbons i.e. the heavy atom is actually
contained within the molecule under study. As the hydrocarbon
is substituted along the series F, Cl, Br, I then fluor-
escence becomes less favourable i.e. the ratio ϕ_P/ϕ_F increases.
This has been well illustrated in the case of 1-substituted
naphthalenes (Table 4).

TABLE 4.[a]

Effect of halogen substitution upon ϕ_P/ϕ_F for naphthalene.

	ϕ_P/ϕ_F
1-Methylnaphthalene.	0.053
1-Fluoronaphthalene.	0.068
1-Chloronaphthalene.	5.2
1-Bromonaphthalene.	6.4
1-Iodonaphthalene.	1000

a. from ref. 54.

Similar work has been carried out for flourescein dyes.[57]
In this series of compounds ϕ_F decreases, but ϕ_P/ϕ_F does not,
this may be due to comparable increases in $S_1 \longrightarrow T_1$ and
$T_1 \longrightarrow S_0$ inter-system crossing processes, hence no signific-
ant increases in phosphorescence intensity would be observed.
It is also possible that substitution by a halogen atom gives
rise to an increase in the rate of $S_1 \longrightarrow S_0$ internal convers-
ion.

1:2:5 FLUORESCENCE QUENCHING BY OXYGEN.

Fluorescence quenching by oxygen is a general phenom-
enon, very few electronically excited organic molecules
are unaffected by its prescence in fluid solution. Hence
all fluorescence and phosphorescence measurements should
ideally be performed with oxygen-free solutions, this is
generally achieved either by nitrogen flushing or outgassing
procedures (freeze-pump-thaw cycles). The drop in fluoresc-
ence or phosphorescence intensity is sometimes due to the
compound undergoing oxidation. There is often no apparent
chemical reaction however, and the quenching is irreversible,
i.e. if the solution is purged of oxygen, the quenching no
longer takes place.

Several mechanisms have been put forward to explain
the efficiency of oxygen as a quencher. Complexes have
been postulated in certain instances as being responsible
for the fluorescence quenching of aromatic hydrocarbons.
Benzene[58] and toluene,[59] in the prescence of oxygen, exhibit

an electronic absorption band that is characteristic of neither the hydrocarbon nor oxygen. Excitation into this band, which is believed to be a charge-transfer absorption band, will result in the formation of an excited state charge-transfer complex. Recent studies have indicated that the primary route of fluorescence quenching of aromatic hydrocarbons is induced inter-system crossing from S_1 to T_1.[60] Furthermore, the efficiency of quenching was found to be dependent upon the solvent polarity. Similar results for fluorescence quenching of various substituted benzenes have been reported.[61] The evidence showed that if the ionisation potential of the benzene was higher than 9 e.v. then a fall off in the quenching rate constant took place as the ionisation potential was raised. The available evidence does therefore suggest that the quenching of aromatic hydrocarbon fluorescence involves charge-transfer interactions.

Quenching of aromatic hydrocarbon triplet states by oxygen leads to the formation of the highly reactive species known as singlet oxygen. The chemistry of singlet oxygen has been the subject of several reviews.[62,63,64]

SECTION TWO: RESULTS AND DISCUSSION.

2:1 EXCIPLEXES FORMED BETWEEN AMINES AND AROMATIC HYDROCARBONS.

Numerous studies have been made on intermolecular exciplex formation, but there have been relatively few investigations on corresponding intramolecular exciplexes. Chandross and Thomas[65] studied the fluorescence of compounds in Series I and II, where the chain length was varied from $n = 1$ to

$(CH_2)_n NEt_2$

I

$(CH_2)_n NEt_2$
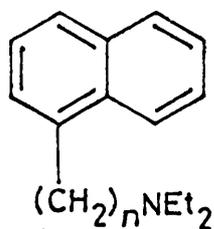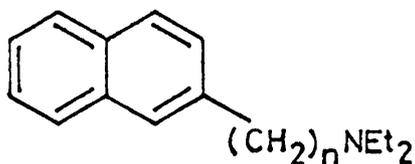
II

$n = 4$. Fluorescence from an excited state charge-transfer complex was detected when $n = 2$, 3 and 4 but not when $n = 1$. The most stable exciplexes were formed when $n = 3$ and in this case, fluorescence was visible at room temperature. The interactions for the compounds with $n = 2$ were judged to be less favourable since the intensity of the exciplex fluorescence was lower under equivalent conditions. Increasing the chain length further, i.e. to $n = 4$, inhibited fluorescence at room temperature and it was only detected by cooling the solutions. For $n = 1$, fluorescence from an exciplex was not observed.

The important feature of these compounds is that the number of conformations available for formation of the

exciplex is restricted by the methylene chain linking the
two interacting chromophores. Hence favourable conform-
ations are available with n = 2 and n = 3, but when n = 4,
although these conformations are still available to the mole-
cule, they are of higher energy as a result of eclipsed
C - H bonds. The absence of emission from an exciplex for
compounds with n = 1 was attributed to poor overlap of the
two groups. These results led the authors to the conclusion
that the geometrical requirements for formation . of the
exciplex were not very strict.

Brimage and Davidson[66,67] have also studied Series I,
as well as the corresponding series of 9-substituted anth-
racenes (Series III) obtaining fluorescence spectra similar

$$(CH_2)_n NEt_2$$
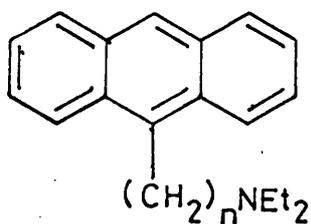
III

to those of Chandross and Thomas. They extended the study
of the compounds and discovered that common photoreactions
of the aromatic hydrocarbon were inhibited. This was
attributed to quenching of the first excited singlet state
of the aromatic hydrocarbon by intramolecular exciplex
formation.

Another series of compounds (IV) has been shown to
exhibit intramolecular exciplex formation.[67] Compounds
with n = 0, 1, 2 and 3 were studied. The compounds with
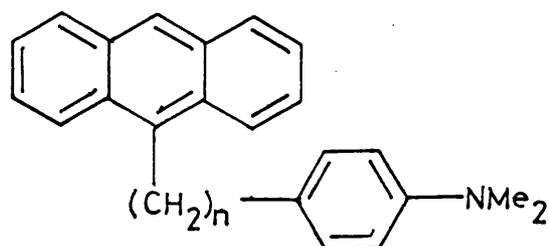
$$\underline{IV}$$

n = 1 and 2 did not show exciplex fluorescence in solvents of low polarity and this was believed to be due to the exciplex energy lying above that of the first excited singlet state of anthracene. The observation of exciplex fluorescence when n = 3 must involve interaction of the aromatic ring of the arylamino group with the anthracene π-system. The situation for n = 0 was found to be somewhat different since a new electronic absorption band was observed which precludes an exciplex mechanism for this compound.

To gain further insight into the chemistry of exciplex formation and decay, the following compounds have been synthesised, where an ester function has been incorporated into the chain linking the donor and acceptor groups.

$CH_2CO_2CH_2CH_2NR'R''$

1. $R'=R''=Me$.
2. $R'=Me$. $R''=Ph$.

$CH_2CO_2CH_2CH_2NR'R''$
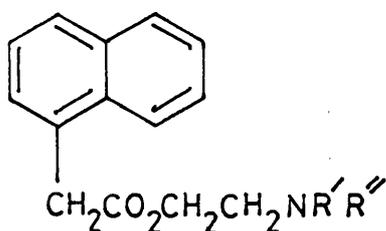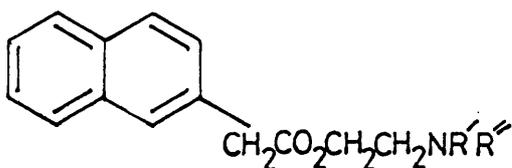
3. $R'=R''=Me$.
4. $R'=Me$. $R''=Ph$.
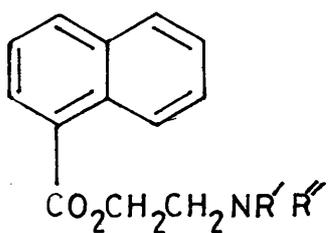
5. $R'=R''=Me$.

6. $R'=Me$. $R''=Ph$.
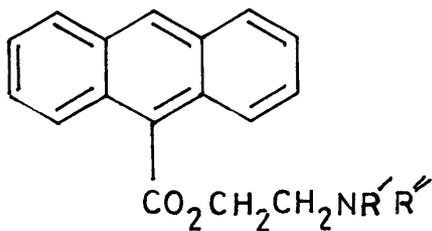
7. $R'=Me$. $R''=Ph$.
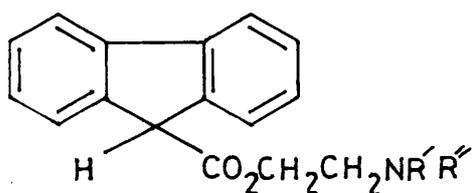
8. $R'=R''=Me$.

9. $R'=Me$. $R''=Ph$.
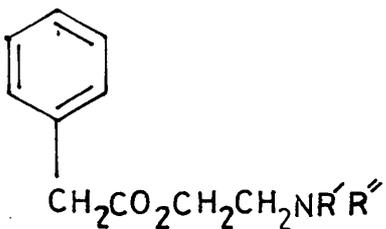
10. $R'=R''=Me$.

The synthesis of the amino-esters, 1 to 10, was achieved by esterification of the corresponding carboxylic acid with either 2-dimethylamino ethanol (11) or 2-(N-methylanilino) ethanol (12).[a]

a. This compound was a gift from Dr. J.F. McKellar, Organics Division, I.C.I. Ltd.

$$Me_2NCH_2CH_2OH \qquad\qquad Ph\ N(Me)CH_2CH_2OH$$
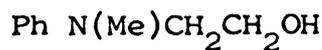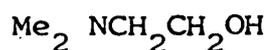
$$\underline{11.} \qquad\qquad\qquad\qquad \underline{12.}$$

The carboxylic acid was always converted to its acid chloride
by refluxing in benzene with oxalyl chloride, the alcohol
was then reacted with the acid chloride.

$$R.CO_2H \xrightarrow[\text{Benzene}]{(COCl)_2} R.COCl \xrightarrow[\text{Benzene}]{R'R''N(CH_2)_2OH} R.CO_2(CH_2)_2NR'R''$$

Oxalyl chloride was found to convert the acid into the
acid chloride very cleanly and was always used in preference
to thionyl chloride for this reason.

Emission studies have been carried out for each comp-
ound (Section 2:1:1) and more detailed investigations (Sections
2:1:2, 3 and 4) performed for selected compounds ($\underline{1}$ and $\underline{2}$).
The effect of solvent upon the fluorescence lifetime of I
(n = 2) has also been studied (Section 2:1:3). Some invest-
igations have also been made on intermolecular exciplexes
(Section 2:1:5).

2:1:1   INTRAMOLECULAR EXCIPLEX FORMATION: ULTRA-VIOLET
        AND EMISSION SPECTRA.

Results.

The ultra-violet absorption spectra of the solutions
used for the emission studies of compounds $\underline{1}$ to $\underline{10}$ were

essentially the same as mixtures of the parent compounds at the same concentrations.

At room temperature, the fluorescence of compounds 1, 2, 3, 4, 6, and 7 was found to consist of two bands. The first, higher energy emission arises from the parent hydrocarbon (monomer) and this was always of lower intensity than that found in the monomer. The second band which was always shifted to the red of the monomer fluorescence, was broad and structureless and shifted further to the red with a decrease in intensity as the polarity of the solvent was raised.

The new emission bands have been attributed to intramolecular exciplex formation.

Compounds 5, 8, 9 and 10 did not exhibit exciplex fluorescence. The monomer fluorescence is quenched in the case of compound 5, and 10 does not fluoresce at all. 8 and 9 are atypical, 8, emits what appears to be fluorescence characteristic of the fluorene chromophore; whereas 9 has an emission spectrum that is dependent upon the excitation wavelength.

Emission typical of these compounds is illustrated by 1 and 2 in Diagrams 1, 2 and 3. Detailed results of the room temperature emission spectra are shown in Table 5.

The dipole moments of the exciplexes were calculated using equation 1, which has been previously derived[68] from formulae given in the literature.[69,70]

$$\tilde{\nu}_{(o)} = \tilde{\nu}_{CT} - \frac{2\mu^2_{CT}}{hca^3} \cdot \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2} \cdot \frac{\eta - 1}{2\eta^2 + 1} \right]$$

TABLE 5.

Wavelengths of maximum emission and relative intensities for compounds 1 - 9.[a]

Compound	Solvent	λmax.(NM) Monomer	λmax.(NM) Exciplex	Relative intensity[b] Monomer	Relative intensity[b] Exciplex
1.	Cyclohexane.	348	440	0.17	0.4
	Benzene.	348	447	0.13	0.39
	Chloroform.	350	-	0.09	-
	Diethyl ether.	350	460	0.11	0.35
	Acetonitrile.	350	520	0.03	0.07
2.	Cyclohexane.	348	415	0.066	0.58
	Benzene.	348	424	0.044	0.53
	Acetonitrile.	350	480	0.04	0.05
	95% Ethanol.	350	490	0.11	0.22
	Glycerol.	350	-	0.9	-

a. Wavelength and relative intensities have all been taken from uncorrected spectra recorded with 10^{-4}M solutions at room temperature.

b. Relative to; 1-naphthylacetate = 1 (for 1, 2, 3, 4); 1-methylnapthoate = 1 (for 5, 6); 9-methyl-anthracene = 1 (for 7); Fluorene = 1 (8, 9).

TABLE 5. (Continued)

Compound	Solvent	λ max.(NM) Monomer	λ max.(NM) Exciplex	Relative intensity Monomer	Relative intensity Exciplex
3.	Cyclohexane.	346	-	0.15	-
	Benzene.	346	446	0.07	0.15
	Ethyl acetate.	348	476	0.04	0.04
	Acetonitrile.	350	505	0.035	0.006
	95% Ethanol.	350	500	0.04	0.016
4.	Cyclohexane.	350	405	0.1	0.3
	Benzene.	350	420	0.04	0.18
	Ethyl acetate.	350	435	0.04	0.09
	Acetonitrile.	353	470	0.02	0.03
	95% Ethanol.	350	470	0.03	0.06
5.	Methyl cyclo hexane.	348	-	0.21	-
	Benzene.	350	-	0.2	-
	Ethylacetate.	350	-	0.16	-
	Acetonitrile.	350	-	0.15	-
	95% Ethanol.	350	-	0.18	-

TABLE 5. (Continued)

Compound	Solvent	λ max. (NM) Monomer	λ max. (NM) Exciplex	Relative intensity. Monomer	Relative intensity. Exciplex
6.	Cyclohexane.	-	375	-	0.16
	Benzene.	-	380	-	0.15
	Ethyl acetate.	350	390	0.02	0.12
	Acetonitrile.	350	400	0.01	0.06
	95% Ethanol.	350	410	0.01	0.09
7.	Cyclohexane.	425	450	0.005	0.001
	Benzene.	425	460	0.001	0.002
	Ethyl acetate.	425	465	0.002	0.002
	Acetonitrile.	-	480	0.0005	0.0004
	95% Ethanol.	-	485	0.001	0.001
8.	Cyclohexane.	305/312	-	1	-
9.	Cyclohexane	342(exn.302)	-	1	-
		348(exn.280)	-	1	-

CH₂CO₂CH₂CH₂CH₂NMe₂ (structure)
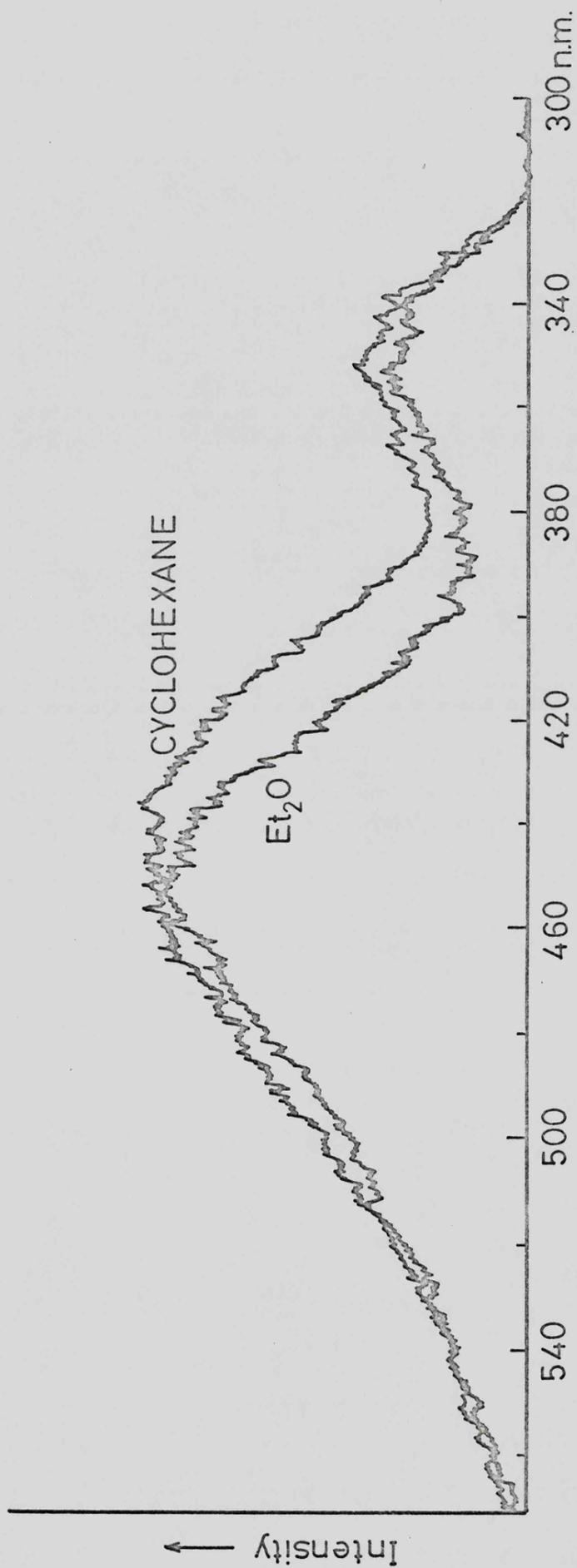
DIAGRAM 1

Fluorescence emission recorded in cyclohexane and diethyl ether.
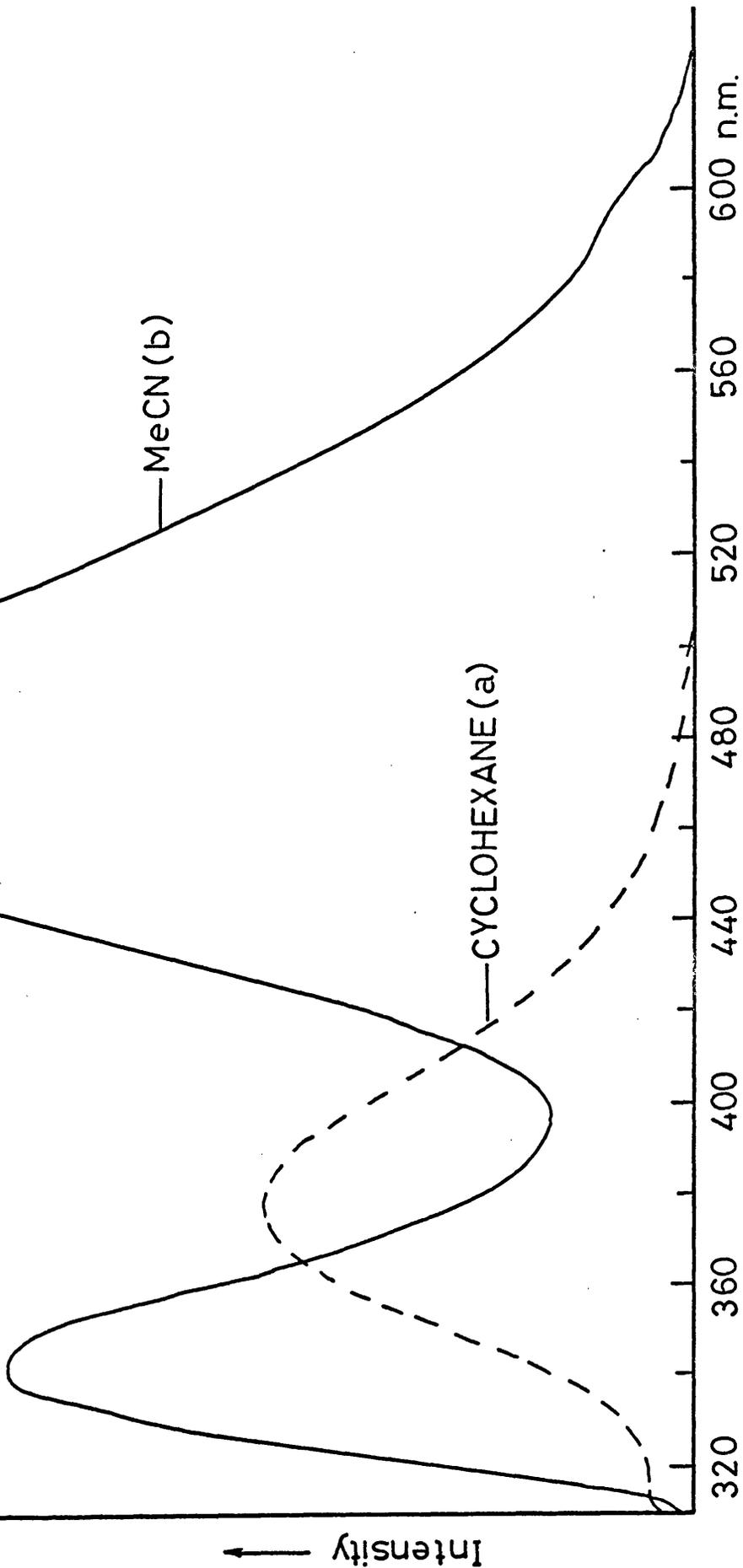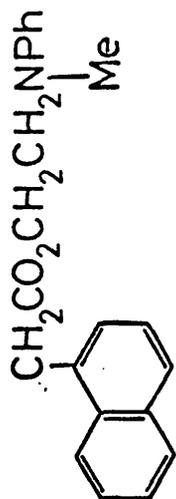
Fluorescence emission recorded in cyclohexane and acetonitrile solution.

Relative intensity (a) x1, (b) x 30.
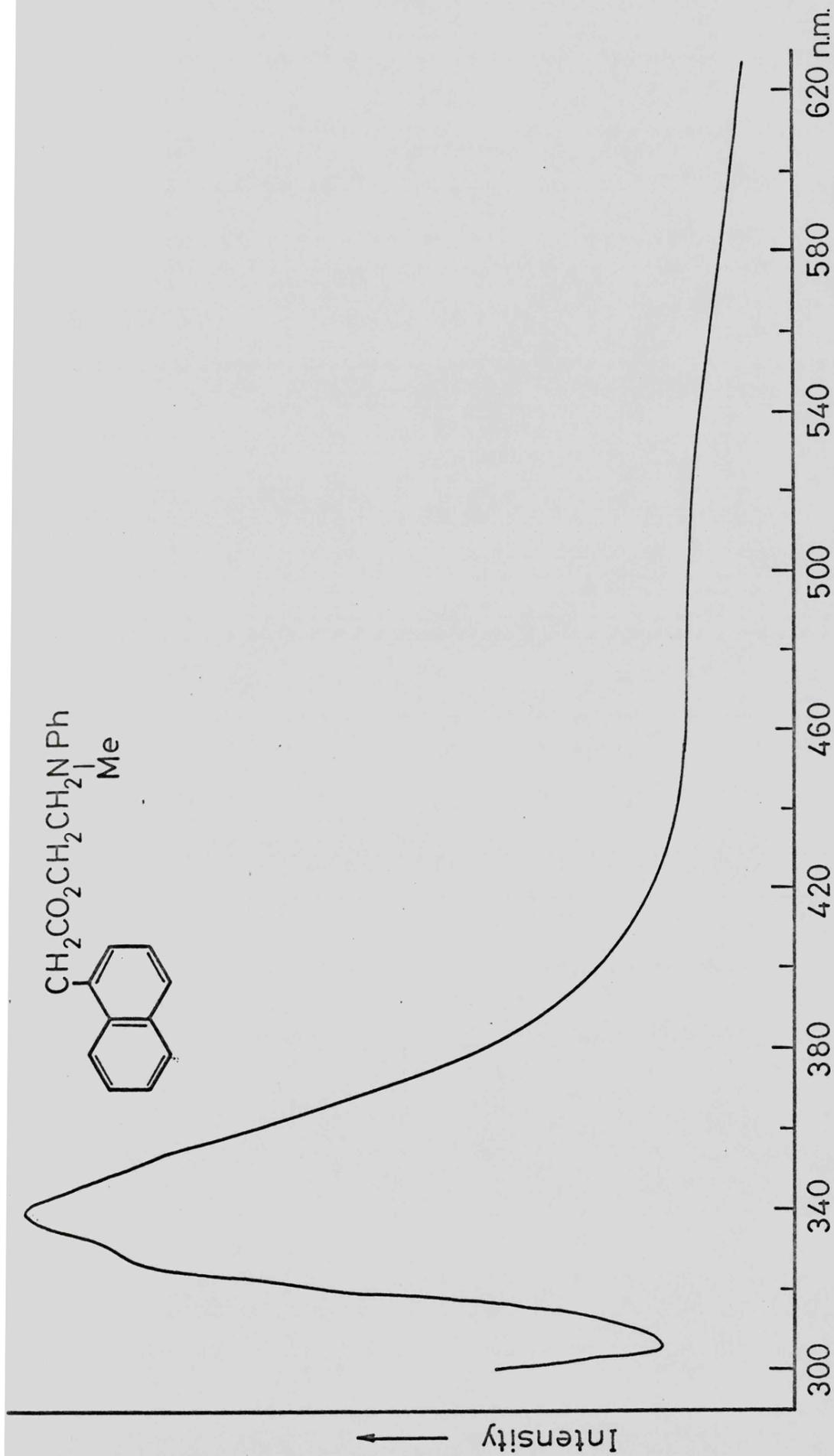
DIAGRAM 2

DIAGRAM 3

Fluorescence emission recorded in glycerol solution.

37.

Where $\tilde{\upsilon}_{CT}$ = wavenumber of maximum complex emission.

$\tilde{\upsilon}_{(o)}$ = wavenumber of the zero-zero transition.

μ_{CT} = dipole moment of complex.

h = Planck's constant.

c = speed of light in vacuo.

a = cavity radius of complex.

ε = dielectric constant of solvent.

η = viscosity of solvent.

The wavenumber of maximum complex emission was plotted against the expression in brackets for compounds 1, 2, 3, 4, 6 and 7. The data are shown in Table 6, together with the slopes obtained in Table 7.

Evaluation of the dipole moment of the exciplexes then requires a value for 'a', the cavity radius of the exciplex. This has been estimated as being slightly greater than the radius of the exciplex and estimated from molecular models of the compounds. The radius for the exciplex formed by the naphthalene compounds is approximately 5.0Å , and for the anthracene compound (7), approximately 5.5Å .

Since the values for 'a' are rather uncertain, the dipole moments have been calculated for three different radii, the results are shown in Table 8.

The emission spectrum of each compound 1 - 7 was studied over a wide range of concentration (10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5}M in benzene solution). Compounds 8 and 9 were studied at 10^{-4} and 10^{-5}M (in cyclohexane solutions). The shape and the wavelength of the fluorescence spectrum were found to be independent of the concentration.

TABLE 6.

Solvent dependence of wavenumber of fluorescence maxima of intramolecular exciplexes.

Solvent	Z^a	Compound.					
					$\tilde{\nu}$ max. $(1000cm^{-1})$		
		1.	2.	3.	4.	6.	7.
Cyclohexane.	0.106	22727	24096	-	24691	26666	22222
Benzene.	0.116	22371	23585	22421	23809	26316	21739
Ethyl acetate.	0.293	-	-	21276	22988	25641	21505
Diethyl ether.	0.256	21739	-	-	-	-	-
Acetonitrile.	0.394	19230	20833	19802	21276	25000	20833
95% Ethanol.	0.42	-	20408	20000	21276	24390	20618

a.

TABLE 7.

Slopes $(cm^{-1})^b$ from plots of $\tilde{\nu}$ max. vs. Z.

Compound.	1.	2.	3.	4.	6.	7.
Slope.	3450	5555	3950	5400	2995	2500

b. $\text{Slope} = -\dfrac{2\mu_{CT}^2}{h\,c\,a^3}$

TABLE 8.

Dipole moments of exciplexes (Debye units).

	a($\overset{o}{A}$)	4.5	5.0	5.5	6.0
Compound 1.[a.]		7.92	9.27	10.7	-
Compound 2.		10.05	11.77	13.58	-
Compound 3.[a.]		8.47	9.92	11.45	-
Compound 4.		9.9	11.6	13.4	-
Compound 6.		7.34	8.64	9.97	-
Compound 7.		6.74	7.89	9.11	10.38

a. Weller has calculated μ =16.8D for naphthalene-triethylamine assuming the full transfer of one electron.

Emission from $\underline{1}$ and $\underline{2}$ in rigid matrix (acetonitrile) and glass (methyl cyclohexane) at -196° was fluorescence and phosphorescence typical of the parent compounds. No anomalous fluorescence or phosphorescence bands were observed under these conditions.

Discussion.

No evidence exists for ground state complex formation i.e. there are no changes in the ultra-violet absorption spectra of $\underline{1}$ - $\underline{10}$ corresponding to those in the fluorescence spectrum. Although no typical charge-transfer absorption bands can be seen, this does not necessarily imply that ground state complexing of some type does not occur but it is assumed that ground state interactions are not important since no changes could be detected. The new fluorescence bands have thus been attributed to an interaction that only takes place in the excited state. This is further substantiated by the fluorescence excitation spectra, in which both exciplex and monomer

spectra are the same. In the case of compound 5, where

fluorescence quenching is present and no new fluorescence

band was detected, the excitation spectrum was found to be

identical to that of 1-methylnapthoate.

The absence of a concentration effect upon the fluor-

escence spectrum is good evidence that the results reported

derive from intra and not intermolecular interactions. The

absence of exciplex fluorescence at -196° is presumably due

to the difficulty encountered by the molecule in reorientating

itself into the exciplex conformation.

The dipole moments calculated for those compounds

exhibiting a new fluorescence band are all fairly high which

suggests that emission is derived from a species that possesses

charge-transfer character.

The results obtained from ultra-violet absorption spectra,

concentration effects and dipole moments are evidence that intra-

molecular exciplex formation is responsible for the new fluor-

escence bands.

The effect of solvent polarity upon the exciplex emission

parallels those found for intermolecular exciplexes although

in each case the dipole moments calculated for the intramolecular exciplexes are lower than their

intermolecular counterparts. Kuzmin and Guseva[70] calculated a

value of approximately 11D for the naphthalene — triethylamine

exciplex assuming a radius of 4.5Å . Knibbe[71] has also deter-

mined the dipole moment for this exciplex, finding a value of

12.5D for a radius of 4.7Å . Their results are thus in good agree-

ment. The values obtained for 1 and 3 are very much lower, being

approximately 8 and 8.5D respectively with a similar radius.

Knibbe[71] has also found values for the dipole moments of the exciplexes formed between naphthalene — N,N-diethylaniline (12.5D, a = 4.8Å) and anthracene — N,N-diethylaniline (12.5D, a = 5.5Å). The corresponding values obtained for compounds 2, 4, 6 and 7 are again lower.

On the basis of the equation used to determine the dipole moments, three reasons can be put forward to explain why the intramolecular exciplexes have lower dipole moments than the equivalent intermolecular exciplexes.

1. The complex radius is larger than expected, i.e. greater than 5.0Å and 5.5 Å respectively, for exciplexes formed by naphthalene and anthracene.

2. The electron transfer process is less efficient in an intra-molecular exciplex despite the close proximity of the donor and acceptor groups.

3. The radius assumed for the intermolecular exciplexes is too high. This is unlikely however, since the size of the larger component, i.e. the aromatic hydrocarbon, will mainly determine the size of the complex.

A possible explanation of both 1. and 2. is that the chain linking the aromatic hydrocarbon with the amino group imposes a restraint that is absent in the intermolecular excip-lex. This may either force the complex to assume a larger radius (which may possibly render the electron transfer process less facile) or else the molecule has to adopt a conformation which has a smaller radius but in which electron transfer is more difficult. Since electron transfer reactions are believed to occur even over large distances, then it would appear that the

molecules possess a larger radius in the stable exciplex conformation, values calculated for 'a' between 5.0 and 5.5 Å (for naphthalene) give reasonable agreement for 1, 2, 3 and 4 with the dipole moments found for the equivalent intermolecular exciplexes. On this basis the dipole moments of compounds 6 and 7 (assuming a = 6.0 Å) are still low and in this case the linking chain probably does force the molecule to adopt an unfavourable conformation.

Dipole moments have been previously calculated for intramolecular exciplexes. The values obtained for compounds in Series I[72] were found to be higher than those for the intermolecular exciplexes and those obtained for Series III[67] were also higher than those determined by Knibbe[71] for anthracene — N,N-diethylaniline. Both series however have relatively short chains compared to 1 - 7 and it would appear that the longer linking chain does impose restraints upon the molecule in forming an exciplex.

Apart from indicating that the exciplexes studied possess considerable charge-transfer character, the effect of solvent polarity also shows a trend that is observed for intermolecular exciplexes, i.e. decreasing intensity of exciplex fluorescence as the polarity of the solvent is raised (See Table 3). This, as has been noted (Section 1:2:2) is due ultimately to the formation of radical ions and triplet aromatic hydrocarbon. The most important point however is the ability of the intramolecular exciplexes to fluoresce in polar solvents, such as acetonitrile, i.e. conditions under which the intermolecular exciplexes formed between

aromatic hydrocarbons and amines do not fluoresce at all. Fluorescence of the exciplex has also been observed in polar solvents for compounds in Series I, II and III, and will be discussed more fully in relation to the fluorescence decay times of the exciplexes (Section 2:1:2).

The data in Table 5 gives some indication of the geometrical requirements for exciplex formation, apart from that derived from the dipole moments. The compounds have a minimum of four atoms linking the donor and acceptor groups yet many of them exhibit exciplex fluorescence at room temperature, a situation not found when the side chain consists entirely of methylene groups. Construction of molecular models shows that the ester group allows the methylene units to adopt a conformation in which the amino group is situated over the aromatic hydrocarbon nucleus. The non-bonding interactions which hinder exciplex formation in I and II $(n = 4)$, have therefore been avoided in these molecules but the dipole moments do indicate that the situation is not as favourable as it is for I $(n = 2)$, $(n = 3)$ and II $(n = 2)$, $(n = 3)$.

The effect of using an aryl amine as an electron donor as opposed to an alkyl amine is illustrated by the pairs 1 - 2; 3 - 4; 5 - 6. The most obvious difference between the two amino groups is that the ionisation potential of the aromatic amine is lower than that of the alkyl amine (N,N-diethylaniline 7.2 e.v.,[73] triethylamine 7.5 e.v.[74]) hence the electron transfer process should be easier for those systems containing an aryl amine. This is reflected

in the higher dipole moments obtained for $\underline{2}$ and $\underline{4}$ as compared to $\underline{1}$ and $\underline{3}$.

It is noticable that the wavelength of maximum emission of $\underline{1}$ and $\underline{3}$ lie at lower energy than $\underline{2}$ and $\underline{4}$ despite the fact that the latter pair have higher dipole moments. The reason for this is believed to be due to a change in the structure of the amine from pyramidal before complexing occurs, to planar in the exciplex itself.[37] Consequently after emission from the exciplex the Franck-Condon ground state so formed will be of higher energy due to the structural change, and hence the light emitted will be of longer wavelength. The activation enthalpy for inversion is known to be 8.2 kcal/mole for trimethylamine.[75]

The effect of the phenyl group is very marked in the case of $\underline{6}$ which does emit from an exciplex whereas $\underline{5}$ with a dimethylamino group does not. Although the exciplex formation should be more favourable in $\underline{6}$ due to the presence of the aryl amine, molecular models of $\underline{5}$ and $\underline{6}$ do indicate that steric reasons may be responsible for the lack of exciplex fluorescence from $\underline{5}$, since the amino group has to lie well away from the naphthalene ring. The situation in $\underline{6}$ is somewhat different, although the amino group itself cannot interact very efficiently with the naphthalene chromophore, the phenyl ring can attain a degree of overlap and as a result may play a part in the transfer of an electron. The two aromatic rings, however, do not lie parallel. The lone pair of electrons cannot be regarded as localised in N,N-dimethylaniline and it appears that they

45.

are delocalised into the benzene ring,[76,77] hence the most favourable overlap in $\underline{6}$ should be when the two aromatic rings lie parallel, and since they do not, then the inter-action should be less favourable although electron transfer should still be possible. Chandross, Taylor and Schiebel[78] in a study on pyrene - dialkylaniline exciplexes concluded that the results with N,N-dimethylaniline were most consist-ant for "the sandwich-pair geometry" in the exciplex config-uration. This may then explain why the dipole moment of $\underline{6}$ is rather low, similar considerations should apply to compound $\underline{7}$, which also has a low dipole moment and the same type of mol-ecular structure as $\underline{6}$.

It has been noted that $\underline{5}$ does not exhibit exciplex fluorescence but emission from the monomer is quenched. Weller,[68] in a study on fluorescence quenching of aromatic hydrocarbons by N,N-diethylaniline obtained quenching rate constants from which the encounter distance was found to vary from 4 - 8Å . He concluded that the quenching of fluor-escence from an aromatic hydrocarbon can occur in an encounter complex. The orientation of the molecules within the encoun-ter complex will be less restricted than in a sandwich-type complex where good overlap is required, consequently fluor-escence quenching can occur without the formation of a stable, fluorescent exciplex. Fluorescence quenching was still apparent in $\underline{5}$ even though the concentration was low, it is therefore assumed that quenching is via an intra rather than an intermolecular process. The results obtained from $\underline{5}$ are reminiscent of those reported for I (n = 1), where only fluor-

escence quenching was detected.

A comparison of the data for compounds 2 and 4 shows
that the exciplex emission band is at shorter wavelength
for 4 (i.e. the 2-substituted naphthalene) and this is also
true for the dimethylamino derivatives 1 and 3. Molecular
models of these compounds do not show any serious non-
bonded interactions for 3 and 4 that are not present for
1 and 2. Indeed, interference occurs in the 1-substituted
series because of interaction between the methylene group
attached to the ring and the hydrogen at C - 8 of the naph-
thalene, this may be sufficient to increase the energy of
the Franck-Condon ground state, thus giving rise to a longer
wavelength emission from the exciplex. Another possible
reason for the wavelength difference is that the 1-substitut-
ed naphthalenes can attain greater overlap of the amino and
naphthalene groups. The amino group in 1 and 2 can interact
inthe regions of C - 1, C - 2, C - 3, C - 7 and C - 8 whereas
3 and 4 can interact only in the regions of C - 1, C - 2 and
C - 3 of the naphthalene ring. Hence the electron transfer
may be more favourable in 1 and 2 for this reason.

The derivatives of fluorene, compounds 8 and 9, do not
exhibit intramolecular exciplex fluorescence, which is rather
suprising. Lamola[79] has reported that intramolecular transfer
of singlet excitation energy can take place between dimethoxy
benzene and fluorene, but in this case the absorption spectrum
did show that some ground state interaction does occur. There
is no evidence however, for association or interaction in the
ground state of either 8 or 9 as judged by the absorption
spectra. Unlike 8, the fluorescence of 9 exhibited a wave-

length dependence. Excitation at shorter wavelengths than 302NM caused the fluorescence spectrum to shift slightly to longer wavelengths (see Table 3).

The emission from 9 appears to be fluorescence, not from the fluorene chromophore, but mainly from the N-methylaniline chromophore and this was substantiated by the fluorescence from a solution of N,N-dimethylaniline which gave an emission band of similar intensity at 355NM. Emission from the aryl amine appears to predominate in the fluorescence spectrum of 9. The slightly shorter wavelength of maximum fluorescence (348NM) from that found in N,N-dimethylaniline (excitation wavelength 302NM) may be due to weak emission from the fluorene chromophore which shifts the band to higher energy. The ultra-violet absorption spectra of these two chromophores do coincide. At 302NM the approximate optical densities (O.D.) for 10^{-4}M solutions in cyclohexane are,

$$\text{Compound 8} \quad \text{O.D.} \ = 0.5.$$

$$\text{Compound 9} \quad \text{O.D.} \ = 0.7.$$

$$\text{N,N-dimethylaniline} \quad \text{O.D.} \ = 0.2.$$

Excitation with light of wavelength 302NM should therefore give rise to fluorene fluorescence as well as amine fluorescence in 9.

An explanation of the wavelength effect can be found in the fluorescence excitation spectra since the amine was found to posess a shoulder at 267NM, a feature which is absent in 8.

It therefore appears that transfer of singlet excitation energy takes place in 9 and since the effect is noticed at 10^{-5}M it is likely that it is an intramolecular process.

The absence of exciplex fluorescence does not appear

to be a function of the molecular structure in either

8 or 9, overlap of donor and acceptor groups is possible and

apparently more favourable than in 5, 6 and 7, although the

energetically most favourable conformation for the exciplex

i.e. the sandwich- pair, cannot be attained. Brimage[80] found

that 13 exhibited intramolecular exciplex formation, and
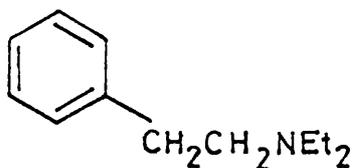
13

the energetics of 8 would be expected to fall between

those of 12 and I(n = 2), which also forms a stable exciplex.

Compound 10 fails to fluoresce at all in fluid solution,

i.e. benzene fluorescence is completely quenched and no

exciplex fluorescence could be detected, this is unexpected

in view of the results reported for 13. A possible reason for

the lack of exciplex fluorescence from 8, 9 and 10 may lie

in both the ester group and the energetics. Under conditions

where favourable conformations cannot be attained for excip-

lexes formed with aromatic hydrocarbons of high singlet energy,

other quenching routes may be preferred.

One final observation from the room temperature emission

data is that fluorescence from 2 in glycerol (Diagram 3) is

different from that in ethanol. Emission in the latter is

similar to that in acetonitrile (Diagram 2). It can be seen

that exciplex formation has been inhibited in glycerol and

purely on the basis of dielectric constants (glycerol,

ε = 37, ethanol, ε = 24; both at 25°[74]) one would expect

to see fluorescence from an exciplex for 2 in glycerol.

It has been found that the rate constants for quenching of

fluorescence of aromatic hydrocarbons exhibit anomalous

behaviour in alcohols and that they are lower than would be

expected on the basis of their polarity.[81] (Selinger and

McDonald[38] have criticised this type of treatment in that

their experiments indicated that the rate of quenching was

governed by viscosity and not by the dielectric constant

of the solvent.)

Two possible explanations have been suggested;

1. The behaviour is due to the long dielectric relaxation

times of the alcohols.

2. Hydrogen bonding can occur between the hydroxyl proton

of the alcohol and the lone pair of the hydrogen atom.

It has been found that the hydroxyl group in 2-(N-methyl-

anilino) ethanol (12) had little effect upon the rate of

fluorescence quenching of aromatic hydrocarbons,[82] there-

fore the result reported here appears to be due to the

long relaxation time. The viscosities of ethanol and glycerol

are 1.2 c.p. and 19.9 c.p. respectively. It is interesting

to note that in this case viscosity can affect intramolec-

ular exciplex formation despite the close proximity of

the donor and acceptor groups. A recent study on intra-

molecular excimer formation supports the view that viscosity

can affect the formation of intramolecular excited state

complexes.[83]

2:1:2 INTRAMOLECULAR EXCIPLEX FORMATION: RADIATIVE

   LIFETIME STUDIES.

Results.

It was noted in the previous section that intramolecular exciplex formation could be observed in polar solvents such as acetonitrile. By contrast, intermolecular exciplexes formed between aromatic hydrocarbons and amines do not fluoresce in this type of solvent. In order to understand the effect of solvent upon the exciplex, the lifetimes of both monomer and exciplex fluorescence were studied.[a]

The fluorescence lifetimes have been determined for three compounds known to exhibit intramolecular exciplex formation; 1, 2, and I(n = 2). The lifetimes were evaluated for both degassed and air saturated solutions in cyclohexane and acetonitrile. The data obtained are summarised in Tables 9 and 10.

TABLE 10.

Time delays for naphthylalkylamines.

Compound.	Delay (ns.)	Solvent.
1.	3	Cyclohexane.
	3	Acetonitrile.
2.	9	Cyclohexane.
	12	Acetonitrile.
I (n = 2)	3	Cyclohexane.
	3	Acetonitrile.

a. This work was carried out in conjunction with Dr. Godfrey Beddard at the Royal Institution, London.

TABLE 9.

Lifetimes (ns.) of the fluorescence from some naphthylalkylamines.

Compound.		Cyclohexane.		Acetonitrile.	
		Monomer.	Exciplex.	Monomer.	Exciplex.
1. naphthyl–$CH_2CO_2CH_2CH_2CH_2NMe_2$	A.	10.6*	11	1.6	a.
	D.	28.0	28	57.0	a.
2. naphthyl–$CH_2CO_2CH_2CH_2CH_2NMe.Ph$	A.	a.	10*	1.5	12.5
	D.	a.	32	50.5	61.5*
I (n = 2). naphthyl–$CH_2CH_2NEt_2$	A.	a.	11.7*	9.2	6.4
	D.	a.	13.6*	57.5	30.0
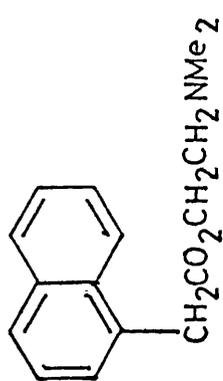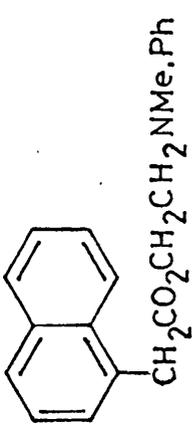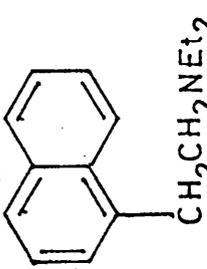
Solvent.

A.   Denotes air saturated solution.

D.   Denotes degassed solution.

*.   Denotes exponential decay.

a.   Emission too weak for decay curve to be measured.

52.

The lifetimes of 1-methylnaphthalene were also determined

in cyclohexane solution$(10^{-4} M)$,

$$\tau_F(\text{degassed}) = 83\text{ns}.$$

$$\tau_F(\text{air saturated}) = 14.8\text{ns}.$$

Discussion.

The first, and perhaps, most important observation is

that the lifetime of the exciplex fluorescence is longer

in acetonitrile that it is in cyclohexane solution. This

is in direct contrast to the early findings that the life-

time of intermolecular aromatic hydrocarbon-amine exciplexes

is shortened by increasing the solvent polarity.[84,85] It

has also been found that the quantum yield of exciplex fluor-

escence decreases as the solvent polarity increases, which is

a common characteristic of exciplex formation. These two

facts can be rationalised if the non-relaxed exciplex is prop-

osed as an intermediate in the quenching mechanism.
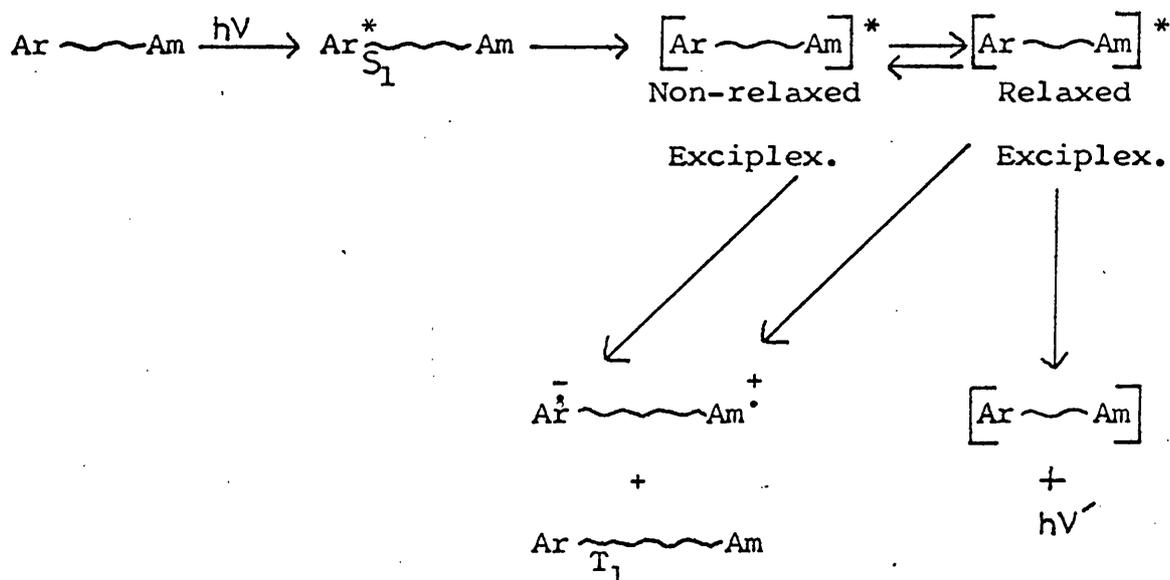
Ar. Denotes aromatic hydrocarbon.

Am. Denotes amine.

Apparently, complete dissociation of the non-relaxed exciplex into radical ions and/or triplet hydrocarbon does not occur in acetonitrile solution for compounds 2 and I (n = 2), the solvent is then able to reorientate itself about the non-relaxed exciplex leading to the relaxed form. This is then capable of emitting light. The longer lifetimes observed for fluorescence from the relaxed exciplexes in acetonitrile solution are due to the greater solvating power of that solvent with respect to cyclohexane.

On the assumption that the lifetime is longer in acetonitrile than it is in cyclohexane it is possible to propose that dissociation of the relaxed exciplex again, either into radical ions, or triplet hydrocarbon, is not important. This leads one to the fact that the dissociation of the non-relaxed exciplex, and not of the relaxed exciplex, is dependent upon the solvent polarity. Hence an increase in the polarity of the solvent causes an increase in the dissociation of the non-relaxed exciplex leading to a lower exciplex fluorescence intensity and a longer lifetime. Compound 1 does not behave in quite the same way, dissociation of the non-relaxed exciplex for this molecule appears to be efficient since it was difficult to observe the decay of the fluorescence. The factors affecting the break up of the non-relaxed exciplex are not fully understood at the present time, but it is interesting to note two points,

1. Brimage and Davidson[66] (Section 2:1:1) found intramolecular exciplex formation inhibited the photoreactivity of both naphthalene and anthracene, in particular it was expected

that in polar solvents intramolecular photocyclisation

reactions of naphthalene compounds (Series I) might take

place via radical ion formation, but the compounds proved

to be stable to irradiation in acetonitrile solution.

2. Reaction has been detected in a similar compound by

Bryce-Smith,[86] irradiation of 14 in methanol gave rise to
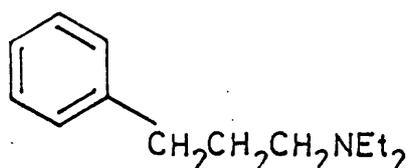
14

a cyclised product i.e. the type of reaction expected of

I(n = 3). The use of a good proton donor as a solvent may

be the reason for the reactivity in this molecule. The

two sets of results may not be incompatible since the react-

ion of 14 was found to be very slow.

These examples serve to illustrate that radical ion

formation for intramolecular exciplexes is not a straight-

forward process.

The time delays observed in the build up of the exciplex

fluorescence reflect the time taken for the amine to react

with the aromatic hydrocarbon. The lifetime of the initially

excited species is an important factor, because a diffusion

controlled process is necessary to form the exciplex and this

must take place before the excited species is deactivated by

other quenching mechanisms i.e. the mean radiative lifetime

imposes a time limit on exciplex formation. Knight and

Selinger,[87] have found that exciplex formation that takes

place from excitation of the naphthalene nucleus shows a relatively long time delay .

The effect of oxygen quenching upon the fluorescence lifetime is quite marked as can be seen by comparison of the values determined for air saturated and degassed solutions. In each case, the lifetimes of both monomer and exciplex have been shortened in air saturated solution.

2:1:3   INTRAMOLECULAR EXCIPLEX FORMATION: FLASH PHOTOLYSIS STUDIES.

Results.

Compounds 1 and 2 were studied using a microsecond flash photolysis apparatus in the spectroscopic mode. Two different solvents, cyclohexane (non-polar) and 95% ethanol (polar), were used for the experiments.

Transient $(T_1 \longrightarrow T_n)$ absorption spectra have been obtained for each of these systems and approximate optical densities of the absorptions measured by inserting neutral density filters between the cell and the spectrograph. The time delay between the photolytic flash and the spectrographic flash was fixed at 20 μs. for this purpose and the spectra then compared directly.

The wavelengths of the absorption spectra are presented in Table 11, together with approximate optical densities for the most intense absorption which was always that of lowest energy. A typical absorption spectrum is illustrated in Diagram 4.
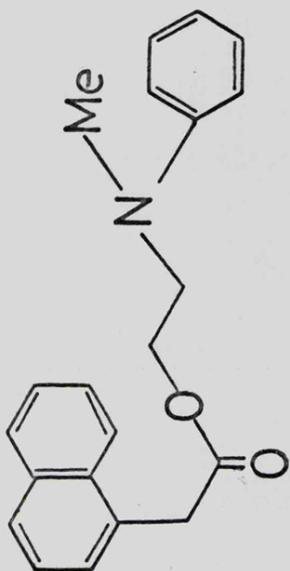
$T_1 \longrightarrow T_n$ Absorption Spectrum in Cyclohexane (10^{-4}M) 20μs delay.
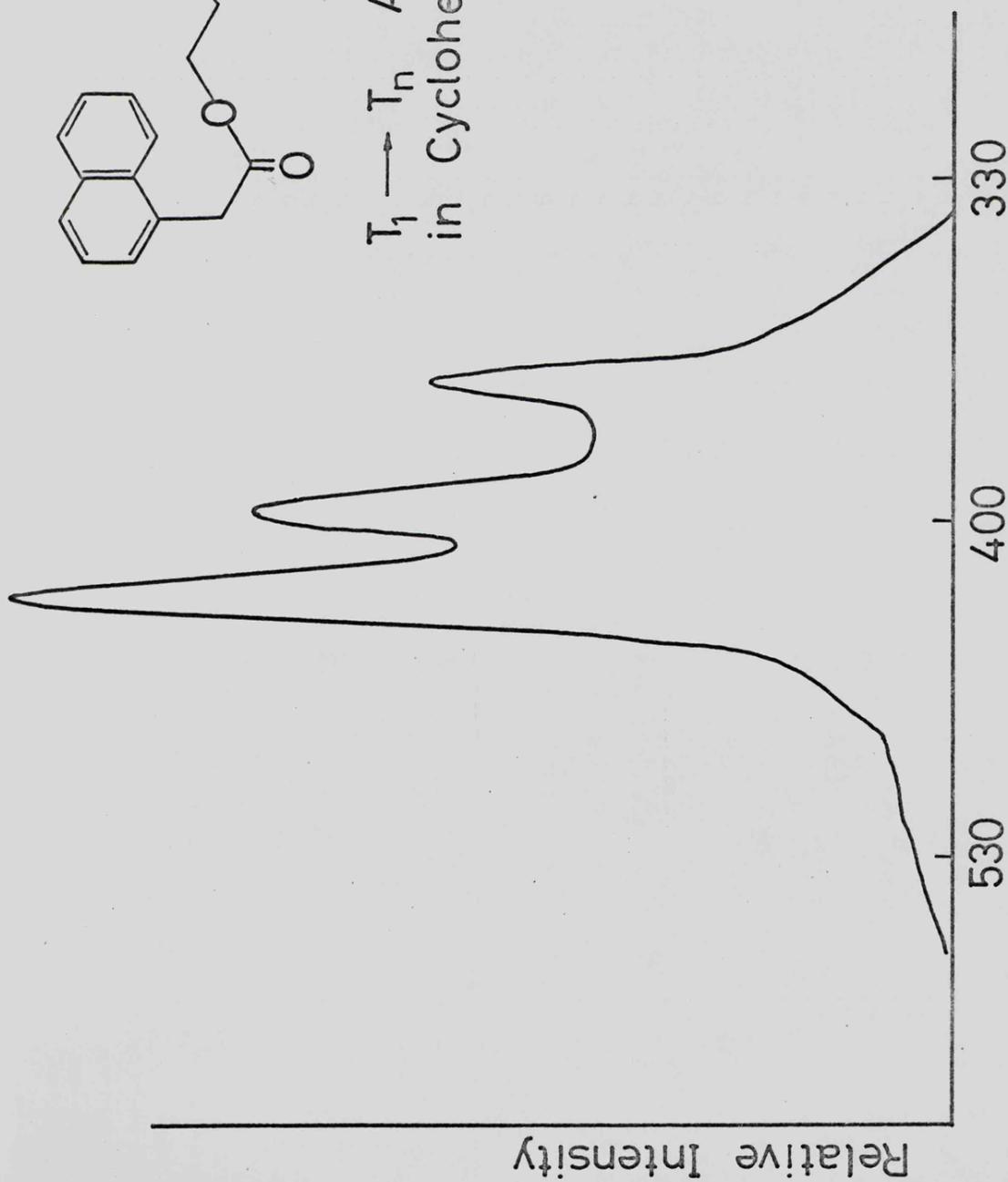
Wavelength (n.m.)
DIAGRAM 4.

Relative Intensity

57.

TABLE 11.

λ max.(NM) and optical densities of transient ($T_1 \longrightarrow T_n$) absorption spectra.[a]

Compound.	Solvent.	λ max.	Optical Density.[b]
naphthalene-$CH_2CO_2CH_2CH_2CH_2NMe_2$	Cyclohexane.	420,398,368	1.4 – 1.6
	95% Ethanol.	416,394,367	1.2 – 1.3
naphthalene-$CH_2CO_2CH_2CH_2CH_2NMe.Ph$	Cyclohexane.	420,396,367	1.6 – 1.8
	95% Ethanol.	416,394,364	1.5 – 1.7
naphthalene-CH_2CO_2Me	Cyclohexane.	420,396,367	1.7 – 2.0
	95% Ethanol.	416,394,368	1.7 – 2.0
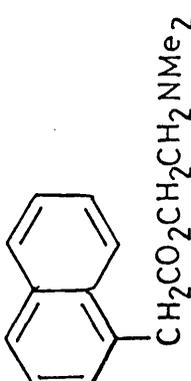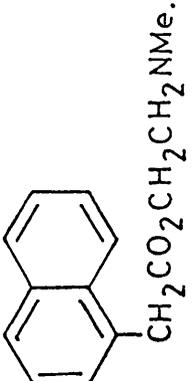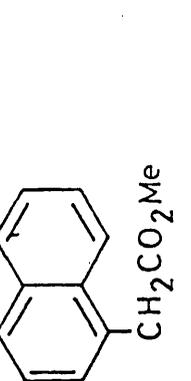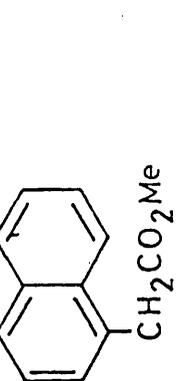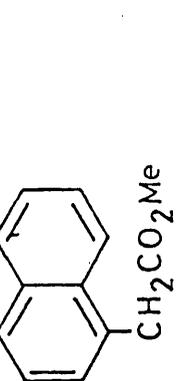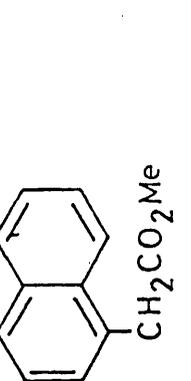
a. Recorded at a solute concentration of 10^{-4}M at room temperature.

b. Approximate optical densities for the most intense absorption (420 or 416NM).

Discussion.

The absorption spectra observed in these experiments are believed to be due to the naphthalene triplet. Comparison with published spectra of this particular species shows that the wavelengths agree fairly well.[88] Furthermore, spectra of exactly the same shape were obtained from the unquenched naphthalene standard.

Radical anions and cations formed as a result of the electron transfer process might be expected in ethanolic solution. Porter and Land[89] have identified the radical cation of p-methyl-N,N-dimethylaniline, it has a triplet absorption maximising at 460NM. This radical cation was not observed in the transient absorption spectra of 2. The radical anion of naphthalene is believed to absorb at 326NM[90] but this species was not observed either. There is also the possibility that the naphthalene radical anion is protonated in ethanol which would give the dihydronaphthyl radical, $C_{10}H_9^{\cdot}$, but this absorbs at a very similar wavelength (330NM) to the radical anion,[91] a region in which the spectra are blank.

It therefore appears that, contrary to the findings that intermolecular exciplexes formed between aromatic hydrocarbons and amines give radical ions in polar solvents, the intramolecular exciplexes studied here do not decay in this manner since only triplet hydrocarbon can be detected. Weller[92] has also failed to observe radical ion formation from the flash photolysis of intramolecular aromatic hydrocarbon-amine exciplexes.

The optical densities calculated from the absorption

spectra for 1 and 2 are fairly high in comparison to those

found for the standard and assuming Beer's Law is valid under

the conditions of the experiments then the concentrations

are also high. The optical densities for the absorptions in

cyclohexane are slightly higher than those in 95% ethanol,

and this would be expected on the basis of the mechanism

proposed to explain the fluorescence lifetimes of 1 and 2.

The mode of formation of the triplet naphthalene cannot be

determined as a result of the relatively long time scale

used for the work, but in cyclohexane it is likely to be

formed directly from the exciplex itself. Radical ion form-

ation is not a probable route in cyclohexane but it is in

ethanol and although such species could not be detected,

their formation cannot be precluded. Back electron transfer

in the solvated ion-pair can produce the triplet, although

this is believed to be a slow process ; the ground state

can also be reached directly in this manner. The formation

of the triplet directly from the non-relaxed exciplex may

also take place in ethanolic solution.

An interesting possibility for the formation of the

aromatic hydrocarbon triplet is that of intersystem crossing

from the singlet state exciplex. The resultant triplet excip-

lex may then decay into the triplet state of the hydrocarbon.

$$^1(Ar^{d-} \cdots Am^{d+})^* \longrightarrow {}^3(Ar \cdots Am)^* \longrightarrow {}^3Ar^* \cdots Am.$$
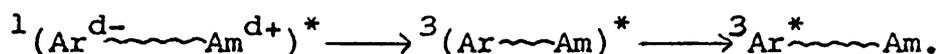
Direct evidence for this process has been found,[93] both

fluorescence and phosphorescence can be observed by excitat-

ion into a charge-transfer absorption band of an aromatic

hydrocarbon-acceptor complex. This is not an exciplex but the excited states obtained by excitation should be comparable.

2:1:4 INTRAMOLECULAR EXCIPLEX FORMATION: EFFECT OF TEMPERATURE UPON THE FLUORESCENCE SPECTRUM.

Results.

The temperature dependence of both monomer and exciplex fluorescence intensities have been recorded for compound $\underline{2}$ at $10^{-4}M$ in toluene solution. A plot of

$$\log_{10} \frac{I_e}{I_m [Q]} \quad \text{against} \quad \frac{1}{T}$$

is shown in Figure 4 where

I_e = intensity of exciplex fluorescence.

I_m = intensity of monomer fluorescence.

$[Q]$ = concentration of quencher.

T = temperature (K).

The plot clearly shows two different regions of linearity. The increase observed in the ratio I_e/I_m as the temperature is raised (i.e. the low temperature portion) reflects the fact that there is an increase in the encounter frequency of the excited and unexcited molecules, hence the rate of formation of the exciplex increases.

The decrease in the ratio at higher temperatures demonstrates that formation of the exciplex is a reversible reaction.

The method of Birks, Lumb and Monro[94] has been used to

FIGURE 4.

$10^{-4}M$ in degassed Toluene

$\log_{10}\left[\dfrac{I_E}{I_M(Q)}\right]$

$10^3/T$ °K
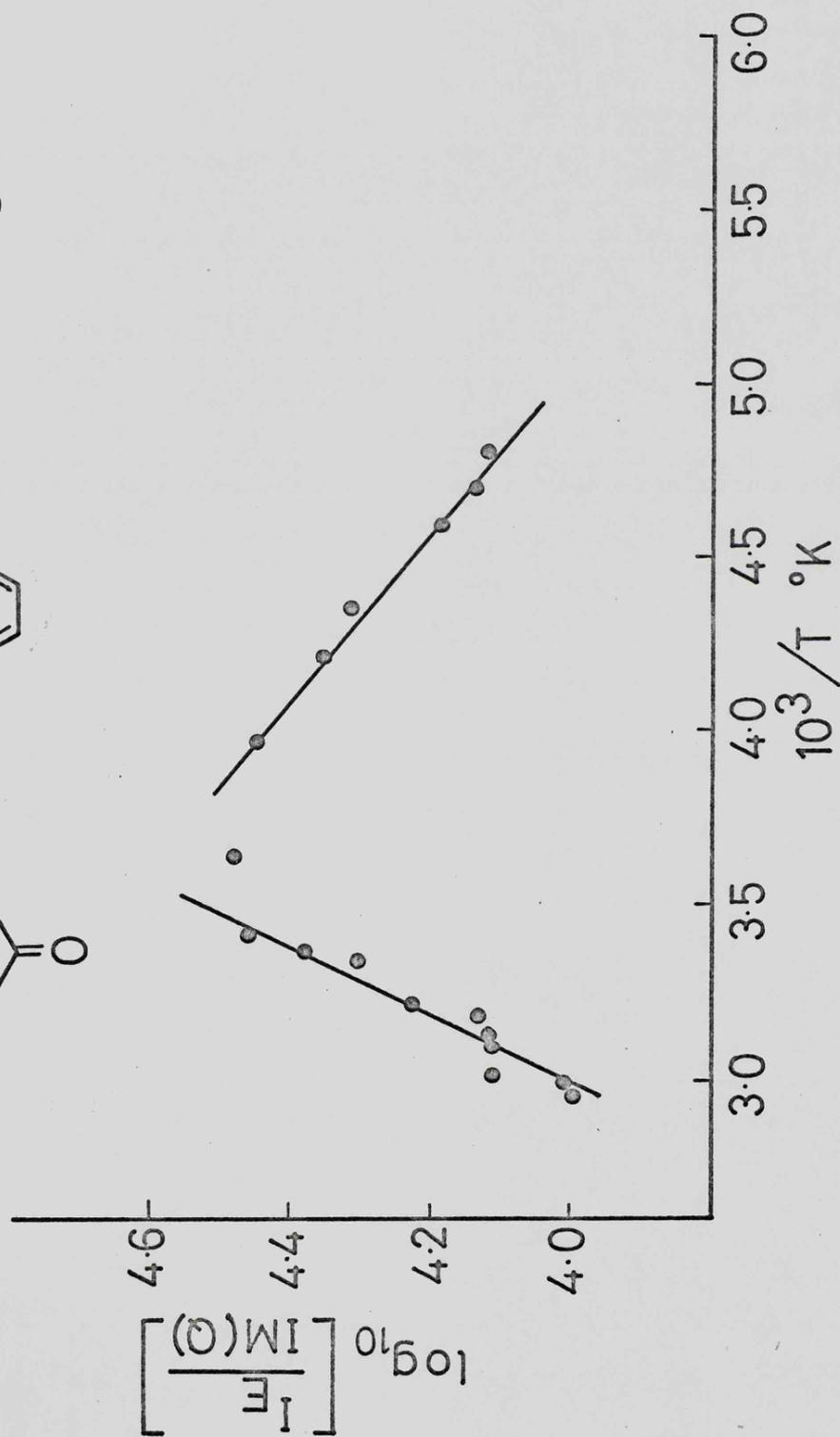
determine the enthalpy of formation ($-\Delta H^*$) of this exciplex from the slope of the high temperature portion of the plot. The low temperature region yields a value for the activation energy of exciplex formation (E_a).[a.]

$$-\Delta H^* = 5 \text{ kcal/mole} (\pm 2 \text{ kcal/mole}).$$

$$E_a = 1.5 \text{ kcal/mole.}$$

Discussion.

The value calculated for $-\Delta H^*$ is relatively low. Typical $-\Delta H^*$ values from the literature are,

    Naphthalene-triethylamine.   8.0 kcal/mole.[70]

    Anthracene-triethylamine.   4.1 kcal/mole.[71]

    Anthracene-N,N-diethylaniline.   10.2 kcal/mole.[71]

No data appear to be available either on intramolecular exciplexes or on the intermolecular naphthalene-N,N-dimethyl-aniline exciplex, from the values presented above it might be expected that $-\Delta H^*$ for this exciplex would be greater than 7 kcal/mole. A sandwich-pair conformation is not possible in this molecule (Section 2:1:1) which may decrease $-\Delta H^*$.

The activation energy required for formation of the exciplex is typical of the values found by Birks[94] for formation of the pyrene excimer. It is possible to calculate the activation energy of the diffusion controlled reaction from the following equation,

$$k_c = \frac{8RT}{3000\,\eta} = N_c \exp.\left[\frac{-E_c}{RT}\right]$$

where k_c = the diffusion controlled rate constant.

    N_c = constant.

    E_c = the activation energy.

a. See Appendix 1 for a kinetic treatment which enables ΔH^* and E_a to be calculated.

E_c for toluene has been calculated as 0.1 e.v. (2.3 kcal/mole).[94] The discrepancy between E_c and E_a for $\underline{2}$ in toluene solution is fairly small, hence E_a indicates that formation of the intramolecular exciplex is controlled by diffusion.

The repulsion energy, E_r, of the complex in its Franck-Condon ground state can be calculated from,

$$h(\tilde{\upsilon}_m - \tilde{\upsilon}_e^{max.}) = -\Delta H^* + E_r$$

where, $\tilde{\upsilon}_m$ is the frequency of the zero-zero transition of the aromatic hydrocarbon,

$\tilde{\upsilon}_e^{max.}$ is the frequency of maximum emission from the exciplex,

$\tilde{\upsilon}_m$ was estimated from the onset of fluorescence (314NM $\equiv$ 31850cm^{-1}) of a solution (10^{-4}M) of 1-naphthylacetic acid methyl ester in toluene. This is in good agreement with the value (315NM $\equiv$ 31750cm^{-1}) published for 1-methylnaphthalene[95]

$\tilde{\upsilon}_e^{max.}$ was taken as 23580cm^{-1} (424NM). Substitution of the known quantities gives E_r = 18.9 kcal/mole, this is high and is approximately the same as E_r values found for exciplexes formed with triethylamine.[71] E_r for $\underline{2}$ may indicate a large degree of "steric crowding" in the repulsive ground state of the complex.

2:1:5 INTERMOLECULAR EXCIPLEX FORMATION: EMISSION SPECTRA.

Results.

The fluorescence spectra of a number of aromatic hydro-carbon-amine mixtures have been recorded. The fluorescence from the hydrocarbon was always quenched but in many cases

a new fluorescence band could not be detected under the

conditions used.

Quenching of fluorescence with triethylamine.

The results of the investigations at room temperature

are summarised in Table 12. Attempts were also made to detect

exciplex fluorescence at lowered temperatures (down to approx-

imately, -100°), these have been noted in Table 12.

Quenching of fluorescence with 1,4-diazabicyclo(2,2,2) octane.

1,4-diazabicyclo(2,2,2) octane (DABCO) was unsuccessful

DABCO

in forming a fluorescent exciplex with both 9-cyano and

9-methylanthracene. The concentration of aromatic hydro-

carbon was 2×10^{-5}M and that of DABCO 10^{-1}M. Toluene sol-

utions were studied over a wide temperature range ($+20$ to

-105°).

Quenching of fluorescence with N,N-dimethylaniline.

A fluorescent exciplex was formed at room temperature

between 9-methylanthracene (2×10^{-5}M) and the aryl amine

(10^{-1}M) in both methylcyclohexane and toluene. The wave-

lengths of maximum exciplex emission were 470 and 501NM res-

pectively. Typical emission spectra are shown in Diagrams

5 and 6.

Stern-Volmer plot.

The rate constant (k_q) for quenching of anthracene

TABLE 12.

Emission from aromatic hydrocarbons in solutions containing triethylamine. [a]

Aromatic Hydrocarbon.	Concentration.	Concentration of Et_3N	Solvent.	Fluorescent. Exciplex.	λ max.(NM).
9-Methyl anthracene.	$2 \times 10^{-5}M$	$2 \times 10^{-3}M$	Methyl	NO	-
	"	$2 \times 10^{-2}M$	cyclohexane	NO	-
	"	$2 \times 10^{-1}M*$	and Toluene.	NO	-
9-Cyano anthracene.	$2 \times 10^{-5}M$	$2 \times 10^{-1}M$	Toluene.	NO	-
	$5 \times 10^{-5}M$	2M	Cyclohexane.	NO	-
	"	1M	"	NO	-
	"	0.5M	"	?	-

a. Room temperature 20 ± 3°.

*. Denotes that the temperature was lowered.

TABLE 12 (Continued.)

Aromatic Hydrocarbon.	Concentration.	Concentration of Et_3N	Solvent.	Fluorescent Exciplex.	λmax.(NM).
Anthracene.	5×10^{-5}M	up to 5×10^{-1}M	Cyclohexane.	NO	-
	"	7×10^{-1}M	"	YES	Broadening.
	"	1.33M	"	YES	490
	"	2M	"	YES	490
Pyrene.	10^{-5}M	7×10^{-2}M	Hexane.	NO	-
	"	7×10^{-1}M	"	YES	475
1-Methyl	2×10^{-5}M	2×10^{-1}M	Toluene.	YES	450
naphthalene.	10^{-4}M	2×10^{-1}M	Methyl cyclohexane.	YES	405
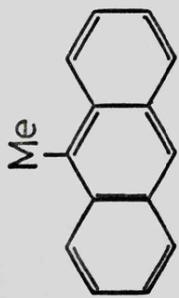
DIAGRAM 5

2×10^{-5} M+ $\left\}\right.$

1. 2×10^{-1} M Et$_3$Ṅ   Degassed methylcyclo—
                                    hexane at +15°.
2. 10^{-1}M Me$_2$N—⬡
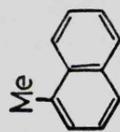
3. 2×10^{-5}M+Et$_3$Ṅ 2×10^{-1}M.
   Degassed methylcyclohexane at -25°.

68.

Et$_3$N̈(2 x 10^{-1}M) + 1.

Me — (anthracene structure) — 2 x 10^{-5}M

2. Me — (naphthalene structure) — 2 x 10^{-5}M

Degassed toluene at +15°

DIAGRAM 6

INTENSITY

350   400   450   500   550
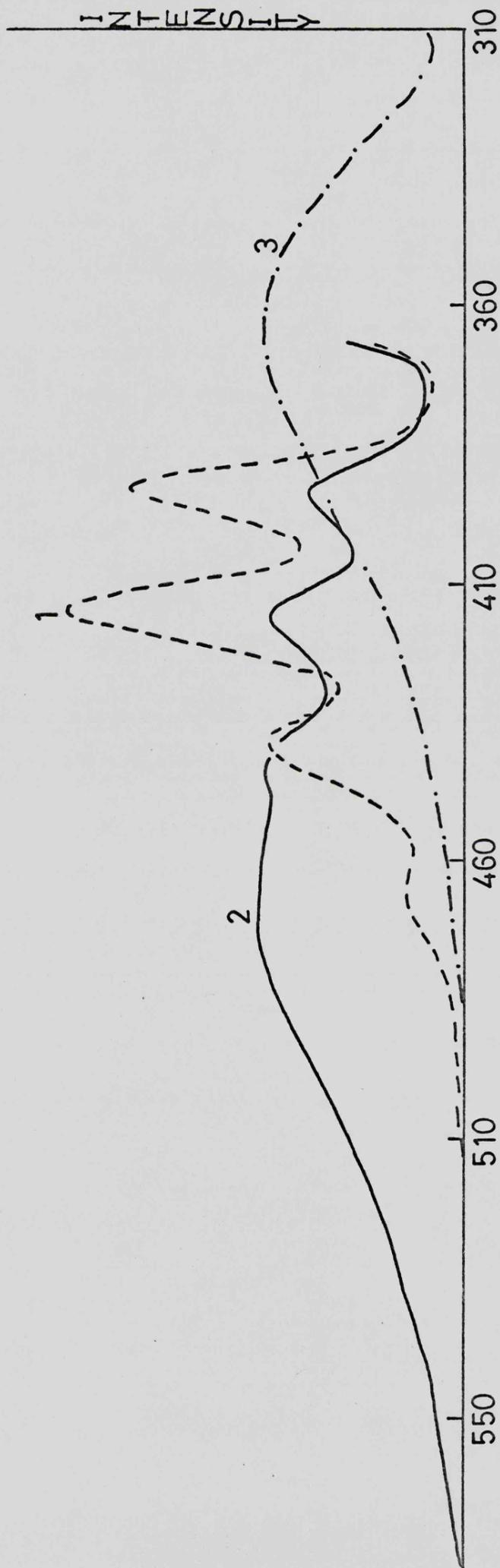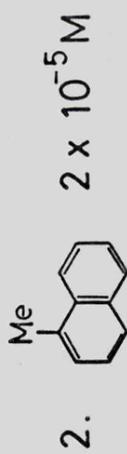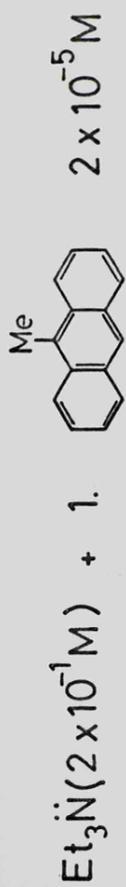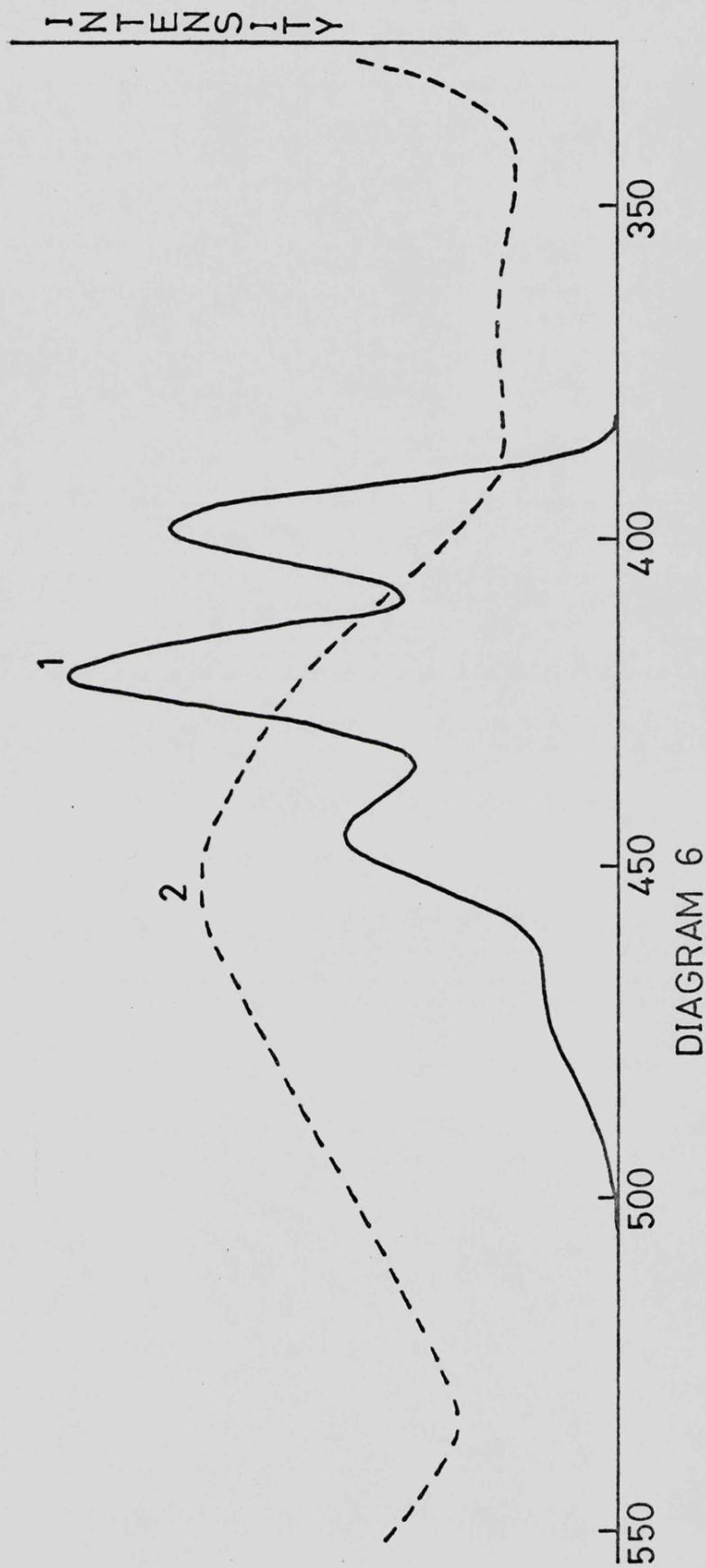
fluorescence by triethylamine has been obtained in cyclo-
hexane solution.

$$k_q = 0.56 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}.$$

It is possible to compare the k_q value with that predicted
for diffusion using $k_d = 8RT/3000\eta$ where η is the viscosity,[a.]
this gives,

$$k_d = 9.6 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}. \quad (18^\circ)$$

Discussion.

Anthracene and pyrene do not form an exciplex with
triethylamine as readily as naphthalene, since lower concent-
rations of the amine are required to produce a fluorescent
exciplex for the latter hydrocarbon. N,N-Dimethylaniline,
by contrast, undergoes electron transfer readily with both
naphthalene and anthracene.

There have been relatively few reports upon anthracene-
trialkylamine exciplexes in the literature. The work of
Knibbe[71] and Mataga[37] has already been noted. Nakajima[96]
has studied the anthracene-tri-n-butylamine exciplex,
finding that its formation was not quite diffusion controlled.
It has been suggested that the structural change of trialk-
ylamines during exciplex formation is responsible for their
lack of reactivity. This does not appear to be the only
reason for the difficulty encountered in the case of anth-
racene- triethylamine because k_q for both naphthalene[72]
and anthracene are not diffusion controlled, further, the
naphthalene-triethylamine exciplex is readily detectable.

a. Viscosity of cyclohexane taken from ref. 74.

The possibility of permanent chemical reaction between anthracene and the amine, leading to fluorescence quenching but no exciplex emission, was discounted for two reasons.

1. No change in the fluorescence intensity of anthracene could be detected during the course of the experiments.

2. Fluorescence quenching with DABCO does not lead to a fluorescent exciplex. DABCO has been found to quench but not react with aromatic hydrocarbons.[72,97]

A study of the energetics of exciplex formation yields what may be an answer to this problem. The energy of the exciplex can be calculated from the following equation,

$$E_e = I.P._Q - {}^1E_S - E.A._A.$$

This is similar to the equation given in Section 1:2 which was for the energetics of the charge-transfer process. The equation does ignore two terms, C the coulombic energy, and $\Delta H_{solv.}$ the energy of solvation of the exciplex. Substitution[a] into the equation gives the energies shown in Table 13.

TABLE 13.

Energies (kcal/mole) of aromatic hydrocarbon-amine exciplexes.

Hydrocarbon.	Triethylamine.	N,N-dimethylaniline.
Anthracene.	80.7	73.8
Pyrene.	81.64	74.83
Naphthalene.	81.73	74.83

These absolute values do not appear to be of importance by themselves, subtraction of the singlet energy of the

a. I.P., E.A. and ${}^1E_S$ values taken from refs., 74, 98 and 95 respectively.

aromatic hydrocarbon gives the energy of the exciplex with respect to the first excited singlet state of the hydrocarbon, the values obtained are presented in Table 14.

TABLE 14.

Energies (kcal/mole) of exciplexes relative to the singlet levels of the aromatic hydrocarbon.

Hydrocarbon.	Triethylamine.	N,N-dimethylaniline.
Anthracene.	+5.2	-1.7
Pyrene.	+4.64	-2.26
Naphthalene.	-9.27	-16.17

Absolute reliance cannot be placed upon the electron affinities and ionisation potentials (which may vary by up to 0.2 e.v.) nevertheless, a trend is apparent. Both anthracene and pyrene exciplexes formed with triethylamine are of higher energy than the singlet state of the parent hydrocarbon, which may explain why fluorescence is difficult to detect. By contrast, the same exciplex formed with naphthalene is of lower energy than the naphthalene singlet. The values obtained for N,N-dimethylaniline are negative, i.e. the exciplex is of lower energy than the singlet hydrocarbon. This treatment is therefore consistent with the experimental results. Emission from anthracene and pyrene-triethylamine exciplexes may be due to one or more factors.

1. High concentrations of amine increase the polarity of the medium thus stabilising the exciplex, although the dielectric constant of triethylamine is low.

2. The $\Delta H_{solv.}$ and C terms are sufficiently important in the solvents used to make the values in Table 14 negative.

3. The quantum yield of fluorescence is low so that high

concentrations of amine are required to see the exciplex

emission.

The emission spectra obtained from compounds in Series

III did not exhibit strong exciplex fluorescence which is

in general accord with the results obtained in this study.

2:1:6 SUMMARY.

The results presented above are consistent with the

previous work on intramolecular exciplexes, indicating that

whilst geometrical requirements do exist for exciplex form-

ation they are not critical.

The properties of intramolecular exciplexes often

parallel those of intermolecular exciplexes, however there

are some differences.

The exciplexes do fluoresce in polar solvents with red-

uced intensity which implies that radical ion formation

takes place, but these species cannot be detected by flash

photolysis. This may imply either that their formation is

rapidly reversible or that they rapidly decay. There is no

direct evidence for either process but the close proximity

of the donor and acceptor groups in an intramolecular excip-

lex may facilitate a back electron transfer from the radical

ions, this would then give rise to the longer fluorescence

lifetimes observed for the exciplexes in polar solvents.

Bolton[99] has in actual fact noted that back electron transfer

in radical ions which are not separated by a large distance

can be very rapid, e.g. for a separation of approximately 10Å the back transfer should take place in about 10^{-12} sec. It may therefore not be unreasonable to expect such a process to occur in an intramolecular exciplex.

2:2 SOME ASPECTS OF THE PHOTOCHEMISTRY OF HYDRAZINES AND HYDRAZIDES.

2:2:1 FLUORESCENCE QUENCHING OF 1-METHYL NAPHTHALENE.

Results.

It is believed that hydrazines and hydrazides have, in their preferred conformations, the two nitrogen atoms so arranged that eclipsing of the lone pair electron does not occur.[100,101] As a consequence, the non-amidic nitrogen of monoacylhydrazines should be able to quench the first excited singlet state of aromatic hydrocarbons by an electron transfer process i.e. in a similar manner to fluorescence quenching by tertiary amines.

The monoacylhydrazines $\underline{Y}$(1), (2) and (3) have been synthesised.
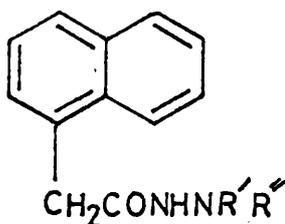
1. $R' = R'' = Me$.
2. $R' = Me$. $R'' = Ph$.
3. $R' = R'' = Ph$.

$\underline{Y}$

The nuclear magnetic resonance spectra of these compounds (see Section 2:2:5) indicate that they exist as two different isomers, termed $\underline{E}$ and $\underline{Z}$, as a result of restricted OC—N bond rotation.

$\underline{E}$ $\underline{Z}$
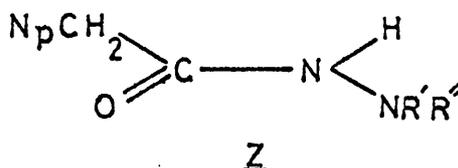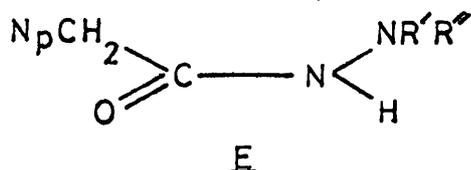
Where Np = 1-naphthyl.

It can be seen that only the E̲ isomer will be capable of intra-
molecular exciplex formation since the naphthalene and amino
groups are on the same side of the molecule. Very little
movement will be required to bring about the interaction nec-
essary for formation of an intramolecular exciplex (see Figure 5)
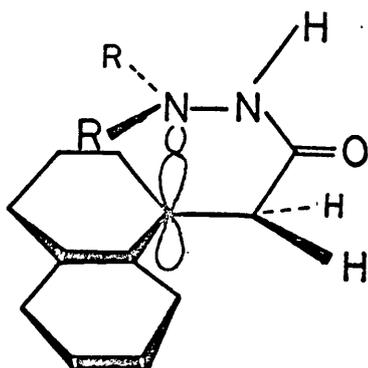
Figure 5.

In this conformation, the lone pairs of the nitrogen atoms
must be at an angle of approximately 90° to each other.

The fluorescence spectrum of each compound does exhibit
a long wavelength fluorescence band, this has been attributed
to exciplex formation. Compound X̲(1) did not exhibit a discrete
band, but a marked broadening of the monomer fluorescence could
be observed. The broadening was more pronounced in acetonitrile
than it was in toluene. The emissions were found to be indep-
endent of concentration in the range 10^{-5}M - 10^{-3}M. The results
are presented in Table 15 and the quantum yields of fluorescence
in Table 16. The fluorescence spectra of X̲(1), (2) and (3)
in acetonitrile are portrayed in Diagram 7.

TABLE 15.

Effect of solvent upon the wavelength(NM) of maximum exciplex emission shown by $\underline{V}$(2) and (3).

Solvent.	Compound.	
	$\underline{V(2)}$	$\underline{V(3)}$
Toluene.	395	410
Chloroform.	425	440
Dichloromethane.	439	450
Acetonitrile.	442	458
Ethanol.	450	470
N-methyl formamide.	480	485

TABLE 16.

Quantum yields of fluorescence of exciplex emission.[a]

Solvent.	Compound.		
	$\underline{V(1)}$	$\underline{V(2)}$	$\underline{V(3)}$
Acetonitrile.	0.0073	0.022	0.01443
Toluene.	–	0.046	0.038

a. Quantum yield of fluorescence was found to be 0.23 for

in acetonitrile.

CH_2CO_2Me
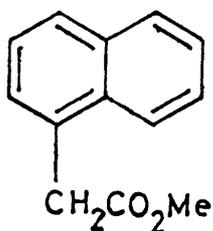
Flourescence Spectra of [naphthalene structure] CH$_2$CONHNR$_1$R$_2$ in Acetonitrile Solution.

A   R$_1$ = R$_2$ = Me
B   R$_1$ = Me. R$_2$ = Ph
C   R$_1$ = R$_2$ = Ph

CH$_2$CO$_2$Me

λ n.m. ⟶

DIAGRAM 7.

Relative Intensity

78.
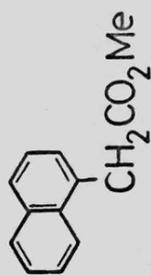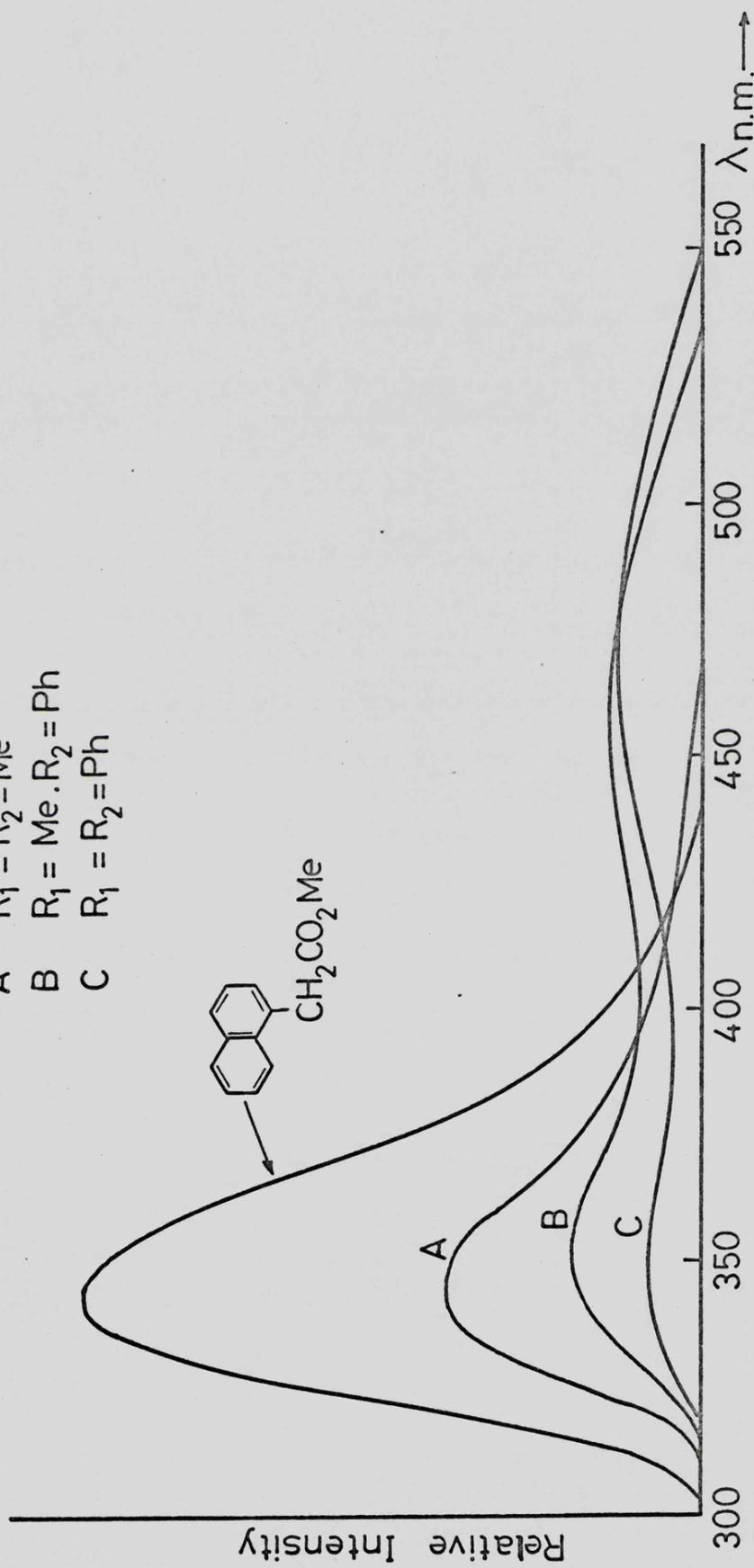
The fluorescence decay curve of the exciplex emission from $\underline{Y}(2)$ has been obtained,[a] it failed to exhibit any appreciable time delay in the build-up of exciplex fluorescence.

The ultra-violet absorption spectrum of each compound (10^{-4}M) was identical to that of mixtures of the parent hydrocarbon and the corresponding acetylhydrazine.

Dipole moments have been calculated for $\underline{Y}(2)$ and (3) using the method described in Section 2:1:1, a complex radius of 5.0 Å has been assumed,

$\underline{Y}(2)$ μ = 8.9 Debye.

$\underline{Y}(3)$ μ =10.0 Debye.

The ionisation potentials[b] have been determined for $\underline{15}$, $\underline{16}$, and $\underline{17}$ by the method of photoelectron spectroscopy.

PhCONHNMe$_2$ PhCONHNMe.Ph   PhCONHNPh$_2$

$\underline{15}$ $\underline{16}$ $\underline{17}$

The results are shown in Table 17.

TABLE 17.

Ionisation potentials(e.v.) of some monoacylhydrazines.

Compound.	Ionisation potential.	
	Adiabatic[c]	Vertical.
PhCONHNMe$_2$	8.02 ± 0.05	8.65 ± 0.04
PhCONHNMe.Ph	7.18 ± 0.06	7.74 ± 0.05
PhCONHNPh$_2$	7.07 ± 0.10	7.67 ± 0.06

a. This experiment was carried out with the help of Dr. C. Lewis of the Royal Institution, London.

b. These measurements were carried out by Dr. R. Lloyd of the University of Birmingham.

c. Measured at the band onset.

Discussion.

The spectral data are consistent with the new emission bands arising from an exciplex formed by electron transfer from the hydrazine moiety to the first excited singlet state of the naphthalene. In view of the data presented in Section 2:2:2 it does not appear possible to conclusively assign the emissions as arising from intramolecular interactions in non-polar solvents, but in ethanol at least, the exciplex will be formed intramolecularly.

The ionisation potentials of 15, 16 and 17 confirm that electron transfer from the non-amidic nitrogen of monoacyl-hydrazines is possible. The values obtained for those compounds with a terminal aryl amino group (16 and 17) are approximately the same as the ionisation potential of N,N-dimethyl-aniline. The ionisation potential of 15, which possesses a terminal N,N-dimethylamino group is appreciably higher as would be expected. The adiabatic ionisation potentials should be more representative of the energies involved in formation of the exciplex provided that the exciplexes themselves have lifetimes long enough to allow relaxation of the components to the most favourable conformation.

An important difference between exciplexes formed by amines and by hydrazides (both intramolecularly) is that the latter compounds exist as two isomers, only one of which can participate directly in exciplex formation. The Z isomer would have to undergo, as an essential step, rotation about the OC-N bond before exciplex formation could take place. It is not known whether sufficient energy is available in the formation of an exciplex for such barriers to be overcome.

The fluorescence decay curve of $\underline{Y}(2)$ did not show any long time delay in the build up of exciplex fluorescence, such a delay might have been expected if the $\underline{Z}$ isomer was capable of exciplex formation. Any possibility of the $\underline{Z}$ isomer participating via the equilibrium with the $\underline{E}$ isomer must be discounted on the basis of the time scale for this process, which is far greater than the fluorescence lifetime of any of the excited species involved.

The $\underline{E}$ isomer is therefore likely to be responsible for the fluorescence quenching of the naphthalene. It might be expected that the preferred conformation would be the sandwich-pair for $\underline{Y}(2)$ and (3) which have an aryl amino group i.e. in common with other exciplexes containing an aryl amine. The conformation shown in Figure 5 does not allow the phenyl ring to form a sandwich-pair unless the amino group lies on the periphery of the naphthalene ring. The restrictions imposed upon the geometry of the molecule may be the reason for the relatively low dipole moments of $\underline{Y}(2)$ and (3) compared to those of similar intermolecular exciplexes.

2:2:2 FLUORESCENCE QUENCHING OF 9-METHYLANTHRACENE.

Results.

The work described in Section 2:2:1 has indicated that monoacylhydrazines are efficient quenchers of the first excited singlet state of naphthalene, for this reason quantitative data have been obtained for the fluorescence quenching of 9-methylanthracene by these compounds using the Stern-Volmer

equation.

1-Methyl-1-phenylhydrazine (<u>18</u>), 1,1-diphenylhydrazine

(<u>19</u>) and 1-acetyl-2-methyl-2-phenylhydrazine (<u>20</u>) were used

to quench the fluorescence from 9-methylanthracene.

$$H_2NNMe.PH \qquad H_2NNPh_2 \qquad MeCONHNMe.Ph$$

<u>18</u>   <u>19</u>   <u>20</u>
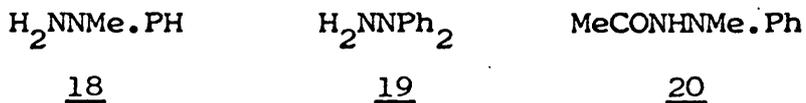
The Stern-Volmer plots showed that, in benzene and

acetonitrile solution, the quenching efficiency did not

increase linearly with an increase in the concentration of

the quencher (Figure 6). The deviation was less pronounced

in acetonitrile than in benzene and was absent when ethanol

was used as a solvent. Values for the quenching rate constant,

k_q, (derived from the Stern-Volmer quenching constant) have

been taken in the two regions of linearity. The values are

shown in Table 18 together with the approximate concentration

ranges in which they apply.

Ultra-violet absorption spectra were recorded for a

range of the solutions used in the Stern-Volmer plots, there

was no indication of ground state interactions or of absorpt-

ion of light by the quencher at the excitation wavelength

used.

No new emission bands were observed during these studies.

Attempts to produce fluorescent exciplexes of 1-methylnaphth-

alene in the prescence of <u>18</u>, <u>19</u> and <u>20</u> (each at 10^{-1}M) were

not sucessful although fluorescence quenching of the naphthal-

ene was evident.

<u>Discussion</u>.

The approximate rate constants, k_d, expected for a

Stern Volmer Plot for the Quenching of 9–Methylanthracene Fluorescence by $PhMeNNH_2$ in a) Benzene b) Acetonitrile and c) Ethanol Solution.
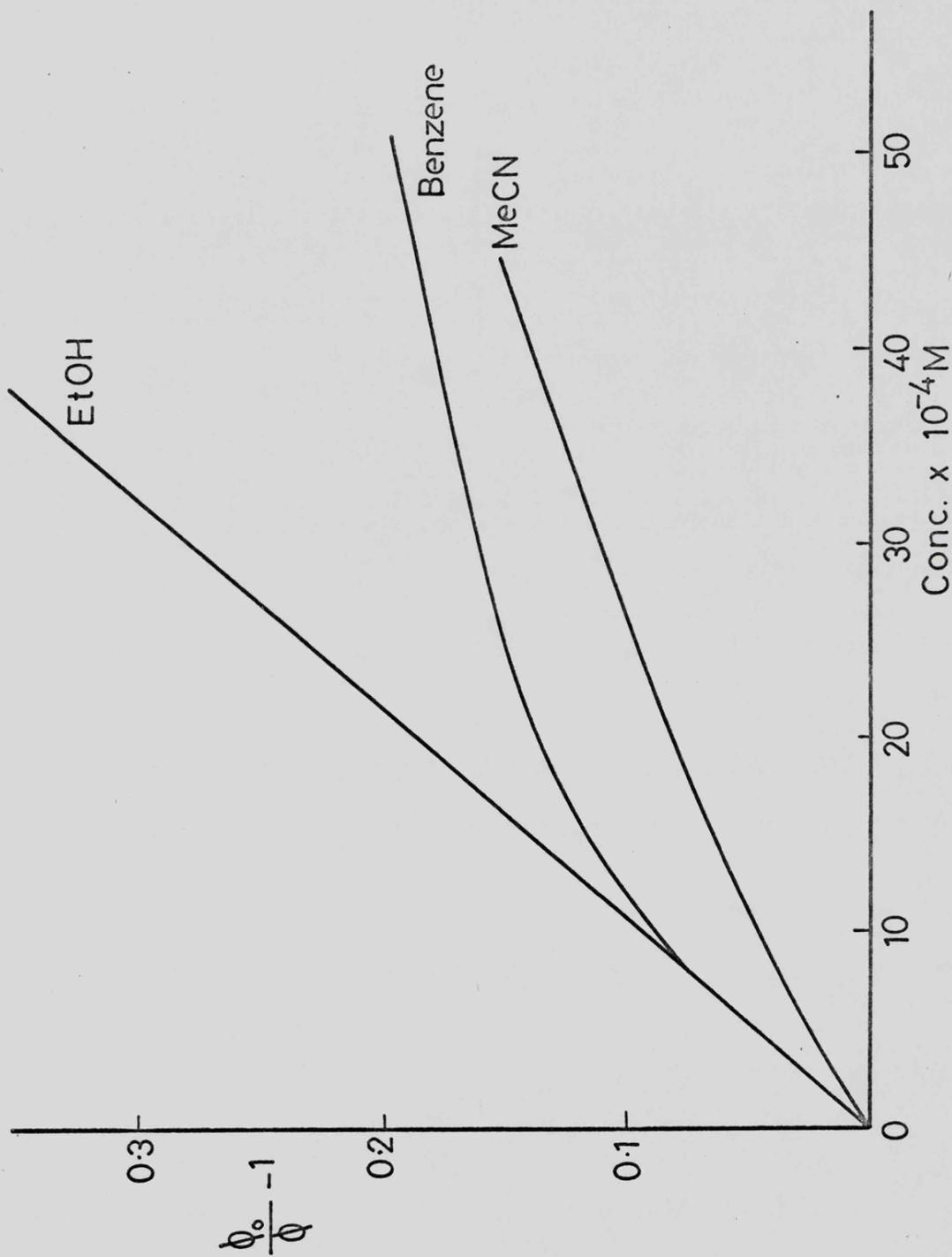
FIGURE 6.

TABLE 18.

Values of k_q^a. for quenching of 9-methylanthracene fluorescence.[b]

Quencher.	Solvent.		
	Benzene.	Acetonitrile.	Ethanol.
MeCONHNPhMe (18)	11.2 ($<1 \times 10^{-3}$M) 2.3 ($>1.25 \times 10^{-3}$M)		
Ph$_2$NNH$_2$ (19)	22.0 ($<6 \times 10^{-4}$M) 6.6 ($>9 \times 10^{-4}$M)	13.6 ($<1.6 \times 10^{-3}$M) 9.5 ($>2.2 \times 10^{-3}$M)	6.2
Ph.MeNNH$_2$ (20)	22.1 ($<1.5 \times 10^{-3}$M) 6.2 ($>1.8 \times 10^{-3}$M)	14.8 ($<1.0 \times 10^{-3}$M) 6.0 ($>1.4 \times 10^{-3}$M)	15.4

a. $\times 10^{-9}$ l mol^{-1} s^{-1}.

b. Calculated from $k_q \tau = K_Q$, where τ is the mean radiative lifetime of 9-methylanthracene taken as 5.0ns. See refs. 71 and 102. The approximate rate constants for diffusion, k_d, (at 18°) are;

Benzene: k_d = 14.8 $\times 10^9$ l mol^{-1} s^{-1}.

Acetonitrile: k_d = 26.8 $\times 10^9$ l mol^{-1} s^{-1}.

Ethanol: k_d = 9.7 $\times 10^9$ l mol^{-1} s^{-1}.

diffusion controlled reaction are shown at the foot of Table 18. It can be seen that when low concentrations of the quencher are used, k_q is of approximately the same magnitude as k_d. This indicates therefore that the fluorescence quenching is diffusion controlled i.e. hydrazines and hydrazides are efficient quenchers of aromatic hydrocarbon fluorescence. The values of k_q at higher concentrations (generally greater than $10^{-3}M$) indicate that the reaction is no longer diffusion controlled.

The variation of k_q with the concentration of the quencher is ascribed to an increase in the degree of association between the quencher molecules as the concentration is increased. The quenching efficiency should therefore be lower at high concentrations and this is reflected in the lower k_q value obtained from the appropriate linear portion of the plot.

A possible reason for the self-association is that hydrogen bonding takes place via the amino groups in both the hydrazines (NH_2-) and the hydrazides ($CONH-$). The straight line Stern-Volmer plots obtained in ethanolic solution can then be explained since the solute-solute interactions present in aprotic solvents would be replaced by solute-solvent interactions.

There is evidence in the literature that amines, amides and similar molecules hydrogen bond.

Hydrazides and amides are known to be associated in the solid state.[103] There is also some evidence that hydrogen bonding takes place in solution. Recently 7-azaindole has been shown to form hydrogen bonded pairs in hydrocarbon solution at room temperature. The appearance of a new fluor-

escence band was attributed to fluorescence from a tautomeric species formed by a double proton transfer after excitation.

The phoshporescence of aromatic amines capable of hydrogen bond formation has been found to be weak at high concentration (10^{-3}M) in non-polar glasses, lowering the concentration gave rise to normal phosphorescence.[105] Addition of small quantities of diethyl ether (to 10^{-3}M solutions) also gave normal phosphorescence. The results were suggested to be a result of hydrogen bonding between solute and solvent and hydrogen bonding which resulted in self-association of the amines.

The concentration dependence of the ultra-violet absorption spectra of aniline[106] and indole[107] has been studied. The changes observed in the spectra were attributed to hydrogen bond formation.

It therefore seems reasonable to explain the non-linearity of the Stern-Volmer plots in terms of self-association due to hydrogen binding, but there is no conclusive evidence that such a process is ultimately responsible for the observations.

It is interesting to note that hydrazines and acyl-hydrazines quench the fluorescence of 1-methylnaphthalene and 9-methylanthracene but do not give rise to exciplex emission. Tertiary amines are known to produce fluorescent exciplexes but primary and secondary amines do not.[108,109] Irradiation of mixtures of aromatic hydrocarbons and primary or secondary amines yields products that are likely to be formed by a radical mechanism.[109,110] Quenching rate constants however, suggest that the quenching process proceeds via the same

mechanism as that for tertiary amines i.e. exciplex form-
ation.[108] It is possible that proton transfer takes place

from the amine to the excited hydrocarbon within the exciplex.

An explanation of the lack of exciplex fluorescence from

the aromatic hydrocarbon-hydrazine system is that a rapid

proton transfer reaction takes place in the excited state.

$$ArH^* + R_2N - NH_2 \longrightarrow \left[\overset{\cdot}{ArH} \ldots\ldots R_2\overset{+}{N} - NH_2 \right]^* \longrightarrow ArH_2^{\cdot} + R_2\overset{+}{N} - \overset{-}{NH}.$$
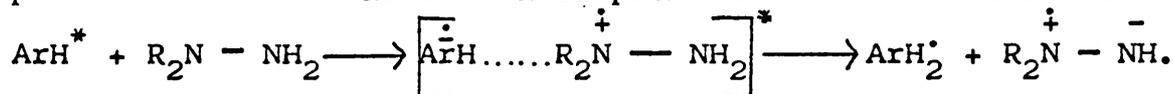
The mechanism is analogous to that proposed for primary and

secondary amines except that the nitrogen atom that part-

icipates in the electron transfer does not transfer the proton.

2:2:3 FLUORESCENCE OF HYDRAZINES AND HYDRAZIDES.

Results.

The indication from the non-linear Stern-Volmer plots

is that self association occurs for hydrazines and hydrazides

in aprotic solvents, it is therefore possible that this

phenomena may be shown by other properties of the compounds.

The fluorescence spectra of a number of these compounds (16,

18, 19, 20 and 21) were therefore recorded in fluid solution

at room temperature.

PhCONH.NMe.Ph   16

H$_2$NNR$'$R$''$ 18   R$'$ = Me.R$''$ = Ph.

    19   R$'$ = R$''$ = Ph.

MeCONHNR$'$R$''$ 20   R$'$ = Me. R$''$ = Ph.

    21   R$'$ = R$''$ = Ph.

Fluorescence bands at longer wavelength than expected were

observed for 18 and 19, whereas the fluorescence from 16, 20

and 21 was very broad. The fluorescence in protic

solvents e.g. ethanol, were similar to those obtained from aryl amines such as N,N-dimethylaniline. The results are summarised in Table 19 and the fluorescence recorded for 1,1-diphenylhydrazine shown in Diagram 8.

The fluorescence spectra were not independent of concentration, it was found that an increase in concentration of the solute led to an increase in the intensity of the long wavelength fluorescence. The effect was quite marked for the hydrazines (18 and 19) whereas the hydrazides (16, 20 and 21) showed only small changes. A concentration range of 10^{-5} - 10^{-2}M was used for these studies.

A further observation was that addition of small quantities (up to 4% by volume) of absolute ethanol or n-butylamine to solutions of 18 and 19 in benzene or cyclohexane led to a complete loss of the long wavelength fluorescence.

The ultra-violet absorption spectra of these compounds were found to be very similar to those of N,N-dimethylaniline and diphenylamine. A bathochromic shift was observed in each case for the lowest energy absorption band when the solvent was decreased in polarity (cyclohexane to 95% ethanol).

Discussion.

The fluorescence spectra of the hydrazines and hydrazides also indicate that self-association takes place in aprotic solvents since the new fluorescence bands are concentration dependent. Hydrogen bonding is indicated as the cause of the self-association since the addition of small quantities of solvents known to be capable of hydrogen bond formation causes the fluorescence spectrum to revert to that found in ethanol.

TABLE 19.

Wavelengths(NM) of maximum emission from hydrazines and hydrazides.[a]

Compound.[b]		Solvent.		
	Ethanol.	Acetonitrile.	Benzene.	Cyclohexane.
16 PhCONHNPhMe.	367	370	350	380
18 $H_2NNMe.Ph.$	358	354	354,410[c]	347,393[c]
19 $H_2NNPh_2.$	370	366	430	432
20 MeCONHMe.Ph.	360	370	360	355
21 $MeCONHNPh_2.$	383	388	375	370

a. All solutions at $10^{-4}M$

b. N,N-Dimethylaniline fluoresces at 346NM in cyclohexane and 365NM in ethanol. Diphenylamine fluoresces at 344NM in cyclohexane and 366NM in ethanol.(from ref. 105)

c. Denotes emission is a shoulder on the most intense band.
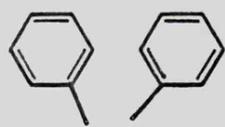
Fluorescence Spectra of $H_2N{-}N$ $10^{-4}M$ in various Solvents.

(a) 95% Ethanol (intensity scale x 2)

(b) Cyclohexane

(c) Benzene
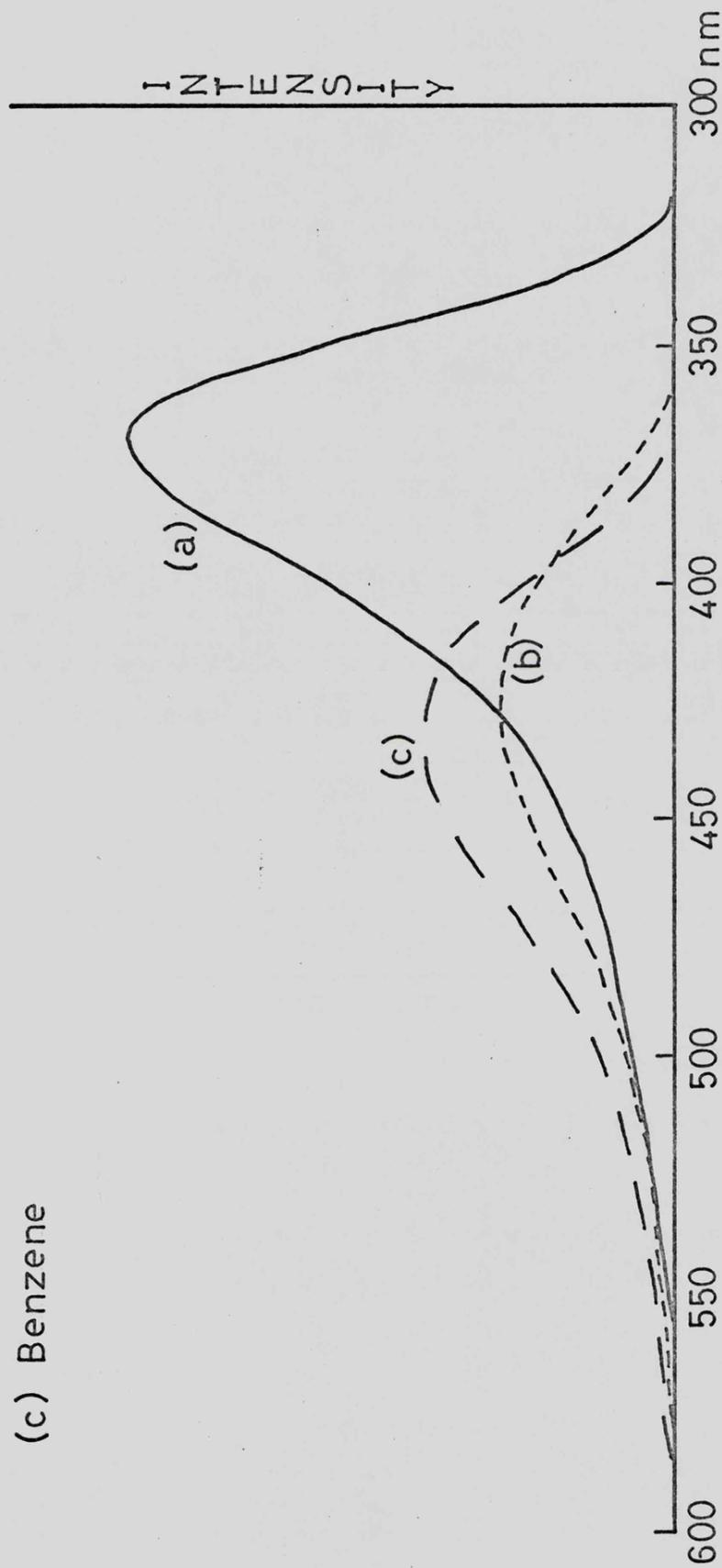
DIAGRAM 8

These results are thus compatible with the non-linear
Stern-Volmer plots and it appears that when the hydrazines
are capable of hydrogen bonding to molecules other than those
of their own type, they behave normally.

The new fluorescence bands observed may be due to
emission from an excited dimer formed between two of the
aryl amine moieties, although more than two molecules may
be involved depending on the degree of association.

2:2:4   IRRADIATION OF ACYL HYDRAZINES: PRODUCT STUDIES.

Results.

It has been noted that compounds exhibiting intra-
molecular exciplex formation are stable to certain photo-
chemical reactions.[66] Compounds $\underline{Y}$(1) and (2) are potentially
capable of undergoing a Norrish Type $\amalg$ reaction, i.e. abstract-
ion of a hydrogen atom by an excited carbonyl group.
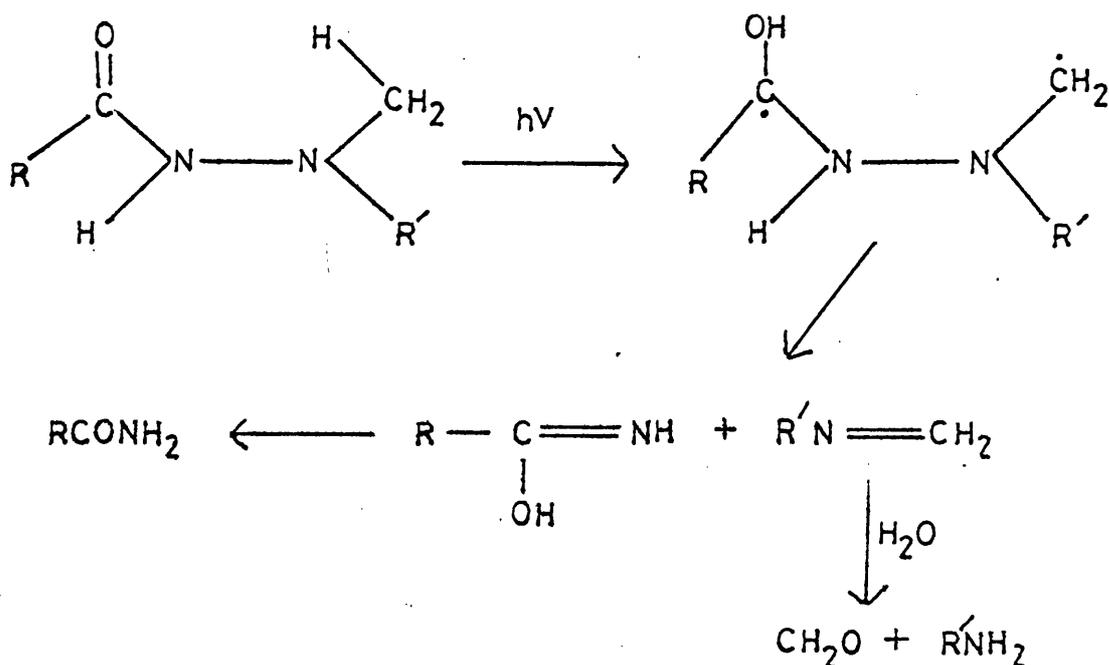
This type of reaction is well known for simple carbonyl compounds,[111] and the geometry of the hydrazides is such that hydrogens attached to the terminal N-methyl group can approach the carbonyl group closely.

Compounds $\underline{\mathbb{V}}(1)$ and (2) proved to be stable to irradiation (254NM) in both acetonitrile and isopropanol solution. A compound exhibiting a charge-transfer transition in its electronic absorption spectrum, N-(N-methylanilino) phthalimide was also found to be stable.

Compounds $\underline{22}$, $\underline{23}$ and $\underline{24}$ were found to react.

PhCH$_2$CONHNMe$_2$ PhCH$_2$CONHNMe.Ph   PhCH$_2$CONHNPh$_2$

$\underline{22}$ $\underline{23}$ $\underline{24}$

Irradiation in acetonitrile solution gave bibenzyl as the only identified product, whereas irradiation in isopropanol gave phenylacetamide and N-methylaniline (from $\underline{23}$), or diphenylamine (from $\underline{24}$). No amines could be identified in the products from $\underline{22}$. It is interesting to note that these compounds are the phenylacetic acid analogues of $\underline{\mathbb{V}}(1)$ and (2), which do not react.

1-Acetyl and 1-benzoylhydrazines were also found to react. No evidence was found for the presence of imines in the products obtained from the reaction of $\underline{16}$ and $\underline{20}$.

MeCONHNMe.Ph   PhCONHNMe.Ph

$\underline{16}$ $\underline{20}$

The expected hydrolysis product of the imine, i.e. aniline, could not be detected. The identified products from irradiation of these compounds was the corresponding acid amide and the amine which would be produced by cleavage of the

N — N bond. Free hydrazines could not be detected in any

of the reactions.

The products identified with the yields obtained are

shown in Table 20. An important point is that the yield

of amide in isopropanol is high compared to that found in

acetonitrile.

Discussion.

The stability of the naphthalene compounds can be due

to one of two reasons.

1. The naphthalene group inhibits reaction via the triplet

state as a result of its low lying triplet levels.

2. Exciplex formation acts as a sink for singlet excitation

energy.

The stability of the phthalimide is probably due to

similar reasons since this compound exhibits a charge-transfer

transition (Section 2:5:1).

The identification of bibenzyl as a product from the

irradiation of 22, 23 and 24, is not consistent with reaction

taking place by a Norrish Type Ⅱ reaction. The fact that

1-acetyl and 1-benzoylhydrazines yield N-methylaniline and

diphenylamine as products is also evidence that this mechanism

is not important.

The formation of the amines in acetonitrile can be

explained by a mechanism in which radicals are formed by

cleavage of the N — N bond.
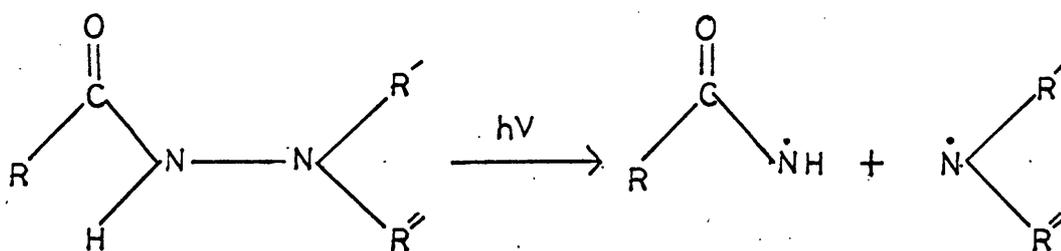
TABLE 20.

Products[a] obtained by irradiation[b] of monoacylhydrazines in acetonitrile and isopropanol.

HYDRAZIDE.	ACETONITRILE.	ISOPROPANOL.
$MeCONHNMe_2$.	$MeCONH_2$ (5%)	$MeCONH_2$ (7%) $HCONHNMe_2$ (<1%)
$MeCONHNMe.Ph$.	$MeCONH_2$ (2%) $PhNHMe$ (15%)	$MeCONH_2$ (76%) $PhNHMe$ (41%)
$PhCONHNMe_2$.	$PhCONH_2$ (13%)	$PhCONH_2$ (49%)
$PhCONHNMe.Ph$.	$PhCONH_2$ (83%) $PhNHMe$ (30%)	$PhCONH_2$ (80%) $PhNHMe$ (8%)
$PhCONHNPh_2$.	$PhCONH_2$ (38%) Ph_2NH (38%)	$PhCONH_2$ (80%) Ph_2NH (50%)
$PhCH_2CONHNMe_2$.	$(PhCH_2)_2$ (21%)	$Ph(CH_2)_2$ (Trace) $PhCH_2CONH_2$ (70%)
$PhCH_2CONHNMe.Ph$.[c]	$(PhCH_2)_2$ (47%)	$Ph(CH_2)_2$ (Trace) $PhCH_2CONH_2$ (61%) $PhNHMe$ (34%)
$PhCH_2CONHNPh_2$.[d]	$(PhCH_2)_2$ (15%)	$Ph(CH_2)_2$ (Trace) $PhCH_2CONH_2$ (39%) Ph_2NH (26%)

a. Yields are corrected for the amount of starting material consumed in the reaction.

b. Irradiation time was four hours with light of wavelength 254NM.

c. Irradiated for two hours in isopropanol.

d. Irradiated for twenty hours in acetonitrile.

Presumably this reaction pathway would be facilitated by R

substituents capable of stabilising the incipient amino

radical.

The formation of bibenzyl could also arise via a radical

mechanism, in this case fission of the benzylic methylene-

carbon bond takes place in preference to the N — N bond, thus

forming the stable benzylic radical.
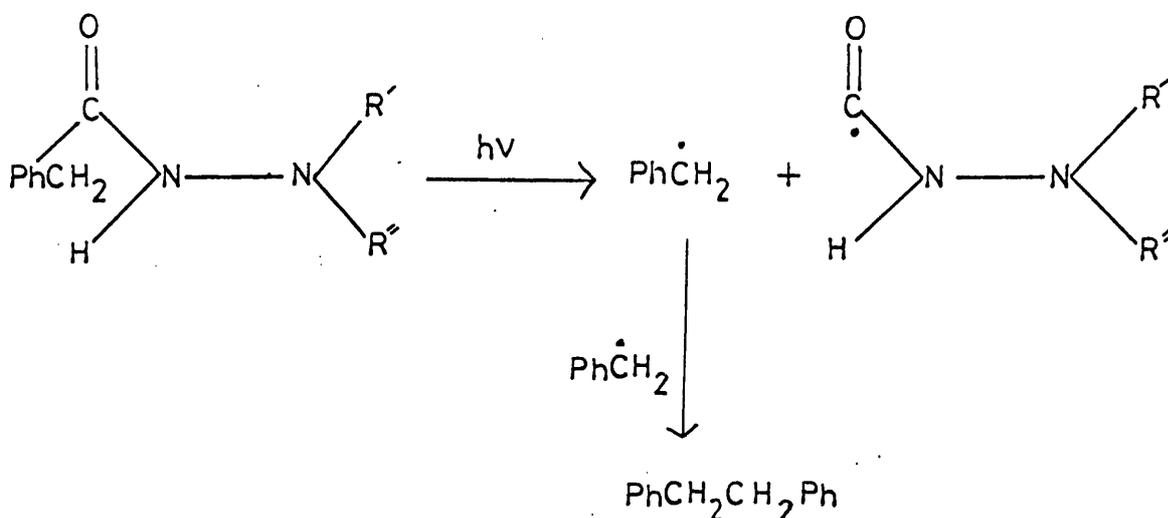
The reactions appear to proceed via a free radical

mechanism rather than a concerted process in acetonitrile,

hence the use of a good hydrogen donor as solvent, e.g. isop-

ropanol, might be expected to increase the amide yields. This

was found to be the case, which is in agreement with a mech-

anism involving N — N bond fission. The products observed

from 22, 23 and 24 change, only trace amounts of bibenzyl are

formed, the major product becoming the amide. It is there-

fore possible that the mechanism changes in isopropanol. Bond

fission may be less important and, in the presence of a good

hydrogen donor, the excited hydrazide may abstract hydrogen

from the solvent. The radical so produced may then undergo

further reaction.

$$R'\!-\!\underset{H}{\overset{O}{\underset{|}{\underset{\displaystyle C}{\|}}}}\!-\!N\!-\!-\!N\overset{R'}{\underset{R''}{\diagup}} \quad \xrightarrow{\text{hV}} \quad R'\!-\!\underset{H}{\overset{OH}{\underset{|}{\underset{\displaystyle C}{\cdot}}}}\!-\!N\!-\!-\!N\overset{R'}{\underset{R''}{\diagup}}$$

$$R'\overset{OH}{\underset{\displaystyle C}{\diagup}}\!=\!NH \quad + \quad \cdot N\overset{R'}{\underset{R''}{\diagup}}$$
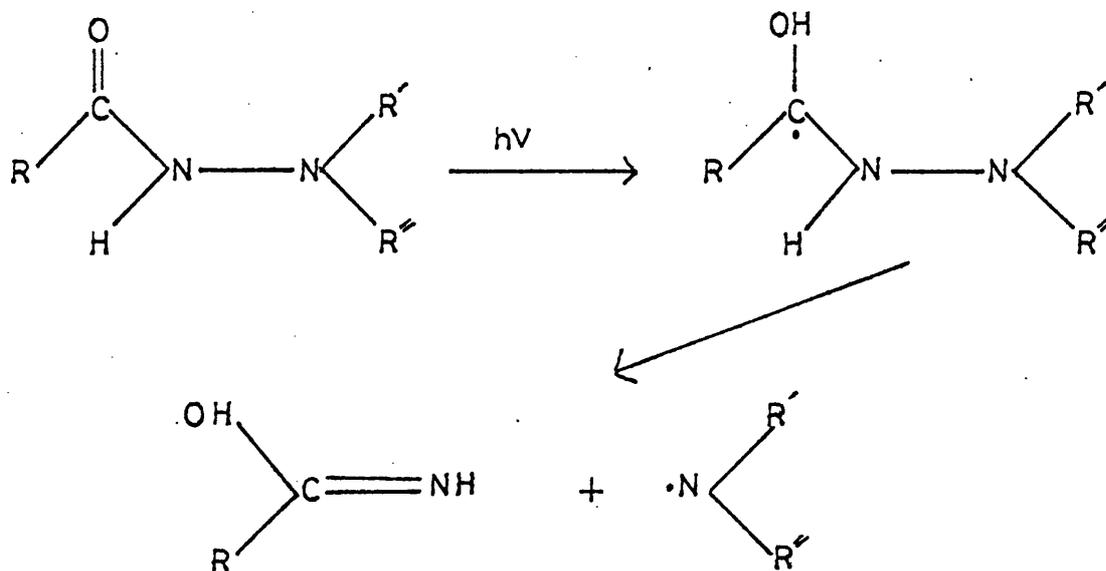
A similar reaction has been observed for the excited carbonyl

group of esters in which hydrogen abstraction followed by

fragmentation of the radicals takes place.[112]

A recent publication[113] describes the products obtained

from irradiation of 2,2-diacylhydrazines. The reactions

do not appear to proceed via N — N bond fission, but the non-

amidic nitrogen is not fully substituted. The presence of the

hydrogen on this amino group will destabilise any incipient

amino radical relative to a disubstituted amino group and

this may be the reason why cleavage of the N — N bond does

not take place. Low yields (1 - 2%) of bibenzyl were obtained

from hydrazides derived from phenyl acetic acid after irradiat-

ion in methanol.

2:2:5   NUCLEAR MAGNETIC RESONANCE SPECTRA OF HYDRAZIDES.

Results.

The N.M.R. spectra of compounds in Series X

were found to be more complex than expected, neither the methylene group, nor the methyl group attached to the terminal amino group, were observed as singlets. The N.M.R. spectrum of one of them, $\underline{Y}(1)$, is shown in Diagram 9. The effect of temperature upon the N.M.R. spectra of $\underline{Y}(1)$ and (2) was studied, the signals (from both $-CH_2-$ and $-NMeR$ groups) were found to collapse to a singlet at high temperature. The exchange rates between the two sites have been determined at the coalescence temperature and the free energies of activation for the rate determining stereochemical process calculated from the Eyring equation,[114]

$$\Delta G^{\ddagger} = 2.303RT(10.319 + \log T - \log k)$$

This equation is only strictly applicable for those systems in which there is an equal population of the two sites. Compound $\underline{Y}(2)$ exhibits a non-equivalent population, consequently the term $\log k$ has to be modified since two k values are involved corresponding to the forward and the backward reactions.

Consider a particular magnetic nucleus involved in a reversible exchange between two sites A and B, and let the residence times in the sites be τ_A and τ_B. The rates of transfer will be given by first order rate constants which are the reciprocal of these quantities,

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B$$
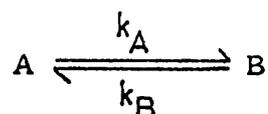
where $k_A = 1/\tau_A$ and $k_B = 1/\tau_B$

The equilibrium constant for the process K, will be given by
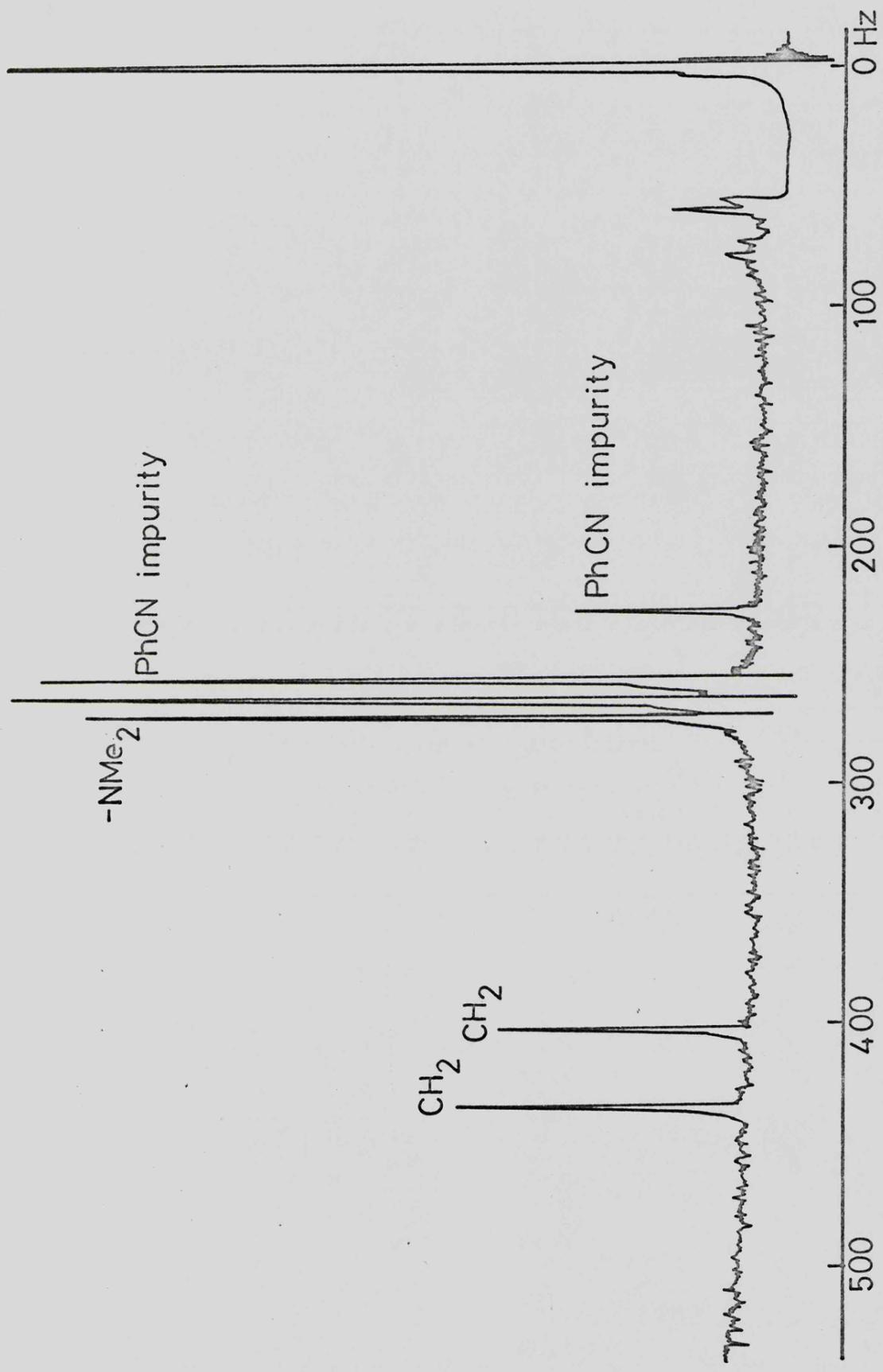
DIAGRAM 9

NMR Spectra of $\overline{V}$ (1) in Benzonitrile solution at room temperature.

$$K = \frac{[A]}{[B]} = \frac{k_A}{k_B} = \frac{\tau_B}{\tau_A}$$

hence, $\quad \tau_A = \dfrac{\tau_B}{K}$ $\qquad\qquad\qquad\qquad\qquad$ 1.

The total relaxation rate of the nucleus, τ , in sites A

and B will be given by

$$\tau = \frac{\tau_A \cdot \tau_B}{\tau_A + \tau_B} \qquad\qquad\qquad 2.$$

Substitution for τ_A from 1. into 2. gives,

$$\tau_B = \tau(K^2 + K)$$

similarly, substitution for τ_B gives,

$$\tau_A = \frac{\tau(1 + K)}{K}$$

τ can be evaluated from the known equation,[114]

$$\tau = \frac{1}{\sqrt{2} \cdot \pi \cdot \Delta v}$$

where Δv is the separation (in Hz) between the signals from

sites A and B. K can be obtained from the integration of the

two signals. τ_A and τ_B can be calculated from these values,

which allows k_A and k_B, and $\Delta G_A^{\ddagger}$ and $\Delta G_B^{\ddagger}$, to be calculated

in turn. The results are shown in Table 21, where A relates

to the minor "isomer".

The changes induced in the N.M.R. spectrum by increas-

ing the temperature were found to be reversible in all cases.

The N.M.R. spectrum of $\mathfrak{L}(2)$ was recorded at temperatures

down to -60° (in $CDCl_3$) but no further splitting of the

signals was observed.

TABLE 21.

Spectral data and Free Energy of Activation for conformational interchange in monoacylhydrazines.[a]

	$V(1)$[b]		$V(2)$[c]		$V(2)$[b]
	$-NMe_2$	$-CH_2-$	$-NMe_2$	$-CH_2-$	$-NMe_2$
$\Delta\nu_{AB}$ (Hz)	6	32	12	11	8
T_c^o	69	80	66	77	71
K	1.0	1.0	0.185	0.175	0.43
k_A (sec^{-1})	26.6	142	8.33	7.3	14.1
k_B (sec^{-1})	26.6	142	243	237	58.1
$\Delta G_A^{\ddagger}$ (kcal/mole)	15.2	14.1	12.9	19.1	18.9
$\Delta G_B^{\ddagger}$ (Kcal/mole)	15.2	14.1	12.4	16.7	17.9

a. $\Delta G^{\ddagger}$ values refer to the coalescence temperature T_c.

b. In benzonitrile solution.

c. In d_3-acetonitrile solution.

Discussion.

    Three intramolecular processes are of importance in relation to the N.M.R. spectra of these compounds.

1.   Inversion at the terminal nitrogen.

2.   Rotation about the N — N bond.

3.   Rotation about the OC—N bond.

The barriers to these processes have been the subject of considerable interest (see for example refs. 103, 115, 116). Recent work[117] on substituted hydrazines has indicated that inversion at nitrogen is unlikely to be the rate determining stereochemical process.   Hence $\Delta G^{\ddagger}$ refers to restricted rotation about OC—N or N — N bonds in these molecules.   Such restrictions can give rise to four different isomers as shown in Figure 7 where R = 1-naphthyl.
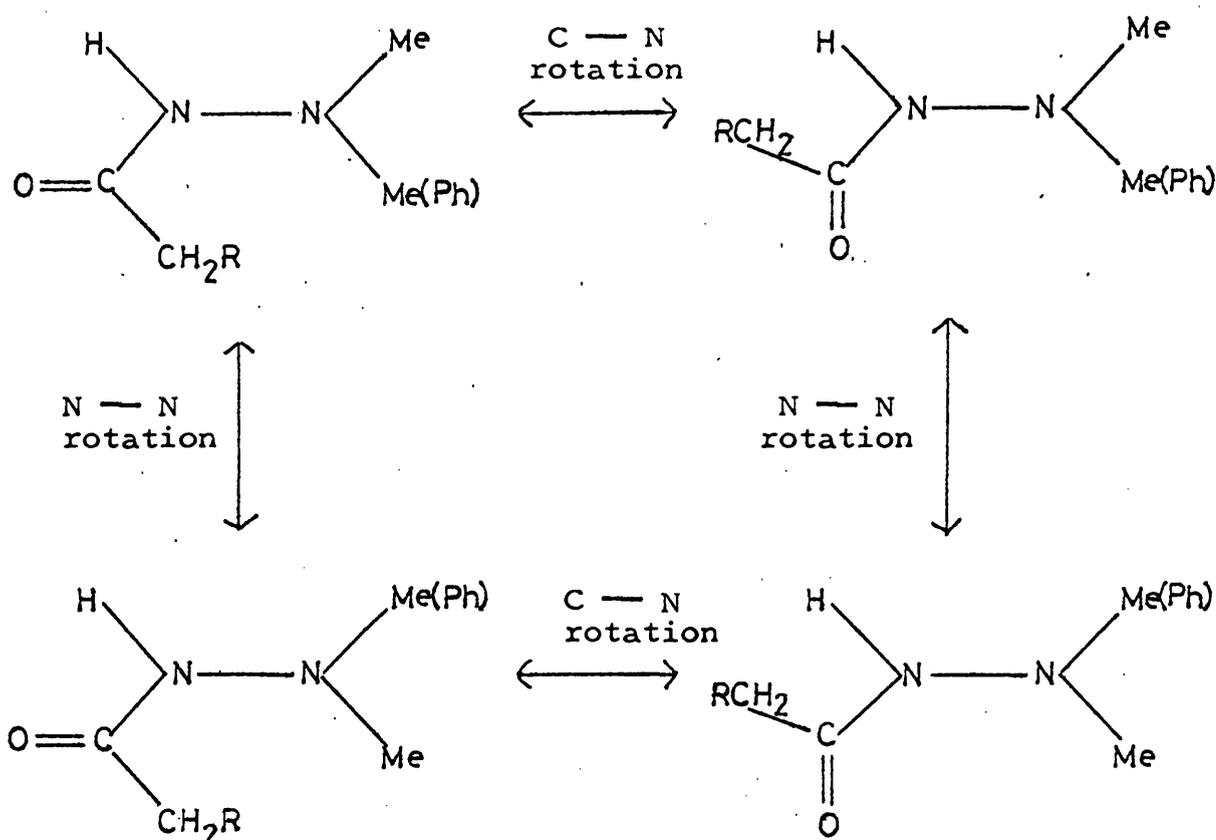
Figure 7.

Isomers obtained due to restricted OC—N and N—N bond rotation.

The two possible restricted bond rotations cannot be distinguished in $\underline{\underline{V}}$(2) since both would give rise to two different environments for the $-CH_2-$ and $-NMePH$ groups. The non-equivalence observed for the $-NMe_2$ group can also be explained by either restricted $N - N$ or $OC-N$ bond rotations. However, the observation of the two signals for the $-CH_2-$ group in $\underline{\underline{V}}$(1) can only be due to restricted rotation about the $OC-N$ bond. This result is in agreement with an N.M.R. study of 2-acetyl-1,1-dibenzylhydrazine in which the onset of fast rotation about the $N - N$ bond was found to take place at $30°$ whereas a temperature of $80°$ was required to induce fast rotation about the $OC-N$ bond.[117] Hindered rotation about the $OC-N$ bond has also been suggested as the reason for the non-equivalence of the methyl groups in various acetyl-hydrazines.[117] It is not possible to tell if hindered $N - N$ bond rotation is important for compounds in Series $\underline{\underline{V}}$ since the geometry of the molecules does not allow this particular effect to be isolated.

The isomers resulting from restricted $OC-N$ bond rotation are termed $\underline{E}$ and $\underline{Z}$,

$\underline{E}$ $\qquad$ $\underline{Z}$
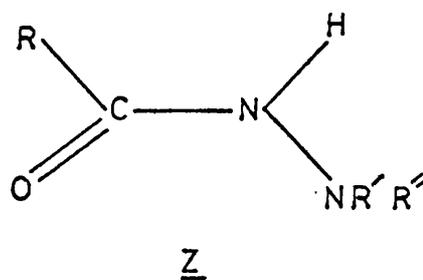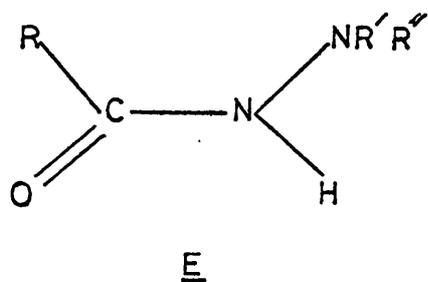
although their existence cannot be proved for $\underline{\underline{V}}$(2) it

seems reasonable to assume that hindered OC–N bond rotation

exists in this molecule since the methylene group does not

appear as a singlet for either $\Psi(1)$ or $\Psi(3)$. The barriers

determined (Table 21) are of a similar magnitude to those

reported in other amides.[116, 118, 119]

Results.

·A number of salts of N,N-diethyl-2-(1-naphthyl) ethyl-amine with hydrogen halides and alkyl halides have been syn-thesised (compounds 25 - 29).
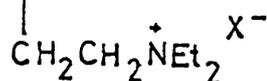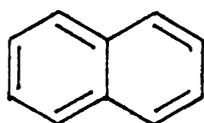
25	R = H	.	X = Cl⁻ .
26	R = H	.	X = Br⁻ .
27	R = H	.	X = I⁻ .
28	R = Et	.	X = Br⁻ .
29	R = Et	.	X = I⁻ .

A similar compound, 30 has also been prepared.
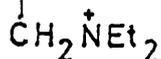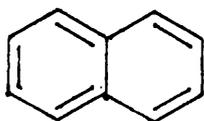
30

The emission spectrum of each compound was recorded, both naphthalene fluorescence and a longer wavelength (solvent dependent) band were observed, although 30 only showed a broad-ening of the naphthalene fluorescence. The effect of solvent polarity was found to be typical of that found for excited state charge-transfer complexes i.e. increasing polarity caused the emission to shift to longer wavelengths. The new fluorescence bands have been attributed to exciplex formation. The quantum yields of fluorescence are shown in Table 22 for 25 - 29.

TABLE 22.

Quantum yields and wavelengths of maximum emission of fluorescence for salts 25 - 29 and 1-methylnaphthalene.[a]

Compound.	Quantum Yield.			
	Monomer	λ max. (NM)	Exciplex	λ max. (NM)
25	0.051	350	0.020	490
26	0.041	350	0.023	490
27	0.037	350	0.041	490
28	0.09	350	0.006	490
29	0.08	350	0.013	490
1-methylnaphthalene.	0.1	350	-	-

a. In acetonitrile solution (approximately 10^{-4}M).

The solvent dependence of 26 was studied for a wide range of solvents, emission from this compound in some of the solvents at room temperature is shown in Diagram 10 and a plot of λ max. (NM) against E_T[b] in Figure 8. The other compounds were not studied in such detail but the effect upon the exciplex fluorescence was found to parallel that obtained for 26 in benzene and acetonitrile solution. Very similar wavelengths were observed for 25 - 29 in the various solvents.

The salts exhibit exciplex fluorescence in aprotic solvents, but a striking difference was observed in protic solvents such as ethanol and water, it was possible to observe only unquenched naphthalene fluorescence.

b. A solvent polarity scale based on the sensitivity of the charge-transfer absorption band of pyridinium phenol betaines to solvent polarity.[120]
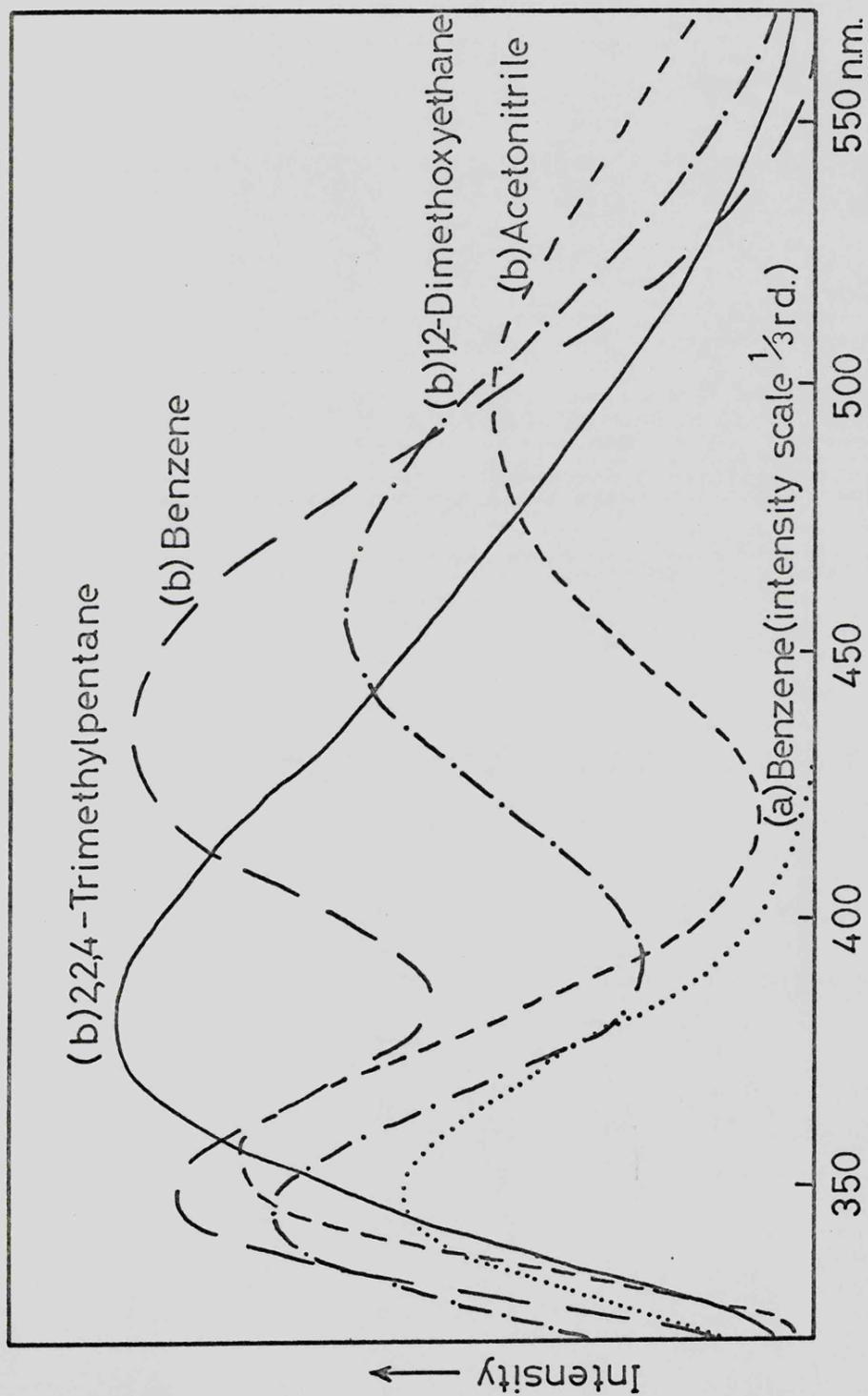
DIAGRAM 10

Fluorescence Spectra of (a) 1-Methylnaphthalene (10^{-4} M),

(b) 26 (10^{-4} M) in various solvents.

Benzene

N-Methylformide

●Dimethylsulphoxide

●MeCN

Dimethylformide

● Pyridine

● 1,2-Dimethoxyethane

●Dichloromethane

520

500

450

460

440

50   60   70   80   90

λ max n.m.
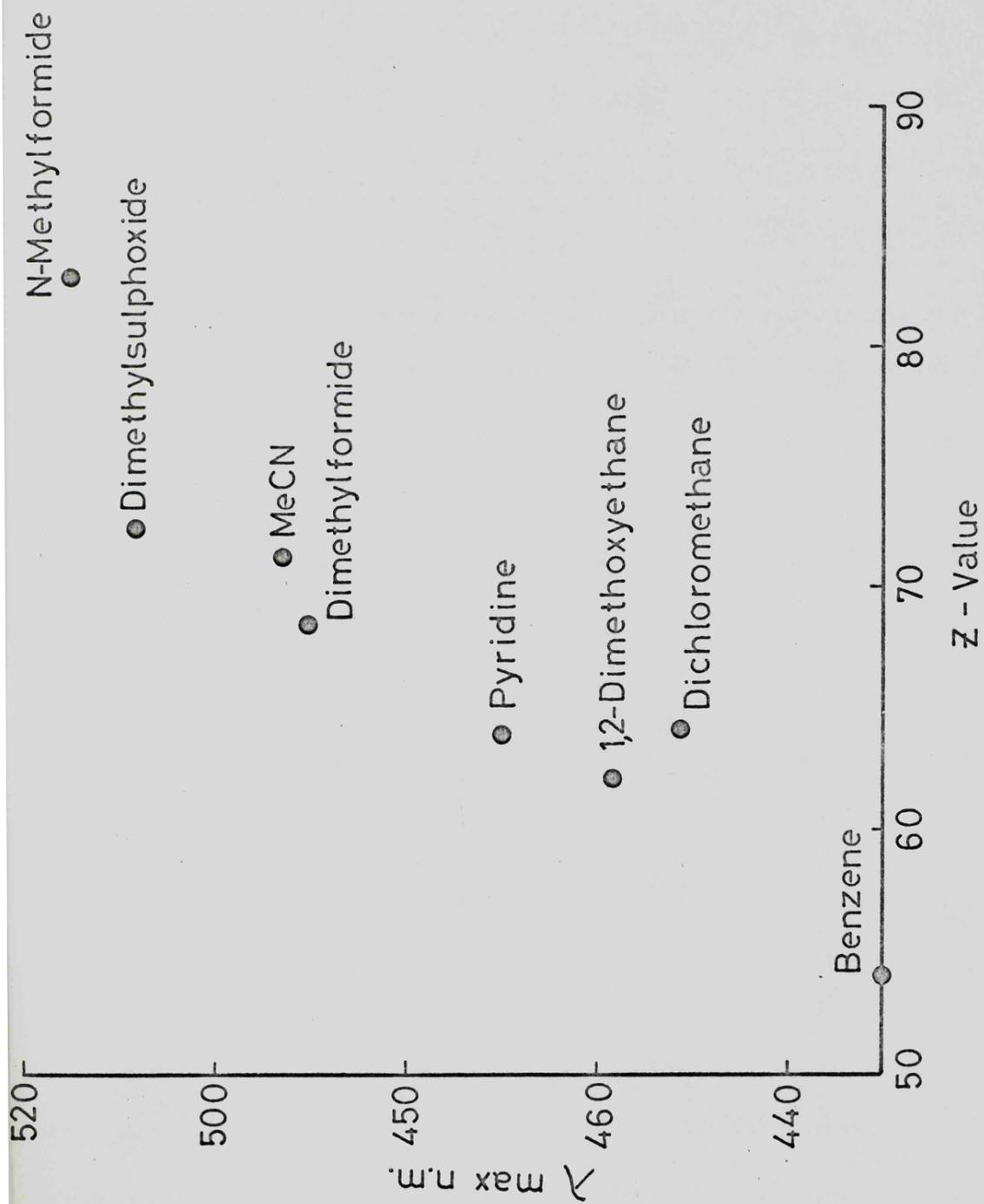
Z - Value

FIGURE 8.   Wavelength of Exciplex Fluorescence
Maximum vs. Z-Values for 26.

106.

Emission from the salts at $-196°$ in both polar and non-polar matrices was found to be that of the naphthalene nucleus only. The intensities of both fluorescence and phosphorescence were comparable to those obtained from 1-methyl-naphthalene.

The ultra-violet absorption spectra of the salts ($10^{-4}M$) failed to show any evidence for charge-transfer absorptions. The spectrum derived from the naphthalene nucleus was unperturbed by comparison with that of 1-methylnaphthalene. Those salts containing an iodide ion (I^-) posessed an absorption at 248NM ($\varepsilon_{molar} = 1.4 \times 10^4$) in acetonitrile solution. The spectrum of sodium iodide ($10^{-4}M$) in acetonitrile exhibits an identical absorption. Similar spectra for this ion have previously been published.[121] The N.M.R. spectra of the salts all showed resonances due to $-CH_2\overset{+}{N}R_3$ (10 - 20% solutions in $CDCl_3$) indicating that the compounds exist as salts at high concentration.

Irradiation of $\underline{30}$ in benzene solution ($3 \times 10^{-3}M$) with 300NM lamps for two days yielded 49% of the parent amine, N,N-diethyl-2-(1-naphthyl) methylamine.

Stern-Volmer quenching constants were obtained for the fluorescence quenching of naphthalene by halogen ions. Tetra-n-butylammonium halides were used as the source of the anion. The values are shown in Table 23.

Ultra-violet absorption spectra of the solutions used for the Stern-Volmer plots did not show any evidence for ground state interactions. New fluorescence bands were not observed from any of the solutions. It can be seen that the solvent

TABLE 23.

Stern-Volmer quenching constants for quenching of naphthalene
fluorescence by halogen anions.[a]

Solvent.	Chloride.	Bromide.	Iodide.
95% Ethanol.	Very low.	19	102
Acetonitrile.	206	54	162
Benzene.	600	253	130

a. Naphthalene ($10^{-4}M$) was excited by light of wavelength 300NM.

has a marked effect upon the quenching efficiency of the anion,
being particularly pronounced for Cl^-. The plots were not
truly linear in many cases but displayed a slight downward
curve with increasing concentration.

The quantum yields of naphthalene fluorescence for 25,
26 and 27 were also determined in several solvents for comp-
arison with the results shown in Table 23. The values obt-
ained are shown in Table 24.

TABLE 24.

Quantum yields of naphthalene fluorescence for 25 - 27.

Solvent.	Compound.		
	25	26	27
95% Ethanol.	0.1	0.1	0.1
Acetonitrile.	0.051	0.041	0.037
1,2-Dimethoxyethane.	0.035	0.02	Not determined
Benzene.	0.004	0.003	0.0035

The quantum yield for the iodide (27) was not determined

in 1,2-dimethoxyethane because interaction occurs between the solvent and the solute. A new absorption band appeared in the electronic absorption spectrum as a tail to the red of the naphthalene absorption. The fluorescence spectra were found to contain a component (λ max. between 400 - 450NM) presumably derived from excitation into this band. This effect was found to be common to all of the iodides studied. Solutions left standing overnight subsequently developed a strong yellow colour, it was not possible to isolate the salt from these solutions. Such interactions were not apparent for the salts containing Cl^- and Br^-.

The emission spectra of 25 — 29 were found to be dependent upon the concentration. Quantitative studies were made for 26 in benzene, emission of solutions of varying concentration of the salt, were compared directly with solutions of 1-methylnaphthalene whichpossessed the same optical density at the excitation wavelength (300NM). It was found that increasing the concentration of the salt gave rise to a decrease in the intensity of the exciplex emission, whilst the monomer fluorescence reached a maximum at approximately $5 \times 10^{-4}M$ and subsequently decreased. The same effect was also found for 25, 27, 28 and 29. A plot of fluorescence intensity against concentration is shown for 26 in Figure 9.

Discussion.

The new fluorescence bands observed for the salts in aprotic solvents exhibit a solvent effect typical of that found for exciplexes and in the absence of any changes in the ultra-violet absorption spectra it seems reasonable
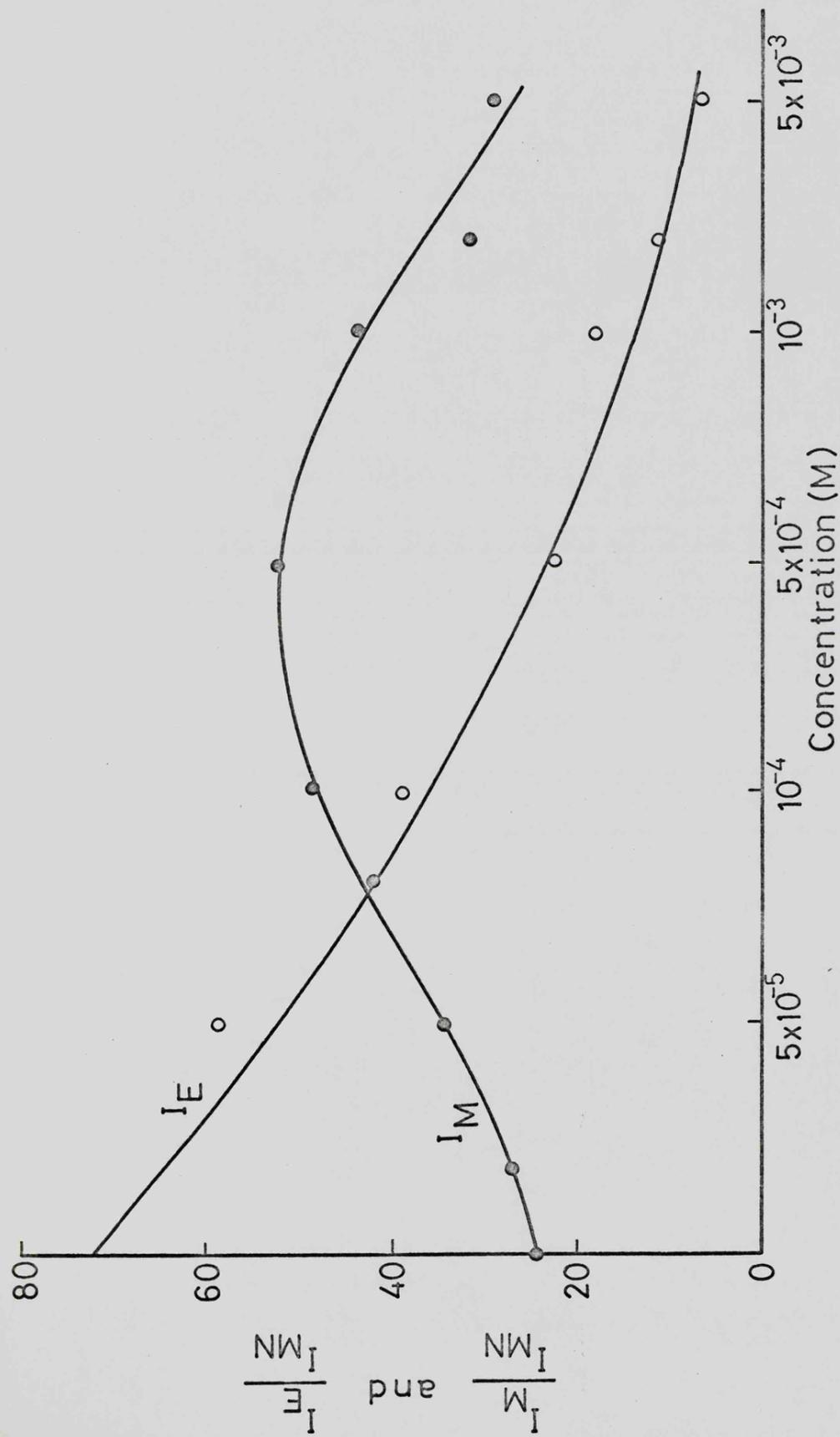
FIGURE 9. Intensities of Monomer (I_M) and exciplex (I_E) Fluorescence Relative to 1-Methylnapthalene (I_{MN}).

to assign them as being due to exciplex formation. The results also suggest that the electron transfer takes place from the halogen anion to the naphthalene chromophore in its first excited singlet state.

Electron transfer reactions involving halogen anions and heterocyclic compounds have previously been proposed, e.g. pyridinium or acridinium ions.[122, 123] Kosower observed an anomalous absorption band in the spectrum of N-alkyl-pyridinium iodides, and attributed it as arising from electron transfer from the iodide ion to the positive pyridinium nucleus within a solvated ion pair. The sensivity of this absorption band to solvent polarity has since been used to construct a solvent polarity scale (Z-values scale). Flash photolysis[124] of 1-methylpyridinium iodide has been shown to yield the free radicals expected of an electron transfer reaction,

$$R^+ \; I^- \xrightarrow{\; h\nu \;} R^\bullet + I^\bullet.$$
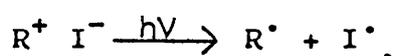
Direct irradiation of trimethylanilinium salts[125] was found to give benzene and trimethylamine, reaction was bel-ieved to be via an electron transfer mechanism,

$$Ar \cdot X^+ \; Y^- \xrightarrow{\; h\nu \;} \left[ArX \; Y\right]^* \longrightarrow Ar^\bullet + X^\bullet + Y^\bullet.$$
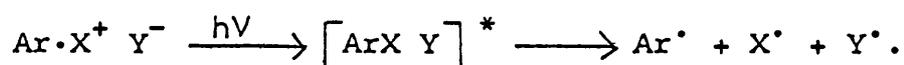
Further evidence for charge-transfer processes involving halogen anions has been provided by fluorescence quenching studies of anthracene.[126, 127] The quenching rate constants were found to depend upon the redox potential of the anion rather than the atomic spin-orbit coupling paramater thus indicating that a charge-transfer mechanism is responsible for the fluorescence quenching. The evidence therefore suggests that charge-transfer from the halogen anion to the

naphthalene in the salts is a feasible process.

Ion-pairing is believed to occur in aprotic solvents and consequently quenching is likely to be efficient due to the close proximity of the donor and acceptor moieties. A possible explanation of the lack of fluorescence quenching in protic solvents is that solvation of the ions takes place, causing the ion pairs to dissociate. The concentration of the anions would then be too low for efficient quenching by a bimolecular process. This is supported by the Stern-Volmer quenching constant obtained for the iodide ion in ethanol (Table 23), substitution of the experimental value, and the concentration $[Q] = 10^{-4}M$, into the Stern-Volmer equation,

$$\frac{\phi_o}{\phi} = 1 + K_Q [Q]$$

gives $\phi_o/\phi = 99$ i.e. 1% quenching, assuming that the salt is fully dissociated. This value (within experimental error) is consistent with the quantum yields obtained for naphthalene fluorescence in ethanol (Table 24).

Proof for the existence of ion-pairing has been found by conductance measurements of tetra-n-alkylammonium salts.[128] It is likely that, in acetonitrile solution, the salts exist partially as ion pairs,

$$R_4\overset{+}{N} X^- \rightleftharpoons R_4\overset{+}{N} + X^-$$
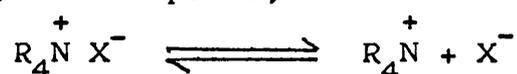
and in less polar solvents, such as acetone, ion-pairing is much more extensive.[129]

The situation in protic solvents such as ethanol and n-butanol is rather different, the association constants for quaternary ammonium salts are relatively high.[130,131]

A multi-step association process has been proposed in which there are solvent separated ion pairs and contact ion pairs.

$$R_4\overset{+}{N} + X^- \ (ROH)_n \rightleftharpoons R_4\overset{+}{N} \ (ROH)_n \ X^- \rightleftharpoons R_4\overset{+}{N} \ X^- \ (ROH)_n$$
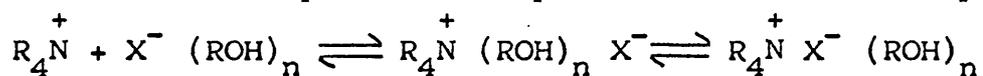
A possible reason for the lack of quenching by the anions in ethanol is that the solvent separated ion pairs predominate.

Dissociation of 27, 29 and 30 into the free amine and hydrogen or ethyl iodide can be discounted by the presence of an iodide absorption band, further the wavelength and exctinction coefficient are very similar to those found for sodium iodide. Hence the iodides, at least, exist as salts at low concentration, whilst the N.M.R. spectra indicate that all of the salts exist as such at higher concentrations.

An important observation is that the wavelength of the exciplex fluorescence bands are all very similar and also resemble those found for the free parent amine.[66,72] A possible explanation is provided by the following mechanism (where Np = 1-naphthyl),
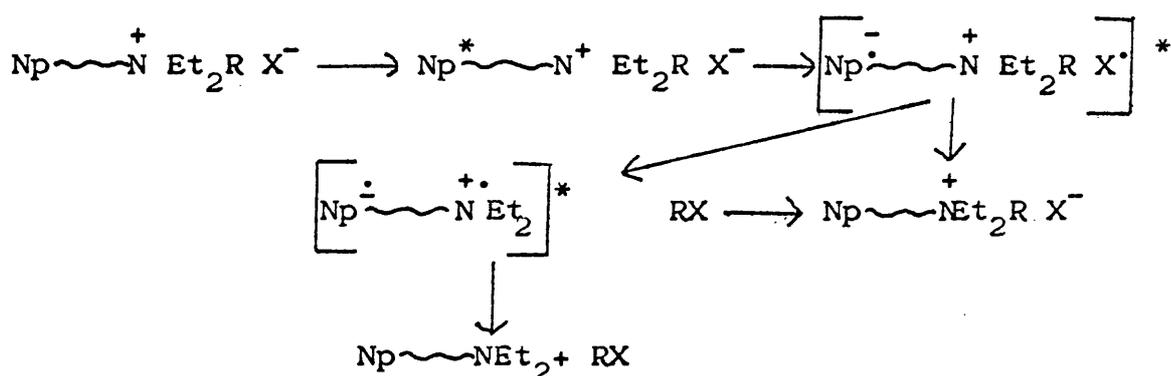
Full transfer of one electron has been shown although this need not necessarily be the case.

The fluorescence quenching thus takes place via an initial electron transfer from the halogen anion to the first excited singlet state of naphthalene. This is reasonable in view of the fact that ammonium moiety does not have vacant orbitals to accept an electron, further the quantum yields in ethanol show that it does not quench naphthalene fluorescence. Cleavage of the N — R bond by reaction with the iodide atom may then be rapid giving rise to the same exciplex as would have been formed by direct excitation of the parent amine. This species can then undergo any of the decay processes typical of that for an amine-hydrocarbon exciplex. The iodide liberated by excitation of the salt may remain close to the solvent shell around the exciplex, hence when the exciplex is deactivated reaction may occur to yield the salt. Photolysis of 30 gave the free amine in 49% yield which does give some support for such a mechanism.

This mechanism would also explain why 30 does not exhibit a discrete exciplex fluorescence band, formation of the free amine in the excited state would not give such an emission because this particular compound is known to be unable to do so.[65] It would therefore appear that the ammonium salts studied here are "special" cases and the observation of an electron transfer from the halogen anion to the excited naphthalene relies upon the ability of the products of the electron transfer to fluoresce. This is in accord with other work on fluorescence quenching of aromatic hydrocarbons (always intermolecular) in which a new fluorescence band was never observed.[127,132] It has recently been proposed[132] that the dependence of quenching rate constants on the redox potential of the anions,[126,127] may be due to

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the collision complex containing contributions from electron

transfer states which couple with both singlet and triplet

states of the aromatic hydrocarbon, thus giving rise to the

observed dependence but not to a true electron transfer process.

This may be true for $\underline{25}$ - $\underline{29}$, but in this case the electron

transfer goes to completion because of the presence of the

ammonium moiety.

Two factors are of importance in attempting to rationalise

the Stern-Volmer quenching constants obtained for the halogen

anions in the three solvents.

1. The effect upon the ability of the ion to react as an

electron donor.

2. The effect of the size of the anion upon the association

constant.

Smaller negatively charged ions are more solvated by protic

solvents than large ones e.g. the negative charge of Cl^- is

more "concentrated" than the charge of I^-, hence the former

ion is more tightly surrounded by a shell of solvent molecules

which will therefore hinder reaction. The K_Q values obtained

do exhibit the expected trend i.e. $I^- > Br^- > Cl^-$ in ethanolic

solution. The use of an aprotic solvent for nucleophilic sub-

stitution is known to cause a change in the reactivity orders

for these anions i.e. $Cl^- > Br^- > I^-$ (see for example refs.

133 and 134). Such an order was obtained for K_Q in benzene

but the values for acetonitrile solution follow a different

order. A possible reason may be due to the second factor

mentioned above i.e. a change in the association constant of the

salts. Substitution reactions are known to be less efficient

by anions when they exist in an ion pair,[133] it is therefore

likely that the degree of association will affect the K_Q

values. Association constants are known to decrease in apro-

tic solvents as the size of the anion becomes greater,[129]

the solvation and association factors thus work against each

other in aprotic solvents which renders interpretation of the

results difficult without a precise knowledge of their effect

upon the quenching ability.

Comparison of the quantum yields (Table 24) with K_Q

(Table 23) is difficult for the same reason because the

state of the salts containing a naphthalene ring is not known

in aprotic solvents. These salts generally exhibit lower

naphthalene quantum yields as the solvent polarity decreases

which would be expected if only the solvation of the anion

was considered.

The effect of concentration upon the fluorescence spectrum

of 26 serves to show a further complicating factor in the

study of these ammonium salts. The dissolution of ionic com-

pounds in polar solvents can lead to micelle formation.[135]

The structure of the micelle is believed to be such that

the hydrophobic part of the molecule s constitute the core

and the polar end groups are located at the micelle-water inter-

face. The dissolution of a polar compound in a non-polar solv-

ent is also known to form aggregates in which the charged

hydrophilic groups are contained in the interior and the

hydrophobic hydrocarbon moiety is in contact with the non-

polar solvent. These aggregates are termed inverted or rever-

sed micelles,[136,137] and have been primarily used as a medium

for investigating reaction rates and interactions of solutes

contained within the interior of the reversed micelle.[137]

There is some evidence of a different nature which

suggests that ammonium salts aggregate in non-polar solvents,

dielectric relaxation measurements of such salts in benzene-

xylene mixtures showed complexities that were attributed to

aggregation of the molecules.[138]

The formation of a reversed micelle may be responsible

for the concentration effects observed for 26, thus an

increase in the concentration of the salt would effectively

remove the species responsible for the fluorescence quenching

from the environment of the naphthalene.

The changes in intensity of the monomer fluorescence are

more difficult to rationalise. The initial increase in

fluorescence intensity observed as the concentration of the

salt is raised may be due to the formation of a reversed mic-

elle containing a small number of molecules, subsequent increas-

es in the concentration might then lead to a reversed micelle

containing more molecules. Self-quenching of fluorescence by

naphthalene may occur within such a micelle i.e. excimer form-

ation and/or a higher polymeric form of naphthalene may be

involved in which the electronic excitation energy is dissip-

ated in a non-radiative manner.

It is well known that micelles are not rigid structures i.e.

they exist in equilibrium with the monomers,

$$(n.R_4\overset{+}{N}\ \overset{-}{X})S \rightleftharpoons n(R_4\overset{+}{N}\ \overset{-}{X})S$$
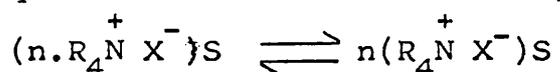
where "n" is the number of monomers per micelle and "S" refers

to the solvent, hence the lifetime of the micelle will obv-

iously be an important factor in the fluorescence quenching

process. Unfortunately, information regarding the effect of micelle or reversed micelle formation upon the fluorescence of aromatic hydrocarbons appears to be scant. Excimer fluorescence has been observed in two cases from aromatic hydrocarbons contained within a micelle of a cationic detergent in aqueous solution thus indicating that the lifetime of the micelle is far longer than that required for excimer formation,[139,140] but whether these results can be extrapolated to account for the results reported here in which a reversed micelle may be formed is uncertain.

2:4 FLUORESCENCE QUENCHING OF AROMATIC HYDROCARBONS BY DIENES, OLEFINS AND HETEROCYCLIC COMPOUNDS.

2:4:1 INTRAMOLECULAR QUENCHING OF NAPHTHALENE FLUORESCENCE.

Results.

A number of naphthalene compounds containing certain quench-
ing groups in the side chain have been synthesised (31 - 38).
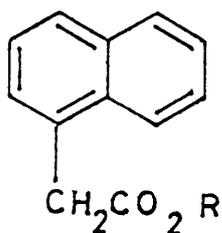
31 R = $CH_2.CH = CH.Ph.$
32 R = $CH_2.CH = CH.CH = CH.Me.$
33 R = 2 —— furfuryl.
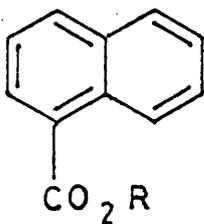
34 R = $CH_2.CH = CH.Ph.$
35 R = 2 —— furfuryl.

36

OCOCH=CH.CH=CH.Me
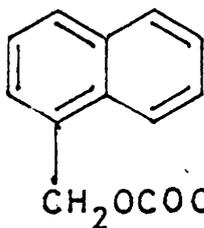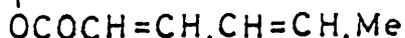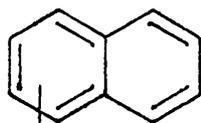
38   1-substituted naphthalene.

39   2-substituted naphthalene.

The emission spectrum of each compound was recorded

in both polar (95% ethanol, acetonitrile) and non-polar

solvents (benzene, cyclohexane) but it was not possible to

detect any new fluorescence bands.   The wavelength of max-

imum emission did not differ greatly from that found for the

naphthalene chromophore i.e. approximately 350NM.   The quantum

yields of fluorescence for 31 - 38 are shown in Table 25.

TABLE 25.

Quantum yields of fluorescence for 31 - 38.[a.]

Compound.	31	32	33	34	35	36	37	38
Quantum yield.	0.08	0.09	0.095	0.1	0.07	0.005	0.004	0.004

a. Recorded in 95% ethanol at a concentration of approximately

10^{-4}M.

The quantum yields for the reference compounds 39, 41 and 42,

were found to be approximately the same, ϕ_F = 0.23, that of
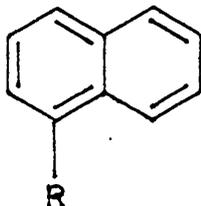
39   R = CH_2CO_2Me.

40   R = CO_2Me.

41   R = CH_2OCOMe.

42   R = OCOMe.

40 was found to be 0.28.

The quenching observed was not a function of concent-
ration since experiments showed that the compounds at con-
centrations lower than 10^{-4}M were still quenched.

Attempts were made to detect complex emission i.e. a new
fluorescence band, at low temperature for 31 - 33; emission
from these compounds in methyl cyclohexane solution (10^{-4}M)
at temperatures down to $-90°$ failed,to exhibit fluorescence
other than that of the naphthalene chromophore. The intensity
of fluorescence from the monomer merely increased as the temp-
erature was lowered.

The ultra-violet absorption spectra of 31 - 36 were
found to be essentially the same as those of the parent comp-
ounds. The spectra of 37 and 38 however, do not posess the
vibrational fine structure characteristic of naphthalene,
possibly indicating a degree of conjugation between the two
chromophores within the molecule.

Discussion.

Ground state interactions are unlikely to be a factor
of importance in the fluorescence quenching observed for 31 -
36, since the ultra-violet absorption spectra are essentially
unchanged. This may not be true of 37 and 38 in view of the
broad, structureless absorption band exhibited by these comp-
ounds.

The mechanism by which fluorescence quenching takes place
is in some doubt. It is assumed that excitation of the mol-
ecules will give rise to an interaction of the two groups,
thus forming a complex within which quenching takes place.
Stabilisation of such a complex could arise from either charge-

transfer or exciton resonance interactions or from a mixture
of these i.e.,

$$ArQ^* \longleftrightarrow Ar^*Q \longleftrightarrow Ar^+Q^- \longleftrightarrow Ar^-Q^+$$
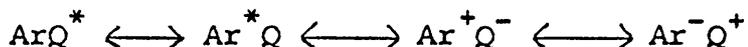
2-Methylfuran has a high ionisation potential (8.39e.v.[141])
hence any excited complex formed by 33 or 35 is unlikely to
posess large contributions from charge-transfer stabilisation.
This is reflected in the relatively high quantum yields for
these compounds, the slightly lower value obtained for 35
compared to 33 may be due to the higher electron affinity of
the naphthalene within that compound. The geometry of 33 does
allow the two rings to lie parallel and this is probably the
most favourable conformation for an excited state complex in
this molecule, it would therefore appear that poor overlap of
the interacting groups is not the cause of a lack of complex
emission.

The ionisation potentials of dienes and styrenes are
high compared to that of triethylamine e.g. 2,5-dimethyl-2,
4-hexadiene and 2-methylstyrene have ionisation potentials of
7.84[142] and 8.23[143] e.v. respectively. Electron-transfer
upon excitation of 31, 32 and 34 is therefore likely to be
inefficient. Taylor[144] has been successful in observing
exciplex fluorescence from 1-cyanonaphthalene and various
olefins and dienes. The presence of the electron withdrawing
cyano group makes electron transfer to the naphthalene ring
more favourable. Both Taylor[144] and Hammond[145] were unable to
detect exciplex fluorescence with naphthalene itself. Exciplex
fluorescence from the compounds containing olefins and dienes
is therefore unlikely.

A reason suggested by Hammond[146] for the lack of exciplex fluorescence is that the transient exciplexes contain a small exciton resonance contribution in which electronic excitation energy is located upon the quencher. The importance of such a contribution is not in its effect upon the binding energy of the complex but from its effect upon the rate of internal conversion, thus the complex "borrows" some of the rapid non-radiative decay characteristics of the quencher groups leading to fluorescence quenching of naphthalene but not to complex fluorescence.

The situation as regards <u>36</u>, <u>37</u> and <u>38</u> appears to be different since the naphthalene fluorescence quantum yields are far lower than those of <u>31</u> - <u>35</u>. The wavelength of light used to excite the compounds (usually 300NM) does give rise, at least initially, to both Ar^* and Q^* since both absorb light in this region. The energies of the singlet levels of the two chromophores will not be separated by such a large amount as they are for the other compounds (<u>31</u> - <u>35</u>), as a consequence exciton resonance contributions should be more important leading to a more stable excited complex. The result of this should be to decrease the naphthalene fluorescence quantum yield.

2:4:2 INTERMOLECULAR FLUORESCENCE QUENCHING OF AROMATIC HYDROCARBONS.

Results.

A study has been made of the fluorescence quenching of

four aromatic hydrocarbons; naphthalene, 1-cyanonaphthalene, 9-cyanophenanthrene and 9-cyanoanthracene, by thiophene, N-methylpyrrole, N-methylindole, furan, 2-methylfuran, and 2,5-dimethylfuran. Additionally, attempts were made to observe a fluorescent, excited state complex between anethole and 1-cyanonaphthalene.

Fluorescent complexes were only observed with two of the hydrocarbons, 1-cyanonaphthalene and 9-cyanophenanthrene. The successful quenchers for both hydrocarbons were N-methylpyrrole, N-methylindole and 2,5-dimethylfuran. A complex was also detected in the quenching of 1-cyanonaphthalene by 2-methylfuran. In each case the new band was found to red shift as the polarity of the solvent was increased. The new fluorescence band could not be detected in ethanol or acetonitrile. The ultraviolet absorption spectra of the systems exhibiting the new fluorescence band, and those that only showed fluorescence quenching, were essentially the same as those of mixtures of the parent compounds.

The new fluorescence bands have been attributed to exciplex formation involving an electron transfer from the heterocyclic compound to the first excited singlet state of the hydrocarbon. The wavelengths of maximum emission of both monomer and exciplex fluorescence, together with the ratio of the relative intensities of the emissions, are shown in Table 26.

The effect of quencher concentration ($10^{-1} - 10^{-2}M$) upon the exciplex fluorescence was studied for 2-methylfuran, 2,5-dimethylfuran, and N-methylpyrrole. The first two quenchers decreased the intensity of the monomer fluorescence and

TABLE 26.

Wavelengths of maximum emission and relative intensities of monomer and exciplex emissions.

Exciplex.	Solvent.	λ max.(NM) Monomer.	λ max.(NM) Exciplex.	I_E/I_M [a.]
1-Cyanonaphthalene	Cyclohexane.	345	395	1.47
-2-methylfuran.	Benzene.	352	414	1.0
	Chloroform.	352	428	1.6
	Dichloromethane.	352	433	2.2
	Ethyl acetate.	350	447	1.7
1-Cyanonaphthalene	Cyclohexane.	345	420	4.6
-2,5-dimethylfuran.	Benzene.	350	432	5
	Chloroform.	351	456	5
	Dichloromethane.	351	460	4
	Ethyl acetate.	350	469	2

a. I_E/I_M is the ratio of the relative intensities of exciplex and monomer emissions respectively.

TABLE 26. (Continued)

Exciplex.	Solvent.	$\lambda_{max.}$(NM) Monomer.	$\lambda_{max.}$(NM) Exciplex.	I_E/I_M
1-Cyanonaphthalene	Cyclohexane.	345	426	1.43
-N-methylpyrrole.	Benzene.	350	452	0.93
	Chloroform.	350	460	0.48
	Dichloromethane.	352	470	0.45
	Ethyl acetate.	350	-	-
1-Cyanonaphthalene	Cyclohexane.	340	435	0.37
-N-methylindole.	Benzene.	350	455	0.26
	Chloroform.	350	470	0.16
	Dichloromethane.	350	485	0.2
9-Cyanonaphenanthrene	Cyclohexane.	390(approx.)	405(approx.)	1.0
-2,5-dimethylfuran.	Benzene.	380(shoulder)	437	2.1
	Chloroform.	380(shoulder)	460	7.3
	Dichloromethane.	380(shoulder)	452	10
	Ethyl acetate.	380(shoulder)	459	3.75

TABLE 26. (Continued)

Exciplex.	Solvent.	λ max. (NM) Monomer.	λ max. (NM) Exciplex.	I_E/I_M
9-Cyanophenanthrene -N-methylpyrrole.	Cyclohexane.	390(approx.)	410(shoulder)	0.85
	Benzene.	390	452	1.25
	Chloroform.	383	456	0.83
	Dichlormethane.	388	461	0.62
	Ethyl acetate.	380	–	–
9-Cyanophenanthrene. -N-methylindole.	Cyclohexane.	380	430	1.00
	Benzene.	380	455	0.5
	Chloroform.	382	470	0.45
	Dichlormethane.	382	480	0.66
	Ethyl acetate.	380	482	0.28

CN

+ Me⟶O⟶Me   in Benzene

1. 8 x10⁻²M
2. 5 x10⁻²M
3. 3 x10⁻²M
4. 1 x10⁻²M

INTENSITY

Wavelength (n.m)

DIAGRAM 11

INTENSITY

CN

+

N—Me
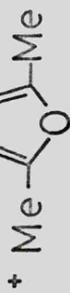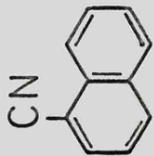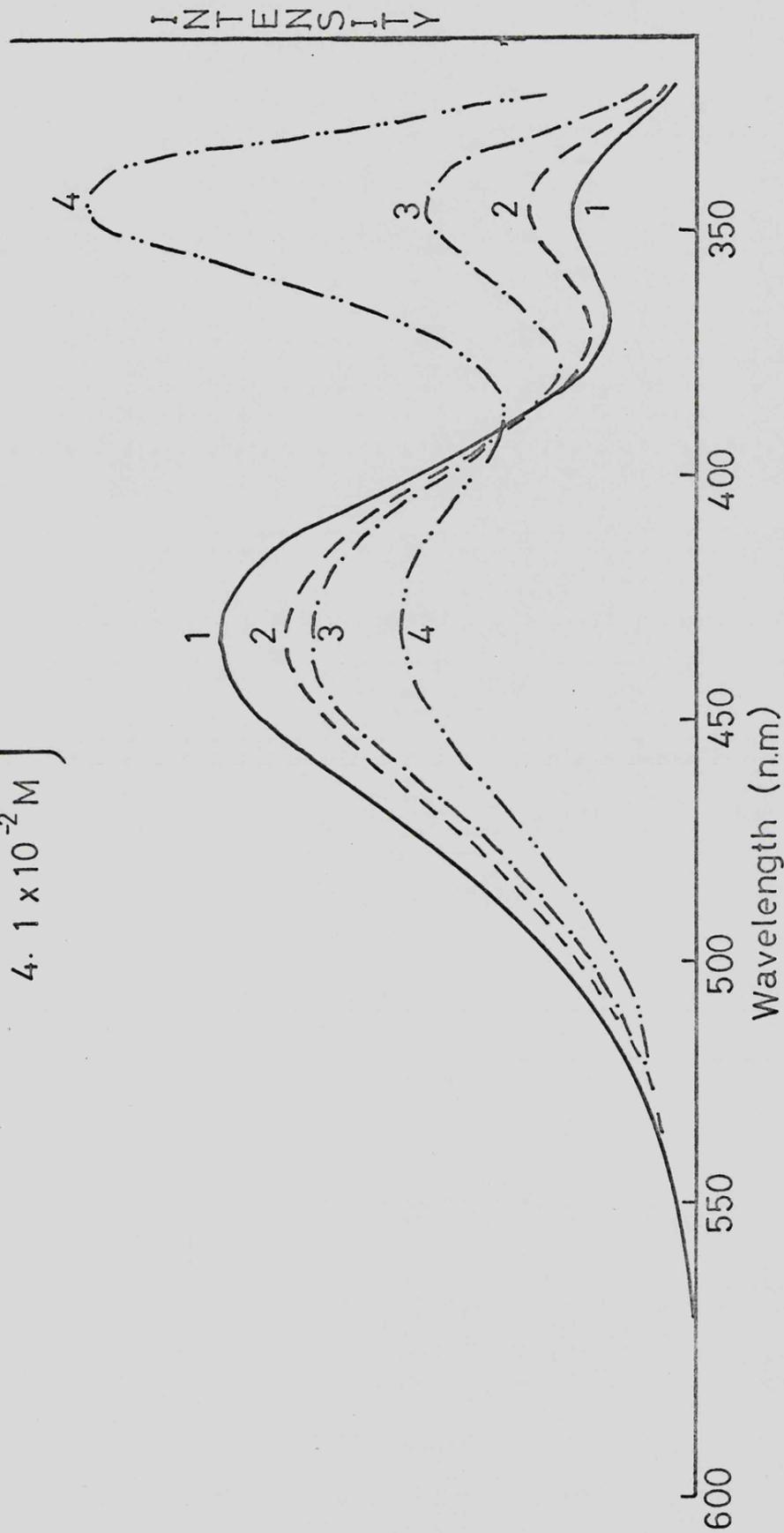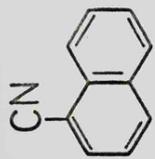
in Cyclohexane

1. 10^{-1} M
2. 2×10^{-2} M
3. 5×10^{-2} M
4. 10^{-2} M

4

3
2

1

Wavelength (n.m.)

DIAGRAM 12

600   550   500   450   400   350

128.
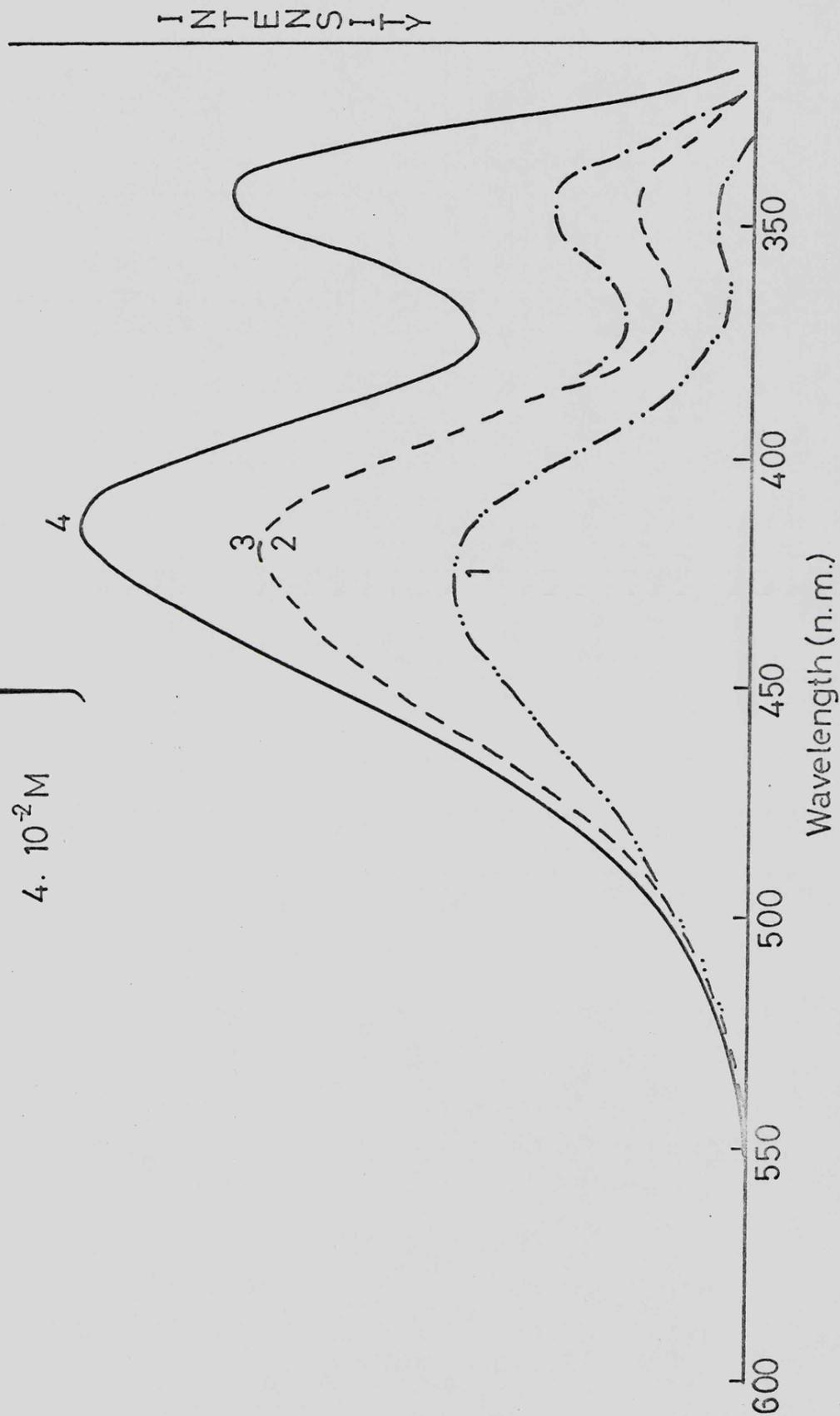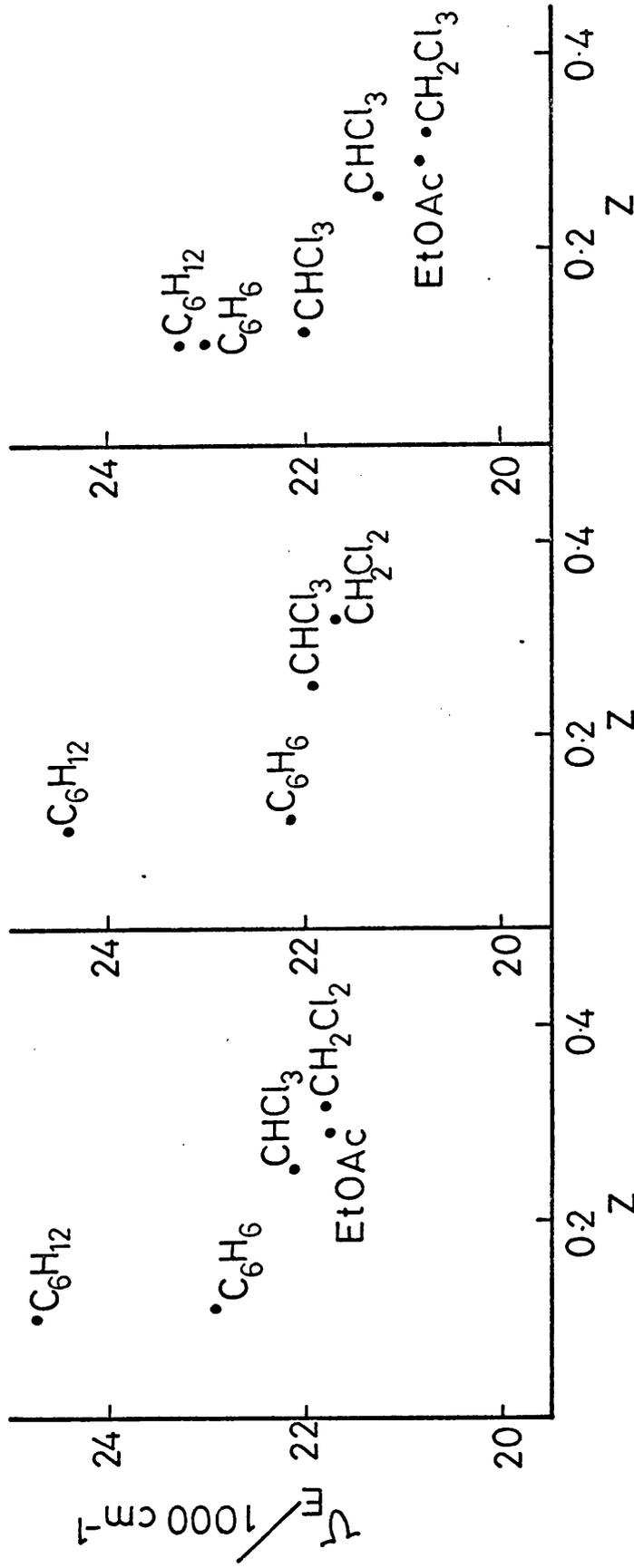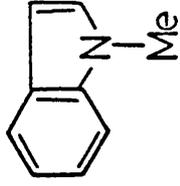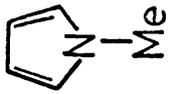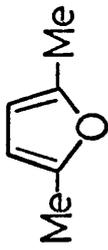
FIGURE 10. Correlation of Exciplex Fluorescence Maxima with Solvent

Polarity for 9-Cyanophenanthrene Exciplexes.
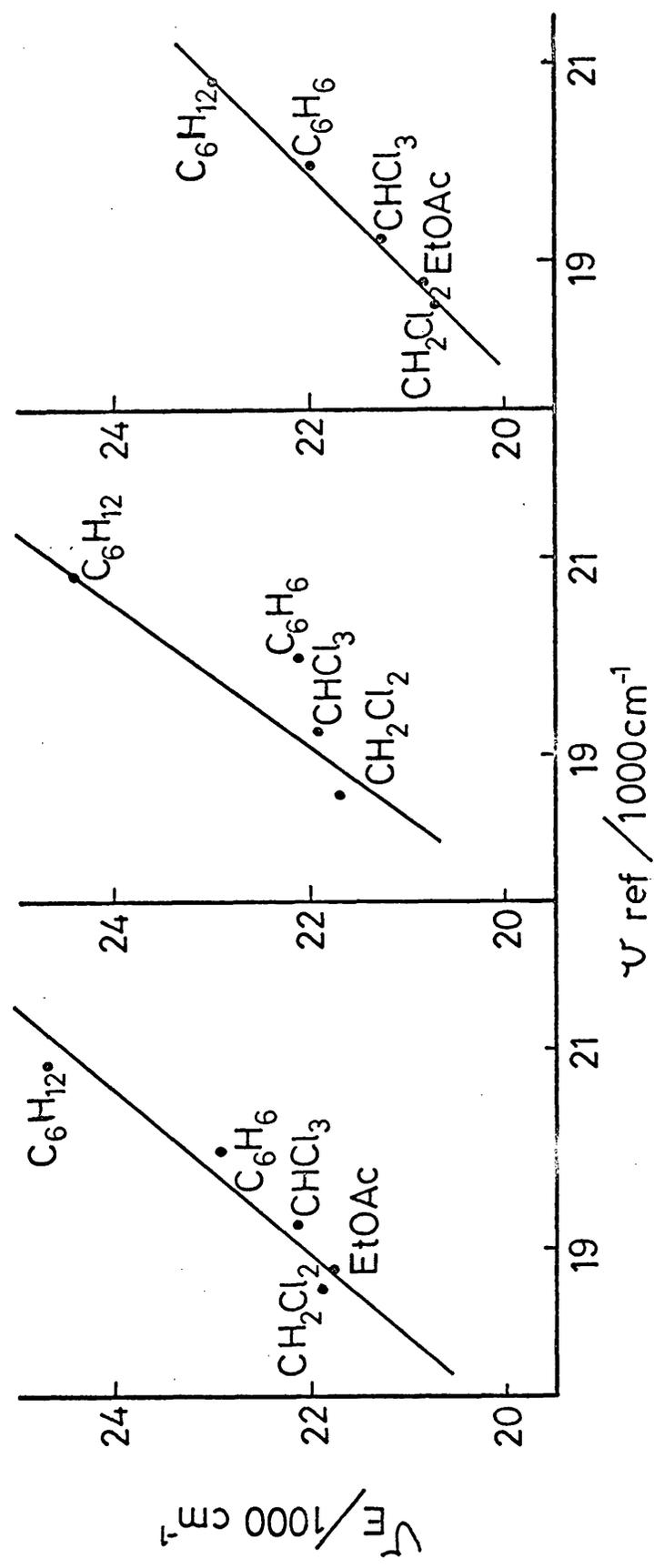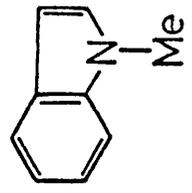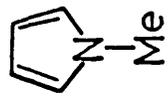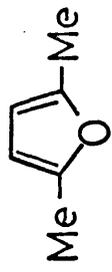
FIGURE 11. Correlation of the Fluorescence Maxima of 9-Cyanophen-anthrene exciplexes with those of Anthracene-N,N-diethylaniline.

increased that of the exciplex fluorescence as the concentration was raised. An isoemissive point was obtained in each case. N-methylpyrrole, with both 1-cyanonaphthalene and 9-cyanonaphthalene, tended to decrease the intensity of the exciplex emission. Further, with 1-cyanonaphthalene, a quite marked red shift of the exciplex fluorescence maximum was observed as the concentration of the quencher increased. Representative spectra are shown in Diagrams 11 and 12.

Dipole moments have been calculated for the exciplexes. The method described in Section 2:1:1 did not give a good correlation between the solvent polarity factor and the wavenumber of maximum exciplex emission (see Figure 10), for this reason the dipole moments have been estimated relative to the anthracene-N,N-diethylaniline exciplex.[71,93] In this method the wavenumber of the exciplex emission is plotted against that found for the anthracene-N,N-diethylaniline exciplex. The slope obtained from such a plot is then treated in the same way as those from a conventional plot. Examples of the plots are illustrated in Figure 11 for the exciplexes formed by 9-cyanophenanthrene, although the plots are not linear the deviations have been largely eliminated. Molecular models indicate that for a sandwich-pair conformation exciplexes formed by 1-cyanonaphthalene and 9-cyanophenanthrene have radii of approximately 5.0 and 5.5 $\overset{o}{A}$ respectively. These values, together with the slopes of the plots, were used to calculate the approximate dipole moments shown in Table 27.

The enthalpies of formation (- ΔH^*) of three of the exciplexes, 1-cyanonaphthalene-2-methylfuran, 1-cyanonaphthalene-

TABLE 27.

Dipole moments (Debye units) of exciplexes formed between

aromatic hydrocarbons and heterocyclic compounds.

Quencher.   Aromatic Hydrocarbon.

	1-Cyanonaphthalene.	9-Cyanophenanthrene
2-Methylfuran.	8.9	-
2,5-Dimethylfuran.	8.7	8.4
N-Methylpyrrole.	7.8	9.5
N-Methylindole.	7.8	7.8

N-methylpyrrole, 9-cyanophenanthrene-N-methylpyrrole, have

been determined from a study of the effect of temperature

upon the fluorescence spectrum. The method used was the same

as described in Section 2:1:4. The plots of log (I_E/I_M) against

$1/T$ showed two linear regions as expected, $-\Delta H^*$ was calculated

from the high temperature portion of linearity, whilst the

energy of activation for formation of the complex, E_a, was cal-

culated from the low temperature portion.

1-Cyanonaphthalene-2-methylfuran: $-\Delta H^* = 2.5$ kcal/mole.

$$E_a = 1.1 \text{ kcal/mole.}$$

1-Cyanonaphthalene-N-methylpyrrole:

$$-\Delta H^* = 9.0 \text{ kcal/mole.}$$

$$E_a = 1.7 \text{ kcal/mole.}$$

1-Cyanophenanthrene-N-methylpyrrole:

$$-\Delta H^* = 9.0 \text{ kcal/mole.}$$

$$E_a = 1.0 \text{ kcal/mole.}$$

In those cases where exciplex emission was not observed

various concentrations of both quencher and quenchee were

studied. Different solvents, usually benzene and cyclohexane

were also used. Attempts were also made to observe exciplex fluorescence at low temperature, but these experiments were unsuccessful.

Anomalous fluorescence bands were observed from two of the compounds studied. N-Methylindole was found to fluoresce at 390NM at 10^{-1}M in cyclohexane. The wavelength of maximum emission at lower concentration (10^{-4}M) is 323NM. 1-Cyanonaphthalene (10^{-2}M in cyclohexane) showed fluorescence bands at 350 and 410NM. For this reason the concentrations of the compounds were kept well below the above values and the emission spectra of the components were also recorded separately to ensure that only monomer fluorescence was visible.

Complex fluorescence could not be detected from mixtures of anethole and 1-cyanonaphthalene, the concentration of both components was varied between 10^{-2} and 10^{-4}M, no attempt was made to judge whether fluorescence quenching took place, since both compounds themselves fluoresce.

9-Cyanophenanthrene has been reported to form an exciplex with anethole since this work was completed.[143] The concentrations employed in the experiments were not stated but a band at 456NM was observed in neat anethole. A preliminary experiment has indicated that anethole itself may be responsible for this emission, it was found to fluoresce strongly at 465NM.

Rate constants have been determined for the fluorescence quenching of 9-cyanoanthracene by furan, 2,5-dimethylfuran, thiophene and N-methylpyrrole. The quenching efficiency was found to be greater in acetonitrile than in cyclohexane for those quenchers known to form a fluorescent exciplex with

1-cyanonaphthalene and 1-cyanoanthracene. Anthracene was

found to be quenched less efficiently by N-methylpyrrole

than 9-cyanoanthracene. The values shown in Table 28 were

calculated from the Stern-Volmer equation using fluorescence

lifetimes (τ) of 9-cyanoanthracene and 1-cyanonaphthalene

determined using a pulse sampling fluorometer.

<div align="center">TABLE 28.</div>

Rate constants[a] for fluorescence quenching of aromatic

hydrocarbons by heterocyclic compounds.

Hydrocarbon.			Quencher.					
	Furan.		2,5-Dimethyl-Furan.		Thiophen		N-Methyl-pyrrole.	
	A.[b]	C.[c]	A.	C.	A.	C.	A.	C.
9-Cyanoanthracene.[d]	0.012	0.01	5.4	3.0	0.01	0.09	6.5	1.7
Anthracene.[e]	-	-	-	-	-	-	0.82	-
1-Cyanonaphthalene.[f]	1.0	0.04	-	-	-	-	8.6	-

a. x 10^{-9} l mol^{-1} s^{-1}.

b. A = Acetonitrile.

c. C = Cyclohexane.

d. τ = 22.7ns (A) and 20ns (C).

e. τ = 5.0ns.[102]

f. τ = 15.3ns (A) and 23.8ns (C).

Discussion.

The new fluorescence bands show behaviour typical of

that expected for an excited state charge-transfer complex and

since the ultra-violet absorption spectra are essentially the

same as those of the parent compounds, the bands have been

attributed to intermolecular exciplex formation.

Reliance cannot be placed upon the absolute values for the dipole moments (Table 27) due to the poor correlation between the solvent polarity factor and the wavelength of maximum exciplex emission. Specific solute-solvent interactions may be responsible for the deviations observed since the formula commonly used to obtain dipole moments of exciplexes utilises the dielectric constant of the medium. This is a macroscopic property of the solvent consequently its use in attempting to define solvent polarity on a microscopic band may not be valid.[120] The effect of the solvent upon the long wavelength fluorescence band does however indicate that it is derived from a species thatpossesses considerable charge-transfer character.

Another method has been suggested by which the charge-transfer character of exciplexes can be estimated.[38]

$$Ar^* + Q \xrightarrow{k_q} \left[ArQ\right]^* \longrightarrow \left[Ar^{d-}....Q^{d+}\right]^*$$

with hv_M, k_1, k_2, hv_E pathways, and

$$Ar^{-\bullet} + Q^{+\bullet}$$

The ratio I_E/I_M, where I_E and I_M are the fluorescence intensities of exciplex and monomer respectively, will depend upon the charge-transfer character of the exciplex. It would be expected that the ratio would decrease as the charge-transfer character of the exciplex increased due to the formation of the solvated radical ions i.e. the rates of k_1 and k_2 should both be greater thus decreasing I_E but leaving I_M unchanged.

This treatment does not therefore rely upon the use of a solvent polarity factor since I_E/I_M can be compared for a given solvent, however, in the absence of a reference system, it does only give a quantitative estimate of the extent to which charge has been transferred.

This method has been applied to the exciplexes formed between aromatic hydrocarbons and heterocyclic compounds; I_E/I_M (from Table 26) were set equal to 1 for cyclohexane solution and I_E/I_M for the other solvents calculated relative to this value. The ratios are shown in Table 29.

It would appear that a reasonable order for the charge-transfer character of the exciplexes formed with 1-cyano-naphthalene would be,

N-methylpyrrole > N-methylindole > 2,5-dimethylfuran

> 2-methylfuran,

and for those formed with 9-cyanophenanthrene,

N-methylindole > N-methylpyrrole > 2,5-dimethylfuran.

The ionisation potentials of 2-methylfuran, 2,5-diemthylfuran, and pyrrole are 8.39, 8.01 and 8.2 e.v. respectively,[141] which gives a reasonable correlation with the degree of charge-transfer estimated, but the above orders can only be regarded as a guide since changes do occur from solvent to solvent. These changes in the order are likely to be a result of a breakdown of the assumptions used. The most important is that quenching of the excited species must be irreversible, such a condition probably applies to amine-hydrocarbon exciplexes, for which the method was originally used, but since k_q (Table 28) is often not diffusion controlled it may not be true for

TABLE 29.

Relative intensities (I_E/I_M) for exciplexes formed between aromatic hydrocarbons and heterocyclic compounds.[a]

Exciplex.	Solvent.			
	Benzene.	Chloroform.	Dichloromethane.	Ethylacetate.
1-Cyanonaphthalene				
2-methylfuran.	0.68	1.1	1.5	1.15
2,5-dimethylfuran.	1.07	0.86	0.43	1.1
N-methylpyrrole.	0.65	0.34	0.32	–
N-methylindole.	0.71	0.42	0.53	0.34
1-Cyanophenanthrene				
2,5-dimethylfuran.	2.1	7.28	10.0	3.75
N-methylpyrrole.	1.5	0.98	0.74	–
N-methylindole.	0.5	0.45	0.66	0.28

a. I_E/I_M is relative to $I_E/I_M = 1$ for each exciplex in cyclohexane.

the exciplexes under consideration here. The effect of reversibility upon I_E/I_M would be to decrease its value thus indicating that the complex contains more charge-transfer character than is necessarily the case.

The isoemissive point obtained by increasing the quencher concentration (except for N-methylpyrrole) is characteristic of the formation of a 1:1 complex between the singlet excited hydrocarbon and the quencher molecule. The decrease in exciplex intensity observed by increasing the concentration of N-methylpyrrole indicates that some further interaction takes place between the exciplex and the quencher. Similar results have been interpreted as being due to the formation of a stoichiometric complex between the two interacting molecules[147,148] or to a polarity change of the solvent induced by the addition of a polar molecule.[38] N-Methylpyrrole is likely to have a relatively high dielectric constant (ε pyrrole = 7.48[74]) whereas cyclohexane has a relatively low dielectric constant (ε = 2.02) the decrease in the exciplex fluorescence intensity and the red shift of the band can be adequately explained by a change in the solvent polarity. N-Methylpyrrole is known to associate in solution e.g. benzene, probably existing as a weakly bound dimer,[149] hence higher concentrations of N-methylpyrrole may lead to an interaction of the singlet excited hydrocarbon and an N-methylpyrrole dimer which would facilitate interaction between the exciplex and the second quencher molecule.

The $-\Delta H^*$ values of the exciplexes formed between N-methylpyrrole and the cyanosubstituted hydrocarbons are high,

in view of the fact that the 1-cyanonaphthalene-2-methylfuran exciplex has a low $-\Delta H^*$ it would appear that the major contribution to the binding energy of the exciplexes is charge-transfer in nature. The values calculated for E_a (between 1 and 2 kcal/mole) are typical of those found for a diffusion controlled reaction.

The lack of exciplex fluorescence from many of the systems studied can be rationalised in terms of the singlet energy levels and electron affinities of the aromatic hydrocarbons and the ionisation potentials of the quenchers. Furan and thiophene both have high ionisation potentials (8.89 and 8.86 e.v. respectively[141]), use of the method described in Section 2:1:5 indicates that the energy of the 1-cyanonaphthalene exciplex will be appreciably higher (approximately 10kcal/mole) than that of the first excited singlet state of the naphthalene. The lower ionisation potential of 2-methylfuran (8.39 e.v.) changes the situation, the energy of the exciplex is lowered relative to that formed with furan and a stable, fluorescent exciplex is formed with 1-cyanonaphthalene.

The singlet energy of 9-cyanophenanthrene however is still too low for exciplex formation to be favourable. The ionisation potentials of 2,5-dimethylfuran (8.01 e.v.[141]) and N-methylpyrrole (8.2 e.v.[141]) are sufficiently low such that both form a stable exciplex with 9-cyanophenanthrene.

Naphthalene, as noted in Section 2:4:1 is less likely to act as an electron acceptor in formation of an exciplex than 1-cyanonaphthalene since the ^1E_S and E.A.$_A$ terms (Section 2:1:5) are less favourable by approximately 13kcal/mole,[144]

as a result the most favourable electron donors i.e., N-methylpyrrole and 2,5-dimethylfuran, fail to form a fluorescent exciplex with naphthalene. The failure to observe fluorescent exciplexes with 9-cyanoanthracene as the electron acceptor is probably due to its low singlet energy, the situation appears to be similar to that of anthracene which will only form fluorescent exciplexes with donors posessing low ionisation potentials.

The quenching rate constants determined for the fluorescence quenching of aromatic hydrocarbons indicate that the quenching efficiency is dependent upon the ionisation potential of the donor. Furan and thiophene are inefficient quenchers of both 9-cyanoanthracene and 1-cyanonaphthalene, k_q being well below that expected of a diffusion controlled reaction, whilst N-methylpyrrole and 2,5-dimethylfuran quench the two cyanosubstituted hydrocarbons at a rate approaching the diffusion controlled limit. This would be expected for a charge-transfer mechanism since the donors with the lower ionisation potentials should be more efficient quenchers. Similar results have been reported for the 1-cyanonaphthalene-furan[150] and naphthalene-pyrrole[151] systems, in both cases kinetic studies showed that the quenching process was relatively inefficient. Exciplexes were proposed to account for the observations.

The importance of the electron affinity of the hydrocarbons is reflected in the higher k_q obtained for 9-cyanoanthracene compared to that of anthracene.

The effect of solvent upon k_q is quite marked, it can be seen that quenching of 9-cyanoanthracene with N-methylpyrrole is far less efficient in cyclohexane than it is in

acetonitrile, further, the difference cannot be accounted
for purely by a change in the viscosity of the solvent, the
ratio of k_q for the two solvents, $k_q(A)/k_q(C)$, is 3.8 whereas
that for the diffusion controlled rate constant $k_d(A)/k_d(C)$
is 2.8. It is also apparent that N-methylpyrrole quenches
1-cyanonaphthalene and 9-cyanoanthracene at approximately
the same rate in acetonitrile despite the difference in the
singlet energies of the two hydrocarbons i.e. it appears that
charge-transfer between 9-cyanoanthracene and N-methylpyrrole
becomes more favourable in acetonitrile solution, presumably
because the exciplex is more stable. This suggests that
formation of the exciplex in non-polar solvents and probably
acetonitrile is a reversible process,

$$Ar + Q \xrightarrow{h\nu} Ar^* + Q \rightleftharpoons (ArQ)^* \rightleftharpoons (Ar^{d-}....Q^{d+})^*$$
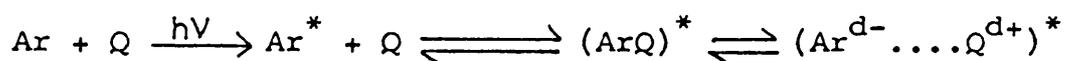
the fact that the donors of high ionisation potential quench
inefficiently also suggests that dissociation of the exciplex
back to the locally excited state may take place.[145,152] The
efficiency of the fluorescence quenching process will thus
be limited by the efficiency of electron transfer within the
exciplex and the more stable the exciplex the less is the
likelihood of the back reaction taking place. It was noted
in Section 1:2:1 that the efficiency of energy transfer bet-
ween two molecules is dependent upon the separation of the
energy levels; similar considerations apply here, hence the
greater solvating power of acetonitrile compared to cyclo-
hexane will give rise to a more stable exciplex rendering the
back reaction less efficient, and giving rise to a larger k_q.

It would be expected that a donor of high ionisation potential,
even in acetonitrile, would form a relatively unstable exciplex
and this should be reflected by a low k_q indicating that the
back reaction from the exciplex is important.

2:5 DONOR-ACCEPTOR COMPLEXES FORMED BY IMIDES.

The formation of a donor-acceptor (DA) complex is usually detected by the presence of a new absorption band in the electronic absorption spectrum, this is commonly called a charge-transfer (CT) transition. Excitation into this band will produce an excited CT complex, the formation and stability of such a complex is affected by the same factors as are intramolecular exciplexes. The ionisation potential of the donor, the electron affinity of the acceptor and the type of chain linking the two groups will therefore be of importance. A sandwich-pair conformation of the molecule is not a necessary prerequisite for the observation of a CT transition i.e. steric factors are not critical, however for a complex of the type,

$$D - (CH_2)_n - A$$
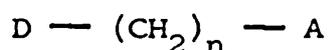
the CT transition is usually most readily observable when n = 2 or 3 and the transition decreases in intensity as n is increased through four and five.[153-156] The situation is not therefore dissimilar to that for the formation of an intramolecular exciplex.

2:5:1 DONOR-ACCEPTOR COMPLEXES FORMED WITH AMINES.

Results.

Phthalic anhydride and tetrachlorophthalic anhydride are known to be good electron acceptors,[98] it is therefore to be expected that the corresponding imides will also be electron acceptors. Amines, especially aryl amines, are known to be

good electron donors, it therefore seems reasonable to expect the amines to form a DA complex with imides. Compounds in Series $\underline{\text{VI}}$, and the closely related compound $\underline{43}$ have been found to exhibit a new electronic absorption

$\underline{\text{VI}}$, n = 0,1,$\overset{a.}{2}$,3,4. $\underline{43}$
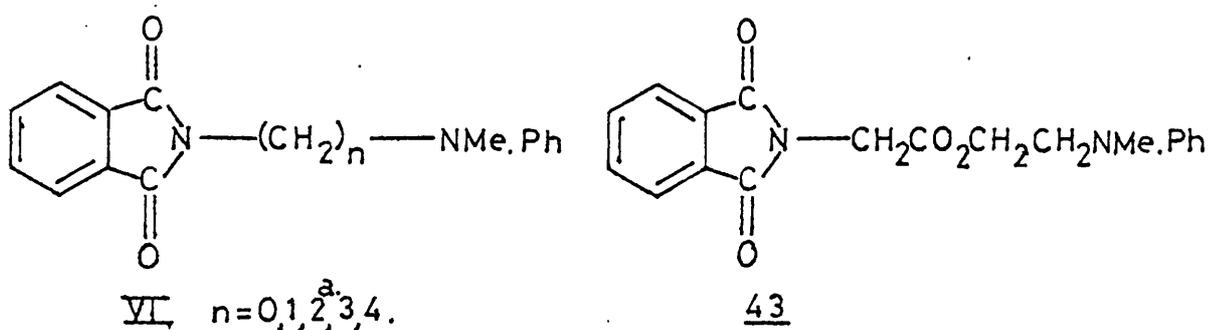
band, this has been attributed to a CT transition. Compounds in Series $\underline{\text{VII}}$, which posess a dialkyl amino group show similar, but less marked, properties to the compounds in Series $\underline{\text{VI}}$.

1. n = 2 . $R' = R'' = Me$.
2. n = 3 . $R' = R'' = Et$.$^{a.}$

$\underline{\text{VII}}$
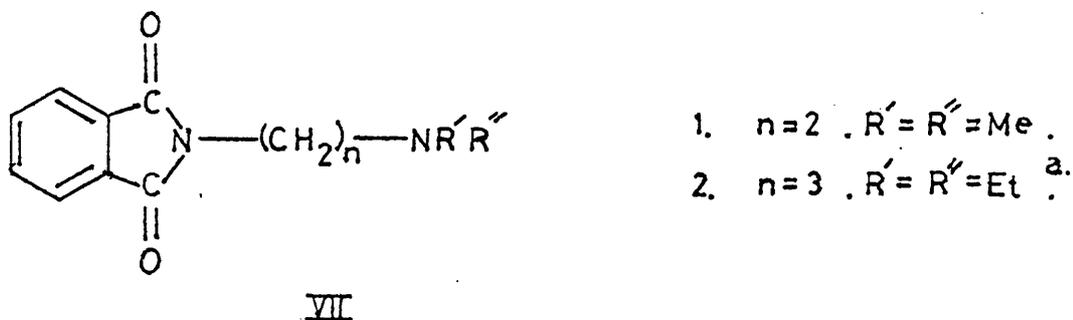
Two compounds derived from tetrachlorophthalimide, $\underline{\text{VIII}}$ (1) and (2), also show CT transitions in their ultra-violet absorption spectra.

1. n = 0 .
2. n = 2 .

$\underline{\text{VIII}}$
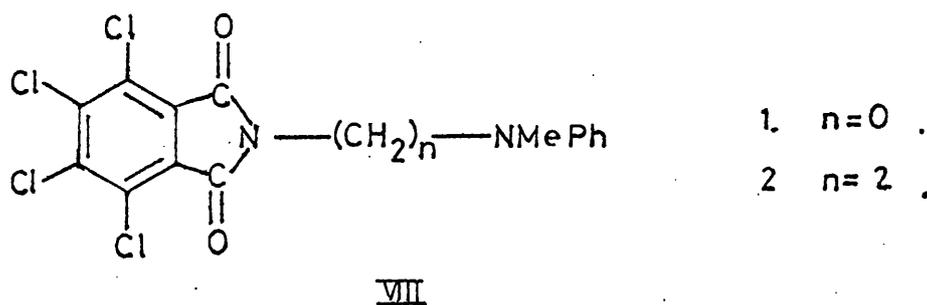
a. These compounds were a gift from Dr. M.J. Harper, I.C.I. Organics Division, Manchester.

144.

The absorption spectrum of each compound was recorded in several solvents. The CT transition was often observed as a discrete band for the compounds containing an aryl amino group, only a broadening of the absorption due to the phthalimide was apparent for $\underline{VII}$ (1) and (2).

The absorption spectrum of each compound was compared to that of a "reference" solution containing equimolar quantities of N-n-butylphthalimide (NBP) or N-n-butyltetrachlorophthalimide (NBTP) and triethylamine or N,N-dimethylaniline. The reference spectra were found to be similar to those produced by addition of the spectra of the separated compounds, higher concentrations (greater than 10^{-2}M) led to CT transitions which are believed to be the result of intermolecular DA complex formation.[157]

Compounds $\underline{VI}$ (0) and (2), $\underline{VII}$ (1) and (2) obey Beer's Law over a wide concentration range (10^{-2}M to 10^{-4}M) in both benzene and 95% ethanol. Compound $\underline{VIII}$(1) obeys Beer's Law in acetonitrile over the same concentration range.

The addition of small quantities of hydrochloric acid to solutions of the compounds caused the CT transition to disappear for those compounds in which the chain insulating the two chromophores contained more than one carbon atom.

The wavelengths of maximum absorption and the molar extinction coefficients for $\underline{VI}$, $\underline{43}$ and $\underline{VIII}$ are shown in Table 30. The ultra-violet absorption spectra of $\underline{VI}$ and $\underline{43}$ are shown in Diagram 13. Difference spectra,obtained by subtraction of the spectrum of NBP - N,N-dimethylaniline from each of the spectra of $\underline{VI}$ and $\underline{43}$ do not show the same wavelengths in many cases, however their use as a method of obtaining
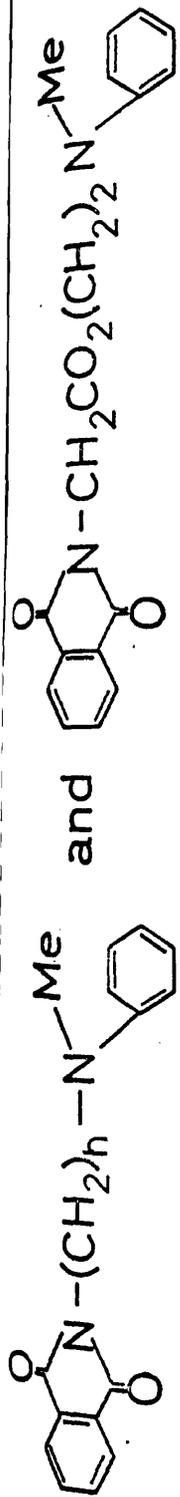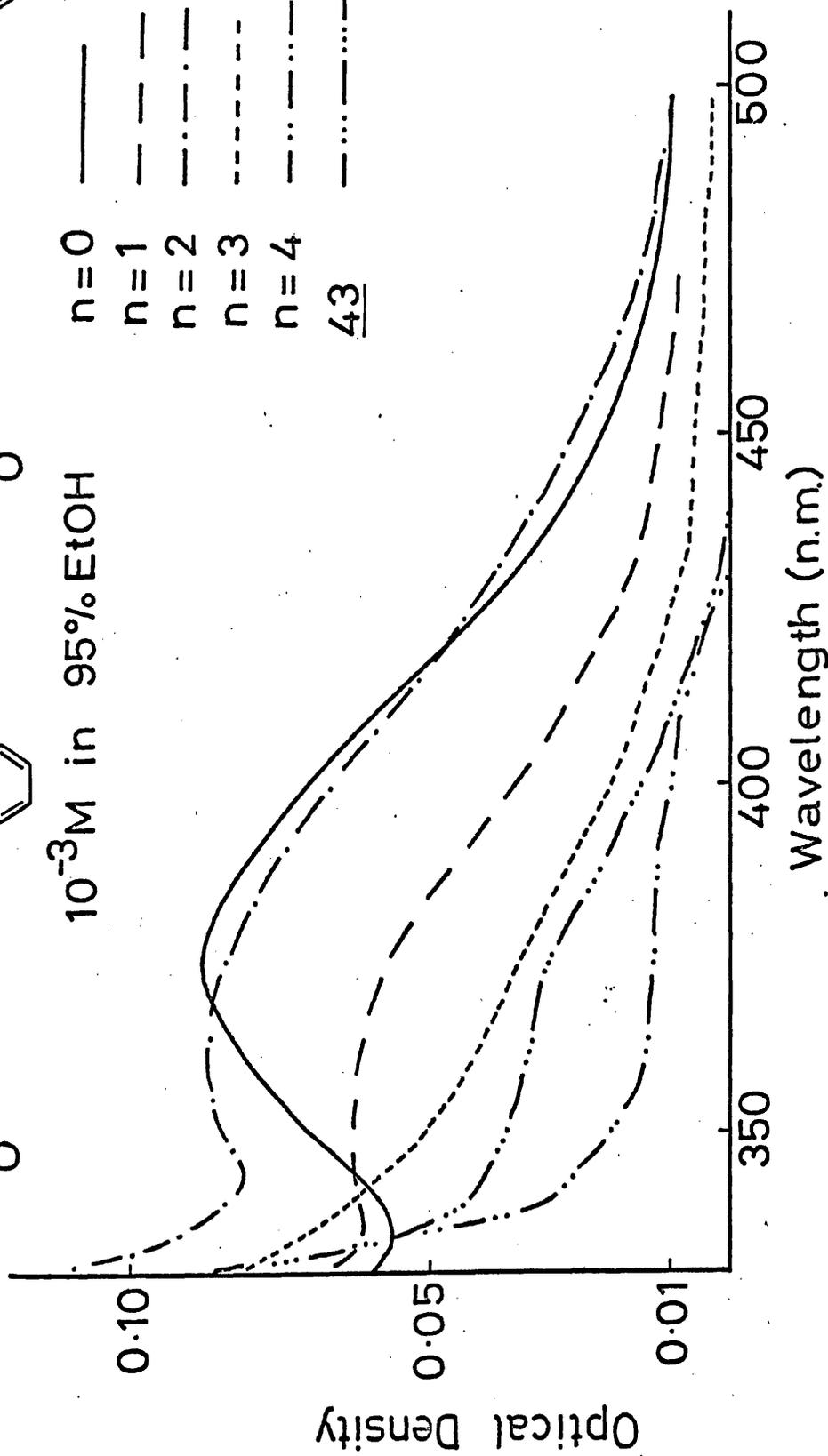
DIAGRAM 13. Ultra-violet absorption spectra of some phthalimides.

TABLE 30.

Wavelengths (NM) of maximum absorption and extinction coefficients[a] of some phthalimides.

Compound.	Cyclohexane.		Benzene.		95% Ethanol.	
	λ max.	ε_m	λ max.	ε_m	λ max.	ε_m
VII (0)	370	88	383	84	378	86
VII (1)	361	67	364	62	350	64
VII (2)	357	97	363	92	359	89
VII (3)[b]	400	16	400	16	400	22
VII (4)[b]	400	8	400	9	400	10
43[b]	400	11	400	15	400	16
VIII (0)[c]	412	65	408	62	402	40[d]
VIII (1)	402	90	400	75	-	-
TNBP - PhNMe$_2$[e]	425	43	-	-	-	-

a. ε_m is the molar extinction coefficient based on the concentration of the compound.

b. The absorption is a shoulder, λ max. and ε_m are given for 400NM (ε_m are in units of $m\ l^{-1}cm^{-1}$).

c. λ max. = 399, ε_m = 45 in acetonitrile.

d. Approximate vaule.

e. λ max. = 421, ε_m = 25 in acetonitrile.

extinction coefficients and wavelengths of maximum absorption have recently been criticised,[153] nevertheless they do serve to show that a "real" intramolecular interaction takes place in these molecules.

The ultra-violet absorption spectrum of N-n-butylmaleimide

has also been found to exhibit a weak CT transition in the presence of N,N-dimethylaniline e.g. ε_{molar} = 4.5 at 398NM in cyclohexane.

The compounds containing an N-methylanilino group fluoresce in non-polar solvents at room temperature, apart from $\underline{VI}$ (0) and $\underline{VIII}$(1). Compounds $\underline{VII}$ (1) and (2) did fluoresce, but the intensity of the bands was too low to allow a positive identification.

The wavelength of the fluorescence bands was found to be extremely sensitive to solvent polarity, shifting to longer wavelengths with a concomitant decrease in intensity as the polarity of the solvent was raised. Emission could not be detected in solvents more polar than benzene, indeed only $\underline{VI}$ (3) and $\underline{43}$ were found to fluoresce in this solvent. The fluorescence maxima of $\underline{VI}$ and $\underline{43}$ are shown in Table 31.

TABLE 31.

Wavelengths (NM) of fluorescence exhibited by $\underline{VI}$ and $\underline{43}$.[a]

Solvent.	Compound.				
	$\underline{V(1)}$	$\underline{V(2)}$	$\underline{V(3)}$	$\underline{V(4)}$	$\underline{43}$
Hexane.	515	525	525	515	510
Cyclohexane.[b]	520[c]	525	535	520	513
	(0.001)	(0.002)	(0.006)	(0.002)	(0.006)
Benzene-Cyclohexane.[d]	e.	551	550	540	540
Benzene.	e.	e.	565[c]	e.	565[c]

a. 10^{-2}M solutions at room temperature, 10^{-4}M solutions produced weaker emissions.

b. Fluorescence quantum yields shown in brackets.

c. Extremely weak emission.

d. Mixture of benzene and cyclohexane in the ratio 26:74

e. No emission observed.

A preliminary investigation of the fluorescence decay times of these compounds has indicated that the lifetime of the fluorescent excited state is short, ranging between approximate values of 10 and 30ns depending upon the compound.

It is possible to produce fluorescence by excitation of the compounds in either the CT absorption bands or the absorption bands arising from the uncomplexed compounds. The fluorescence excitation spectra were found to show two bands at approximately 315 and 390NM, corresponding to the complexed and uncomplexed states of the molecules.

Fluorescence was observed from solutions containing equimolar quantities (10^{-2}M) of NBP and N,N-dimethylaniline in cyclohexane (λ max. 510NM). This fluorescence was not detected when lower concentrations of the donor and acceptor were used or in solvents more polar than benzene. The equivalent complex formed with N-n-butylmaleimide does not exhibit CT fluorescence, only weak emission from the aryl amine was observed.

Compound $\underline{VIII}$ (2) was found to fluoresce in cyclohexane (5×10^{-4}M) at 570NM (λ max.) but not in benzene. Fluorescence from the equivalent intermolecular complex (each compound 5×10^{-3}M) was also detected (λ max. 560NM).

Discussion.

The long wavelength absorption of the compounds cannot be attributed as being due to either of the separate chromophores, further, since Beer's Law holds over a wide concentration range it is believed that the transitions are due to intramolecular interactions. This is substantiated by the fact that the equivalent intermolecular complex cannot be detected

at the concentrations used.

The position of the new absorption band does not appear to be dependent upon the solvent polarity which may indicate that the degree of charge-transfer in the ground state is small, nevertheless excitation into the new absorption band i.e. wavelengths where the separated chromophores do not absorb light, produces a fluorescence band that is sensitive to the solvent polarity. This is good evidence that excitation does produce charge-transfer.[158] The new absorption bands have thus been assigned to CT transitions but this does not necessarily imply that charge-transfer takes place in the ground state. Discrete CT transitions were not observed in many of the compounds, i.e. the association only causes a broadening of an absorption band of the components, although relatively few of the reactant molecules are correctly orientated to give a strong CT transition in these cases, this does not mean that quite a large proportion of the reactant molecules are not complexed.

The interaction between the two groups is likely to be "through-space", this is indicated by the observation that the wavelength of the CT band does not appear to depend markedly on the length of the linking chain i.e. the σ electrons of the chain are not involved in the CT transition. Although the chain linking the two chromophores does not contribute to the CT transition it does impose restraints upon the orientation of the two groups towards each other, as it does for intramolecular exciplex formation. The most favourable conformation should therefore be attained by $\underline{\text{VI}}$ (2) and (3) and this is observed to

be the case as judged by the intensity of the absorption band.
Longer chains, as in $\overline{\text{VI}}$ (4), give rise to a decrease in the
intensity of the CT transition, this is attributed to a lack
of association between the donor and acceptor groups as a result
of severe non-bonded interactions i.e. the energy gained by the
interaction of the groups barely overcomes the energy require-
ments for making the polymethylene chain adopt what is undoubt-
edly an unfavourable conformation. The fact that both a CT
transition and a CT fluorescence can be observed from $\overline{\text{VI}}$ (4)
at room temperature whereas N,N-dimethyl-4-(1-naphthyl)butyl-
amine ($\overline{\text{I}}$, n = 4) requires a lower temperature for observation
of an intramolecular exciplex fluorescence may reflect that
the DA complex has a higher $-\Delta H^*$, more energy is thus available
to overcome the eclipsing of C—H bonds in the polymethylene
chain.

The introduction of an ester group into the methylene
chain in <u>43</u> gives rise to a more intense absorption than for
$\overline{\text{VI}}$ (4), thus interaction of the donor and acceptor groups
is facilitated. This result is therefore analogous to those
reported in Section 2:1:1 regarding intramolecular exciplex
formation.

The observation of discrete CT transitions in $\overline{\text{VI}}$ (0)
and (1) is interesting since the geometry of the molecules does
not allow extensive overlap of the interacting groups and a
conformation in which the donor and acceptor groups form a
sandwich-pair is impossible. The situation in $\overline{\text{VI}}$(0) is such
that interaction is restricted to an overlap of the phthalimido
nitrogen <u>p</u>-orbital and the <u>p</u>-orbital of the C-1 carbon of the

phenyl ring (C-1 is the carbon by which the phenyl group is bonded to the amino nitrogen). The molecular framework is not as rigid for $\underline{VI}$ (1) and interaction may occur between the phthalimido nitrogen $\underline{p}$-orbital and the $\underline{p}$-orbitals of either the amino nitrogen or the C-1 carbon of the phenyl ring. The proposed conformations in which the CT transition takes place in these molecules are very similar to those suggested by de Boer for compounds of the type D — CH_2 — A in which overlap between the highest occupied molecular orbital of the donor and the first vacant orbital of the acceptor is poor.[153] The observation of a strong CT transition in $\underline{VI}$ (0) and (1) would thus presuppose that the orbitals which can overlap contribute to the relevant molecular orbitals.

A comparison of the wavelengths and extinction coefficients for the tetrachlorophthalimide-amine CT transitions shows that ε_m is higher in the intramolecular case, $\underline{VIII}$ (2), but λ max. is at a shorter wavelength. This suggests that whilst intramolecular formation of a DA complex is energetically less favourable since the most favourable conformation cannot be adopted[156] (or is energetically more difficult to attain) the close proximity of the two groups allows a greater number of molecules to interact.

The fact that the fluorescence lifetimes of the emissions from some of the compounds is short makes it possible to assign the emissions to fluorescence from a singlet state CT complex, the short lifetime should also preclude the possibility of delayed fluorescence contributing to the emission. The quenching of fluorescence in polar solvents is presumably due to a break up of the complex to form radical ions.[159]

Excitation into a CT absorption band has been shown to produce the complex in a Franck-Condon excited state, the complex subsequently relaxes to the most favourable conformation.[159,160] The formation and decay of the excited CT complex can thus be represented by the following mechanism in which the various non-radiative processes of the excited species have been omitted.

$$D + A \; \rightleftharpoons \; DA$$

$$h\nu \downarrow \qquad h\nu' \downarrow \qquad h\nu'' \downarrow \qquad \nearrow h\nu_F$$

$$^1D^* \qquad ^1A^* \qquad \qquad ^1(D^{d+} A^{d-})^*$$

$$^1D^* \rightleftharpoons \;\; ^1A^* \;\rightleftharpoons\; D, A \;\rightleftharpoons\; ^1(DA)^* \longrightarrow \;^3(DA)^*$$
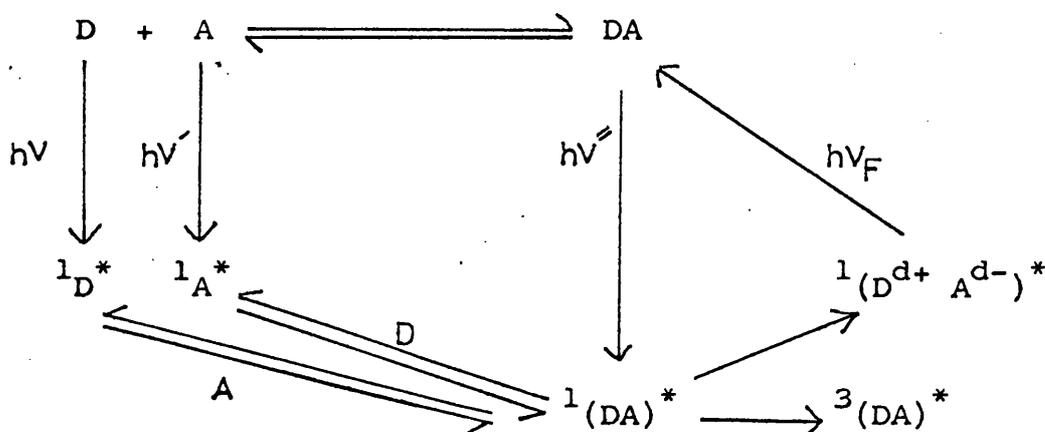
The interactions between $^1D^*$ and $^1A^*$ and ground state A and D groups respectively have been represented as equilibria although there is no direct evidence that this is the case.

There is the possibility of intersystem crossing from any of the excited species involved including the singlet complex which would thus give rise to the triplet excited complex $^3(DA)^*$. The formation of this latter species has been shown for other DA complexes to occur not from the relaxed singlet state but from the Franck-Condon state[159] i.e. a similar route to that found for the formation of the triplet hydrocarbon in amine-hydrocarbon exciplexes. The triplet

complex may dissociate into either of the locally excited states i.e., $(^3D^*A)$ or (D^3A^*), phosphorescence was detected from the acceptor (Section 2:5:2) but this is likely to have been formed by intersystem crossing from the acceptor and not from the complex since the energy of the triplet acceptor is appreciably higher than that of the singlet state of the complex. Although no new phosphorescence bands were detected it is possible that the emission from the triplet complex is at very low energy and consequently was not detected.

The similar wavelengths of maximum emission observed for each of the compounds in Series $\underline{VI}$ indicates that the relaxed excited states of the complexes have a similar conformation which is likely to be a sandwich-pair type in which the donor and acceptor groups are parallel, the lack of fluorescence from $\underline{VI}$ (0) and the low quantum yield for $\underline{VI}$ (1) may therefore be due to their inability to adopt such a conformation.

2:5:2 EFFECT OF SOLVENT AND TEMPERATURE UPON THE CHARGE-TRANSFER FLUORESCENCE OF DONOR-ACCEPTOR COMPLEXES FORMED WITH AMINES.

Results.

The emission spectra of $\underline{VI}$ and $\underline{43}$ were studied in three matrices, cyclohexane, acetonitrile and 95% ethanol, at $-196°$. CT fluorescence could be observed in both the polar solvents under these conditions, whereas at room temperature the emission is quenched.

The behaviour of the compounds was found to be different
in ethanol than in cyclohexane and acetonitrile. The main
emission from the latter solvents was found to be CT fluor-
escence. Phosphorescence expected from the phthalimide was
extremely weak if present at all. A yellow colour was found
to develop upon freezing of the solutions in cyclohexane or
acetonitrile and a corresponding change was observed in the
fluorescence excitation spectrum i.e. the most intense band
was found to be 400NM, and not 320NM as at room temperature.
This effect was noticed for solute concentrations of both 10^{-4}
and 10^{-2}M and in all cases the changes observed on freezing
could be reversed by thawing the solutions.

The emissions observed using an ethanol matrix were
dependent upon both the solute concentration and the wavelength
of exciting light. Phosphorescence from the phthalimide res-
idue (λ exn. 315NM) and CT fluorescence (λ exn. 390NM) were
observed for a solute concentration of 10^{-2}M, at 10^{-4}M only
phthalimide phosphorescence was observed and an excitation
band corresponding to a CT transition was absent.

The emission from matrices containing equimolar quantities
of NBP and N,N-dimethylaniline were also recorded for comparison
with those of $\underline{\text{VI}}$ and $\underline{43}$, the trend was exactly the same as
that previously observed except that complexing was not as eff-
icient at either 10^{-4} or 10^{-2}M since phthalimide phosphorescence
could always be detected.

The results are summarised in Tables 32 and 33 and an
example of the emission spectra is shown in Diagram 14.

TABLE 32.

Wavelengths (NM) at which maximum intensity of fluorescence (F) and phosphorescence (P) occurs for VI and 43 in degassed solutions at -196° a.

(Excitation wavelength NM)

Solvent	Concn.	n = 0 F.	n = 0 P.	n = 1 F.	n = 1 P.	n = 2 F.	n = 2 P.	n = 3 F.	n = 3 P.	n = 4 F.	n = 4 P.	43 F.	43 P.
Cyclohexane	10^{-4} M	b.	b.	535 (390)	b.	540 (400)	b.	540 (400)	b.	540 (400)	b.	540 (400)	b.
Ethanol	10^{-2} M	b.	468 (336)	525 (400)	450 (314)	535 (400)	b.	535 (400)	490 (362)	510 (314)	470	535 (350)	478 (321)
	10^{-4} M	b.	470 (330)	b.	450 (300)	b.	457 (310)	b.	455 (310)	b.	455 (312)	b.	478 (334)
Acetonitrile	10^{-2} M	b.	b.	545 (400)	b.	545 (400)	b.	545 (400)	b.	550 (450)	b.	548 (400)	b.
	10^{-4} M	b.	b.	540 [b] (380)	b.	545 (400)	b.	540 (400)	b.	549 (320)	b.	549 (400)	b.

a. N-n-butylphthalimide exhibits phosphorescence at 450, 460 and 470 NM in cyclohexane, ethanol and acetonitrile.

b. Very weak emission.

TABLE 33.

Wavelengths (NM) at which maximum intensity of fluorescence and phosphorescence for mixtures of N-n-butylphthalimide and N,N-dimethylaniline occur.

Solvent.	Solute Concn.	Temp.	Fluorescence. (Excitation wavelength NM)	Phosphorescence. Excitation wavelength NM
Cyclohexane.	10^{-4}M	20°	a.	a.
		-196°	530 (400)	440 (310)
Ethanol.	10^{-2}M	-196°	540 (400)	466 (326)
	10^{-4}M	-196°	a.	435 (310)
Acetonitrile.	10^{-2}M	-196°	545 (400)	a.
	10^{-4}M	-196°	545 (310 or 400)	450 (310)

a. No emission detectable.

10^{-2} Min degassed 95% EtOH −196°

1. Total emission spectrum λ exn. 350 n.m.

2. Phosphorescence spectrum λ exn. 321 n.m. (Intensity x 50)

Relative Intensity

650   600   550   500   450   400

Wavelength (n.m.)

DIAGRAM 14.

1

2
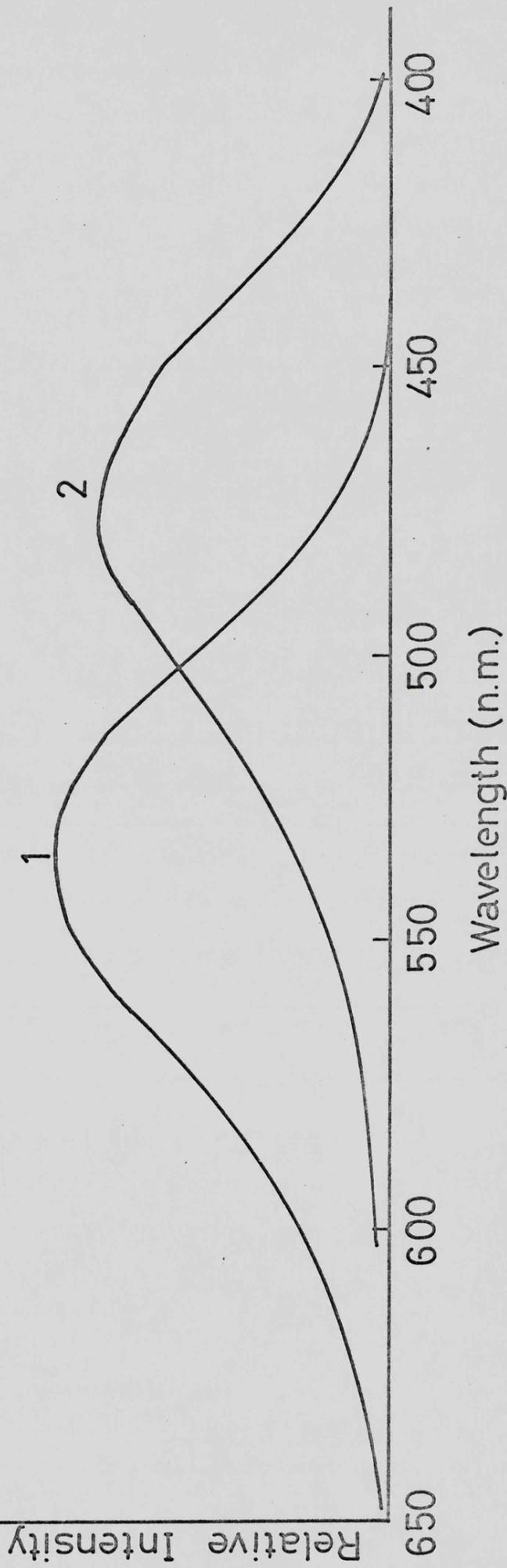
Discussion.

The freezing process appears to aid the formation of a DA complex when cyclohexane or acetonitrile are used as solvents, the developement of the yellow colour and the corresponding changes in the fluorescence excitation spectra both substantiate this point. The failure to detect phosphorescence from the phthalimide indicates that a large number of the molecules exist as DA complexes. Intersystem crossing from the singlet complex is unlikely to produce triplet phthalimide since NBP phosphoresces at approximately 450NM which is of higher energy than the fluorescence of $^1(DA)^*$.

The freezing of ethanolic solutions of the compounds does not appear to aid formation of a complex, CT fluorescence cannot be observed at a solute concentration of $10^{-4}M$ and there is not an excitation band attributable to a CT transition. A high concentration ($10^{-2}M$) of solute in ethanol does produce CT fluorescence, but excitation at 315NM gives NBP phosphorescence, thus indicating that not all of the molecules are complexed.

These results suggest that the solvating properties of ethanol and acetonitrile are affected by the freezing process to such an extent that they cannot aid the dissociation of the complex as they can in fluid solution. The reason for the weak CT fluorescence from the ethanolic matrices may be the result of specific solute-solvent inte.. .....ons, thus the formation of a hydrogen bond between the N-methylanilino group and the ethanol may inhibit DA complex formation, energy will have to be expended to break this bond in order that a complex may

form. A similar reason has been proposed[82] to explain the effect of alcohols reducing the potential of amines to participate in exciplex formation.

The results presented in Table 33 show that CT fluorescence can be observed as a result of intermolecular DA complex formation, indeed the same yellow colour was noted upon freezing of 10^{-2}M solutions of the components in acetonitrile and cyclohexane, it is therefore possible that the emissions derived from $\underline{VI}$ and $\underline{43}$ are due to intermolecular interactions. It is not possible in fact, to assign DA complex formation as arising entirely from intramolecular interactions in any case, it can be seen that intermolecular complex formation takes place under the same conditions as does intramolecular complex formation. The observation of NBP phosphorescence from a mixture of NBP and N,N-dimethylaniline upon excitation with light at 310NM shows that all the solute molecules are not complexed except at 10^{-2}M in acetonitrile. It is therefore probable that CT fluorescence from $\underline{VI}$ and $\underline{43}$ takes place from complexes formed both inter and intramolecularly.

There are several possible reasons for the enhancement of DA complex formation upon freezing of the solutions.

1. The compounds crystallise from solution.

2. Aggregates of the molecules are formed.

3. The equilibrium between complexed and uncomplexed molecules is changed.

The formation of crystals of $\underline{VI}$ and $\underline{43}$ in frozen cyclohexane and acetonitrile would in fact explain the yellow colour

that is produced since the crystals of the compounds are all

yellow. The effect does not appear to be isolated to the comp-

ounds already mentioned, similar effects have been observed

for DA complexes formed between imides and aromatic hydrocarb-

ons (Section 2:5:3) and for aromatic hydrocarbons (Section

2:6:2). There are also precedents in the literature for the

formation of aggregates and microcrystals e.g. aggregation of

ketones[161] and crystallisation of pyrene,[162] but the enhance-

ment of formation of an intermolecular DA complex appears

to be unknown. It is interesting to note that the effect

could not be detected for the intermolecular NBP-1-methyl-

naphthalene DA complex which exhibits only a weak CT transition

(Section 2:5:3) but it could for the intermolecular NBTP-

anthracene complexes which show a relatively intense CT trans-

ition, hence it is possible that the prior existence of a

"strong" DA complex is necessary to observe the effect inter-

molecularly. The equilibrium in these cases may be changed

by the freezing process such that a large number of molecules

become complexed.

2:5:3   DONOR-ACCEPTOR COMPLEXES FORMED WITH AROMATIC HYDRO-
        CARBONS.

Results.

Intermolecular complex formation between aromatic

hydrocarbons and anhydrides or imides is well known; phthalic

anhydride, tetrachlorophthalic anhydride, and pyromellitic

anhydride are commonly used as acceptors; pyrene, anthracene,

naphthalene and various substituted benzenes often being used
as the donors (see for example Refs. 163-165). A few examples
of intramolecular complexes of this type have been reported
(see for example Refs. 154, 166, 167).

Compounds IX (1), (2) and (3) do exhibit a new fluor-
escence band in non-polar solvents at room temperature.
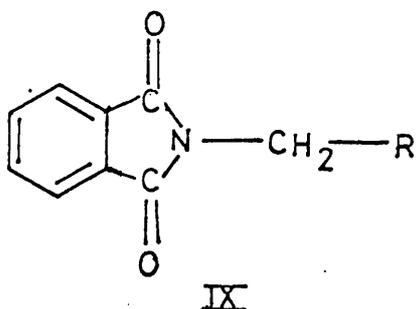
1   R = CH_2-(1-naphthyl).
2   R = $CH_2OCO(CH_2)_2$-(1-naphthyl)
3   R = CH_2-(3-indolyl).

IX

The emissions could be observed with exciting light of wave-
lengths up to 360NM, a region in which neither the phthalimide
nor hydrocarbon chromophores absorb. The wavelengths of max-
imum emission in cyclohexane were found to be 415 and 419NM
respectively for IX(1) and (2). Fluorescence could not be
detected in polar solvents such as acetonitrile. Emission from
mixtures of NBP and 1-methylnaphthalene was found to be fluor-
escence from the aromatic hydrocarbon in both cyclohexane
and acetonitrile.

The ultra-violet absorption spectrum of each compound
was found to possess a long wavelength tail, this was quite
pronounced for IX(3). The spectrum of mixtures of NBP and
1-methylnaphthalene did not show a tail, but those of NBP and
3-methylindole did, but the intensity of the latter absorption
was found to be weaker than that for IX(3).

The emission from these compounds was also studied in matrices of cyclohexane, acetonitrile and 95% ethanol at -196°. The compounds containing naphthalene emitted intense naphthalene phosphorescence compared to 1-methylnaphthalene at low solute concentrations (10^{-4}M). The new fluorescence band observed at room temperature was also detected, the wavelength of maximum emission was found to vary between 430 and 450NM. Phosphorescence from the phthalimide group and fluorescence from the naphthalene group were not observed. It was possible to detect naphthalene phosphorescence by exciting with light of wavelength up to 360NM, the new fluorescence was also observed under these conditions.

Breen and Keller[166] have also studied $\underline{IX}$(1) at room temperature and in rigid matrix (-196°), their findings are in agreement with those reported here, the only difference is that the new fluorescence band was not observed by them at room temperature in t-butanol-isopentane (3:7). An interesting point from their work is that the absorption spectrum of $\underline{IX}$ (1) at -196° shows a relatively intense long wavelength absorption with a molar extinction coefficient of approximately 500 at 330NM, this compares with a value of 50 taken from a spectrum recorded at room temperature for this work. The excitation spectra show a corresponding change upon freezing i.e, they shift to longer wavelengths.

The compound containing indole, $\underline{IX}$(3), was found to emit a strong fluorescence band at approximately 500NM, similar emissions were observed from matrices containing NBP and 3-methylindole at the same concentrations as used for $\underline{IX}$(3),

only very weak indole and phthalimide phosphorescence were observed.

Matrices containing a higher solute concentration (10^{-2}M) of the naphthalene compounds showed the same fluorescence bands but the naphthalene phosphorescence was found to be "distorted" i.e. the emission lost much of the vibrational fine structure and there was also a slight red shift (the emission spectrum of IX(1) is shown in Diagram 15). Emission from a cyclohexane matrix containing NBP and 1-methylnaphthalene (both 10^{-2}M) did not show this distortion, further no anomalous fluorescence bands were detected.

The absorption and fluorescence spectra of mixtures of NBTP and various anthracenes also exhibit new bands. The absorption bands were only observed as a tail or shoulder on the absorption of the phthalimide, ε_{molar} (cyclohexane) at 430NM for solutions containing equimolar quantities of the two components were found to be, anthracene 20; 9-methylanthracene 64; 9,10-dimethylanthracene 8; 9,10-diphenylanthracene 2.

Fluorescence bands corresponding to these absorptions were observed both at room temperature and at -196° in cyclohexane, the frozen solutions were always yellow. The wavelength of maximum fluorescence was found to vary depending upon the hydrocarbon used: anthracene 505NM; 9-methylanthracene 525NM; 9,10-dimethylanthracene 538NM. A new fluorescence band could not be detected using 9,10-diphenylanthracene.

Discussion.

Aromatic hydrocarbons and anhydrides are known to form DA complexes, it is therefore likely that the new absorption

1. Fluorescence (20°) λ exn. 330n.m. Intensity x 8

2. Total emission (-196°) λexn. 300n.m. Intensity x 1

3. Phosphorescence (-196°) λexn. 350n.m. Intensity x 10

5 x 10⁻³M in Cyclohexane

Wavelength n.m.

DIAGRAM 15

Relative Intensity
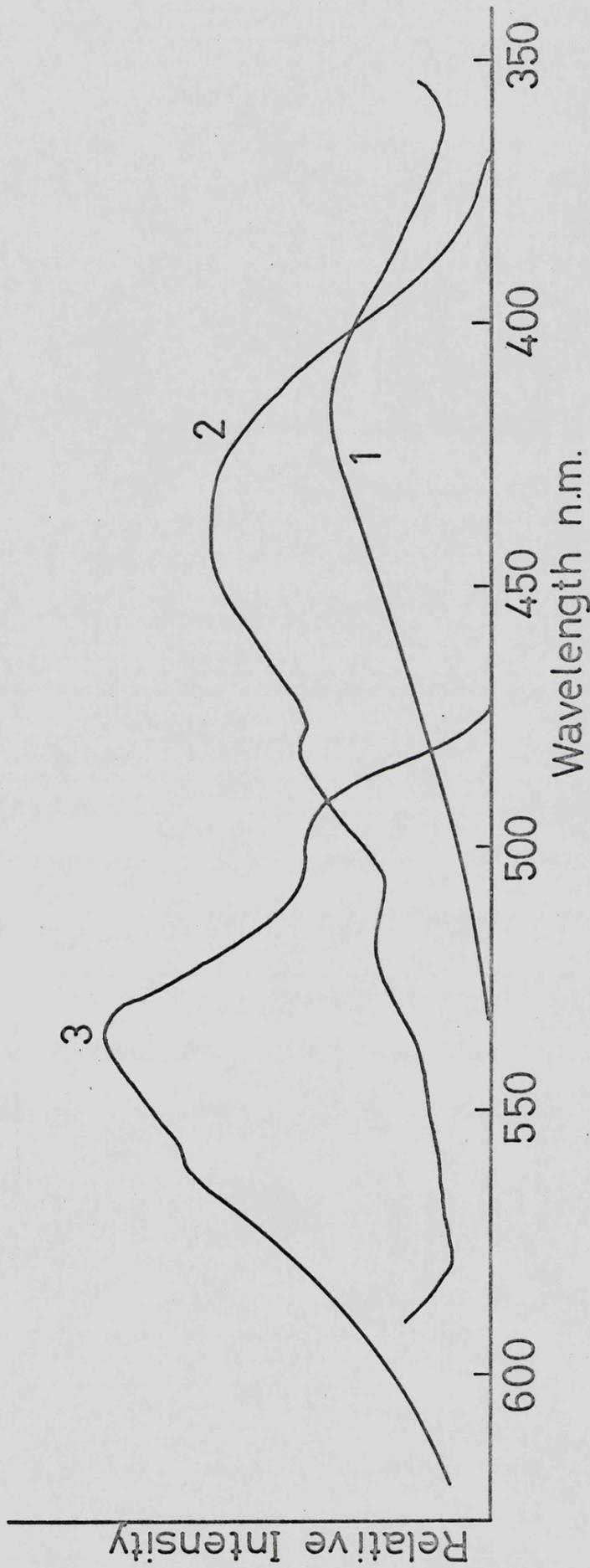
165.

bands observed for IX are charge-transfer in nature i.e. the absorption corresponds to a CT transition and the fluorescence is emission from an excited state CT complex. The fact that the fluorescence maxima of the NBTP-anthracene complexes shift to longer wavelength as the ionisation potential of the donor decreases also suggests that the excited complexes formed between imides and hydrocarbons possess charge-transfer character. The quenching of fluorescence in polar solvents can then be attributed to a dissociation of the complex into radical ions.[159] The results also indicate that the new fluorescence and absorption bands are derived largely from intramolecular interactions in fluid solution.

Breen and Keller also attributed the new fluorescence band of IX(1) to CT fluorescence, their failure to observe it at room temperature is probably a consequence of the high solvent polarity thus leading to a dissociation of the excited complex. The absence of naphthalene fluorescence and phthalimide phosphorescence was believed to be the result of efficient energy transfer, the most important processes are represented by the following mechanism,
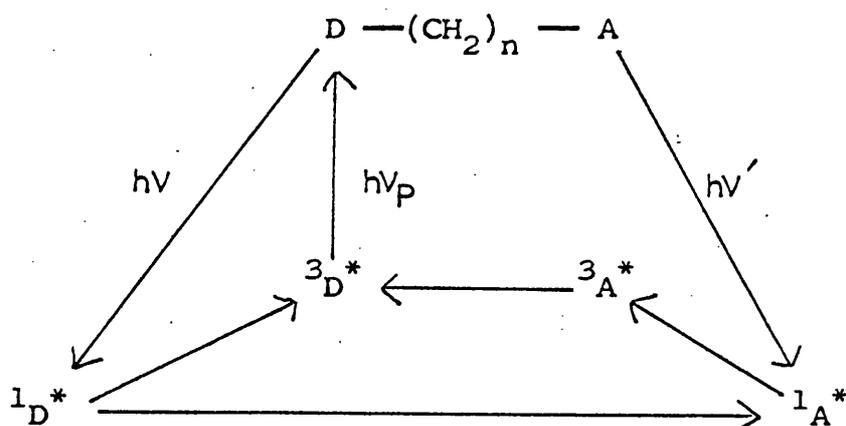
Thus excitation of naphthalene yields its first excited singlet

state, energy transfer to the phthalimide chromophore followed

by intersystem crossing yields the phthalimide triplet. The

naphthalene triplet is of lower energy than that of the phthal-

imide hence the electronic excitation energy is observed as

naphthalene phosphorescence. This mechanism was substantiated

by the fact that excitation of the phthalimide yielded naphthal-

ene phosphorescence. It was inferred from these results that

complete energy transfer is possible from all conformers of the

molecule in rigid matrix at -196°.

The presence of a DA complex however, does indicate

another possibility i.e. energy transfer within the complex.

The intensity of the CT transition at -196° is greater than at

room temperature which suggests that freezing aids complex form-

ation (Section 2:5:2). Energy transfer in IX(1) may thus take

place within the complex i.e. a conformation in which the two

groups are close together, and consequently it may not be

necessary to propose that transfer takes place from all conf-

ormers.

Excitation with light of wavelength 360NM was observed

to give rise to both CT fluorescence and naphthalene phosphor-

escence, this provides direct evidence for intersystem crossing

from the singlet complex to the triplet complex. It seems

reasonable therefore to add the following steps to the mechanism,

$$(DA) \xrightarrow{\quad h\nu \quad} {}^1(DA)^*$$

$$h\nu_P \qquad h\nu_F$$

$${}^1(D^{d+} A^{d-})^*$$

$$({}^3D^*A) \xleftarrow{\qquad\qquad} {}^3(DA)^*$$
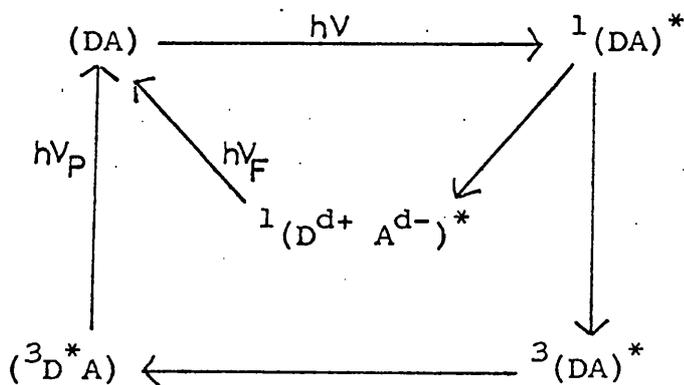
The step involving localisation of the electronic excitation energy upon the donor molecule is reasonable since the triplet state of naphthalene is the lowest in energy,[168] it may however be idealised since the vibrational fine structure of the naphthalene phosphorescence was sometimes observed to be distorted, this may be due to the species $^3(DA)^*$ being stabilised by contributions from charge-transfer states.[159,163,169] There is also the possibility that the broadening is due to phosphorescence from a triplet complex, such emissions have been observed from phthalic anhydride - substituted benzene complexes,[170] however the CT phosphorescence in these cases was always at lower energy than the phosphorescence of either the donor or the acceptor, the broadening is therefore unlikely to be due to CT phosphorescence in IX(1) and (2). A further possibility is that a triplet excimer is formed by interaction of the triplet complex with an uncomplexed donor molecule. Briegleb[171] has studied the DA complexes of naphthalene with tetrachlorophthalic anhydride in n-propylether between -117 and -153° observing a structureless, red shifted phosphorescence dependent upon both the concentration and the temperature which was believed to be phosphorescence from $(^3DD^*A)$,

$$(DA) \xrightarrow{h\nu} {}^1(DA)^* \longrightarrow {}^3(DA)^* \longrightarrow (^3D^*A) \xrightarrow{D} (^3DD^*A)$$
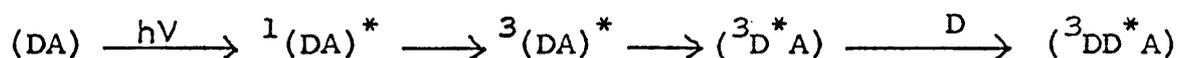
The temperature would appear to preclude such a mechanism for IX(1) and (2) since the slightly higher temperatures allow diffusion of a donor molecule to interact with $(^3D^*A)$, but since the distortions appear to be concentration dependent it is possible that interactions of this type take place.

The longer wavelength of maximum fluorescence from IX

(3) may reflect that indole has a lower ionisation potential

than naphthalene hence electron transfer is more favourable,

the wavelength of the emission is indeed similar to those

found for the complexes formed between phthalimides and aryl

amines (Section 2:5:1).

The lack of CT fluorescence from mixtures of NBTP and

diphenylanthracene is probably due to the fact that the phenyl

rings are not in the same plane as the anthracene nucleus, the

dihedral angle between the aromatic ring planes is 67° [172]

Thus steric hindrance inhibits approach of the two molecules

and as a consequence DA complex formation is inefficient. This

result parallels the findings that 9-methyl and 9,10-dimethyl-

anthracene form fluorescent excimers but 9,10-diphenylanthracene

does not.[168]

The formation of excimers parallels that of exciplexes
in many respects, the essential differences are;

1. the excimer fluorescence maximum does not depend upon
the solvent polarity,

2. the steric requirements for the excimer are rigorous
compared to those of the exciplex.

The most favourable conformation is normally assumed to be a
symmetrical sandwich-pair in which the molecules are parallel
to each other and separated by approximately 3.0Å,[168,173] but
theoretical calculations have indicated that minor deviations
from a perfect sandwich-pair are necessary to account for the
excimer fluorescence.[174]

Two definitive studies on intramolecular excimer formation
have shown that a sandwich-pair is necessary for the observation
of excimer fluorescence. Diphenyl and triphenyl alkanes[175] and
dinaphthyl alkanes[176] i.e. compounds of the general type

$$Ar - (CH_2)_n - Ar$$
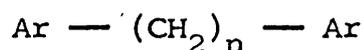
have been shown to form a stable, fluorescent excimer only
when n = 3. A sandwich-pair conformation can be attained when
n = 4 but this involves eclipsed C—H bonds which will lower
$-\Delta H^*$. The situation for n = 1 and n = 2 is such that the rings
cannot lie parallel and as a result intramolecular excimer form-
ation does not take place. The naphthalene compounds[176] were
found to exhibit strong excimer fluorescence only if symmetric-
ally substituted, restricted overlap (about 25%) can be achieved
when the two rings are parallel which gives further support to

the proposal that good overlap is necessary in an excimer.

Two groups of compounds only were known to exhibit intra-molecular excimer fluorescence, 1,3-diarylpropanes and para-cyclophanes[93] (q.v.), but very recently a paper[177] has described intramolecular excimer fluorescence involving pyrene nuclei separated by a linking chain of up to ten carbon atoms, intense excimer fluorescence was observed for compounds with n = 5 and 6, whilst weak fluorescence could still be detected when n = 8. Pyrene is known to have a high stabilisation energy $(-\Delta H^* = 9.2$ kcal/mole[179]) whereas naphthalene is more weakly bound $(-\Delta H^* = 6.2$ kcal/mole[180]), the magnitude of the stabilisation energy of the pyrene excimer appears to be sufficiently greater than that of naphthalene to allow unfavourable conformations to be adopted by the linking chain when the pyrene chromophores are in the excimer state.

2:6:1 INTRAMOLECULAR EXCIMER FORMATION.

Results.

A number of ethers (44 - 47) have been synthesised in which the chain separating the two naphthalene rings consists of three or more atoms,[a]
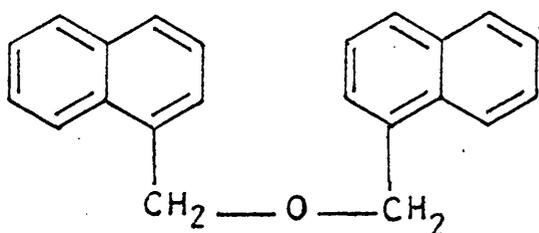
CH_2 —— O —— CH_2 44

a. These compounds were prepared with the assistance of Miss M Schmidt.

$CH_2O(CH_2)_n$ $\underline{45}$, n = 1
$\underline{46}$, n = 2

$CH_2O(CH_2)_2OCH_2$ $\underline{47}$.
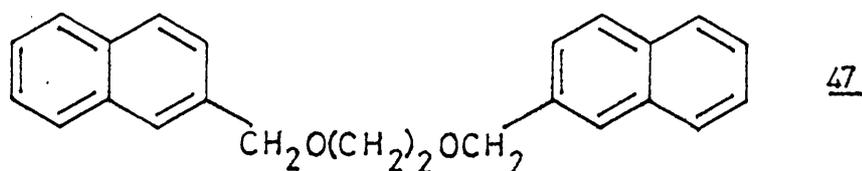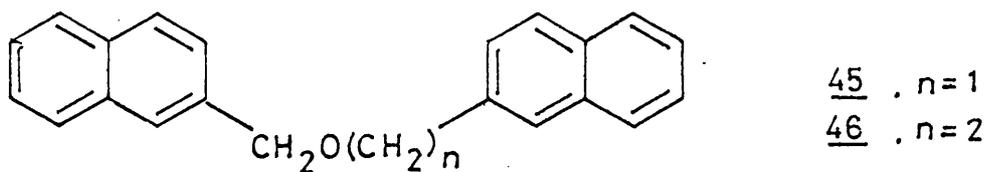
The ethers have been found to exhibit fluorescence bands other than those of the parent compounds $\underline{48}$ and $\underline{49}$.

CH_2OMe $\underline{49}$

CH_2OMe $\underline{48}$
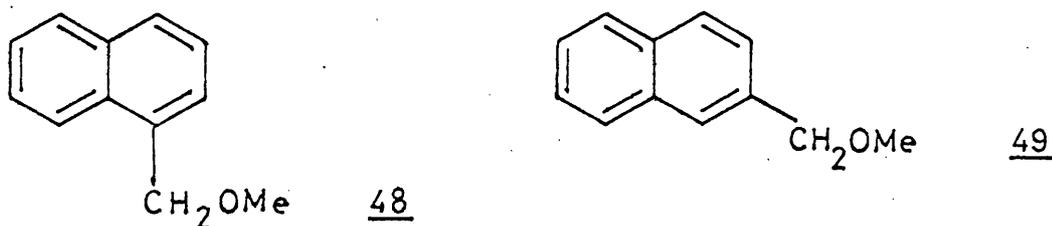
Discrete new fluorescence bands were observed for $\underline{44}$ and $\underline{45}$ whereas $\underline{46}$ and $\underline{47}$ were found to exhibit a very broad fluorescence band at approximately 380NM. The emissions from $\underline{44}$ - $\underline{49}$ were found to be independent of concentration in the range 10^{-3} - 10^{-5}M and of solvent polarity, the wavelength of maximum emission only shifting by about 2NM between cyclohexane and acetonitrile. The wavelengths of the fluorescence maxima are shown in Table 34 for one solvent and the fluorescence and fluorescence excitation spectra of $\underline{44}$ and $\underline{45}$ shown in Diagram 16.

1. Fluorescence of 44 λexn. 300 n.m.

2. Excitation Spectrum of 44 for 420 n.m.

3. Fluorescence of 45 λexn. 300 n.m.

4. Excitation Spectrum of 45 for 400 n.m.
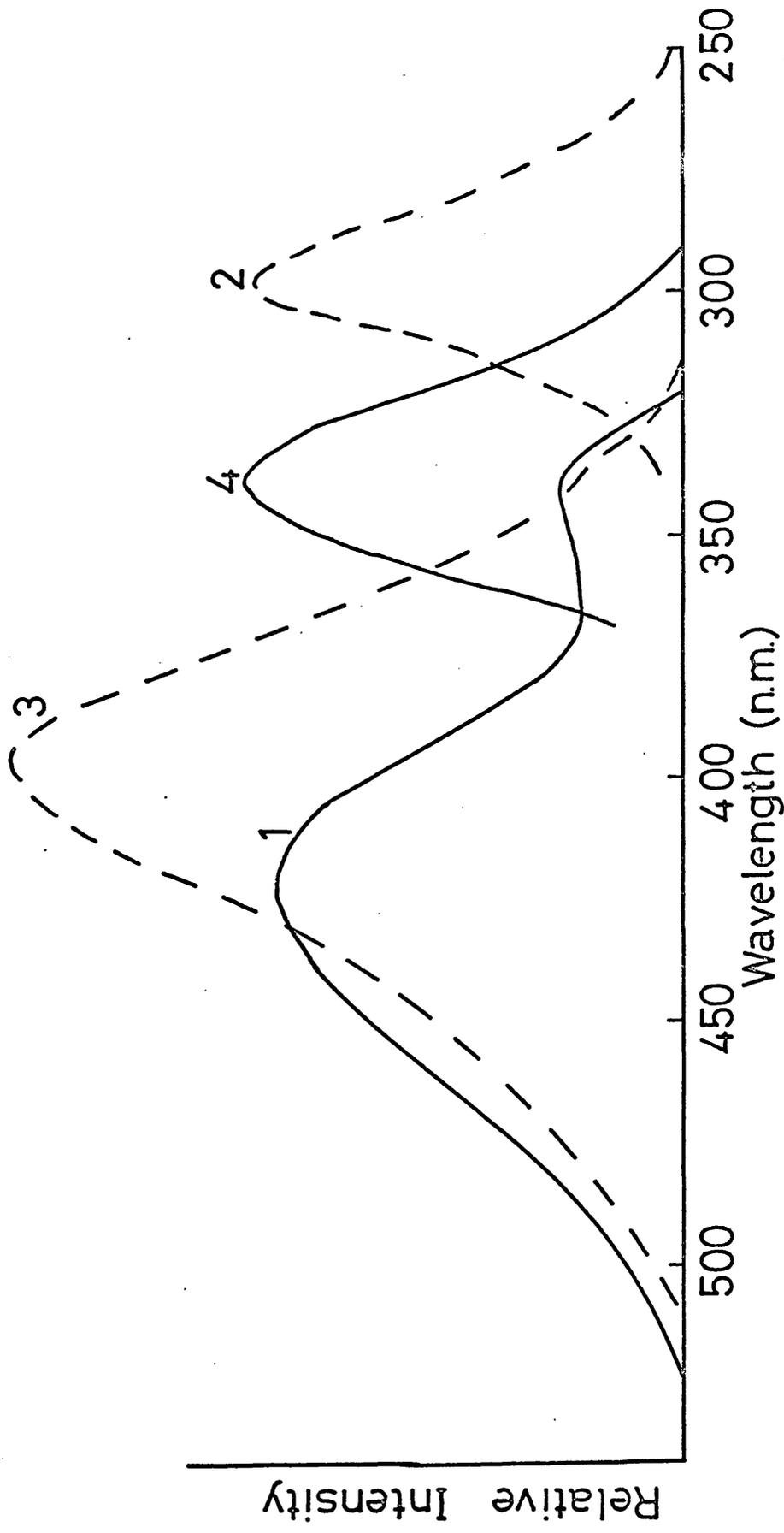
DIAGRAM 16. Fluorescence and Fluorescence Excitation of 44 and 45 in Acetonitrile (10^{-4}M).

TABLE 34.

Wavelengths (NM) of maximum fluorescence for 44 - 49.[a.]

44	45	46	47	48	49
345/422	398	379	380	348	347

a. 10^{-4} M solutions in 95% ethanol at room temperature.

The ultra-violet absorption spectra of 44 and 45 are essentially the same as those of the parent compounds, but it can be seen that the fluorescence excitation spectrum of 45 has a maximum at 340NM. The excitation spectrum of the parent compound 49, resembles that of 44 shown in Diagram 16. The absorption spectra of 46 and 47 both show a marked long wavelength broadening as compared to 49 and there is a similar change in the excitation spectra of these compounds, the maximum being at around 350NM for both. It is unlikely that these changes are due to impurities since three different compounds exhibit what appears to be the same effect, further, the fluorescence spectrum of 45 in methyl cyclohexane (10^{-4} M solution) at -196° does not show a fluorescence at 400NM, a broad monomer emission is seen with a fluorescence excitation maximum of 305NM.

Another group of compounds (50 - 53) have been studied in which the two aromatic hydrocarbons are joined by a linking chain containing an ester group,
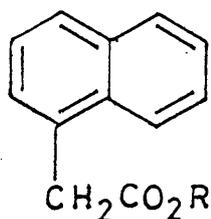
50 R = CH_2(1-naphthyl).
51 R = 1-naphthyl.
52 R = CH_2(9-anthryl).

CH_2CO_2R

174.
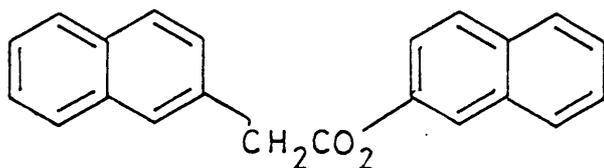
53

New fluorescence bands could not be detected from any

of these compounds although the fluorescence intensity of the

naphthalene residue was found to be less that that from the

parent compounds 39, 41 and 42 (Section 2:5:1).
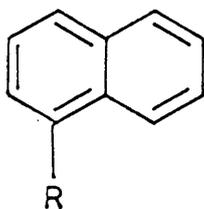
39   R = $CH_2CO_2CH_3$

41   R = CH_2OCOCH_3

42   R = $OCOCH_3$

The intensities of naphthalene fluorescence for 50, 51

and 53 (in degassed 95% ethanol at approximately 10^{-4}M) rel-

ative to the fluorescence intensity of 39 = 1.0 were found to

be: 50, 0.11; 51, 0.18; 53, 0.34.

Compound 52 was found to fluoresce mainly from the anth-

racene chromophore, excitation with light of wavelength 280NM,

at which the naphthalene absorbs about 71% of the light, gives

rise to a barely detectable naphthalene fluorescence, whilst

an equimolar mixture of 39 and 9-methylanthracene shows relativ-

ely strong fluorescence from both of the aromatic hydrocarbons.

The ultra-violet absorption spectra and the fluorescence

excitation spectra of the esters containing two naphthalene

rings were all found to be essentially the same as those of

the parent compounds. The spectra of 52 were found to contain
contributions from both naphthalene and anthracene but no
evidence was found for any abnormalities.

Discussion.

The new fluorescence bands observed for the ethers
show the characteristics of intramolecular excimer formation
in that the new band is independent of concentration and solvent
polarity, further, the fluorescence maxima of 44 and 45 are in
good agreement with those reported for 1,3-dinaphthyl propanes[176]
i.e. approximately 400 and 420NM for 1,1′ and 2,2′ -substituted
naphthalenes respectively.

The fact that new absorption bands appear for 46 and 47
and new fluorescence excitation bands for 45 - 47 suggests that
the new fluorescence does not emanate from an excimer, i.e.
via a true photoassociation process,

$$A + A \xrightarrow{\ h\nu\ } A^* + A \longrightarrow (AA)^*$$

but from an excited dimer in which association occurs before
and not after excitation of naphthalene,

$$A + A \rightleftharpoons (AA) \xrightarrow{\ h\nu\ } (AA)^*$$
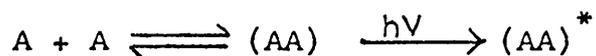
The problem then arises as to whether a true association process
actually takes place in the ground state or whether absorption
of light by pairs of molecules adjacent to each other gives
rise to $(AA)^*$. Specific interactions leading to association
do not seem feasible since the parent ether (49) does not
display atypical fluorescence or absorption bands even at high
concentrations, it therefore seems likely that the naphthalene
nuclei are close together in the ground state. The fact that
the fluorescence spectrum of 45 exhibits mainly monomer fluor-

escence at -196° in a rigid glass does demonstrate that the
fluorescence quenching does take place, at least in part, by a
dynamic process and, more important, it shows that the molecules
are not rigidly held together in fluid solution at room temp-
erature. A full overlap of the two naphthalene rings may not
be necessary for the observation of the new absorption and
excitation bands and a close proximity of the two rings may only
be required i.e. the favoured ground state conformation of these
molecules does not necessarily have to be that which is preferred
for the excimer. Indeed for such a conformation to be stable
would require that non-bonding repulsions in the linking chain
are minimal and this is really only possible for <u>45</u>,
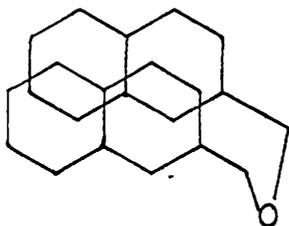
the separation between the two rings in this conformation is
about 3.0Å. Similar conformations are available for <u>46</u> and <u>47</u>
but due to the longer linking chain they are not as favourable
as for <u>45</u>.

The ultra-violet absorption and fluorescence spectra of
the <u>para</u>-cyclophanes[178] have some relevance with regard to
<u>45</u> - <u>47</u>, the compounds are of the general type shown in which
the benzene rings are forced to lie parallel (or nearly so),
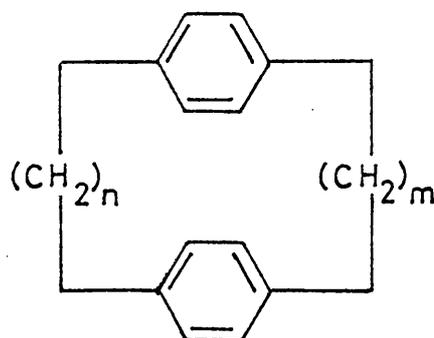
The closest contact between the rings occurs when m = n = 2

and in this case the electron clouds of the benzene rings

penetrate each other, this is manifested by the appearance of

a new absorption band. The cyclophanes with m = 2,n = 3

m = n = 3 and m = 3,n = 4 show similar but progressively

less pronounced absorption bands and when m = n = 4 interaction

cannot be detected in the absorption spectrum. The emission

spectra of these compounds all show anomalous fluorescence bands

which can only be attributed to excimer formation when m = n = 4.

The new absorption bands observed for 45 - 47 could thus be due

to transannular interactions of the type found in the cyclo-

phanes, the difference between the two being that the ethers

are not forced to adopt a conformation in which the two aromatic

rings are parallel.

It seems that on the basis of the absorption and fluor-

escence excitation spectra that an excimer mechanism must be

precluded for the 2,2′ -substituted naphthalene compounds 45 -

47 although it is likely that the singlet excited states produced

will be approximately the same as those which would be formed

by a photoassociation in fluid solution.

The difference in the wavelengths of maximum emission for 44 and 45 parallels that found for compounds exhibiting intramolecular exciplex formation (Section 2:1:1). On the assumption that the "excimer" state of 45 is not affected by the ground state interactions then the longer wavelength of maximum excimer emission from 44 suggests that the Franck-Condon ground state is of higher energy than it is for 45. The higher energy would be caused by repulsion between the C-8 hydrogen and the methylene group attached to the 1-substituted naphthalene. This may correlate with the anomalous absorption and excitation bands observed for 45 - 47 in that overlap of the naphthalene rings in 44 is unlikely in the absence of a driving force i.e. excimer formation.

It can be seen that the "n = 3 rule" first proposed by Hirayama[175] appears to be obeyed since those compounds with a longer chain do not show an appreciable "excimer" fluorescence, however the monomer bands are considerably red shifted and it therefore appears that introduction of an ether linkage has aided interaction between the naphthalene rings.

The fact that the fluorescence quantum yields of 50, 51 and 53 are lower than that of the reference compound shows that fluorescence quenching takes place as a result of interactions between the two naphthalene rings. The lack of excimer fluorescence from these esters is probably a function of the geometry of the molecules. Compounds 51 and 53 cannot attain a parallel arrangement of the two naphthalene rings i.e., they are forced to lie at an angle to each other. Compound 50 can attain a sandwich-

pair conformation but it is unfavourable for three reasons.

1. The methylene groups attached to the rings are forced out of plane.

2. The rings cannot approach much more closely than 4.0Å , a distance greater than that normally assumed necessary for excimer formation to take place.

3. Interference occurs between the methylene group and the C —8 hydrogen.

It is not suprising then that this compound does not exhibit excimer fluorescence.

Compound 52 exhibits transfer of electronic excitation energy i.e. excitation of naphthalene gives rise to anthracene fluorescence because the anthracene has a lower energy singlet excited state. Intramolecular energy transfer has previously been demonstrated for a similar compound (54)[181]

$$-CH_2CH_2CH_2-$$ 54
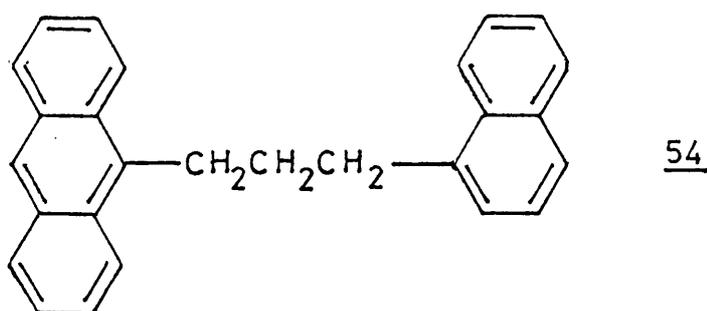
The effect was also observed when the polymethylene chain consisted of one and two carbon atoms.

2:6:2   FLUORESCENCE OF AROMATIC HYDROCARBONS FROM MATRICES.

Results.

The emission spectra of those compounds containing an

ester group, <u>50</u> - <u>53</u>, have been found to exhibit anomalous
fluorescence bands when contained in a solid matrix such as
cyclohexane or acetonitrile. The concentration of the solute
was generally 10^{-4}M. The new band was sometimes the only emiss-
ion that could be detected i.e. both fluorescence and phosphoresc-
ence from the monomer were quenched. The fluorescence maxima
were found to lie between 400 and 430NM for those compounds
containing only naphthalene (<u>50</u>, <u>51</u> and <u>53</u>) whilst <u>52</u> which
possesses an anthracene chromophore was found to fluoresce at
around 470NM. The fluorescence excitation spectra of these
bands were also recorded and often found to be red shifted from
those obtained in fluid solution.

The parent naphthalene compounds <u>39</u>, <u>41</u> and <u>42</u> and the
parent anthracene, <u>55</u>,[a] were also studied to see if the same
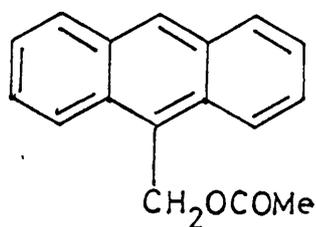
$\overset{|}{C}H_2OCOMe$ <u>55</u>

effects could be observed, similar fluorescence bands were
actually observed from <u>41</u> and <u>55</u>.

The maximum wavelengths of the fluorescence and fluorescence
excitation spectra are shown in Table 35 for 19° and -196°.
The matrices at -196° were all obtained by rapid cooling.

The emissions from the compounds were found to be those
of the parent hydrocarbon at 10^{-4}M in methyl cyclohexane matrix,

a. A sample of this compound was donated by Mr. K. Trethewey.

TABLE 35.

Wavelengths of maximum fluorescence (NM)[a] for some naphthalene compounds in cyclohexane and acetonitrile.[b]

Compound.	Cyclohexane.		Acetonitrile.	
	+19°	-196°	+19°	-196°
50	345	345, 408	347	408
	(295)	(295)(295)	(300)	(303)
51	342	403	346	400
	(297)	(320)	(297)	(297)
52	415,395,441	473	415,395,441	420,470Sh.[c]
	(390)	(395)	(395)	(400)
53	350	350, 430	350	350, 403
	(290)	(300)(308)	(290)	(303)(318)
39	345	348	350	350
	(297)	(298)	(297)	(297)
41	350	410	347	347, 410
	(302)	(302)	(293)	(305)(305)
42	345	345	-	-
	(295)	(295)		
55	415,395,441	480	-	-
	(390)	(395)		

a. Fluorescence excitation maxima in brackets.

b. 10^{-4}M.

c. Sh = Shoulder on most intense fluorescence.

the only exception was that of 53 which exhibited practically

the same emissions as in cyclohexane.

The fluorescence spectra were also recorded at temp-

eratures between 19 and -196°, it was found that in each case

the new fluorescence band appeared shortly after the solvent

had frozen although it was not apparent before this (see Diagram

17), further, the parent compounds 39 and 42 were found to possess

a fluorescence at about 410NM but this gradually decreased in

intensity as the temperature was lowered. Changes in the emiss-

ion spectrum of 39 were also observed upon fast cooling, the

spectrum was monitored by an oscilloscope (rather than a chart

recorder) over a period of one minute after insertion of the

sample (contained in a quartz tube) into liquid nitrogen.

The monomer fluorescence was replaced by a band at approximately

410NM after about 5 sec., this gained in intensity (up to 25 sec.)

and was subsequently replaced by naphthalene fluorescence and

phosphorescence. Plate 1 shows the oscilloscope photographs in

which these changes can be clearly seen.

Permanent changes were not detected for any of the compounds

i.e. on thawing of the matrix the emission reverted to its orig-

inal shape and intensity.

In view of the results reported in Section 2:5 it seemed

likely that aggregates or microcrystals would be responsible

for the anomalous fluorescence bands, consequently the emiss-

ion from the crystalline compounds was studied, in general only

fluorescence could be observed which was often very similar to

that from the compounds in a solid matrix. The greatest diff-

erence was noticed for the anthracene compounds in which the
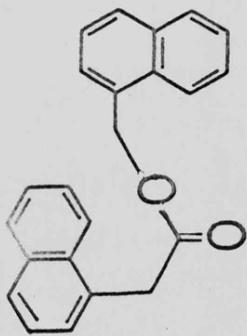
10^{-4} Min degassed MeCN
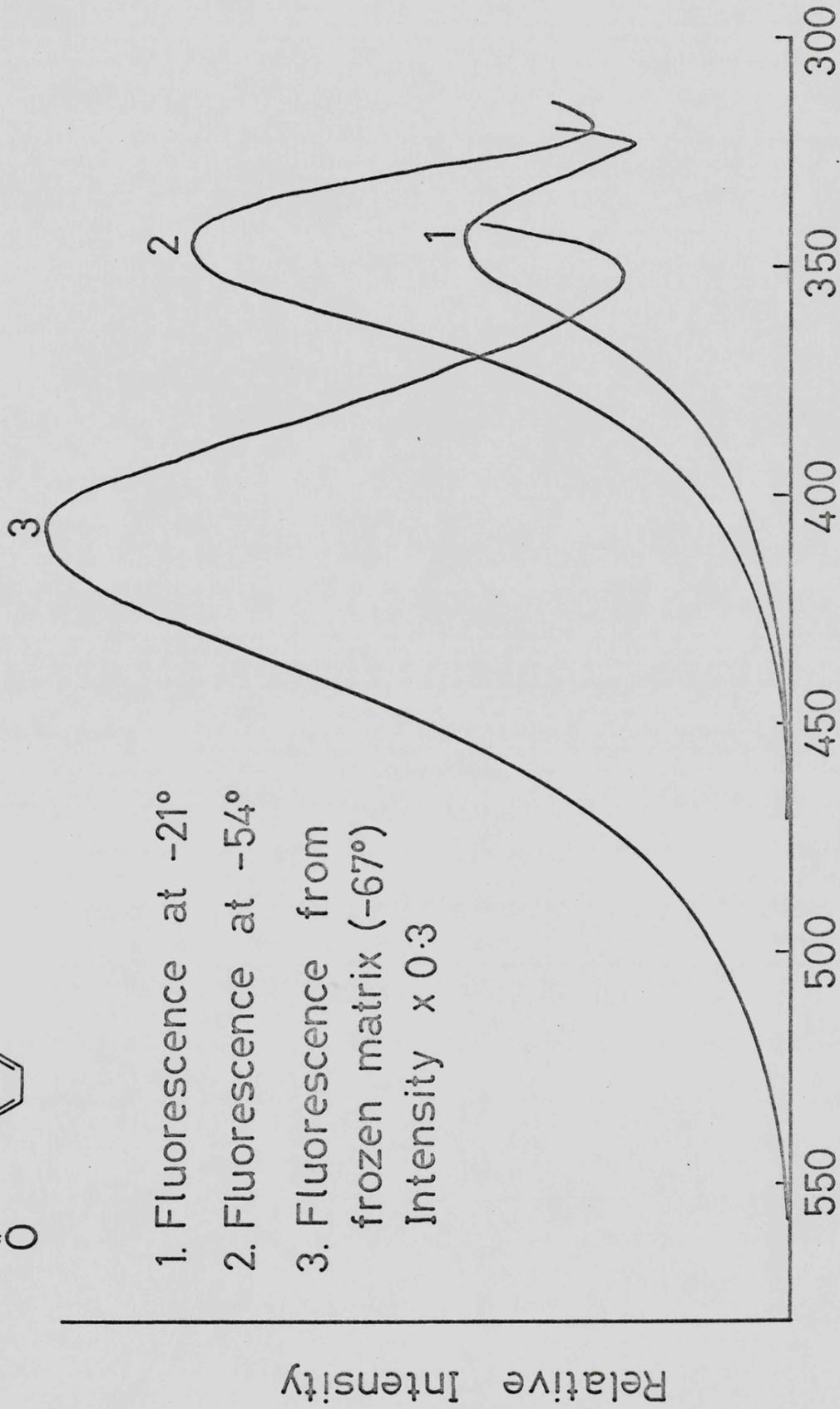
1. Fluorescence at −21°
2. Fluorescence at −54°
3. Fluorescence from frozen matrix (−67°) Intensity × 0.3

Relative Intensity

Wavelength (n.m.)
DIAGRAM 17
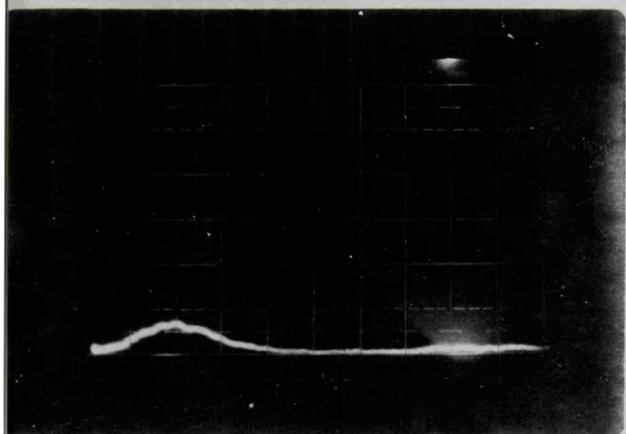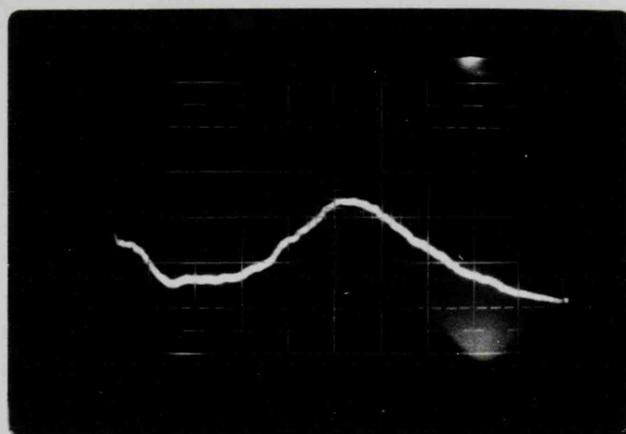
t = 0　　　　　　　　　　t = 25
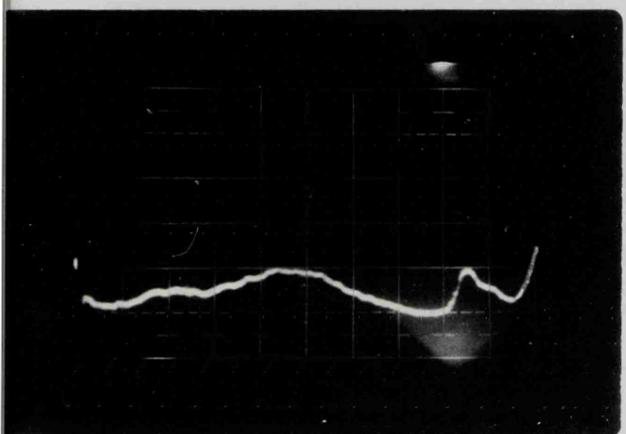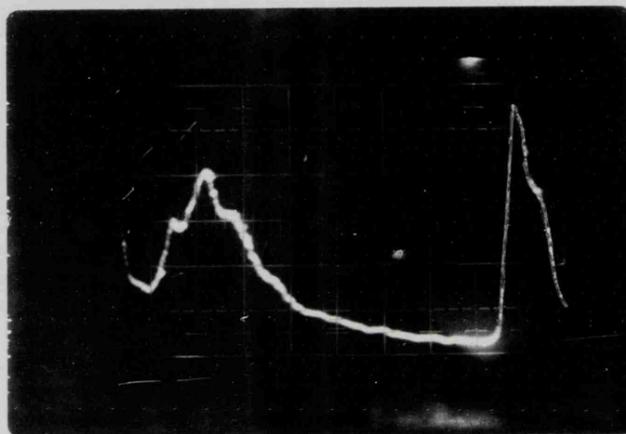
t = 40　　　　　　　　　　t = 60
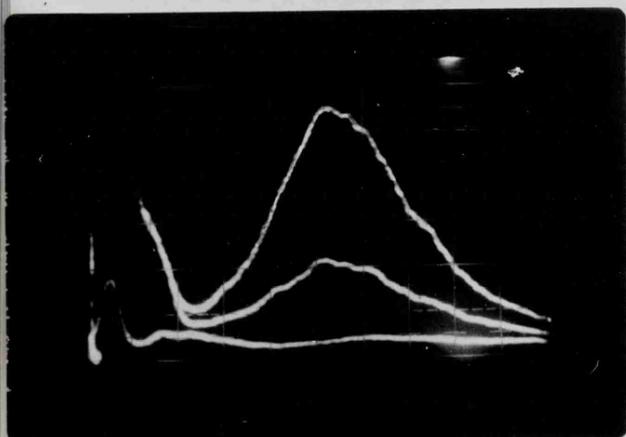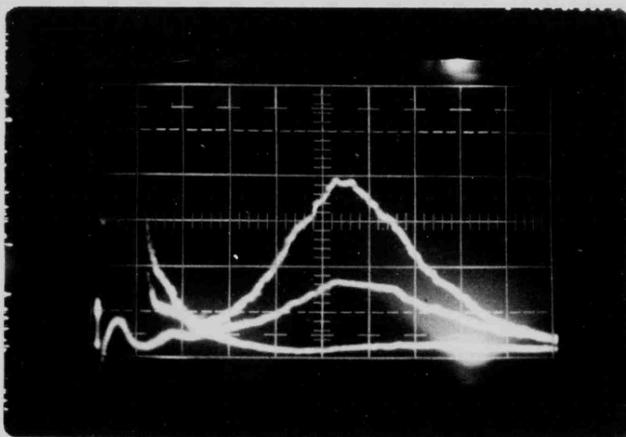
t = 4,16,28　　　　　　　　t = 5,16,27

LATE 1. Fluorescence Spectra of 39 (10^{-4} M in Cyclo-exane) at various times (t sec) after Insertion into iquid Nitrogen. Wavelength Range 300-500 nm.

185

470NM band observed in solid matrix was absent, the emission

being similar to that in fluid solution, Diagram 18 shows the

fluorescence spectra of 52 from solution, matrix and crystal.

The maximum wavelengths of the fluorescence and fluorescence

excitation spectra are shown in Table 36.

Discussion.

The results obtained from the compounds containing two

naphthalene groups suggest that the new fluorescence bands

are derived from an excimer or an excited dimer. It would also

appear that since the parent compounds give rise to very similar

bands the emissions do not arise from intramolecular interact-

ions, a view that is supported by the absence of anomalous

fluorescence in fluid solution. It is unlikely that the bands

are due to impurities for the same reason, further, permanent

chemical reaction does not take place since the monomer fluores-

cence can be restored by thawing the matrix. It therefore seems

reasonable to attribute the bands to excimer or excited dimer

formation following excitation of aggregates or microcrystals

formed by the freezing process.

Excimer fluorescence from crystals is well known (see

for example Refs. 50, 93 and 168) Stevens[182] has suggested

that a general relationship exists between the fluorescence

spectrum and the crystal structure of aromatic hydrocarbons.

The so-called "A" lattice (found for example in naphthalene and

anthracene) does not allow the formation of a symmetric sandwich-

pair i.e. overlap between neighbouring parallel molecules is

small. Weak coupling between molecules generally gives rise to

a small red shift of the fluorescence spectrum, the molecular

TABLE 36.

Wavelengths of maximum fluorescence (NM)^a of crystalline

aromatic hydrocarbons.

Compound.	Temperature.	
	+19°	-196°
50	412	412
	(330)	(330)
51	405	350 (very broad)
	(360)	(320)
52	440,464Sh.,493Sh.	464, 442
	(417,400Sh.)	(408,390Sh.)
53	355, 410	355, 410
	(356,320Sh.^{b})	(356,320Sh.)
39 ^{c}	430	408
	(328)	(321)
41	430	403
	(328)	(321)
42	365, 410Sh.	365, 410
	(332)	(332)
55	466,493Sh.,457Sh.	465,437Sh.
	(417,400Sh.)	(418,390Sh.)

a. Fluorescence excitation maxima in brackets.

b. Sh = Shoulder on most intense fluorescence.

c. Liquid at room temperature.

1. 10^{-4} Min Cyclohexane +6°.
2. 10^{-4} Min Cyclohexane (frozen) −120° intensity × 3.
3. Crystals +19°.
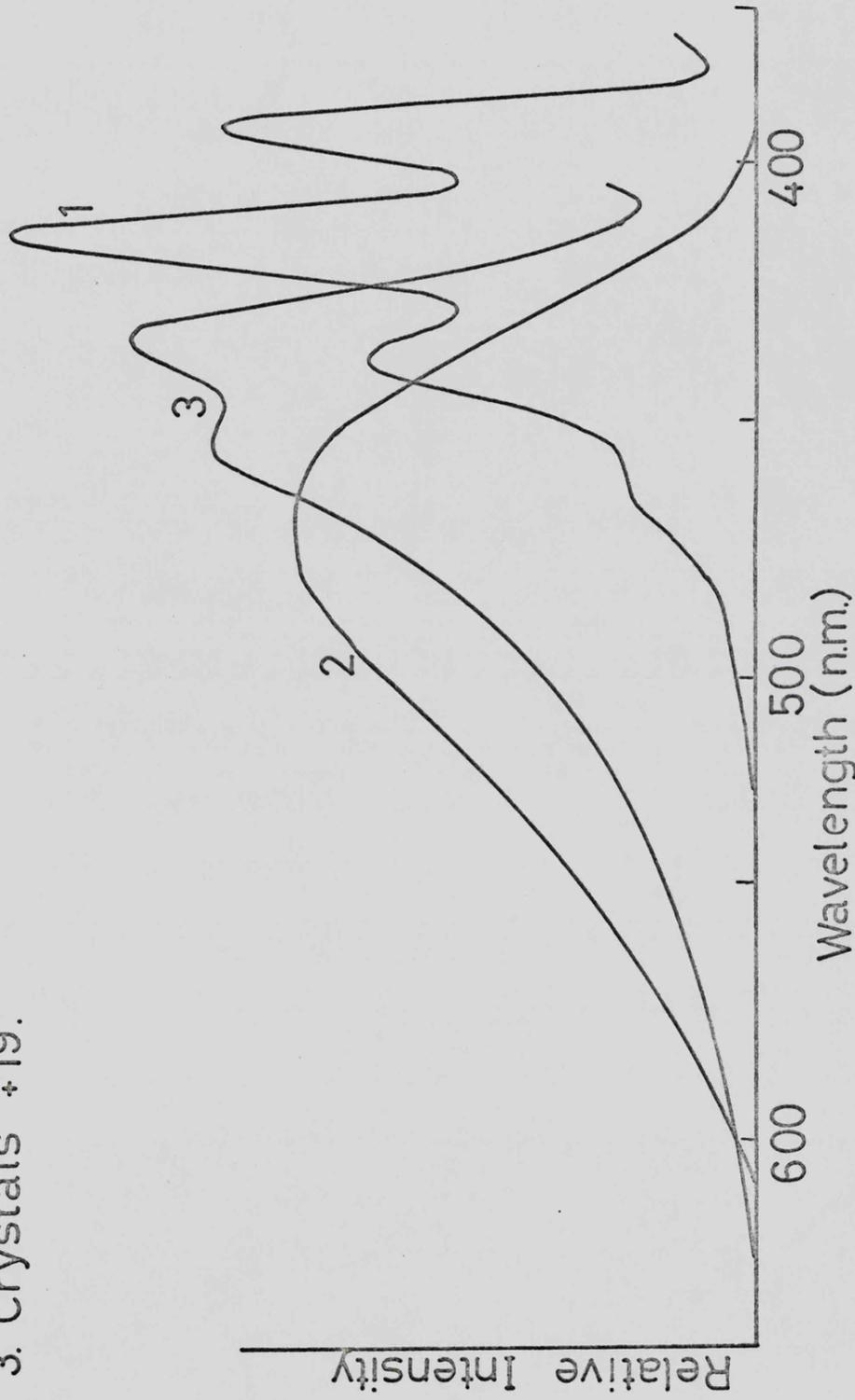
DIAGRAM 18.   Fluorescence Spectra of 52.

fine structure being preserved. A second lattice is the "B"

type in which the molecules are situated such that overlap

can occur between molecules in parallel planes, the fluorescence

of a "B" lattice is characteristic of the excimer, the best

known example is that of crystalline pyrene which fluoresces at

about 475NM.[183]

It has also been suggested that pyrene exists as crystals

in cyclohexane matrix (-196°) and the anomalous fluorescence

bands observed were thus attributed to excimer formation.[162]

It is also possible that "molecular pairs" rather than crystals

are responsible for the emission.[184,185] Both Selinger and

Mataga observed changes in the fluorescence excitation spectrum

e.g. Mataga found the excitation maxima to shift from circa.

335NM in solution to 360NM in cyclohexane matrix. The changes

observed in the fluorescence excitation spectra thus indicate

that a different species exists in solid matrix as compared

to fluid solution.

It would therefore appear that the fluorescence bands

observed can be adequately explained by the formation of either

aggregates or crystals. A comparison of the fluorescence data

of the crystals with those of the matrices for the compounds

containing only naphthalene does not give any correlation i.e.

it is not possible to attribute the emissions observed from the

matrix to emission from a crystalline species. However it is

possible that the shape of the solvent cage affects the way in

which the compounds crystallise, leading to a different orient-

ation of the molecules towards one another and consequently to

a different fluorescence spectrum. In the absence of identical

spectra however, the results could equally well be explained

by proposing that "molecular pairs" or aggregates are formed.

It is possible to distinguish between aggregation and crystall-

isation in only one case, i.e. 51, which only shows a broad

monomer fluorescence from the crystals at -196° whereas an

intense excimer band appears in cyclohexane or acetonitrile

at the same temperature.

The fluorescence band observed for the anthracene compound

52 could arise in theory from any of three different interactions

i.e., naphthalene-naphthalene, naphthalene-anthracene, or

anthracene-anthracene. The long wavelength of the band should

exclude naphthalene-naphthalene interactions whilst the fact that

the parent compound 55 gives a very similar band (λ max. 480NM)

indicates that the band is derived from anthracene-anthracene

interactions. Compound 52 has the potential of forming a

naphthalene-anthracene exciplex, Chandross[186] has in fact obs-

erved fluorescence from such a species by excitation of the

photo-adduct of 1-(9-anthryl)-3-(1-naphthyl) propane (derived

from 54) in a rigid matrix at low temperature, the wavelength of

maximum fluorescence was found to be at 450NM. In view of the

similarity of the band wavelength, such a process cannot be dis-

counted but it is less likely than an excimer emission because

of the fact that the emission from 52 is concentration depend-

ent. It is therefore believed that the emission is derived

from an anthracene excimer.

The large difference between the crystal emission spect-

rum and that from solid matrix for 52 suggests that aggregat-

ion of the anthracene compound occurs. Ferguson[187] has shown

that anthracene possesses a weak excimer component in cyclo-hexane at low temperature (-253°) which has been attributed to emission from "molecular pairs",[188] excimer fluorescence from crystals is unlikely in this case since anthracene possess-es an "A" lattice.

The wavelength maxima of the fluorescence bands observed from 52 and 55 in solid matrix are very much shorter than those found for typical anthracenes e.g. 9-methylanthracene and 9,10-dimethylanthracene excimers fluoresce at around 560NM, in fluid solution.[189] This suggests that there is not a close approach of the molecules within the "molecular pair" responsible for the emission, such an effect has recently been observed for an anth-racene compound with a bulky side chain in which the excimer fluorescence maximum was found to be at about 475NM.[190]

The observation of a "transient" fluorescence in the freez-ing of a cyclohexane solution of 39 may be due to a change in the crystal structure of the solvent with temperature. Cyclo-hexane is known to undergo a phase transition at approximately -90° in which the crystal structure changes from cubic to monoc-linic,[162] hence the change in the crystalline arrangement of the solvent may influence the way in which the solute is arranged, such that they cannot interact to form an excimer. This type of effect has been observed for pyrene in solid cyclohexane solutions where the intensity of the excimer fluorescence was found to decrease rapidly at around -90°, a similar interpret-ation involving a change in the solvent crystal structure was proposed.[184] The fact that the fluorescence spectrum does change

with temperature for 39 suggests that crystallisation does not take place for this compound since it is unlikely that the crystal structure of 39 will be grossly changed by a change in the solvent crystal structure. It is more likely that aggregates are initially formed upon freezing and a subsequent change in the solvent structure forces the "molecular pairs" apart.

The fact that excimer emission can be observed from the crystals of the compounds containing only naphthalene is interesting since naphthalene itself only exhibits monomer fluorescence in the crystalline state (at atmospheric pressure). This may be due to the compounds adopting a type "B" lattice, the side chain of the compounds thus influencing the way in which they crystallise. It must be borne in mind that the observation of excimer fluorescence from the crystals does not necessarily imply the presence of a "B" lattice, the effect could be explained in other ways. First, the molecules are relatively complex compared to the unsubstituted hydrocarbons for which the "A" and "B" lattices strictly apply, hence a different crystal structure altogether may be adopted. Second, the presence of defects in Type "A" crystals can cause excimer fluorescence, this requires that the arrangement of adjacent molecules differs at the defect sites such that the molecules are within the range of excimer interaction. The electronic excitation energy may then "migrate" i.e. energy transfer takes place and the molecular excitation will tend to localise at a defect site because they are lower in energy, this will result in the appearance of an excimer band in the fluorescence spectrum.[168]

The emission from the crystalline anthracene compounds

<u>52</u> and <u>55</u> is typical of that for anthracene itself which suggests that the crystals adopt a type "A" lattice, although the complexity of the molecule may again preclude the possibility of an "A" lattice. The fluorescence of <u>52</u> is in fact very broad, this may be caused by a contribution from the excimer component fluorescing at around 470NM brought about either by poor overlap of adjacent anthracene moieties in parallel molecular planes or by the presence of defects in the crystals.

SECTION THREE : EXPERIMENTAL

Instrumentation and Materials.

Melting points were determined on a Kofler block and are uncorrected.

Infra-red spectra were recorded on a Perkin-Elmer 257 spectrometer in nujol mull unless stated.

Nuclear magnetic resonance spectra were recorded on a Varian Model T60 in deuteriochloroform using tetramethylsilane as an internal standard unless stated.

Mass spectra were obtained on an A.E.I. M.S.9. mass spectromoter (mass peaks of structural significance are quoted).

Benzene, toluene, diethyl ether and petroleum spirit (b.p. 40 - 60°) were dried over sodium wire prior to use, other solvents were dried and purified as necessary.

All solvents used for spectroscopic measurements were established to be free from all absorbing and emitting impurities before use, as judged by the ultra-violet absorption and emission spectra. Acetonitrile, benzene and cyclohexane were Merck "Uvasol" grade and were used without further purification; ethanol was 95% and benzene free; toluene was dried over sodium wire and fractionated; chloroform and dichloromethane were dried over molecular sieve and redistilled; diethyl ether, tetrahydrofuran and 1,2-dimethoxyethane were refluxed over lithium aluminium hydride and distilled from it; methyl cyclohexane was Hopkin and Williams reagent grade and was used with-

out further purification.

Ultra-violet absorption spectra were recorded on a Pye-Unicam SP 800, Pye-Unicam SP 700 or a Hilger-Gifford spectrophotometer.

Emission spectra were obtained with a Baird Atomic Fluorispec SF100E, fitted with an E.M.I. 9781B photomultiplier, in conjunction with a Servoscribe RE516.20 X-t recorder and were uncorrected for instrumental response. Samples were generally contained in $1cm^2$ quartz cells for work at room temperature. Samples for emission at other temperatures were contained in circular quartz or pyrex tubes of 2mm. internal diameter. Emissions at -196° were obtained by inserting the tube into a quartz dewar filled with liquid nitrogen. A similar container was used for work at other temperatures except that provision was made to pass nitrogen gas over the sample. The nitrogen was previously cooled by passing through liquid nitrogen or heated by an electric coil. The temperature was monitored by a calibrated Colmarck electronic thermometer and is believed to be accurate to $\pm 2^\circ$. Phosphorescence could be isolated from fluorescence (at -196°) by rotating a "chopper" around the sample at such a speed as to cut off all short-lived emissions. Oxygen was removed from the samples by a minimum of four freeze-pump-thaw cycles using liquid nitrogen for freezing and a high vacuum line incorporating a mercury diffusion pump for pumping.

3:1 EXCIPLEXES FORMED BETWEEN AMINES AND AROMATIC HYDROCARBONS.

Preparation of the amino-esters.

The general method used was as follows. The carboxylic acid chlorides were prepared by adding oxalyl chloride (1.4g, 0.011 mole) to the acid (0.01 mole) in benzene (25cm^3). The mixture was heated under reflux for 1 hour, benzene and the excess of oxalyl chloride were removed under reduced pressure, leaving the crude acid chloride:

1-Naphthylacetyl chloride, $V_{max.}$ (film) 1793cm^{-1}.

2-Naphthylacetyl chloride, $V_{max.}$ (film) 1800cm^{-1}.

1-Naphthoyl chloride, $V_{max.}$ (film) 1750cm^{-1}.

Anthracene-9-carboxylic acid chloride, $V_{max.}$ (film) 1755cm^{-1}.

Fluorene-9-carboxylic acid chloride, $V_{max.}$ (film) 1795cm^{-1}.

Phenyl acetyl chloride, $V_{max.}$ (film) 1800cm^{-1}.

The crude acid chloride was taken up in benzene (10cm^3) and added dropwise to a stirred, ice-cooled solution of the amino-alcohol (0.01 mole) in benzene (10cm^3). The mixture was allowed to warm up to room temperature and stirred for approximately 6 hours. After this period a solid (generally white) had precipitated from the benzene solution. 2N hydrochloric acid (15cm^3) was added and the aqueous layer extracted with diethyl ether (3 x 15cm^3), then made basic by addition of 2N aqueous sodium hydroxide and extracted with diethyl ether (3 x 20cm^3). The organic layer was washed with water (3 x 15cm^3) and dried over anhydrous magnesium sulphate. Evaporation of the ether under reduced pressure, followed by distillation in vacuo and re-crystallisation where necessary yielded;

<u>2-dimethylaminoethyl-(1-naphthyl)acetate</u> as a clear, colourless oil (0.85g, 33%) b.p. 175° at 0.003 mmHg; hydrogen iodide salt m.p. 156° (from aqueous ethanol); τ 1.9 - 3.0 (7H,m), 6.0 (2H,t,$\underline{J}$ 6Hz), 6.1 (2H,s), 7.7 (2H,t,$\underline{J}$ 6Hz) and 8.0 (6H,s); $\nu_{max.}$ (film) 1730, 1596, 1160, and 785cm^{-1}; m/e 257 (M^{+}), 214, 186, 169, 141 (M^{+} - 116), 115 and 72. (Found, as hydrogen iodide salt: C, 49.6; H, 5.2; N, 3.6. C_{16} H_{20} NO_2 I requires C, 49.8; H, 5.2; N, 3.6%).

<u>2-N(N-methyl)anilinoethyl-(1-naphthyl)acetate</u> as a clear, colourless oil (2.1g, 67%) b.p. 210° at 0.002 mmHg; hydrogen iodide salt m.p. 153 - 154° (from aqueous ethanol); τ 1.8 - 3.6 (12H,m), 5.8 (2H,t,$\underline{J}$ 6Hz), 6.1 (2H,s), 6.6 (2H,t,$\underline{J}$ 6Hz) and 7.3 (3H,s); $\nu_{max.}$ (film) 1730, 1600, 1150, 790, 780, 750 and 690cm^{-1}; m/e 319 (M^{+}), 186, 141 (M^{+} - 178), 120 and 115. (Found, as hydrogen iodide salt: C, 56.3; H, 5.0; N, 3.15. C_{21} H_{22} NO_2 I requires C, 56.3; H, 4.95; N, 3.1%).

<u>2-dimethylaminoethyl-(2-naphthyl)acetate</u> as a clear, colourless oil (1.49g, 58%) b.p. 182° at 0.005 mmHg; τ 2.0 - 2.7 (7H,m), 5.8 (2H,t,$\underline{J}$ 6Hz), 6.2 (2H,s), 7.5 (2H,t,$\underline{J}$ 6Hz) and 7.8 (6H,s); $\nu_{max.}$ (film) 1730, 1600, 1150, 810, 755 and 730cm^{-1}; m/e 257 (M^{+}), 214, 169, 141 (M^{+} - 116), 115 and 72. (Found: C, 74.1; H, 7.5; N, 5.4. C_{16} H_{19} NO_2 requires C, 74.7; H, 7.4; N, 5.4%).

<u>2-N(N-methyl)anilinoethyl-(2-naphthyl)acetate</u> as plates (1.56g, 49%) m.p. 59 - 60° (from ethanol) b.p. 206° at 0.0005 mmHg; τ

2.0 - 3.6 (12H,m), 5.9 (2H,t,J6Hz), 6.5 (2H,s), 6.7 (2H,t,J

6Hz) and 7.4 (3H,s); $V_{max.}$ 1730, 1600, 1145, 805, 745 and

690cm^{-1}; m/e 319 (M$^+$), 186, 141 (M$^+$ - 199) and 115. (Found:

C, 79.0; H, 6.6; N, 4.4. $C_{21}H_{21}NO_2$ requires C, 79.0; H, 6.6;

N, 4.4%).

2-dimethylaminoethyl-naphthalene-1-carboxylate as a clear,

colourless oil (1.48g, 61%) b.p. 130 - 132° at 0.0005 mmHg;T

1.7 - 2.8 (7H,m), 5.6 (2H,t,J 6Hz), 7.4 (2H,t, J 6Hz) and 7.8

(6H,s); $V_{max.}$ (film) 1710, 1594, 1140, 815 and 780cm^{-1}; m/e

243 (M$^+$), 200, 172, 155 (M$^+$ - 88), 127, 102 and 72. (Found:

C, 73.5; H, 7.2; N, 5.5. $C_{15}H_{17}NO_2$ requires C, 74.0; H,

7.01 N, 5.8%).

2-N(N-methyl)anilinoethyl-naphthalene-1-carboxylate as a clear,

colourless oil (1.92g, 63%) b.p. 208 - 210° at 0.001 mmHg; T

1.6 - 3.1 (12H,m), 5.4 (2H,t,J 6Hz), 6.2 (2H,t,J 6Hz) and 6.9

(3H,s); $V_{max.}$ (film) 1735, 1610, 1135, 800, 770, 735 and 680

cm^{-1}; m/e 305 (M$^+$) 172, 155, 127, 120 (M$^+$ - 185) and 102. (Found:

C, 78.6; H, 6.3; N, 4.4. $C_{20}H_{19}NO_2$ requires C, 78.7; H, 6.3;

N, 4.6%).

2-N(N-methyl)anilino ethyl-anthracene-9-carboxylate as plates

(1.2g, 68%) m.p. 81 - 82° (from ethanol) b.p. 240 - 243° at

0.001 mmHg; T 1.4 - 3.3 (14H,m), 5.1 (2H,t,J 6Hz), 6.1 (2H,t,

J 6Hz) and 7.0 (3H,s); $V_{max.}$ 1735, 1600, 1140, 876, 849, 781,

740 and 690cm^{-1}; m/e 355 (M$^+$), 196, 134 and 120 (M$^+$ - 235).

(Found: C, 81.0; H, 5.95; N, 4.0. $C_{24}H_{21}NO_2$ requires C, 81.1;

H, 6.0; N, 3.9%).

2-dimethylaminoethyl-fluorene-9-carboxylate as a clear, colour-

less oil (1.4g, 55%) b.p. 140 - 142° at 0.01 mmHg; τ 2.2 -

3.0 (8H,m), 5.3 (1H,s), 5.8 (2H,t,$\underline{J}$ 6Hz), 6.6 (2H,t,$\underline{J}$ 6Hz) and

7.9 (6H,s); $V_{max.}$ (film) 1730, 1615, 1604, 1192, 1031 920

and 739cm^{-1}; m/e 281 (M$^+$), 238, 210, 193, 165 (M$^+$ - 116) and

72. Satisfactory analysis could not be obtained for this comp-

ound.

2-N(N-methyl)anilinoethyl-fluorene-9-carboxylate as plates

(2.2g, 69%) m.p. 62 - 63° (from ethanol); b.p. 240° at 0.01

mmHg; τ 2.35 - 3.5 (13H,m), 5.35 (1H,s), 5.85 (2H,t,$\underline{J}$ 6Hz),

6.4 (2H,t,$\underline{J}$ 6Hz) and 7.3 (3H,s); $V_{max.}$ 1738, 1600, 1510, 1316,

1275, 1195, 1030, 745 and 692cm^{-1}; m/e 343 (M$^+$), 165 and 120

(M$^+$ - 223). (Found: C, 80.4; H, 6.3; N, 3.95. $C_{23} H_{21} NO_2$

requires C, 80.4; H, 6.2; N, 4.1%).

2-dimethylaminoethyl phenyl acetate as a clear, colourless

oil (1.84, 89%) b.p. 135° at 0.035 mmHg; τ 2.8 (5H,s), 5.9

(2H,t,$\underline{J}$ 6Hz), 6.4 (2H,s), 7.6 (2H,t,$\underline{J}$ 6Hz) and 7.8 (6H,s);

$V_{max.}$ (film) 1730, 1150, 735 and 695cm^{-1}; m/e 207 (M$^+$), 163

136 and 91 (M$^+$ - 116). (Found: C, 68.9; H, 8.3; N, 6.6. C_{12}

$H_{17} NO_2$ requires C, 69.5; H, 8.3; N, 6.8%).

Preparation of methyl esters.

The methyl esters were prepared by the Fischer-Speier

esterification procedure,[191] distillation of the crude product

in vacuo yielded;

Methyl-naphthalene-1-carboxylate as a clear, colourless oil

b.p. 95 - 97° at 0.02 mmHg, (lit.,[74] 100 - 102° at o.o4 mmHg);

τ 2.1 - 2.7 (7H,m) and 7.6 (3H,s); $V_{max.}$ 1725, 1600, 1140 and 790cm^{-1}.

Methyl-(1-naphthyl)acetate as a clear, colourless oil b.p. 110 - 114° at 0.01 mmHg (lit.,[192] 165 - 167° at 9 mmHg); τ 2.2 - 2.9 (7H,m), 6.0 (2H,s) and 6.4 (3H,s); $V_{max.}$ (film) 1730, 1595, 1150, and 785cm^{-1}.

3:1:1 INTRAMOLECULAR EXCIPLEX FORMATION.

Ultra-violet absorption spectra were recorded in cyclohexane and acetonitrile at room temperature using 10^{-4}M solutions. The spectra were essentially the same as those of the parent compounds.

Emission spectra at room temperature were recorded at a concentration of 10^{-4}M, the solutions were not degassed. The wavelength of the exciting light was varied according to the aromatic hydrocarbon contained in the molecule: naphthalene, 290 - 300NM; anthracene, 350NM; fluorene, 290 - 300NM; benzene, 250NM. The results from these experiments are shown in Table 5 and representative spectra in Diagrams 1 - 3. Fluorescence excitation spectra were recorded under the same conditions as the emission spectra, no changes were detected in these spectra as compared to those of the parent compounds.

The emission spectra of the amino-esters containing naphthalene and anthracene were recorded at four different concentrations (10^{-2}, 10^{-3}, 10^{-4} and 10^{-5}M) in benzene solution. The emission spectra from those compounds containing fluorene were recorded at 10^{-4}M abd 10^{-5}M in cyclohexane solution.

No changes, apart from those of intensity due to the change of concentration, were observed in these experiments.

Degassed solutions of 2-dimethylaminoethyl-(1-naphthyl) acetate and 2-N(N-methyl)anilinoethyl-(1-naphthyl)acetate in methyl cyclohexane and in acetonitrile (10^{-4}M solutions) were studied at -196°. Exciplex fluorescence bands were not observed under these conditions, the emissions were typical of those found for the parent compounds. The intensity of the emissions was not reproducible, variations of approximately 50% were noted and for this reason no attempts were made to obtain relative quantum yields at this temperature, however, the intensities were of the same order as those of the parent compounds under the same conditions.

3:1:2 FLUORESCENCE LIFETIME STUDIES.

Preparation of N,N-diethyl-2-(1-naphthyl)ethylamine.

This compound was prepared as previously described by Brimage,[72] infra-red and N.M.R. spectra were identical with those reported.

Measurement of fluorescence decay curves.

The fluorescence decay curves were measured using the single photon counting technique. The excitation source was a light pulse obtained from a free running spark lamp operating at 8KHz in an oxygen atmosphere. The half-width of the light pulse was approximately 4ns. The wavelength of the exciting light was chosen by a Bausch and Lomb monochromator type 33-86-02. The emissions were observed through wide band

filters (30NM) centered at 340NM for monomer emissions and at 400 or 490NM for exciplex emissions. The emissions were detected by a water-cooled E.M.I. 9813 KB photomultiplier. The fluorescence lifetimes are shown in Table 9 and the time-delays in the build up of exciplex fluorescence shown in Table 10.

3:1:3 FLASH PHOTOLYSIS STUDIES.

The flash photolysis apparatus was basically an FP-1-ph unit from Northern Precision Co. Ltd., comprising a horizontal cell compartment with two horizontal quartz flash lamps. The lamps were attached to a capacitor unit of 10 μF capacity. The spectral flash was obtained from a "Garton Type" flash tube which was charged from a 10μF rapid discharge capacitor supp-lied by Hivatronic Ltd. The delay-time between photolytic and spectral flashes was fixed by a Type W.3. Unit (Chelsea Inst-ruments Ltd.,). The reaction vessel was a quartz tube 20cm long and 1.8cm in diamater. A side-arm connecting this tube to a 250cm^3 round bottomed flask, fitted with a tap, allowed rem-oval of oxygen from the solutions by freeze-pump-thaw cycles. Absorption spectra of transient species were obtained with a Hilger quartz spectrograph and recorded on Ilford H.P.3 photo-graphic plates.

Plate photometry was carried out on a Joyce-Loebl double beam recording microdensitometer. The spectra, recorded both before and after the photolytic flash were scanned and the diff-erence in the densities of the two scans plotted, in arbitary

units, against wavelength at approximately 7NM intervals thus giving the transient absorption spectra. Optical densities were obtained by inserting neutral density filters between the cell and the spectrograph. The plates were then scanned on the microdensitometer and a calibration curve obtained for "observed density", again in arbitary units, against % Transmission. The approximate optical densities (shown in Table 11) for the transient absorptions were obtained from this curve. It was necessary to construct a calibration curve for each plate to avoid errors due to slightly different developing conditions etc.

3:1:4 EFFECT OF TEMPERATURE UPON THE FLUORESCENCE SPECTRUM.

The solutions used to obtain the variable temperature fluorescence spectrum of 2-N(N-methyl)anilinoethyl- (1-naphthyl) acetate were degassed prior to use. The overall emission spectrum was recorded at each temperature and then the intensities of both monomer and exciplex fluorescence recorded a minimum of four times at 350 and 450NM respectively. An average of these readings was taken and the values obtained gave the plot shown in Figure 4, the slopes of the plot in the high and low portions of linearity were used to determine $-\Delta H^*$ and E_a respectively.

3:1:5 INTERMOLECULAR EXCIPLEX FORMATION.

Anthracene was B.D.H. "blue fluorescent" grade, 9-methyl-anthracene and 9-cyanoanthracene (both from Aldrich Chemical

Co.,) were all used without further purification. 1-cyano-
naphthalene (m.p. 36 - 37°) was recrystallised from petroleum
spirit. Pyrene (m.p. 149 - 150°) was recrystallised from dieth-
yl ether. Triethylamine was refluxed over potassium hydrox-
ide, distilled under a stream of dry nitrogen gas and stored
over potassium hydroxide. N,N-dimethylaniline was distilled
in vacuo. DABCO was used as received.

The solutions used to obtain the emission spectra were
all degassed before use. Light of wavelength 350NM was used to
excite anthracene and pyrene; 300NM light was used to excite
naphthalene. The results are shown in Table 12 and represent-
ative spectra in Diagrams 5 and 6.

Stern-Volmer plot.

Solutions of the fluor (anthracene) containing varying
amounts of the quencher (triethylamine) in cyclohexane were
made up by dilution from stock solutions and their fluorescence
intensities determined at a fixed wavelength (415NM). Each
reading was repeated at least twice to ensure a constant fluor-
escence intensity was recorded and the fluorescence intensity
of a reference solution (anthracene in the absence of quencher)
was recorded in between each of these readings to ensure that
the response from the spectrofluorimeter was constant. The
intensity of fluorescence is directly related to the quantum
yield of fluorescence hence the values obtained for the int-
ensity were substituted directly into the Stern-Volmer equat-
ion (Section 1:2:1). The slope of a plot of ϕ_o/ϕ - 1 against
quencher concentration gave the Stern-Volmer quenching constant
K_Q. This value together with a value for the fluorescence

lifetime of anthracene taken from the literature gives k_q, the quenching rate constant, from the relationship $K_Q = k_q \tau$. The relative intensities of anthracene fluorescence and the concentrations of triethylamine are shown in Table 37.

<u>TABLE 37.</u>

<u>Data for fluorescence quenching of anthracene by triethylamine.</u>[a]

Concentration (M)	0	0.14	0.28	0.422	0.56	0.70
I		55	42.9	32.0	28.5	22.1	18.2
$I_0/I - 1$		0	0.28	0.72	0.93	1.49	2.02

a. Concentration of anthracene was 5×10^{-5}M. Light at 350NM was used to excite anthracene.

3:2 SOME ASPECTS OF THE PHOTOCHEMISTRY OF HYDRAZINES AND HYDRAZIDES.

3:2:1 FLUORESCENCE QUENCHING OF 1-METHYL NAPHTHALENE.

Preparation of 1-(1-naphthyl)acetyl-2,2-disubstituted hydrazines.

The general method used was as follows. 1-Naphthylacetyl-chloride (0.01 mole), prepared as described in Section 3:2, was taken up in benzene ($10cm^3$) and added dropwise to a stirred, ice-cooled solution of the hydrazine (0.01 mole) in benzene ($10cm^3$). The mixture was allowed to warm up to room temperature and stirred for 1 hour, during this period a white precipitate had formed, 2N aqueous sodium hydroxide ($20cm^3$) was then added, the benzene separated and washed with water ($3 \times 20cm^3$). The aqueous layer was washed with diethyl ether ($3 \times 20cm^3$) and the organic layers combined and washed with water ($3 \times 15cm^3$). Evaporation of the organic extracts under reduced pressure gave a white solid, subsequent recrystallisation yielded;

1-(1-naphthyl)acetyl-2,2-dimethylhydrazine as needles (2.0g, 87%) m.p. 139 - 140° (from ethanol); τ 1.5 - 2.6 (7H,m), 3.4 (1H,s), 6.05 and 5.7 (2H,s) and 7.6 and 7.58 (6H,s); $V_{max.}$ 3160, 3020, 1645, 1590, 1555, 1505, 1252, 1160, 810, and $770cm^{-1}$; m/e 228 (M^+), 185, 141 and 59. (Found: C, 73.0; H, 7.0; N, 12.3. $C_{14} H_{16} N_2 O$ requires C, 73.6; H, 7.1; N, 12.3%).

1-(1-naphthyl)acetyl-2-methyl-2-phenylhydrazine as needles (1.0g, 61%) m.p. 148 - 149° (from ethanol); τ 2.0 - 3.5 (12H,m), 6.0 and 5.95 (2H,s) and 7.1 and 6.95 (3H,s); $V_{max.}$

3260, 1660, 1600, 1525, 1503, 1258, 974, 800, 780, 740 and 683cm^{-1}; m/e 290 (M$^+$), 185, 141 and 121. (Found: C, 78.4; H, 6.2; N, 9.4. $C_{19} H_{18} N_2$ O requires C, 78.6; H, 6.25; N, 9.65%).

1-(1-naphthyl)acetyl-2,2-diphenylhydrazine as needles (1.1g, 60%) m.p. 206 - 207° (from ethanol); Υ (in d_6 -dimethylsulph- oxide) 1.8 - 2.1 (17H,m) and 5.95 and 5.9 (2H,s); $V_{max.}$ 3260, 3030, 1660, 1585, 1260, 965, 780, 760 and 695cm^{-1}. (Found: C, 81.6; H, 5.7; N, 8.0. $C_{24} H_{20} N_2$ O requires C, 81.8; H, 5.7; N, 7.95%).

Ultra-violet absorption and emission spectra.

Spectra were recorded at a routine concentration of 10^{-4}M in 1cm^2 quartz cells at room temperature. The ultra-violet absorption spectra of the naphthalene compounds were compared with those of mixtures of the parent compounds, no essential differences were detected. Details of the fluorescence spectra are shown in Table 15 and representative spectra in Diagram 7. The fluorescence decay curve of 1-(1-naphthyl)acetyl-2-methyl-2-phenylhydrazine was determined in essentially the same was as described in Section 3:1:2.

Fluorescence quantum yields.

The fluorescence quantum yields were determined relative to quinine sulphate using solutions that had an optical density of 0.1 at 300NM,[193] the Hilger-Gifford fixed wavelength spect-rophotometer was used to make up these solutions. The solutions were degassed and the total fluorescence spectrum recorded.

The quantum yields were determined from the area of the fluorescence spectrum. The dipole moments of the naphthalene compounds were determined from the effect of solvent polarity upon the exciplex fluorescence maxima using the data shown in Table 15, the wavelength values (NM) were converted to cm^{-1} and the slope of a plot of the solvent polarity factor (Z) against $\tilde{U}_{max.}$ used to evaluate the dipole moments (Section 2:1:1).

Preparation of 1-benzoyl-2,2-disubstituted hydrazines.

The method used was identical to that used for the 1-(1-naphthyl)acetyl derivatives (page 206) except that benzoyl chloride was used in place of 1-naphthylacetyl chloride. The same work-up yielded;

1-benzoyl-2,2-dimethylhydrazine as needles (0.8g, 49%) m.p. 105 - 106° (from ethanol)(lit.,[193] 105 - 106°); Υ 2.0 - 2.6 (5H,m) and 7.4 (6H,s); $V_{max.}$ 3230, 3050, 1635, 1600, 1510, 1300, 1162, 1015, 730 and 690cm^{-1}.

1-benzoyl-2-methyl-2-phenylhydrazine as needles (1.5g, 66%) m.p. 152 - 153° (from ethanol)(lit.,[195] 154 - 155°); Υ 1.7 - (1H,s), 2.0 - 3.3 (10H,m) and 6.8 (3H,s); $V_{max.}$ 3270, 1655, 1600, 1580, 1525, 1310, 1255, 1026, 745 and 688cm^{-1}.

1-benzoyl-2,2-diphenylhydrazine as needles (1.1g, 38%) m.p. 192 - 193° (from ethyl-acetate-petroleum spirit, b.p. 40 - 60°) (lit.,[196] 189°); Υ 2.1 - 3.1 (15H,m) and 1.5 (1H,s); $V_{max.}$ 3240, 1655, 1600, 1590, 1520, 1250, 1080, 1030, 760, 750, 730 and 690cm^{-1}; m/e 288 (M^{+}), 183 and 106.

The ionisation potentials of the 1-benzoyl-2,2-disubstituted

hydrazines were determined by Dr. R. Lloyd of the University of

Birmingham.

3:2:2   FLUORESCENCE QUENCHING OF 9-METHYLANTHRACENE.

1-Methyl-1-phenylhydrazine was distilled in vacuo,

1,1-diphenylhydrazine hydrochloride was neutralised by 2N

aqueous sodium hydroxide, extracted with diethyl ether and

distilled in vacuo. The hydrazines were stored under nitrogen

in the dark.

Preparation of 1-acetyl-2-methyl-2-phenylhydrazine.

The method was identical to that used previously (page

206) except that acetyl chloride was reacted with 1-methyl-1-

phenylhydrazine. The same work-up yielded 1-acetyl-2-methyl-

2-phenylhydrazine as needles (1.3g, 79%) m.p. 92 - 93° (from

ethanol) (lit.,[118] 92.5 - 93°); τ 2.4 - 3.25 (5H,m), 6.82

(3H,s) and 1.95 and 2.08 (3H,s); $V_{max.}$ 3240, 3030, 1670, 1600,

1530, 1500, 1278, 1120, 1040, 979, 879, 750, 720 and 692cm^{-1};

m/e 164 (M^{+}), 122, 121 (M^{+} - 43), 105 and 77.

Stern-Volmer plots.

The procedure used to determine the quenching rate const-

ants of fluorescence of anthracene by the hydrazines was ident-

ical to that outlined in Section 3:1:5. The values obtained

from the experiments are shown in Table 18. A minimum of four

ultra-violet absorption spectra were recorded from the solutions

used for each Stern-Volmer plot; 9-methylanthracene with no

quencher added and three of the solutions containing both the

hydrocarbon and the quencher. It was not possible to detect

any absorptions other than those of the separate components.

The absorption spectrum of the quencher at the highest concent-

ration used in obtaining the plot was also recorded, in no case

did the quencher absorb light at the excitation wavelength used.

9-Methylanthracene rather than naphthalene was used for this

reason. The relative intensities of 9-methylanthracene fluor-

escence and the concentrations of hydrazines are shown in

Table 38.

TABLE 38.

Data for the fluorescence quenching of 9-methylanthracene

by hydrazines.

1. 1-acetyl-2-methyl-2-phenylhydrazine in benzene.

Concentration x 10^4M	I	$I_o/I - 1$
0	14.9	-
2	14.8	0.007
6	14.4	0.035
10	14.25	0.046
14	14.2	0.049
20	14.1	0.057
30	13.95	0.068
40	13.80	0.079
50	13.75	0.084

TABLE 38. (Continued)

2. 1,1-diphenylhydrazine in benzene.

Concentration x 10^4M	I	$I_o/I - 1$
0	9.1	-
2	9.05	0.005
4	8.5	0.07
6	8.6	0.06
10	8.2	0.11
14	8.0	0.14
18	8.05	0.13
22	7.7	0.18
26	7.65	0.19
30	7.4	0.23
36	7.1	0.28
44	7.0	0.30
48	6.9	0.32

3. 1,1-diphenylhydrazine in acetonitrile.

Concentration x 10^4M	I	$I_o/I - 1$
0	11.8	-
2	11.7	0.008
4	11.3	0.044
6	10.95	0.078
10	10.8	0.092
14	10.55	0.12
18	10.3	0.146
22	10.3	0.146
26	10.25	0.153

TABLE 38. (Continued)

3. 1,1-diphenylhydrazine in acetonitrile (continued).

Concentration x 10^4M	I	$I_o/I - 1$
30	10.0	0.18
36	9.5	0.24
42	9.43	0.25
48	9.3	0.27

4. 1,1-diphenylhydrazine in 95% ethanol.

Concentration x 10^4M	I	$I_o/I - 1$
0	11.2	-
4	11.1	0.009
6	10.75	0.042
10	10.8	0.037
14	10.8	0.037
18	10.55	0.062
22	10.3	0.087
26	10.25	0.093
30	10.2	0.1
36	9.8	0.14

5. 1-methyl-1-phenylhydrazine in benzene.

Concentration x 10^4M	I	$I_o/I - 1$
0	9.35	-
2	9.15	0.022
4	9.1	0.027
6	8.85	0.056
10	8.6	0.087

TABLE 38 (Continued)

5. 1-methyl-1-phenylhydrazine in benzene (continued).

Concentration x 10^4M	I	$I_o/I - 1$
14	8.25	0.13
18	8.2	0.14
22	8.2	0.14
26	8.15	0.147
30	8.05	0.16
44	7.7	0.214

6. 1-methyl-1-phenylhydrazine in acetonitrile.

Concentration x 10^4M	I	$I_o/I - 1$
0	15.1	-
2	14.9	0.0134
4	14.8	0.02
6	14.55	0.038
10	13.9	0.086
14	14.0	0.078
18	13.8	0.094
22	13.6	0.11
26	13.5	0.12
30	13.25	0.14
36	12.9	0.17
42	12.85	0.175
48	12.7	0.19

TABLE 38 (Continued)

7. 1-methyl-1-phenylhydrazine in 95% ethanol.

Concentration $\times 10^4$ M	I	$I_o/I - 1$
0	9.5	-
2	9.0	0.055
4	9.25	0.027
6	9.25	0.027
10	8.75	0.085
14	8.3	0.144
18	8.25	0.152
22	7.8	0.22
26	7.25	0.31
30	7.2	0.32
36	7.25	0.31
42	7.0	0.356
48	6.65	0.426

3:2:3 FLUORESCENCE OF HYDRAZINES AND HYDRAZIDES.

Preparation of 1-acetyl-2,2-diphenylhydrazine.

This method was identical to that used previously for 1-acetyl-2-methyl-2-phenylhydrazine (page 209). The same work-up yielded 1-acetyl-2,2-diphenylhydrazine as plates (1.3g, 79%) m.p. 190 - 191° (from ethanol) (lit.,[197] 188.5°); τ 2.6 - 3.3 (10H,m) and 7.95 (3H,s); $V_{max.}$ 3260, 1670, 1590, 1525, 1278, 745 and 690cm^{-1}; m/e 226 (M$^+$), 184, 183 (M$^+$ - 43), 169 and 168.

Fluorescence spectra.

The fluorescence spectra were recorded in $1cm^2$ quartz cells at room temperature in various solvents (see Table 18) at a routine concentration of $10^{-4}M$. The fluorescence spectrum of each compound was also recorded over a wide concentration range $(10^{-5} - 10^{-2}M)$ in benzene, cyclohexane and 95% ethanol, only the spectra of the 1,1-disubstituted hydrazines changed markedly.

The solvents (absolute ethanol or n-butylamine) added to the solutions of the hydrazines in non-polar solvents were previously established to be free from absorbing and fluorescing impurities in the wavelength region used for recording the fluorescence spectra.

The ultra-violet absorption spectra of these compounds were recorded using solutions at the same concentration as those used for the fluorescence spectra, no changes corresponding to those in the fluorescence spectra were detected.

3:2:4 PRODUCT STUDIES.

Preparation of 1-acetyl-2,2-dimethylhydrazine.

The method was identical to that used previously for 1-acetyl-2-methyl-2-phenylhydrazine (page 209). The same work-up yielded 1-acetyl-2,2-dimethylhydrazine as a clear colourless oil (0.7g, 70%) b.p. 100 - 105° at 20 mmHg; (lit.,[118] 93 - 95° at 14 - 16 mmHg); τ 1.0 (1H,s), 7.1 (3H,s), and 7.9 (3H,s); $\nu_{max.}$ 3400, 3200, 1710, 1230, 1035 and 983cm^{-1}; m/e 102 (M$^+$), 59 and 43.

Preparation of 1-phenylacetyl-2,2-disubstituted hydrazines

The general method was as follows. Phenylacetyl chloride (0.01 mole) prepared as described in Section 3:2 was reacted with the corresponding 1,1-disubstituted hydrazine as previously described for the 1-(1-naphthyl)acetyl derivatives (page 206). The same work-up yielded;

1-phenylacetyl-2,2-dimethylhydrazine as needles (1.2g, 67%) m.p. 104 - 105° (from ethyl acetate-petroleum spirit) (lit.,[198] 105°); τ 2.6 (5H,s), 6.15 and 6.4 (2H,s) and 7.4 and 7.5 (6H,s); $V_{max.}$ 3200, 3030, 1648, 1570, 1170, 720 and 695cm^{-1}; m/e 178 (M^{+}), 135 (M^{+} - 43), 91 and 59.

1-phenylacetyl-2-methyl-2-phenylhydrazine as needles (1.8g, 75%) m.p. 137 - 138° (from ethanol); τ 2.2 - 3.35 (10H,m), 6.25 and 6.4 (2H,s) and 6.8 and 7.0 (3H,s); $V_{max.}$ 3230, 3030, 1665, 1540, 1500, 1110, 755 and 690cm^{-1}. (Found: C, 75.0; H, 6.7; N, 11.7. $C_{15}H_{16}N_2$O requires C, 75.0; H, 6.7; N, 11.7%).

1-phenylacetyl-2,2-diphenylhydrazine as needles (1.8g, 60%) m.p. 187 - 187.5 $^{\circ}$ (from ethanol); τ 2.2 - 3.2 (15H,m) and 6.2 and 6.3 (2H,s); $V_{max.}$ 3280, 3270, 1635, 830, 790, 745, 725, 685 and 675cm^{-1}. (Found: C, 79.2; H, 6.2; N, 9.1. $C_{20}H_{18}N_2$O requires C, 79.5; H, 6.0; N, 9.3%).

Preparation of 1,1-phthaloyl-2-methyl-2-phenylhydrazine.

Phthalic anhydride (1.48g, 0.01 mole) was heated under reflux with 1-methyl-1-phenylhydrazine (1.22g, 0.01 mole) in glacial acetic acid (15cm^3) for 1 hour. Acetic acid was then

removed under reduced pressure leaving a dirty, yellow solid. Recrystallisation yielded 1,1-phthaloyl-2-methyl-2-phenylhyd-razine as yellow needles (2.3g, 90%) m.p. 125.5 - 127° (from ethanol) (lit.,[199] 125°); τ 1.8 - 2.2 (4H,m), 2.3 - 3.3 (5H, m) and 6.55(3H,s); $V_{max.}$ 1784, 1735, 1600, 1500, 1300, 1210, 1115, 990, 950, 872, 738, 707 and 682cm^{-1}.

Preparation of 1-formyl-2,2-dimethylhydrazine.

Equal weights (1.2g, 0.02 mole) of methyl formate and 1,1-dimethylhydrazine were. mixed and stirred at room temperature for 2 days. The mixture was stored at -18° overnight, after which time crystallisation had occured. The crystals were washed with petroleum spirit and recrystallised yielding 1-formyl-2,2-dimethylhydrazine (0.5g, 28%) m.p. 49 - 51° (from diethyl ether) (lit.,[200] 50 - 52°); τ 1.5 (1H,s), 1.95 (1H,s) and 7.35 (6H,s); $V_{max.}$ 3400, 3185, 1680, and 895cm^{-1}.

Irradiation Procedure.

The solutions (25cm^3) were generally 10^{-2}M in hydrazide and contained in 100cm^3 quartz tubes fitted with a Dreschel head through which a continuous stream of dry nitrogen was passed both before (for $\frac{1}{2}$ hour) and during the irradiation period. Irradiations were carried out in a Southern New England Co., Rayonet Reactor fitted with 16 lamps (15w each) having maximum emission at 253.7NM. The standard reaction time was four hours unless stated (see Table 20).

Product Analysis.

Product analyses were performed with a Pye 104 Gas Liquid Chromatograph. The products from the reactions were identified

by comparison with authentic samples which had all been previously purified. Percentage yields of the products were obtained by comparison of the product and authentic sample peaks, errors due to the injection of different amounts of material were minimised by the use of internal standards. The reproducibility of the yields was found to be approximately $\pm$ 5%. Each product was always identified on at least two columns (all standard Pye-Unicam Series 104 attachments). 10% E30 and 3% OV17 packings proved suitable for all of the products. Additionally, acetamide, N-methylaniline and diphenylamine were also detected on a 10% PEG 20M column, whilst benzamide, phenylacetamide and bibenzyl were detected on a 10% APL column.

The products from the irradiation of 1-acetyl and 1-benzoyl-2-methyl-2-phenylhydrazines were subjected to column chromatography (Laporte Type "H" alumina). Acetamide and benzamide, as well as N-methylaniline were detected by N.M.R. and I.R. spectroscopy, but aniline was not present in either case.

3:2:5 NUCLEAR MAGNETIC RESONANCE SPECTRA.

The effect of temperature upon the N.M.R. spectra of 1-(1-naphthyl)acetyl-2,2-disubstituted hydrazines was studied on a Jeol PS100 spectrometer. The temperature was measured internally and checked externally (by a Colmarck electronic thermometer) for each temperature at which a spectrum was run. The accuracy of the temperature measurement is believed to be $\pm$ 2°. In each case the temperature was raised above that of

coalescence to ensure that the observations were not merely
a function of a change of chemical shift with temperature.
A room temperature spectrum was recorded after each run to
ensure that the processes were reversible.

A typical N.M.R. spectrum showing the $-NMe_2$ and $-CH_2-CO$
groups is presented in Diagram 9, the spectral data and free
energies of activation are shown in Table 21.

Preparation of the ammonium salts.

The parent amines were prepared by routes described in the literature.[72] The general method for preparation of the hydrogen halide salts was as follows. The amine (0.01 mole) was taken up in diethyl ether ($20cm^3$) and a stream of the hydrogen halide gas bubbled through the solution until precipitation of the salt was complete. The crude product was filtered and washed with diethyl ether (3 x $10cm^3$). The quaternary ammonium salts were prepared by mixing the amine (0.01 mole) with an excess of ethyl iodide or ethyl bromide ($3cm^3$). The mixture was allowed to stand for 5 minutes and then warmed on a steam bath. The crude product generally crystallised at this stage.

The crude product was obtained as an oil in some cases, trituration with petroleum spirit at 0° then caused it to solidify.

Crystallisation of the crude products yielded;

N,N-diethyl-2-(1-naphthyl)ethylamine hydrochloride as plates (1.9g, 71%) m.p. 162 - 163° (from aqueous ethanol); τ 0.0 - 0.7 (1H,broad), 1.4 - 2.7 (7H,m), 5.9 - 7.0 (8H,m) and 8.55 (6H,t,$\underline{J}$ 6Hz); $V_{max.}$ 2550, 2470, 2320, 1930, 1590, 790, 780 and 770cm^{-1}. (Found: C, 72.5; H, 8.3; N, 5.2. $C_{16} H_{22}$ N Cl requires C, 72.8; H, 8.4; N, 5.3%).

N,N-diethyl-2-(1-naphthyl)ethylamine hydrobromide as needles (2.0g, 68%) m.p. 173 - 174° (from aqueous ethanol); τ 1.6 - 2.9 (7H,m), 5.95 - 6.95 (8H,m) and 8.5 (6H,t,$\underline{J}$ 7Hz); $V_{max.}$

2620, 2480, 1810, 1590, 790, 778 and 768cm^{-1}. (Found: C, 62.3; H, 7.1; N, 4.5. $C_{16} H_{22} N$ Br requires C, 62.4; H, 7.1; N, 4.55%).

N,N-diethyl-2-(1-naphthyl)ethylamine hydroiodide as needles (1.8g, 50%) m.p. 146 - 147° (from aqueous ethanol) τ 0.3 - 0.1(1H,broad), 1.95 - 2.95 (7H,m), 5.97 - 7.0 (8H,m) and 8.5 (6H,t,$\underline{J}$ 7Hz); $\nu_{max.}$ 2740, 2630, 2480, 1590, 800 and 775cm^{-1}. (Found: C, 54.3; H, 6.2; N, 4.0. $C_{16} H_{22} N$ I requires C, 54.2; H, 6.2; N, 3.9%).

N,N-diethyl-2-(1-naphthyl)ethylamine ethyl bromide as plates (1.14g, 34%) m.p. 162 - 163° (from ethyl acetate-acetone); τ 1.5 - 2.8 (7H,m), 6.1 - 6.7 (10H,m), 8.4 - 8.9 (9H,t,$\underline{J}$ 7Hz); $\nu_{max.}$ 2615, 2470, 1590, 790 and 772cm^{-1}. (Found: C,64.4; H. 8.0; $C_{18} H_{26} N$ Br requires C, 64.3; H, 7.8%).

N,N-diethyl-2-(1-naphthyl)ethylamine ethyl iodide as plates (1.49g, 39%) m.p. 188 - 189° (from ethanol-petroleum spirit); τ 1.4 - 2.6 (7H,m), 6.05 - 6.8 (10H,m) and 8.6 - 8.2 (9H, t,$\underline{J}$ 7Hz); $\nu_{max.}$ 2610, 2465, 1590, 800 and 780cm^{-1}. (Found: C, 56.6: H, 6.75; N, 3.85. $C_{18} H_{26} N$ I requires C, 56.4; H, 6.8; N, 3.65%).

N,N-diethyl-2-(1-naphthyl)methylamine hydroiodide, as plates (1.9g, 56%) m.p. 177 - 178.5° (from ethanol-petroleum spirit); τ 0.1 - 1.1 (1H,broad), 1.55 - 2.7 (7H,m), 5.15 (2H,s), 6.65 (4H,q,$\underline{J}$ 7Hz) and 8.5 (6H,t,$\underline{J}$ 7Hz); ν_{max} 2735, 2630, 2480, 1590

790 and 770cm^{-1}. (Found: C, 52.9; H, 6.1; N, 4.1. $C_{15} H_{20}$ N I requires C, 52.8; H, 5.9; N, 4.1%).

Emission spectra.

Fluorescence spectra at room temperature were recorded in 1cm^2 quartz cells using an excitation wavelength of approximately 300NM. The quantum yields of fluorescence were determined by the method previously described (page 207).

Emission at -196° from the salts was found to be that of the naphthalene chromophore. Quantum yields of fluorescence and phosphorescence were not determined at this temperature since the intensities could not be measured reliably, apparently depending upon the matrix of the solvent.

Ultra-violet absorption spectra.

Ultra-violet absorption spectra were recorded at a standard concentration of 10^{-4}M on Pye-Unicam SP700 and SP800 spectrophotometers. Sodium iodide was Fisons "Reagent" grade and was used without further purification.

Photolysis of N,N-diethyl-2-(1-naphthyl)methylamine hydroiodide.

N,N-Diethyl-2-(1-naphthyl)methylamine hydroiodide (0.44g) was irradiated in benzene (500cm^3) for 2 days using a Rayonet Reactor fitted with 16 lamps having maximum emission at 300NM. Dry nitrogen gas was bubbled via a capillary through the solution during the photolysis. Benzene was removed by evaporation under reduced pressure and the resulting brown oil chromatographed on alumina (Laporte Type "H", elution with benzene). N,N-diethyl-2-(1-naphthyl)methylamine was isolated (0.17g, 49%), and identified by comparison of the N.M.R. and I.R.

spectra with those of an authentic sample and by thin layer chromatography.

Stern-Volmer plots.

The procedure used to determine the Stern-Volmer quenching constants, K_Q, was the same as that described in Section 3:1:5.

Naphthalene (m.p. 80 - 80.5°) was zone-refined before use.

The concentration of naphthalene was fixed at 10^{-4}M, light of wavelength 300NM was used for excitation of the samples. All solutions were degassed prior to use.

The relative intensities of naphthalene fluorescence and the concentrations of the ammonium salts used are shown in Table 39.

TABLE 39.

Data for the fluorescence quenching of naphthalene by halogen anions.

1. Tetra-n-butylammonium bromide in 95% ethanol.

Concentration (M) x 10^3	I	$I_o/I - 1$
0	84	-
5	76.35	0.1
9.8	69.4	0.21
14.8	65.1	0.29
19.5	60.0	0.4
25.5	57.5	0.46
29.0	60.0	0.4

TABLE 39. (Continued)

2. <u>Tetra-n-butylammonium iodide in 95% ethanol</u>.

Concentration (M) x 10^3	I	$I_o/I - 1$
0	78	-
5.2	50.65	0.54
9.2	39.0	1.0
15.2	30.95	1.52
20.0	26.0	2.0
29.3	20.0	2.89

3. <u>Tetra-n-butylammonium chloride in acetonitrile</u>.

Concentration (M) x 10^3	I	$I_o/I - 1$
0	91	-
0.1	88.9	0.022
0.2	86.9	0.047
0.3	85.0	0.07
0.4	83.6	0.088
0.5	82.0	0.11

4. <u>Tetra-n-butylammonium bromide in acetonitrile</u>.

Concentration (M) x 10^3	I	$I_o/I - 1$
0	87	-
1	82.85	0.05
2	76.3	0.14
4	71.3	0.22
6	66.4	0.31
9	58.8	0.48
10	58.8	0.48

TABLE 39 (Continued)

5. Tetra-n-butylammonium iodide in acetonitrile.

Concentration (M) x 10^3	$\underline{I}$	$I_o/I - 1$
0	92	-
1	79.3	0.16
2	68.65	0.34
4	56.8	0.62
6	46.45	0.98
9	37.7	1.44
10	36.1	1.55

6. Tetra-n-butylammonium chloride in benzene.

Concentration (M) x 10^4	$\underline{I}$	$I_o/I - 1$
0	68	-
5	51.9	0.31
10	43.3	0.57
15	35.6	0.91
20	30.6	1.22
25	27.8	1.45

7. Tetra-n-butylammonium bromide in benzene.

Concentration (M) 10^4	$\underline{I}$	$I_o/I - 1$
0	89	-
1	86.8	0.025
2	84.3	0.056
3	82.7	0.076
4	80.5	0.106
5	78.75	0.13

8. Tetra-n-butylammonium iodide in benzene.

Concentration (M) x 10^4	I	$I_o/I - 1$
0	85	-
8	77.3	0.1
10	74.55	0.14
20	66.4	0.25
30	61.15	0.39
40	55.5	0.53
50	52.1	0.63

Concentration dependence of fluorescence.

The dependence of the fluorescence spectrum of N,N-diethyl-2-(1-naphthyl)ethylamine hydrobromide upon concentration was studied in the range 10^{-5} - 5×10^{-3}M in benzene. Solutions of the salt were made up to a known concentration by dilution of a stock solution and their optical densities recorded at 300NM (the wavelength used for excitation of the samples) on a Hilger-Gifford fixed wavelength spectrophotometer. Solutions of 1-methylnaphthalene were made up in the same way and any slight difference in the optical density from the solution of the salt were adjusted by dilution, or addition of small quantities of the stock solution, such that the optical densities of the solutions of the two compounds at a given concentration were the same. The solutions were then degassed and the ultra-violet absorption and emission spectrum of each solution recorded. The results of these experiments have been presented in Figure 9 as ratios of I_M/I_{MN} and I_E/I_{MN} (%) where I_M and I_{MN} are the relative fluorescence intensities of naphthalene in

the salt and in 1-methylnaphthalene respectively and I_E is

the relative fluorescence intensity of the exciplex in the

salt.

The fluorescence spectra of the other salts were rec-

orded over the same concentration range, a decrease in the

intensity of exciplex emission relative to that of the naph-

thalene was observed.

3:4:1 INTRAMOLECULAR QUENCHING OF NAPHTHALENE FLUORESCENCE.

Preparation of 3-phenyl-prop-2-enyl-(1-naphthyl)acetate.

   Pyridine (0.79g, 0.01 mole) was added to ice-cooled

1-naphthylacetyl chloride with stirring. 3-Phenyl-2-propen-

1-ol (1.34g, 0.01 mole) in benzene (10cm^3) was then added

with stirring to this mixture, which was subsequently allowed

to warm up to room temperature and then stirred overnight.

2N aqueous sodium hydroxide was added and the benzene layer

separated, the aqueous layer was extracted with diethyl ether

(3 x 15cm^3) and the organic layers combined and dried over

anhydrous magnesium sulphate. Evaporation of the solvent

under reduced pressure, followed by distillation of the crude

product yielded;

3-phenyl-prop-2-enyl-(1-naphthyl)acetate as a clear, viscous

oil (2.4g, 79%) b.p. 195 - 200° at 0.001 mmHg; τ 1.85 - 2.85

(12H,m), 3.6 - 3.95 (2H,m), 5.4 (2H,d,$\underline{J}$ 5Hz) and 6.05 (2H,s);

   $V_{max.}$ (film) 3060, 1730, 1595, 1510, 1250, 1140, 965, 790,

775, 740, and 690cm^{-1}; m/e 302 (M$^+$), 141 (M$^+$ - 261), 117, 115

and 91. Satisfactory elemental analysis could not be obtained

for this compound.

Preparation of 1-(hexa-2,4-dienyl)-(1-naphthyl)acetate.

Hexa-2,4-diene-1-ol.

   Hexa-2,4-dienoic acid (3.8g, 0.03 mole) was taken up in

diethyl ether (80cm^3) and added dropwise to lithium alum-
inium hydride (1.2g, 0.031 mole) in diethyl ether (10cm^3)
under dry nitrogen, a vigorous reaction ensued and the add-
ition rate was adjusted such as to maintain reflux. Ethyl acet-
ate was added dropwise until frothing ceased, the organic
layer was filtered off and dried over anhydrous sodium sul-
phate. Evaporation of the solvents under reduced pressure
followed by distillation in vacuo yielded; hexa-2,4-diene-1-
ol as a clear, colourless oil (2.0g, 68%); τ 3.6 - 4.8 (4H,m),
5.6 (1H,s), 5.95 (2H,d,$\underline{J}$ 5.5Hz) and 8.3 (3H,d,$\underline{J}$ 6Hz); $V_{max.}$
(film) 3300, 3005, 2945, 1655, 1450, 1250, 985 and 781cm^{-1}.

1-(Hexa-2,4-dienyl)-(1-naphthyl)acetate.

1-Naphthylacetyl chloride (0.01 mole) was reacted with
pyridine (0.01 mole) as before, hexa-2,4-diene-1-ol (0.98g,
0.01 mole) in benzene (10cm^3) was added dropwise to the ice-
cooled mixture with stirring. The mixture was allowed to
warm up to room temperature and stirred for 36 hours. The
same work-up yielded 1-(hexa-2,4-dienyl)-(1-naphthyl)acetate
as a clear, colourless oil (1.75g, 66%) b.p. 150 - 154° at
0.001 mmHg; τ 1.8 - 2.7 (7H,m), 3.7 - 4.7 (4H,m), 5.45 (2H,d,
$\underline{J}$ 5Hz), 4.0 (2H,s) and 8.25 (3H,d,$\underline{J}$ 6Hz); $V_{max.}$ (film) 3005,
2950, 2910, 1720, 1590, 1250, 1160, 1130, 785 and 770cm^{-1};
m/e 266 (M^+), 186, 141 (M^+ - 145), 121, 115 and 81. Satisfact-
ory elemental analysis could not be obtained for this compound.

Preparation of 2-furfuryl-(1-naphthyl)acetate.

1-Naphthylacetyl chloride (0.01 mole), pyridine (0.01 mole)

and furfuryl alcohol (0.01 mole) were reacted together in benzene in the same way for 18 hours, the same work-up yielded 2-furfuryl-(1-naphthyl)acetate as a clear, colourless oil (1.25g, 47%) b.p. 180° at 0.003 mmHg; τ 1.95 - 2.8 (8H,m) 3.85 (2H,s), 5.05 (2H,s) and 6.1 (2H,s); $V_{max.}$ (film) 3150, 3120, 3030, 2950, 1740, 1600, 1505, 1250, 1150, 970, 790 and 775cm^{-1}. m/e 266 (M$^+$), 141 (M$^+$ - 125), 115 and 81. (Found: C, 77.0; H, 5.4. $C_{17}H_{14}O_3$ requires C. 76.7; H, 5.3%).

Preparation of 3-phenyl-prop-2-enyl-1-naphthalene-carboxylate.

1-Naphthoyl chloride (0.01 mole), pyridine (0.01 mole) and 3-phenyl-2-propen-1-ol (0.01 mole) were reacted together in benzene in the same way and stirred for 16 hours. The same work-up yielded 3-phenyl-prop-2-enyl-1-naphthalene-carboxylate as plates (1.7g, 58%) m.p. 43 - 44.5° (from benzene-petroleum spirit); τ 1.7 - 2.9 (12H,m), 3.15 - 3.9 (2H,m), and 5.0 (2H,d,$\underline{J}$ 5Hz); $V_{max.}$ 3050, 3020, 2935, 1705, 1590, 1575, 1510, 1245, 1200, 1130, 965, 810, 780, 740 and 690cm^{-1}; m/e 288 (M$^+$), 155 (M$^+$ - 133), 141 and 127. (Found: C, 83.7; H, 5.6. $C_{20}H_{16}O_2$ requires C, 83.3; H, 5.5%).

Preparation of 2-furfuryl-1-naphthalene-carboxylate.

1-Naphthoyl chloride (0.01 mole), pyridine (0.01 mole) and furfuryl alcohol (0.01 mole) were reacted together in benzene in the same way and stirred for 20 hours. The same work-up yielded 2-furfuryl-1-naphthalene-carboxylate as a clear, colourless oil (1.7g, 68%) b.p. 160 - 164° at 0.001 mmHg; τ 1.7 - 2.9 (8H,m), 3.90 (2H,s) and 4.65 (2H,s); $V_{max.}$ (film)

3030, 2960, 1710, 1590, 1570, 1510, 1240, 1195, 810, 780 and

745cm^{-1}; m/e 252 (M$^+$), 155 (M$^+$ - 97), 127 and 81. (Found:

C, 76.4; H, 4.9. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.8%).

Preparation of 1-naphthylmethyl-hexa-2,4-dienoate.

1-Naphthylmethyl alcohol.

1-Naphthoic acid (5.16g, 0.03 mole) was taken up in diethyl

ether (100cm^3) and added dropwise to an ice-cooled suspension

of lithium aluminium hydride (1.14g, 0.03 mole) in diethyl

ether (20cm^3). The mixture was allowed to warm up to room

temperature and stirred for a further 4 hours. Ethyl acetate

was added dropwise until frothing ceased, the organic layer

was filtered off and dried over anhydrous sodium sulphate.

Evaporation of the solvents under reduced pressure followed by

trituration and recrystallisation yielded 1-naphthylmethyl-

alcohol (2.6g, 55%) m.p. 63 - 64° (lit.,[202] 64°); τ 1.8 - 2.9

(7H,m), 5.0 (2H,s) and 8.1 (1H,s); $V_{max.}$ 3310, 1600, 1000,

800, 790 and 771cm^{-1}.

Hexa-2,4-dienoic acid chloride.

This compound was prepared by heating under reflux with

oxalyl chloride in benzene as previously described ($V_{max.}$

1750cm^{-1}).

1-Naphthylmethyl-hexa-2,4-dienoate.

Hexa-2,4-dienoic acid chloride (0.01 mole) was reacted

with pyridine (0.01 mole) and 1-naphthylmethylalcohol in the

same way and stirred for 24 hours. The same work-up yielded

1-naphthylmethyl-hexa-2,4-dienoate as a clear, colourless oil

(1.0g, 41%) b.p. 175 - 180° at 0.0025 mmHg; τ 1.8 - 2.8 (9H,

m); 3.75 - 4.15 (2H,m), 4.4 (2H,s) and 8.3 (3H,d,$\underline{J}$ 6Hz); $V_{max.}$

3030, 2970, 1715, 1645, 1620, 1515, 1240, 1134, 800, 792 and

778cm^{-1}; m/e 252 (M$^+$), 157, 141 (M$^+$ - 111) 127, 115 and 95.

(Found: C, 80.25; H, 6.45. $C_{17} H_{16} O_2$ requires C, 80.9; H,

6.35%).

Preparation of 1-naphthyl-hexa-2,4-dienoate.

Hexa-2,4-dienoic acid chloride (0.01 mole) was reacted with

pyridine (0.01 mole) and 1-naphthol in the same way and stirred

for 24 hours. The same work-up yielded 1-naphthyl-hexa-2,4-

dienoate as plates (1.5g, 63%) m.p. 83 - 84° (from benzene-

petroleum spirit); τ 1.9 - 2.8 (9H,m), 3.7 - 4.1 (2H,m) and

8.3 (3H,d,J 5Hz); $V_{max.}$ 1720, 1645, 1600, 1215, 1110, 800 and

700cm^{-1}; m/e 238 (M$^+$), 115, 95 (M$^+$ - 143), 67 and 41. (Found:

C, 81.0; H, 6.0. $C_{16} H_{14} O_2$ requires C, 80.7; H, 5.9%).

Preparation of 2-naphthyl-hexa-2,4-dienoate.

Hexa-2,4-dienoic acid chloride (0.01 mole) was reacted with

pyridine (0.01 mole) and 2-naphthol in the same way, the mixt-

ure was stirred for 24 hours. The same work-up yielded

2-naphthyl-hexa-2,4-dienoate as plates (1.6g, 66%). m.p. 70.5 -

72.5° (from benzene-petroleum spirit); τ 2.0 - 3.0 (9H,m),

3.9 - 4.35 (2H,m), 8.4 (3H,d,J 5Hz); $V_{max.}$ 1724, 1645, 1602,

1500, 1240, 1150, 1120, 815, 790 and 760cm^{-1}; m/e 238 (M$^+$),

115, 95 (M$^+$ - 143), 67 and 41. (Found: C, 80.85; H. 5.9. C_{16}

$H_{14} O_2$ requires C, 80.7; H, 5.9%).

Preparation of the methyl esters.

The methyl esters were prepared by reaction of acetyl

chloride with 1-naphthol or 1-naphthylmethyl alcohol in the usual way. Distillation in vacuo and recrystallisation yielded 1-naphthylacetate m.p. 40 - 41° (lit.,[202] 42°); τ 2.05 - 2.7 (7H,m) and 7.8 (3H,s); $\nu_{max.}$ (film) 3020, 1730, 1600, 1258, 800, 790 and 775cm^{-1}. Distillation in vacuo yielded 1-naphthyl-methyl acetate as a clear colourless oil b.p. 85 - 90° at 0.01 mmHg; (lit.,[202] 134 - 136° at .15 mmHg); τ 2.0 - 2.7 (7H,m) and 7.7 (3H,s); $\nu_{max.}$ (film) 3015, 1750, 1600, 1250, 800 and 780cm^{-1}.

Ultra-Violet absorption and emission spectra.

Ultra-violet absorption spectra were recorded at a concentration of 10^{-4}M in cyclohexane and benzene. Emission spectra were also recorded at a standard concentration of 10^{-4}M. The quantum yields of fluorescence (Table 25) were determined in 95% ethanol using the method previously described (page 207).

3:4:2   INTERMOLECULAR FLUORESCENCE QUENCHING.

Furan, thiophene, 2-methylfuran and 2,5-dimethylfuran were refluxed and distilled from lithium aluminium hydride under a stream of dry nitrogen gas. N-Methylpyrrole was distilled under dry nitrogen.

Fluorescence spectra.

The fluorescence spectra (see Table 26) were obtained using solutions containing 10^{-4}M 1-cyanonaphthalene or 9-cyanophen-anthrene and 10^{-1}M 2-methylfuran, 2,5-dimethylfuran or N-methyl pyrrole; N-methylindole was used at 10^{-2}M. The solutions were degassed prior to use. The ultra-violet absorption spectra of

these systems were found to be essentially the same as those of the separated components.

The effect of quencher concentration upon the fluorescence spectrum was studied under the same conditions, the quencher concentration being varied between 10^{-2} and 10^{-1}M. The ultra-violet absorption spectra of each solution showed no changes corresponding to those in the fluorescence spectrum.

The systems which failed to exhibit a new fluorescence band were studied under a number of conditions in which solvent, concentration of quencher, concentration of hydrocarbon and temperature were varied.

The enthalpies and activation energies of formation of the exciplexes were determined using the method described in Section 3:1:4. The concentration of the hydrocarbon was always 2×10^{-5}M and that of the quencher 10^{-1}M, toluene was used as the solvent.

Stern-Volmer plots.

The rate constants for the fluorescence quenching of aromatic hydrocarbons were determined using the method described in Section 3:1:5, the concentration of anthracene and 9-cyano-anthracene was fixed at 5×10^{-5}M, 1-cyanonaphthalene was used at 10^{-4}M. The relative intensities of hydrocarbon fluorescence and the concentrations of quencher used are shown in Table 40.

TABLE 40.

Data for fluorescence quenching of aromatic hydrocarbons

by heterocyclic compounds.

1. 9-cyanoanthracene-furan in acetonitrile.

Concentration (M)	I	$I_o/I - 1$
0	70.5	-
0.1	66.6	0.06
0.2	66.6	0.06
0.5	61.2	0.15
0.8	58.1	0.21
1.0	55.5	0.27

2. 9-cyanoanthracene-furan in cyclohexane.

Concentration (M) x 10	I	$I_o/I - 1$
0	80	-
0.6	79	0.012
1	78.2	0.023
2	77.0	0.038
5	72.6	0.1
8	68.7	0.165

3. 9-cyanoanthracene-2,5-dimethylfuran in acetonitrile.

Concentration (M) x 10^3	I	$I_o/I - 1$
0	69.5	-
2	19.3	2.6
4	11.6	5.0
6	8.7	7.0
8	6.6	9.53
10	5.3	12.15

TABLE 40 (Continued.)

4. **9-cyanoanthracene-2,5-dimethylfuran in cyclohexane.**

Concentration (M) x 10^3	I	$I_o/I - 1$
0	75	-
2	31.25	1.4
4	18.75	3.0
6.	14.55	4.15
8	11.6	5.46
10	9.4	6.98

5. **9-cyanoanthracene-thiophene in acetonitrile.**

Concentration (M)	I	$I_o/I - 1$
0	86	-
1	76.9	0.118
2	66.15	0.3
2.5	54	0.59
4	43	1.0
5	39.9	1.15

6. **9-cyanoanthracene-thiophene in cyclohexane.**

Concentration (M)	I	$I_o/I - 1$
0	84.0	-
1	72.4	0.16
2	67.4	0.25
2.5	57.85	0.45
4	49.9	0.68
5	45.5	0.85

TABLE 40 (Continued)

7. 9-cyanoanthracene-N-methylpyrrole in acetonitrile.

Concentration (M)	I	$I_o/I - 1$
0	71.0	-
1	64.0	0.11
2	53.0	0.34
5	42.15	0.68
8	28.5	1.49
10	28.5	1.49

8. 9-cyanoanthracene-N-methylpyrrole in cyclohexane.

Concentration (M)	I	$I_o/I - 1$
0	82.0	-
1	44.65	0.84
2	33.5	1.31
5	31.1	1.64
8	23.5	2.49
10	20.5	3.0

9. Anthracene-N-methylpyrrole in acetonitrile.

Concentration (M) x 10^3	I	$I_o/I - 1$
0	74.0	-
1	73.6	0.005
4	73.0	0.014
6	72.0	0.027
8	71.75	0.031
10	71.0	0.042

TABLE 40 (Continued)

10. <u>1-cyanonaphthalene-furan in acetonitrile.</u>

Concentration (M) x 10	I	$I_o/I - 1$
0	81.5	-
1	71.5	0.14
2	68.5	0.19
5	56.6	0.44
8	48.5	0.68
10	44.65	0.825

11 <u>1-cyanonaphthalene-furan in cyclohexane.</u>

Concentration (M) x 10	I	$I_o/I - 1$
0	82.0	-
1	38.0	1.16
2	30.0	1.73
5	8.15	9.06
8	6.15	12.4
10	5.1	15.1

12. <u>1-cyanonaphthalene-N-methylpyrrole in acetonitrile.</u>

Concentration (M) x 10^2	I	$I_o/I - 1$
0	85.0	-
1	36.9	1.3
2	18.1	3.7
5	8.75	9.77
8	4.45	18.1
10	2.95	27.8

Determination of Fluorescence Lifetimes.

The lifetimes used to determine the quenching rate constants
(via the Stern-Volmer equation) were measured using a PS-3 pulse
sampling fluorometer supplied by Applied Photophysics Ltd. The
optical system consisted of a lamp, operated at approximately
22KV (by an Applied Photophysics supply unit) in an atmosphere
of nitrogen gas (at 2 atmospheres), and trigger and signal
photomultipliers E.M.I. Types 931A and 9813KB respectively, the
power supply for which was a Farnell Model E2 unit. The signals
were monitored by a Bradley Sampling Adaptor Type 158 in conjun-
ction with either an Advance Model HR-100 X-Y recorder or a
Dynamco 7110 storage oscilloscope.
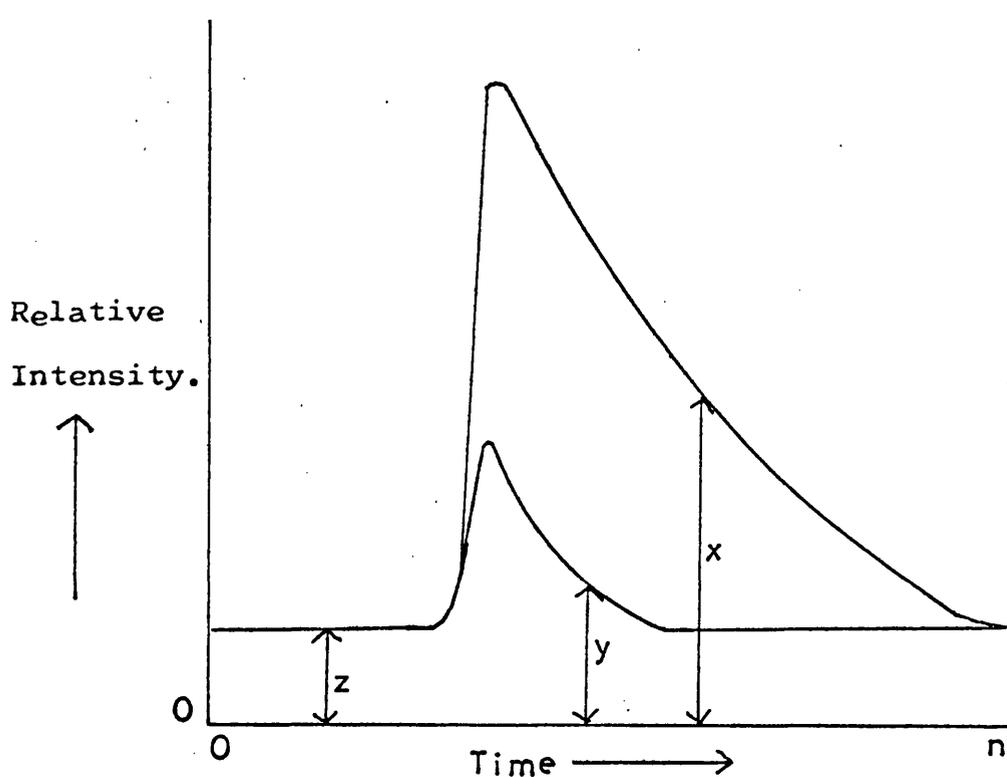
Figure 12.

Schematic representation of decay curves obtained from the PS-3

pulse sampling fluorometer.

The decay curves were analysed with the help of the University of Leicester Computer Service[a] using the procedure outlined by Demas and Adamson.[203] The programme used requires four data inputs.

1. Fluorescence decay of the sample: the relative intensity of the sample decay "x" was taken at regular intervals along the total length of the decay $(0 \rightarrow n)$.

2. Scattered light decay: the relative intensity, "y", was taken at the same intervals as was "x".

3. Time base: the time base is linear, consequently it is possible to allocate each reading of "x" and "y" with a time.

3. Data and pulse backgrounds: these are single integer and are generally the same, they represent the relative intensity "z" (exaggerated in Figure 12) and are the level above zero from which the decay curves start.

The fluorescence decay curves of 1-cyanonaphthalene (10^{-4}M degassed solutions) were obtained as outlined above using an OX7 filter for the excitation light, the decay curves of 9-cyanoanthracene were obtained using an OX7 filter for the exciting light and a Balzer K2 filter for the emitted light.

3:5 DONOR-ACCEPTOR COMPLEXES FORMED BY IMIDES.

3:5:1 DONOR-ACCEPTOR COMPLEXES FORMED WITH AMINES.

Preparation of N- [(N-methyl)anilino] methylphthalimide.
N-Hydroxymethylphthalimide.

This compound was prepared as described in the literature.[204]

N- [(N-methyl)anilino] methylphthalimide.

N-Hydroxymethylphthalimide (1.56g, 0.01 mole) was taken up in methanol (15cm^3) and N-methylaniline (1.07g, 0.01 mole) added. The mixture was heated under reflux for 1 hour and cooled, a yellow solid precipitated, subsequent crystallisation yielded N- [(N-methyl)anilino] methylphthalimide as pale yellow needles(1.6g, 59%) m.p. 92 - 93°(from ethanol); τ 2.1 - 2.65 (4H,m), 2.7 - 3.4 (5H,m), 4.9 (2H,s) and 6.9 (3H,s); $V_{max.}$ 1775, 1710, 1600, 1505, 1290, 1230, 998, 988, 944, 934, 755, 745, 730 and 690cm^{-1}; m/e, 266 (M$^+$) 161, 120, 106 and 77. (Found: C, 72.1; H, 5.3; N, 10.3. $C_{16} H_{14} N_2 O_2$ requires C, 72.2; H, 5.3; N, 10.5%).

Preparation of N- [3-(N-methyl)anilino] propylphthalimide.

N-(3-bromo)propylphthalimide (2.78g, 0.01 mole) was heated with N-methylaniline (2.14g, 0.02 mole) in decalin (15cm^3) at 170° for 5 hours with stirring. Dry nitrogen gas was passed continuously over the reaction mixture. The reaction mixture was then cooled to room temperature and 2N hydrochloric acid (20cm^3) added, the aqueous layer was separated and the decalin washed with 2N hydrochloric acid (2 x 5cm^3). The aqueous layers

were combined and neutralised with 2N sodium hydroxide and extracted with diethyl ether ($3 \times 25\text{cm}^3$). The ethereal extracts were combined and dried over anhydrous magnesium sulphate and the ether removed under reduced pressure. Distillation in vacuo yielded N-methylaniline and the crude product which was crystallised yielding N- $\boxed{3\text{-}(\text{N-methyl})\text{anilino}}$ propylphthalimide as pale yellow plates (1.9g, 67%) m.p. 73 - 74° (from ethanol); b.p. 210° at 0.05 mmHg; τ 2.05 - 2.55 (4H,m), 2.6 - 3.2 (5H,m), 6.2 (2H,q,$\underline{J}$ 7Hz), 6.7 (2H,q,$\underline{J}$ 7Hz), 7.0 (3H,s) and 7.9 (2H,dd,$\underline{J}$ 7Hz); $V_{\text{max.}}$ 1780, 1710, 1600, 1504, 1035, 990, 910, 876, 750, 715, and 690cm^{-1}; m/e 294 (M$^+$), 147, 120 (M$^+$ - 174) and 77. (Found: C, 73.4; H, 6.2; N, 9.5. $C_{18}H_{18}N_2O_2$ requires C, 73.45; H, 6.2; N, 9.5%).

Preparation of N- $\boxed{4\text{-}(\text{N-methyl})\text{anilino}}$ butylphthalimide.

N-(4-Bromo)butylphthalimide (2.92g, 0.01 mole) was reacted with N-methylaniline (2.14g, 0.02 mole) in decalin (15cm^3) as described in the preparation of N- $\boxed{3\text{-}(\text{N-methyl})\text{anilino}}$ propylphthalimide. The same work-up followed by distillation in vacuo and recrystallisation yielded N- $\boxed{4\text{-}(\text{N-methyl})\text{anilino}}$ butylphthalimide as yellow plates (1.2g, 39%) m.p. 71 - 72° (from ethanol); τ 2.1 - 2.5 (4H,m), 2.6 - 3.4 (5H,m), 6.2 (2H,t,$\underline{J}$ 7Hz), 6.7 (2H,t,$\underline{J}$ 7Hz), 7.1 (3H,s) and 8.0 - 8.55 (4H,m); $V_{\text{max.}}$ 1770, 1710, 1600, 1506, 1045, 915, 860, 748, 720 and 688cm^{-1}; m/e 308 (M$^+$), 147, 120 and 77. (Found: C, 74.0; H, 6.55; N, 9.0. $C_{19}H_{20}N_2O_2$ requires C, 74.0; H, 6.5; N, 9.1%).

Preparation of [2-(N-methyl)anilinoethyl] -N-phthalimido acetate.

Phthalylglycine.

Phthalic anhydride (2.96g, 0.02 mole) was heated with glycine (1.5g, 0.02 mole) for 15 minutes at 150 - 190°. The mixture was allowed to cool and the product recrystallised from water.

Phthalylglycl chloride.

Phthalylglycine (2g, 0.01 mole) was heated under reflux with thionyl chloride ($4cm^3$) for 30 minutes. Excess thionyl chloride was removed under reduced pressure leaving phthalylglycyl chloride, $V_{max.}$ 1806, 1770 and $1720cm^{-1}$.

[2-(N-methyl)anilinoethyl] -N-phthalimido acetate.

Phthalylglycyl chloride (0.01 mole) was taken up in benzene ($10cm^3$) and added dropwise to an ice-cooled solution of 2-(N-methylanilino)ethanol (1.5g, 0.01 mole) in benzene ($5cm^3$). The mixture was allowed to warm up to room temperature and stirred for 4 hours. 2N Hydrochloric acid ($25cm^3$) was added and the benzene layer separated, the aqueous layer was washed with diethyl ether (3 x $15cm^3$), made basic by addition of 2N sodium hydroxide and extracted with diethyl ether (3 x 20 cm^3). The ethereal extracts were combined, washed with water (2 x $15cm^3$) and dried over anhydrous magnesium sulphate. Evaporation of the solvent under reduced pressure followed by recrystallisation yielded [2-(N-methyl)anilinoethyl] -N-phthalimido acetate as yellow needles (2.0g, 59%) m.p. 90 - 92° (from cyclohexane); τ 2.1 - 2.6 (4H,m), 2.7 - 3.6 (5H,m), 5.7 (2H,s), 5.8 (2H,t,$\underline{J}$ 5Hz), 6.5 (2H,t,$\underline{J}$ 5Hz) and 7.1 (3H,s); $V_{max.}$ 1770, 1740, 1720, 1600, 1508, 1248, 1015, 954, 890,

750, 740, 705 and 690cm^{-1}; m/e 338 (M$^+$), 161, 120 (M$^+$ - 188) and 77. (Found; C, 67.5; H, 5.3; N, 8.1. C$_{19}$H$_{18}$N$_2$O$_4$ requires C, 67.4; H, 5.4; N, 8.3%).

Preparation of N-(2-dimethylamino)ethylphthalimide.

Phthalic anhydride (2.96g, 0.02 mole) was heated under reflux with 2-dimethylaminoethylamine (1.76g, 0.02 mole) in glacial acetic acid (25cm^3) for 2 hours. The solvent was removed under reduced pressure leaving a dark brown oil, trituration with petroleum spirit and recrystallisation yielded N-(2-dimethylamino)ethyl phthalimide as plates (2.35g, 43%) m.p. 103.5 - 104.5° (lit.,^{205} 104 - 105°); τ 2.1 - 2.5 (4H,m), 6.2 (2H,t,$\underline{J}$ 7Hz), 7.4 (2H,t,$\underline{J}$ 7Hz) and 7.7 (6H,s); $V_{max.}$ 1770, 1710, 1600, 1190, 1110, 1015, 934, 859, 800, 767 and 718cm^{-1}.

Preparation of N-(N-methyl)anilinotetrachlorophthalimide.

Tetrachlorophthalic anhydride (2.86g, 0.01 mole) was heated under reflux with 1-methyl-1-phenylhydrazine (1.22g, 0.01 mole) in glacial acetic acid (25cm^3) for 1 hour, after which time the product had precipitated, recrystallisation yielded N-(N-methyl) anilinotetrachlorophthalimide as yellow needles (3.7g, 95%) m.p. 252 - 253° (from acetonitrile); $V_{max.}$ 1793, 1740, 1600, 1502, 1310, 1210, 1132, 790, 745, 738 and 686cm^{-1}; m/e 388 (M$^+$), 105 and 77. (Found: C, 46.2; H, 2.0; N, 7.1; Cl, 36.5. C$_{15}$H$_8$N$_2$O$_2$Cl$_4$ requires C46.15; H, 2.0; N, 7.2; Cl, 36.4%).

Preparation of N-[2-(N-methyl)anilino]ethyltetrachlorophthalimide.

2-Bromoethylamine (1.24g, 0.01 mole) was heated at 170° with

N-methylaniline (1.07g, 0.01 mole) for 1 hour under a stream of dry nitrogen gas. The mixture was cooled to room temperature upon which it set to a glass, 2N sodium hydroxide was added and the mixture extracted with diethyl ether (3 x 10cm^3). The ethereal layers were combined and added to tetrachlorophthalic anhydride (2.86g, 0.01 mole) in glacial acetic acid (25cm^3) and the ether distilled from the mixture which was then heated under reflux for 2 hours. An orange solid precipitated which was filtered off (3.2g.). Crystallisation of a small sample yielded N- $\boxed{\text{2-(N-methyl)anilino}}$ ethyltetrachlorophthalimide as orange needles m.p. 280 - 281.5° from benzene);

$V_{max.}$ 1770, 1710, 1595, 1508, 1305, 1200, 1100, 795, 740 and 690cm^{-1}; m/e 416 (M$^+$), 120 (M$^+$ - 296), 105 and 77. (Found: C,48.7; H, 2.85; N, 6.5; Cl, 33.85. $C_{17} H_{12} N_2 O_2 Cl_2$ requires C, 48.8; H, 2.9; N, 6.7; Cl, 34.0%).

Preparation of the N-n-butylimides.

N-n-butylphthalimide m.p. 31 - 33° (from ethanol) lit.,[191] 34°) and N-n-butyltetrachlorophthalimide m.p. 153 - 154° (from acetic acid-ethanol) (lit.,[206] 153 - 154°) were prepared as previously described in the literature[191], N-n-butylmaleimide b.p.50° at 0.05 mmHg, (lit.,[207] b.p. 103 - 104° at 20mmHg.) was prepared by a known procedure.[201]

Ultra-violet absorption spectra.

The absorption spectra were recorded on Pye-Unicam SP800 and SP700 spectrophotometers, the details are shown in Table 30 and examples portrayed in Diagram 13. The Beer's Law plots were obtained at a fixed wavelength (usually that of maximum

absorption) using a Hilger-Gifford spectrophotometer.

Fluorescence spectra.

The fluorescence spectra were recorded with air-saturated solutions except for those used for the quantum yields. Quantum yields were determined by the method described in Section 3:2:1. Details of the fluorescence spectra are shown in Table 31.

The fluorescence lifetimes were estimated from the fluorescence decay curves obtained using a pulse sampling fluorometer (Section 3:4:2). Solutions containing the phthalimide at 10^{-3}M were used, and were all degassed prior to use. An OX7 filter was used for the excitation light and a Balzer K3 filter for the emitted light.

3:5:2 EMISSION OF DONOR-ACCEPTOR COMPLEXES FROM MATRICES.

The emission spectra were recorded under standard conditions, the solutions were either 10^{-4} or 10^{-2}M in the phthalimide. The results are presented in Table 32.

The emission spectra of equimolar mixtures of the N-n-butylimide and N,N-dimethylaniline were also recorded under standard conditions, the results are presented in Table 33.

3:5:3 DONOR-ACCEPTOR COMPLEXES FORMED WITH AROMATIC HYDROCARBONS.

Preparation of N-[2-(1-naphthyl)]ethylphthalimide.

This compound was prepared as described by Breen and Keller,[166] recrystallisation yielded N-[2-(1-naphthyl) ethyl]-

246.

phthalimide (0.7g, 23%) as needles m.p. 144 - 145° (from
ethanol) (lit.,[166] 144 - 145°); τ 1.6 - 2.85 (11H,m), 5.8 -
6.2 (2H,m) and 6.4 - 6.85 (2H,m); $V_{max.}$ 1763, 1708, 1610,
1595, 1508, 1100, 981, 862, 795, 777, 720 and 710cm^{-1}; m/e
301 (M^{+}) and 141 (M^{+} - 160). (Found: C, 79.6; H, 5.0; N, 4.9.
Calculated for $C_{20} H_{15} N O_2$ C, 79.7; H, 5.0; N, 4.65%).

Preparation of 2-(N-phthalimido)ethyl-(1-naphthyl)acetate.

2-(N-hydroxy)ethylphthalimide.

Phthalic anhydride (2.96g, 0.02 mole) was heated under
reflux with ethanolamine (1.22g, 0.02 mole) in glacial acetic
acid (30cm^{3}) for 2 hours. The solvent was removed under red-
uced pressure leaving a brown oil, trituration with petroleum
spirit followed by crystallisation yielded 2-(N-hydroxy)ethyl-
phthalimide (3.6g, 94%) as needles m.p. 124 - 125° (from
ethanol) (lit.,[208] 126 - 127°); $V_{max.}$ 3480, 1770, 1710, 1610,
1190, 1060, 900, 800 and 728cm^{-1}.

2-(N-phthalimido)ethyl-(1-naphthyl)acetate.

1-Naphthylacetyl chloride (0.005 mole) in benzene (10cm^{3})
was reacted with pyridine (0.6g) in benzene (10cm^{3}). A solut-
ion of 2-(N-hydroxy)ethylphthalimide (0.95g, 0.005 mole) in
benzene (10cm^{3}). The mixture was allowed to warm up to room
temperature and stirred for 45 hours, after which time a solid
had precipitated, this was filtered off and the resultant benz-
ene solution evaporated to leave a yellow oil. Trituration
with petroleum spirit, followed by recrystallisation yielded
2-(N-phthalimido)ethyl-(1-naphthyl)acetate (0.75g, 38%) as
plates m.p. 121 - 123.5^{o} (from ethanol); τ 2.0 - 2.95 (11H,m)

5.8 (2H,t,$\underline{J}$ 5Hz), 6.15 (2H,s) and 6.3 (2H,t,$\underline{J}$ 5Hz); $V_{max.}$

1778, 1740, 1710, 1600, 1513, 1150, 1020, 855, 792, 785, 730

and 718cm^{-1}; m/e 395 (M$^+$), 174, 168 and 141 (M$^+$ - 254).

(Found: C, 73.05; H, 4.8; N, 3.95. $C_{22} H_{17} N O_4$ requires 73.5;

H, 4.8; N, 3.9%).

Preparation of N-$\boxed{\text{2-(3-indolyl)}}$ethylphthalimide.

Phthalic anhydride (0.74g, 0.005 mole) was heated under

reflux with tryptamine (0.8g, 0.005 mole) in glacial acetic

acid (25cm^3) for 3 hours and then left to cool overnight, after

which time a solid had precipitated. The solid was filtered

off, recrystallisation yielded N-$\boxed{\text{2-(3-indolyl)}}$ethylphthalimide

(0.5g, 34%) as plates m.p. 167 - 168° (from ethanol); $\mathcal{T}$ 2.0 -

2.6 (4H,m), 2.6 - 3.1 (4H,m), 5.45 (1H,s), 6.05 (2H,t,$\underline{J}$ 6Hz)

and 6.9 (2H,t,$\underline{J}$ 6Hz); $V_{max.}$ 3360, 1768, 1700, 1615, 1100, 995

988, 870, 745 and 715cm^{-1}; m/e 290 (M$^+$), 130 (M$^+$ - 160), 98 and

95. (Found: C, 74.2; H, 4.9; N, 9.6. $C_{18} H_{14} N_2 O_2$ requires

C, 74.5; H, 4.9; N, 9.65%).

Ultra-violet absorption and fluorescence spectra.

Absorption and fluorescence spectra were recorded for solut-

ions of the phthalimides at a standard concentration of 10^{-4}M.

The solutions used to obtain the fluorescence spectra were all

degassed before use.

The fluorescence spectra of equimolar mixtures of N-n-butyl-

tetrachlorophthalimide and anthracene, 9-methylanthracene,

9,10-dimethylanthracene or 9,10-diphenylanthracene were recorded

at a concentration of 5 x 10^{-3}M. The solutions were degassed

prior to use.

3:6 EXCIMER FORMATION.

3:6:1 INTRAMOLECULAR EXCIMER FORMATION.

Preparation of di-1-naphthylmethyl ether.

1-Naphthylmethylbromide.

1-Methylnaphthalene (4.26g, 0.03 mole) was heated under reflux with N-bromosuccinimide (6.4g, 0.036 mole) in carbon tetrachloride ($65cm^3$) for 2 hours, during which time succinimide gradually formed. The mixture was cooled in ice and the succinimide filtered off, the filtrate was shaken with 2N aqueous sodium hydroxide (2 x $15cm^3$) and then with water (3 x $15cm^3$) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure leaving a yellow oil. Distillation in vacuo and crystallisation yielded 1-naphthylmethylbromide as pale yellow plates (4.5g, 68%) m.p. 44 - 45° (from petroleum spirit (lit.,[209] 45° - 46°) b.p. 85° at 0.02 mmHg; τ 7.9 - 3.2 (7H,m) and 5.4 (2H,s).

Di-1-naphthylmethyl ether.

Dimethylsulphoxide ($20cm^3$) was added to crushed pellets of potassium hydroxide (0.89g, 0.016 mole) and the mixture stirred for five minutes. 1-Naphthylmethyl alcohol (0.65g, 0.004 mole) was added and the mixture stirred for 45 minutes. 1-Naphthylmethyl bromide (0.89g, 0.004 mole) was added and the mixture stirred for a further 45 minutes. Water ($20cm^3$) was added and the aqueous layer extracted with diethyl ether (3 x $50cm^3$). The ethereal extracts were combined, washed with water (3 x $50cm^3$) and dried over anhydrous calcium chloride. The ether

was removed under reduced pressure leaving a solid, recrystallisation yielded di-1-naphthylmethyl ether as plates (0.58g, 48%) m.p. 120 - 121° (from benzene-petroleum spirit) (lit.,[202] 121°); τ 1.85 - 2.9 (14H,m) and 5.1 (4H,s); $V_{max.}$ 1600, 1510, 1080, 1062, 1040, 800, 790, and 775cm^{-1}; m/e 298(M$^+$), 157, 141 (M$^+$ - 157), and 78. (Found: C, 88.4; H, 6.1. Calculated for $C_{22}H_{18}O$, C, 88.6; H, 6.1%).

Preparation of di-2-naphthylmethyl ether.

2-Naphthylmethyl alcohol.

The method used was identical to that described for 1-naphthylmethyl alcohol (page 231); τ 2.1 - 3.0 (7H,m), 5.35 (2H,s) and 7.6 (1H,s); $V_{max.}$ 3230,1605, 1055, 1040, 814 and 790cm^{-1}.

2-Naphthylmethyl bromide.

The method used was identical to that described for 1-naphthylmethyl bromide; τ 2.1 - 3.1 (7H,m), and 5.45 (2H,s); $V_{max.}$ 1600, 1215, 1145, 826 and 754cm^{-1}.

Di-2-naphthylmethyl ether.

2-Naphthylmethyl alcohol (0.8g, 0.005 mole) and 2-naphthylmethyl bromide (1.1g, 0.005 mole) were reacted in the presence of potassium hydroxide (1.1g) in dimethylsulphoxide as described for di-1-naphthylmethyl ether. Recrystallisation yielded di-2-naphthylmethyl ether (0.6g, 40%) as plates m.p. 120 - 121° (from ethanol); τ 2.2 - 2.9 (14H,m) and 5.4 (4H,s); $V_{max.}$ 1602, 1172, 1130, 1110, 820 and 740cm^{-1}; m/e 298 (M$^+$), 157, 141 (M$^+$ - 157), 127, 105 and 78. (Found: C, 88.5; H, 6.1. $C_{22}H_{18}O$ requires C, 88.6; H, 6.1%).

Preparation of 2-(2-naphthyl)ethyl-(2-naphthyl)methyl ether.

2-(2-naphthyl)ethyl alcohol.

2-Naphthylacetic acid (3.9g, 0.02 mole) was reduced with lithium aluminium hydride (0.76g, 0.02 mole) by the method described for 1-naphthylmethyl alcohol (page 231).

2-(2-Naphthyl)ethyl-(2-naphthyl)methyl ether.

2-Naphthylmethyl bromide (1.1g, 0.005 mole) and 2-(2-naphthyl)ethyl alcohol (0.86g, 0.005 mole) were reacted in the presence of potassium hydroxide (1.1g) in dimethyl sulphoxide in the manner previously described. The same work-up yielded 2-(2-naphthyl)ethyl-(2-naphthyl)methyl ether as plates (0.65g, 42%) m.p. 98 - 99° (from ethanol); τ 2.1 - 2.7 (14H,m), 5.3 (2H,s), 6.1 (2H,t,$\underline{J}$ 6Hz) and 6.8 (2H,t,$\underline{J}$ 6Hz); $V_{max.}$ 1600, 1128, 1108, 862, 825 and 738cm^{-1}; m/e 312 (M^{+}) 156, 141 (M^{+} - 171), 127 and 115. (Found: C, 88.5; H, 6.4. $C_{23}H_{20}O$ requires C, 88.4; H, 6.45%).

Preparation of O,O-di-(2-naphthylmethyl)-ethane-1,2-diol.

2-Naphthylmethyl bromide (1.1g, 0.005 mole) and ethylene glycol (0.31g, 0.005 mole) were reacted in the presence of potassium hydroxide (1.1g) in dimethyl sulphoxide as before. The same work-up yielded O,O-di-(2-naphthylmethyl)-ethane-1,2-diol (1.0g, 57%) as plates m.p. 98 - 99° (from ethanol); τ 2.1 - 2.9 (14H,m), 5.2 (4H,s) and 6.2 (4H,s); $V_{max.}$ 1600, 1215, 865, 824, 756 and 741cm^{-1}; m/e 342 (M^{+}), 201, 157 and 141 (M^{+} - 201). (Found: C, 84.1; H, 6.3. $C_{24}H_{22}O_{2}$ requires C, 84.2; H, 6.5%).

Preparation of methyl 1-naphthylmethyl ether.

1-Naphthylmethyl alcohol (0.8g, 0.001 mole) and methyl iodide (0.7g, 0.005 mole) were reacted in the presence of potassium hydroxide (1.1g) in dimethyl sulphoxide as before. The same work-up followed by distillation in vacuo yielded methyl 1-naphthylmethyl ether as a clear, colourless oil (0.55g, 63%) b.p. 62° at 0.002 mmHg: (lit.,[202] 101 - 103° at 1.5 mmHg); τ 2.25 - 2.9 (7H,m), 5.65 (2H,s) and 6.8 (3H,s).

Preparation of methyl 2-naphthylmethyl ether.

The method was identical to that described for methyl 1-naphthylmethyl ether. The same work-up and distillation in vacuo yielded methyl 2-naphthylmethyl ether as a clear, colourless oil (0.6g, 69%) b.p. 62° at 0.02 mmHg; τ 2.3 - 2.9 (7H,m), 5.6 (2H,s) and 6.7 (3H,s); $\nu_{max.}$ 1608, 1590, 1222, 1198, 853, 818 and 750cm^{-1}.

Preparation of 1-naphthylmethyl-(1-naphthyl)methyl acetate.

1-Naphthylacetyl chloride (0.01 mole) in benzene (10cm^3) was added dropwise to an ice-cooled solution of 1-naphthylmethyl alcohol (0.01 mole) in benzene (10cm^3), the mixture was allowed to warm up to room temperature and stirred for a further 12 hours. 2N sodium hydroxide (20cm^3) was added and the benzene layer separated. The aqueous layer was extracted with diethyl ether (2 x 15cm^3) and the organic layers combined, washed with water (3 x 15cm^3) and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure leaving a yellow

oil, trituration with petroleum spirit at $0°$ and recrystall-
isation yielded 1-naphthylmethyl-(1-naphthyl)methyl acetate
as plates (1.6g, 49%) m.p. 103 - 104° (from benzene-petroleum
spirit); τ 2.0 - 2.9 (14H,m), 4.45 (2H,s) and 5.95 (2H,s);
$\nu_{max.}$ 1719, 1590, 1157, 1121, 952, 780, 765, 755 and 730cm^{-1};
m/e 326 (M$^+$), 168, 141 (M$^+$ - 185) and 105. (Found: C, 84.6;
H, 5.7. $C_{23}H_{18}O_2$ requires C, 84.6; H, 5.6%).

Preparation of 1-naphthylmethyl-(1-naphthyl)acetate.

1-Naphthylacetyl chloride (0.01 mole) was reacted with
1-naphthol (0.01 mole) in benzene as described above. The
same work-up yielded 1-naphthylmethyl-(1-naphthyl)acetate.
(1.0g, 32%) as plates m.p. 96 - 98.5° (from benzene-petroleum
spirit); τ 1.7 - 3.0 (14H,m) and 5.65 (2H,s); $\nu_{max.}$ 1755,
1601, 1130, 800 and 722cm^{-1}; m/e 312 (M$^+$), 168, 141 (M$^+$ - 171)
and 105. (Found: C, 84.7; H, 5.3. $C_{22}H_{16}O_2$ requires C, 84.6;
H, 5.1%).

Preparation of 2-naphthylmethyl-(2-naphthyl)acetate.

2-Naphthylacetyl chloride (0.01 mole) was reacted with
2-naphthol (0.01 mole) in benzene as described for 1-naphthyl-
methyl-(1-naphthyl)acetate. The same work-up yielded 2-naphthyl-
methyl-(2-naphthyl)acetate (1.2g, 38%) as plates m.p. 155 - 156°
(from benzene-petroleum spirit); τ 2.0 - 2.8 (14H,m) and 5.95
(2H,s); $\nu_{max.}$ 1750, 1602, 1183, 1168, 954, 828, 780, 750 and
740cm^{-1}; m/e 312 (M$^+$), 185 (M$^+$ - 127), 141 and 105. (Found:
C, 84.7; H, 5.2. $C_{22}H_{16}O_2$ requires C, 84.6, H, 5.2%).

Preparation of 1-naphthylmethyl-(9-anthryl)methyl acetate.

9-Anthraldehyde.

The method of preparation was identical to that described in the literature[210]. 9-Anthraldehyde was obtained in 62.5% yield, m.p. 101 - 102° (lit.,[210] 104 - 105°).

9-Anthrylmethyl alcohol.

Reduction of 9-anthraldehyde with sodium borohydride was carried out as described by Stewart[211] in 70% yield, m.p. 155 - 156° (lit., 156 - 158°).

1-Naphthylmethyl-(9-anthryl)methyl acetate.

1-Naphthylacetyl chloride (0.01 mole) was reacted with 9-anthrylmethyl alcohol (0.01 mole) as described for 1-naphthyl-methyl-(1-naphthyl)acetate. The same work-up yielded 1-naphthyl-methyl-(9-anthryl)methyl acetate (1.8g, 48%) as plates m.p. 160 - 162° (from benzene-petroleum spirit); τ 1.5 - 2.9 (16H,m), 3.9 (2H,s) and 6.0 (2H,s); $V_{max.}$ 1730, 1605, 1129, 965, 792 and 730cm^{-1}; m/e 376 (M^+), 191 (M^+ - 185), 141 and 78. (Found: C, 85.9; H, 5.4. $C_{27} H_{20} O_2$ requires C, 86.1; H, 5.4%).

Ultra-violet absorption and fluorescence spectra.

Absorption and fluorescence spectra were recorded at a standard concentration of 10^{-4}M, the solutions were not degassed except for those used for quantum yield measurements. Details of the fluorescence spectra are presented in Table 34 and Diagram 16.

3:6:2 FLUORESCENCE OF AROMATIC HYDROCARBONS FROM MATRICES.

Fluorescence spectra of the hydrocarbons contained in a solid matrix were recorded with degassed solutions containing 10^{-4}M of the solute. The results are presented in Table 35 and representative spectra in Diagram 17.

The effect of freezing upon the fluorescence spectrum of 1-naphthylmethyl acetate (10^{-4}M in degassed cyclohexane) is shown in Plate 1. The fluorescence spectra in the range 300 - 500NM were obtained by using a Dynamco 7110 storage oscilloscope as the recorder, the "x" axis drive unit employed was that of the Baird Atomic Fluorispec.

The fluorescence spectra of the crystals (see Table 36 and Diagram 18) were obtained from samples of the compounds contained in pyrex tubes (1mm internal diameter) suspended in a quartz tube (2mm internal diameter). The samples were not degassed.

APPENDIX 1.

The Kinetics of the Temperature Dependence of Fluorescence.

Consider the following scheme for the formation and decay of an excimer,

		Rate.
$A \xrightarrow{\ h\nu\ } A^*$		I
$A^* \longrightarrow A + h\nu'$		$k_1[A^*]$
$A^* \longrightarrow A$		$k_2[A^*]$
$A^* \longrightarrow {}^3A$		$k_3[A^*]$
$A^* + A \longrightarrow A_2^*$		$k_4[A^*][A]$
$A_2^* \longrightarrow A^* + A$		$k_5[A_2^*]$
$A_2^* \longrightarrow A + A + h\nu''$		$k_6[A_2^*]$
$A_2^* \longrightarrow A + A$		$k_7[A_2^*]$
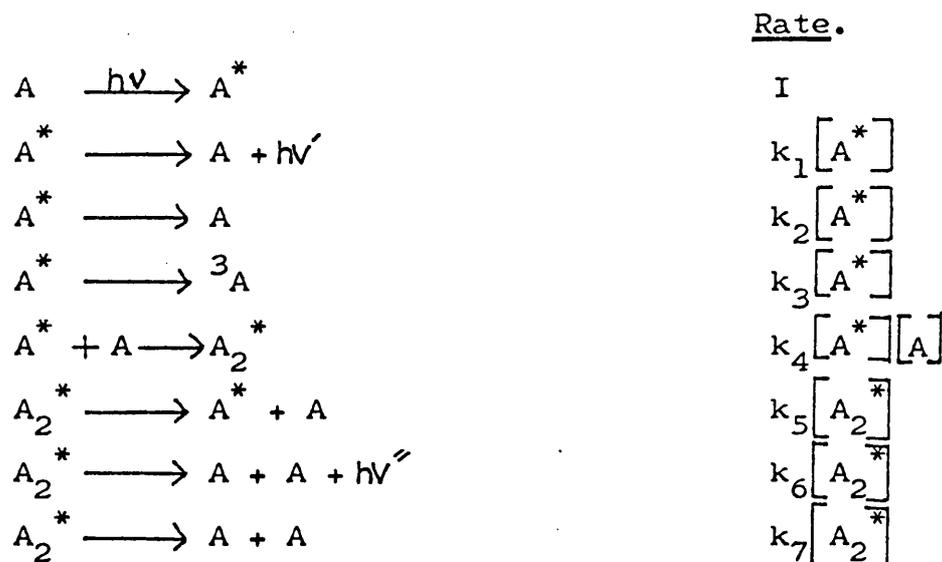
The stationary state equations for A^* and A_2^* can be solved and if $[A]$ is the concentration of the solute then

$$\frac{\phi_{A^*}}{\phi_{A_2^*}} = \frac{k_6[A_2^*]}{k_1[A^*]} = \frac{k_6\, k_4[A]}{k_1(k_5+k_6+k_7)}$$

where ϕ_{A^*} and $\phi_{A_2^*}$ are the fluorescence quantum yields of monomer and excimer respectively. These values will be directly related to the fluorescence intensity as recorded by the spectrofluorimeter, hence the equation becomes,

$$\frac{I_E}{I_M} = \frac{k_6\, k_4[A]}{k_1(k_5+k_6+k_7)}$$

where I_E and I_M and the fluorescence intensities of excimer and

monomer respectively.

The low temperature limit is then defined by the condition that the rates of dissociation and of radiationless decay (k_5 and k_7) tend towards zero, thus the equation reduces to

$$\frac{I_E}{I_M} = \frac{k_4[A]}{k_1}$$

Now, k_2, k_3, k_4, k_5 and k_7 are normally assumed to posess an activation energy term i.e., they are generally expressed in the form,

$$k = N \exp(-E/RT)$$

Measurements made on a system under these conditions thus yield information about the diffusion processes leading to complex formation since a plot of log I_E/I_M against $1/T$ will yield the activation energy term which can then be compared with the activation energy for a diffusion controlled process.

The high temperature limit is defined by the condition that $k_5 \gg k_6 + k_7$, hence the equation becomes

$$\frac{I_E}{I_M} = \frac{k_6 k_4[A]}{k_1 k_5}$$

The intensities of fluorescence from the monomer and the excimer will indicate the relative concentrations of each of the excited species and the decrease in I_E/I_M at high temperature illustrates that the excimer dissociates. A plot of log I_E/I_M against $1/T$ in this temperature range will therefore give a value for $-\Delta H^*$, the enthalpy of formation of the excited complex.

This treatment requires that k_1 and k_6 are temperature independent, such an assumption may not be valid for k_6 since

the observation of excimer fluorescence requires a destruction of the perfect sandwich-pair which may be a thermally activated process. A further limitation is that the solvent refractive index is dependent upon temperature.

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SUMMARY.

The emission spectra of some alkylnaphthalenes containing amino or hydrazine moieties in the side chain exhibit anomalous fluorescence bands. The spectral data are consistent with the proposal that the bands are derived from intramolecular exciplexes. The steric and electronic requirements for intramolecular exciplex formation are discussed on the basis of the dipole moments, wavelengths of fluorescence maxima and, in the case of the hydrazines, the N.M.R. spectra. Irregularities in the rate constants for intermolecular quenching of 9-methylanthracene fluorescence by hydrazines and in the fluorescence spectra of hydrazines are believed to be due to solute association, probably via hydrogen bond formation. A study of the products obtained by irradiation of certain monoacylhydrazines has been made, it is proposed that reaction proceeds by a photoinduced homolysis of the N — N bond.

Salts of N,N-diethyl-2-(1-naphthyl)ethylamine with hydrogen halides and alkyl halides have been shown to exhibit exciplex formation in aprotic solvents. The results are interpreted in terms of electron transfer from the halogen anion to the singly excited naphthalene, followed by a rapid elimination of hydrogen halide or alkyl halide.

The fluorescence quenching of cyanosubstituted aromatic hydrocarbons has been shown to proceed via exciplex formation when the hydrocarbons possess a high singlet energy. Intramolecular fluorescence quenching of naphthalene by dienes and olefins does not give rise to a fluorescent complex, this has

been explained in terms of the character of the quenching groups.

Donor-acceptor complexes formed between imides and amines or aromatic hydrocarbons have been shown to give an excited state charge-transfer complex upon excitation. Enhanced complex formation has been observed upon freezing cyclohexane or aceto-nitrile solutions of the compounds.

Ester and ether groups have been used to separate two naphthalene moieties. Excitation yields excited state naph-thalene complexes even when the linking chain consists of more than three atoms. Similar complexes have been detected in cyclohexane and acetonitrile matrices, it is suggested that excitation of aggregates or crystals formed upon freezing give rise to the new fluorescence bands.