SOME EXCITED STATE

CHARGE-TRANSFER INTERACTIONS

by

Kenneth R. Trethewey

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STATEMENT

The experimental work in this thesis has been
carried out by the author in the Department of
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for any other degree.

K.R.Trethewey.

Department of Chemistry,
University of Leicester.

November, 1976.

To C.B.

PREFACE

Whilst it is almost certain that the first reactions of the primordial soup were photochemical ones, the study of materials in their electronic excited states has taken a long time to get off the ground. In the last thirty years however, the development of sophisticated electronics has enabled the chemist to investigate extremely fast processes and as a consequence photochemistry has expanded enormously. Its use in the preparation of materials is still looked upon by many as a black art. But given that thermochemistry has had a head start the eventual everyday use of compounds in their excited states is inevitable when the physical aspects have been evaluated.

The work in this thesis is not concerned with the synthetic use of photochemistry but with the way species interact in their excited states. It represents four extremely enjoyable years spent with Dr. Stephen Davidson whom I wish to thank most sincerely, firstly for enabling me to embark on a photochemical career, secondly for providing me with so many fruitful ideas and thirdly for his friendship.

Also, I would like to express my appreciation to others without whose help this work would not have been possible. To Mrs. Maria Szpek for her considerable help in all aspects of the work, not least for uncomplainingly keeping me supplied with dry solvents! To Dr. Godfrey Beddard of the Davy-Faraday

Publications by R. Stephen Davidson and Kenneth R. Trethewey

1. The Mechanism of the Dye Sensitised Photooxygenation of
    Amines. J.C.S. Chem. Comm., 674, (1975).

2. Factors Affecting Dye Sensitised Photooxygenation
    Reactions. J.C.S. Perkin II, (in press).

3. Photosensitised Oxidation of Amines: Mechanism of
    Oxidation of Triethylamine. J.C.S. Perkin II, (in press).

4. Concerning the Use of Amines as Probes for Participation
    of Singlet Oxygen in Dye Sensitised Oxygenation Reactions.
    J.C.S. Perkin II, (in press).

5. The Role of the Excited Singlet State of Dyes in Dye
    Sensitised Photooxygenation Reactions. J. Amer. Chem.
    Soc., 98, 4008, (1976).

6. The Geometrical Requirements for Fluorescent Intramolecular
    Exciplex Formation and Fluorescence Quenching. J.C.S. Chem.
    Comm., 827, (1976).

7. The Role of Carotenoids in Photosynthesis (with Godfrey
    Beddard). Nature, submitted for publication.

COMPOUND ABBREVIATIONS

General aromatic:		Ar.
Types:	1-Naphthyl–	1-Np, α.
	2-Naphthyl–	2-Np, β.
	9-Anthryl–	9-An, An.
	1-Pyryl–	1-Py, Py.
	Phenyl–	Ph.
Linking chains:	–(CH$_2$)–	1
	–(CH$_2$)$_2$–	2
	–(CH$_2$)$_n$–	n
	–CH$_2$O(CH$_2$)$_2$–	4'
	–CH$_2$OCOCH$_2$–	4(0)
	–CH$_2$CO$_2$(CH$_2$)$_2$–	5
Amines:	–NHtBu	T
	–NEt$_2$	E
	–NHPh	P
	–NMePh	N
Examples:	2-Np(CH$_2$)$_3$I	β3I
	9-AnCH$_2$X	An1X (X=Hal.)
	1-Np(CH$_2$)$_2$NMePh	α2N
	ArCH$_2$OCOCH$_2$Cl	Ar4(0)Cl

All other abbreviations are those in common use in the chemical literature.

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CHAPTER TWO

The Intramolecular Excited State Interactions of Amine Containing

Aromatic Hydrocarbon Derivatives.

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CHAPTER 1:

The intramolecular excited

state interactions of halogen-

containing polycyclic aromatic

hydrocarbon derivatives and

the heavy atom effect.

And God said, Let there be light: and
there was light.

—Genesis:1:3

1.1. History

As long ago as the evening of Friday, June 17th, 1859, Professor Michael Faraday[1] addressed a meeting of the Royal Institution on the subject of "phosphorescence and fluorescence". He described that when a calcined oyster shell, a piece of white paper, or even the hand were exposed to the sun's rays and then instantly placed in a dark room they could still be seen. Even a 'decoction of horse chestnut bark' was said to have a glow of its own after illumination, known as phosphorescence.

Although those effects might appear somewhat naive, he went on to describe Becquerel's original design of one of the first phosphoroscopes and showed a remarkable degree of experimental observation for a worker of well over a century ago. Even the most skilled of workers however could not observe processes as fast as those occurring in excited states without sophisticated electronics and so it was nearly ninety years before the theory of the excited states began to take shape.

It was the assignment of the phosphorescent state as the triplet state that really caused the problems. Originally it was supposed that a molecule absorbed a quantum of light into an excited and short-lived fluorescent state F, where it relaxed into a lower energy metastable state P (Fig.1.1a). The emission from this state P was of longer wavelength and was much longer lived in comparison to the well-established fluorescence and so
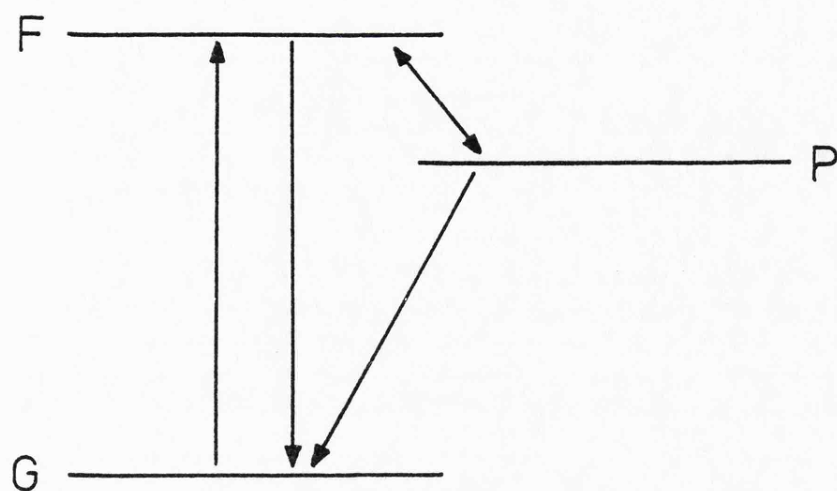
Fig 1·1a.
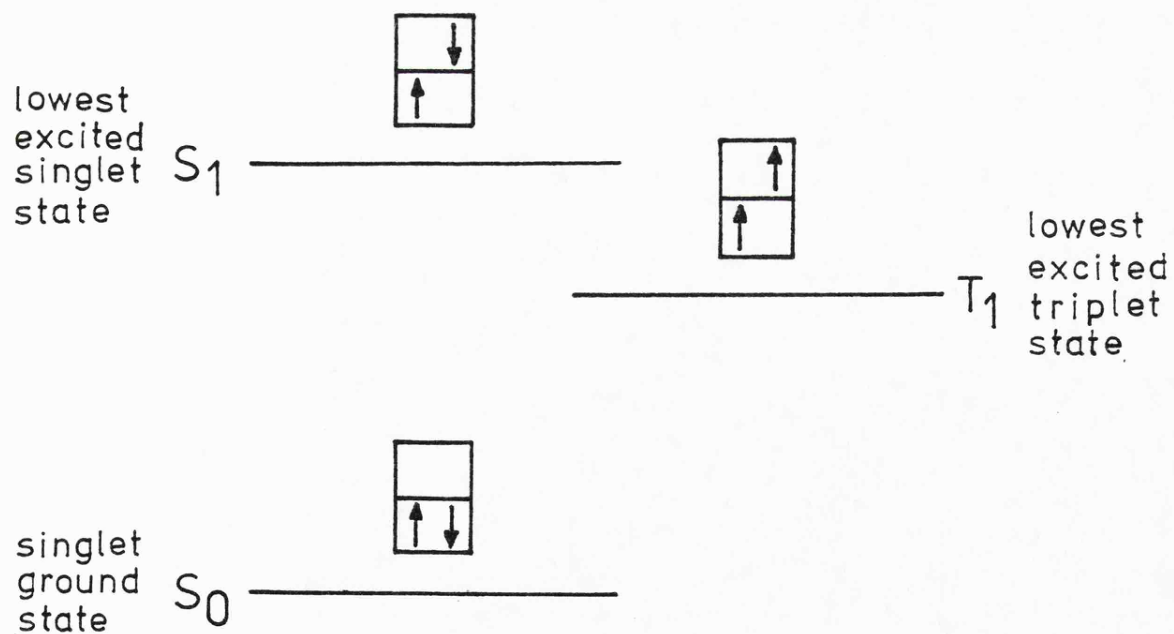
Fig 1·1b.

the transition to the ground state G was assumed to be forbidden. Just what this metastable state was, was not clear until 1944 when a Russian called Terenin[2] and the Americans, Lewis and Kasha[3] independently proposed that the metastable state was the triplet state where the excited electron had flipped its spin, in accordance with Hund's rule of maximum multiplicity, to a lower energy configuration (Fig.1.1b).

The main difficulty in proving the assignment lay initially in distinguishing between two types of phosphorescence that could be detected. These two types were observed to have two different wavelengths but the same lifetime. One type gave a spectrum identical to the fluorescence spectrum (the mirror image of the absorption spectrum) and the other gave a spectrum which was completely new. The first was dependent on temperature and the second was not. Jablonski[4] was the first to propose with a diagram such as Fig.1.1a that phosphorescence was emission from the state P but thermal energy could promote conversion back to F where a delayed fluorescence would be observed.

Lewis, Lipkin and Magel[5] showed that with increasing illumination on a solution of fluorescein, as many as 80% of the molecules could be obtained in the long lived phosphorescent state, and they measured the absorption spectrum of the P state. An important fact is that the excited molecules always returned to the P state and not to the F state - one of the factors which aided the assignment by Lewis, Kasha and Terenin. Surprisingly,

many workers seemed to find it hard to accept that the phosphorescent state was the triplet state and despite much evidence between 1944 and 1958 they tried to prove otherwise in best scientific traditions. It was in 1958 that no lesser person than Jablonski himself[6] put forward a rigorous identification of the phosphorescent state as the singlet, but in the same year the e.s.r. spectrum of the naphthalene triplet[7] was first reported and the case of the triplet state seemed conclusively proved thereafter.

Having finally removed all uncertainty about major assignments there was room for significant break-throughs and it was due largely to the work of Norrish and Porter at Cambridge, together with the development of the laser which enabled the processes which are about to be described to be fully investigated.

1.2. The Fundamental Processes

The basic processes affecting the distribution of electrons in an atom or molecule as we understand them today are shown in Fig.1.2. The energy levels of the electrons in the system are divided into discrete levels, S_0, S_1...S_i; T_1, T_2...T_j , which are themselves divided into levels associated with the vibrational energy of the atoms in the molecule. S_i is used to denote the ith. level of the singlet state where the total spin multiplicity $S(=\Sigma s)=0$. Similarly T_j denotes the jth. level of the triplet manifold where $S = 1$.

AN ENERGY LEVEL DIAGRAM.
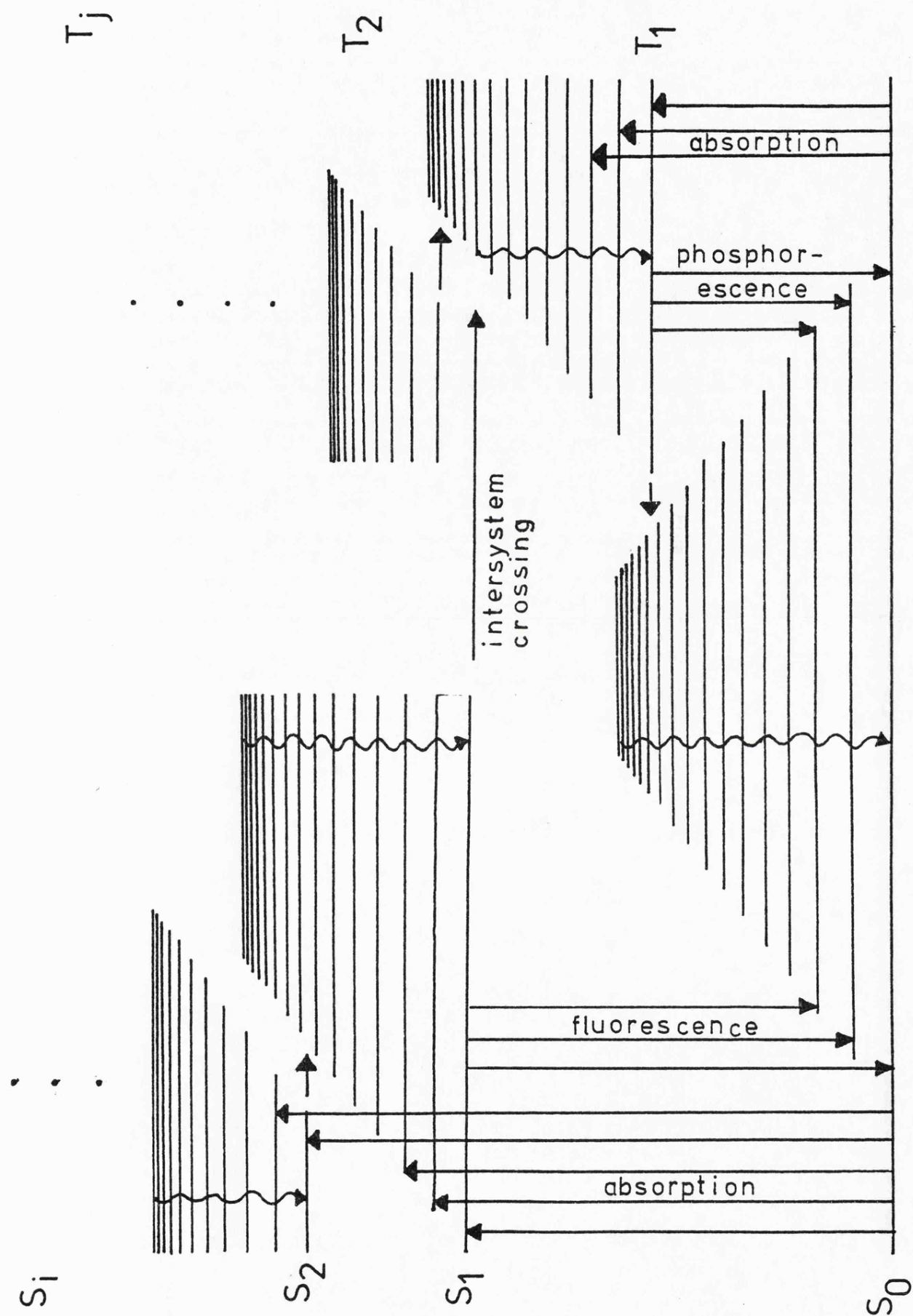
Fig.1.2.

THE FUNDAMENTAL PROCESSES.

Approximate Rate Constants.

S_1

S_0

intersystem
crossing
$S_1 \rightarrow T_1$ 10^{4-12} s^{-1}
$T_1 \rightarrow S_0$ 10^{-1-5} s^{-1}

T_1

S_2

S_1

S_0

absorption
10^{15-16} s^{-1}

internal
conversion
$S_n \rightarrow S_{n-1}$ $>10^{12}$ s^{-1}
$S_1 \rightarrow S_0$ 10^{6-12} s^{-1}

vibrational
relaxation
$>10^{12}$ s^{-1}

fluorescence
10^{6-9} s^{-1}

phosphorescence
10^{-2-4} s^{-1}
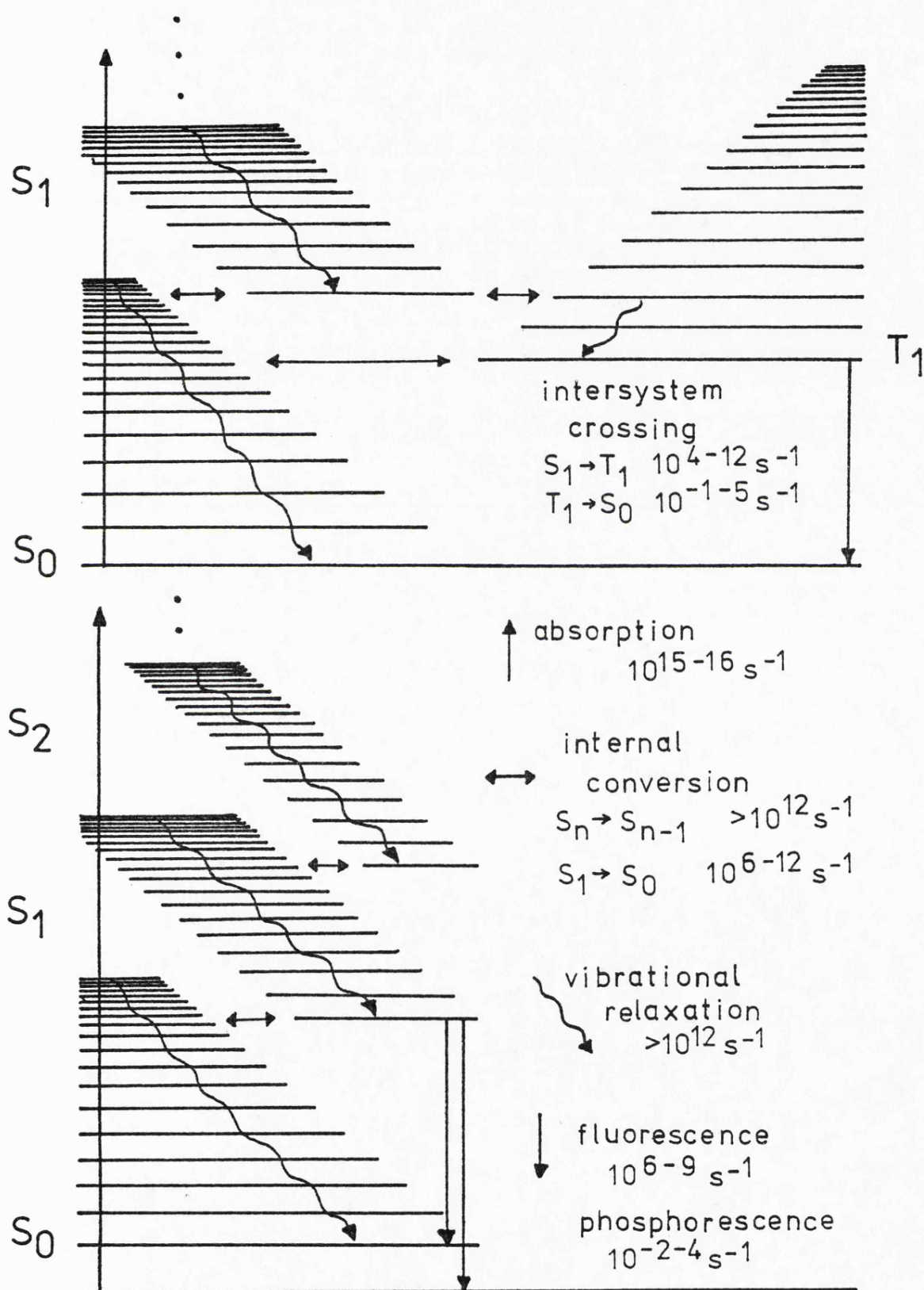
Fig.1.3.

Fig.1.3 illustrates in more detail the various processes, together with the approximate order of magnitude of their rate constants.

The initial absorption of light, i.e. the energy transfer process between a photon and an electron, takes place in a time span approaching 10^{-16}S, the electron occupying an upper level dependent on the energy of the photon. Heisenberg's uncertainty principle dictates that we shall probably not be able to measure such fast processes and for most purposes the absorption time can be neglected. All other processes take place within longer times which can range into seconds in some cases. The electron in an excited vibrational level of an electronic state rapidly relaxes to the lowest vibrational level largely by intermolecular collisions with a rate constant $>10^{12}s^{-1}$. It then undergoes a radiationless passage between two different electronic states with the same multiplicity, e.g. $S_1 \rightsquigarrow S_2$. This process is mostly under intramolecular control but is subject to external stimulation. Since potential energy surfaces overlap internal conversion occurs via two nearly equienergetic levels. The probability is the same for $S_1 \rightsquigarrow S_2$ or $S_2 \rightsquigarrow S_1$ but the large vibrational energy of the lower electronic state disturbs the equilibrium in that direction. Whilst internal conversion is highly efficient for $S_{i-1} \rightsquigarrow S_i$ (k $\sim 10^{12}s^{-1}$), for a reason which is not quite clear $S_0 \rightsquigarrow S_1$ is relatively inefficient (k $\sim 10^{6-12}s^{-1}$) and radiative processes are often the most important from the S_1 level.

Arriving at the lowest vibrational level of S_1 the molecule can spontaneously emit a quantum of light in a process known as fluorescence. Alternatively it can lose its energy in a vibrational deactivation, which as we have seen is inefficient, or it can undergo intersystem crossing to the triplet manifold. This involves a spin flip by an electron, a process which is normally forbidden, but as we shall see later can be influenced by certain factors. Having crossed to the triplet manifold the molecule once more relaxes and arrives at the lowest vibrational

\state of T_1. Here it can lose its energy in a radiative process known as phosphorescence. Because of the forbidden nature of this process the triplet molecule is usually quite stable when compared to other excited states and can exist sometimes for many seconds. The crossing $S_0 \leftsquigarrow T_1$ is very inefficient ($k = 10^{-1-5}s^{-1}$) and rarely compares with $T_1 \leftsquigarrow S_1$. Sometimes the ratio of these two rates can be as high as 10^9 and it might appear somewhat surprising that two similar processes should have such vastly different rates. Kasha[8] suggested that the difference in rates was connected with the energy gap between the pure electronic states. Since $\Delta E_{T_1-S_0} > \Delta E_{S_1-T_1}$ then $k_{ISC\ T_1 \leftsquigarrow S_1}$ > $k_{ISC\ S_0 \leftsquigarrow T_1}$. Hence the probability of $T_1 \leftsquigarrow S_1$ increased as the energy gap between them decreased. The same argument can be used to explain the rate discrepancy between $S_{i-1} \leftsquigarrow S_i$ and $S_0 \leftsquigarrow S_1$ since $\Delta E_{S_1-S_0} > \Delta E_{S_i-(S_{i-1})}$.

1.3. The Heavy Atom Effect

The processes previously mentioned which involve the change of spin of an electron have long been known to be influenced by the presence of a so-called 'heavy atom', i.e. one with a high atomic number. This has become universally known as the 'heavy atom effect'. Since this chapter is concerned with the heavy atom effect it is necessary to incur a short diversion into the field of quantum theory.

An electron moving in an orbit about a nucleus possesses orbital angular momentum. This is a vector quantity and so it must possess a magnitude and direction. (Vector quantities will hereafter be represented by $\underline{x}$). The orbital quantum number is denoted by l and can have any integral value up to $(n-1)$ where n is the principal quantum number. Letters to denote the type of orbital are used as follows:

$$l = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad ...$$
$$ s \quad p \quad d \quad f \quad g \quad ...$$

According to the quantum theory the magnitude of the orbital angular momentum $\underline{l}$ is given by $\sqrt{l(l+1)}$ atomic units, (a.u.). Thus for an electron in a p orbital the magnitude of $\underline{l}$ is $\sqrt{2}$ a.u. A reference direction (z) can be specified by means of a magnetic or electric field and then the vector may have only integral values in that direction, Fig.1.4.

orbital

z↑

1

0

-1

spin

z↑

1/2

0

-1/2
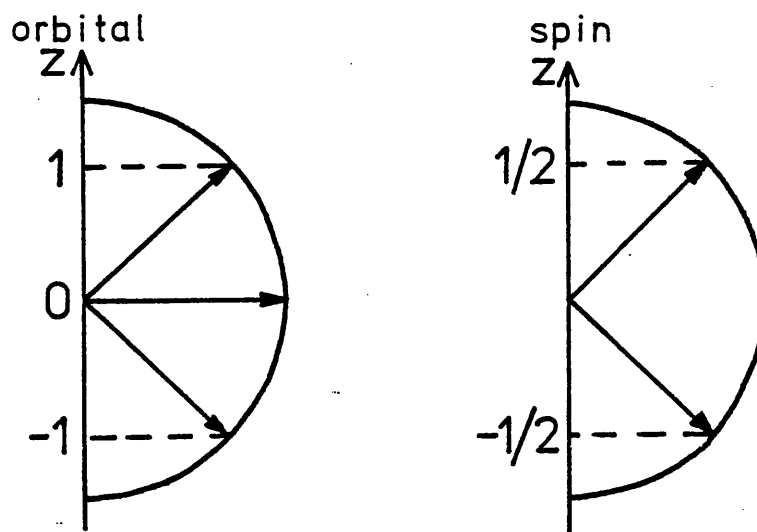
Fig 1.4

Thus, again for a p electron, $l = 1$ and the magnitudes of $\underline{l}$ in the z direction, l_z, are 1, 0, -1. Hence $l_z = m$ the magnetic quantum number.

Not only do electrons orbiting a nucleus possess orbital angular momentum but they spin about an axis through themselves and therefore possess spin angular momentum. The magnitude of this vector $\underline{s}$ is given by $\sqrt{s(s+1)}$ which, since $s = \frac{1}{2}$ is $(\sqrt{3}/2)$. This vector must have a half integral component in the reference direction (see Fig.1.4). The total angular momentum $\underline{j}$ of an electron is obviously the sum of the spin and orbital contributions. However since we are adding vector quantities it is not as simple as it might appear. Mathematically we write $\underline{j} = \underline{l} + \underline{s}$. This is the only way of arriving at the angular momentum of a single electron but for a many electron system there are two possibilities.

SPIN-ORBIT COUPLING.
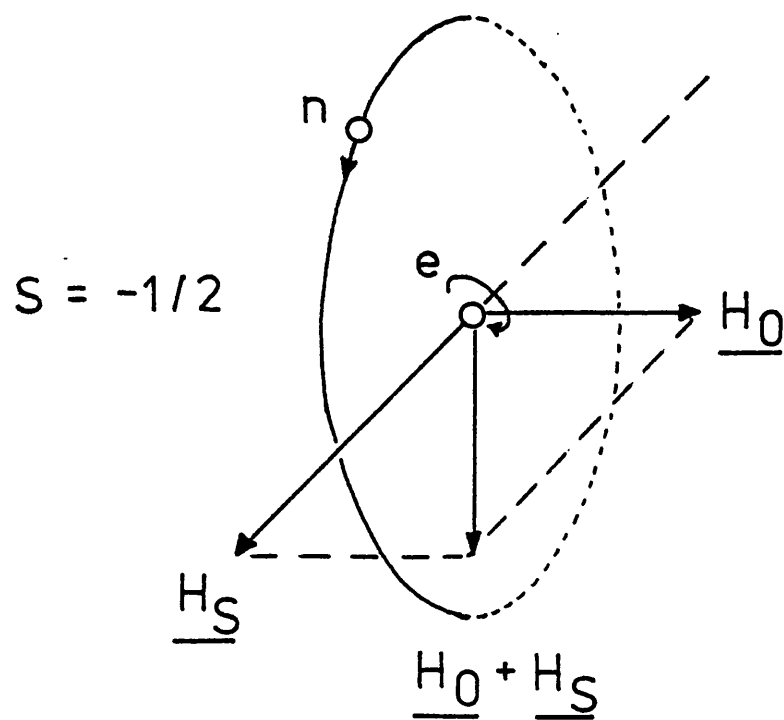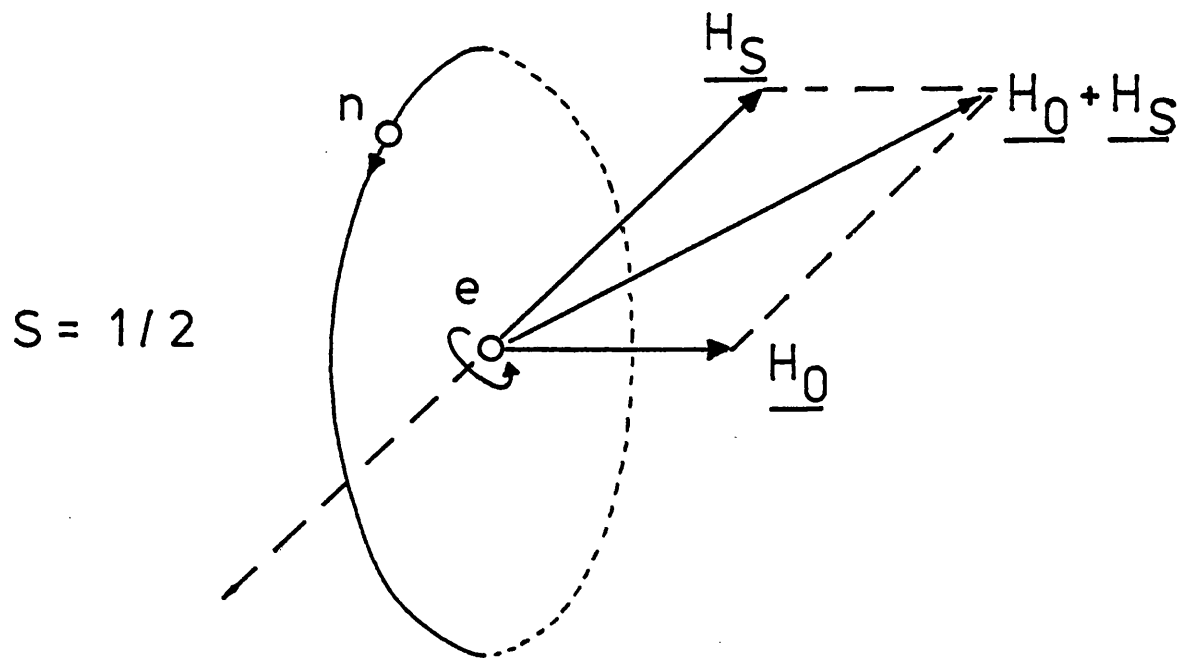
Fig. 1.5.

The first is the so-called Russell-Saunders coupling where all the spin momenta interact to give the total spin vector $\underline{S}$ and similarly all the orbital contributions sum to give the vector $\underline{L}$. The total angular momentum is then $\underline{J}_{RS} = \underline{L} + \underline{S}$. (Another name for this is spin-spin, orbit-orbit coupling). This method assumes little coupling of $\underline{s}$ and $\underline{l}$, that is, a small non-interacting nucleus.

A much more realistic approach for the heavier elements is to take the total angular momentum for each electron and sum these to give the total value $\underline{J}_{SO} = \Sigma \underline{j}i$. (It should be remembered that $\underline{J}_{RS}$ and $\underline{J}_{SO}$ are not necessarily equivalent in vector addition). Diagrammatically this is shown in Fig.1.5. An observer on the spinning electron sees the nucleus apparently orbiting it. The nucleus will produce a magnetic field along the axis perpendicular to its orbit, $\underline{Ho}$. The spinning electron will also produce a magnetic field along the axis of its spin, $\underline{Hs}$, and the interaction of these two fields is spin orbit coupling, ($\underline{Ho} + \underline{Hs}$). Obviously if the nuclear charge is small then $\underline{Ho}$ is small and $\underline{Hs}$ is not greatly affected, but if Z, the atomic number, is large the S-O coupling will also be large. In fact calculation shows that spin-orbit coupling denoted by ζ is given by the following expression.

$$\zeta_{nl} = \frac{e^2 h^2}{2m^2 c^2 a_0^3} \cdot \frac{Z^4}{n^3 (l+1)(l+\frac{1}{2})l}$$

Since $\beta \propto Z^4$ the effect is very large for the heavier nuclei.
It is however decreased a little by the inverse dependence on
the orbital parameters corresponding to the greater distance
of the electron from the nucleus. The dependence on Z^4 is
the origin of the term 'heavy atom effect'.

1.4. Selection Rules and Spin-Orbit Coupling

Quantum theory has provided many rules concerning trans-
itions between various states whether radiative or non-radiative.
These are called 'selection rules'. Strictly speaking a select-
ion rule states whether a process is allowed or not but in
practice it is found that the variation of molecular parameters
will induce different amounts of 'allowedness'.

Platt[9] proposed that a perfectly allowed $\pi\pi^*$ transition
can be represented by a parameter called the oscillator strength,
F_A. Any other transition will then have an oscillator strength,
F, given by

$$F = fs.fo.fm.fp.F_A.$$

For the perfectly allowed transition the f terms are unity whilst
for others the various selection rules reduce the respective f
term. fs is for spin forbidden transitions. It is by far the
most important and can be 10^{-5} commonly. fo relates to a change
of orbital (e.g. $n\pi^*$) and is often 10^{-2}. fm is for a forbidden
change of linear angular momentum and varies between 10^{-1}-10^{-3}
while fp is the symmetry forbidden term, usually 10^{-1}.

Since S-0 coupling changes fs it can dramatically affect the extent to which a transition takes place, more so than a change in any other selection rule.

The $\pi^* \leftarrow \pi$ transition in ethylene has a value of $\epsilon(T_1 \leftarrow S_0) < < 1$. Thus in general spin forbidden transitions can only be observed if there is significant perturbation of the selection rules, usually in the form of spin-orbit coupling. The effect of this sort of perturbation is to mix the characters of the two different states forming, in effect, two new states thus:

$$\Psi_T^1 = \Psi_T^0 + \lambda_{TS} \Psi_S^0$$

$$\Psi_S^1 = \Psi_S^0 + \lambda_{TS} \Psi_T^0$$

Here ^{0} represents a pure state, ^{1} represents a hybrid state and λ is a mixing coefficient. As has already been seen λ_{ij} increases as $(E_i - E_j) \rightarrow 0$. Therefore, in the simplest case such as Fig.1.3a the mixing of S_1 and T_1 is greater than of S_0 and T_1. A point to note which will be discussed further is that the intersystem crossing pathway is via the most effectively mixed singlet and triplet state. Because of extremely rapid relaxation to S_1 this state will always be involved but the triplet state involved is not necessarily the lowest in energy but merely the most nearly energetic. A consequence

X	τ_T PhX s^{-1}	τ_T NpX s^{-1}
H	7·0	2·6
F		1·5
Cl	0·004	0·3
Br	0·0001	0·018
I		0·0025

All at 77K.   D.McClure, ref.12

TABLE 1.1a.

	Φ_F	Φ_P	Φ_P/Φ_F	τ_P	k_{ISC}
NpMe	0·85	0·044	0·05	2·1	2×10^5
NpF	0·84	0·056	0·07	1·5	2×10^5
NpCl	0·058	0·30	5·2	0·3	$1·5 \times 10^7$
NpBr	0·0016	0·27	164	0·02	5×10^8
NpI	0·0005	0·38	>1000	0·002	$>3 \times 10^9$

All at 77K.   Ermolaev et al., ref.13-15

TABLE 1.1b.

of the mixing of states which has been missed by many workers

is that as mixing increases it becomes less meaningful to talk

about singlet and triplet states. This is important in relation

to the inorganic complexes which are being used as sensitisers,

and in particular tris-(2,2'-bipyridyl)ruthenium II chloride

mentioned in 3.2.2. Here the heavy ruthenium ion makes it

nonsense to refer to the emissive state as the triplet as

Crosby et al[10] have pointed out.

1.5. Observations of the Heavy Atom Effect

1.5.1. Photophysical

A physical demonstration of the perturbation of the

$T_1 \leftarrow S_0$ selection rule was first reported by Kasha[11] who ob-

served that on mixing ethyl iodide and 1-chloronaphthalene

he obtained a yellow colouration from colourless starting

materials. He attributed this not to any sort of charge-transfer

or other ground state molecular complex but to a collisional

spin-orbit perturbation, that is, the iodide coupling with the

naphthalene nucleus during collisions to enhance the $T_1 \leftarrow S_0$

transition of the aromatic system. The break-down of this

selection rule by the heavy atom causes an increased transition

probability not only for $T_1 \leftarrow S_0$ but for $S_0 \leftarrow T_1$ and hence

effectively reduces the observed phosphorescent lifetime.

The direct intramolecular effect of a heavy atom was first

reported by McClure[12] who observed the dramatic reduction in triplet lifetime of a number of benzene and naphthalene derivatives reproduced in Table 1.1a. As is to be expected the lifetime is progressively reduced on increasing the atomic number of a halogen substituent.

$$S_0 \xrightarrow{\quad I \quad} \longrightarrow S_1$$

$$S_1 \xrightarrow{\quad k_F \quad} S_0 + h\nu$$

$$S_1 \xrightarrow{\quad k_{IC} \quad} S_0$$

$$S_1 \xrightarrow{\quad k_{ISC} \quad} T_1$$
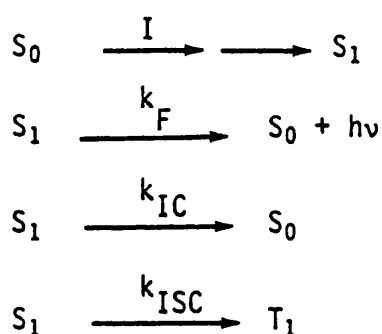
<u>Scheme 1</u>   •

As we have seen, the largest perturbation by a heavy atom can be of the lowest excited singlet state with a closely energetic triplet state. The consequent increase in allowedness of the $T_j \leftrightsquigarrow S_1$ transition leads to much more efficient competition with the emissive process. From Scheme 1 the quantum yield of fluorescence is given by

$$\Phi_F = \frac{k_F}{k_F + k_{IC} + k_{ISC}}$$

Hence if k_{ISC} is increased by the heavy atom then Φ_F decreases. Whilst the natural lifetime of fluorescence is represented by $(k_F)^{-1}$, the observed fluorescence lifetime $\tau_F = (k_F + k_{IC} + k_{ISC})^{-1}$.

Hence similarly it will be reduced by the same effect. Table 1.1b reproduces results obtained by Ermolaev and co-workers[13-15] and illustrates the effects just described. Whilst it is true to say that the increased yield of triplet state molecules leads to an increase in the quantum yield of phosphorescence (Φ_p) relative to Φ_F, it can be seen from the values for $\Phi_F + \Phi_p$ that radiationless modes of decay become much more important with increasing atomic weight.

That the relation $\Phi_F + \Phi_T = 1$ was demonstrated by Medinger and Wilkinson[16] who used the quenching of the fluorescence of anthracene by bromobenzene and the examination of the triplet yield by flash photolysis to obtain their data. Further comment in relation to this will be made in 1.9.

Very little work has been done to correlate the effect of a non-conjugated heavy atom on a chromophore in terms of molecular geometry. In an elegant piece of work Turro[17] described some unusual results with naphthonorbornane systems in which the various physical parameters were examined for molecules having a bromine atom at different positions of the norbornane skeleton.

7-syn-   7-anti-
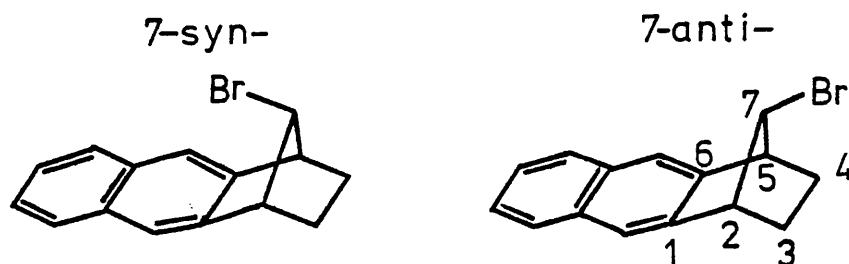
Fig 1.6

Most surprisingly the molecule containing the bromine in the
7-syn position (Fig.1.6) and in which the heavy atom perturbation
might be expected to be greatest in fact was the least affected -
less even than the 3-exo or 3-endo molecules. The one in which
the parameters such as Φ_F and Φ_p were most affected by bromine
substitution was the 7-anti compound. In a further piece of
work[18] he found that substituting a second bromine into the
most perturbed 7-anti molecule, there was actually a reduction
in the heavy atom effect on the molecular parameters. Turro
was unable to further any suggestion as to the reason for these
extraordinary results other than that particular importance
must be attached to the back lobe of the C-Br bond. To date
no satisfactory explanation of the results has been put forward.
Work described later in this chapter has attempted to provide
more information about the intramolecular interaction between
non-conjugated heavy atoms and chromophores, albeit in non-rigid
molecules.

1.5.2. Photochemical

The first example of a heavy atom influence on the products
of a chemical reaction was supplied by Cowan and Disko.[19]
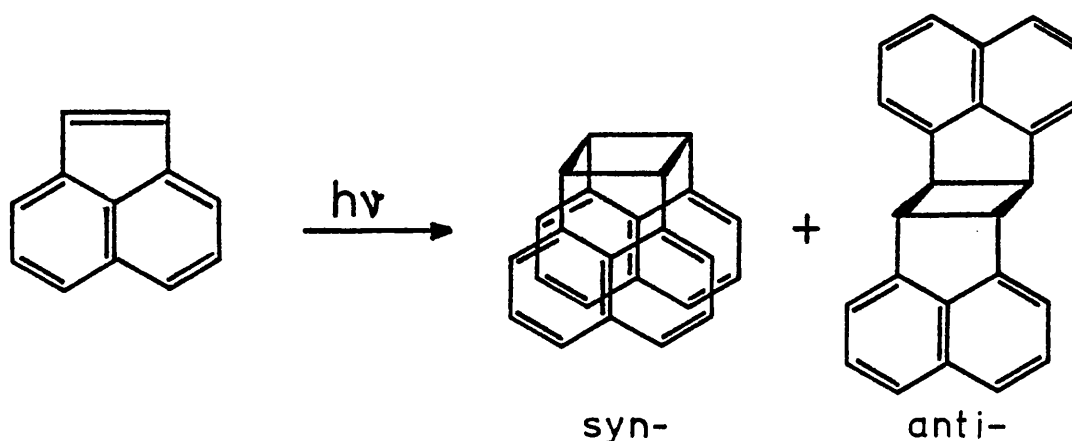
Fig.1.7

They studied the photodimerisation of acenaphthylene in different solvents to give the syn- and anti-dimers (Fig.1.7). Although a small change in the syn/anti ratio was observed with change of solvent, by far the largest effect was in n-propyl bromide where the amount of anti-isomer was dramatically increased. Further, they found that the amount of anti- could be reduced almost to zero by introduction of oxygen, a well known triplet quencher, to the solution. These results were consistent with the mechanism whereby the syn-isomer was produced from a molecular complex in the singlet state whilst the anti- came from triplet intermediates. As Ferree and Plummer[20] pointed out, this effect is greatest only on systems where the initial triplet yield is small. A heavy atom solvent would have little effect on the dimerisation of 5-bromo-acenaphthylene, that is, the intramolecular perturbation is by far the most important.

As yet the direct use of the heavy atom effect in synthesis has been limited but a noteworthy example is the report of Meinwald[21] of the synthesis of pleiadiene. Whilst the previous optimum route had succeeded with an overall yield of $2\frac{1}{2}\%$ a new route involving a dimerisation of acenaphthylene and maleic anhydride in a heavy atom solvent afforded 28% overall.

Since the bulk of this chapter is concerned with photophysical aspects of halogen containing compounds little more will be said on this topic.

1.6. Temperature dependence of intersystem crossing and the relative positions of singlet and triplet levels

An important effect on the intersystem crossing process in aromatic hydrocarbons became apparent with the report by Bowen and Sahu[22] that the fluorescence of 9- and 9,10-disubstituted anthracenes was temperature dependent at ambient temperatures. Other substituted anthracenes were subsequently examined[23,24] and finally Hunter and Wyatt[25] showed that anthracene itself exhibited temperature dependence where variations in Φ_F occurred at low temperatures but not greater than $\sim$-100°C, (Fig.1.8). It was known from absorption spectroscopy that the transitions in anthracene were bathochromically shifted as the molecule was substituted and the most logical answer to the observations of temperature dependence was to put the interacting triplet level slightly higher in energy than S_1. This level could not be T_1 since $E_{S_1} > E_{T_1}$ and was most likely to be T_2. Thus in anthracene where the difference in energies was least, dependence of Φ_F on temperature was only observable at low temperatures. The lowering of S_1 by substitution and the consequent increase in the energy gap led to an increase in the energy required to complete intersystem crossing and hence temperature dependence of Φ_F at much higher values. (Coupling of S_1 with the much lower energy T_1 is small because of the large energy gap). This can be rationalised mathematically by the expression

$$\Phi_F = \frac{k_F}{k_F + k_{IC} + k_{ISC} + k'_{ISC}\, \exp(-\Delta E/RT)}$$

Fig.1.8
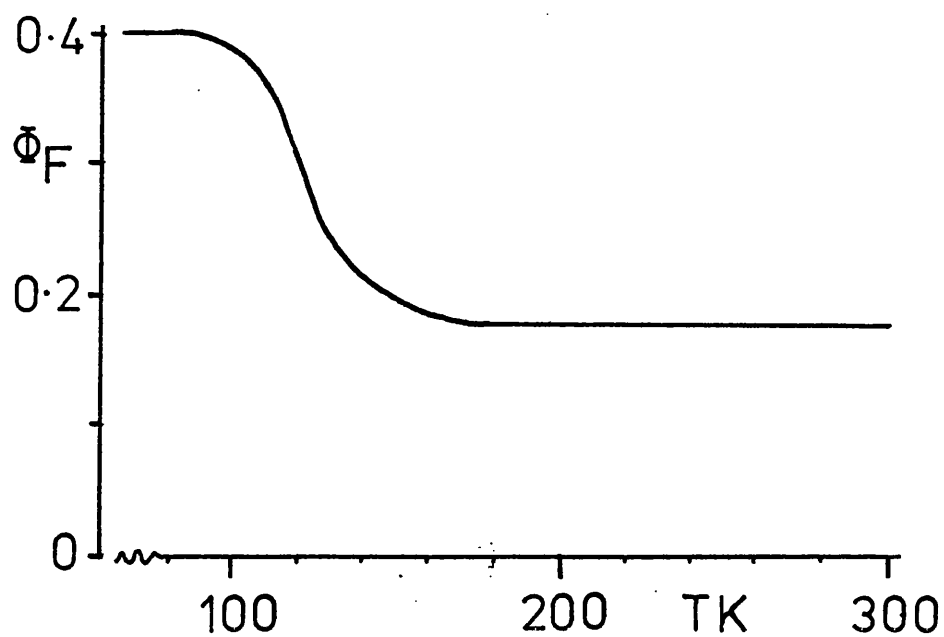
Hunter and Wyatt, Chem. Phys. Letts., <u>6</u>, (1970), 221.

Fig.1.9

Class A	Class B	Class C
e.g. BrNp, BrPy.	e.g. BrAn.	e.g. BrPer.

Zander et al., Chem. Phys. Letts., <u>31</u>, (1975), 251.

where k_{ISC} is the intersystem crossing rate for $T_1 \leftsquigarrow S_1$ and

k'_{ISC} that for $T_2 \leftsquigarrow S_1$. ΔE is the energy gap between S_1 and T_2.

Further light has been shed on the matter by Zander and co-workers[26] who examined the fluorescence of 3-bromo and 3,9-dibromoperylene and found no heavy atom effect, the fluorescence yields being 0.96 and 0.95 respectively, whilst for perylene $\Phi_F = 0.98$. This was in marked contrast to 9-bromoanthracene which showed a temperature dependent heavy atom effect, and 3-bromopyrene which showed a strong effect independent of temperature. Using a certain amount of known information about the energy levels[27,28] Zander explained the results by means of a diagram reproduced in Fig.1.9. Platt's notation was used to correlate the levels. (For an explanation of Platt's notation see Ref.28, pp.294-303). It has long been known that the longest wavelength absorption band in the spectra of aromatic hydrocarbons does not arise from the same transition in each case. Platt's explanation of the spectra shows that for the two lowest energy $\pi\pi^*$ transitions labelled $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ (where ^1A is his label for the ground state) the energy of the transition and hence the relative position of the levels in the energy diagram vary with the hydrocarbon. Thus in naphthalene and pyrene the lowest energy transition is $^1L_b \leftarrow {}^1A$, whilst in anthracene and perylene it is $^1L_a \leftarrow {}^1A$. However, the relative positions of the corresponding triplet levels to their singlet states does not vary significantly. Hence ^3L_a is quite a lot lower than ^1L_a whilst ^3L_b is quite close to ^1L_b in all cases. So in naphthalene and pyrene intersystem crossing occurs from $S_1(^1L_b)$

to $T_2(^3L_b)$ almost exclusively. In anthracenes however the closest triplet level $T_2(^3L_b)$ is higher in energy hence the large temperature dependence. Coupling and hence intersystem crossing still occurs with $T_1(^3L_a)$ although to a smaller extent. In perylene however $S_1(^1L_a)$ is now so far below $S_2(^1L_b)$ that thermal activation into $T_2(^3L_b)$ is out of the question. Crossing to $T_1(^3L_a)$ is still very weak and so the fluorescence yield approaches unity and is unaffected by heavy atom substitution which is only effective on strongly coupled states.

Aromatic hydrocarbon derivatives used in this chapter are of naphthalene, anthracene and pyrene.

1.7. Excited State Charge Transfer Complexes

The formation of ground state charge transfer (CT) complexes has been known for a long time owing to the ease with which they may be detected. The presence of new bands in an absorption spectrum of the mixture but not of the separate components provides sound evidence. The formation of such complexes is usually between an electron donor and an acceptor and hence considerable amounts of CT character are often obtained. (Note that while the donor and acceptor are in 'contact' the complete transfer of an electron is not necessary and indeed rarely observed).

In the excited state molecules have a quite different electronic structure and hence there is no reason why a molecule should not then become an electron donor or acceptor which would not in the ground state. Indeed CT interactions must be vastly more important in photochemistry since molecules in their excited states have unpaired electrons and are anxious either to donate one or to accept a spin-paired counterpart. The observation by Forster and Kasper[29] of new bands in the fluorescence spectrum of pyrene at medium concentrations provided the first evidence of an <u>excited state complex</u>, now termed an 'exciplex'. Further developments occured in the field concerning exciplexes of aromatic hydrocarbons with species other than themselves, the biggest advances being with amine exciplexes.[30] Chapter two describes these in detail. After a period of intensive study by many workers it is now possible to paint a fairly detailed picture of the general properties of exciplexes. A comprehensive review of the subject has been published by Davidson.[31]

1.7.1. Formation

It has been necessary, for reasons which will become apparent, to involve two complexes in the theory.[32,33] The first is an encounter complex formed by the initial coming-together of the two reactants. The second is a so-called relaxed exciplex where the solvent molecules have rearranged to accommodate and stabilise the new species. In either case the wavefunction of the species can be described by equation 1.(1).

$$\psi_C = C_1\phi(A^-D^+) + C_2\phi(A^*D) + C_3\phi(AD^*) + C_4\phi(A^+D^-) + C_5\phi(AD) \quad .. \; 1.(1)$$

$$\text{where } \Sigma C_i^{\,2} = 1$$

In the simplest, but by no means trivial, case of a non-interacting collision

$$\psi_C = C_5\phi(AD) \text{ where } C_5 = 1 \quad\quad\quad\quad .. \; 1.(2)$$

Otherwise, the complex can be composed both of CT components, where transfer can be large or small, and also of contributions due to exciton resonance.

In the special case where A = D = M (as in Forster's pyrene example) then the compound is called an excimer (excited dimer). These types of complex have been well studied[34,35] and symmetry dictates that $C_1 = C_4$ and $C_2 = C_3$. Hence

$$\psi_C = C_6\phi(M^+M^-) + C_7\phi(M^*M) + C_5\phi(MM) \quad\quad\quad .. \; 1.(3)$$

The major contribution has been suggested[36] as coming from the exciton interaction, i.e. $C_7 \gg C_6$.

When A and D are not identical, the one with the lowest ionisation potential becomes the donor (D) and the other the acceptor (A). A charge transfer complex formed between them will be seen to have a dipole moment whose size is dependent on the degree of CT (i.e. $C_1 - C_4$) and on the radius of the complex. The dipole moment will obviously be maximised when $C_1 = 1$, i.e.

$$\psi_C = C_1 \phi (A^- D^+) \qquad \qquad \dots 1.(4)$$

but in the excimer case where $C_1 = C_4$ then $\mu = 0$. Calculation of the dipole moment is obviously of value in determining the nature of the exciplex and can be carried out where a discrete emission is observed.[37]

The energy of the complex formed depends on a number of factors. Its heat of formation, ΔH_F can be expressed by 1.(5).

$$\Delta H_F = -\Delta H_{SI} + C_1 I.P._D + C_2 E.A._A - C_3 - \Delta H_{SO} \qquad \dots 1.(5)$$

ΔH_{SI} is the singlet excitation energy of the absorbing species, $I.P._D$ is the ionisation potential of the donor and $E.A._A$ the electron affinity of the acceptor. C_3 is a coulombic interaction for the stabilisation of the partial ions in the gaseous state and $-\Delta H_{SO}$ the heat of solvation. The last factor provides the main difference between the encounter and the relaxed exciplex. Reorientation of the molecules around the encounter complex will occur to maximise ΔH_{SO} and provide more stabilisation. This process requires a finite time and has been observed by time resolved spectroscopy.[38,39] Using this technique the birth and decay of exciplexes have been examined and the complex emission was shown to 'grow in' significantly after the fluorescence from the monomer. This was taken as indicative of the reorientation processes required since the observed emission occurs only from the relaxed species.

The most important point to note with regard to results

in this chapter is that the solvent will most affect the energy of

the relaxed species; the encounter complex will be much less affected.

1.7.2. Decay

Similar decay processes are open to exciplexes as for a

simple excited state. Included in this of course is an emissive

process. The absence of an emission however must not be taken

as the absence of an exciplex since non-radiative processes can

be extremely important. Fig.1.10 is a diagram by Knibbe[30]

illustrating the formation of an exciplex and the emission from it.

Since emission from the exciplex occurs to a dissociative ground

state complex, no fine structure is observed and the emission is

always a broad structureless band bathochromically shifted from

the fluorescence of the monomer. Emissions have been observed

from complexes involving aromatic hydrocarbons and a number of

other species both inter-and intra-molecularly. Those include

amines[40-48] olefins,[49,50] and halogen anions.[51] To date none

has been observed from an exciplex involving a halogen atom.

Fig.1.11 illustrates the various possible decay modes

of exciplexes. Detailed discussion of them will occur after

the presentation of results in chapters one and two. It is

sufficient at this stage to point out the possibilities.

DIAGRAMS
OF EXCIPLEX FORMATION

E

$(AD)^*$

$A^* + D$

r

exciplex emission monomer
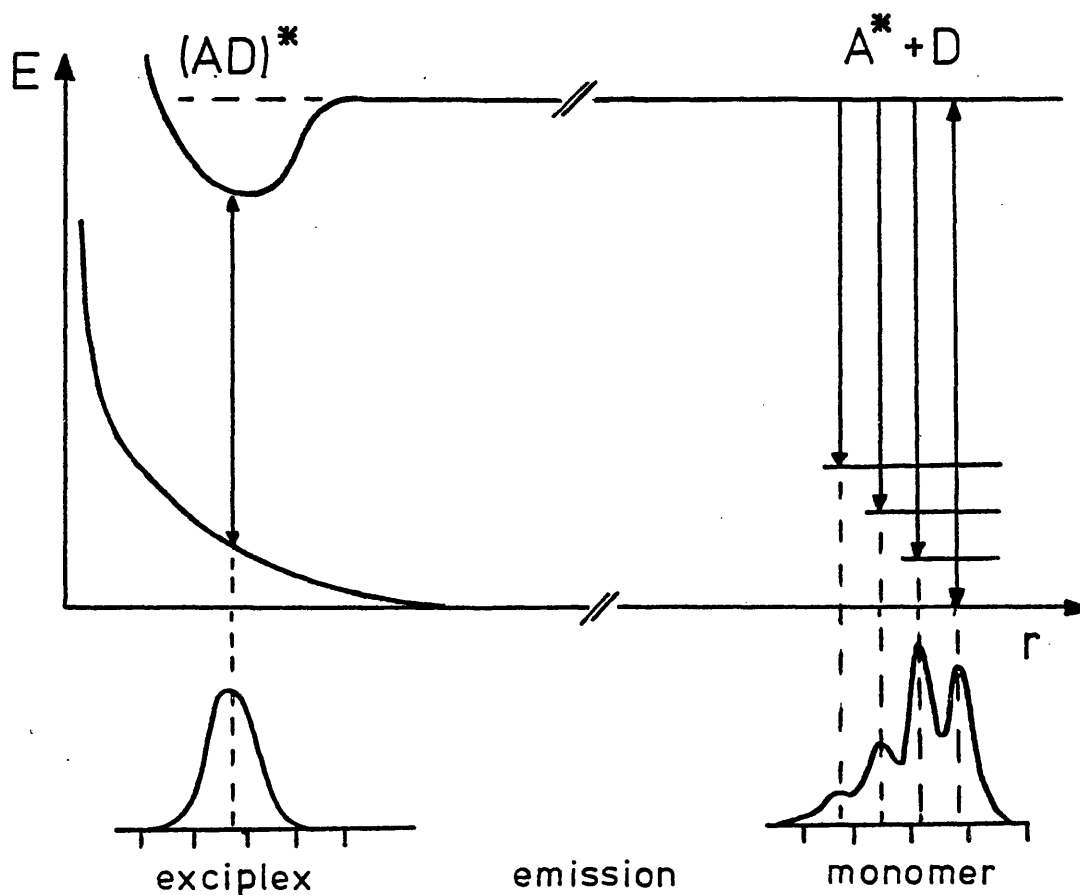
Fig.1.10 (after Knibbe, ref.30)

E

non relaxed
exciplex

$(D \cdots A)^*$

$D^{\oplus} + A^{\ominus}$

relaxed
exciplex

$(DA)^*$

radical
ions

triplets

$D_{T(S)}^+ A_{S(T)}$

D + A

ground state
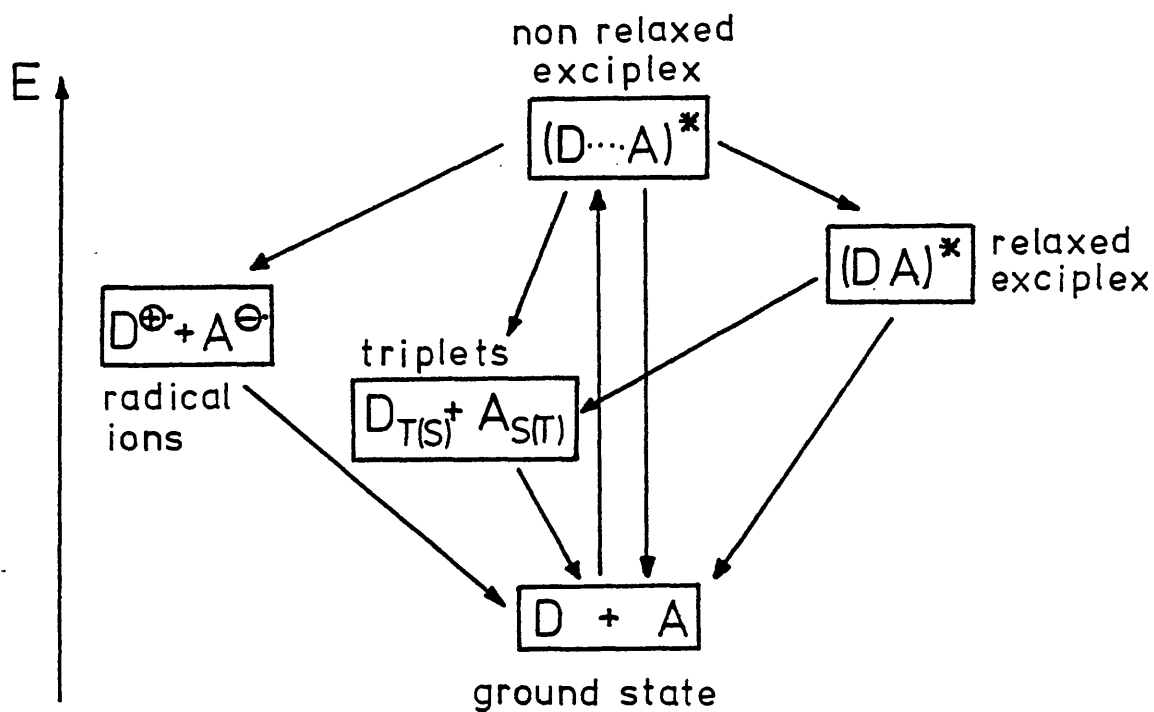
Fig.1.11 (after Davidson, ref.31)

Whilst maximum stabilisation of the exciplex is expected in polar solvents therefore, radical ion formation can be so stabilised as to compete effectively and even eliminate the emissive process. Indeed intermolecular exciplexes cannot be observed in polar solvents for this reason. This type of deactivation is thought to occur only from the non-relaxed exciplex.[33,52-54] Further discussion of this point occurs in 2.4.7.

In non-polar solvents relaxed exciplexes have been shown to yield triplet states[55-57] but whether they do in polar solvents is debatable, evidence being available on both sides.[54-58]

Lastly both exciplexes can undergo radiationless deactivation to the ground state molecules without going via radical ions or triplet states. This too will be developed later in the chapter.

1.8. Results and Discussion of Absorption and Fluorescence Studies

1.8.1. Introduction

The interaction of halogen atoms with the excited states of aromatic hydrocarbons has been studied by many workers either in terms of the direct spin-orbit perturbations of halogens substituted directly into aromatic rings[17,18,19] or the intermolecular interaction by alkyl halides with aromatic systems.[11]

Despite two stimulating reports[17,18] on the remote intramolecular

effect of a heavy atom in which questions remain unanswered,

virtually no other work has been done on the intramolecular inter-

actions and their geometrical requirements. Results described

in this section attempt to fill that gap.

From the outset it should be pointed out that research

began in the hope of detecting for the first time emission from

an intramolecular exciplex of an aromatic hydrocarbon and a

halogen atom. This has not been observed with any of the compounds

containing halogen prepared in this laboratory. Compounds were

synthesised in groups of chlorides, bromides, iodides and the

non-halogen containing derivative where possible. Four aromatic

systems were employed, 1- and 2-substituted naphthalenes, 9-

substituted anthracenes and 1-substituted pyrenes. By far the

greater number of compounds were in the naphthalene series. (For

a complete list of the compounds synthesised see the compound

index at the end of Chapter 4). The linking chain employed was

a matter of convenience rather than design and three types were

used: $-(CH_2)_n-$, (n = 1-3), $-CH_2OCOCH_2-$ and $-CH_2CO_2(CH_2)_2-$.

Again, for convenience the various derivatives will often be

referred to by a code explained in the abbreviations section at

the front of this thesis.

1.8.2. Absorption Spectra

Absorption spectra were not run on a quantitative basis

but were qualitatively examined for all compounds synthesised to

determine the extent (if any) of ground state perturbations. In the series Ar3X, Ar4(0)X and Ar5X no significant differences in the spectra from those of the non-halogen containing compounds were observed.

The series ArX, Ar1X and Ar2X however, showed perturbations of the ground state absorption bands from those of the unsubstituted compounds. The spectra of the equivalent phenyl and benzyl derivatives have been examined by Shorygin and co-workers[59-61] and their results are illustrated in Table 1.2, together with data for An1X and An2X. The absorption spectra of αX, α1X, βX and β1X are shown in Figs.1.12 and 1.13 and illustrate similar perturbations to those described in the Russian work. Whilst the heavy atom in ArX caused a bathochromic shift of the transitions together with a general broadening of the vibrational structure, the same magnified effect was observed in the Ar1X series. A very small shift to longer wavelength was observed in the An2X series whilst for α2X and β2X the only apparent changes were reduction in the absorption coefficients of the sharp bands in the region 300-325 nm. There did not seem to be any wavelength shift in these last two series.

The largest perturbations thus occurred when the interacting species are separated by a methylene unit. The nature of this interaction seems to be a hyperconjugative through bond effect, the extra stability of the benzyl radical contributing to the

Absorption spectra (λmax.)

Ph	H	254	203	183	
	F	260	203	182	
	Cl	261	204	189	
	Br	261	215	192	
	I	260	230	194	
PhCH$_2$	H	262	205	188	
	F	262	205	187	
	Cl	264	215	190	
	Br	272	225	194	
	I	272	235	202	

(refs. 59–61)

An	H				
AnCH$_2$	H	385	365	347	330·5
	Cl	391	371	352	338
	Br	396	376	358	342
An(CH$_2$)$_2$	Cl	385·5	365·5	347	331
	Br	386	366	347·5	331·5
	I	388	368	349	333

Table 1.2

Absorption spectra in cyclohexane.
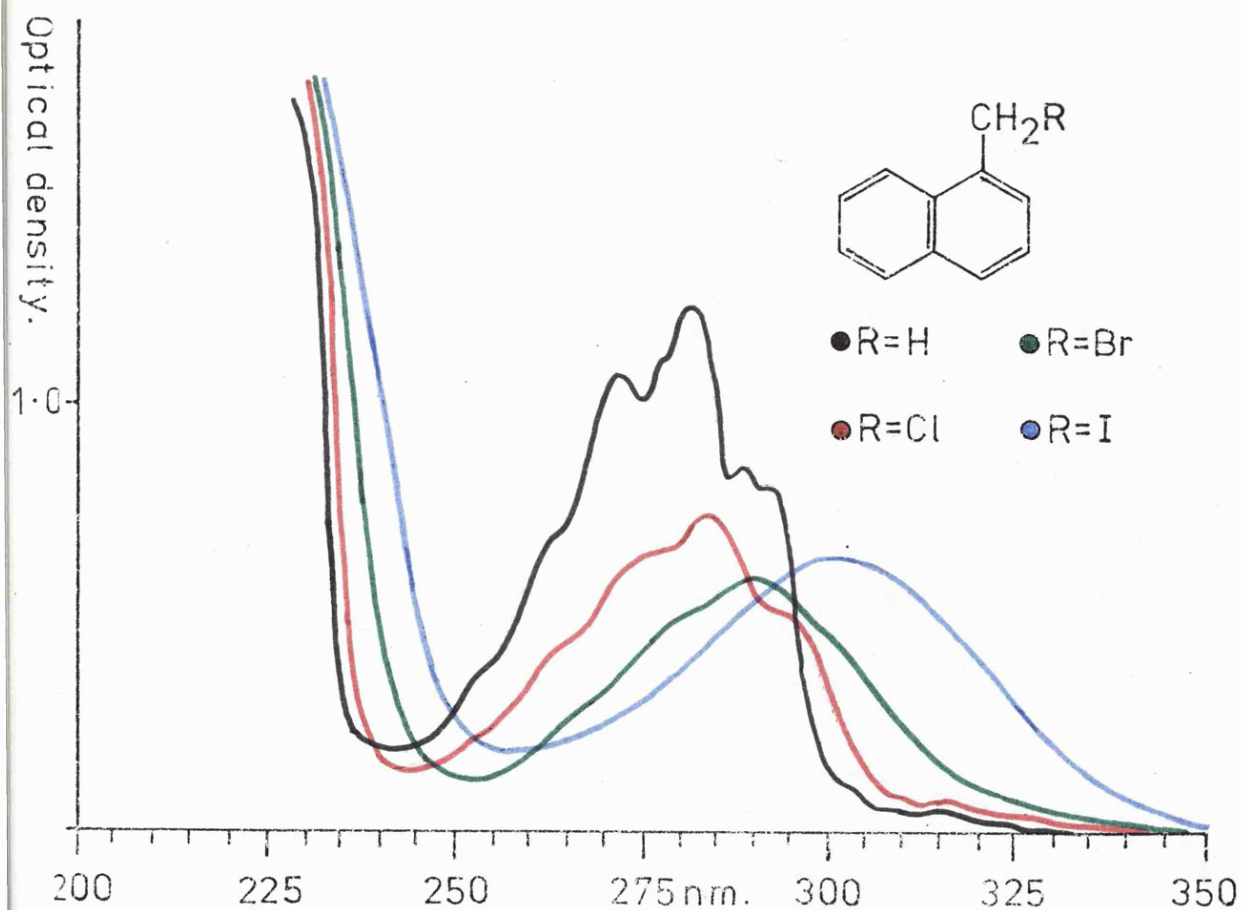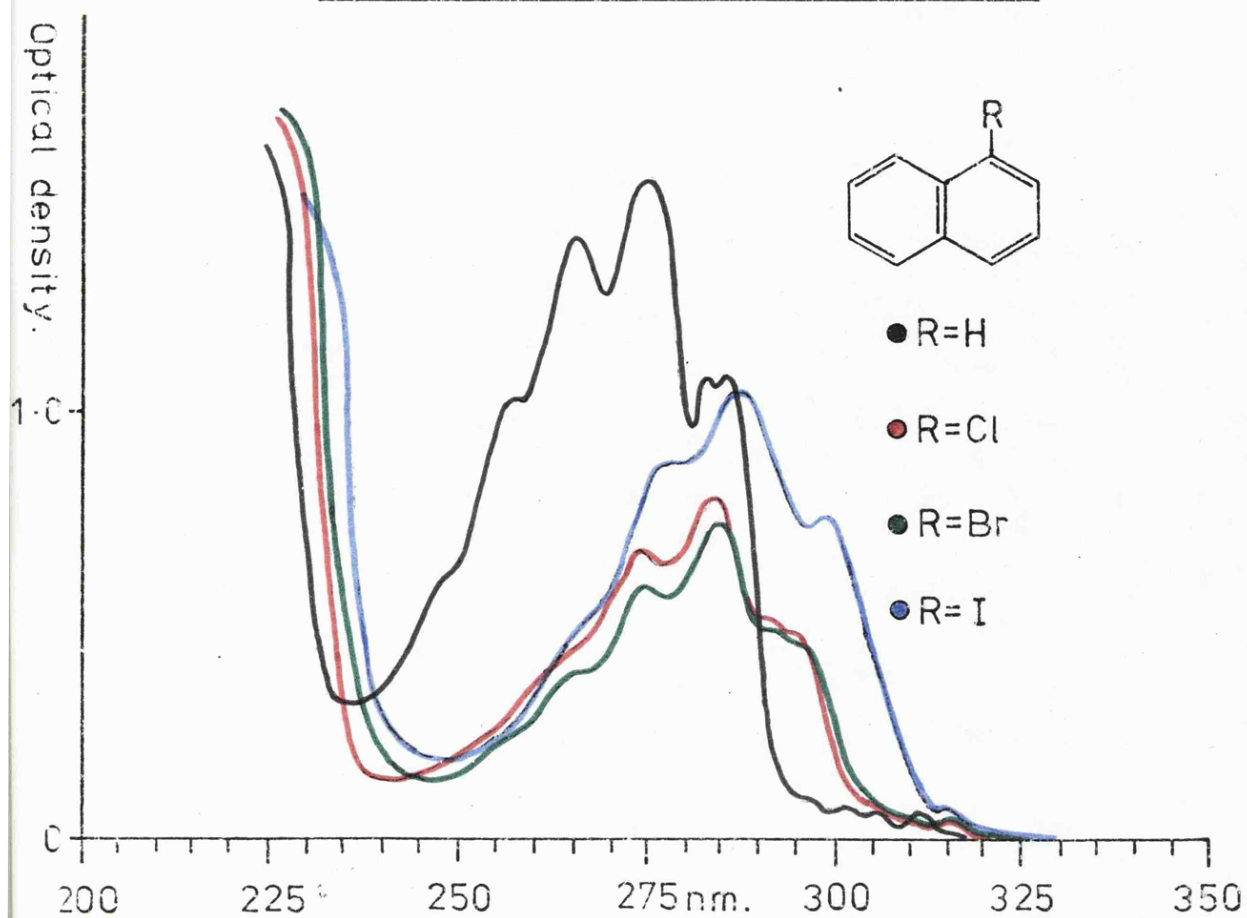
Fig.1.12

Absorption spectra in cyclohexane.
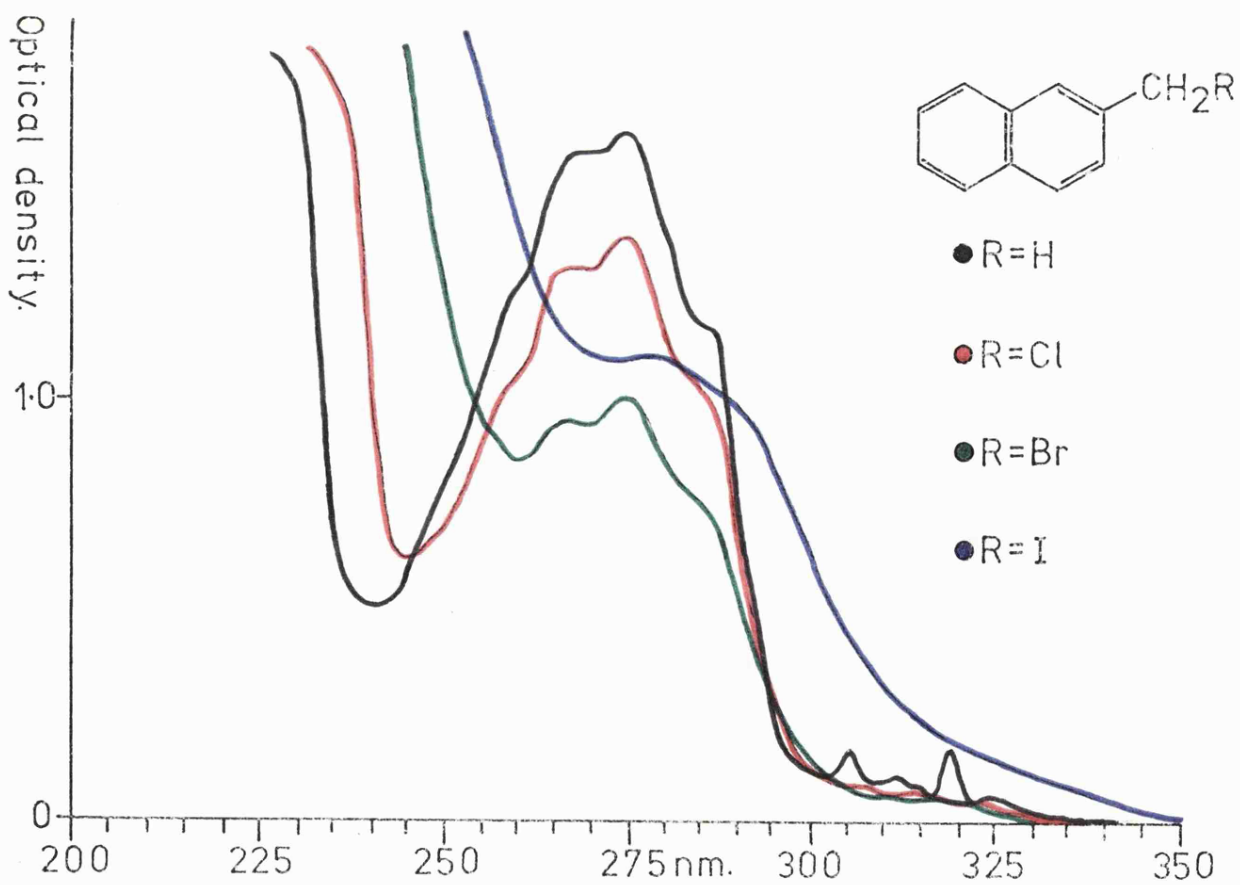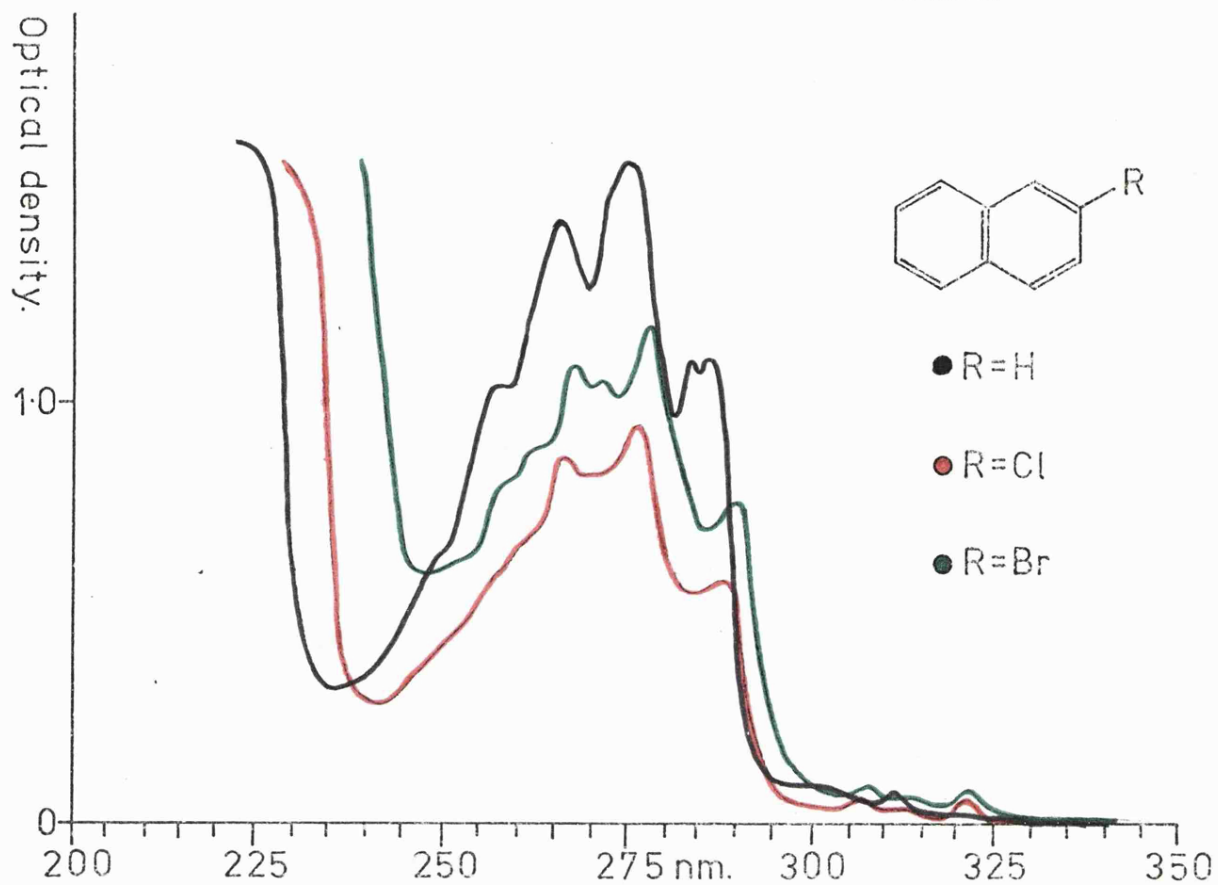
Fig. 1.13.

wavefunction of the molecule. That is to say, $ArCH_2\cdot + \cdot X$ is much closer in energy to $ArCH_2X$ than $Ar\cdot + \cdot X$ is to ArX. Consequently the radical description mixes with the pure sp^3 hybridised state giving the ArC carbon more of the sp^2 character of the benzyl radical. Thus the sp^3 hybridised C-X bond acquires p-character and the more labile is the bond the more it will become like a p-orbital. As p-character increases in C-X so, also, $Ar\overarc{-C-}X$ will decrease towards $90°$. Thus since the bond strength follows the order $H > Cl > Br > I$ it follows that the carbon-iodine bond has most p-character and is most readily disposed to overlap with the aromatic system. The iodide is indeed observed to be the most heavily perturbed.

The small effects in the Ar2X series show that an extended through bond effect is present. The nature of this interaction is discussed in 1.8.4.

1.8.3. Fluorescence Spectra

The fluorescence spectra of all the compounds used in this chapter exhibited the characteristic structure of the root aromatic hydrocarbon. The spectra have not been reproduced other than to illustrate the monomer emissions. Figs.1.14 and 1.15 show the standard spectra of the naphthalenes and Fig.1.16 those of the pyrenes. The emission spectrum typical of the anthracenes can be found in Fig.2.17 where that for 9-MeAn is illustrated. No new emission bands were observed for any of

FLUORESCENCE SPECTRA OF 1-MeNp

λ_{exc} 305nm

x3:MeCN

x3:C$_6$H$_{12}$
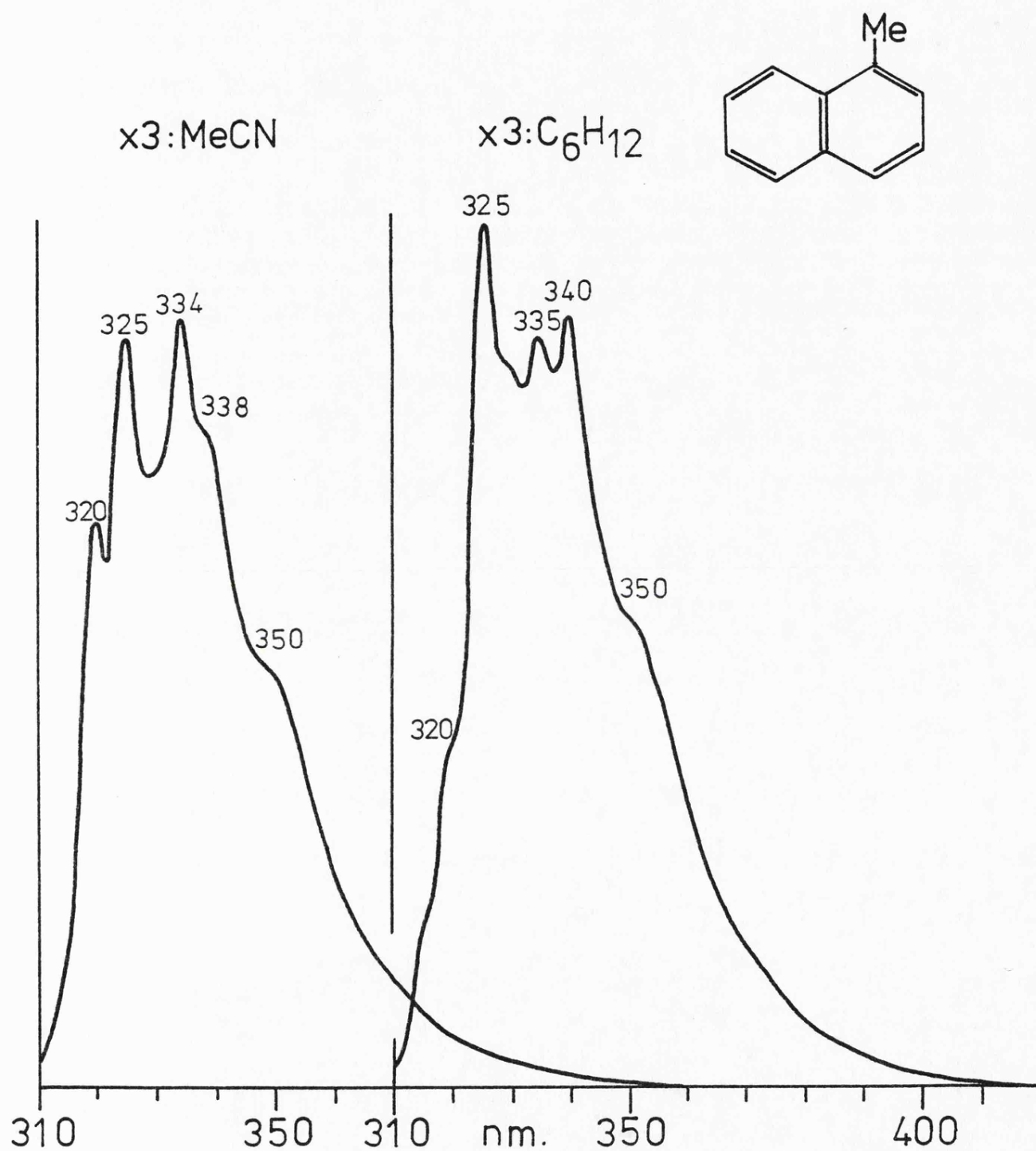
Fig.1.14.

FLUORESCENCE SPECTRA OF Np AND 2-MeNp.

x3:MeCN (a)

x1:MeCN (b)

x1:C_6H_{12} (c)   do.

Me

λ_{exc} 305nm.
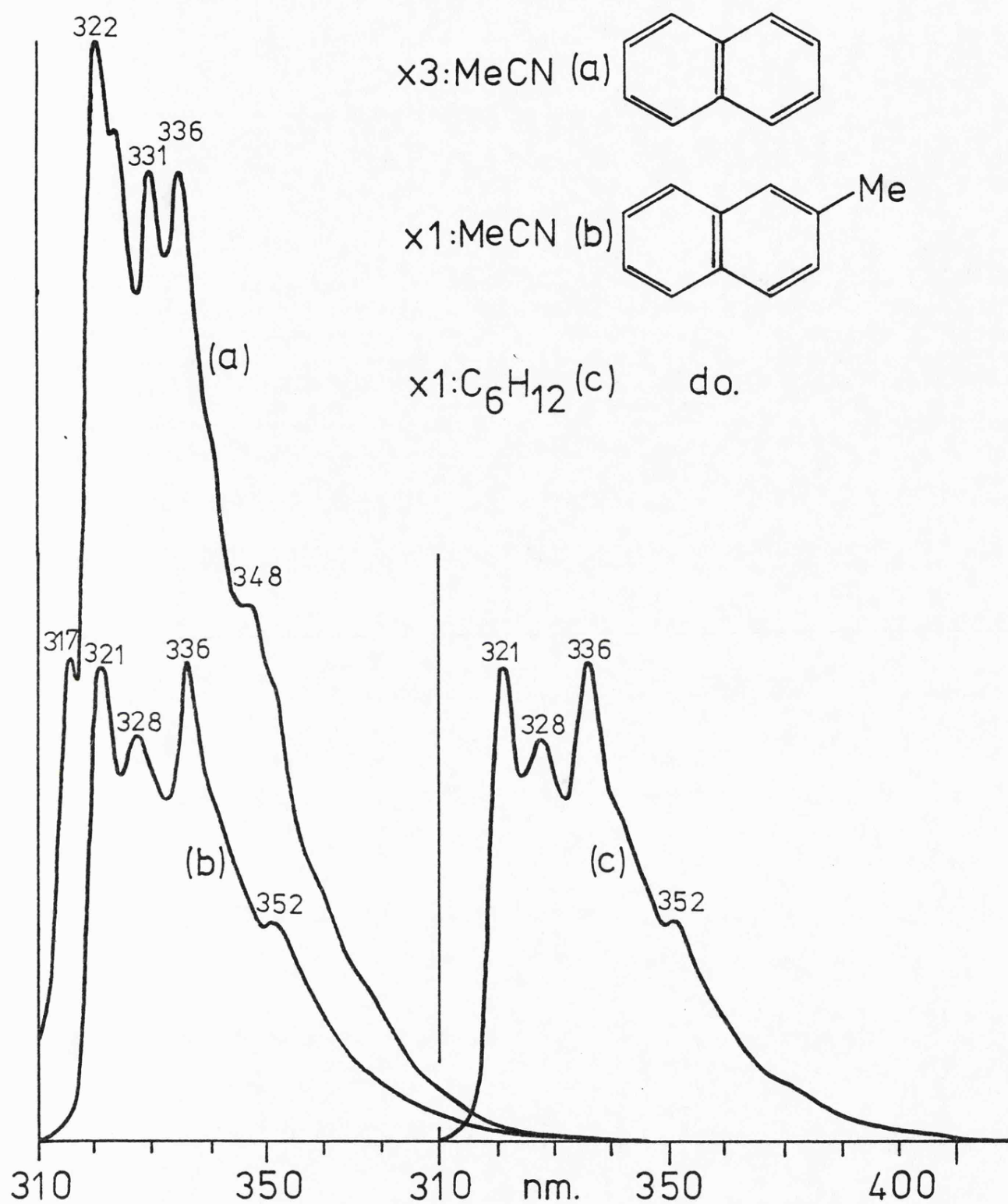
Fig. 1.15.

FLUORESCENCE SPECTRA OF PYRENE AND SOME DERIVATIVES IN CYCLOHEXANE.

$\lambda_{exc} = 340\,nm.$

R = OCOCH$_2$X.
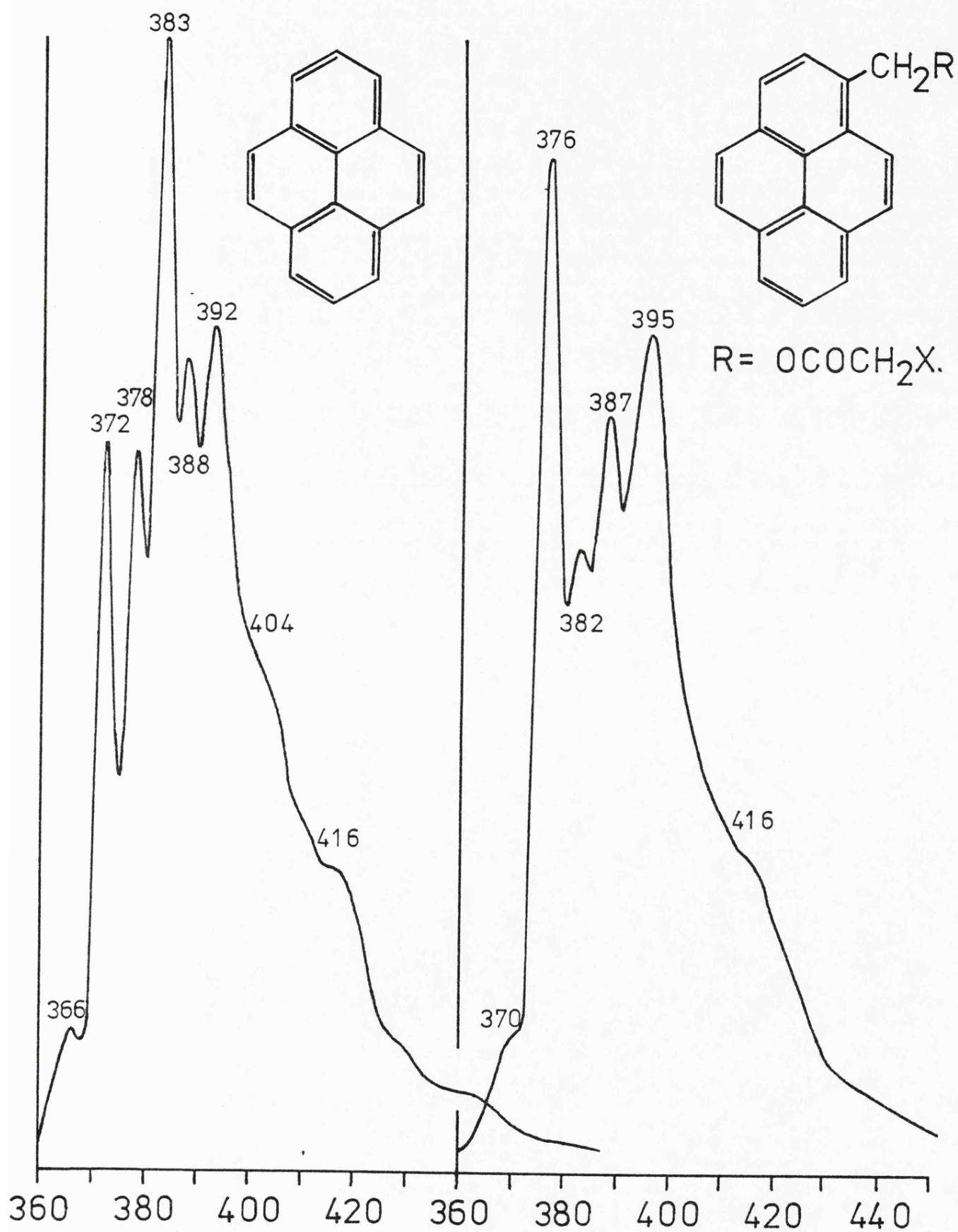
Fig.1.16.

QUANTUM YIELDS FOR

1-Np(CH$_2$)$_n$X.
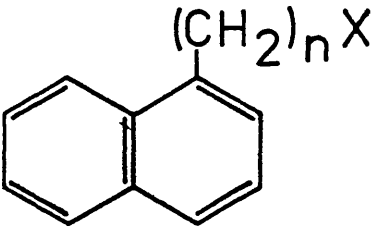
(CH$_2$)$_n$X			
benzene			
X \ n	0	1	2	3
---	---	---	---	---
H	0·175	0·230		
Cl	0·014	0·0029	0·068	0·119
Br	0·0032	0·0011	0·012	0·025
I		0·0011	0·0039	0·0060
acetonitrile				
H	0·182	0·200		
Cl	0·011	0·0008	0·050	0·127
Br	0·0026	0·0008	0·011	0·023
I		0·0011	0·0034	0·0056

Table 1.3.

QUANTUM YIELDS FOR

$2\text{-}Np(CH_2)_n X.$
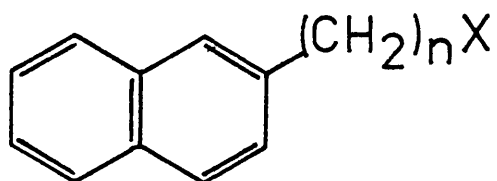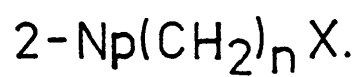
benzene				
X \ n	0	1	2	3
H	0·175			
Cl		0·0022	0·070	0·137
Br	0·0040	0·0027	0·006	0·030
I		0·0023	0·0032	0·0043
acetonitrile				
H	0·182			
Cl		0·0018	0·079	0·111
Br	0·0029	0·0024	0·005	0·021
I		0·0021	0·0023	0·0031

Table 1.4.

QUANTUM YIELDS FOR

9-An(CH_2)_nX.
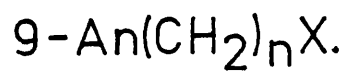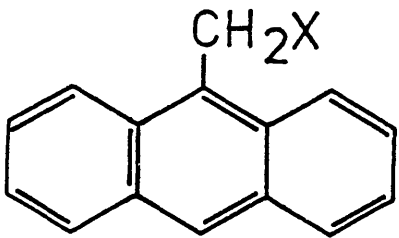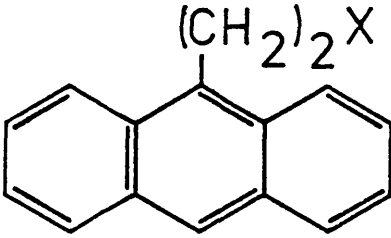
	CH_2X	$(CH_2)_2X$
X	cyclohexane	
H	0.290	
Cl	0.011	0.195
Br	0.0005	0.041
I		0.031
	acetonitrile	
H	0.350	
Cl	0.001	0.224
Br	0.0005	0.047
I		0.017

Table 1.5.

QUANTUM YIELDS FOR

1-AND 2-$NpCH_2OCOCH_2X$.
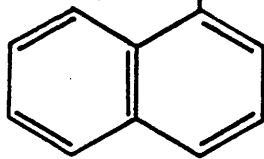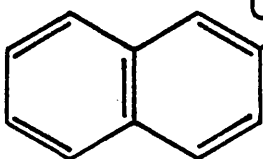
CH_2OCOCH_2X	CH_2OCOCH_2X
X	benzene
H	0.125	0.139
Cl	0.109	0.084
Br	0.011	0.010
I	0.006	0.002
	acetonitrile
H	0.123	0.134
Cl	0.100	0.057
Br	0.008	0.010
I	0.002	0.002

TABLE 1.6.

QUANTUM YIELDS FOR

9-An- and 1-PyCH$_2$OCOCH$_2$X.
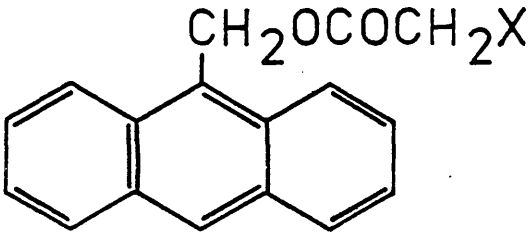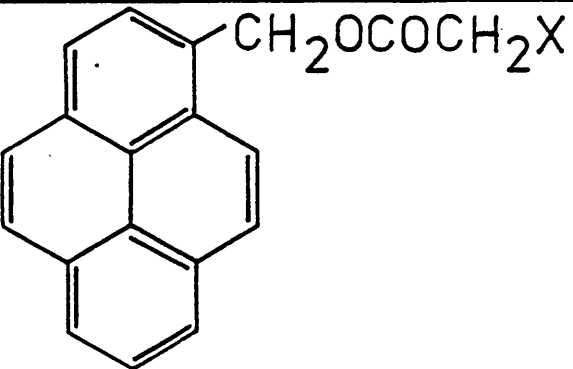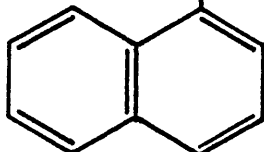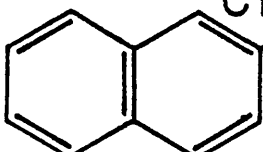
	CH_2OCOCH_2X (9-An)	CH_2OCOCH_2X (1-Py)
X	cyclohexane	
H	0·290	0·820
Cl	0·220	0·811
Br	0·210	0·479
I	0·030	0·085
	acetonitrile	
H	0·314	0·830
Cl	0·245	0·831
Br	0·226	0·101
I	0·038	0·032

Table 1.7

QUANTUM YIELDS FOR

1-AND 2-NpCH$_2$CO$_2$(CH$_2$)$_2$X

![1-Np structure] CH$_2$CO$_2$(CH$_2$)$_2$X	![2-Np structure] CH$_2$CO$_2$(CH$_2$)$_2$X
X	benzene
H[1]	0·114	0·113
Cl	0·100	0·112
Br	0·032	0·088
I	0·010	0·028
	acetonitrile
H[1]	0·126	0·128
Cl	0·090	0·122
Br	0·023	0·086
I	0·011	0·031

[1] H=NpCH$_2$CO$_2$Me

TABLE 1.8.

EMISSION YIELDS IN C_6H_{12} AT 77K.

Compound	αNp-		βNp-	
	Φ_P	Φ_F	Φ_P	Φ_F
-Me	0·044[1]	0·85[1]	0·03	0·6
-1Cl	0·10	0·034	<0·01	<0·01
-2Cl	0·20	0·255	0·06	0·1
-3Cl	0·06	0·57		0·45
-1Br	<0·01	<0·01		<0·05
-2Br	0·55	0·05	0·18	<0·05
-3Br			<0·15	0·045
-1I				
-2I	0·30	0·025	<0·15	<0·015
-3I				0·03
-5Br	<0·01	0·15		
-5I	<0·01	0·15	<0·01	0·15

[1] Refs 13-15

Table 1.9.

FLUORESCENCE AND PHOSPHORESCENCE OF

Me

$(CH_2)_2Br$

and

in methylcyclohexane at 77K.

1-NpMe   ● x3   ● x100

1-Np$(CH_2)_2$Br   ● x30   ● x10

Intensity.
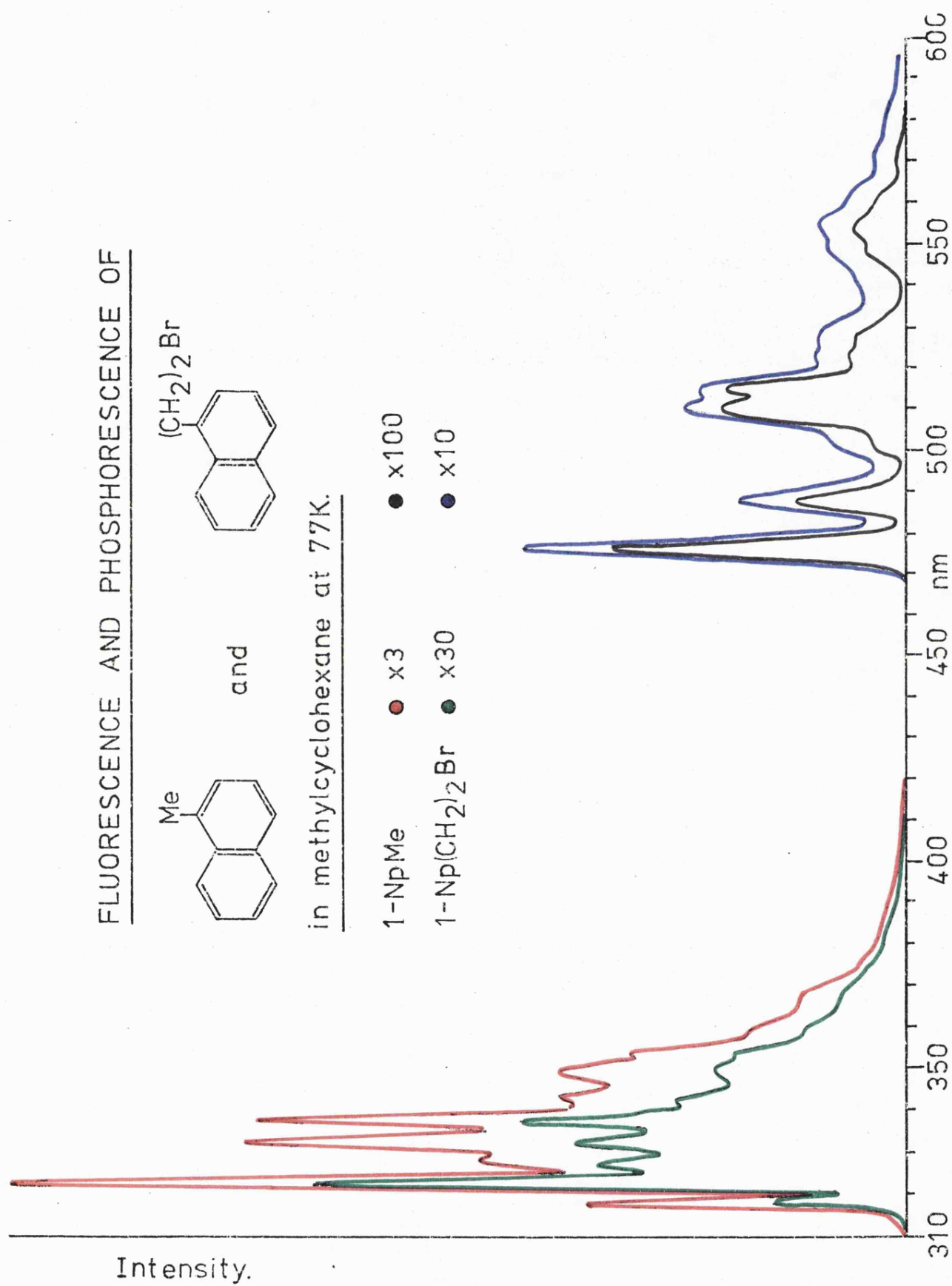
Fig.1.17.

CORRELATION DIAGRAM FOR VARIATION OF $\log_{10}\Phi_F$ WITH n.

1-Naphthyl derivatives.
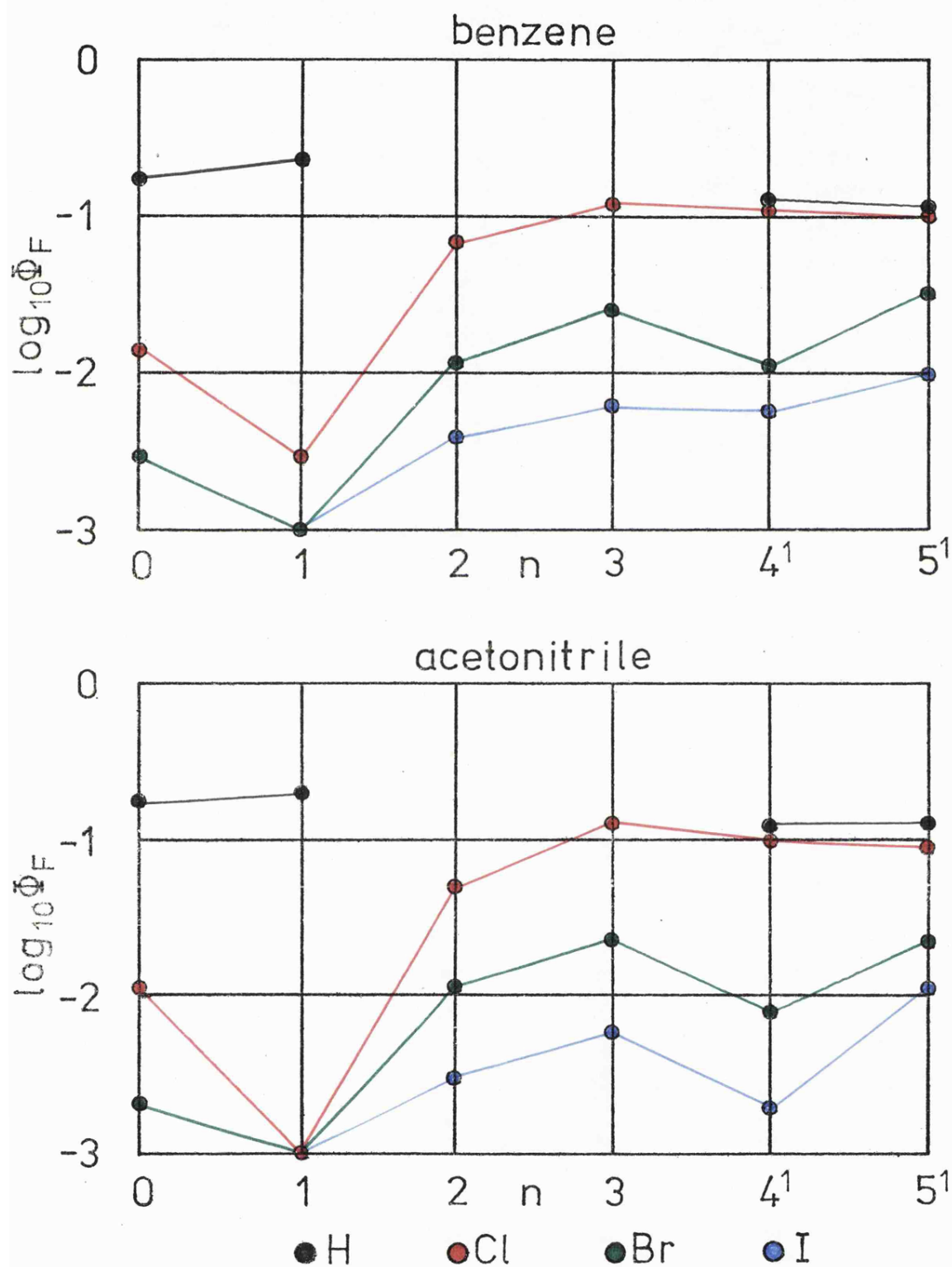
Fig. 1.18.

[1]contains ester link.

CORRELATION DIAGRAM FOR
VARIATION OF $\log_{10}\Phi_F$ WITH n.
2-Naphthyl derivatives.
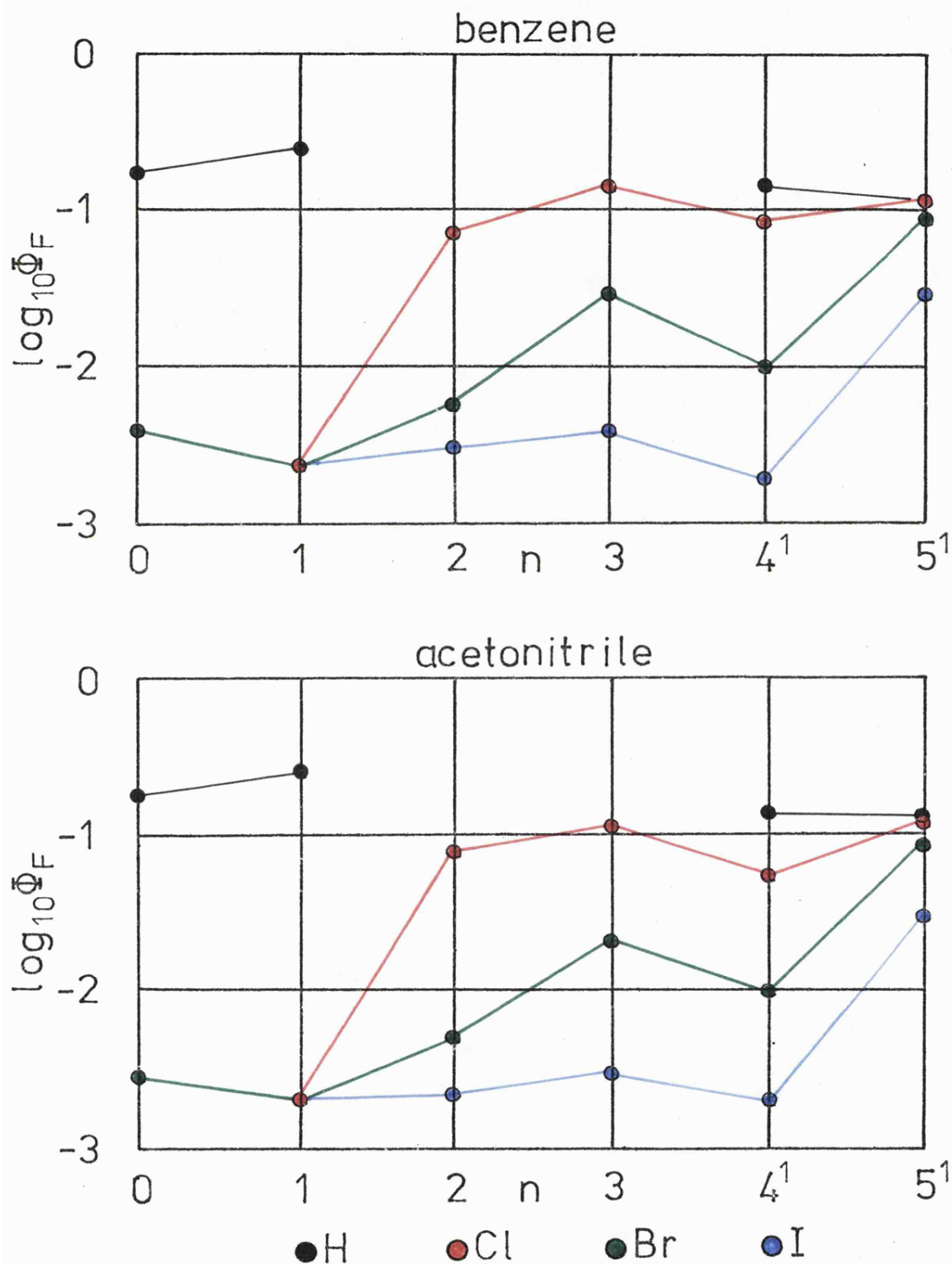
Fig.1.19.

^{1}contains ester link.

the halogen containing compounds.

Tables 1.3-1.8 inclusive list quantum yields of fluorescence for the derivatives prepared. Naphthalene compounds were examined in benzene and acetonitrile whilst anthracene and pyrene compounds were run in cyclohexane and acetonitrile. Tables 1.3, 1.4 and 1.5 concern the series αnX, βnX and $AnnX$ respectively. Tables 1.6 and 1.7 illustrate $\alpha 4(0)X$, $\beta 4(0)X$, $An4(0)X$ and $Py4(0)X$. Table 1.8 contains values for $\alpha 5X$ and $\beta 5X$. (In this chapter X refers to Cl, Br and I and occasionally to the unsubstituted derivative where X = H. No fluorides were prepared).

As well as examining the spectra at room temperature the majority of the compounds were cooled to 77K in methylcyclohexane and their fluorescence and phosphorescence yields were obtained. Table 1.9 lists the approximate quantum yields calculated by comparison with literature values from Table 1.1b. In fact whilst the phosphorescence spectra of the naphthalene derivatives were well defined (see Fig.1.17) it was not possible to obtain similar spectra for any of the anthracene derivatives because of their very high fluorescence yields.

The variation of quantum yield with the length of the linking chain for the naphthalene derivatives has been illustrated in Figs.1.18, 19 where $\log_{10} \Phi_F$ has been plotted against the number of intervening atoms n. The chains containing the ester

linkage have been included in the diagram as illustrative of the n = 4 and n = 5 case although it is obvious from the non-halogen containing derivative that the ester group has an effect. (In fact, comparison with the Φ_F values for NpCH$_2$OMe in Table 2.4 show the ether linkage to have a significance).

General trends are immediately apparent. In all cases within the limits of experimental error (which has been estimated as 10-20%) the order of quenching is I > Br > Cl > H, in accordance with other observations in the literature noted earlier. Perhaps the most striking result obtained is that the order of quenching for Ar(CH$_2$)nX as n is varied does not follow quite the expected pattern. It might have been anticipated that the quenching effect would drop with increasing n. This is true by and large but for the n = 1 case the quenching is greatest (greater than for n = 0). A similar observation has been noted by Ichimura and co-workers[62] who noted while working in a solid matrix that Φ_F PhCH$_2$Cl << Φ_F PhCl. The effect is biggest for αlCl which is much more strongly quenched than αCl by a factor of about 10. The same applies to the bromides and iodides although the effect is not so great. This is because the compounds in the series NplX are quenched to the same extent. In the anthracene case AnlBr was more strongly quenched than AnlCl but the chloride still had a very weak emission.

As n was increased from 1 to 3 a gradual increase in quantum yield was observed with a marked increase for chlorides but only a small increase for iodides. (Bromides were intermediate in degree). As the chain increased in length the amount of quenching obtained was still quite remarkable. Thus, even with five linking atoms the quenching of the iodide was >10 times in the 1-Np series and ∿4 in the 2-Np series relative to the standard compounds which did not contain a halogen.

Differences between the two positions of naphthalene substitution were noted. In the 1-position the quenching was greater when n = 1 than for the 2-series but as n increased the fluorescence recovered faster in the 1-series. The 2-series remained heavily quenched for n = 2, 3 (in particular for the bromides and iodides) but at n = 5 there was much less difference between halides. In other respects however there were many similarities between the series.

Very little effect of solvent was observed throughout this work, a factor which will occur in the discussion.

The properties of the anthracene derivatives which have been synthesised can be seen to fit into the same pattern as has been established for the naphthalenes. The difference in observed quenching between AnlX and An2X was much more marked, with AnlBr > NplBr but Np2X > An2X.

CORRELATION DIAGRAM OF
$\log_{10}(\text{rel}.\Phi_F)$ FOR $ArCH_2OCOCH_2X$
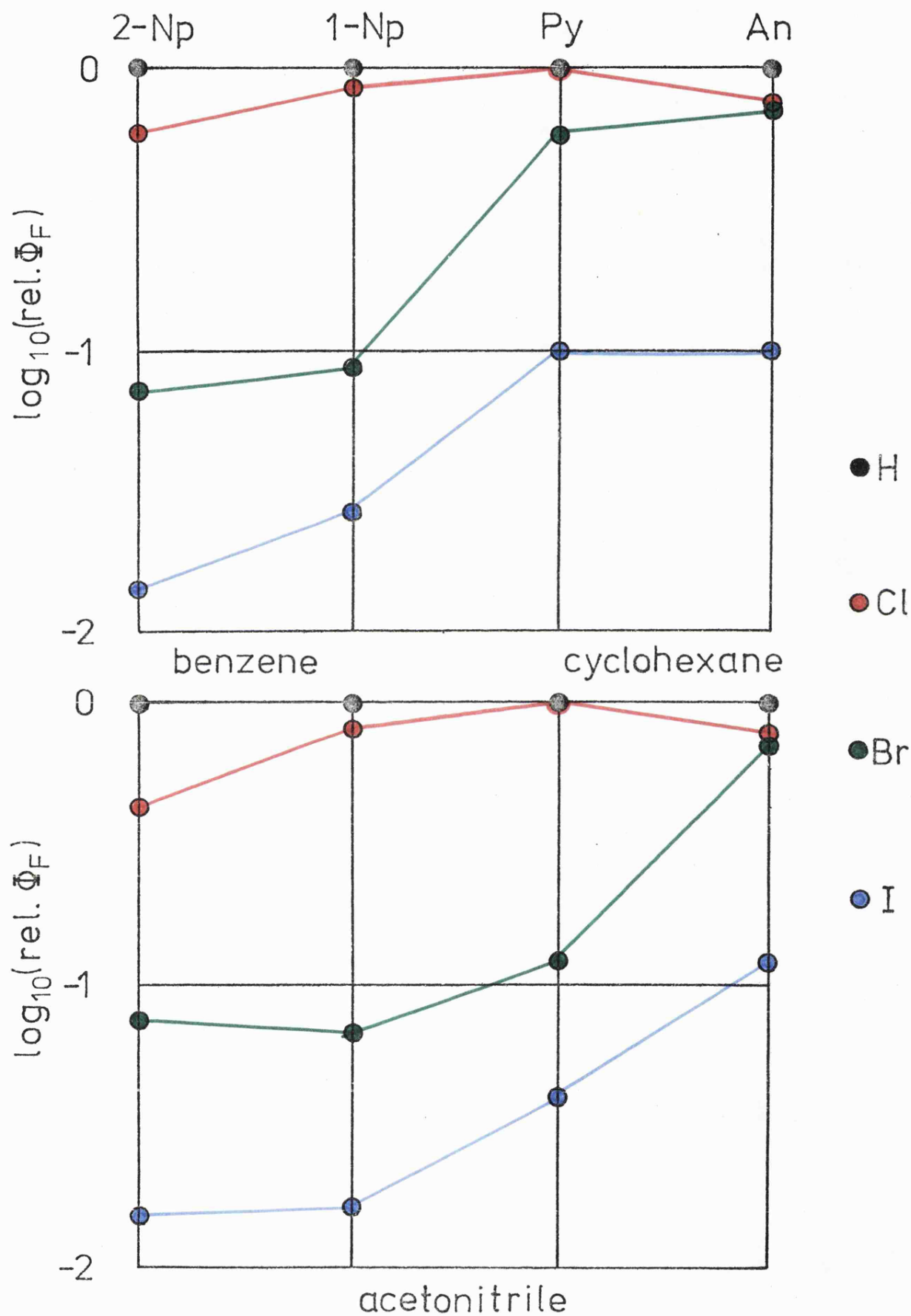
Fig. 1.20.

Fig.1.20 shows the correlation of quantum yield for the series Ar4(0)X although in this case to obtain a better comparison of the halogen effect the logarithm of the relative quantum yield was plotted for the different aromatic systems used. Here again there was little difference between the naphthyls although quenching was slightly better in the β case. These were both better than the pyrene series and in anthracene the effect seemed to be least.

Further data which have been obtained are shown in Table 1.10. This is a table of the lifetimes of the fluorescence observed which have been calculated from the fluorescence yields in degassed and aerated solution. The method of calculation was as described below. For a compound whose lifetime is known in a particular solvent the following Stern-Volmer relationship for oxygen as a singlet quencher holds,

$$\frac{\Phi_{F_0}}{\Phi_F} = 1 + k_q \tau_0 [O_2]$$

where Φ_{F_0} is the quantum yield in degassed solution and Φ_F that in aerated solution. k_q is the quenching constant for oxygen with the excited singlet state and τ_0 is the lifetime of the excited singlet in degassed solution.

Approximate Singlet Lifetimes (ns)

1-Np-

n	0	1	2	3	4	5
benzene						
H	110[1]	83[1]			40	46
Cl	5	27	19	56	38	48
Br	27	13	16	11	16	40
I			19	24		40
acetonitrile						
H	118[1]	84			36	59
Cl	4		21	61	44	63
Br	17		27	10	10	25
I			23	13	19	27

2-Np-

n	0	1	2	3	4	5
benzene						
H	110[1]	60			54	51
Cl		21	32	56	29	48
Br	27		5	13	5	40
I			27	16	21	40
acetonitrile						
H	118[1]	74			55	65
Cl		25	34	59	25	63
Br	6	21	2	10	8	38
I			25	17	19	36

[1] ref 63

Table 1.10.

If $R_o = \dfrac{\Phi_{F_o}}{\Phi_F}$ for the known compound and if

$K_o = k_q[O_2]$ is constant for the same solvent then $R_o = 1 + K_o\tau_o$

and $(R_o - 1) = K_o\tau_o$.

Now for a compound whose lifetime is unknown a similar relation holds in the same solvent

i.e. $(R-1) = K_o\tau$

Hence $\dfrac{(R_o - 1)}{(R-1)} = \dfrac{\tau_o}{\tau}$

and so the unknown lifetime is given by

$$\tau = \tau_o\frac{(R-1)}{(R_o-1)}$$

In Table 1.10 the known lifetimes and their sources have been indicated. Owing to the lack of data for the fluorescent lifetime of naphthalene in benzene a value was used in toluene as solvent on the basis that other measurements with anthracene show no difference in lifetime in these two solvents.[63] The tabulated values are probably subject to ~20% error where τ is large but the shorter lifetimes could well have a large error since the method of calculation involves a ratio of two areas. A short lifetime will necessarily mean a small ratio of areas and thus magnify the error considerably. The lifetimes are however not intended to be any more than an approximate guide to the halogen

effect and to illustrate trends. Some interesting observations

emerge. As would be expected where a quenching of fluorescence

is involved there is a shortening of the lifetime when a halogen

is contained in the molecule. The shortening of lifetime follows

in general the pattern of fluorescence quenching with one major

difference and that is that the iodides have in many cases longer

lifetimes than the corresponding bromide. It would seem from

the differences between ArnCl and ArnBr that this is due to an

unusual lengthening of $_\Lambda$the iodide rather than a shortening of$_\Lambda$

τ for $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ τ for

the bromide. (This is not due to error in measurements of area

because the actual spectra obtained showed less quenching by

oxygen for bromides compared to iodides and this is reflected

in the lifetimes).

1.8.4. Static or Dynamic Interaction?

In general, the problem posed in this chapter (and indeed

in Chapter two) is how exactly two sites separated by a linking

chain can interact. This has received a good deal of attention

in the literature from which useful conclusions can be drawn.

However in chemistry no two problems are alike and each must

be considered separately.

The model for the problem will be abbreviated to

$D-(CH_2)_n-A$ where D is a donor and A an acceptor in the broadest

sense of the terms. There are several ways in which D and A

can interact, dependent on the character of D and A and the
length of the chain.

If the chain is short then the possibility that the
electrons of D and those of A can interact through the σ-bonding
framework without D ever approaching A must be considered.
Inductive effects when n = 0 and 1 are well documented. In
relation to the present work it has been observed that Φ_F
NpMe > Φ_F NpCH$_2$OMe, and similarly for the Np4(O)H compounds.
Elsewhere[64] it was observed that the rate of dye sensitised
photo-oxidation of the aromatic system of anthracene derivatives
(Fig.1.21) was substantially affected by substituents on the
α carbon. Even when compounds having n = 2 were used retarded
oxidation rates were noted. Thus a remote substituent was
altering the electron density at the 9,10 positions.

Fig.1.21.
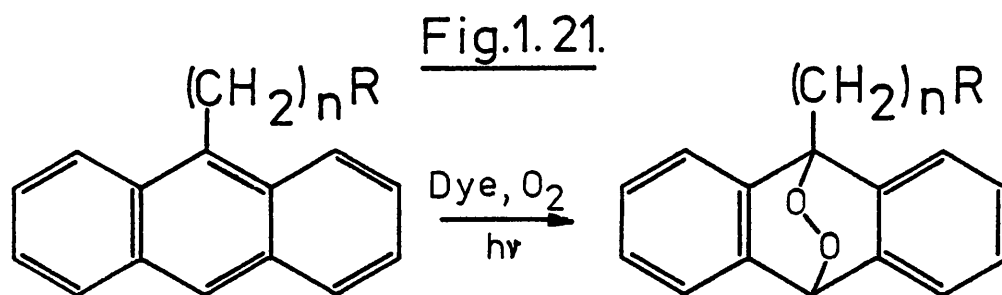
As was seen in 1.8.2. there can be a hyperconjugative effect
when n = 1 particularly as the C-R bond gets weaker. There is
evidence in the literature[65-67] that this type of 'through-bond'
effect operates over much larger values of n although it should
be pointed out that most of these occur where the molecular

geometry is fixed. A case in point is the low ionization potential of 1,4-diazabicyclo[2,2,2]octane where it is believed that the non bonding nitrogen lone pairs are stabilised by interaction via the parallel 2-3, 5-6 and 7-8 σ bonds.[65] The anomalous ionisation potentials of toluene, ethylamine and benzylamine will also be noted in 2.4.2. in relation to this point. In the same way as hyperconjugation aids the $n = 1$ interaction it can be present when $n = 3$. A weak C-X bond could communicate with the aromatic system via overlap with the σ_{1-2} bond.

$Ar\,CH_2X$

$Ar(CH_2)_2X$

$Ar(CH_2)_3X$

$-CH_2OCOCH_2X$
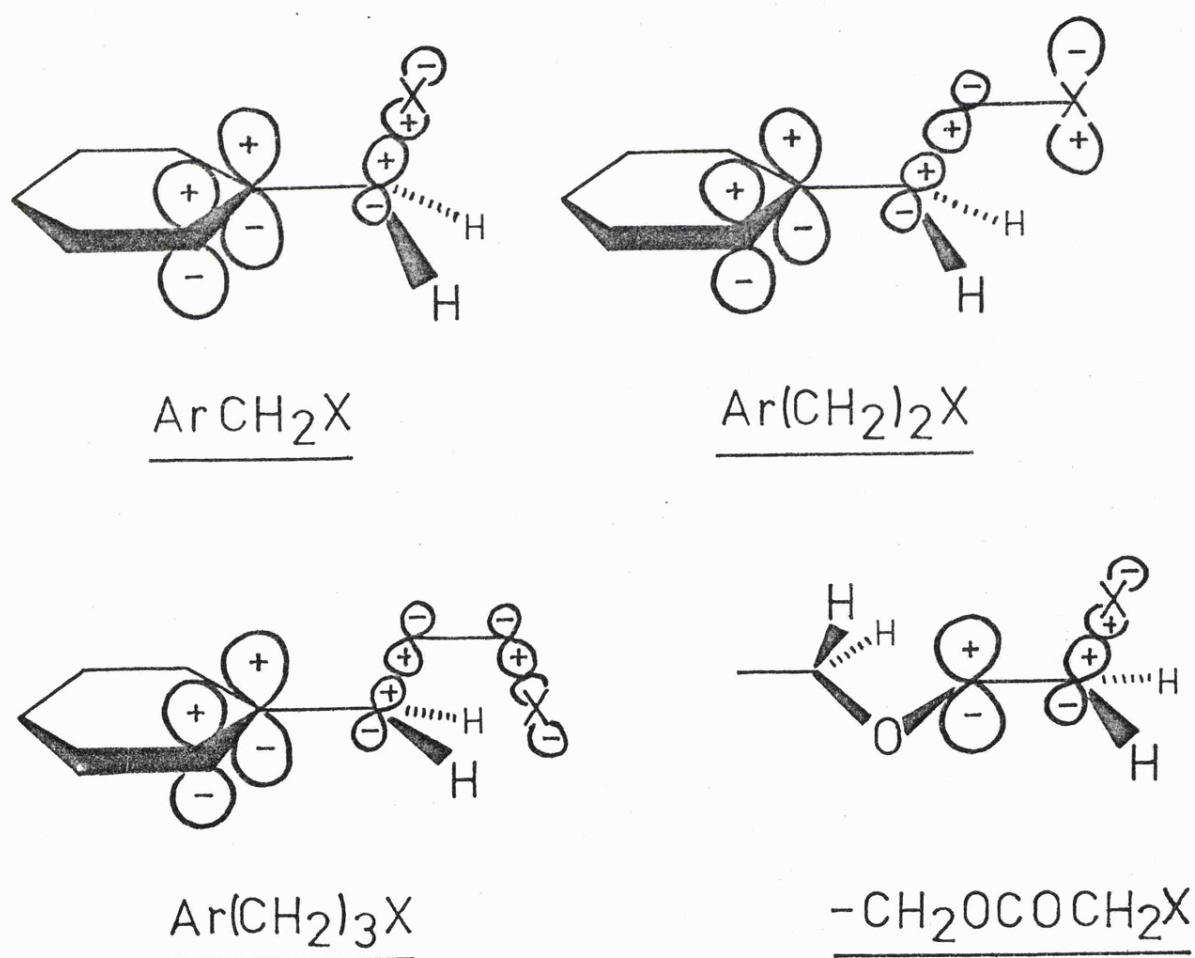
Fig.1.22.

Fig.1.22 illustrates the mode of interaction of the cases in point. When n = 2 the non-bonding electrons of the halogen itself are open to a possible interaction with the same σ_{1-2} bond. It should be noted that if such an interaction were present it would imply a hindered rotation about the $Ar-C_1$ bond. The interpositioning of an ester group in the chain could cause a similar interaction[68] where again the C-X bond is weakened by the ability of the α-carbonyl to stabilise the radical. As yet this type of interaction has not been well established in molecules without fixed geometry.[65] It would be expected to diminish rapidly with the increase in the number of conformations of the side chain. In molecules containing only a methylene chain it is unlikely to extend beyond n = 3 for this reason. A 'through bond' static effect when n is small must therefore be considered.

Another effect is the dynamic interaction of D and A caused by the molecular and solvent movements. This can also be called a 'through space' interaction. In the simplest sense one can imagine the chain bending to allow D and A physical contact. In considerations of this sort it is necessary to distinguish between the possible types of interaction. It has been shown by Shimada and Szwarc[69] that an electron transfer process between a naphthalene and a naphthalene radical anion can occur over quite large distances (typically 9$\overset{\circ}{A}$) such that three or four solvent molecules actually separate D and A.

This observation was backed up by Weller[70] who found a distance
of 7Å in amine-aromatic hydrocarbon exciplexes. However it is
well known[34,71-73] that for intramolecular excimer formation
to occur stringent geometrical requirements must be met. In
the first place the aromatic rings should be parallel and
separated ideally by ~3.5Å; in the second the methylene chain
should adopt a staggered conformation. These requirements led
to the observation[72-74] that n = 3 is the optimum for intra-
molecular excimer formation. Whilst aromatic hydrocarbon-
amine exciplex formation requires a fairly close approach, the
requirements are nothing like so stringent[75,76] (see chapter two).
In the compounds used here it is unlikely that the requirements
of excimer formation will be necessary for the interaction to
occur and evidence in support of this occurs in chapter two.
There is almost certainly some type of charge transfer inter-
action and so the presence of a halogen orbital within the
'effective interaction radius' of 9Å must be considered as
possibly leading to a partial charge transfer interaction with
its attendent quenching.

Inspection of molecular models indicates that in fluid
solution the dynamic 'through space' interaction is possible
in all of the compounds used, the linking chain adopting a
conformation such that the halogen can approach close to the π
cloud. The two exceptions are for ArX and ArlX where the
linking chain is not long enough to allow this. However,

other interactions already discussed occur in these compounds.
Several factors influence the 'through space' interaction. As
the chain length is increased, the number of degrees of freedom
increases allowing the molecule to adopt statistically more
conformations where the halogen is not close to the π cloud -
a dilution effect. Balancing this to some extent is the ability
of the halogen to interact with more parts of the π cloud.
Quenching must further depend on the efficiency of the fluores-
cent process being affected. These last two factors mean
that for different aromatic systems different degrees of quenching
will be observed, all other factors remaining constant. An
obvious difference is between anthracene and pyrene. In the
Ar4(0)X series the 9-anthryl derivatives allow interaction over
all three rings of the system whilst in the 1-pyryl derivatives
two rings are almost 'out of reach'. On the other hand the
fluorescent process in anthracene derivatives is highly efficient
($\tau_F \sim$ 4ns) whilst in pyrene compounds it is much less efficient
($\tau_F \sim$ 450ns). The balance between these two affects the ob-
served quenching in Fig.1.20 and from the results it would seem
that the lifetime of anthracene over pyrene and naphthalene is
the deciding factor. However comparing naphthalene and pyrene
(Np $\tau_F \sim$ 100ns) the poor overlap of the halogen and the pyrene
π-system tips the balance in favour of the strongest quenching
in the naphthalene series.

1.8.5. Solid Matrix Studies

To examine the amount of dynamic versus static quenching present, the fluorescence and phosphorescence spectra of some of the derivatives were examined at 77K in methylcyclohexane. The results are summarised in Table 1.9. It was observed that fluorescence quenching was present, even in a solid matrix, for most of the naphthalene compounds, being largest for n = 1 and falling off as n increased. The quenching also followed the order I > Br > Cl > H. Thus it was small for $\alpha,\beta3Cl$ but quite large for $\beta3I$. Except in the n = 1 case where comparison was difficult because of the heavy quenching, fluorescence yields were higher in the matrix for all the compounds examined. In the case of the anthracene compounds studied, the quantum yields were all identical in the solid matrix, i.e. there was no fluorescence quenching at 77K despite perturbations in the absorption spectra. This observation agrees with the results of Zander.[26]

Because of the very large fluorescence quantum yield at 77K (~1.0[26]) no phosphorescence of anthracene derivatives was observed. In contrast, the surprising result was obtained that phosphorescence   of many of the naphthalene derivatives showed an increase in quantum yield above that of methyl naphthalenes. In the compounds n = 1 where the bonds were most labile however, a sharp reduction in quantum yield was observed.

Hence in the series of chlorides $\alpha Cl \rightarrow \alpha 3Cl$ there was an overall decreasing trend for Φ_p with increasing n whilst for $\alpha 1Cl$ phosphorescence was perhaps reduced below what it would have been if the C-Cl bond had not been so labile. Neither phosphorescence nor fluorescence was observable for $\alpha 1Br$ whilst for $\alpha 2Br$ the phosphorescence was much enhanced, more so even than αBr; the fluorescence was however strongly quenched. These effects are illustrated in Fig.1.17.

When $\alpha, \beta 5I$ and $\alpha 5Br$ were examined, phosphorescence was weak and fluorescence slightly quenched. However, the fluorescence and phosphorescence are undoubtedly affected by the ester function rather than the halogen, since all three compounds gave identical spectra. The series An4(O)X showed no quenching at 77K relative to the non-halogen containing compound.

The results for the anthracene are in agreement with results reported elsewhere and support the endothermic inter-system crossing process described in 1.6. Unfortunately they shed no light on the mechanism of the quenching process. For the naphthalene compounds however the results show quite clearly that both static and dynamic interactions are occurring in these compounds. The dynamic interaction is removed by freezing the compounds into a crystal lattice and the quenching observed in

this state is therefore due to static mechanisms. When n > 4

static interactions are not present and the quenching process

is entirely a dynamic one. However, the presence of a labile

bond in the molecule will provide an efficient decay mode if

energy transfer is possible. This will result in a loss of both

fluorescence and phosphorescence. The fact that AnlCl and AnlBr

fluoresce strongly at 77K indicates that there is no longer

sufficient energy to promote bond homolysis as in the case of

the naphthalene compounds. The nature of the static interaction

will be discussed further in 1.8.7.

1.8.6. Halogen Excited State C-T Complexes

There is already much evidence that the dynamic inter-

action and quenching occurs via a charge transfer exciplex

intermediate in intermolecular models. Hammond and co-workers[77]

have examined the intermolecular fluorescence quenching of 1,4-

dimethoxybenzene in acetonitrile by various alkyl chlorides, and

similarly Harriman and Rockett[78] have studied the intermolecular

quenching of alkanone fluorescence by alkyl halides in cyclo-

hexane. Both groups made quenching rate constant measurements

(which are quite obviously not possible by standard methods

for studies of intramolecular interactions) and then attempted

to correlate $\log_{10} k_q$ with ionisation or redox potential.

They found acceptable correlation, for example, for a series of

chlorides, or a series of iodides, but not for the compounds as

a whole. Indeed Rockett found that whilst chlorides and iodides formed distinct relationships the bromides seemed to be transitionary in character. When he looked at aryl halides however the relationship was good for PhCl, PhBr and PhI.

Further studies of the substituent effects on benzyl halides by both groups gave interesting results. Hammett type plots in both cases gave small positive ρ values for chlorides, 0.85 in acetonitrile[77] and 1.35 in cyclohexane,[78] indicative of the development of negative charge in the aromatic system. Rockett found that for the bromides and iodides the ρ values in cyclohexane were -0.41 and -1.85 respectively, suggesting that in this case the benzyl compound was acting as a donor.

The fact that aryl halides show a good correlation for $\log_{10} k_q$ vs I.P. but alkyl halides do not is argued as evidence that the lability of the C-X bond is a crucial factor. Aryl halides have stronger bonds than alkyl halides. Thus the easier it is for the C-X bond to dissociate then the larger is the quenching rate constant. Again this was borne out in Rockett's results where the order of quenching was tertiary > secondary > primary halide. This hypothesis is consistent with the results reported in this chapter.

The quenching mechanism is seen by Hammond as involving initially formation of an exciplex. The same mechanism can

hold for the intramolecular compounds studied in this chapter having n > 2, since the implication is of quencher and quenchee diffusing together to form the exciplex. Once communication between the electrons of the two species is established by means of the complex, coupling of vibrational modes and in particular with those of the C-X bond which could act as an energy sink can provide an excellent mode of radiationless deactivation.

The effect of solvent in this mechanism is important since any diffusional process will be subject to solvent parameters. As has already been noted very little solvent effect has been observed in the results reported here. In section 1.7 it was pointed out that the major effect of solvent might be expected to occur on the reorientation process between an initial encounter complex and a relaxed exciplex. If a relaxed exciplex is to be proposed as taking part in these interactions a significant effect of solvent might be expected. Numerous kinetic examinations[79,80] have been made which have omitted the non-relaxed species and any reactions occurring from it. Ware[80] has undertaken a complex analysis of rate constants and found excellent agreement between calculated values and those derived from observed data without including a non-relaxed exciplex in his equations. In his systems however the major intermediate was the relaxed exciplex since his calculations were based on the emissions observed from them. In

such systems as those in this chapter the particularly effect-
ive deactivating process which could occur before solvent
reorientation is probably far more important. This would
further explain why emission from an exciplex has not been
observed.

Brooks and Davis[81] studied the fluorescence quenching
of anthracene by anions. They found using a kinetic scheme
similar to one which will be discussed below, that there was
quite good correlation of log k_q vs ionisation potential but
not when spin-orbit coupling parameters were included. From
this they deduced that the quenching mechanism was one involving
an exciplex where the rate constant for heavy atom induced
triplet formation was less important than other deactivating
processes. Further evidence in support of this will be given
in 1.9.

The amount of C-T involved in the exciplex is a matter
of speculation. Hammond's and Rockett's results on the benzyl
halides suggest small amounts of charge transfer but this
would not necessarily apply to alkyl halides and could well
be even less. It has been suggested that it cannot be large
in view of the low C-T character observed in electron-poor
aromatic electron rich donor exciplexes studied by Taylor.[82]
Consequently it would be expected that exciplexes between

less electron poor aromatics and less electron rich donors

would have even less C-T character. Alkyl halides have, in

general, the facility of being able to donate or accept charge.

A non-bonding electron can conceivably be donated to a

sufficiently energetic acceptor whilst on the other hand the

lowest energy transition is of the type $\sigma^* \leftarrow n$ and addition

of an electron to the σ^* orbital is known to result in dis-

sociation. The order of ionisation potentials is usually

RI < RBr < RCl whilst the order of electron affinities is

RI > RBr > RCl. Prediction of the direction of charge donation

is therefore difficult and must depend on the ionisation pot-

ential and electron affinity of the quenchee. The change

over in charge donation to charge acceptance reported by the

halides in Rockett's study is undoubtedly due to the positioning

of the potentials for the alkanone on the scale, it seeming

likely that they fall in the middle, i.e. $\sim$9.7-10.0 eV, with

iodides at lower potentials and chlorides higher. (Alkyl

iodides have values typically 9.2-9.6 eV and chlorides 10.1-

11.0 eV). The use in this study of naphthalene, anthracene

and pyrene with ionisation potentials of 8.1, 7.4 and 7.4 eV

respectively indicates that donation from the aromatic to

the halogen is most likely but in the absence of the observation

of the exciplex this cannot be proved. This would be opposite

to the observations that amines and halogen anions[51] act as the

donors in exciplexes with aromatic hydrocarbons. These species

have lower ionisation potentials than alkyl halides and there are in any case no suitable vacant orbitals to accept an electron. In both these examples a high degree of charge transfer is present as evidenced by the large observed shift in λ_{max} for the exciplex in different solvents.

In the absence of any other conclusive evidence it seems that where dynamic complex formation applies to the molecules studied in this work, the wavefunction of the complex mentioned in 1.7 contains contributions from all of the terms. The amount of the contribution from each relative to the other will vary with the nature of R, X and possibly solvent. It seems likely that the contribution from the exciton resonance terms is the most appreciable.

1.8.7. The Mechanism in Intramolecular Quenching Reactions

The search for a mechanism to account for the various processes must first consider how to describe kinetically the dynamic quenching of the molecule $D-(CH_2)_n-A$. In his study of the naphthalene electron transfer system Szwarc[69] pointed out that where there is no 'through bond' effect of D and A they can be considered as separate species coming together in a 'bimolecular' interaction. If D is at the centre and A at the surface of an 'active sphere', the radius of the sphere R is dependent on the number of bonds (n + 1). This model

would cause A to have a minimum concentration within the sphere which he calculated and called C_{min}. However when he calculated the 'effective concentration' C_{eff} of A from his data he found that $C_{eff} < C_{min}$. In other words the linking chain was restricting the movement of D with respect to A, a not unnatural conclusion. In fact he found that $C_{eff} \propto (n + 1)^{1/2}$ when $n > 5$ but when $n < 5$ C_{eff} was reduced even more below C_{min}.

The quenching action involving the formation of the exciplex in a purely dynamic mechanism will be considered as a pseudo-bimolecular interaction:
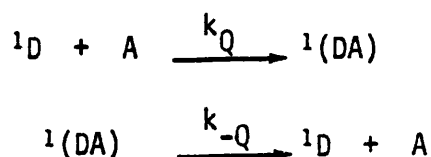
$$^1D + A \xrightarrow{k_Q} {}^1(DA)$$

$$^1(DA) \xrightarrow{k_{-Q}} {}^1D + A$$

$$\text{where } \frac{d}{dt}{}^1(DA) = k_Q [^1D][A]$$

(It will be assumed that the hydrocarbon is acting as the donor. This may not be true in all the molecules). The rate constant for the complex forming process is denoted by k_Q and for the reverse step by k_{-Q}. [A] can be called C_{eff} and is constant for each compound. The consequent dynamic quenching for a fixed concentration of substrate in solution will be a temperature dependent constant.

MECHANISM OF EXCITED STATE INTERACTIONS
IN HALOGEN CONTAINING AROMATIC SYSTEMS

$D\sim\sim A$ non-interacting

$(D\ A)$..........interacting

$$^{1}D\sim\sim A \underset{k_{-Q}}{\overset{k_Q}{\rightleftharpoons}} (D^*A) \leftrightarrow (D\ A^*) \leftrightarrow (D^+A^-) \leftrightarrow (D^-A^+) \leftrightarrow (^{1}D^{\sim}A)$$

Encounter complex

k_{ISC}

k_T

$^{3}D\sim\sim A$

k_F

k_{IC}

k_D

k_R

k_P

$D\sim\sim A$

Products
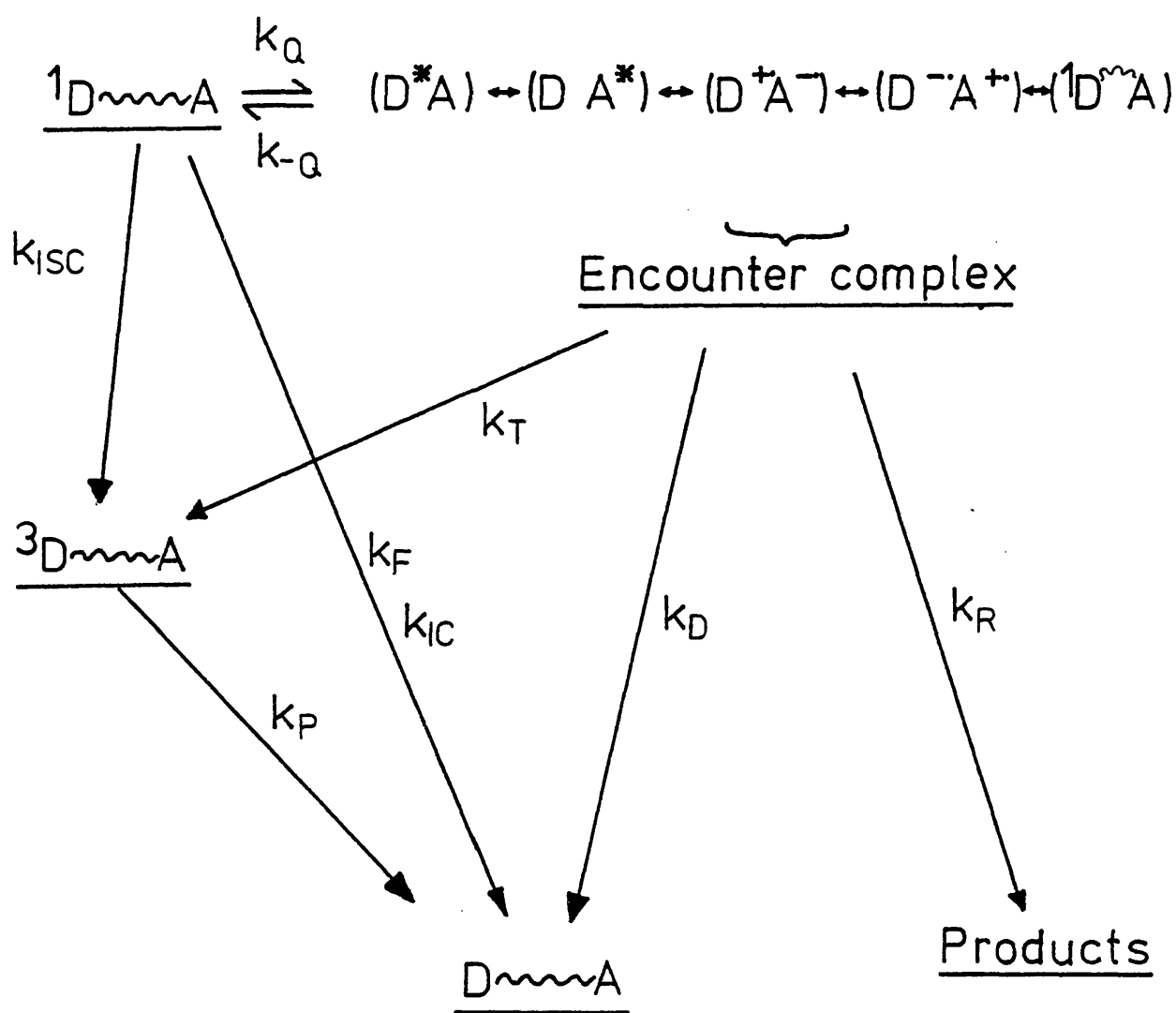
Fig.1.23.

A mechanism illustrating the various interactions is shown in Fig.1.23. It does not include the relaxed exciplex or any of its decay processes since there is no evidence for such a species in these compounds. A useful tool in understanding the results is the concept of an interaction surface. 'Surface' is used rather than 'sphere' because there must be a directional element attached to these interactions. In chapter two where aliphatic amines are discussed the interaction is via a strongly directional lone pair. It will also be shown how the angle of overlap appears to be unimportant but that the amine lone pair must be able at least to approach the aromatic system. A halogen has much more non-bonded electron density and the interaction surface will be larger and less directional than a single lone pair. Indeed the surface can be very large for an iodine or bromine in a molecule. The encounter complex is therefore deemed to be formed when the surface due to the quencher and that due to the quenchee intersect. The surface concept is useful because it gets away from the idea of the two species actually being in contact. There is enough evidence to show that complexation occurs over distances up to 9$\overset{o}{A}$. The surface can be thought of as following approximately the same shapes as the orbitals involved but probably extending farther in all directions. This approach leads to the possibility of two sorts of static interaction - one where the surfaces intersect and the other where they do not, the effect being relayed through the bonds

alone. The three types of interaction are thus

(1)   A dynamic through space interaction

(2)   A static through bond interaction

(3)   A static through space interaction

The simplest example of (1) is a molecule having a long enough chain such that the surfaces do not intersect when it is fully extended. Molecules having n > 3 appear to fall into this category. At normal temperatures the dynamic flexing motion brings the surfaces into contact to cause the observed perturbations but at low temperatures these are erased when the flexing is stopped. Interaction (3) occurs when the chain length is short enough to cause surface intersection at full extension. It may even be that full extension shows no overlap but other conformations cause interaction. In either case quenching will be observed at 77K, in the first because interaction is always present, and in the second because a large number of the statistical conformations lead to interaction. Examples of such compounds probably have n = 2, 3. Note that the dynamic interaction is probably present also and that whilst cooling will considerably increase the fluorescence yield, the reduction in observed quenching will not be complete in the solid matrix.

The series of compounds having n = 1 are probably a special case in that they are effectively complexes in the ground state. The interaction surfaces are permanently intersecting

and consequently the absorption bands are strongly perturbed. There can be very little of the dynamic mechanism in the halogen derivatives at least, and certainly there is very little difference in the emissions observed either at room or liquid nitrogen temperature, both being extremely weak. The interaction is of types (2) and (3) and the lability of the C-X bonds determines the properties of these compounds.

The through bond interaction (2) is perhaps a useful way of by-passing the need for the surfaces to intersect since the effect is transmitted through the linking chain. Since it is normally associated with short chains however it is found in conjunction with (3). Some of the compounds prepared by Turro[17] however appear to be exhibiting the through bond effect in isolation (Fig.1.6). It is hard to see how surfaces could intersect in the 3-exo and 7-exo derivatives and there is no question of a dynamic effect being involved. The perturbation in these compounds is so large that the through bond effect must be very much more significant than the static through space effect. The differences between the derivatives may well be due to the relative reactivities of the various types of C-Br bond which we have shown to be important. The 2-bromo compound where the halogen is 'benzylic' must have an exceptionally strong bond for its type because of the total lack of participation of the aromatic system. Nevertheless such perturbation as is observed is due to the surface intersection alone. The 3-endo and 7-endo probably have elements of (2) and (3) but it seems likely that

a strong steric repulsion of the aromatic and bromine in the

3-endo derivative will force the C_2-C_3 bond into a less favour-

able position for a through bond overlap. A small change in

bond angle can make a dramatic difference (cf. the opposite effect

of ArlX, 1.8.2.) thus explaining why the derivative is in fact

the least perturbed of all. There seems no doubt therefore of

the operation of through bond effects which while dominating

in rigid cyclic compounds are probably much less important in

acyclic compounds in solution at room temperature. It is

difficult to conclude further on the balance between the two

static effects other than to suggest that experiments could be

performed on highly sterically hindered molecules where both

aromatic and quencher are shielded. A static through space

interaction would be much more affected by strong steric inter-

actions. The results for the anthracene derivatives at 77K

unfortunately shed no light on the mechanism of the quenching

because of their   properties at low temperatures.

1.9. Results and Discussion of Triplet Studies

As has been discussed, the formation of the triplet

state of an aromatic hydrocarbon is affected by the presence

of heavy atoms such as halogens. Several definitive studies

exist[16,83,84] whereby triplet quantum yields of compounds can

be determined. One of these[83] involves the use of an external

heavy atom such as xenon which is ideally suited because of its

lack of reactivity. Studies described in this section with

some anthracene derivatives however show that an increase in

Φ_T, the quantum yield of triplet formation, is not always a

consequence of the introduction of a halogen atom into a system.

A halogen can influence triplet formation of an aromatic

hydrocarbon in two ways. If it is substituted close to the

ring it can directly alter the rate parameters such as k_{IC} and

k_{ISC} as we have seen. If it is present either in the molecule,

as in compounds described here, or as an intermolecular quencher

in solution, it can increase Φ_T by means of an exciplex inter-

mediate, the equations for which have already been indicated.

It has been assumed until now that by means of these two

mechanisms the heavy atom always causes an increase in Φ_T

(together with a decrease in the fluorescence quantum yield).

Results presented here show that this was not the case in the

TRIPLET YIELDS AND LIFETIMES OF ANTHRACENE DERIVATIVES.

	C_6H_{12}		MeCN	
	Φ_T	τ_T(ms)	Φ_T	τ_T(ms)
AnMe	0·71	0·42	0·65	0·35
$AnCH_2Cl$	0·51	0·26	0·37	0·11
$AnCH_2Br$	0·08	0·19		
$An(CH_2)_2Cl$	0·62	0·30		
$An(CH_2)_2Br$	0·53	0·24		
$An(CH_2)_2I$	0·53	0·23		
$AnCH_2OCOCH_3$	0·74	0·45	0·57	0·31
$AnCH_2OCOCH_2Cl$	0·62	0·31	0·59	0·36
$AnCH_2OCOCH_2Br$	0·88	0·50	0·53	0·35
$AnCH_2OCOCH_2I$	0·50	0·21	0·20	0·35

Table 1.11.

FLASH PHOTOLYSIS OF AnCH$_2$X IN CYCLOHEXANE
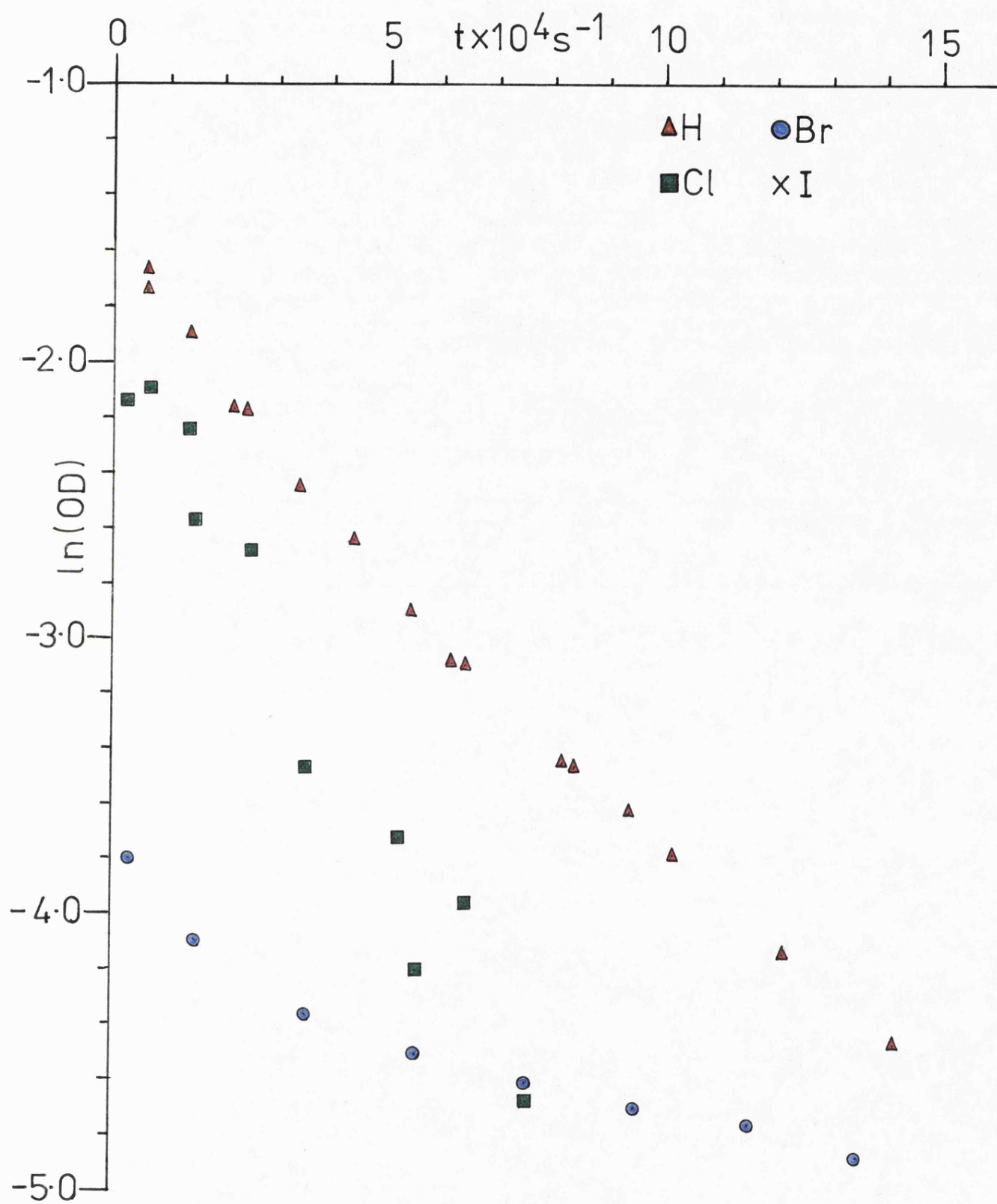
FIG.1.24.

FLASH PHOTOLYSIS OF An(CH₂)₂X IN CYCLOHEXANE
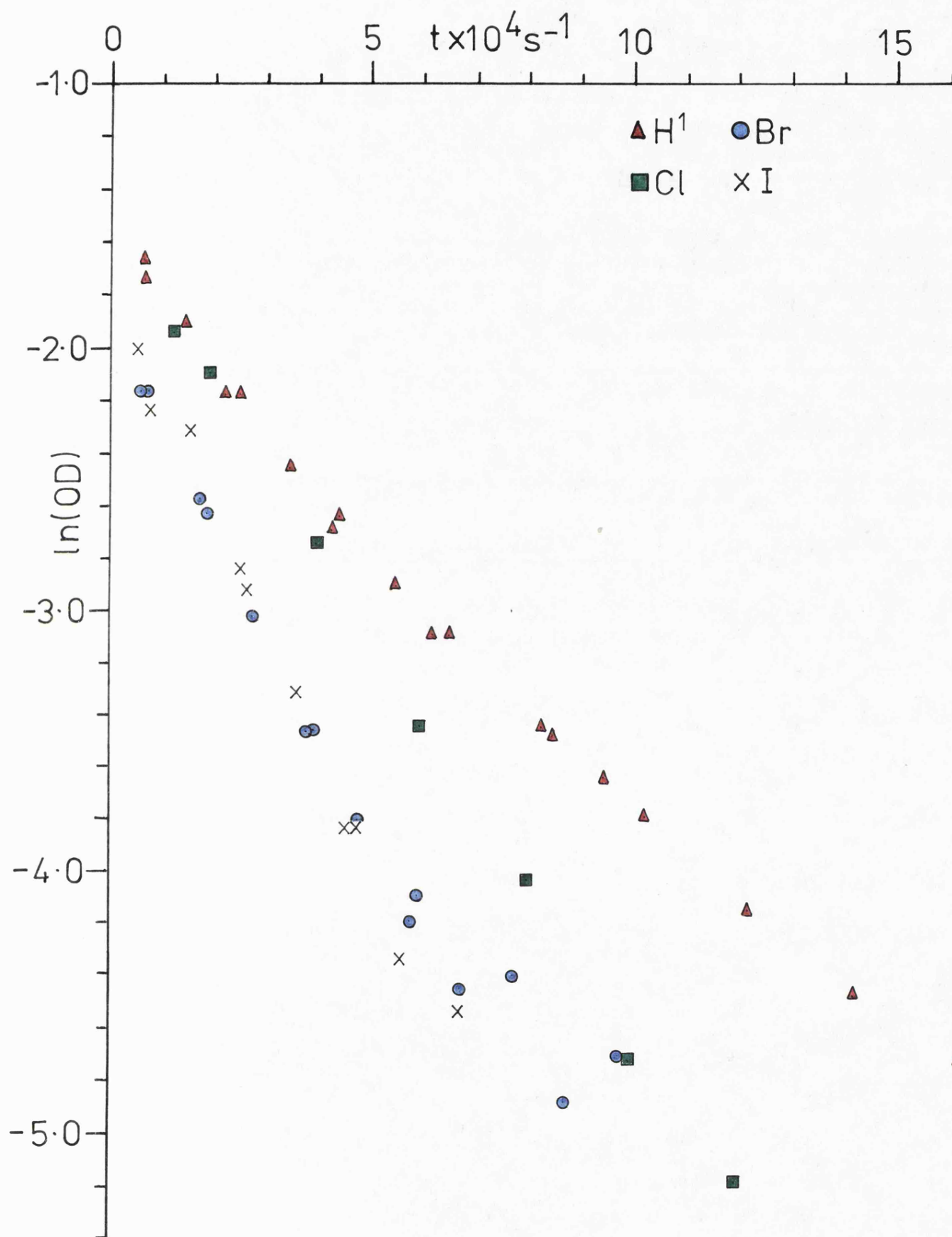
FIG. 1.25.

FLASH PHOTOLYSIS OF AnCH$_2$OCOCH$_2$X
IN CYCLOHEXANE
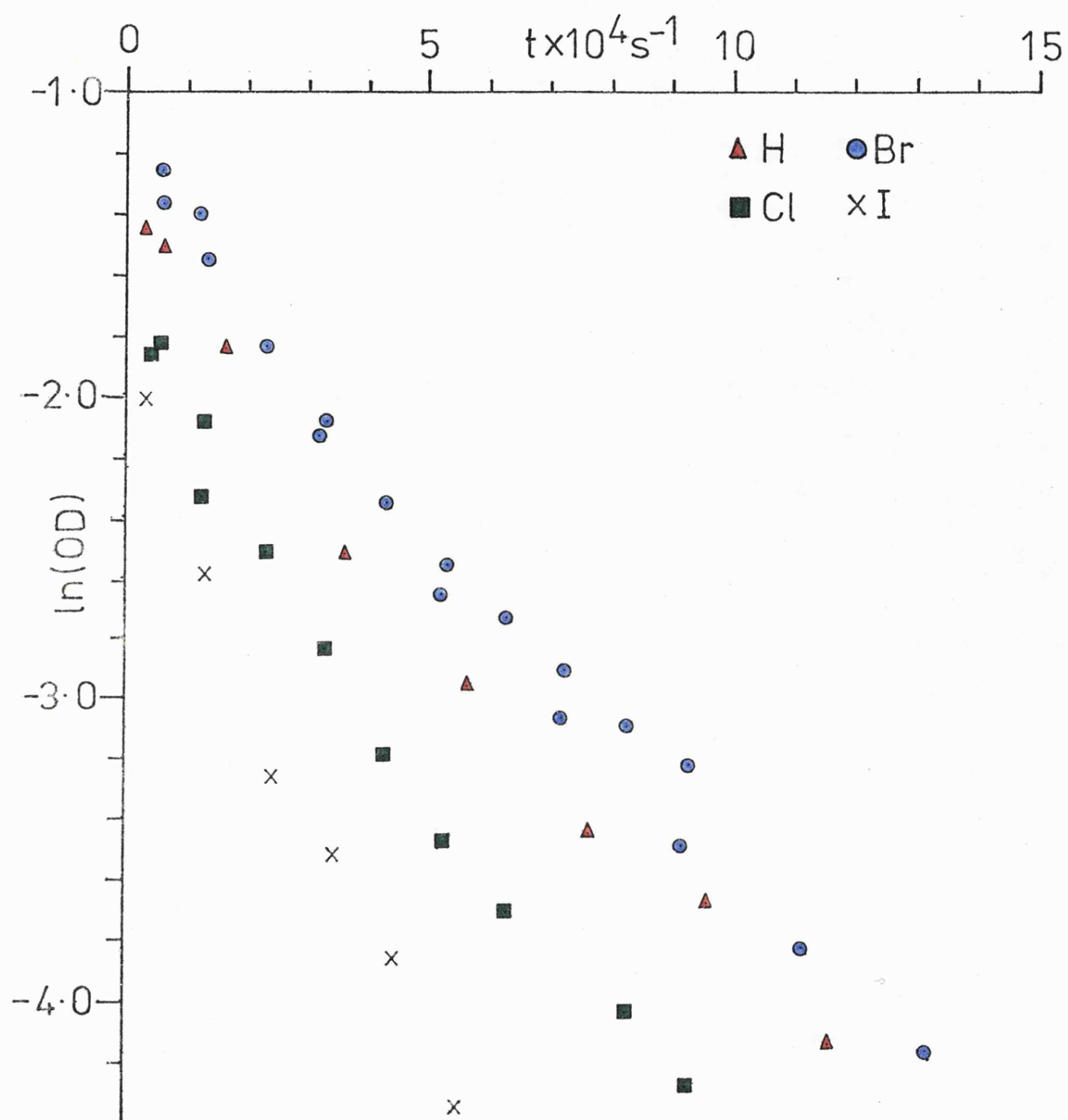
FIG.1.26.

FLASH PHOTOLYSIS OF An CH$_2$X
IN ACETONITRILE
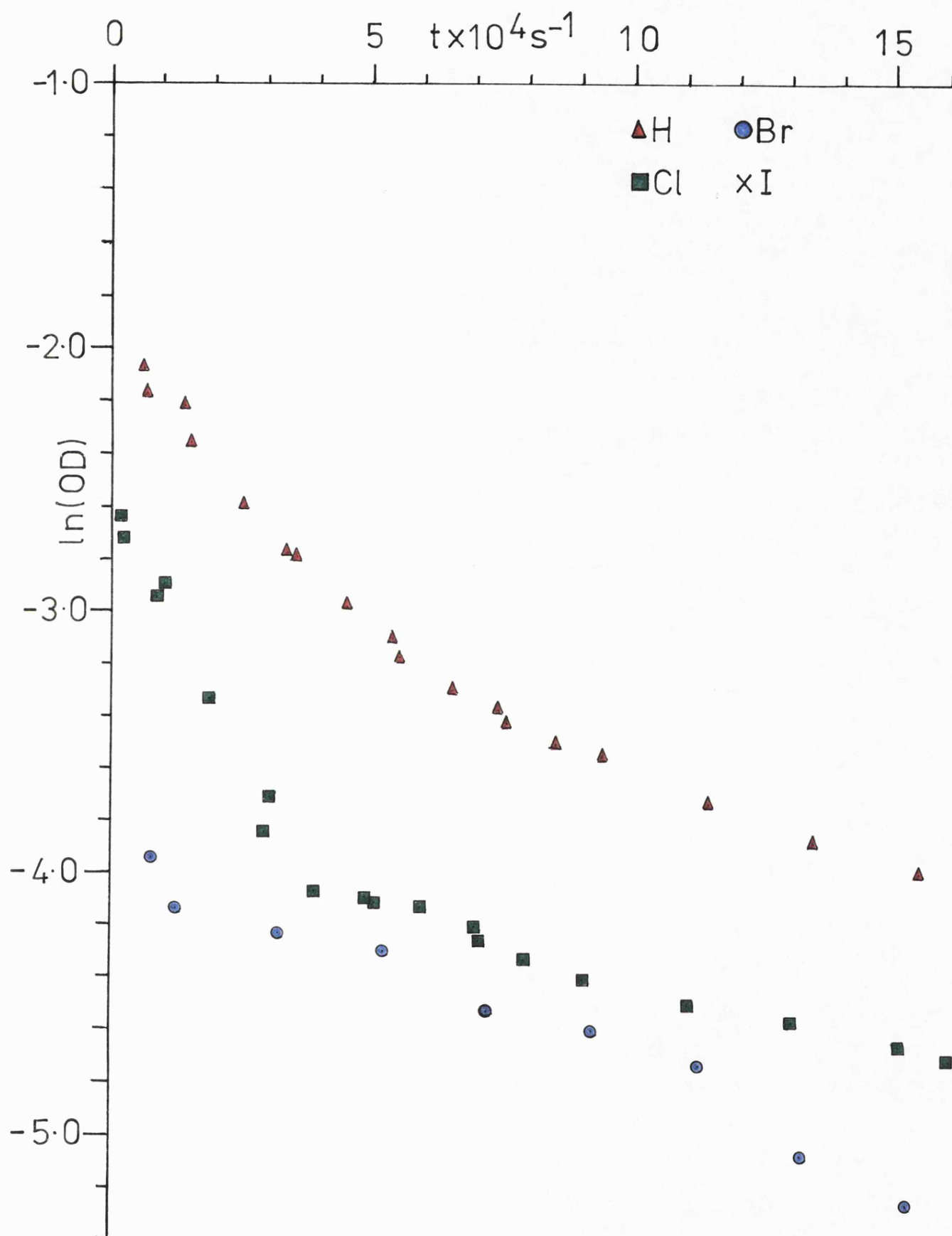
FIG. 1.27

FLASH PHOTOLYSIS OF $AnCH_2OCOCH_2X$ IN ACETONITRILE

84
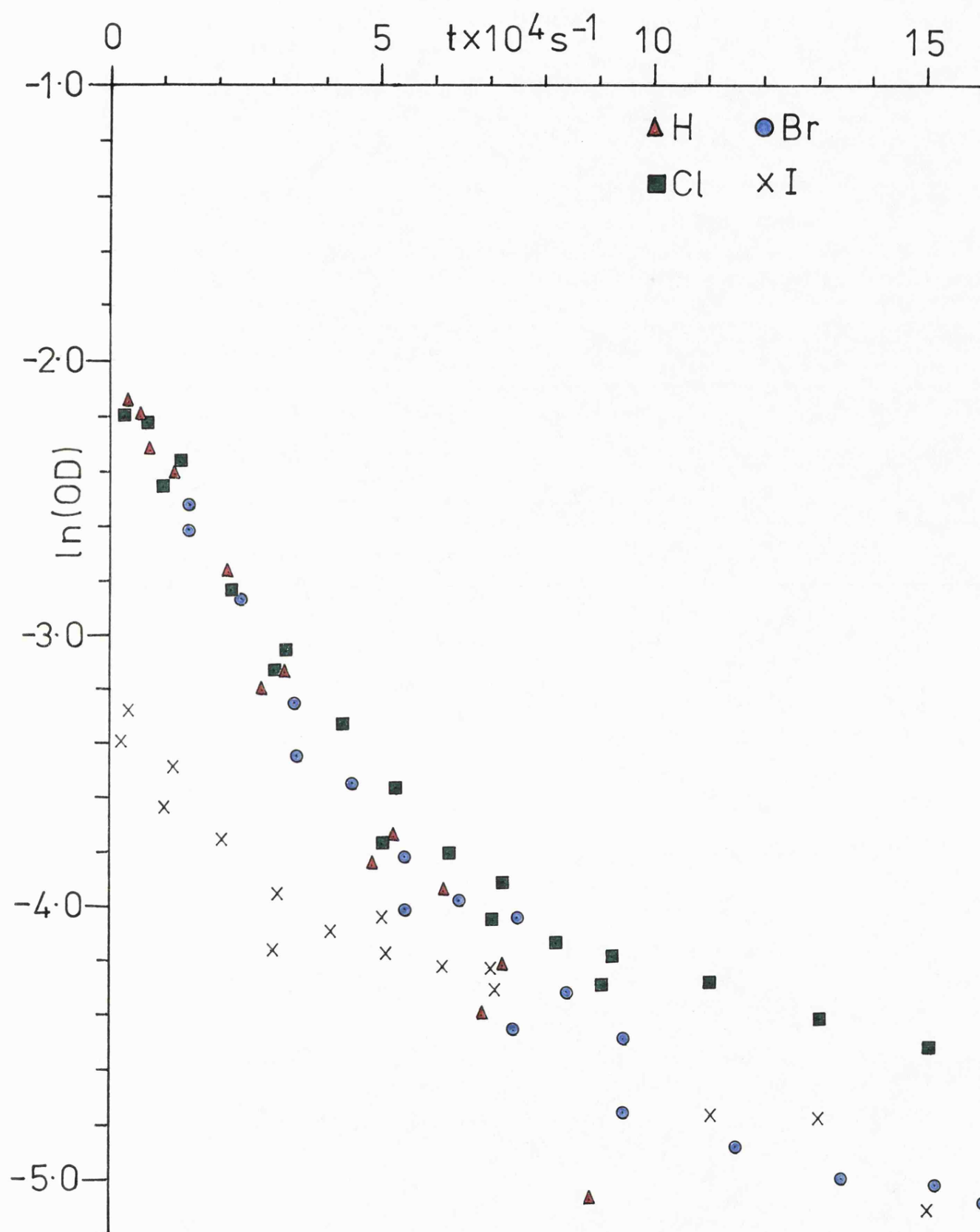
FIG.1.28.

compounds AnlX, An2X and An4(O)X.

The triplet-triplet absorption spectra were obtained by a standard flash photolysis technique using photographic plates. The spectra were then translated into graphical form using a microdensitometer. In order to obtain the triplet quantum yields and lifetimes the solutions were monitored at 425 nm using an oscilloscope and the traces recorded photographically. The changes in optical density with time were calculated from the photograph and assuming a first order decay mechanism a plot of $\log_e$ OD vs time was made. Extrapolation of the line to time zero gave the initial optical density of the triplets and the slope of the plot gave the rate constant for decay ($\tau_T = k^{-1}$). The assumption[16] was made that $\Phi_F + \Phi_T = 1$ for the standard compound 9-methyl anthracene and since $\Phi_F = 0.29, 0.35$ in cyclohexane and acetonitrile respectively then corresponding Φ_T values were 0.71 and 0.65. All other triplet yields were then calculated using the initial optical densities relative to the standard compound. A complete discussion of the analysis of the data is given in the Appendix (1.9). Figures 1.24 to 1.28 inclusive illustrate first order decay plots of the series examined. The results obtained in cyclohexane (1.24-1.26) all show reasonable first order decay although slight curvature is apparent in some of the components. (In almost every case a plot for a particular compound is a combination of two separate sets of results). Particularly well-

behaved was the series An2X. In acetonitrile (1.27-1.28) considerable deviations from linearity were observed in all cases. Reasons for this will be discussed later. Unfortunately the series An2X was not used in this solvent.

Table 1.11 contains the parameters evaluated and in cyclohexane meaningful conclusions can be made. The most important observation is that there is no dramatic increase in Φ_T counter-balancing the large decrease in Φ_F. (The unique result for An4(0)Br may be in error.) Indeed the trend is rather of decreasing Φ_T as the atomic weight $_\wedge$increases. There

$$of\ X$$

is a trend of reducing lifetime with atomic weight$_\wedge$although

$$of\ X$$

the reduction is small and can be taken as insignificant. It can be fairly concluded that in cyclohexane the relation[16]

$\Phi_F + \Phi_T = 1$ does not necessarily hold when a halogen is present in the molecule, such that there is a possibility of intra-molecular interaction. The reason for the lack of an increase in Φ_T is easy to discover when the processes of exciplex decay discussed in 1.7 and illustrated in Fig.1.23. are considered. Competing with the possible formation of triplets from the exciplex is a deactivating mechanism to ground state starting material together with a mechanism giving product formation. Either involves transfer of energy into the C-X bond and it seems quite certain that the product formation mechanism is important via dissociation of C-X. Inspection of the photo-

graphic plates where the ground state absorption spectra were recorded both before and after the series of flashes showed that in several cases depletion of the substrate had occurred. In particular the compound AnIBr showed high reactivity and probably provides an explanation for the particularly low Φ_T value in the table. It has already been noted that the C-X bond is especially labile in compounds of this type and depletion of the substrate may have occurred during the degassing process.

The flash photolysis results in acetonitrile presented problems of interpretation. Marked deviation from linearity of the first order decay plots for all except An4(O)H meant that extraction of meaningful rate data was difficult. The only firm conclusion which could be drawn was that there was again no increase in Φ_T as predicted by the simple heavy atom theory.

The results as a whole were not consistent with either a first or second order decay. The results for the early part of the decay were approximately consistent with a first order decay.

It is possible to imagine anthracene triplet decay in the presence of a heavy atom. This could cause deviations from linearity of the decay such as are exhibited by these results. Since the lifetimes concerned are longer,

a change of solvent would have a larger effect in this case

than in the fluorescence decay. (Deviations are present in

cyclohexane although to a lesser degree than in acetonitrile.)

There is also the possibility that radical ions may be present

although they normally have absorptions in a different region

of the spectrum. There was no indication on the photographic

plate of absorptions other than those of the anthracene ground

and triplet states. There is good evidence[85,86] to support

the formation of $ArCH_2 \cdot$ radicals in solution. This has been

observed for $PhCH_3$, αMeNp, βMeNp and the absorption band was

close to the triplet absorption in all cases. A conflicting

argument however is that the same behaviour might have been

expected in cyclohexane. Whether the slight deviations from

linearity in this solvent can be attributed to this explanation

is a matter of speculation. Again, if this were the case

An4(0)H in MeCN might not have been expected to be so well-

behaved. If a radical species were an intermediate it would

be likely to decay by more than one mechanism, leading to

decay kinetics of intermediate order in agreement with the data.

The behaviour of the compounds in acetonitrile solution

can only be explained in terms of a complex mechanism leading

to a composite picture of more than one decaying species if

they are not taken as the product of an artefact. Deviations

from linearity of the compounds AnlX and An4(0)X in cyclohexane

together with the known lability of the C-X bond indicate that

the presence of intermediates other than the triplet state molecule is not only possible but likely. The much more stable An2X compounds and the good linearity obtained supply reliable results which are reinforced by the trends of the other compounds.

The comparison with the results showing phosphorescent enhancement for the naphthalene compounds in solid matrix at 77K is surprising. This observation must lead to the conclusion that an enhancement of the triplet yield is occurring in these compounds where there is not a particularly reactive carbon-halogen bond. Unfortunately no flash photolysis data on the naphthalene derivatives are available to confirm this prediction.

1.10. Conclusions

The intramolecular interactions of halogen containing aromatic compounds consist either of a simple heavy atom effect or a partial charge transfer complex (or both) depending on the compound. The mode of interaction is by dynamic through space, static through space or static through bond mechanisms and the balance between them has been discussed. Remarkable perturbations have been observed in 'benzyl' type compounds due largely to the extreme lability of the $C-X$ bond, a factor which is of importance in the decay mechanisms even of unactivated halogens. Enhancement of phosphorescence has been observed by

halogens 'remote' from the aromatic ring in solid matrix,
evidence of the distance over which static interactions can
occur. Other effects on the parameters of the aromatic by
remote quenchers have been observed and attributed to static
effects of either the molecule itself or its encounter complex.
Studies on the anthracene triplet yields showed that there was
not necessarily a heavy atom induced enhancement of triplet
states, the yield being strongly dependent on the reactivity
of the C-X bond present.

1.11. Experimental

The compounds used in this chapter were prepared or pur-
chased as detailed in Chapter four.

1.11.1. Fluorescence

All quantum yield and other emission determinations were
carried out using a Perkin-Elmer MPF-4 spectrofluorimeter.
Solutions were made up to an optical density of 0.1 at the
following wavelengths of excitation: 1- and 2-naphthalenes,
305 nm; 9-anthracenes, 350 nm; 1-pyrenes, 340 nm. Solution
optical densities were obtained on a Pye-Unicam SP1800 spectro-
meter and absorption spectra run on a Pye-Unicam SP800 spectro-
meter. 1 cm path length quartz cells were used in all cases.
Solutions of naphthalene and pyrene derivatives were degassed

using three consecutive freeze-thaw cycles in liquid nitrogen, evacuating to a pressure of 10^{-3} mmHg or less. A specially designed reusable quartz cuvette was used in this procedure. Benzene cyclohexane and methyl cyanide spectroscopic solvents were all Merck 'Uvasol' grade supplied by Anderman and Co. Ltd., and showed no emission at maximum gain over the wavelengths used. Quantum yields were all determined relative to an aerated solution of a standard compound at the same excitation wavelength. The standard compounds used were 1- and 2-methyl naphthalene, 9-methyl anthracene and pyrene. Values for the quantum yields of these compounds were taken from ref.63. 1-Methyl naphthalene was distilled prior to use; 2-methyl naphthalene was distilled and chromatographed. The quantum yields were determined by measuring the areas contained by the spectra using a planimeter and comparing with the standard compound. Approximate fluorescent lifetimes were obtained by comparing the quantum yields in degassed and aerated solution.

1.11.2. Flash Photolysis

These results were obtained using a standard microsecond flash photolysis apparatus equipped to give either an absorption spectrum directly onto a photographic plate or a decay curve at a pre-determined wavelength via a Dynamco oscilloscope with a 'Polaroid' photographing attachment. A specially designed degassing cell with pyrex windows and pathlength of 20 cm was

used. All solutions were 10^{-5} M in substrate. Cyclohexane

was May and Baker reagent used unpurified, and acetonitrile

Koch Light puriss fractionated from phosphorus pentoxide.

All solutions were degassed using the same procedure as in the

fluorescence measurements. Results were calculated by a method

described in Appendix 1.9 and using a PDP11 computer.

1.11.3. Matrix Emission Studies

The compounds were examined by preparing solutions O.D.

0.3 at 305 nm in 1 cm cells. The emission spectra were obtained

by means of thin circular cells, internal radius 1 mm in frozen

methylcyclohexane at liquid nitrogen temperature, 77K. All

solutions were degassed. Quantum yields were obtained by com-

parison with 1-methyl naphthalene using the values quoted in

Table 1.1b.
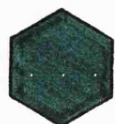
CHAPTER 2:

The intramolecular excited state interactions of amine-containing polycyclic aromatic hydrocarbon derivatives.

I'm beginning to see the light.
                                        —Popular.

2.1. Introduction

This chapter is devoted to the study of intramolecular excited state interactions between aromatic hydrocarbons and amines to form charge transfer complexes. These are commonly known as exciplexes. The first exciplex of this kind was observed in 1963 by Leonhardt and Weller[87] when they noted a new structureless fluorescence band in the spectrum of perylene quenched by aromatic amines. It was observed only in non-polar solvents and there was no sign of a change in the absorption spectrum. The new emission was attributed to the formation of an intermolecular charge transfer complex in the excited state and christened 'exciplex' by way of abbreviation.

An introduction to the formation of exciplexes has been given in section 1.7. and some of the processes by which deactivation can occur have been discussed.

The intramolecular exciplex formation by aromatic hydro-carbons and amines similar to those described here has already received attention. Having established the geometrical requirements for intramolecular excimer formation in a series of compounds of the type $Np-(CH_2)_n-Np$, Chandross and his co-workers[34] went on to look at the geometrical requirements of compounds such as $Np(CH_2)_nNMe_2$,[75] for 1- and 2-naphthalene derivatives and n = 1 to 4. Brimage and Davidson[88,89] looked at the series $1-Np(CH_2)_nNEt_2$ and $9-An(CH_2)_nNEt_2$ for n = 1 to 3, and Davidson and Lewis[33,90] have

studied molecules of the type 1- and 2-$NpCO_2(CH_2)_2NR_2$ and 1- and 2-$NpCH_2CO_2(CH_2)_2NR_2$.

Work in this chapter has extended the studies of the previous workers and in particular of Chandross and Thomas,[75] both qualitatively and quantitatively.

In their classic study on intramolecular excimer formation Chandross and Dempster[34] found the geometrical requirements for the formation of an excimer to be quite strict, as also did Hirayama[71] in similar studies of benzene excimers. Emission from an excimer was only observed when three methylene units formed the linking chain and the two naphthalene rings were substituted in the same position. The conclusion from this result was that only in these cases could the molecules adopt a configuration where the aromatic planes were parallel and in the form of a 'sandwich'.

The conditions for the formation of an exciplex with amines, for example, were found to be far less demanding. Chandross and Thomas[75] found no exciplex emission for n = 1 and observed it from n = 4 only at low temperature. In the cases where n = 2, emission was observable from an exciplex at room temperature but in n = 3 the exciplex emission was very strong to the point of almost total suppression of the monomer emission. Some of the spectra obtained are illustrated in

Fig.2.1. As the temperature was reduced the exciplex emission reached a maximum intensity and ultimately disappeared leaving only monomer emission in the frozen matrix.

The lack of observation of an exciplex when n = 1 was ascribed to the poor overlap between the nitrogen lone pair and the π cloud. When n = 4 it was assumed that whilst overlap was possible it was rendered less favourable by the necessity for eclipsed hydrogens in the best conformation for overlap. Whilst a similar situation pertained in the n = 2 case, the most favourable n = 3 compound (as in the excimer case) seemed to combine all the optimum requirements of lone pair π cloud overlap and staggered conformation of the linking chain. The fluorescence intensity of the monomer was observed to parallel the exciplex intensity for n = 2 - 4, strong quenching of the monomer occurring when the complexation was large and vice versa. In the cases where apparently no exciplex formation was possible strong quenching of the monomer was observed (n = 1).

When the amine was altered from a dimethyl to a diethyl derivative, Brimage and Davidson[88] observed some interesting differences. The n = 2 case showed a stronger exciplex emission than had been observed by Chandross and a small exciplex emission was observed when n = 1 in benzene and acetonitrile. The general trend of the results however was the same as obtained by Chandross and the differences could be ascribed to a lower ionisation potential

in the diethyl case allowing a greater degree of complex formation.
The dipole moments were calculated and found to be 11.4 D for
n = 2 and 14.0 D for n = 3. The value calculated for the complete
transfer of an electron is 16.8 D, indicating that a high degree
of charge transfer had occurred.

Results reported here form an extension to the work
summarised above and exhibit relationships to that described in
Chapter one. Parts of the discussion in that chapter are there-
fore strongly relevant to the arguments in this. The compounds
synthesised are described in chapter four and were prepared by
standard procedures. The compounds are all derivatives of 1- and
2-naphthalene and 9-anthracene. The linking chains used were
$-(CH_2)_n-$ for n = 1 to 4, $-CH_2OCH_2CH_2-$ and $-CH_2OCOCH_2-$. The amines
used were derivatives of diethylamine, tertiary butylamine, aniline
and N-methylaniline. For brevity the compounds will be referred
to by abbreviations which are described at the start of this thesis.
The absorption spectra of Ar4N and Ar4(O)P, together with the
anilines are shown in Fig.2.2. The fluorescence spectra for the
compounds studied in cyclohexane and acetonitrile at room temperature
are shown in Fig.2.3.-2.16. The quantum yields for $\alpha,\beta nE$ and
$\alpha,\beta nN$, both of the monomer and exciplex (where it was possible to
distinguish between them) are listed in Tables 2.1.-2.3. Table
2.4. shows the fluorescence yields for the compounds having an
ether (4') link and Table 2.5. the yields for compounds with an
ester (4(O) link. The data listed in Table 2.6. are fluorescence
yields for the An4(O)Am series.

FLUORESCENCE SPECTRA OF RELATED COMPOUNDS.

1-Np(CH$_2$)$_n$NMe$_2$

methylcyclohexane

2-Np(CH$_2$)$_n$NMe$_2$

- n=2
- n=3
- n=4
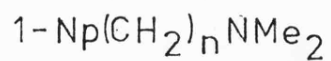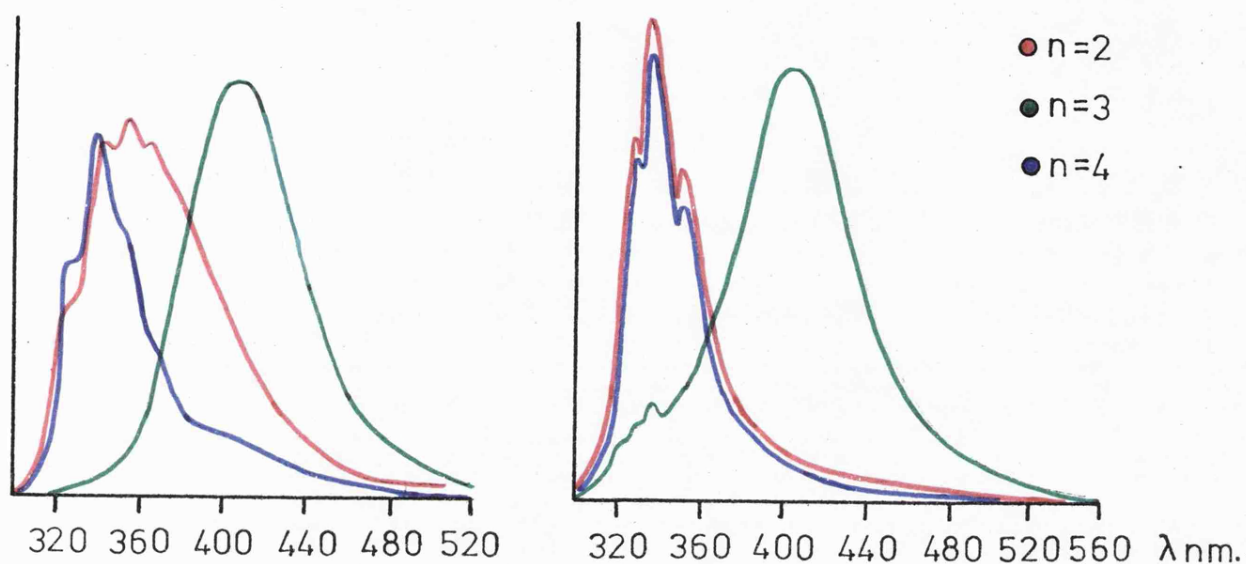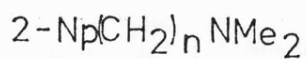
Chandross and Thomas, Chem. Phys. Letts., 9, 393, (1971).

Fig. 2.1

Emission spectra of 2-NpCH$_2$NEt$_2$ in different solvents.

Solvent	$\Phi_{mon.}$	$\Phi_{exc.}$	λ_{max}
cyclohexane	0·019[1]		
benzene	0·001	0·006	405
dichloromethane	0·003	0·004	440
ethyl acetate	<0·001	0·004	445
ethanol	0·003	0·002	470
acetonitrile	0·018	0·006	495

[1]Total emission.

Table 2.1

Absorption spectra in cyclohexane

Fig. 2.2.

Emission spectra of

CH$_2$NEt$_2$

in

- benzene
- dichloromethane
- ethyl acetate
- ethanol

(λ_{ex} 290nm.)

Intensity

Fig.2.3.

Emission spectra of

(CH$_2$)$_n$NEt$_2$

in cyclohexane

n = 1   ● X100
n = 2   ● X3
n = 3   ● X10
n = 4   ● X30

Intensity

nm.

Fig. 2.4.

Emission spectra of
(CH₂)ₙNEt₂

in acetonitrile

n=1 ● X100
n=2 ● X30
n=3 ● X30
n=4 ● X100

Intensity.

nm.

Fig. 2.5.

Emission spectra of
(CH₂)ₙNEt₂

in cyclohexane

n=1 ● X30
n=2 ● X3
n=3 ● X3
n=4 ● X10

Fig.2.6.

Emission spectra of
(CH₂)ₙNEt₂

in acetonitrile

n=1 ● X30
n=2 ● X30
n=3 ● X10
n=4 ● X100

Intensity

nm.

310 350 400 450 500 550 600 650

Fig.2.7.

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Emission spectra of
(CH$_2$)nNMePh

in cyclohexane

n=1   X100
n=2   X3
n=3   X10
n=4   X30

Intensity.

105

500 nm.

450

400

350

310

Fig.2.8.

Emission spectra of

(CH₂)ₙNMePh

in acetonitrile

n=1	●	X100
n=2	●	X10
n=3	●	X10
n=4	●	X100

Intensity.

nm.

106

Fig.2.9.

Emission spectra of
(CH₂)ₙNMePh
in cyclohexane

n=1 ● X100
n=2 ● X10
n=3 ● X3
n=4 ● X30

Intensity.

Fig. 2.10.

Emission spectra of

(CH₂)ₙNMePh

in acetonitrile

n=1 ● X100
n=2 ● X10
n=3 ● X30
n=4 ● X100

Intensity.

nm.

Fig.2.11.

108
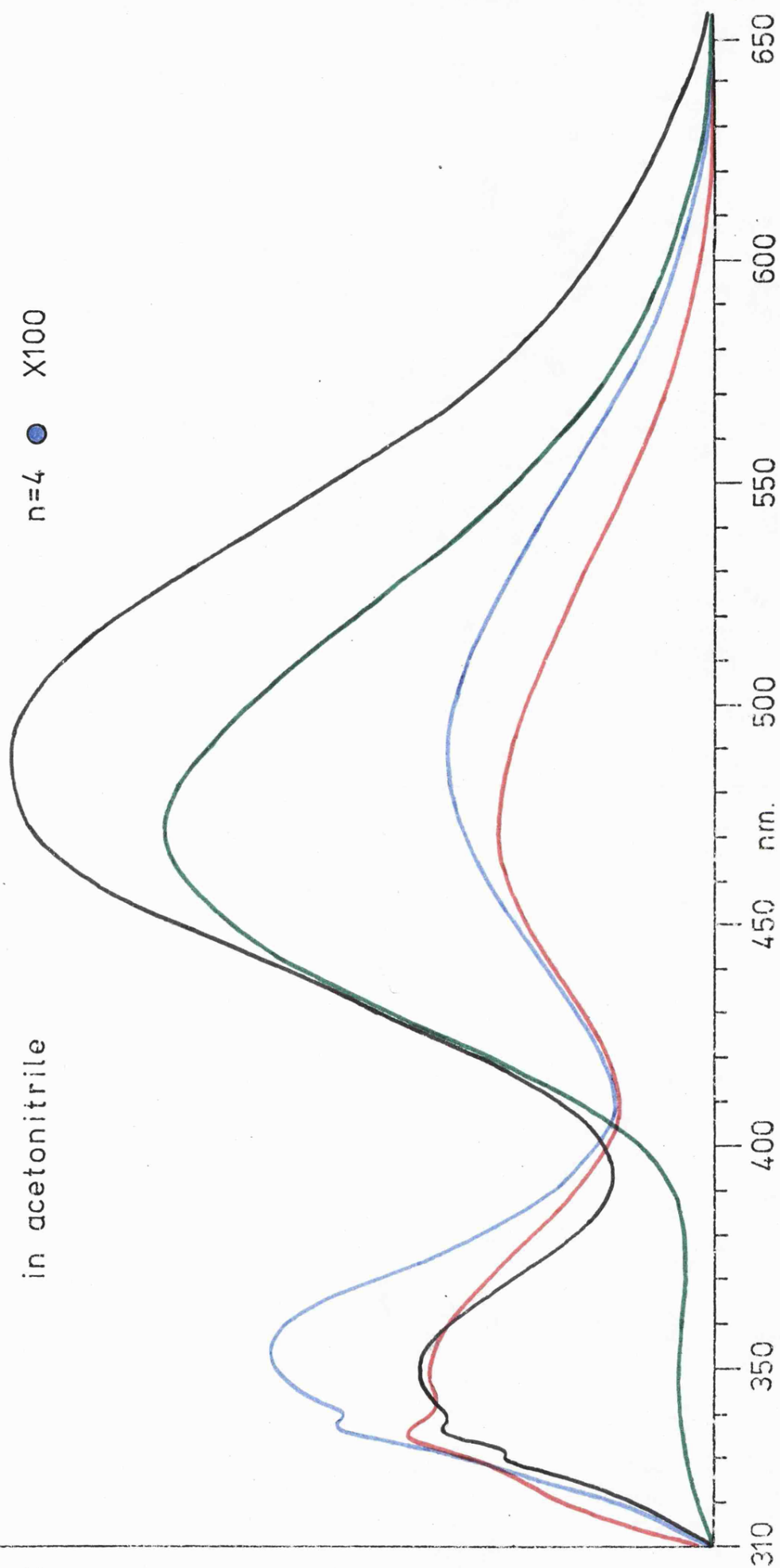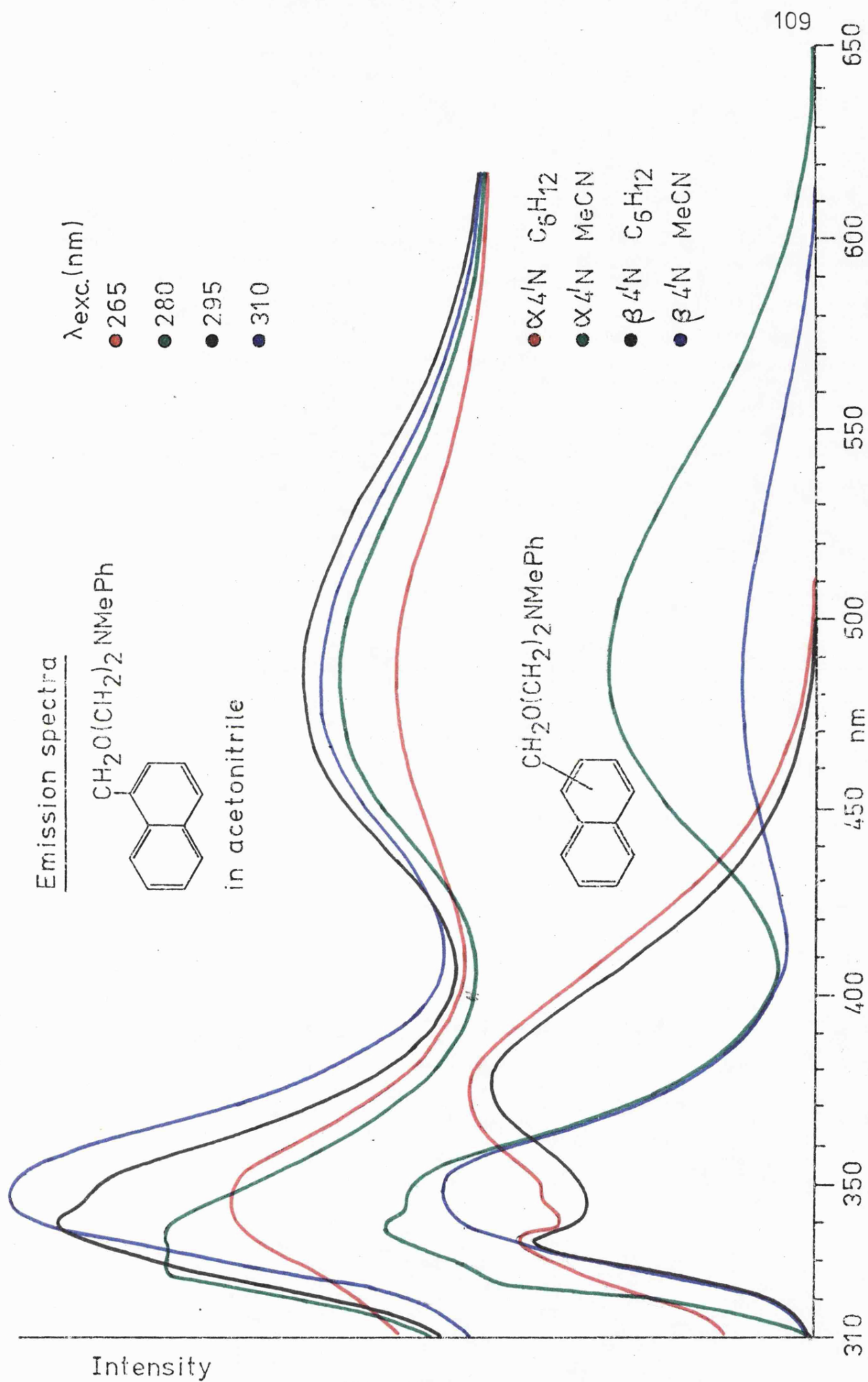
Fig. 2.12.

EMISSION SPECTRA OF 1- AND 2-NpCH$_2$OCOCH$_2$NR$_2$ IN CYCLOHEXANE

2-Np

NH^{t}Bu ● ×3
NEt$_2$ ● ×30
NHPh   ● ×30
NMePh   ● ×100

1-Np

NH^{t}Bu ● ×10
NEt$_2$ ● ×100
NHPh   ● ×100
NMePh   ● ×30

Intensity.

Fig. 2.13.

Emission spectra of

$CH_2OCOCH_2NR_2$

in acetonitrile

NH^tBu	●	x30
NEt_2	●	x100
NHPh	●	x100
NMePh	●	x100

Intensity.

Fig. 2.14.

Emission spectra of

CH₂OCOCH₂NR₂ — (2-naphthyl structure)

in acetonitrile

NH^tBu ● x3
NEt₂ ● x30
NHPh ● x100
NMePh ● x100

Intensity

nm.
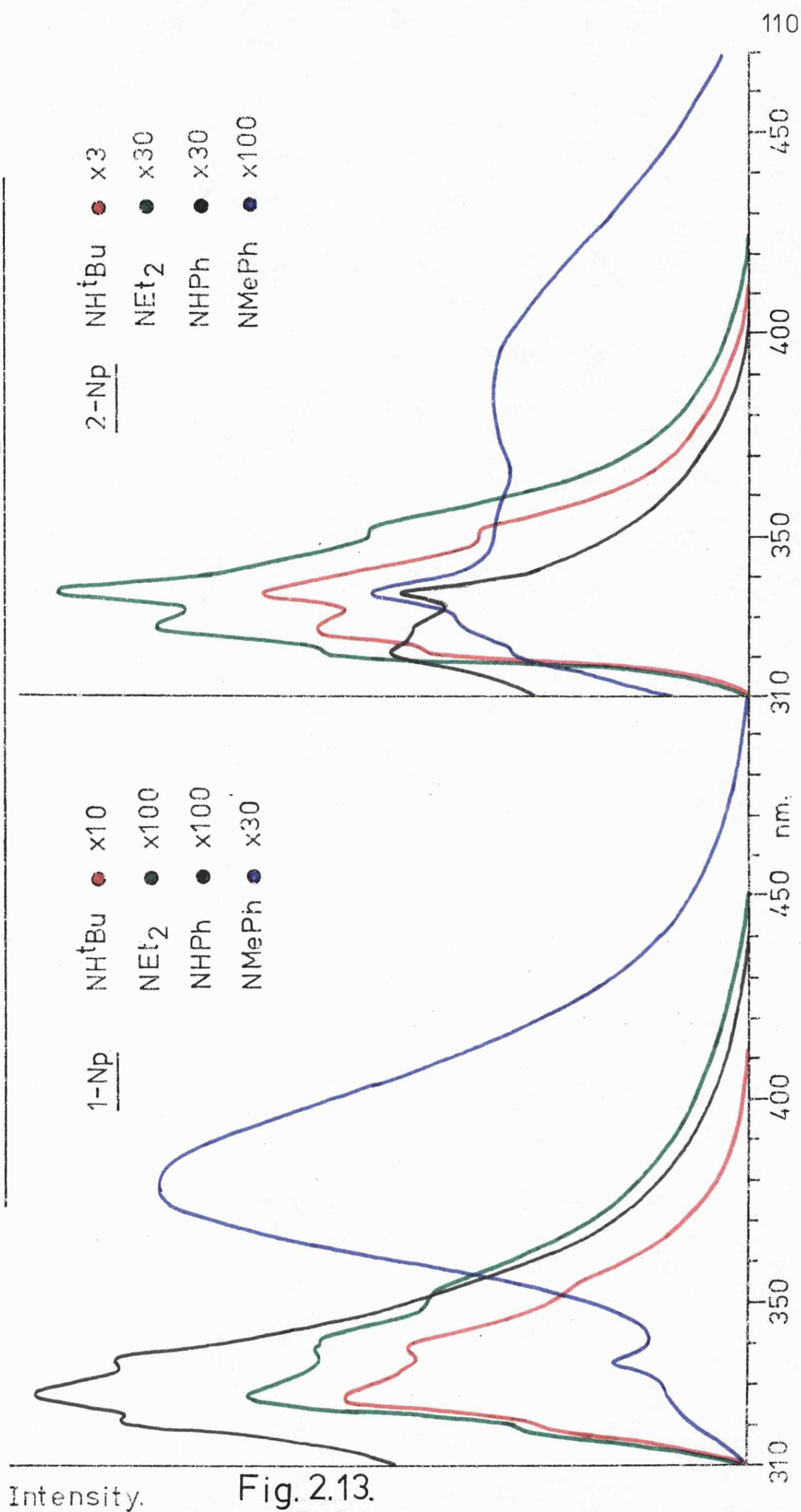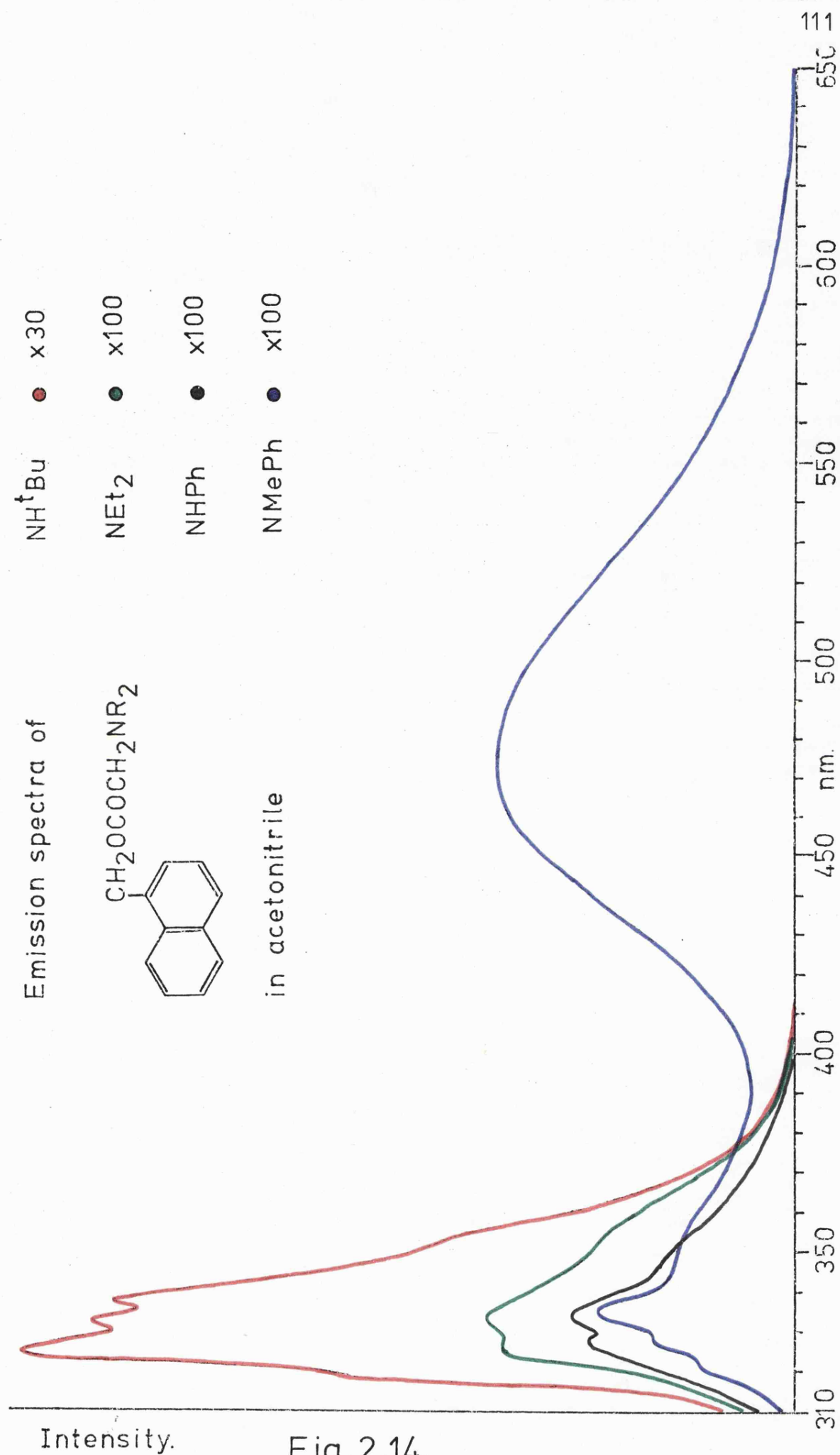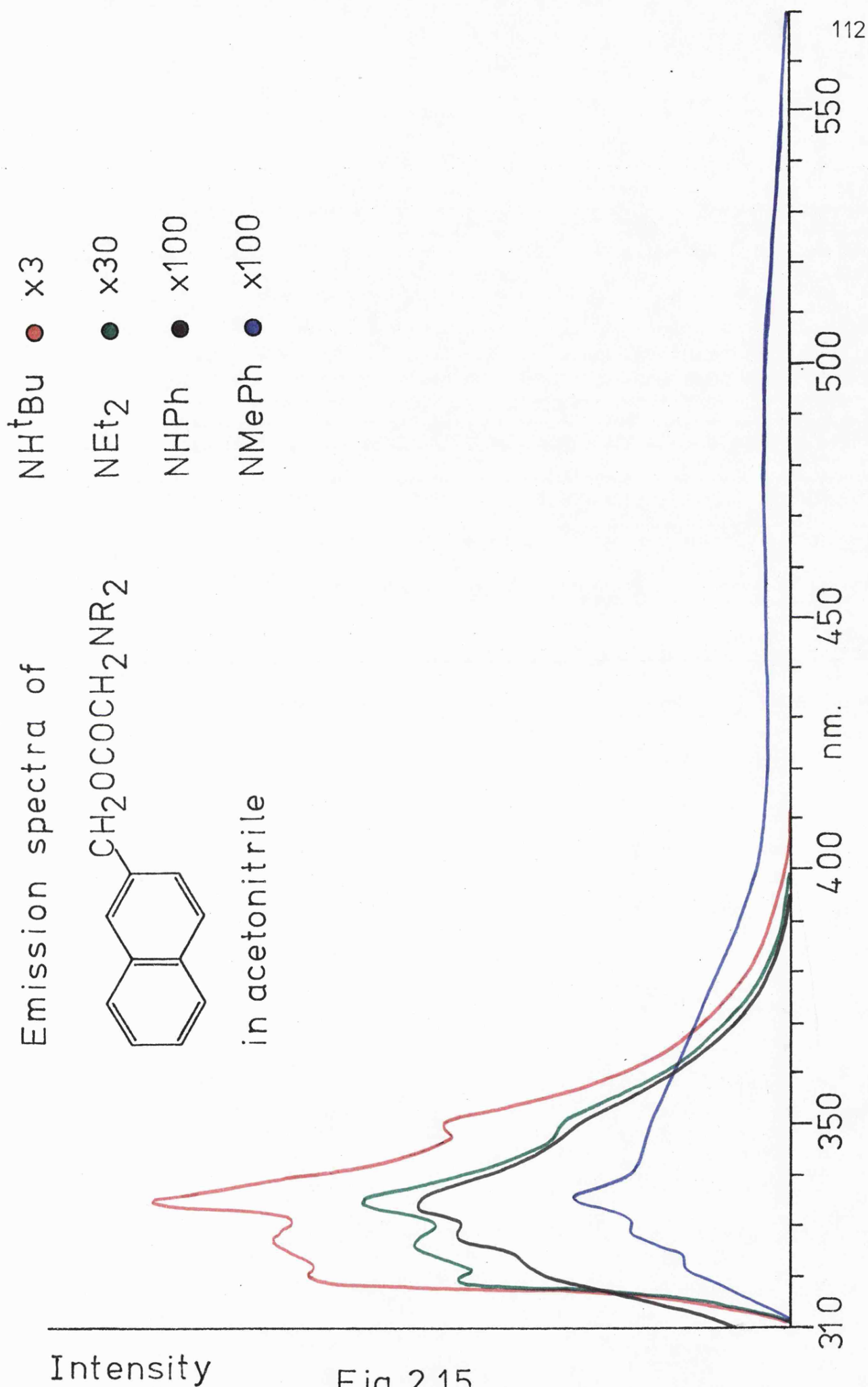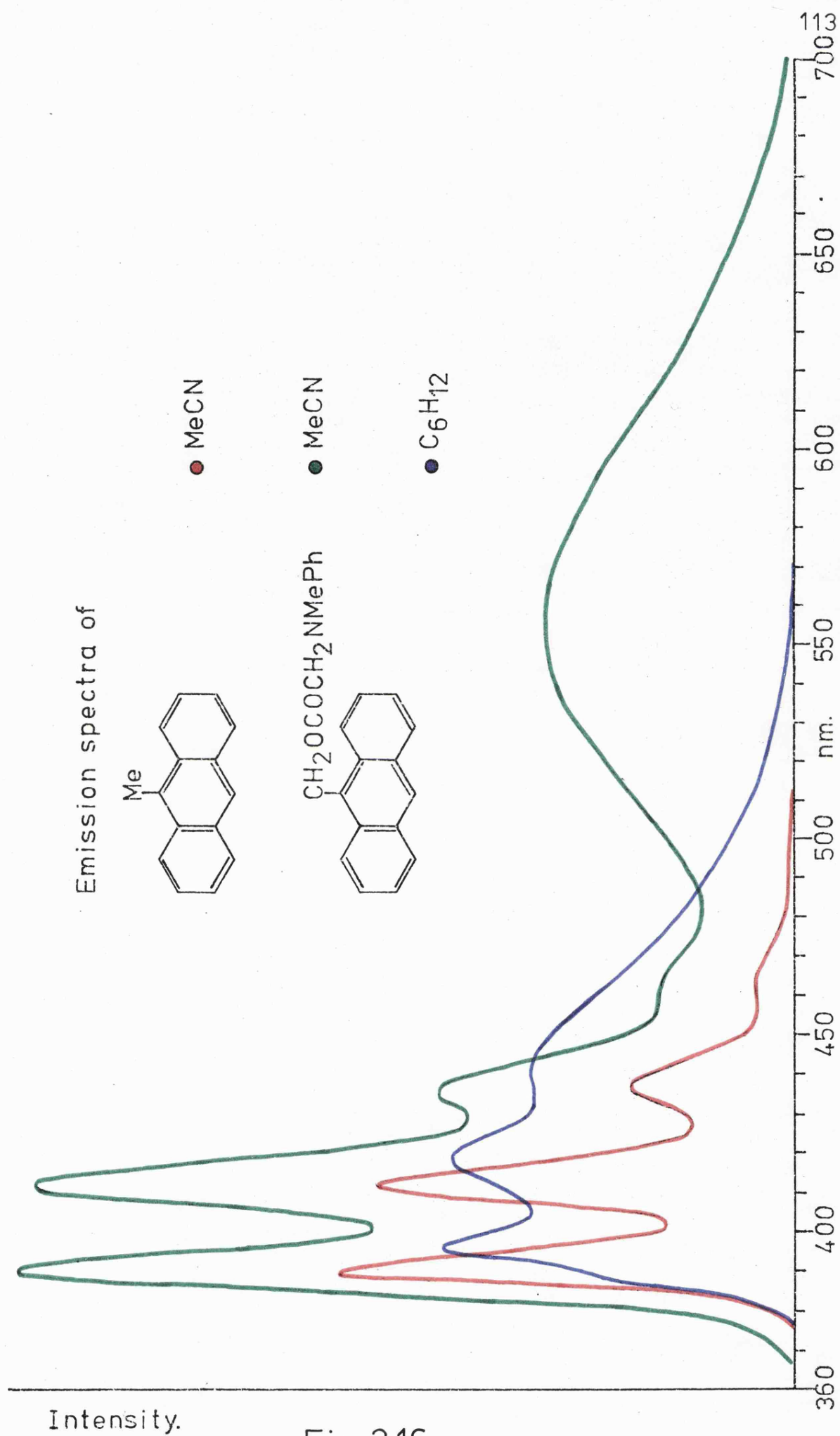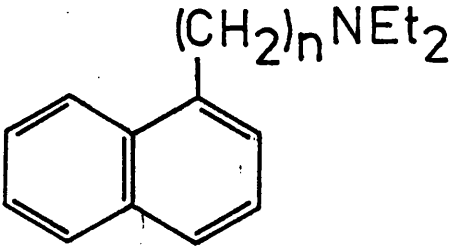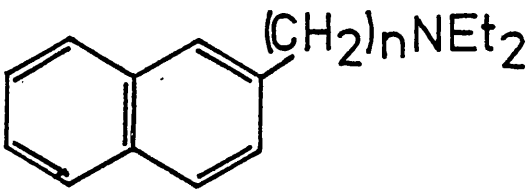
Fig. 2.15.

Fig. 2.16.

QUANTUM YIELDS FOR

1-AND 2-Np$(CH_2)_n$NEt$_2$.
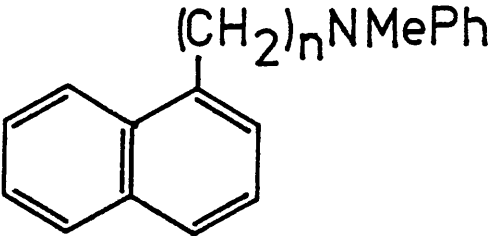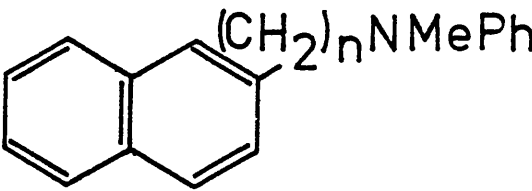
n	$(CH_2)_n$NEt$_2$ (1-naphthyl)		$(CH_2)_n$NEt$_2$ (2-naphthyl)	
	cyclohexane			
	Φmonomer	Φexciplex	Φmonomer	Φexciplex
1	0·005[1]		0·019[1]	
2	<0·001	0·406	0·186[1]	
3	0·010	0·200	0·115	0·216
4	0·031	0·034	0·113	0·034
	acetonitrile			
1	0·006[1]		0·018	0·006
2	0·008	0·040	0·003	0·028
3	0·012	0·015	0·070	0·010
4	0·008	0·002	0·012	0·002

[1] Φ Total emission

TABLE.2.2.

QUANTUM YIELDS FOR

1-AND 2-Np(CH$_2$)$_n$NMePh.
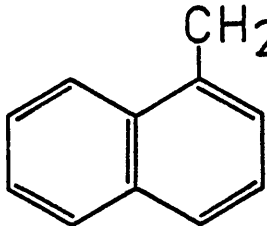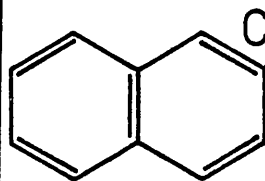
n	$(CH_2)_n$NMePh (1-naphthyl)		$(CH_2)_n$NMePh (2-naphthyl)	
cyclohexane				
	Φmonomer	Φexciplex	Φmonomer	Φexciplex
1	0·005[1]		0·007[1]	
2	0·008	0·214	0·002	0·055
3	0·018	0·172	0·008	0·180
4	0·007	0·069	0·003	0·106
acetonitrile				
1	0·006	<0·001	0·005	0·007
2	0·007	0·102	0·005	0·143
3	0·066	0·028	0·009	0·050
4	0·012	0·010	0·011	0·016

[1] Φ Total emission

TABLE.2.3.

QUANTUM YIELDS FOR

1-AND 2-NpCH$_2$O(CH$_2$)$_2$NR$_2$.

CH$_2$O(CH$_2$)$_2$NEt$_2$		CH$_2$O(CH$_2$)$_2$NEt$_2$	
cyclohexane			
Φ monomer 0·007	Φ exciplex 0·006	0·014	0·001
acetonitrile			
0·008	<0·001	0·012	<0·001

1-NpCH$_2$OMe Φ$_F$ 0·055 C$_6$H$_{12}$ 2-NpCH$_2$OCH$_3$ Φ$_F$ 0·043 C$_6$H$_{12}$
                0·091 MeCN   0·109 MeCN
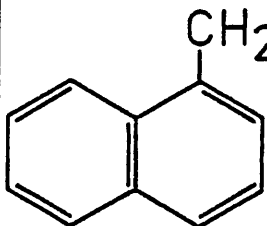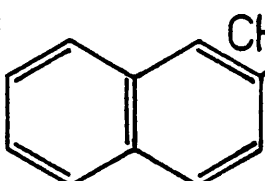
CH$_2$O(CH$_2$)$_2$NMePh		CH$_2$O(CH$_2$)$_2$NMePh	
cyclohexane			
0·005	0·019	0·007	0·023
acetonitrile			
0·009	0·007	0·017	0·010

TABLE.2.4.

QUANTUM YIELDS FOR
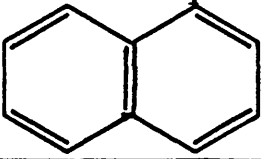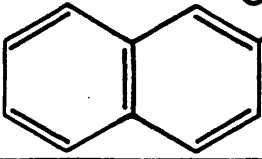
1-AND 2-NpCH$_2$OCOCH$_2$NR$_2$

X	CH$_2$OCOCH$_2$X (1-Np)		CH$_2$OCOCH$_2$X (2-Np)	
	cyclohexane			
	Φ monomer $\quad$ Φ exciplex		Φ monomer $\quad$ Φ exciplex	
H	0·125		0·130	
NHtBu	0·071		0·111	
NEt$_2$	0·011		0·015	
NHPh	0·006		0·009	
NMePh	0·001	0·018	0·002	0·004
	acetonitrile			
H	0·123		0·134	
NHtBu	0·048		0·115	
NEt$_2$	0·008		0·008	
NHPh	0·002		0·002	
NMePh	0·001	0·006	0·001	0·0005

TABLE.2.5.

QUANTUM YIELDS FOR

9-AnCH$_2$OCOCH$_2$R.
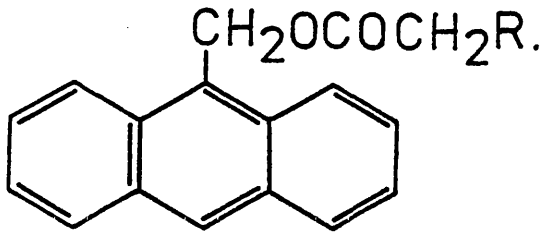
CH$_2$OCOCH$_2$R.		
R	**cyclohexane**	**acetonitrile**
NH^{t}Bu	Φmonomer Φexciplex 0·166	Φmonomer Φexciplex 0·020
NEt$_2$	0·145	0·023
NMePh	0·022 0·030	0·002 0·0005

TABLE.2.6.

DIPOLE MOMENTS[1]

	n=1	n=2	n=3	n=4
αnE		16·8	15·1	15·6
αnN		14·6	17·1	15·6
βnE	14·4		13·3	11·8
βnN	14·0	14·0	15·6	16·3

[1] Values in Debye units.

Table 2.7.

EXCIPLEX λ_{max} VALUES.[1]

Compound	C_6H_{12}	MeCN	Compound	C_6H_{12}	MeCN
$\alpha 1E$		495	$\beta 1E$		495
$\alpha 2E$	365	482	$\beta 2E$		470
$\alpha 3E$	397	505	$\beta 3E$	393	470
$\alpha 4E$	400	520	$\beta 4E$	430	500
$\alpha 4'E$	375	500	$\beta 4'E$	415	
$\alpha 1N$			$\beta 1N$	390	475
$\alpha 2N$	377	465	$\beta 2N$	390	475
$\alpha 3N$	377	510	$\beta 3N$	380	485
$\alpha 4N$	383	490	$\beta 4N$	375	490
$\alpha 4'N$	380	470	$\beta 4'N$	380	480
$\alpha 4(O)N$	380	475	$\beta 4(O)N$	390	470
$\alpha 4(O)P$		470	$\beta 4(O)P$		470

[1] Values in nm.

Table 2.8.

Dipole moments were calculated using the method of Knibbe[30] and are tabulated, together with the λ_{max} values of exciplex emission from which they were calculated, in Tables 2.7. and 2.8.

2.2. Results of Absorption Studies

Absorption spectra were not analysed on a quantitative basis but checked for perturbations of the ground state as in chapter one. The qualitative absorption spectra of all the aliphatic amine derivatives were identical with those of the respective substituted aromatic compounds. (A slight difference noted was that substitution of the methyl group in 2-methylnaphthalene rendered the sharp bands at 306, 320- nm less intense, presumably by a reduction in the symmetry of the system. Comparison of methyl with ethyl naphthalene was not possible). The compounds containing the aromatic amines showed bands characteristic of the two individual chromophores with a slight bias in favour of the aniline moiety at longer wavelengths. No variation with the type of linking chain was observed; hence Ar4N, Ar4'N and Ar4(O)N showed identical bands. The spectrum was also independent of n, αlN, for example, having the same absorptions as α4N. No variation in the absorption spectra of the aliphatic amines either with chain type or length was observed. Perturbations for the compounds ArlAm equivalent to those observed in the halogen derivatives ArlX and reported in chapter one were not observed.

2.3.   Results of Fluorescence Studies

n = 1   Fluorescence from these compounds was very weak in all

cases.   In agreement with the observation of Brimage,[88] exciplex

emission was obviously present from the shape of the spectra but

in cyclohexane it was not possible to distinguish it quantitatively

from the monomer emission: the λ_{max} was obviously very close to

that of the naphthalene.   The yields given in the tables are

therefore often combinations of exciplex and monomer emissions.

In other solvents of intermediate polarity it was easier to dis-

tinguish the emitting species since discrete new bands were

obtained.   In particular β1E was examined and the spectra obtained

are illustrated in Fig.2.3. and the quantum yields in Table 2.1.

n = 2   Exciplex formation occurred with extraordinary efficiency

in this case, (greater than appears to have been observed for

the dimethylamino derivatives) and the quantum yields are largest

for this value of n whether the amine is aromatic or aliphatic.

In particular α2E in cyclohexane was almost totally emissive

from an exciplex with an efficiency twice as large as for methyl

naphthalene.   The N-amines were less efficient at complexing than

the E-amines in cyclohexane but on changing to acetonitrile the

dramatic reduction in complex formation for the aliphatic relative

to the aromatic amines inverted this order.   The dipole moments

were less in the aromatic amine derivatives.

<u>n = 3</u>   When n = 3 the yield of complex was found to be less than

when n = 2 although it was still very efficient. (In Chandross's

work with excimers[34] and amines[75] n = 3 was found to be the most

favourable chain length). The same observations about complex form-

ation in aromatic vs aliphatic amines pertained here as were made

for n = 2. In contrast however, the dipole moments were larger

for the aromatic amines. Fluorescence quenching was less than

for either n = 1 or n = 2.

<u>n = 4</u>   When n was increased to four it was observed that the

fluorescence quenching of the naphthalene which had been gradually

decreasing with increasing n, became suddenly more efficient.

Complex formation however was less efficient than for n = 2, 3 and

for the first time the yields were higher for the aromatic amines

in both solvents. Charge transfer seemed to be greater too, as

evidenced by the dipole moments. A further observation which

apparently contradicted the last was that the λ_{max} values were at

lower energy for the aliphatic amines.

<u>n = 4'</u>   The substitution of an ether link for a methylene unit

had very little effect on either aliphatic or aromatic derivatives

in acetonitrile but in cyclohexane there was more monomer quenching

but less complex emission, the greater effect occurring for aliphatic

derivatives.

<u>n = 4(O)</u> The further introduction of a carbonyl group to give an ester caused the complex emission from the diethyl amine to become very weak. It was observable using very wide slits but the quantum yield was too small to measure. Fluorescence quenching was unaffected in either solvent for the aliphatic but was considerably increased for the aromatic amines. Exciplex emission was the same for α4(O)N as for α4'N but in the β series was much reduced in the ester containing compound.

In this series also, other amines were prepared. A tertiary butyl-amino derivative showed a small amount of fluorescence quenching but no trace of exciplex emission was detected. A derivative of aniline seemed to come between the diethyl and the N-methylaniline compounds in that fluorescence quenching was intermediate in magnitude and exciplex emission, whilst detectable, was not quite enough to measure quantitatively. Results obtained for a similar series of anthracene derivatives correlated with the observations in the naphthalene series.

2.4. <u>Discussion</u>

2.4.1. <u>The mechanism of the interactions</u>

A simple method of understanding the processes occurring in this type of interaction is by means of a potential energy diagram similar to those used by Knibbe[30] but altered slightly to deal with the intramolecular case (Fig.2.17.). The diagram attempts

POTENTIAL ENERGY DIAGRAM FOR EXCIPLEX FORMATION.

Non-polar solvent
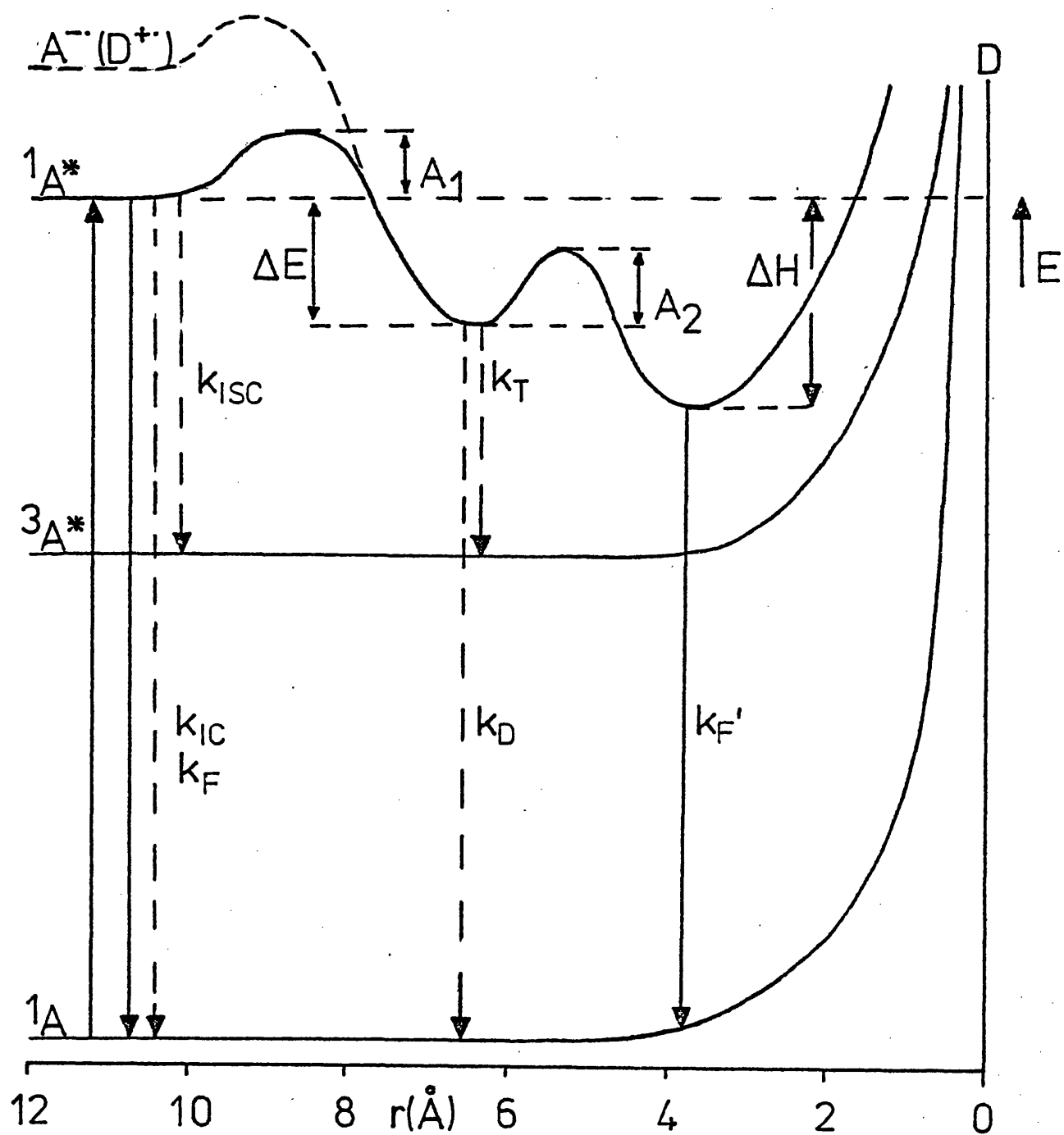
Fig. 2.17

to show how the energy of the molecule varies as the two inter-
acting species at the ends of a long chain are brought together.
(In many respects, the distance apart is very difficult to define
when they are close together because of the finite sizes of the
orbitals involved. A strict analysis would involve quantum mechanical
overlap factors but the concept of intersection of surfaces as out-
lined in chapter one is useful. For simplicity however the distance
apart r may be referred to).

Szwarc[69,91] pointed out that for a long chain there is
an intrinsic property which he called the 'dynamic flexibility'.
It is independent of the length of the chain and simply reflects
its ease of bending. It will consequently determine the activation
energies between interconverting conformations. The activation
energies were found to be 3-5 Kcals/mole for a methylene chain and
$\sim$8 Kcals/mole for a $(CH_2CH_2O)_n$ chain. Not surprisingly therefore
he was able to show that the linking chain imposes a restriction
on the diffusion together of the reacting species in comparison to
the intermolecular case. A similar interpretation was placed on
a result reported by Chuang[92] where intermolecular charge transfer
between anthracene and dimethylaniline took place in $\sim$10ps whilst
in $An(CH_2)_3$-p-$C_6H_4NMe_2$ it occurred in 900ps.

When the distance between the two species is large the
normal processes can occur and are shown on the left hand side
of the figure. As diffusion together occurs and the molecule crosses

Szwarc's flexibility barrier A_1, a point will be reached where

an encounter complex can be formed by partial electron transfer.

The optimum distance for this varies with the substrate, the

solvent and also with the actual configuration which can alter

the type of overlap, but has been calculated as 7-9 $\overset{o}{A}^{32,69,93}$

(The scale of distance apart in Fig.2.17 is only intended as a

very rough approximation). Normally approach of the interacting

species will be allowed to this point and only in the most

severely hindered (i.e. rigid, cyclic) systems will it not be

possible. The stabilisation $-\Delta E$ of the encounter complex will

depend on the degree of interaction and therefore on its wave-

function (1.7.). In the compound Ar4(0)T for example, the ionisation

potential is high and the wavefunction will be similar to the

uncomplexed state with C_5 the largest of the constants. This

means that fluorescence quenching will be small. When an aromatic

amine is present however, as in Ar4(0)N, the low ionisation potential

makes $-\Delta E$ more negative and the radiationless processes from the

encounter complex become more important. Monomer fluorescence

quenching therefore increases. An added complication however is

that for the same separation a number of different conformations

of the linking chain are possible. If some of these conformations

have increased non-bonded interactions (such as eclipsed rather

than staggered hydrogens) then the stability and hence the quenching

of one conformation may be different from another. The reaction

coordinate is thus seen to have a complex dependency on a large

number of variables and the explanations given here must be much simplified.

Having formed an encounter complex, what the molecule next chooses to do depends on the kinetics and energetics of the pathways open to it. It was shown in chapter one how halogen containing compounds are very rapidly deactivated back to the ground state because of a particularly favourable vibrational route. In the absence of such a favourable route in these compounds, and given a much larger degree of charge transfer, fluorescent exciplex formation occurs. However, it requires closer approach of the orbitals involved to a distance of ~ 4 $\overset{o}{A}$ [32] and the geometry of the molecule will interpose an activation energy, A_2, between these two conformations, where $A_2 > A_1$. (In an intermolecular model such as used by Knibbe it is likely that A_1 and A_2 are close to zero except perhaps in the case of unusually hindered molecules such as those of Taylor et al[94] described in 2.4.2.) It will be subject to solvent effects since close approach requires solvent rearrangement, but will be most sensitive to geometrical constraints. In short chain compounds the constraint by the linking chain on the interacting species acquiring the desired degree of overlap could be enough to make fluorescent exciplex formation slow relative to the deactivating processes occurring from the encounter state. In the intramolecular excimer model the barrier is prohibitively high when $n \lesssim 3$ either because the chain does not allow the correctly orientated overlap of the π orbitals or because there are serious

non-bonding interactions. From the results obtained for β1E this is not so. Whilst the barrier is high enough to cause only a little fluorescent complex formation, the complex, once formed, is nearly as stable as for some of the more geometrically favourable complexes viz. dipole moment. Nevertheless the processes from the encounter state are fast enough to compete effectively with further complexation and severe fluorescence quenching results.

Returning to the Ar4(0)T example it should be noted that the ^{t}Bu group will not prevent the formation of the encounter complex but will make A_2 sufficiently large to preclude the observation of an emissive state. Consequently the small amount of fluorescence quenching is more attributable to the high ionisation potential than to steric interference by the ^{t}Bu. In Ar4(0)N however, steric interactions will be less and A_2 will be reduced somewhat thus enabling emissive complexation. Ionisation potential must also be a factor in determining the size of A_2 because compounds which would be expected to have similar geometries show different exciplex emission efficiencies. Thus Ar4(0)N is stronger than Ar4(0)P and Ar1E is better than the dimethylamino compounds. Even if the Ar4(0)T compound was sterically allowed to form an emissive complex it might be precluded from doing so because of its high ionisation potential.

2.4.2. Short Chain Interactions and Orbital Orientations

The model used this far to explain the results is not very satisfactory for the very short chain compounds such as ArlAm when thought of in terms of r. In such compounds the geometry does not allow separation of Ar and Am by as much as 5 $\overset{\text{o}}{\text{A}}$ and the molecule might be thought to exist totally in a charge transfer state when excited. Whilst this may be largely true, it is the actual orientation of the lone pair which will determine the type of excited state and thus the concept of interaction surface becomes useful. The activation energies between the few conformations open to it would be much larger than Szwarc's flexibility barrier. Indeed, he noted in his studies that when n < 5 the activation energies did indeed increase by a factor of 2 for n = 5 → 3. Shorter chains would be expected to produce even higher barriers. The energies will not be quite as big here as in his binaphthyl molecules where much larger steric interactions might be expected at close range.

A further factor becomes important in short chains. When n is large the proportion of the total number of conformations where the molecule is in an interacting position is very small. This number will increase however as n decreases and for n = 1 is significant. This means that the excitation occurs into a quenching configuration in a relatively large number of the total number of molecules. The effect is a 'static' one: that is, it is temperature independent, and if diffusional processes are pro-

hibited, as in a solid matrix, quenching will be observed. Chandross noted that the naphthalene emission for his compounds when n = 1 was weak at 77K in solid methylcyclohexane.

For n = 1, as we have seen, the activation barriers are larger. This explains why the emissive complex formation is so weak in comparison to the fluorescence quenching which is strong because of the shortness of the chain. The relaxed exciplex, whilst energetically difficult to form, has a high degree of charge transfer, as evidenced by the dipole moment, and an apparently large -ΔH in view of the λ_{max}^{-}. The exact orientation required for the interaction of the amine and the aromatic orbitals is still rather enigmatic, however. It has already been pointed out that excimers require so-called 'sandwich' orientations, with the aromatic rings parallel, but whilst this is desirable, particularly for the aromatic amines, it is not necessary in amine exciplexes. In an intramolecular study, Taylor[94] and co-workers examined the formation of exciplexes between pyrene and two anilines. One was N,N-dimethylaniline and the other its 3,5-ditertiary butyl-analogue. Obviously, large steric interactions in the latter prevented the benzenoid part of the molecule getting close to the pyrene moiety. Strong exciplex emission was observed from both systems and it was concluded that in the hindered case the amine was interacting as a localised lone pair. The authors drew the amine as sp^3 hybridised interacting at right angles to the plane of the pyrene

(Fig.2.18.). It is surely just as likely that the molecule, which must be planar [95] interacts angularly.
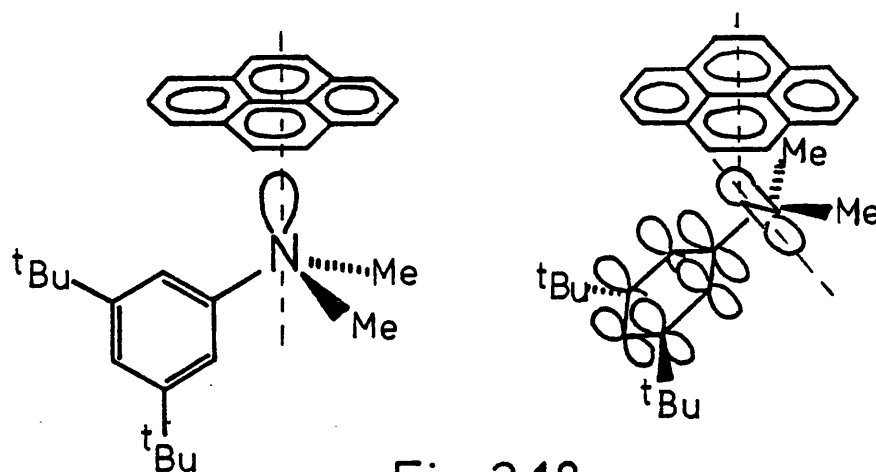
Fig 2.18.

The loss of overlap due to the angular approach would perhaps not be as great as that due to the loss of conjugation with the π cloud. It has already been pointed out[96] that aliphatic amines appear to transform from pyramidal to planar in an exciplex and there does not seem to be good reason why the geometry of the aniline should be distorted from its normal shape in which the lone pair is strongly mixed into the π cloud.[95] In the compounds studied here the orbital alignment cannot possibly occur in the way Taylor suggested when n = 1 or 2 and exciplex formation must result from angular overlap.

Two points should be noted in considering possible conformations. Firstly in the α-derivatives a significant interaction with the 'peri' hydrogen at C8 restricts rotation about the Np-C bond. (A similar situation exists in the An derivatives with
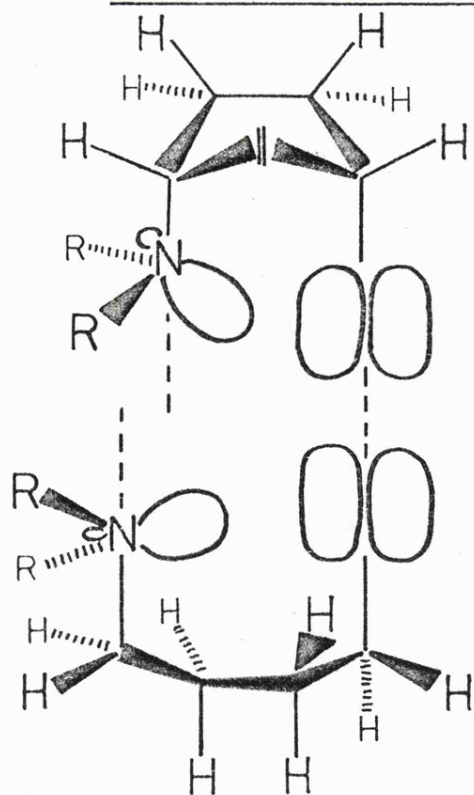
$Ar(CH_2)_4NR_2.$
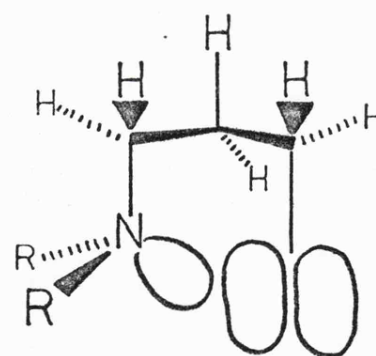
$Ar(CH_2)_3NR_2.$
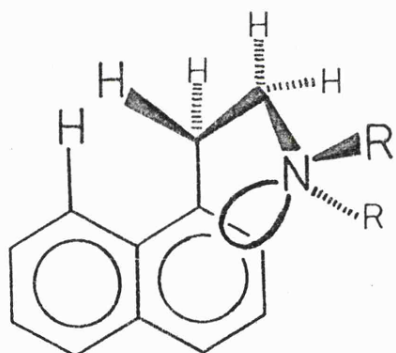
$1\text{-}Np(CH_2)_2NR_2.$
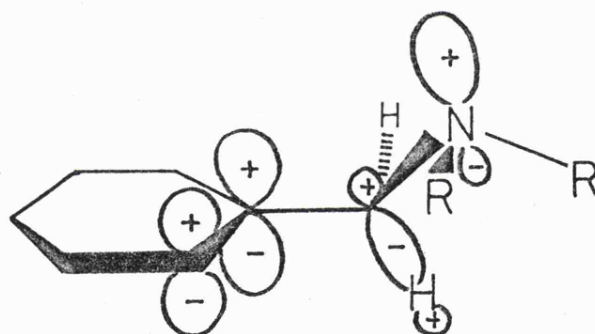
$Ar\,CH_2\,NR_2.$
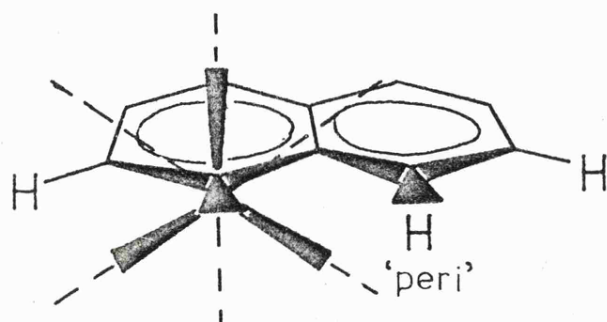
$1\text{-}NpCH_2\text{-}$
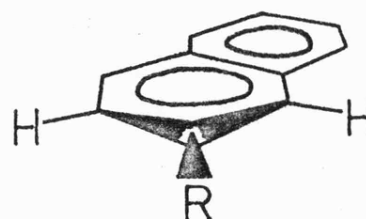
'peri'

$2\text{-}NpCH_2\text{-}$

Fig. 2.19.

peri hydrogens at Cl and C8). This interaction is not present

in β compounds. Secondly, conformations in which hydrogens

are eclipsed are to be avoided. Given these preferences, the

most likely conformations adopted by some of the molecules can

be determined, some of which are shown in Fig.2.19. A further

interaction in this series must be considered. It is possible

to envisage an overlap between the lone pair of the nitrogen

and the pπ orbitals via the C-H σ bonds in a hyperconjugative

interaction (Fig.2.19.). This 'through bond' interaction similar

to those discussed in chapter one cannot be ruled out merely

because of the absence of new absorption bands. Inspection of

the ionisation potentials of toluene (8.82 ev),[97] ethylamine

(8.86 ev)[97] and benzylamine (7.56 ev)[98] are sufficient to indicate

an interaction between the nitrogen and the aromatic system not

shown in the absorption spectrum. In the absence of photo-

electron spectroscopy data it is not possible to be more specific

other than to predict that an effect will be detectable in the

ionisation energies of the ArlAm compounds.

2.4.3. Exciplex Stability

When n is increased to 2 and 3 it has been seen that the

quantum yield of complex emission is at its largest. With the

amines used here there was slightly more for n = 2 than for n = 3

but in the dimethylamino compounds (Fig.2.1.) the reverse was true.

Although the yield of the emission is an indication of the favour-

ability of exciplex formation it is not possible to conclude which

is the most energetically stable from these results alone. Considerations of the λ_{max} of exciplex are unfortunately not very helpful because molecules in their excited states have different geometries and bond lengths. Consequently emission from the excited state is followed by some molecular and/or solvent rearrangement to stabilise the molecule. The observed emission does not correspond exactly to the difference in energy between the ground state and the exciplex (i.e. a measure of -ΔH). This reasoning has been adopted[90] to explain why the λ_{max} of aromatic amine exciplexes often appear at shorter wavelengths than those of aliphatic amines which have a larger ionisation potential (see Table 2.8.). Indeed it has been postulated[96] that in the excited state complex aliphatic amines are planar rather than pyramidal, a factor which would cause the exciplex emissions to be red shifted from their true positions and bring them to lower energy than those of the aromatic amines.

The stability of the complex, -ΔH, as we have seen is a function of a number of parameters including ionisation potential of the donor, electron affinity of the acceptor, the coulombic stabilisation term and the heat of solvation of the charge transfer state. Added to these is a rather vague quantity dependent on the molecular geometry which will determine the extent of possible overlap. The complex stability can only be assessed by a study of both the monomer and exciplex emission dependency on temperature followed by analysis using the method of Birks.[99] Lewis[90] cal-

culated -ΔH for 1-NpCH$_2$CO$_2$(CH$_2$)$_2$NMePh in toluene to be 5 ± 2

Kcals/mole. The intermolecular exciplex between naphthalene

and triethylamine in hexane was found to have -ΔH = 8 Kcals/mole.[100]

The lower stabilisation for the intramolecular compound reflects

the lower dipole moments compared to those of intermolecular

compounds (see 2.4.6.).

Given a situation where the only parameter being varied

is the nature of the amine it would seem that the differences

in the amounts of exciplex observed for the dimethylamino and

the diethylamino compounds are explained by the difference in

ionisation potential. For Me$_3$N it is 7.8 ev[101] and for Et$_3$N

it is 7.5 ev.[97] Although these values cannot be assumed for the

naphthalene compounds it illustrates how the significantly lower

ionisation potential for the diethyl derivatives would account

for the generally larger exciplex yields. The ionisation potential

for aromatic amines is low (dimethylaniline = 7.2 ev[97]) but in

this case the emission will also be affected by the different

geometry of the amine.

2.4.4. Longer Chain Interactions

The observation of slightly stronger quenching for n = 4

compared to n = 3 must be accounted for by an increase in the ease

of attainment of a quenching configuration. This might be ex-

pected to some extent as the number of degrees of freedom increase.

There is a competing factor however. Because of the fact that

quenching does not require such close approach as relaxed complex formation, the former is a more statistically favoured interaction at any point in time. Consequently quenching would be much less affected by change in concentration of the quencher than would the exciplex quantum yield. The effective concentration of quencher, which decreases as n increases, is a factor which has already been discussed (1.8.7.). Suffice to say, both exciplex formation and quenching will be expected to decrease as n increases by this simple dilution effect. As Szwarc pointed out, geometrical differences are not evened out until n ⩾ 5 hence the unusual increase in quenching for n = 4 can be attributed to a geometrical effect. The trend of a reducing Φ_{exc} starting at n = 2 is expected to continue as n increases. Work is presently in progress by other workers in this laboratory to study the effect of longer methylene chains.

2.4.5. Ether and Ester Linkages

The substitution of an ether link into the chain will next be considered. When no amine is present (ArCH$_2$OMe) there is fluorescence quenching which can be explained either by a hyperconjugative interaction or a simple electronic inductive effect. In the first chapter the former was argued to be more important. Charge transfer can occur equivalent to that observed for ArlAm as well as for the halogen containing compounds such as ArlCl. The electronegativity of oxygen is usually regarded as

being close to that of chlorine and whilst the lability of the
C-X bond was used to aid the explanation of the properties of
ArlCl, the quenching for the ether is far less in accordance with
its greater bond strength. Any interaction of this sort is
bound to hinder rotation both of the Np-C, and of the αC-O bonds
and will make exciplex formation for Ar4'Am more difficult com-
pared to Ar4Am, in agreement with the observations. The effect
is increased in the Ar4(O)Am series because the carbonyl is able
to stabilise charge variation on the ether oxygen and increases
the hyperconjugative effect. Reversal of the ester group giving
the chain $-CH_2CO-O-CH_2$ makes no difference since the carbonyl π
orbital in the correct orientation has similar symmetry to a
lone pair. Thus (cf. chapter one) the quantum efficiencies of
$ArCH_2CO$ Me are reduced by the same degree as for Ar4(O)H.

2.4.6. The aromatic amine derivatives

The absorption spectra of some of the aromatic amine
derivatives have already been illustrated in Fig.2.2. and partly
discussed in section 2.2. The naphthalene derivatives are un-
usual in so far as they are able to absorb the exciting light
at either end of the molecule. Further, since both N-methyl and
N,N-dimethylaniline fluoresce, emission can occur from either the
naphthalene, the amine or the exciplex. By careful examination
of the excitation and emission spectra at different wavelengths

some interesting observations can be made. Fig.2.20. shows the
excitation and emission spectra of 1-methylnaphthalene together
with the two amines in acetonitrile. (This solvent is perhaps
the most convenient since any exciplex emission is well separated
from that of the other species.) Several points should be noted
from this figure. Firstly the aniline emission is a structureless
band bathochromically shifted from the naphthalene. The emission
for DMA occurs at 350 nm and its excitation spectrum has two
maxima at 265 nm and 308 nm with a minimum at 280 nm. The
excitation spectrum of the naphthalene however has a maximum at
294 nm and drops off sharply at longer wavelengths. Fig. 2.12
illustrates the emission spectrum of $\alpha 4'N$ at various excitations.
It can be clearly seen that the emission bands in the 300-380 nm
region are strongly excitation-dependent whilst the exciplex
emission is not. (Variations in intensity are caused by the
variation in light absorbed at λ_{exc}.) A similar effect is noted
in the emission spectra of $\beta 3N$ illustrated in Fig.2.21. Thus
excitation at 280 nm where there is a minimum in the excitation
spectrum of DMA gives rise to an emission with some structure and
centred on 335 nm, i.e. containing naphthalene characteristics.
Moving the excitation to 300 nm however causes the emission to
take on the characteristic shape and λ_{max} of DMA as in Fig.2.20.
The λ_{max} of the complex however is constant. Inspection of the
spectra of other compounds discussed in this chapter shows that
the monomer emission invariably takes on the characteristics of
DMA at the 305 nm excitation wavelength used.

EXCITATION AND EMISSION SPECTRA OF 1-MeNp AND PhNR$_2$
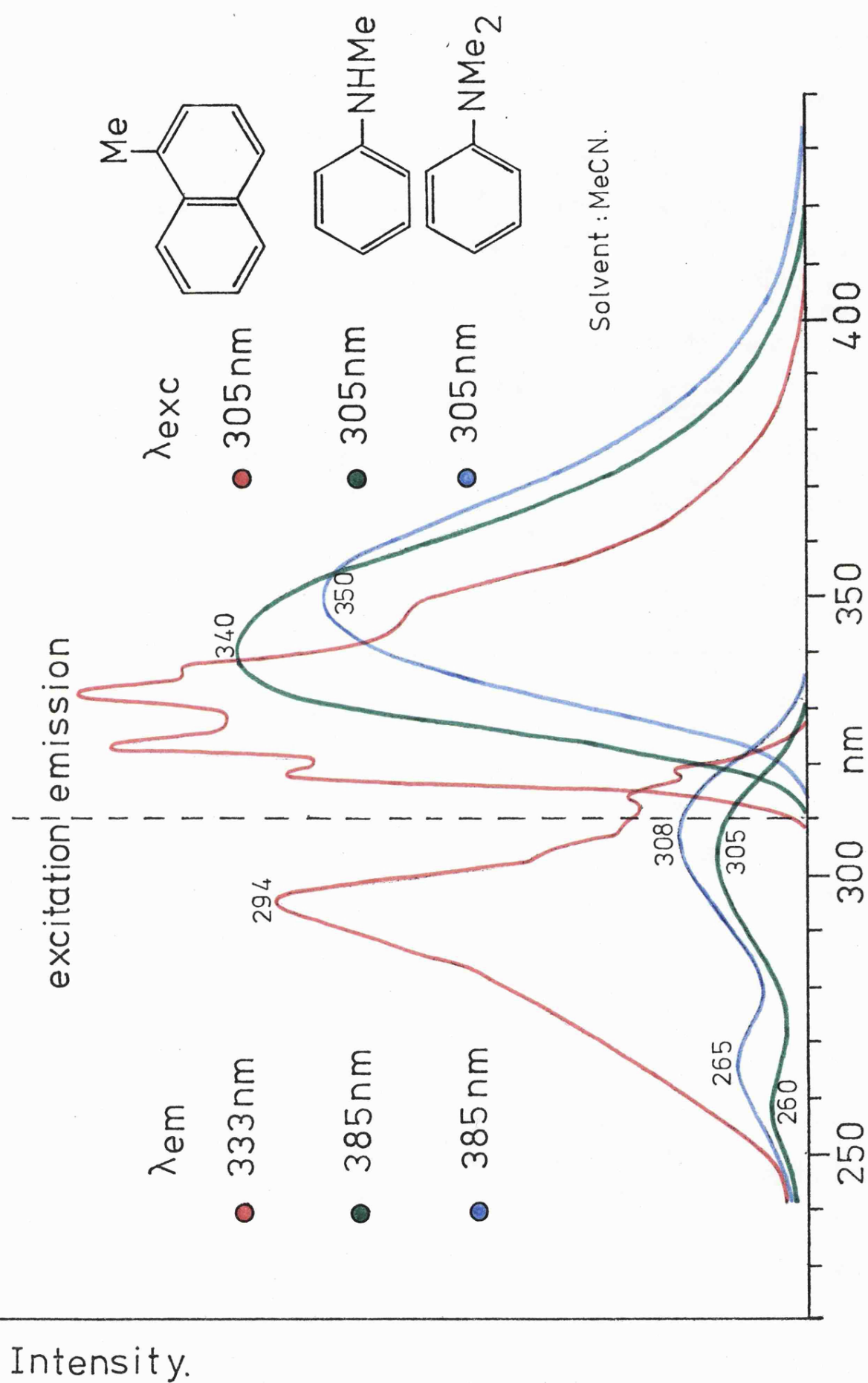
Fig. 2.20.

EXCITATION AND EMISSION
SPECTRA OF β3N AND
α4'N IN MeCN

excitation: α4'N
λem.
● 340nm
● 360nm
● 495nm

excitation: β3N
λem.
● 350nm
● 500nm

emission: β3N
λexc.
● 280nm
● 300nm
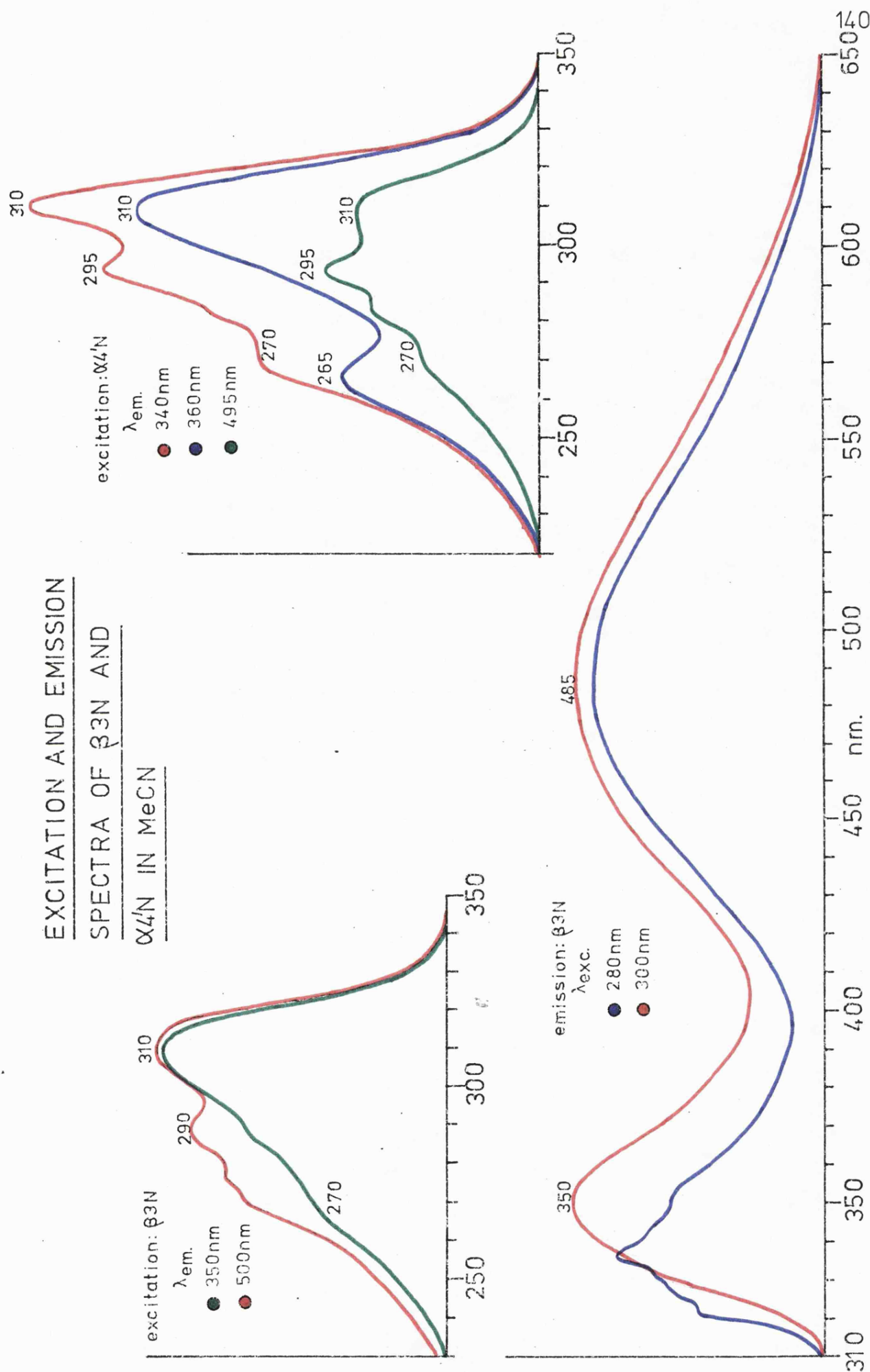
Fig. 2.21.

Further evidence of these properties is provided by the
excitation spectra illustrated in Fig.2.21. for α4'N. Examination
of the spectrum for the emission at 360 nm (where naphthalene
monomer emission is small) shows an excitation spectrum almost
identical to that of DMA. However shifting the monitoring wave-
length to 340 nm causes the λ_{max} at 295 nm to appear which can
be ascribed to the naphthalene.

Another interesting point is that the efficiency of complex
emission relative to that obtained from the other species is variable
with wavelength of excitation. Thus for α4'N in Fig.2.21. complex
formation is very much less efficient relative to the monomer
emission when excited at 310 as opposed to 280 nm. This would
seem to be a function of the lifetime of the species being excited.
The lifetime of DMA would be expected to be much shorter than of
methylnaphthalene (τ_F for aniline = 3.9 ns[63]). Consequently
quenching and complex formation would compete less effectively
with the emissive process from the aniline when it received the
excitation energy rather than the naphthalene.

Dipole moment calculations have previously shown lower
values for aromatic amines than for aliphatic amines despite the
former group having smaller ionisation potentials. Table 2.7.
shows that similar results occur for some of the compounds studied
here. It is important not to place too much emphasis on such
calculations which rely on 'guestimates' of cavity radius and
λ_{max} measurements which can only be obtained within ±5 nm. The
values in the Table have assumed the same cavity radius for all

of the derivatives: 5 $\overset{o}{A}$.[89,90] The only observation of value is

that the dipole moments are remarkably large through the whole

range of n values and possibly maximise at n = 2 for the aliphatics

and n = 3 for the aromatics. If, indeed, this is so it may in-

dicate that the geometrical requirements for n = 1 and n = 2 in

the aromatic series are such as to give less charge transfer than

n = 3 and hence lower dipole moments. The lower values reported

for aromatic amines compared to aliphatic amines can thus be put

down either to variations in the geometrical requirements or

the cavity radius of the complex.

2.4.7. Solvent and the Role of Radical Ions

So far the discussion has ignored the role of solvent with

respect to the formation of radical ions. The discussion of Fig.2.17.

has been aimed mainly at behaviour in non-polar solvents where

the energy of the radical ions is high and can be neglected. In

highly polar media however the ions are stabilised (as, too, is

the exciplex) to a level below that of the encounter complex.

The pathways and energy levels in such a situation were omitted

from the diagram for simplicity but certain points may now be made.

Reference to Fig.2.22. in which all the important processes are

summarised may be found useful. The existence of radical ions in

intermolecular interactions has been well established[102] in polar

solvents and characterised by conventional laser flash photolytic

techniques. So far however, efforts by Lewis[90] and Weller[70]

to observe ions in intramolecular compounds by microsecond experiments in ethanol have failed. This can be explained by Chuang's result[92] reported above (2.4.1.) which demonstrated the retarding influence of the chain. It can be envisaged that in an intermolecular example radical ions when once formed would be likely to diffuse apart very much faster than in an intramolecular case where the chain tends to restrict this motion. Hence the reverse electron transfer would be likely to occur before the two species had separated, precluding their observation on a microsecond or even a nanosecond timescale. To what extent the reverse electron transfer yields the encounter complex, vibrationally excited ground state or triplet molecule is uncertain. All three processes must be considered but some conclusions can be drawn. In non-polar solvent k_R, as we have seen, is small because of the destabilisation of the ions relative to the complex. In this case k_D and k_T are the most important. In polar media k_R is large and because of the stabilisation of the ions k_{D_1} and k_{T_1} important relative to k_{-R}. k_T and k_D would be relatively unaffected. This mechanism would lead to a decrease in Φ_F for both the exciplex and monomer, in agreement with the observations for all compounds in acetonitrile. Further support of this was provided by Beddard, Davidson and Lewis[33] where the lifetimes of some exciplexes actually increased in polar media. This meant that radical ion formation from the relaxed exciplex could be neglected and that decay occurring from the encounter complexes was much more important in polar media.

DIAGRAM OF PROCESSES INVOLVED
IN EXCIPLEX FORMATION

Fig. 2.22.
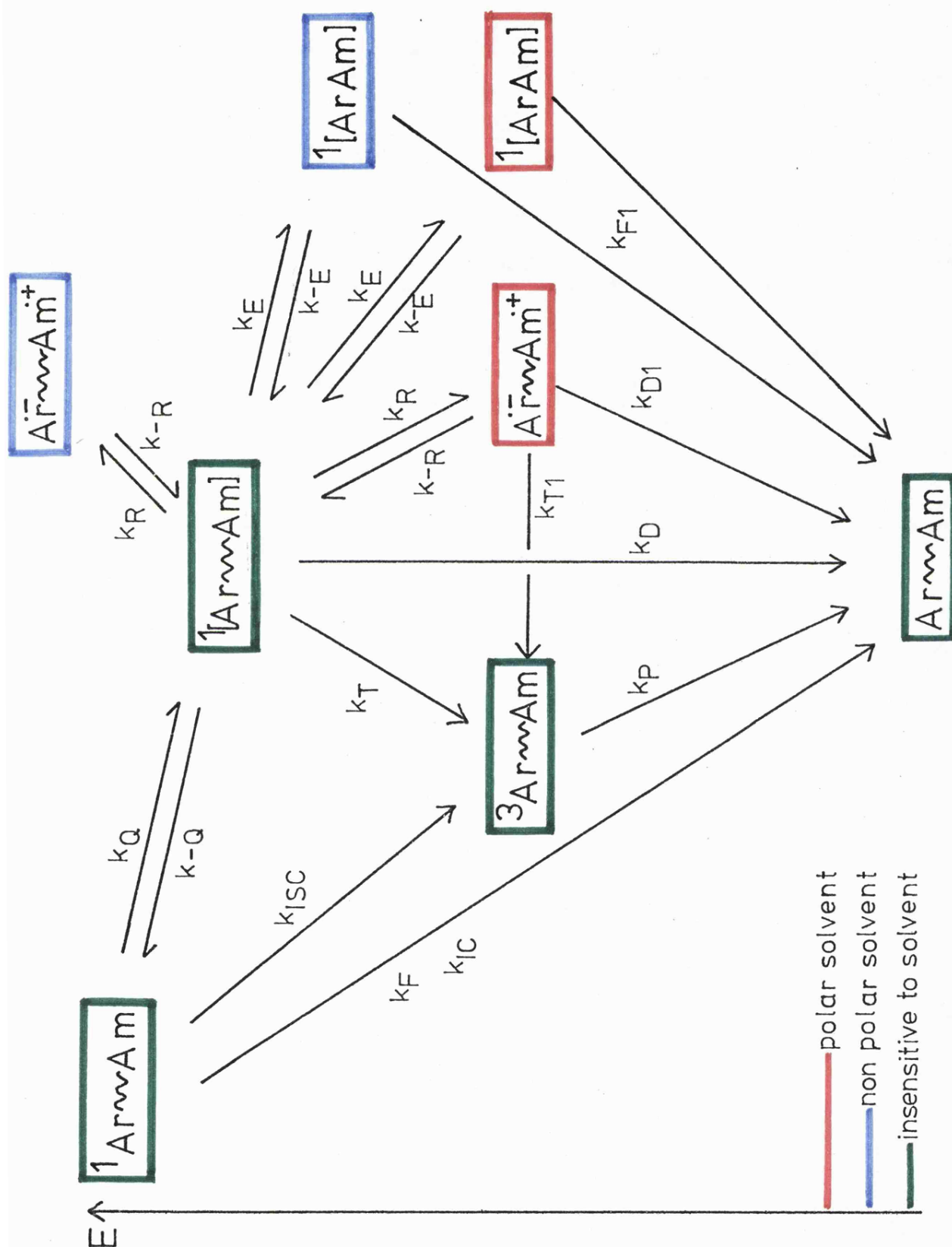
2.5. Conclusions

The study of intramolecular exciplex formation between aromatic hydrocarbons and amines has been extended by synthesising a range of new compounds for examination. The geometrical requirements for complexation were discussed in terms of the energetics of interconversion of conformations. It was conclusively shown that the geometrical requirements for fluorescence quenching of the hydrocarbon were far less rigid than those for emissive exciplex formation. Even so, both types of complex were formed more easily than emissive excimers where strict orientational requirements must be met. It was shown that angular interaction of orbitals is sufficient for complexation in contrast to the rigidly colinear orientations for excimers. The complexes were shown to have a large degree of charge transfer but the efficiency of complex formation was strongly dependent on the ionisation potential of the amine involved. The compounds containing aromatic amines exhibited interesting properties whereby both ends of the molecule could be excited leading to different efficiencies of emission from both monomer and complex.

2.6. Experimental

The apparatus and procedures involved in this work were identical to those described in 1.11. The syntheses and sources of all material are described in chapter four.
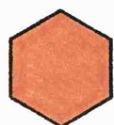
CHAPTER 3:

Excited state interactions

of photosensitisers.

Science is spectrum analysis:art is
photosynthesis.

— Kraus.

3.1. Introduction

When the vital molecules had been made and the very light which had provided the energy was becoming destructive, a natural filter of ozone was formed around the Earth. Evolution had to make do with only a fraction of the ultraviolet radiation that it had once received. And so, in order to perform the vital processes which were to provide us with our birthright a large number of very complex molecules evolved to make use of less energetic visible radiation.

Man was a late starter - by several thousand million years. In the creation of his world he too synthesised molecules. With his love of colour he used natural pigments at first but as nature's molecules became more expensive he made his own which were just as bright and colourful. The trouble was that the colours faded.

The discovery of singlet oxygen and its generation provided the first clue as to why materials were oxidised so easily in the presence of light. The obvious desire to produce materials which were resistant to oxidation prompted considerable research into the behaviour of natural molecules. Concern over the energy requirements of the future also has led to intensive studies into excited state photochemistry particularly in the field of photosynthesis.

The work reported in this chapter attempts to add broadly to the whole field of photosensitisers and their excited state reactions. This begins with a brief outline of sensitised photooxygenation and the role of the sensitiser. The properties of the sensitisers in solution are examined and their interactions with various substrates are reported, mainly with reference to the singlet state, but some mention of triplet state interactions is made. An important point concerning the quenching of excited chlorophyll singlet states by β-carotene is also made.

3.2.1. Dye Sensitised Photooxidation

The mechanism by which light, oxygen and molecules interact has attracted considerable scrutiny and can be classified under the broad heading of dye-sensitised photooxidation. An idea of the scope of the research can be obtained from several reviews.[103-105] For many years the reactive agent in the area under study has been thought to be the lowest lying excited state of molecular oxygen spectroscopically denoted by $^1\Delta gO_2$ and commonly referred to as 'singlet oxygen'. Its participation in photofading processes has been ascribed to its efficient generation by energy transfer from the triplet states of the dyes, followed by chemical reaction with a substrate. Whilst singlet oxygen can be generated by other techniques[106-108] dye sensitised reactions have been used extensively not only because of their applicability to the problems in question but because of the ease with which they may be carried out. Consequently the use of photochemical rather than photophysical methods of singlet oxygen generation introduces a number of possible

excited state interactions and complicates the elucidation of the

mechanisms involved. Particular problems have been encountered

in the mechanism of amine photooxidation. Amines have been shown

to quench singlet oxygen both physically[109,110] and chemically,[108,111,112]

but reaction with dye triplets has also been observed.[113] This

has resulted in a controversy as to whether the photooxidation of

amines proceeds via a singlet oxygen[114-117] or a radical[113,117,118]

mechanism, or both.[119,120] Amines have been recognised as quenchers

of singlet states of aromatic hydrocarbons (cf. chapter two) but

so far the quenching of dye singlets has been deemed unimportant.[117,121]

Elsewhere[119,120,122] this has been shown not to be the case and the

role of singlet quenching in the kinetics of dye sensitised photo-

oxidations has been examined.[123]

Examination of the role of the sensitisers in these

reactions requires firstly a study of their physical properties in

solution, a topic covered by the next section.

3.2.2. The Photosensitisers and their Properties

The two most used fluorescent dyes in photooxidation

reactions are rose bengal and methylene blue. The former is a

member of the xanthene series of dyes and the latter belongs to

the thiazine class. Both have been used in the present work and

their structures, excitation and emission spectra are illustrated

in Figs.3.1. and 3.2.

EXCITATION AND EMISSION SPECTRA OF ROSE BENGAL IN MeOH/H$_2$O (50/50)
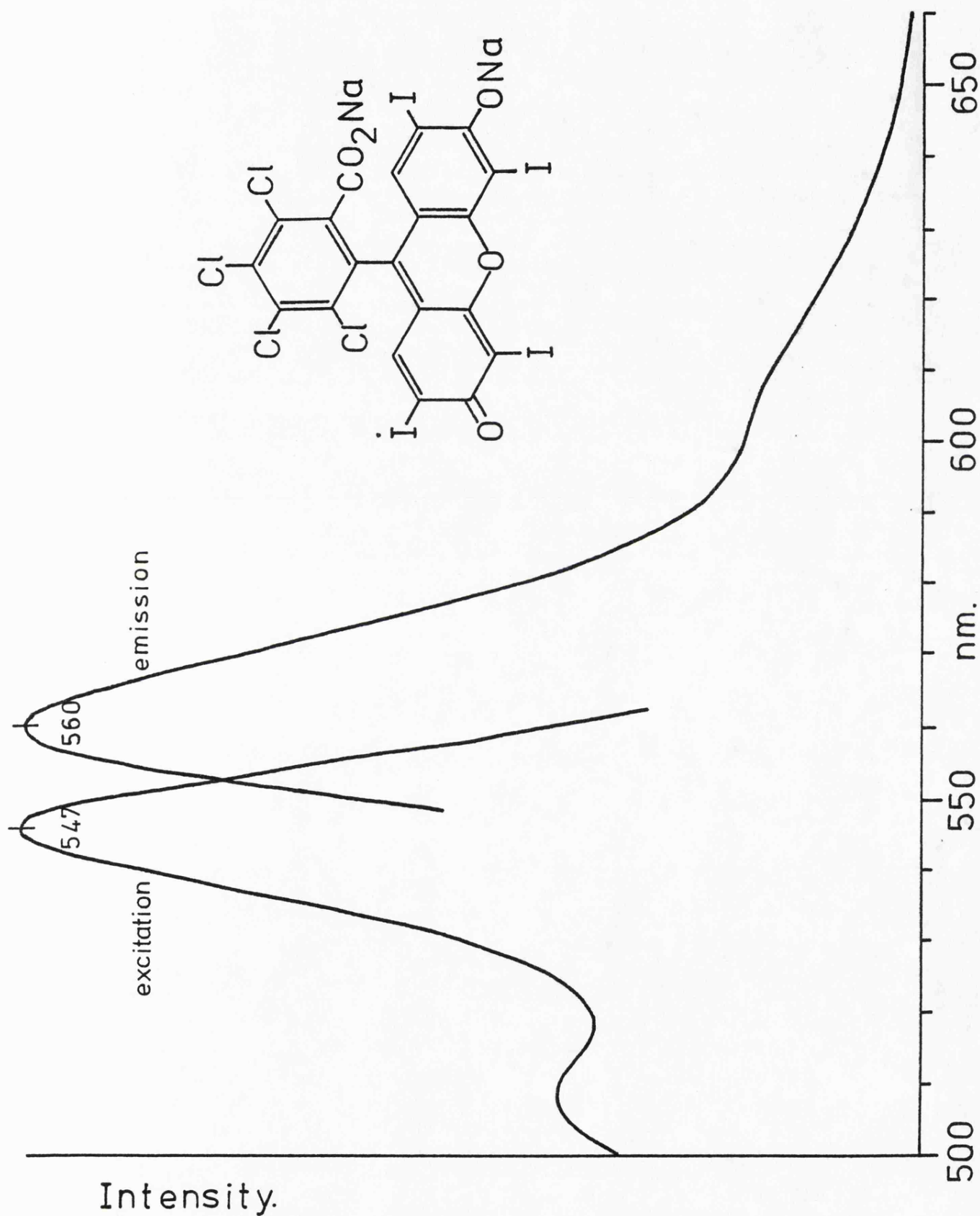
Fig. 3.1.

EXCITATION AND EMISSION SPECTRA OF METHYLENE BLUE IN METHANOL.
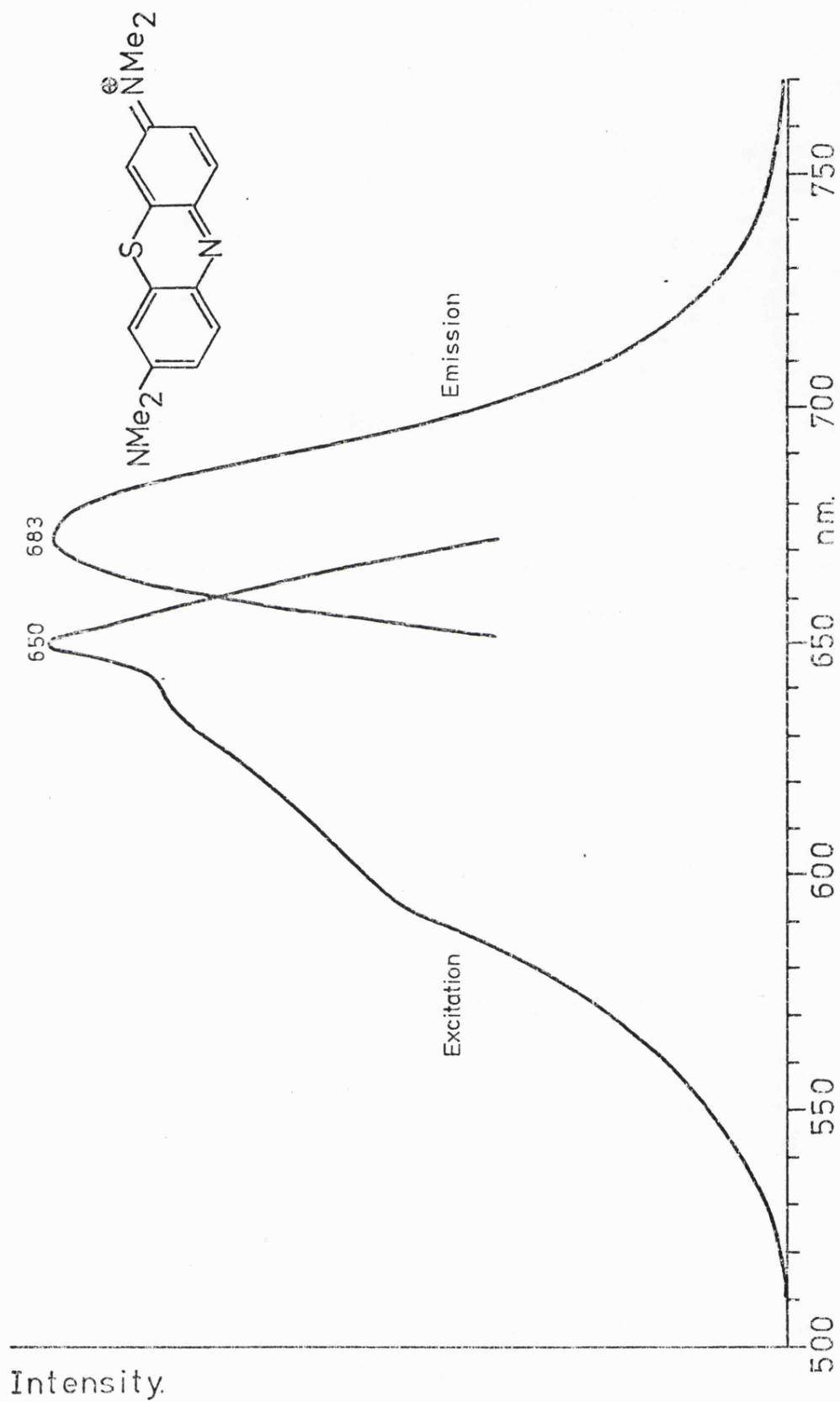
Fig.3.2.

EXCITATION AND EMISSION SPECTRA OF TRIS (2,2'-BIPYRIDYL) RUTHENIUM II CHLORIDE IN METHANOL
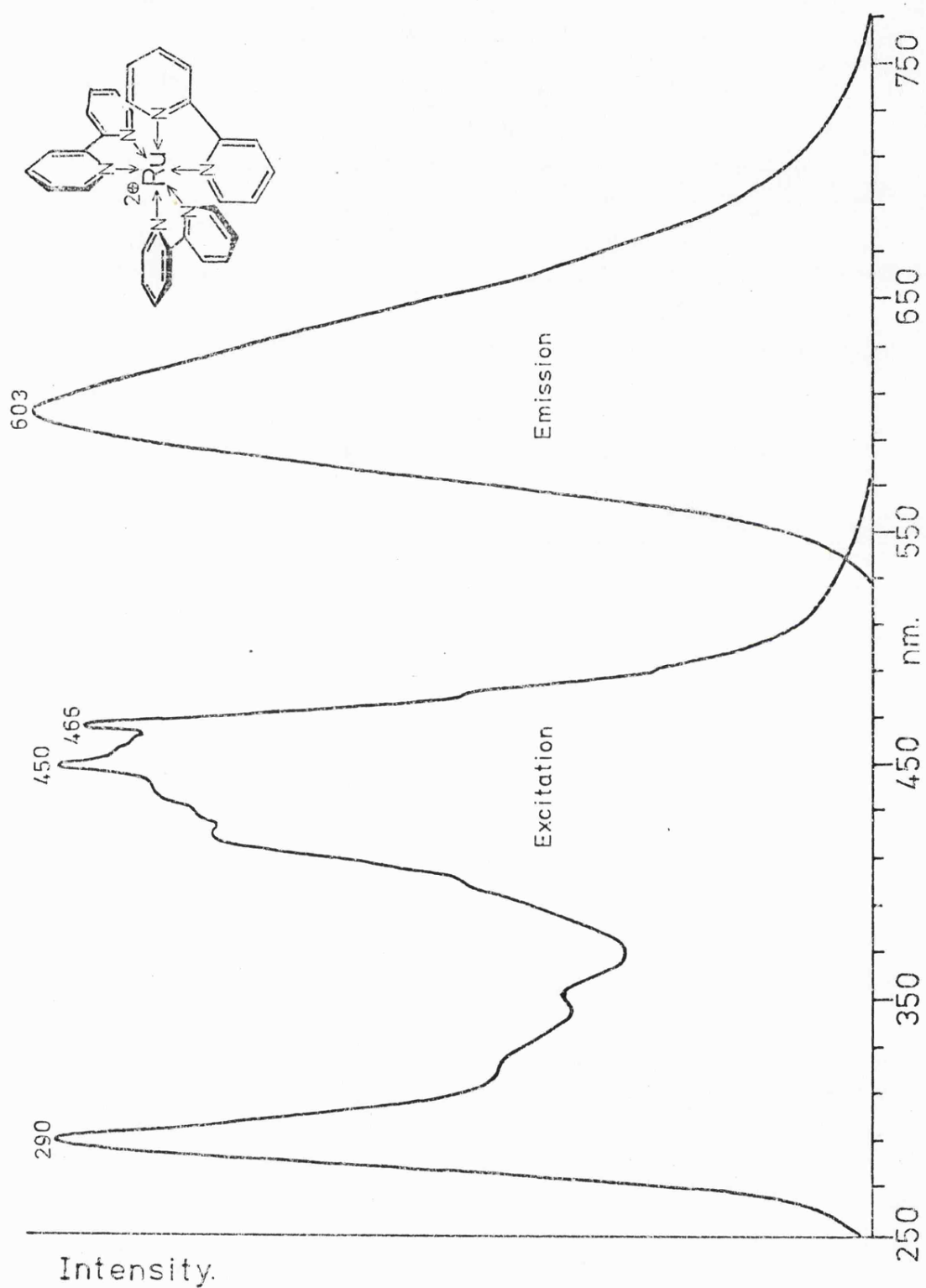
Fig. 3.3.

Another compound which has been used is tris(2,2'-bipyridyl)-ruthenium II chloride, an inorganic complex with a strong charge transfer absorption in the visible region. It has been shown[124] to sensitise the production of singlet oxygen and has been used in a kinetic study of photooxidation reactions of amines.[125] Its spectroscopy has been examined by Crosby and co-workers[126-128] who concluded that the emissive state cannot be defined as either a singlet or a triplet because of its internal heavy atom effect. Nevertheless it has been shown to act in an analogous way to the dyes in sensitised photooxygenation reactions.[124,125] Its structure, excitation and emission spectra are shown in Fig.3.3.

The sensitisers used in this chapter all exhibit variations in fluorescence yield and lifetime in different solvents. The maximum of the emission wavelength however is relatively insensitive to solvent. In pyridine however a ground state solvolysis occurs with the ruthenium complex and the absorption of rose bengal is hypsochromically shifted leading to distortion of the emission by self absorption because the emission is so close to the excitation wavelength. Both the quantum yields and the lifetimes have been obtained for a selection of solvents and the results are tabulated in Tables 3.1. and 3.2. (We are very grateful to Dr. G. Beddard of the Royal Institution, London, for his measurements of the lifetimes. The technique of time-resolved single photon counting was employed.) The lifetimes of the dyes are so short that the effect of oxygen is negligible. Consequently these results were

PROPERTIES OF ROSE BENGAL AND
METHYLENE BLUE IN VARIOUS SOLVENTS.

Solvent	Rose Bengal Φ_F	$\tau_F(ns)$	Methylene Blue. $\Phi_F(rel.)$
MeOH	0.080^1	3.2	1.0
MeOD	0.080	3.21	1.0
EtOH	0.083	3.27	1.13
H_2O	0.017		0.50
MeCN	0.126	4.07	
$(CH_3)_2CO$	0.095	4.3 ± 0.5	
C_5H_5N	0.029		

Table 3.1.

[1]Ref 105

obtained using aerated solutions with optical densities of 0.1 at the excitation wavelength. The ruthenium complex however has a much longer lifetime and quantum yields were obtained in both degassed and aerated solution with the same optical density as for the dyes. Lifetimes were measured in degassed solution only.

PROPERTIES OF $Ru(bipy)_3Cl_2$ IN VARIOUS SOLVENTS AT 293K.

SOLVENT	λmax Absorption	λmax Emission	Φ_E Degassed	Φ_E Aerated	$\tau_E \times 10^9 s^{-1}$ Degassed
H_2O	452·5	608	0·042[1]	0·032	580[1]
D_2O	452·5	610	0·070[1]	0·035	1020[1]
MeOH	448	608	0·062	0·018	865
MeOD	449		0·115	0·036	830
EtOH	447	602	0·096	0·014	700
nPrOH			0·087	0·017	
C_5H_5N	454·5	600	0·082	0·024	
CD_3CN		608	0·088	0·016	
MeCN	449	605	0·073	0·015	940
MeCN/H_2O 80/20			0·073	0·015	
MeCN/H_2O 60/40			0·068	0·018	

[1] Ref 130

TABLE 3.2.

The results reported for the dyes show that fluorescence in acetonitrile is most efficient whilst in water it is least efficient. No effect of solvent deuteration was observed either on the yield or the lifetime. The shortness of the lifetimes involved (cf. the inorganic complex) undoubtedly contribute to the lack of a deuterium effect. The lifetime of methylene blue in EPA at room temperature has been measured as 1.00 ± 0.05 ns.[129]

The inorganic complex showed significantly different behaviour from that of the dyes. The measured parameters were markedly dependent not only on solvent deuteration but on the solvent itself. The quantum yield was temperature sensitive at ambient temperatures decreasing as the temperature increased. Measurements were all made therefore at room temperature (293K). Van Houten and Watts[130,131] in their recently published work have reported similar observations. They have examined in much more detail than could be carried out here the temperature, solvent and isotope dependence of lifetime and emission yield. Their analysis has extended the work of Crosby and co-workers[126-128] who examined the complex at temperatures below 273K and found the decay processes to occur from three closely grouped excited states. These were assigned as d-π^* charge-transfer-to-ligand (CTTL) states. Working between 273-373K, Van Houten and Watts found that other states became important and were linked with the CTTL states by a temperature dependent intersystem crossing.

The new states were proposed to be d-d ligand field (LF) states; their exact nature remains to be demonstrated conclusively however. Fig.3.4. illustrates the states and their decay processes.
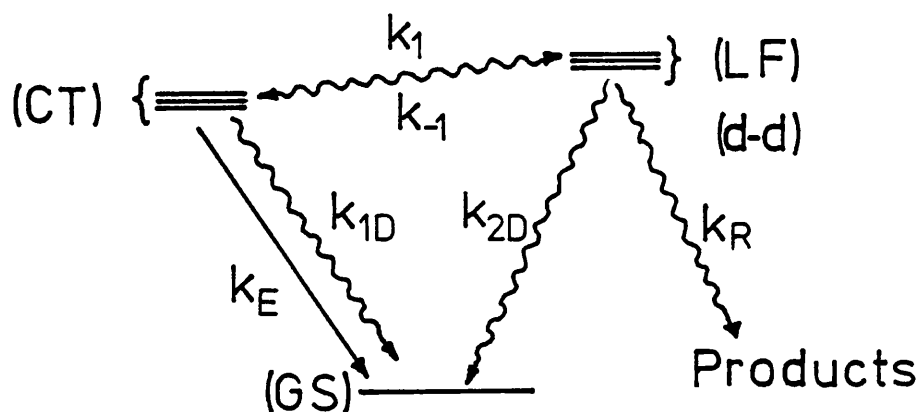
$$\text{Fig. 3. 4.}$$

The parameters denoted by k_E, k_{1D}, k_{2D} and k_R represent average values for decay processes from each group of very closely-spaced levels. Emission occurs from the CTTL states whilst extremely efficient radiationless decay[131] as well as less efficient product formation are the decay modes of the LF states. Thus when $T > 273$ the temperature induced population of the LF states causes emissive yield and lifetime to decrease with increasing temperature, in agreement with observation.

The presence of the non-emissive photoreactive LF states was also proposed by Hintze and Ford[132] who demonstrated that the different states exhibited different photoreactivity. These results are critical in the explanation of the data obtained by

Van Houten and Watts and that described here. The last authors proposed that charge-transfer to solvent interactions with the CTTL states were causing the observed changes in molecular parameters on solvent deuteration. The absence of such changes when the ligand was exchanged for its per-deutero analogue was used in support of this theory. On the other hand, CTTS mixing should imply significant absorption and emission wavelength dependency on solvent.[133] Whilst small variations are observable, much larger effects might have been expected. There is also a surprising lack of effect of addition of water to acetonitrile solutions.

The data listed in Table 3.2. together with those of Van Houten and Watts can be explained by means of the following equations derived from Fig.3.4. (CT)* and (LF)* are the two groups of excited states and k_{1Q}, k_{2Q} the rate constants for their interactions with solvent molecules.

$$C \xrightarrow{I} (CT)*$$

$$(CT)* \xrightarrow{k_E} C + h\nu$$

$$(CT)* \xrightarrow{k_{1D}} C$$

$$(CT)* \xrightarrow{k_1} (LF)*$$

$$S + (CT)* \xrightarrow{k_{1Q}} C + S$$

$$(LF)* \xrightarrow{k_{2D}} C$$

$$(LF)* \xrightarrow{k_{-1}} (CT)*$$

$$S + (LF)* \xrightarrow{k_{2Q}} C + S$$
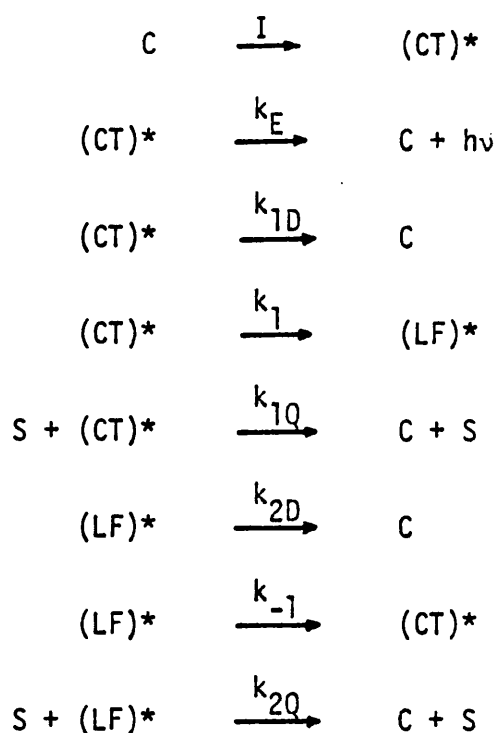
From which it can be shown that

$$\Phi_E = \cfrac{k_E}{k_E + k_{1D} + k_1 \exp(-\Delta E/RT) + k_{1Q}[S] - \cfrac{k_1 k_{-1}}{k_{2D} + k_{-1} + k_{2Q}[S]}} \qquad \ldots 3.(1)$$

The excited state interaction could be in the form of either nucleophilic attack or a protonation step. Certainly the quenching of emission is reduced as the acidity of the protic solvent decreases. Deuteration of the solvent also leads to a reduction of the quenching process as might therefore be predicted. In order to explain the lack of an effect on the lifetime in MeOH/MeOD it is necessary to conclude that there is little quenching of the CTTL states ($k_{1Q} \sim 0$). Quenching of these states may well be small except in the case of H_2O, the most powerful protonating agent. Quenching of the (LF) states however by all of the solvents in different degrees seems to be responsible for the bulk of the effects and indeed it is from this set of states that reaction has been proposed to occur.[131] Because oxygen is such an efficient quencher of the emissive state[124] this process eliminates most of the solvent effects and produces a remarkable invariance of quantum yield in aerated solution compared to the degassed case. Hence

the most efficient solvent quencher, water, is least affected

by oxygen introduction ($\Phi_{deg.}/\Phi_{aer.}$ = 1.3), whilst a much poorer

quencher such as ethanol is dramatically quenched by oxygen

($\Phi_{deg.}/\Phi_{aer.}$ = 6.9).

Having obtained quantum yield and lifetime data for the

photosensitisers and having considered their excited state

properties it is now possible to study the types of compounds

which are able to effectively interact with sensitisers in

photochemical reactions. These are considered in the next four

sections.

3.2.3. The Excited State Interactions of Photosensitisers with Amines

As was reported in chapter two and 3.2.1., the quenching

of aromatic hydrocarbon fluorescence by amines involving a charge

transfer process is well documented. Surprisingly despite the

considerable discussion[103-105] centred around charge transfer

interactions of dye triplets, hardly any consideration has been

paid to the participation of dye singlets in excited state

reactions. At best the singlet quenching by amines has been

discounted as negligible.[116,121] Elsewhere[119,120,122] we have

shown that this is not the case. Table 3.3. summarises the Stern-

Volmer quenching constants together with the quenching constants

themselves measured for the dyes in methanol. From these it is

plain that many of the interactions are far from negligible with

FLUORESCENCE QUENCHING OF DYES BY VARIOUS AMINES[1,2,3].

AMINE	Rose Bengal		Methylene Blue	
	K_{SV} $\times M$	k_q $\times 10^{-10} Ms$	K_{SV} $\times M$	k_q^3 $\times 10^{-10} Ms$
N,N-dimethylaniline	32.5	1.0	20.6	2.1
N-methylaniline	30.4	0.95	22.3	2.2
Diphenylamine	29.4	0.92	36.7	3.7
Aniline	18.6	0.58	18.9	1.9
Tribenzylamine			5.0	0.5
DABCO	6.0	0.19	2.6	0.26
Triethylamine	1.1	0.034	1.0	0.1
Gramine	10.4	0.32	14.0	1.4
Indole	11.9	0.37	19.7	2.0
Indoleacetic acid	15.8	0.49	195	2.0
Indoleacetic acid[1]			24.8	2.5
Tryptamine	23.0	0.72	17.0	1.7
N-acetyltryptophan			19.9	2.0
Tryptophan[1]			200	2.0
Skatole	23.0	0.72	24.0	2.4

[1]Me ester used; [2]MeOH solvent; [3]assumes $\tau_F = 1$ ns, ref 129

TABLE 3.3.

FLUORESCENCE QUENCHING OF ROSE BENGAL BY Et₃N IN VARIOUS SOLVENTS

Solvent	$K_{SV} \times M$	$k_q \times 10^{-8} Ms$
C_5H_5N	0·25	0·7
$(CH_3)_2CO$	0·40	0·92
CH_3OH	1·1	3·4
CH_3OH/H_2O 50/50	1·3	
CH_3CN	1·5[1]	3·7
EtOH	1·5	4·6
H_2O	4-5[1,2]	

[1]curvature in S-V plot   [2] 1% MeOH added

Table 3.4.

EMISSION QUENCHING OF Ru(bipy)₃Cl₂ AT 293K

Amine	$k_q \times 10^{-8} Ms$ MeOH	$k_q \times 10^{-8} Ms$ MeCN
4-Methoxyaniline	15	6
N,N-Dimethylaniline	1·3	0·75
N-Methylaniline	1·0	0·22
Aniline	0·036	<0·01
DABCO	<0·01	1·3
Triethylamine	<0·01	<0·01

Table 3.5.

quenching rate constants in the vicinity of the diffusional controlled limit. The selection of anilines and their order of quenching of $PhNMe_2$ > $PhNHMe$ > $PhNH_2$ shows that quenching follows the order of ionisation potentials (vide infra), a good indication that the interaction is indeed one of charge transfer, i.e.

$$Dye\ S_1\ +\ Am\ \rightleftharpoons\ Dye^{-\cdot}\ +\ Am^{+\cdot}$$
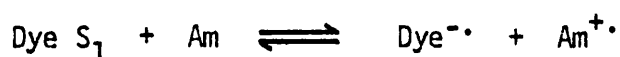
An idea of the importance of this interaction in biological systems is given by the series of substituted indoles where again quenching constants are very high. The lack of variation seems to show that the indole nucleus is the dominating factor and the presence of an amine in the side chain causes little effect. In fact, the amino-indole, gramine ($C_8H_6N.CH_2NMe_2$) is one of the poorest quenchers. On the other hand, the increase in ring charge for skatole over indole does indeed result in more efficient quenching capability consummate with a lowering of the ionisation potential. It is quite apparent that the photo-oxidation of indole and tryptophan derivatives which has received a good deal of attention[134-137] should take into account the possibility of dye singlet participation when concentrations of substrate exceed 10^{-3} M (as they invariably do in this type of reaction.) Doubts must be shed upon mechanisms which fail to do this.[134-137] Further, the widespread practice of using amine-induced photooxidation rate retardation results as evidence for the participation of singlet oxygen[138] is highly dubious unless

low concentrations of amine are used. A consequence of the singlet quenching is that rates of photooxidation of substituted indoles are not substantially increased by increasing the concentration of substrate.[64] (There are however significant rate differences between the derivatives.) In the instance where a dye is absorbed onto a proteinous substrate at a site next to a tryptophyl residue then the oxidation mechanism could well give entirely radical derived products with singlet oxygen playing no part. In solution however oxidation mechanisms combine elements of singlet and triplet dye and singlet oxygen participation.[119,120]

The elucidation of oxidation mechanisms is further complicated however by a solvent dependency of the singlet quenching process. Data for the singlet quenching of rose bengal by triethylamine in different solvents is given in Table 3.4. Quenching is surprisingly efficient in water and quite inefficient in pyridine, other solvents having intermediate values.

Solvent dependency of quenching by amines is observed also in the case of the ruthenium complex where the quenching constants were substantially less than for the dyes (Table 3.5.). Indeed it was the relatively inefficient excited state interaction that prompted its use in the mechanistic investigations of the amine photooxidation processes.[120,125] Again, the rate constants followed an order related to the ionisation potential of the amines suggesting a charge-transfer process. This is the first report

of the luminescence quenching of a ruthenium complex by organic

compounds acting as electron donors. The quenching by electron

acceptors[139-142] and inorganic donors[143-145] has already been

reported. A reductive quenching process is easier to understand

if the excited complex contains the metal as Ru^{III} which has

undergone a metal-to-ligand transition. The original oxidation

state can be attained by the acquisition of an electron from a

suitable donor via a half vacant diffuse d-orbital. Back transfer

to the amine radical cation or reaction with it can occur from

the ligand orbital.

3.2.4. The Excited State Interactions of Photosensitisers with Anions

The quenching of the fluorescence of hydrocarbons[81] and

dyes[129,146] by anions is not novel. Nevertheless it has escaped

the notice of workers who, in the knowledge that azide ion

quenches singlet oxygen,[147,148] have used it to test photo-

oxygenation reactions for the participation of singlet oxygen. A

number of quenching constants are therefore reproduced in Table

3.6. The quenching is much more efficient for methylene blue

than for rose bengal and this can be attributed to a coulombic

interaction since the dyes are respectively cationic and anionic.

Thus, in the same way as amines, anions can act as donors

in excited state charge transfer quenching of dyes leading to

FLUORESCENCE QUENCHING OF

DYES BY ANIONS

Substrate	$K_{SV} \times M$	
	ROSE BENGAL	METHYLENE BLUE
Sodium iodide	$2 \cdot 0^1$	$14 \cdot 6^1, 15 \cdot 4^2$
Sodium azide	$0 \cdot 6^1$	$3 \cdot 6^2$
Sodium thiosulphate		$3 \cdot 1^2$
Sodium bromide	$0 \cdot 1^1$	$0 \cdot 8^2$
Sodium chloride	$0 \cdot 05^1$	$0 \cdot 2^2$

^{1} MeOH/H_2O (50/50) ^{2} MeOH/H_2O (20/80)

Table 3.6.

radicals and derived products. This is relevant to the report[149] that addition of azides to photooxygenation reactions of olefins leads to azido-hydroperoxide formation. Presumably the product occurs via the attack of the azide radical formed from interaction with the dye. Reaction of the radical thus formed with oxygen in solution can be seen to give the observed product after a final hydrogen abstraction step.

Anionic quenching follows the expected order in accordance with their redox potentials. Brooks and Davis[81] obtained similar

THE EFFECT OF IONS ON THE EMISSION

FROM Ru(bipy)$_3$Cl$_2$.
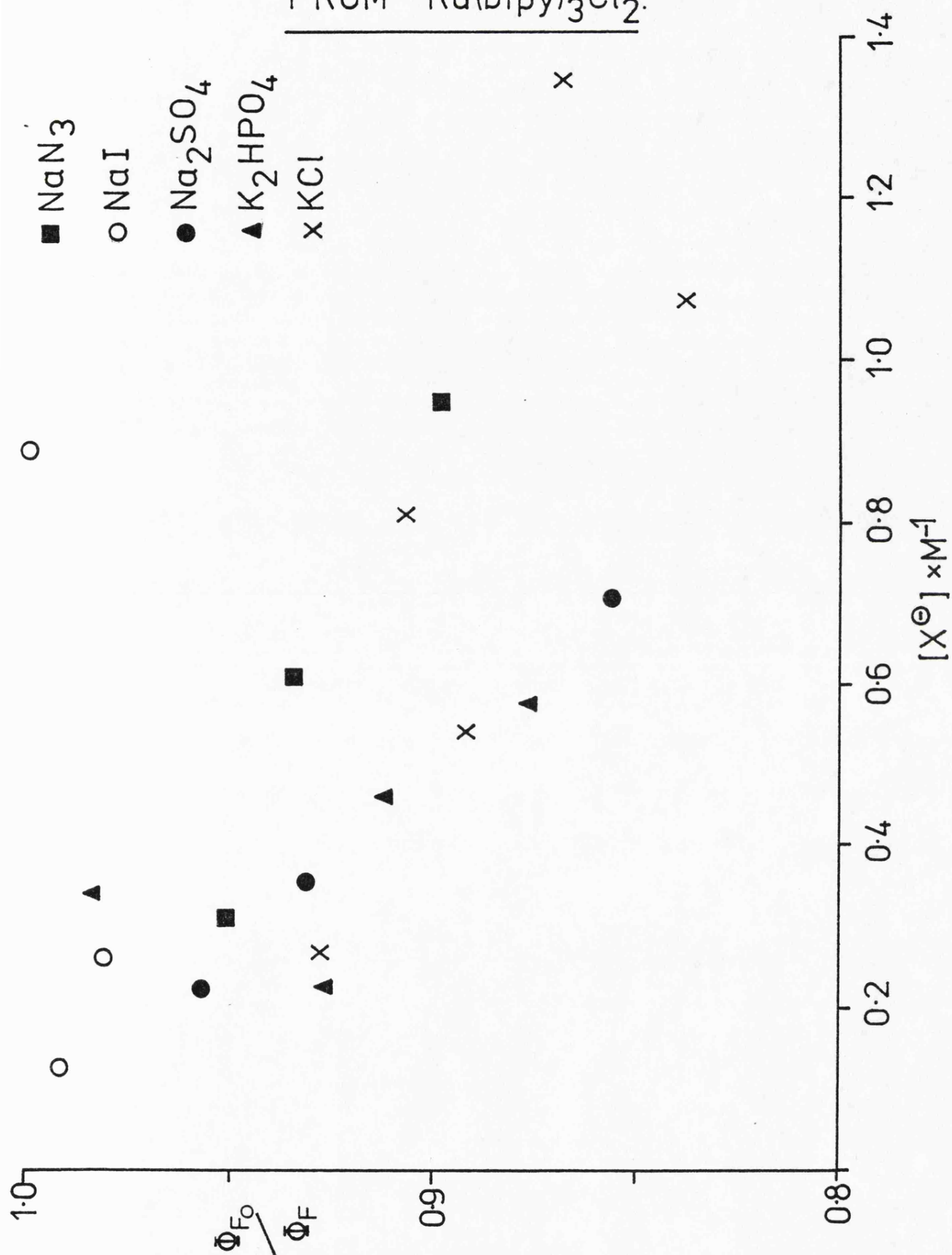
Fig. 3.5.

results in their study of the quenching of anthracene fluorescence. Recent work by Watkins[150-152] on quenching of the fluorescence of aromatic hydrocarbons by anions suggests that electron transfer may not be the mode of interaction in the sense that discrete radical species are formed. Watkins found no evidence of the existence of such species by means of flash photolysis techniques. He proposed that the mechanism of quenching was via an encounter exciplex in which mixing of charge transfer and exciton resonance states occurred in a similar way to that described in 1.7. This allowed efficient formation of the triplet hydrocarbon rather than simple deactivation to the ground state in agreement with the experimental observations. That the heavy atom effect was not involved was evidenced by the quenching of nitrate and thiocyanate being as good as halides (cf. this section, N_3^- vs I^-, Br^-). The degree of quenching was proposed to be dependent on the energetics of the species involved which in turn were related to redox potentials.

When the effect of anions on the luminescence of the ruthenium complex was examined it was found that there was actually an increase in intensity (Fig.3.5.). Reproducibility of results was difficult because of the smallness of the effect. The results for iodide showed hardly any increase. This was taken as an indication that it was quenching the luminescence in opposition to the effect which was causing the enhancement. It was also noted that the

enhancement seemed to be proportional to the anionic charge and that therefore the luminescence was susceptible to ionic strength. However an attempt to correlate the results with ionic strength was not successful. The amounts of substrate necessary were large enough however to be interfering with the sensitiser solvent inter- actions and were undoubtedly causing the enhancement by altering the solvent composition.

3.2.5. The Excited State Interactions of Photosensitisers with Aromatic Hydrocarbons and Related Compounds

After noticing discrepancies in the quantitative photo- oxygenation of 9-methyl anthracene[64] it was found that the substrate was quite efficiently quenching the excited singlet state of the dye and causing a rate retardation. In view of this a number of other substituted anthracenes and naphthalenes were examined and their quenching constants measured. The values obtained are listed in Table 3.7. A variety of other related compounds were also tested and the results for these summarised in Table 3.8.

It was observed that quenching ability was approximately proportional to ionisation potential in so far as anthracene derivatives were better quenchers than naphthalene derivatives. There were small variations within each group of aromatic compounds so that, for example, the electronically deactivated 9-nitro- anthracene was a poor quencher whilst 9-methoxyanthracene was a good one. Surprisingly 9,10-dimethylanthracene was poor in relation to 9-methylanthracene.

FLUORESCENCE QUENCHING OF DYES BY

NAPHTHALENE AND ANTHRACENE COMPOUNDS[1,2]

Substrate	ROSE BENGAL		METHYLENE BLUE	
	$K_{SV} \times M$	$k_q \times 10^{-10} Ms$	$K_{SV} \times M$	$k_q \times 10^{-10} Ms$
Anthracene	7.8^3	0.24		
9-Methyl-	22.7	0.71	28.0	2.8
9,10-Dimethyl-	7.0	0.22	28.7	2.9
9-Hydroxymethyl-	1	0.03	25.3	2.5
9-Hydroxyethyl-	16.2	0.51	35.6	3.6
9-Acetyl-	7.4	0.23	31.8	3.2
9-Carboxaldehyde	10.4	0.32	30.3	3.0
9-Methoxy-	16.6	0.52	35.2	3.5
9-Carboxylic acid			34.7	3.5
9-Nitro-			13.4	1.3
1-Methyl Naph.	0.5	0.016	2.6	0.26
2-Methyl-	0.6	0.019	1.3	0.13
2,3-Dimethyl-	0.8	0.025	8.6	0.86
2,6-Dimethyl-	1.4	0.044	10.4	1.04
Acenaphthylene	1.0	0.03	4.7	0.47
Acenaphthene	3.4	0.11	18.2	1.82

[1] MeOH solvent   [2] assumes $\tau_F = 1$ ns for M.B.   [3] EtOH solvent

Table 3.7

FLUORESCENCE QUENCHING OF DYES[1,2]

Substrate	ROSE BENGAL		METHYLENE BLUE	
	$K_{SV} \times M$	$kq \times 10^{10} Ms$	$K_{SV} \times M$	$kq \times 10^{10} Ms$
1,2-Benzanthracene	$<10^3$	$<0.3^3$		
Pyrene	12.4^3	0.38^3		
Indene	0.2	0.006	0.4	0.04
t Stilbene	2.3	0.073	12.8	1.3
1,4-Diphenylbutadiene	14.8	0.46	28.0	2.8
p-Methoxystyrene			13.4	1.3
β-Carotene			57^4	
Vitamin D_3	5.5	0.17	7.6	0.8
Ergosterol			29.2	2.9
DPBF			57	5.7
Acridene	3.0^3	0.091^3	1.6^3	
Phenazine	14.1^3	0.43^3		
Fluorenone			<0 1	<0 01
Xanthone			2.8	0.3
Thioxanthone			12.1	1.2
Benzophenone			<1	<0.1

[1] MeOH solvent [2] assumes $\tau_F = 1ns$ for M.B. [3] EtOH solvent
[4] MeOH/C_6H_6 (20/80)

Table 3.8.

Two compounds which will prove of interest later in this
chapter are 1,3-diphenylisobenzofuran (DPBF) and β-carotene. Both
compounds have been used extensively in sensitised photooxygen-
ations[153,154] the former because of its extremely high reactivity
with singlet oxygen[155] and the latter because of its role in photo-
dynamic action.[156] Further, both compounds showed extremely
efficient interactions with methylene blue singlet states. (The
data observed had to be corrected because of the substrate
molecules' finite absorptions in the excitation and emission regions
of the dye. The method of correction is the same as that described
in 3.7.3. For these reasons the compounds could not be examined
with rose bengal.) Although the interactions are so efficient it
is unlikely that they will affect the quantitative method of
Young et al[153] for determinations of β-values, or the use of β-carotene
as a test for singlet oxygen.[157] Significant singlet quenching will
only occur at concentrations $> 10^{-3}$ M and both the above procedures
involve substrate concentrations below this threshold level.

The ability of such a wide range of compounds to quench
excited states and the apparent correlation of quenching power
with ionisation potential was put to the test by means of a graph
of $\log_{10} k_q$ vs ionisation potential similar to those of Guttenplan
and Cohen.[158,159] The adiabatic ionisation potentials used,
their sources and code numbers in Fig.3.6. are shown in Table 3.9.
and their correlation with $\log_{10} k_q$ is shown in Fig.3.6. for both
dyes. It can be readily seen from the figure that there is a

Substrate	I P (eV)	Ref	No.fig3.6
N,N-Dimethylaniline	7.1	97	1
N Methylaniline	7.3	97	2
Aniline	7.7	97	3
Diphenylamine	7.25, 7.1	97, 197	4
DABCO	7.52	97	5
Triethylamine	7.5	97	6
Indole	7.86	198	7
Anthracene	7.5	97	8
9-Methyl-	7.17	199	9
9,10-Dimethyl-	7.04	199	10
1-Methyl Naph.	7.96	97	11
2-Methyl-	7.95	97	12
2,3-Dimethyl-	8.2	200	13
2,6-Dimethyl-	8.4	200	14
Acenaphthylene	8.02	201	15
Acenaphthene	7.66	202	16
Indene	8.6, 8.8	97	17
Fluorenone	9.42	203	18
Acridine	7.9, 8.1	204, 198	19
Pyrene	7.53, 7.45	202, 201	20
1,2-Benzanthracene	7.56	201	21
t-Stilbene	7.76	201	22
1,4-Diphenylbutadiene	7.5	205	23
DPBF	7.09	188	24

Table 3.9.

CORRELATION DIAGRAM OF $LOG_{10}k_q$ WITH IONIZATION POTENTIAL
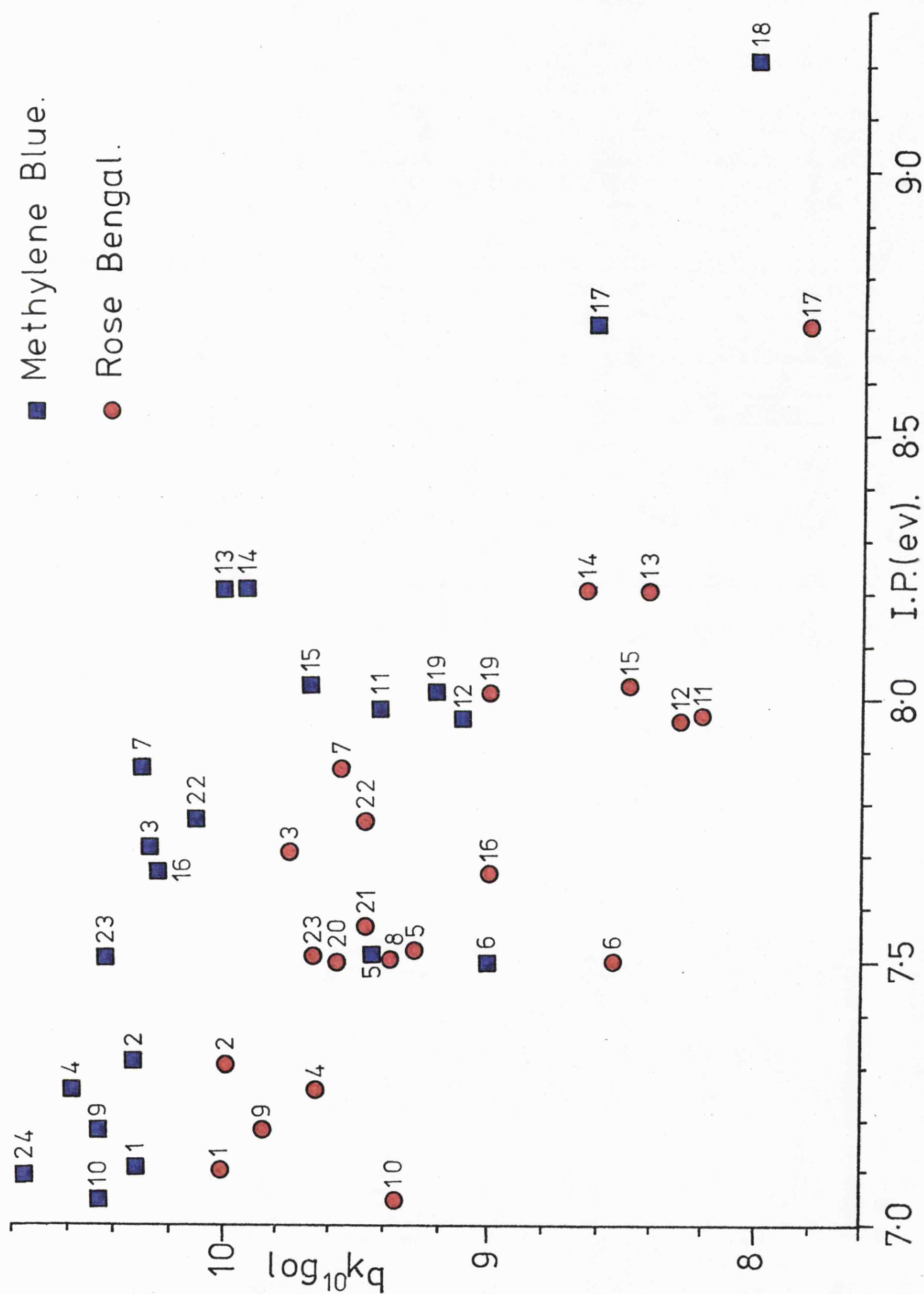
FIG. 3.6.

correlation between the parameters with a more efficient interaction with methylene blue. The flattening off observed at low ionisation potential is due to the proximity of the quenching constants to the diffusional controlled limit. The fairly large scatter can be attributed to the lack of sufficiently accurate ionisation potential data. Even when more than one value exists there is considerable variation and the majority of the values are subject to at least ± 0.1 eV error. The use of compounds with a wider range of ionisation potentials is of course precluded by the experimental difficulty in observing quenching at values below $k_q = 10^8$ M^{-1} s^{-1}. The k_q values are also subject to errors in the region of $\pm 10\%$ and possibly more at low quenching efficiencies. It is possibly unfair therefore to expect a better correlation in view of the inadequacy of the available data. It can reasonably be concluded therefore that since the singlet energy levels of the quenchers preclude energy transfer as a quenching mechanism, and since there is a correlation of quenching ability with ionisation potential, then quenching is occurring via a charge-transfer excited state interaction. This can involve either complete transfer to give discrete radical species or partial transfer in an excited encounter complex such as proposed by Watkins[150,152] and discussed in detail in the first two chapters.

3.2.6. Excited State Interactions of Rose Bengal with Molecules of the Type $Ar(CH_2)_n NR_2$

In view of the fact that amines (3.2.3.) and aromatic hydro-

FLUORESCENCE QUENCHING OF

ROSE BENGAL BY $Ar(CH_2)_n NR_2$.[1]

Substrate	$K_{SV} \times M$	$k_q \times 10^{-8} Ms$
α1E	3·6	11·25
α2E	2·0	6·25
α3E	1·9	5·9
α4E	3·6	11·25
β1E	2·8	8·75
β2E	2·1	6·6
β3E	1·2	3·75
β4E	3·8	11·9
$PhCH_2NEt_2$	2·9	9·1
$Ph(CH_2)_2NMe_2$	1·2	3·75
Et_3N	1·1	3·4

[1] MeOH solvent.

Table 3.10.

carbons (3.2.5.) quenched the excited states of dyes, some of the compounds prepared in chapter two which combined both groups in the same molecule were examined with rose bengal. The results for αnE and βnE are summarised in Table 3.10. Also shown are quenching values for $PhCH_2NEt_2$ and $Ph(CH_2)_2NMe_2$.

The surprising result obtained was that in every case the net quenching power of the molecule was greater than the sum of the two individual groups. Thus, for example, αlE was found to have a K_{SV} of 3.6 M^{-1} whilst triethylamine and α-methyl-naphthalene have been shown to have values of 1.1 and 0.5 M^{-1} respectively. As n was increased from 1 to 3 the quenching power dropped to values close to the sum of the components but when n = 4 the power suddenly increased, equalling if not exceeding the large values obtained when n = 1.

For the phenyl derivatives examined similar properties were noted. Toluene might reasonably be expected to have even smaller quenching properties than naphthalene in view of its larger ionisation potential of 8.82 eV.[97] Nevertheless surprising-ly large K_{SV} values were measured for these derivatives and it was thoughtthere might be a small ground state electronic effect of the aromatic electrons on the amino group. In view of the earlier discussion on through-bond effects it was considered that the technique of [13]C n.m.r. might be sensitive enough to measure this effect by unusual chemical shifts of the carbon atoms in the

linking chain. The ^{13}C n.m.r. spectra were therefore obtained and the chemical shifts computed. (For details see Appendix 3.2.6.). No unusual effects were measured.

Davidson and Whelan[160] have observed unusually large K_{SV} values in their studies of the fluorescence quenching of rose bengal by molecules of the type $Np(CH_2)_nNp$ and $Et_2N(CH_2)_nNEt_2$. In all cases the K_{SV} values are larger than for the sum of the individual quenchers. They have also found that when n = 4 the quenching power is maximised, in agreement with results in this section. Surprisingly however they found this property to be unique to rose bengal; quenching of hydrocarbon fluorescence was found to exhibit a quite different relationship to chain length. No satisfactory explanation is available at present for these results and further work is in progress to investigate these interactions.

3.3. Concerning the Role of β-Carotene in Photosynthesis

3.3.1. Introduction

It has been conservatively estimated that the total annual carotenoid production in nature is 10^8 tons.[161] Given this information the statement that carotenoids play an extremely important role in photosynthesis seems superfluous. Nevertheless, carotenoids are associated with all known photosynthetic systems with a very few exceptions. The recent demands of society for cheap energy

have resulted in an enormous concentration of effort into un-
ravelling the mysteries of the most efficient energy conversion
process known to man. The importance of excited state interactions
of chlorophyll needs therefore no stress. Detailed considerations
of photosynthetic mechanisms are beyond the scope of this short
section but numerous reviews of the subject are available.[161-165]

The close association of carotenoids with chlorophyll
molecules in the chloroplast structure has been well established[166]
and they are believed to play a direct role in photosynthesis.
They have been proposed to act as light harvesters, cofactors for
oxygen transport and evolution, cofactors for the photosynthetic
reactions and as agents to protect the cells against lethal photo-
oxidations. It is believed[164] that the last of these is the true
role of the carotenoids and it has consequently received much
attention. The reason for this is the well known destructive
agent singlet oxygen which is formed extremely efficiently by the
action of light and oxygen on photosensitisers. Carotenoids have
been considered able to protect the cells from destruction by
several modes of action:

(a)   as a light filter

(b)   by development of mechanisms to repair
       the damage caused by oxidation reactions

(c)   by deactivation of the photosensitiser

(d)   by development of compounds to act as
       preferred substrates for the oxidation
       reactions.

SOME EXCITED STATE INTERACTIONS IN GREEN PLANTS

PHOTOSYNTHESIS

^{1}CHL

^{3}CHL ^{3}CHL

CHL

$h\nu$

$^3O_2$ Energy   CAR

$^1O_2$ CAR*
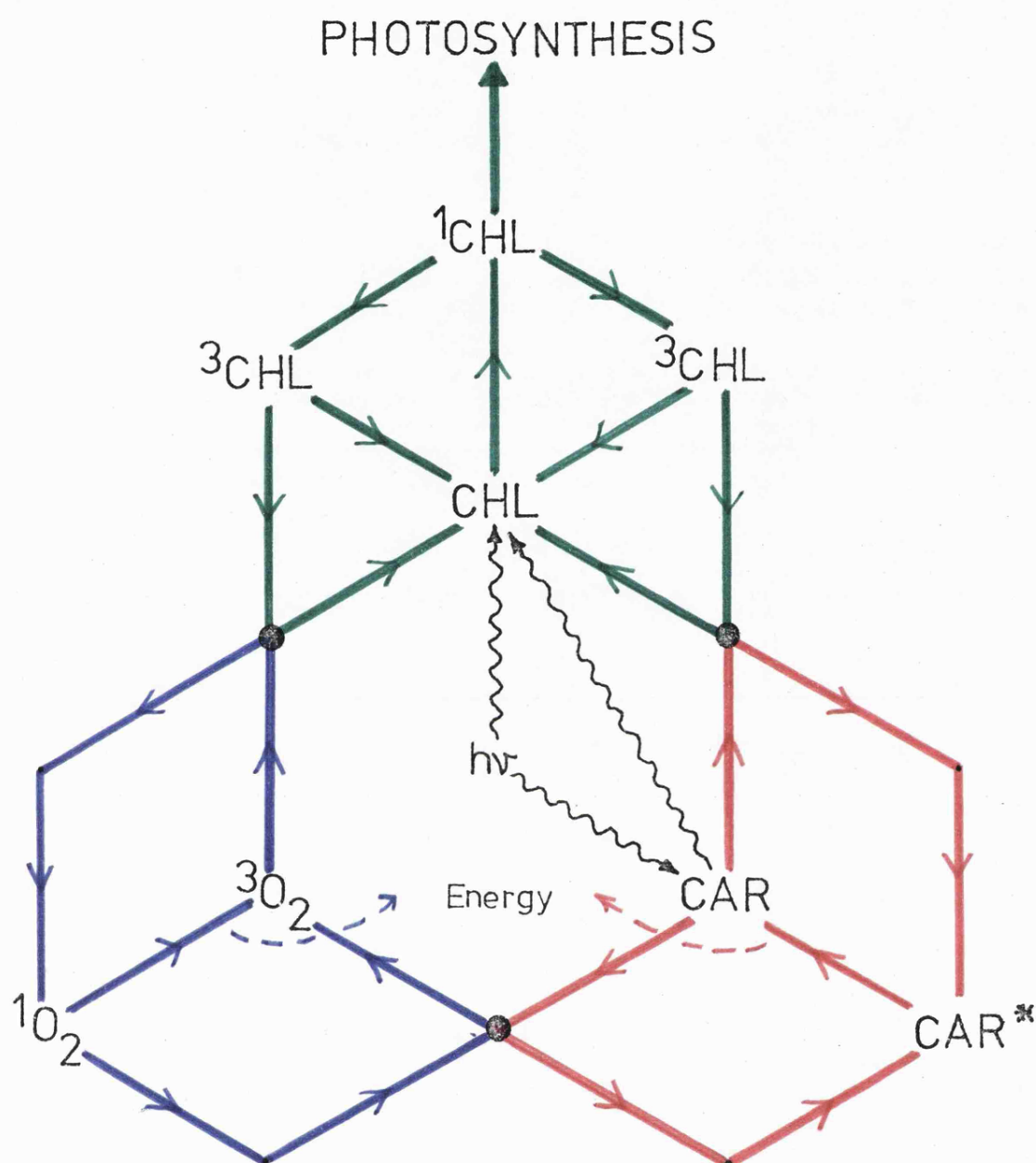
Fig. 3.7.

The mechanisms are illustrated schematically in Fig.3.7. (A more complete discussion occurs in a review by Krinsky in refs. 161, 164). Of these mechanisms there is no doubt that those of (c) are most important.

Foote[154] showed that β-carotene efficiently quenched singlet oxygen and that the rate of quenching was proportional to the length of the polyene chain.[156] Quenching of singlet oxygen has been proposed as occurring via a charge-transfer-like intermediate[121] and hence the ionisation potential of the quencher is important. Increasing the polyene chain length will reduce the ionisation potential and hence increase the quenching of singlet oxygen. As is apparent from 3.2.5. however, low ionisation potentials also increase sensitiser substrate interactions.

Excited state interactions of chlorophyll and β-carotene have been well studied and the quenching of chlorophyll triplet states has been conclusively proved.[167] Excited singlet state quenching has also been reported[168-171] but the results have been shown to be in error.[171] The fluorescence lifetime of chlorophyll a has been measured as 5 ns[162] and therefore from a simple consideration of the Stern-Volmer quenching kinetics it is apparent that a quencher concentration of $>10^{-3}$ M is required for it to be observable. The report[168] of quenching by a concentration of 10^{-5} M is therefore obviously in error. The results in this section however unequivocally demonstrate that β-carotene efficiently quenches the excited singlet state of chlorophyll a, thus providing a

further excited state interaction to be taken into consideration

of the role of β-carotene in photosynthesis.

3.3.2. Results of Singlet Quenching Studies

The greatest problem in carrying out experiments of this

nature is that the absorption bands of β-carotene overlap both

the absorption and the emission bands of chlorophylla. This has

necessitated correction of intensities of emission and the details

of this are outlined in 3.7.3. Chlorophylla was extracted from

Poa Annua and used immediately. Details of the extraction are

given in 3.7.4. and the experimental details of the quenching

measurements in 3.7.2. Because of the difficulty in obtaining

reliable results the effect of β-carotene on the lifetime of

emission of chlorophylla was determined by Dr. G.S. Beddard of

the Royal Institution, London. Table 3.11. contains the extinction

coefficients necessary for the correction of fluorescence intensity.

Tables 3.12.-3.14. list the fluorescence quenching results obtained

using 1 cm square cells and thin tubes. The information from the

Tables has been used in Fig.3.8. to illustrate the results. From

this figure which also shows the shortening of the lifetime, it

can be clearly seen that the independent measurements are quite

consistent. Using the lifetime of the unquenched singlet state of

5 ns[162] the results lead to quenching constants of $4.5 \times 10^9 \ M^{-1} \ s^{-1}$

for the lifetime measurements and $\sim 5 \times 10^9 \ M^{-1} \ s^{-1}$ from the

fluorescence quenching, all in benzene. Benzene-methanol yielded

β-CAROTENE EXTINCTION COEFFICIENTS[1]

λnm	ε±1	λnm	ε±1
700	1	664	16·5
690	3·5	663	17·5
680	6	662	18
678	7·5	661	19
675	9·75	660	20
670	12·5	655	24·5
669	13	652	27
668	13·75	650	29
667	14·5	645	34
666	15	642	37
665	16	640	39

[1] in C_6H_6

Table 3.11.

FLUORESCENCE QUENCHING OF CHLOROPHYLL A BY β-CAROTENE

$[\beta\text{-Car}] \times 10^3 M^{-1}$	$(F_0/F)_{obs.}$	F_0/F
2·09 ±0·1	1·127 ±0·02	1·047 ±0·05
4·19	1·267	1·093
6·29	1·439	1·154
8·38	1·532	1·141
10·37	1·818	1·263

Square cells; C_6H_6 solvent; λ_{exc} 662, λ_{em} 670; [chl] = $4\cdot5\times10^{-6}M$; 'best-fit' K_{sv} = 26±5

Table 3.12.

FLUORESCENCE QUENCHING
OF CHLOROPHYLL A BY β-CAROTENE

[β-Car] $\times 10^3 M^{-1}$	$(F_0/F)_{obs}$	F_0/F
0.7 ±0.1	1.064±0.02	1.040±0.05
1.1	1.086	1.047
1.4	1.082	1.035
2.1	1.129	1.055
2.25	1.139	1.059
2.8	1.165	1.064
3.4	1.277	1.145
4.5	1.400	1.211

Square cells; C_6H_6/MeOH (80/20)solvent; λ_{exc} 662, λ_{em} 669; [chl]=10^{-6}M; 'best-fit' K_{sv} 45 ± 5

Table 3.13.

FLUORESCENCE QUENCHING
OF CHLOROPHYLL A BY β-CAROTENE

[β-Car] $\times 10^3 M^{-1}$	$(F_0/F)_{obs.}$	F_0/F
2.5 ±0.1	1.104±0.02	1.081±0.05
5.0	1.236	1.185
7.5	1.351	1.269

Thin tubes; C_6H_6 solvent; λ_{exc} 650, λ_{em} 678; [chl]=10^{-5}M; 'best-fit' K_{sv} 37±5

Table 3.14.

SINGLET QUENCHING OF CHLOROPHYLL A BY β-CAROTENE.
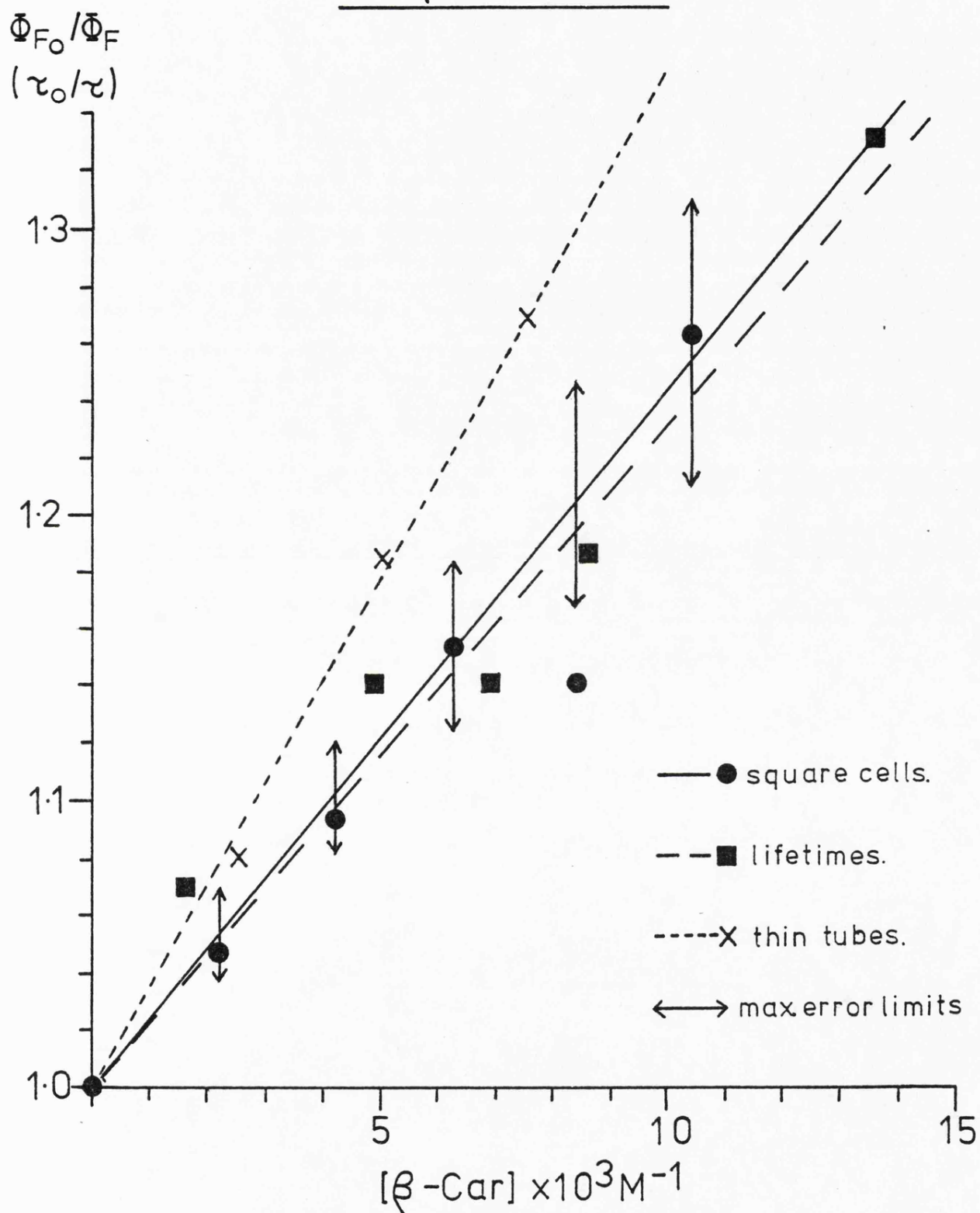
Fig. 3.8.

the higher constant of 9×10^9 $M^{-1}s^{-1}$ presumably as a result of a slight decrease in viscosity.

Surprisingly, during the examination of the lifetimes of chlorophyll fluorescence it was observed that a mixture of carotene and chlorophyll showed many more 'dark counts' than the chlorophyll solution alone. It was apparent therefore that a chemiluminescent reaction was taking place on mixing the two, the emission being due to the chlorophyll. It may be that a report[172] of fluorescence enhancement on addition of β-carotene to a solution of chlorophyll and benzoquinone is due to this reason.

3.3.3. Discussion

The quenching cannot be attributed to an energy transfer process since the singlet energy of chlorophylla lies below that of β-carotene. The results reported in 3.2.5. showed that the quenching of fluorescence of sensitisers by aromatic hydrocarbons and related compounds was probably by a charge transfer process and that β-carotene quenched the fluorescence of methylene blue. The mechanism can therefore be proposed as

$$Car + Chl(S_1) \longrightarrow Car^{+\cdot} + Chl^{-\cdot}$$
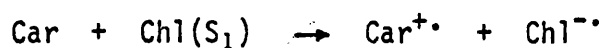
The idea of chlorophylla acting as an electron acceptor is in opposition to the generally accepted participation of the radical cation in photosystem 1. However both the chlorophyll radical ions

have recently been reported[173] as being formed in efficient electron transfer reactions from the respective β-carotene radical ions thus:

$$Car^{+\cdot} + Chl \rightarrow Chl^{+\cdot} + Car$$

$$Car^{-\cdot} + Chl \rightarrow Chl^{-\cdot} + Car$$
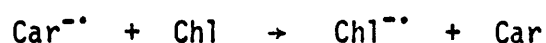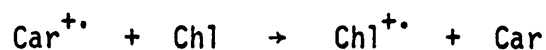
Hence the mechanism proposed here leads to the net production of a chlorophyll radical cation and a chlorophyll radical anion in which the carotene is acting catalytically:

$$Car + Chl(S_1) \rightarrow Car^{+\cdot} + Chl^{-\cdot}$$

$$\underline{Car^{+\cdot} + Chl \rightarrow Car + Chl^{+\cdot}}$$

$$Chl + Chl(S_1) \rightarrow Chl^{-\cdot} + Chl^{+\cdot}$$
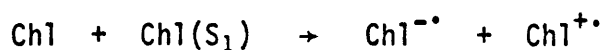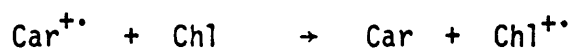
Thus it may be that β-carotene is acting as a catalyst for exciton production as well as being present to deactivate singlet oxygen if it is formed. Its other role as a light harvester has been shown by the presence of a band due to the carotene in the chlorophyll excitation spectrum.[174-178] The processes involved can therefore be represented diagrammatically as in Fig.3.8.

$$Chl(S_1) \xleftarrow{\quad Chl(S_0) \quad} Car(S_1)$$

$$\underset{Car(S_0)}{\searrow} \qquad \underset{Chl(S_0)}{\swarrow}$$

$$Chl^{-\cdot} \; Car^{+\cdot}$$

$$\Big\downarrow Chl(S_0)$$

$$Chl^{-\cdot} Chl^{+\cdot} \; Car$$

$$Chl(S_0) \qquad Car(S_0)$$

Photosynthesis
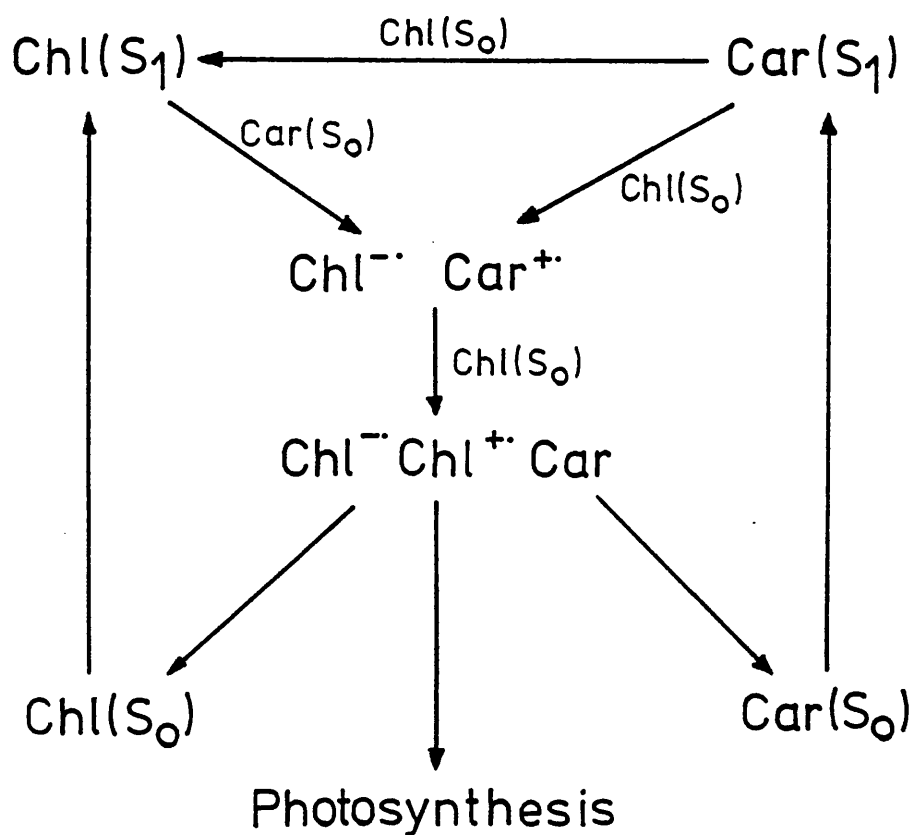
Fig. 3.8.

3.4. Photosensitised Aromatic Hydrocarbon Triplet Formation

Results reported in the last two sections are of a pre-
liminary nature and intended as a guide for possible further
investigation.

The processes of intermolecular energy transfer are many
and have been thoroughly investigated.[179-181] In particular, some
dyes have been shown to undergo triplet energy transfer to aromatic
hydrocarbons.[182,183] The conclusion from these studies has been

that the rate of energy transfer is largely proportional to the energy difference between the states involved. Thus for a donor (D) and acceptor (A) where $E_{T(D)} \gg E_{T(A)}$ then the rate approaches the diffusional controlled limit (with some qualifications[184]). An equilibrium develops however when $E_{T(D)} \sim E_{T(A)}$ but when the energy of the donor drops below that of the acceptor energy transfer becomes strongly temperature dependent (and if the energy is too low does not occur at all).

Our experiments examined energy transfer from various sensitisers, and in particular rose bengal, to 9-methylanthracene to complement results previously obtained for the singlet state (3.2.5.). The technique of conventional microsecond flash photolysis was used. Fig.3.10. illustrates the results obtained using rose bengal with various concentrations of 9-methylanthracene, all traces representing a time delay of 8 µs. The exciting light was suitably filtered such that only the rose bengal absorbed any radiation. When 10^{-5} M substrate was used no trace of the typical triplet-triplet absorption was observed. Bands attributable to the dye triplet absorption were not noted, neither do they appear to have been observed elsewhere. The ground state absorption band of the dye however was taken as an approximate measure of the proportion of triplet molecules present. Thus their depletion for 10^{-5} M substrate indicated that the dye was present mostly in the triplet state.

TRIPLET ENERGY TRANSFER FROM
ROSE BENGAL TO 9-METHYLANTHRACENE.
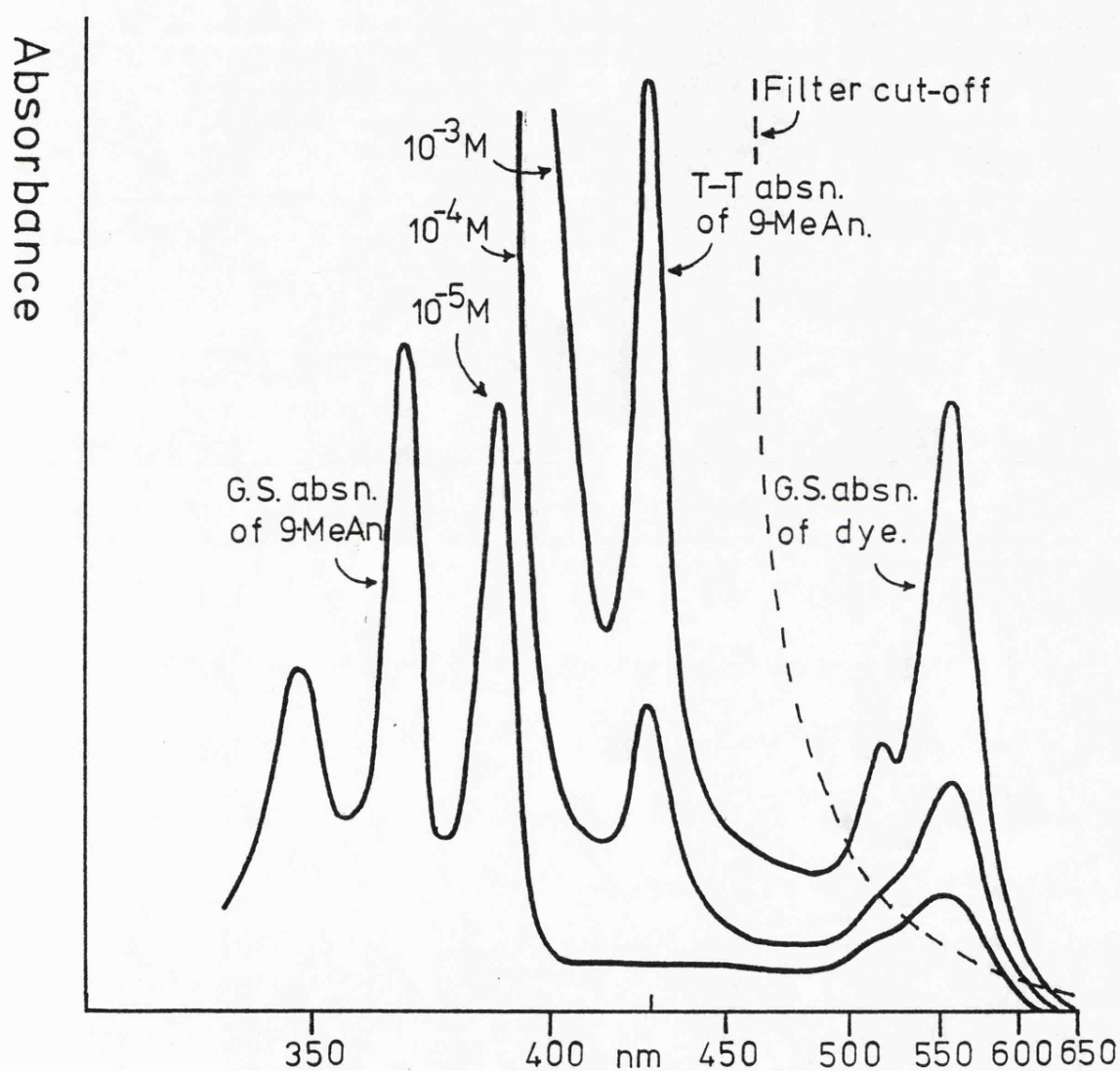
Fig. 3.10.

When 10^{-4} M substrate was used a weak absorption could be clearly seen at the wavelength of the anthracene triplet (425 nm) and the observed increase in the rose bengal absorption bands showed that the dye triplets had been quenched. The effect was increased when 10^{-3} M 9-methylanthracene was used; the anthracene triplet absorption was strong and the rose bengal absorption had reached an intensity approaching total ground state population. In order to ensure that the presence of the anthracene triplet was due to energy transfer an identical solution containing 10^{-3} M 9-methylanthracene was examined in the absence of dye. The spectrum obtained showed no trace of triplet species and was consistent with complete population of the ground state.

An indication that the energy transfer was inefficient was obtained when a 10^{-5} M solution of 9-methylanthracene was flashed in the absence of dye and filter solution. A strong absorption comparable to the 10^{-3} M case in the presence of dye was obtained. However there was undoubtedly an increased flash intensity at the exciting wavelength than in the previous cases and so the energy transfer may well have been more efficient than this experiment indicated.

In the second group of experiments several sensitisers with different triplet energies were used in combination with constant (10^{-5} M) concentration of 9-methylanthracene. The sensitisers used in order of triplet energy were the ruthenium

complex > fluorescein > eosin > rose bengal. In agreement with expectations, the yield of anthracene triplet was observed to follow the same order, i.e. strong for the ruthenium complex and not observable for rose bengal with the others in between. Again, a cautionary note must be added with regard to the variation of exciting light intensity at the different wavelengths required. However, the variation in λ_{ex} was not more than 100 nm (450-550 nm) and it is anticipated that this would not alter the order observed.

The results confirm that energy transfer is occurring from the excited sensitiser to the substrate. The energies of the donor states are known; 49[185] for the complex, 46.8[186] for eosin and 44.6[186] for rose bengal (all Kcals/mole). The value for λ Fluorescein however does not appear to have been obtained but is anticipated to be higher than the other more substituted xanthene dyes. The E_T values quoted by Gollnick[105] appear to be somewhat low. The triplet energy of 9-methylanthracene has been quoted as 41.3 Kcals/mole[182] and if Gollnick's figure were correct would lead to E_T for rose bengal being 1.9 Kcals/mole below that for the anthracene. Rose bengal has been used efficiently to sensitise the dimerisation of acenaphthylene[186] which has been reported to have an E_T of ∿40 Kcals/mole. The results reported therefore are consistent with those of other laboratories.

3.5. The Excited State Interactions of Photosensitisers with 1,3-Diphenylisobenzofuran

1,3-Diphenylisobenzofuran (DPBF) has been used extensively in sensitised photooxygenation reactions.[153,187] It is exceptionally reactive toward singlet oxygen[155] and has a low ionisation potential (7.09 eV[188]). The combination of these factors together with its capacity to stabilise a radical centre has led to the elucidation of numerous excited state pathways and possible products.[189-193] Its use as an indicator of reactions involving singlet oxygen is therefore by no means simple.

In 3.2.5. it was noted that DPBF reacts with the excited singlet state of methylene blue with a rate constant at the diffusional controlled limit. However because of the positioning of the absorption bands the same method could not be applied for rose bengal. In view of the other results reported in this chapter it is almost certain that a similar situation will apply.

The triplet energy of DPBF does not appear to have been reported and its triplet-triplet absorption spectrum has not been observed either in this work or elsewhere. In view of the results noted in 3.2.7. it was thought likely that energy transfer from the rose bengal triplet state to the DPBF might occur.

When a N_2-flushed methanolic solution of DPBF and rose
bengal was irradiated such that only the dye absorbed the light,
a white precipitate which was believed to be the photodimer[194,195]
was obtained in nearly quantitative yield. Irradiation of an
identical solution under the same conditions but in the absence of
the dye showed no change whatever. It was therefore clear that
sensitised photo-dimerisation was occurring. (Indeed the photo-
dimer was formed with far greater efficiency than in the literature
preparation.[195] Using the latter method it was necessary to
irradiate a benzene solution for 48 hours, whilst the sensitised
method required only 1 hour.)

Cowan and Drisko[186] have used a similar method to examine
the dimerisation of acenaphthylene. Their results obtained from
identical unsensitised reactions have been partly discussed in 1.5.2.
DPBF is expected to photodimerise in an analogous way to acenaphthyl-
ene, the scheme for which is shown in Fig.3.11.

syn-   anti-
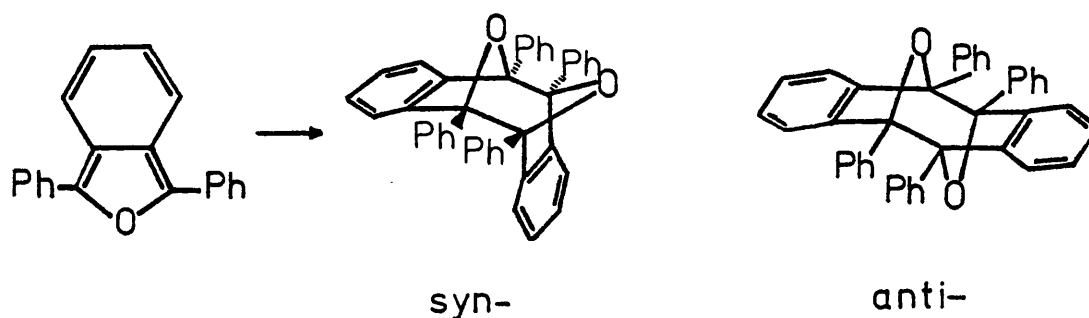
Fig.3.11.

Despite the apparently well known product[173,174] there has been

no report of geometrical isomerisation of the photodimer. This

is undoubtedly due to difficulties of characterisation. The

product obtained from reactions in this laboratory was virtually

insoluble in all solvents tried and the technique of n.m.r. could

not be used. The melting point occurred with decomposition at

145-148°C (cf. lit.m.pt. 210-220°C,[195] 190-200°C[196]). However

the mass spectrum and infrared spectrum compared exactly with

data of LeBerre and Lonchambon.[174] No indication could be found

that the photodimer was present in its two geometrical isomers

other than the discrepancy over the melting points. Indeed the

product obtained cannot definitely be characterised as having

either or both of the structures in Fig.3.8. Molecular models

indicate that the anti-isomer will be slightly more favoured as

it minimises steric interactions. Cowan and Drisko found the

anti-isomer of acenaphthylene to be formed from the triplet hydro-

carbon. This may provide a clue as to the large difference in

dimerisation efficiency for sensitised and unsensitised reactions

of DPBF. The fluorescence yield of DPBF is very high. This means

that not only will dimerisation from the singlet state be inefficient

but a low yield of triplet states will be obtained which can lead

to the favourable anti-isomer. Sensitisation however produces

triplet DPBF in good yield from which dimerisation readily occurs.

3.6. Conclusions

Photosensitisers and dyes in particular have been shown to undergo excited state charge transfer interactions with amines, anions, aromatic hydrocarbons and related compounds. In general, the size of the interaction (which is easily measured by the extent of the fluorescence quenching of the sensitiser) is directly related to the ionisation potential of the quencher. Where two quenching groups are present in the same molecule an interaction greater than that of the sum of the individual quenchers is often obtained.

Quenching of the excited singlet state of chlorophylla by β-carotene has been conclusively demonstrated and the participation of both the chlorophyll radical cation and radical anion suggested in photosynthetic processes.

Triplet-triplet energy transfer has been demonstrated from photosensitisers to 9-methylanthracene and a sensitised photo-dimerisation of 1,3-diphenylisobenzofuran has been observed.

3.7. Experimental

3.7.1. Fluorescence Quenching Studies

Tris 2,2-bipyridyl ruthenium II chloride hexahydrate was prepared by the method of Burstall, J. Chem. Soc., 173, (1936). Otherwise materials sources are listed in 4.6.

Absorption spectroscopy was performed on a Pye-Unicam SP800 spectrophotometer and fluorescence measurements made on a Perkin-Elmer MPF-4 spectrofluorimeter. Methanol was BDH dried and fractionated, as also was ethanol.

Solutions of the sensitiser and substrate were prepared to an optical density of 0.1 for the sensitiser at the λ_{exc}. Excitation and emission wavelengths were the maxima indicated by the spectra in Figs.3.1.-3.3. Stern-Volmer quenching constants were calculated from computed 'best-fit' straight line plots of the data.

3.7.2. Experimental procedure for chlorophyll a quenching by β-carotene

In view of the controversial nature of the results, full experimental details are given.

Chlorophyll a was extracted from Poa Annua and its purity checked by its absorption bands at 662, 430 and 410 nm.[162] It was used immediately after extraction. Synthetic all trans-β-carotene was obtained from Sigma Chemicals and stored in the dark in a deep freeze. Its absorption spectrum was identical to the literature spectrum and its purity was checked by preparing a solution in petroleum ether of $4 \pm 0.6 \times 10^{-6}$ M. The measured optical density was 0.51 ± 0.01 and the calculated absorption coefficient at its λ_{max} of 450 nm was found to be $127,5000 \pm 20,000$. This compares with the literature value of $135,000$[161] in the same solvent. β-Carotene has a measurable absorption in the region of the exciting

and emitting wavelengths of chlorophylla. The extinction co-efficients at different wavelengths were measured; they are the mean of two independent sets of measurements and are shown in Table 3.11. Optical densities were measured using Pye Unicam SP8000 and SP1800 spectrophotometers. Fluorescence measurements were made on a Perkin-Elmer MPF-4 spectrofluorimeter. Benzene was Merck 'UVASOL' and MeOH was BDH (dried).

Steady-state measurements were made both in 1 cm square cells and in thin tubes of internal radius 1 mm to reduce the corrections necessary. Both benzene and benzene-methanol 80:20 (v/v) were used as solvents. The results obtained are tabulated in Tables 3.12.-3.14.

Lifetime measurements were carried out by Dr. G.S. Beddard of the Royal Institution, London. The technique of time-correlated singlet photon counting was used. Excitation was at 550 nm and the fluorescence detected above 670 nm with a cut off filter in front of a cooled 56-TUVP photomultiplier tube. (Similar results were obtained at 620 nm excitation but difficulties with scattered light preferred the first excitation wavelength.) The fluorescence was observed through the back of a 1 mm path length cell. All decays were exponential.

3.7.3. Correction of Chlorophyll Fluorescence Intensities in the Presence of β-Carotene

Consider the fluorescence from the centre O of a square cell illuminated at X by light of intensity I and observed at Y.
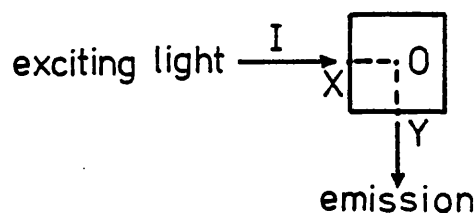
(a)   In the absence of a quencher:

Let the transmittance of the solution over XO and OY be

a and b respectively, and the fluorescence quantum yield be Φ_{F_0}.

Then the fluorescence intensity at Y will be I ab Φ_{F_0} = F_0.

(b)   In the presence of a quencher which absorbs at the excitation

and emission wavelengths:

If the transmittance of a solution of pure quencher is α

and β over XO and OY, then the new observed fluorescence intensity

of the quenched solution with quantum yield Φ_F is given by

Iab$\alpha\beta\Phi_F$ = F.   (Note that the transmittances due to the chlorophyll

remain constant whether in the presence or absence of quencher.)

Hence the observed Stern-Volmer quenching $(F_0/F)_{obs}$ is given by

$$\left(\frac{F_0}{F} \right)_{obs} = \frac{1}{\alpha\beta} \frac{\Phi_{F_0}}{\Phi_F}$$

Since $\log_{10}(1/\text{transmittance})$ = OD

Then α^{-1} = antilog$_{10}$ (OD$_{XO}$)   and β^{-1} = antilog$_{10}$(OD$_{OY}$)

and hence the true Stern-Volmer quenching

$$\frac{F_0}{F} = \left(\frac{F_0}{F} \right)_{obs} [(\text{antilog}_{10}OD_{XO}) \times (\text{antilog}_{10}OD_{OY})]^{-1}$$

3.7.4. The Extraction of Chlorophyll a

The extraction of chlorophylls is usually carried out on spinach leaves. However the availability of fresh spinach is sometimes a problem. Freshly picked green grass appears to be a good source. Poa Annua was used in these experiments. A handful of grass provides an ample working solution. Since chlorophyll deteriorates rapidly it should be extracted each time before use. The following method takes an average worker 2 hours but can be done in less.

The grass was ground in portions with acetone until the latter was a dark green. The acetone was poured off and a little more added to the residue. When the grass had lost most of its colour the next portion was used. The final volume of acetone solution was ~300 mls. This was filtered and then evaporated under reduced pressure using a tepid water bath. (N.B. Since there was some water present it was not evaporated to dryness.) To the residue 100 ml of 40-60 petroleum ether was added together with 20 ml water. After shaking and separating the petroleum layer it was dried with $MgSO_4$ and filtered. Evaporation to dryness on a cool water bath left a dark green residue. A chromatography column ('quick-fit' CR 32/40) was set up without a tap. The packing was chromatographic alumina type H with petrol (40-60) - isopropanol 95:5 (v/v) as solvent. After adding some solvent to a conical flask containing the alumina and shaking well, the mixture was poured quickly into the column so that when the alumina

had settled it was about $\frac{2}{3}$ full. (The solvent should drip quite quickly at this point. It is necessary to have a fast flow through the column to avoid decomposition.) After adding no more than 5 ml of solvent to the chlorophyll extract the solution was quickly pippetted onto the column when the solvent level had fallen to the level of the alumina. When the extract was absorbed the reservoir was filled with solvent. The optimum time for the elution process was found to be 10 minutes. The extract split into its component parts and as many fractions (in 3" x 1" sample tubes) as possible (more than ten) were collected. The bright orange band containing the carotenoids was eluted first. The chlorophylla band came next as a turquoise coloured solution. This changed into an emerald green as chlorophyll b was eluted from the column. The fractions were examined by absorption spectroscopy and those containing the correct absorption bands were collected together and used in the experiment.

3.7.5. Energy Transfer Studies

The experiments were carried out using conventional microsecond flash photolysis apparatus with spectrographic attachment. The flash tubes were enclosed by specially designed pyrex casings containing a filter solution to allow control of excitation wavelengths. Potassium chromate (λ >470 nm) and potassium nitrite (λ >410 nm) were used in aqueous solution. The spectra were

obtained from the photographic plates by means of a micro-densitometer and were corrected by computation to give the curves in Fig.3.10. Methanol was BDH dried and fractionated. Materials sources are listed in 4.6.

3.7.6. Photoreaction of 1,3-Diphenylisobenzofuran

The experiments were carried out using a bank of eight 'daylight, fluorescent' tubes arranged concentrically around the solution under examination. The reaction vessel was contained in a bath of aqueous potassium chromate as filter and nitrogen continuously passed slowly through the solution. Materials sources are listed in 4.6.

CHAPTER 4:

Preparation of materials.

The art of cookery flourished long
before chemistry.

—Mrs. Beeton.

Introduction

The preparation of materials has been divided into sections relating to the type of compound as follows:

4.1   Benzene derivatives

4.2   1- and 2- Naphthalene derivatives

4.3   9-Anthracene derivatives

4.4   1-Pyrene derivatives

4.5   Miscellaneous

4.6   Sources of other compounds used

Comparison of physical data (m.pt., b.pt.) with literature values is given where available, with reference. Melting points are uncorrected and were performed on a Reichert micro-heating apparatus.

Proton magnetic resonance spectra were performed on a Varian T60 spectrometer using tetramethylsilane as internal reference. All spectra are quoted in δ field units together with integrated peak heights and the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants for triplets and quintets are not quoted, being 6-7 Hz in all cases. Other coupling constants are quoted. Solvents used were deuterochloroform ($CDCl_3$), carbon tetrachloride (CCl_4) or trifluoroacetic acid (T.F.A.).

Infrared spectra were obtained on Perkin Elmer 237

and 257 grating spectrophotometers either as nujol mulls or thin films.

Analyses results are quoted in percentages and were performed by CHN Analysis Ltd., S. Wigston, Leicester, and Alfred Bernhardt, Elbach uber Engelskirchen, W. Germany.

Solvents benzene and ether were sodium dried for use in reactions. Acetone for the Finklestein reactions was distilled from anhydrous copper II sulphate.

All compounds prepared as oils were distilled under reduced pressure using a Buchi Kügel oven. Boiling points quoted are uncorrected.

Carbon-13 NMR spectra were obtained for the amines indicated and these are detailed in the appendix. The spectra were run by the P.C.M.U., Harwell, Oxon. Mass spectra were obtained using a V.G. Micromass 16B spectrometer.

4.1   Benzene derivatives

(1)   N,N-diethyl-benzylamine

Benzyl bromide (1 g) was reacted with excess (5 ml) diethylamine in 10 ml of dry ether, stirring for half an hour at room temperature. Acid, base work up followed by evaporation of the ether and excess diethylamine gave the product in nearly quantitative yield as a yellow oil. Reduced pressure distillation rendered it colourless.

$PhCH_2NEt_2$:   b.pt.   94°C, 15 mm. lit. 125°C, 12 mm.[207]

NMR ($CDCl_3$)   : 7.2-7.5 δ, 5H, m; 3.6 δ, 2H, s; 2.15-2.7 δ,

4H, q; 0.9-1.2 δ, 6H, t.

IR (FILM)   : 3080, 3060, 3020, 2960, 2920, 2780, 1600, 1500,

1460, 1390, 1375, 1060, 740, 700 cm^{-1}.

4.2   1- and 2- substituted naphthalene derivatives

Each preparation described refers to the 1-substituted naphthalene derivative. The procedure for the preparation of 2-substituted derivatives is the same, except where stated. The most apparent difference between the two derivatives is that the 2- series is often crystalline when the 1- series is an oil, but when both are crystalline they usually crystallise from the same solvent.

(1)   1-Hydroxymethylnaphthalene

Reduction of 1-naphthoic acid (1 g) with excess lithium aluminium hydride in dry ether (100 ml) yielded the product in excellent yield (>90%) as a white crystalline solid recrystallisable from petroleum ether (60-80). (Reduction of larger quantities of 1-naphthoic acid or 1-naphthylacetic acid is not convenient except via the methyl ester, see 4.2.(20), owing to the lack of solubility of the acid in ether).

1-NpCH$_2$OH: m.pt. 57-59°C; lit. 59-60°C [208]

NMR (CDCl$_3$): 7.2-8.1 δ, 7H, m; 5.05 δ, 2H, s; 1.9 δ, 1H, b.s.

IR (NUJOL) : 3350, 1600, 1000, 800, 790, 770 cm^{-1}.

2-NpCH$_2$OH : m.pt. 76-78°C; lit. 80-81°C [208]

NMR (CDCl$_3$): 7.3-8.1 δ, 7H, m; 4.9 δ, 2H, s; 2.05 δ, 1H, s.

IR (NUJOL) : 3200, 1600, 1270, 1050, 1040, 980, 960, 950, 890,

855, 810, 740 cm^{-1}.

(2)   1-Chloromethylnaphthalene

1 g of 1-hydroxymethyl naphthalene from the preceding section was added to 25 ml of dry benzene. Excess (~2-3 equivalents) of thionyl chloride was diluted with 5 ml of benzene and added slowly to the stirred reaction mixture over a period of ten minutes. When the addition was complete the mixture was refluxed for three hours or until hydrogen chloride ceased to be evolved. The solvent was evaporated under reduced pressure and then pumped dry under

vacuum. The crude product was obtained in excellent yield and purified by distillation (or recrystallisation from petroleum ether for the 2-derivative).

1-NpCH$_2$Cl : b.pt. 92°C, 0.01 mm; lit. m.pt. 31-32°C[208]

b.pt. 168°, 20 mm.

NMR (CDCl$_3$): 7.2-8.2 δ, 7H, m; 4.9 δ, 2H, s.

IR (film) : 3060, 2960, 1610, 1465, 1360, 1285, 1270, 1180, 1030, 880, 810, 800, 790, 745, 720, 700 cm^{-1}.

2-NpCH$_2$Cl : m.pt. 46-47°C; lit. m.pt. 47°C [208]

NMR (CDCl$_3$): 7.35-8.0 δ, 7H, m; 4.7 δ, 2H, s.

IR (NUJOL) : 3060, 1600, 1275, 1260, 1125, 890, 860, 825, 770, 750, 720, 700 cm^{-1}.

(3)   1-Bromomethylnaphthalene

This compound was readily made by refluxing overnight 1-methyl naphthalene (5 g) in carbon tetrachloride (250 ml) with 1:1 equivalents of slightly impure N-bromosuccinimide. Filtration of the precipitated succinimide followed by removal of the solvent by reduced pressure evaporation yielded the crude product (in ∿75% yield) which was recrystallised from petroleum ether (60-80). (Failure to use pure 1-methyl naphthalene resulted in poorer yield).

1-NpCH$_2$Br : m.pt. 55-56°C; lit. 56°C[208]

NMR (CDCl$_3$): 7.4-8.5 δ, 7H, m; 5.1 δ, 2H, s.

IR (NUJOL) : 3040, 1600, 1500, 1240, 1205, 1170, 1015, 865, 800, 770, 730, 705 cm^{-1}.

2-NpCH$_2$Br : m.pt. 52-54°C; lit. 54°C[208]

NMR (CDCl$_3$): 7.3-8.05 δ, 7H, m; 4.65 δ, 2H, s.

IR (NUJOL) : 3040, 1600, 1500, 1210, 1125, 970, 955, 910, 895, 870, 825, 750, 660 cm⁻¹.

(4)   1-Iodomethylnaphthalene

This compound was prepared by a standard Finklestein reaction on 1-bromomethylnaphthalene, 4.2.(3). 1 g of the bromide was added to 1 equivalent of sodium iodide in 10 ml of dry acetone and shaken for six hours. The acetone was removed under reduced pressure. To the residue 25 ml of ether was added and the resulting solution washed with water and dilute sodium thiosulphate solution to remove any free iodine. After drying and evaporating the ether, the product remained in ~90% yield. Both compounds were recrystallised from petroleum ether (60-80) but are unstable.

1-NpCH$_2$I :   m.pt. 62-64°C (decomp.); lit. 58-60°C[209]

NMR (CDCl$_3$): 7.1-8.1 δ, 7H, m; 4.9 δ, 2H, s.

IR (NUJOL) : 3040, 1590, 1230, 1170, 1140, 850, 790, 780, 770 cm⁻¹.

2-NpCH$_2$I :   m.pt. 75-77°C; lit. 78°C[209]

NMR (CDCl$_3$): 7.4-8.2 δ, 7H, m; 4.7 δ, 2H, s.

IR (NUJOL) : 1600, 1160, 900, 870, 830, 755, 745 cm⁻¹.

(5)   1-(2'-Hydroxyethyl)-naphthalene

This derivative was prepared by the reduction of 1-naphthyl acetic acid with lithium aluminium hydride in dry ether and standard

work up, c.f. 4.2.(1). Yields of 80% were obtained. Both deriv-
atives were recrystallised from petroleum ether (60-80).

1-NpCH₂CH₂OH : m.pt. 58-59°C; lit. 59-61°C [208]
_____

NMR (CDCl₃) : 7.3-8.3 δ, 7H, m; 3.9-4.2 δ, 2H, t; 3.2-3.5 δ, 2H,

t; 1.7 δ, 1H, s.

IR (NUJOL) : 3350, 3040, 2940, 1600, 1500, 1050, 800, 780 cm⁻¹.

2-NpCH₂CH₂OH : m.pt. 66-67°C; lit. 68°C [208]
_____

NMR (CDCl₃) : 7.3-8.0 δ, 7H, m; 3.8-4.1 δ, 2H, t; 2.9-3.2 δ,

2H, t; 2.2 δ, 1H, s.

IR (NUJOL) : 3250, 3030, 1600, 1500, 1270, 1050, 1020, 970,

950, 900, 860, 830, 755, 745 cm⁻¹.

(6)   1-(2'-Chloroethyl)-naphthalene

Reaction of 1-(2-hydroxyethyl)-naphthalene, 4.2.(5), with
excess (∿3 equivalents) thionyl chloride in dry benzene as in
4.2.(2) yielded the product in good yield (80-90%). The 2-
derivative was recrystallised from petroleum ether (40-60).

1-NpCH₂CH₂Cl : b.pt. 90-95°C, 0.004 mm; lit. 167-8°C, 17 mm [208]
_____

NMR (CDCl₃) : 7.4-8.2 δ, 7H, m; 3.3-4.05 δ, 4H, m.

IR (Film) : 3040, 2940, 1600, 1530, 800, 780, 700 cm⁻¹.

2-NpCH₂CH₂Cl : m.pt. 47.5-48.5°C; lit. 46.5-47.5°C [210]
_____

NMR (CDCl₃) : 7.2-7.9 δ, 7H, m; 3.65-3.95 δ, 2H, t; 3.05-3.35 δ,

2H, t.

IR (NUJOL) : 3040, 1600, 900, 860, 830, 760, 740, 700 cm⁻¹.

(7) 1-(2'-Bromoethyl)-naphthalene

Preparation of this compound was effected by refluxing for 3 hours ∿1 g of the alcohol from 4.2.(5) in 15 ml of 48% hydrobromic acid. After cooling, the products were extracted into ether and worked up washing with a little dilute alkali. Drying and evaporating the ether yielded the product in 60-70% yield. The 2-derivative was recrystallised from petroleum ether (60-80) as a white crystalline material.

1-NpCH$_2$CH$_2$Br	: b.pt. 130-135°C, 0.5 mm; lit. 130-135°C, 0.3 mm[211]
NMR (CDCl$_3$)	: 7.3-8.2 δ, 7H, m; 3.7 δ, 4H, s.
IR (Film)	: 3050, 2960, 1600, 1520, 1210, 800, 780 cm^{-1}.

2-NpCH$_2$CH$_2$Br	: m.pt. 63.5-64.5°C; lit. 64.5-66.5°C[212]
NMR (CDCl$_3$)	: 7.1-7.8 δ, 7H, m; 3.1-3.8 δ, 4H, m.
IR (Film)	: 3050, 1600, 900, 865, 830, 755 cm^{-1}.

(8) 1-(2'-Iodoethyl)-naphthalene

This derivative was prepared by the method of 4.2.(4) from the bromide made in 4.2.(7). Note that it was necessary to shake for 16-20 hours in this case. The 2-derivative was recrystallised from petroleum ether (60-80).

1-NpCH$_2$CH$_2$I	: b.pt. 175-180°C, 3 mm
NMR (CDCl$_3$)	: 7.3-8.2 δ, 7H, m; 3.2-3.9 δ, 4H, m.
IR (Film)	: 3050, 2960, 1600, 1520, 1140, 800, 775 cm^{-1}.
MASS SPEC.	: 127 (Ar$^+$), 141, 155, 282 (M$^+$).

2-NpCH$_2$CH$_2$I   : m.pt. 81.5-82.5°C

NMR (CDCl$_3$)	: 7.5-8.3 δ, 7H, m; 3.5-3.65 δ, 4H, m.
IR (NUJOL)	: 3060, 1600, 1175, 900, 865, 830, 755 cm^{-1}.
MASS SPEC.	: 127 (Ar$^+$), 141, 155, 282 (M$^+$).

(9)   3-(1'-Naphthyl)-acrylic acid

27 g of 1-naphthaldehyde were added to 27 g of malonic acid in 100 ml of pyridine and a few drops of piperidine added as a catalyst. The mixture was heated on a steam bath for 1$^1_2$ hours and the resulting mixture poured into a litre of water containing 100 ml c. hydrochloric acid. The product precipitated and was filtered off, washed with water and dried over P$_2$O$_5$ giving a yield of 80-90%. The product was a mixture of cis- and trans-isomers and so the melting point was not determined. The product was used in the next step without purification.

(10)   3-(1'-Naphthyl)-propionic acid

10 g of the acrylic acid from 4.2.(9) were added to 300 ml of acetic acid and 1 g of palladised charcoal was then added as a catalyst. The mixture was stirred under an atmosphere of hydrogen until it had absorbed 1 equivalent of gas. The acetic acid solution was then separated from the charcoal by filtration and the acid removed under reduced pressure. The product was obtained in nearly quantitative yield and recrystallised from aqueous ethanol.

1-NpCH$_2$CH$_2$CO$_2$H : m.pt. 154-155°C; lit. 156°C[208]

NMR (CDCl$_3$) : 7.1-8.0 δ, 7H, m; 3.2-3.5 δ, 2H, t; 2.7-3.0 δ,

                2H, t.

IR (NUJOL) : 3300-2500, 3040, 1700, 1600, 1520, 1300, 1225,

                940, 800, 780, 760 cm^{-1}.

2-NpCH$_2$CH$_2$CO$_2$H : m.pt. 132-134°C; lit. 134-135°C[208]

NMR (CDCl$_3$) : 11.0 δ, 1H, b,s; 7.2-8.0 δ, 7H, m; 2.4-3.0 δ, 4H, m.

IR (NUJOL) : 3700-3100, 3050, 2985, 2900-2500, 1720, 1600,

                1505, 1450-1150, 1080, 1040, 870, 850, 810, 740 cm^{-1}.

(11) 1-(3'-Hydroxypropyl)-naphthalene

This compound was prepared by reduction of 1-naphthyl-propionic acid with lithium aluminium hydride in ether as described in 4.2.(1). The 2-derivative was recrystallised from petroleum ether (40-60).

1-NpCH$_2$CH$_2$CH$_2$OH : b.pt. 100-110°C, 0.005 mm; lit. 130°C, 0.05 mm[213]

NMR (CDCl$_3$) : 7.2-8.2 δ, 7H, m; 3.5-3.8 δ, 2H, t; 3.0-3.3 δ,

                2H, t; 2.7 δ, 1H, s; 1.7-2.2 δ, 2H, quintet.

IR (Film) : 3400, 3050, 2940, 1600, 1520, 1400, 1100-1000,

                800, 780 cm^{-1}.

2-NpCH$_2$CH$_2$CH$_2$OH : m.pt. 37-38°C; lit. 36.5-38.5°C[212]

NMR (CDCl$_3$) : 7.2-8.0 δ, 7H, m; 3.55-3.85 δ, 2H, t; 2.7-3.0 δ,

                2H, t; 2.75 δ, 1H, s; 1.65-2.15 δ, 2H, quintet.

IR (NUJOL) : 3320, 3040, 2920, 2860, 1600, 1520, 1050, 900,

                850, 815, 740 cm^{-1}.

(12) 1-(3'-Chloropropyl)-naphthalene

The procedure described in 4.2.(2) was used to prepare this compound using the alcohol, 4.2.(11) as starting material.

1-NpCH$_2$CH$_2$CH$_2$Cl : b.pt. 170-175°C, 2 mm; lit. 108°C, 1 mm[214]

NMR (CDCl$_3$)	: 7.4-8.3 δ, 7H, m; 3.55-3.8 δ, 2H, t; 3.15-3.45 δ, 2H, t; 2.0-2.5 δ, 2H, quintet.
IR (Film)	: 3060, 2960, 1600, 1520, 1240, 900, 800, 775 cm^{-1}.

2-NpCH$_2$CH$_2$CH$_2$Cl : b.pt. 89°C, 0.025 mm; lit. 120°C, 0.5 mm[214]

NMR (CDCl$_3$)	: 7.4-8.2 δ, 7H, m; 3.4-3.7 δ, 2H, t; 2.95-3.25 δ, 2H, t; 2.05-2.55 δ, 2H, quintet.
IR (Film)	: 3050, 2940, 2860, 1600, 1520, 1275, 900, 860, 820, 750 cm^{-1}.

(13) 1-(3'-Bromopropyl)-naphthalene

The same method as in 4.2.(7) was used for this preparation, the alcohol from 4.2.(11) being the starting material.

1-NpCH$_2$CH$_2$CH$_2$Br : b.pt. 100-105°C, 0.01 mm; lit. 127-130°C, 0.4 mm[215]

NMR (CDCl$_3$)	: 7.4-8.25 δ, 7H, m; 3.35-3.6 δ, 2H, t; 3.1-3.35 δ, 2H, t; 2.0-2.5 δ, 2H, quintet.
IR (Film)	: 3040, 2940, 1600, 1530, 1250, 800, 780 cm^{-1}.

2-NpCH$_2$CH$_2$CH$_2$Br : m.pt. 40-42°C; lit. 43.5-44.5°C[212]

NMR (CDCl$_3$)	: 7.3-8.0 δ, 7H, m; 3.3-3.55 δ, 2H, t; 2.8-3.05 δ, 2H, t; 2.0-2.5 δ, 2H, quintet.
IR (Film)	: 3060, 2960, 2920, 1600, 1510, 1450, 1430, 1270, 1240, 890, 850, 820, 745, 630 cm^{-1}.

(14) 1-(3'-Iodopropyl)-naphthalene

Starting from the bromide, 4.2.(13) this preparation was the same as described in 4.2.(4). Shaking in this case was for 16 hours.

1-NpCH$_2$CH$_2$CH$_2$I : b.pt. 95°C, 0.001 mm

NMR (CDCl$_3$) : 7.4-8.4 δ, 7H, m; 3.05-3.45 δ, 4H, m; 2.0-2.5 δ, 2H, quintet.

IR (Film) : 3040, 2950, 2920, 1600, 1510, 1450, 1140, 800, 780 cm^{-1}.

2-NpCH$_2$CH$_2$CH$_2$I : m.pt. 45-47°C (from ethanol)

NMR (CDCl$_3$) : 7.1-7.9 δ, 7H, m; 3.0-3.25 δ, 2H, t; 2.7-2.95 δ, 2H, t; 1.9-2.4 δ, 2H, quintet.

IR (NUJOL) : 3050, 1600, 1285, 1220, 1210, 1170, 950, 905, 870, 820, 810, 760, 745 cm^{-1}.

MASS SPEC. : 127 (Ar$^+$); 141, 155, 169, 296 (M$^+$).

(15) 1-Naphthylmethyl-acetate

1 g of hydroxymethylnaphthalene, 4.2.(1), was added to 15 ml of dry ether and 1.05 equivalents of pyridine. To the magnetically stirred mixture 1.05 equivalents of acetyl chloride were added and stirring was continued for ^{1}$_2$ hour. Dilute hydrochloric acid was then added and the ether layer separated. After washing and drying it was evaporated to leave the product in >90% yield.

1-NpCH₂OCOCH₃ : b.pt. 102°C, 0.0005 mm; lit. 172°C, 13 mm^{208}

NMR (CDCl₃) : 7.5-8.4 δ, 7H, m; 5.7 δ, 2H, s; 2.05 δ, 3H, s.

IR (Film) : 3040, 2960, 1725, 1590, 1500, 1360, 1225, 1060, 1020, 960, 800, 770 cm⁻¹.

MASS SPEC. : 127, 128 (Ar⁺), 141, 158, 200 (M⁺).

2-NpCH₂OCOCH₃ : m.pt. 57.5-58.5°C; lit. 51-3°C^{208}

NMR (CDCl₃) : 7.5-8.3 δ, 7H, m; 5.5 δ, 2H, s; 2.2 δ, 3H, s.

IR (NUJOL) : 3050, 1730, 1600, 1240, 950, 900, 860, 830, 740, 730 cm⁻¹.

MASS SPEC. : 127, 128 (Ar⁺), 141, 158, 200 (M⁺).

(16) 1-Naphthylmethyl-chloroacetate

The same procedure as 4.2.(15) was used except that chloro-acetyl chloride was substituted for acetyl chloride. The 2-derivative was recrystallised from petroleum ether (60-80).

1-NpCH₂OCOCH₂Cl : b.pt. 145-149°C, 0.0005 mm

NMR (CDCl₃) : 7.4-8.4 δ, 7H, m; 5.75 δ, 2H, s; 4.05 δ, 2H, s.

IR (Film) : 3060, 2960, 1750, 1600, 1520, 1300-1150, 970, 800, 780 cm⁻¹.

2-NpCH₂OCOCH₂Cl : b.pt. 140-150°C, 0.0005 mm; m.pt. 51-52°C

NMR (CDCl₃) : 7.5-8.3 δ, 7H, m; 5.55 δ, 2H, s; 4.2 δ, 2H, s.

IR (NUJOL) : 3040, 1755, 1610, 1415, 1320, 1205, 980, 970, 960, 935, 905, 870, 835, 760, 740 cm⁻¹.

C₁₃H₁₁ClO₂ requires C: 66.5; H: 4.7; Found

C: 66.2; H: 4.6%.

(17)   1-Naphthylmethyl-bromoacetate

The same conditions as 4.2.(15) were used except that bromoacetyl bromide was substituted for acetyl chloride.

1-NpCH₂OCOCH₂Br : b.pt. 130°C, 0.01 mm

NMR (CDCl₃)	: 7.3-8.2 δ, 7H, m; 5.5 δ, 2H, s; 3.65 δ, 2H, s.
IR (Film)	: 3060, 2970, 1750, 1605, 1515, 1300-1100, 970, 800, 780 cm⁻¹.

C₁₃H₁₁BrO₂ requires C: 55.7; H: 3.9; Br: 28.9;

Found, C: 55.7; H: 3.9; Br: 28.9%.

2-NpCH₂OCOCH₂Br : b.pt. 140-150°C, 0.0005 mm; m.pt. 49-50°C

NMR (CDCl₃)	: 7.4-8.3 δ, 7H, m; 5.45 δ, 2H, s; 3.9 δ, 2H, s.
IR (NUJOL)	: 3040, 1740, 1605, 1510, 1300-1100, 990, 900, 870, 830, 820, 760 cm⁻¹.

C₁₃H₁₁BrO₂ requires C: 55.7; H: 3.9; Br: 28.9;

Found, C: 55.45; H: 3.9; Br: 29.1%.

(18)   1-Naphthylmethyl-iodoacetate

A similar reaction to that described in 4.2.(4) was carried out using the bromoacetate, 4.2.(17), and shaking overnight. Both derivatives are white crystalline compounds recrystallisable from petroleum ether (60-80).

1-NpCH₂OCOCH₂I : m.pt. 54-55°C

NMR (CDCl₃)	: 7.4-8.2 δ, 7H, m; 5.7 δ, 2H, s; 3.7 δ, 2H, s.
IR (NUJOL)	: 3050, 1710, 1510, 1275, 1090, 970, 800, 780 cm⁻¹.

C₁₃H₁₁IO₂ requires C: 47.85; H: 3.4; I: 39.0;

Found, C: 47.9; H: 3.2; I: 39.2%.

2-NpCH$_2$OCOCH$_2$I   : m.pt. 39-40°C

NMR (CDCl$_3$)   : 7.3-8.1 δ, 7H, m; 5.4 δ, 2H, s; 3.75 δ, 2H, s.

IR (NUJOL)   : 3040, 1710, 1600, 1270, 1250, 1090, 960, 880,

860, 810, 740 cm^{-1}.

C$_{13}$H$_{11}$IO$_2$ requires C: 47.85; H: 3.4; Found,

C: 48.1; H: 3.4%.

(19) 1-Naphthylacetyl chloride

10 g of naphthyl acetic acid was added to 150 ml dry benzene

and 1.05 equivalents of oxalyl chloride. The mixture was refluxed

for 3 hours or until evolution of hydrogen chloride gas ceased.

The benzene was evaporated off after cooling the mixture and 100 ml

of ether added to the residue. The resulting solution was washed

with sodium bicarbonate solution and the ether layer separated.

After drying, the solvent was evaporated to leave the product as

an oil in >80% yield. The product was not characterised but used

immediately in reactions described below.

(20) Methyl-1-Naphthylacetate

1 g of naphthyl acetic acid was added to 20 ml of methanol

and saturated for 10 min with HCl gas. The mixture was then refluxed

for 2 hours on a steam bath and finally cooled. The methanol was

removed under reduced pressure and 25 ml of ether added to the

residue. This solution was washed with dilute HCl and dilute NaOH

solutions, dried and evaporated to yield the products in >80% yield.

1-NpCH$_2$CO$_2$Me   : b.pt. 102°C, 0.005 mm; lit. 165-7°C, 9 mm[208]

NMR (CDCl$_3$)   : 7.3-8.2 δ, 7H, m; 4.1 δ, 2H, s; 3.7 δ, 3H, s.

IR (Film)   : 3040, 2950, 1740, 1600, 1520, 1435, 1335, 1265, 1160, 1010, 800-780 cm^{-1}.

2-NpCH$_2$CO$_2$Me   : m.pt. 50-52°C; lit. 51-53°C[90]

NMR (CDCl$_3$)   : 7.2-8.0 δ, 7H, m; 3.8 δ, 2H, s; 3.7 δ, 3H, s.

IR (Film)   : 3040, 2940, 1740, 1610, 1510, 1440, 1370, 1340-1130, 1020, 970, 910, 860, 820, 800, 760, 740, 705 cm^{-1}.

(21) 2-Chloroethyl-(1'-Naphthyl)acetate

1 g of 1-naphthyl acetyl chloride, 4.2.(19), was added to 15 ml of dry ether and 1.05 equivalents of triethylamine. To the mixture 1 equivalent of ethylene chlorohydrin was added and stirred for an hour at room temperature. After this time an equal volume of dilute HCl was added and the ether layer separated, washed, dried and evaporated. The product was obtained in excellent yield (>80%). The 2-derivative was recrystallised from petroleum ether (60-80).

1-NpCH$_2$CO$_2$CH$_2$CH$_2$Cl: b.pt. 160-170°C, 0.001 mm

NMR (CDCl$_3$)   : 7.4-8.3 δ, 7H, m; 4.15-4.4 δ, 2H, t; 4.1 δ, 2H, s; 3.4-3.65 δ, 2H, t.

IR (Film)   : 3060, 2960, 1740, 1600, 1530, 1450-1150, 1020, 800-780 cm^{-1}.

MASS SPEC.   : 127, 128 (Ar$^+$), 141, 168, 186, 212, 248, 250 (M$^+$).

2-NpCH$_2$CO$_2$CH$_2$CH$_2$Cl: m.pt. 51-53°C

NMR (CCl$_4$)	: 7.4-8.1 δ, 7H, m; 4.2-4.5 δ, 2H, t; 3.8 δ, 2H, s; 3.5-3.75 δ, 2H, t.
IR (NUJOL)	: 3050, 1725, 1600, 1520, 1450-1150, 1020, 890, 865, 840, 810, 735 cm^{-1}.
MASS SPEC.	: 127, 128 (Ar$^+$), 141, 168, 186, 212, 248, 250 (M$^+$).

(22) 2-Bromoethyl-(1'-Naphthyl)acetate

The preparation was carried out as described in 4.2.(21) using ethylene bromohydrin instead of the chlorohydrin. The 2-derivative recrystallised from petroleum ether (60-80).

1-NpCH$_2$CO$_2$CH$_2$CH$_2$Br: b.pt. 170°C, 0.001 mm

NMR (CDCl$_3$)	: 7.35-8.2 δ, 7H, m; 4.25-4.5 δ, 2H, t; 4.1 δ, 2H, s; 3.25-3.5 δ, 2H, t.
IR (Film)	: 3060, 2960, 1740, 1600, 1520, 1450-1150, 1000, 800-780 cm^{-1}.
MASS SPEC.	: 127, 128 (Ar$^+$), 141, 168, 186, 213, 292, 294 (M$^+$).

2-NpCH$_2$CO$_2$CH$_2$CH$_2$Br: m.pt. 48-49°C

NMR (CCl$_4$)	: 7.3-8.1 δ, 7H, m; 4.25-4.5 δ, 2H, t; 3.8 δ, 2H, s; 3.35-3.6 δ, 2H, t.
IR (NUJOL)	: 3040, 1730, 1600, 1520, 1470-1150, 1000, 895, 865, 835, 810, 740 cm^{-1}.
MASS SPEC.	: 127, 128 (Ar$^+$), 141, 168, 186, 213, 292, 294 (M$^+$).

(23) **2-Iodoethyl-(1'-Naphthyl)acetate**

This compound was prepared by the method of 4.2.(4) using

the bromides from 4.2.(22) and shaking for 16 hours. The 2-

derivative was recrystallised from petroleum ether (60-80).

1-NpCH$_2$CO$_2$CH$_2$CH$_2$I : b.pt. 175°C, 0.001 mm

NMR (CCl$_4$)	: 7.35-8.25 δ, 7H, m; 4.15-4.4 δ, 2H, t; 4.05 δ, 2H, s; 2.95-3.25 δ, 2H, t.
IR (Film)	: 3050, 2980, 1740, 1600, 1525, 1450-1130, 1065, 990, 800-780 cm^{-1}.
MASS SPEC.	: 127, 128 (Ar$^+$), 141, 168, 186, 213, 340 (M$^+$).

2-NpCH$_2$CO$_2$CH$_2$CH$_2$I : m.pt. 32-34°C

NMR (CDCl$_3$)	: 7.4-8.3 δ, 7H, m; 4.5-4.8 δ, 2H, t; 4.1 δ, 2H, s; 3.4-3.7 δ, 2H, t.
IR (NUJOL)	: 3060, 1730, 1600, 1520, 1470-1120, 1060, 990, 950, 860, 830, 800, 775, 760, 735 cm^{-1}.
MASS SPEC.	: 127, 128 (Ar$^+$), 141, 168, 186, 213, 340 (M$^+$).

(24) **N,N-Diethyl-1-aminomethylnaphthalene**

1 g of bromomethylnaphthalene, 4.2.(3), was added to excess

diethylamine (5 ml) in ether (15 ml) and stirred for $^1/_2$ hour. The

mixture was then added to 25 ml of dilute HCl and the aqueous layer

separated. The solution was made alkaline and the products ex-

tracted into ether. After drying and evaporating the product

remained in >90% yield. Both 1- and 2-derivatives were purified

by vacuum distillation.

1-NpCH₂NEt₂ : b.pt. 86°C, 0.01 mm; lit. 101-105°C, 0.5 mm[88]

NMR (CDCl₃) : 7.0-8.3 δ, 7H, m; 3.9 δ, 2H, s; 2.3-2.7 δ,

4H, q; 0.9-1.2 δ, 6H, t.

¹³C NMR obtained

IR (Film) : 3040, 2960, 2920, 2790, 1600, 1505, 1450, 1370,

1200, 1160, 1050, 800-770 cm⁻¹.

2-NpCH₂NEt₂ : b.pt. 90°C, 0.01 mm

NMR (CCl₄) : 7.4-8.1 δ, 7H, m; 3.75 δ, 2H, s; 2.4-2.8 δ,

4H, q; 0.9-1.2 δ, 6H, t.

¹³C NMR obtained

IR (Film) : 3060, 2980, 2940, 2800, 1600, 1520, 1460, 1380,

1205, 1170, 1120, 1070, 860, 820, 750 cm⁻¹.

(25) N-methyl-N-phenyl-1-aminomethyl naphthalene

1 g of bromomethyl naphthalene, 4.2.(3), was added to 1 equivalent of N-methyl aniline and 1 equivalent of triethylamine in 15 ml of dry ether. The mixture was refluxed for 1 hour after which time it was added to 50 ml of water and the ether layer separated. After an acid base extraction and removal of the ether the product remained in >80% yield.

1-NpCH₂NMePh : b.pt. 100-105°C, 0.01 mm

NMR (CDCl₃) : 6.8-8.4 δ, 12H, m; 5.1 δ, 2H, s; 3.2 δ, 3H, s.

IR (Film) : 3060, 2900, 1600, 1510, 1375, 1260, 1220, 1120,

1040, 995, 940, 790, 770, 750, 690 cm⁻¹.

2-NpCH$_2$NMePh   : b.pt. 100-105° C, 0.01 mm

NMR (CDCl$_3$)   : 6.8-8.2 δ, 12H, m; 4.95 δ, 2H, s; 3.1 δ, 3H, s.

IR (Film)   : 3050, 2900, 1600, 1500, 1225, 1190, 1100, 1010,

                     990, 900, 850, 815, 740, 690 cm⁻¹.

(26) N,N-Diethyl-1-naphthylacetamide

1 g of naphthylacetyl chloride, 4.2.(19), was reacted with
excess diethylamine (5 ml) in a reaction otherwise the same as
4.2. (24). Both derivatives were used in 4.2.(27) unpurified.

(27) N,N-Diethyl-1-(2'-aminoethyl)-naphthalene

The amide from 4.2.(26) was reduced to the amine with lithium
aluminium hydride in ether. The amine was purified by an acid-base
extraction after the inorganic salts had been removed into water.

1-NpCH$_2$CH$_2$NEt$_2$: b.pt. 90°C, 0.01 mm; lit. 115-118°C, 0.05 mm[88]

NMR (CDCl$_3$)   : 7.0-7.9 δ, 7H, m; 2.35-3.3 δ, 8H, m; 0.9-1.2 δ,

                      6H, t.

^{13}C NMR obtained

IR (Film)   : 3060, 2970, 2930, 2800, 1605, 1520, 1480, 1400,

                      1220, 1075, 800-770 cm⁻¹.

2-NpCH$_2$CH$_2$NEt$_2$: b.pt. 92°C, 0.002 mm

NMR (CCl$_4$)   : 7.25-8.0 δ, 7H, m; 2.3-3.0 δ, 8H, m; 0.8-1.2 δ,

                      6H, t.

^{13}C NMR obtained

IR (Film)   : 3050, 2960, 2920, 2860, 2800, 1600, 1510, 1470,

                      1380, 1200, 1070, 850, 810, 740 cm⁻¹.

(28) N-Methyl-N-phenyl-1-naphthylacetamide

The reaction was carried out as described in 4.2.(25) using 1-naphthylacetyl chloride, 4.2.(19), instead of bromomethyl naphthalene. The amide was used in 4.2.(29) unpurified.

(29) N-Methyl-N-phenyl-1-(2'-aminoethyl)-naphthalene

This amine was prepared by the reduction of the amide from 4.2.(28), as described in 4.2.(27). Both derivatives were re-crystallised from petroleum ether (60-80).

1-NpCH$_2$CH$_2$NMePh   :   m.pt. 86-87°C; lit. 85-86°C [88]

NMR (CDCl$_3$)   :   6.7-8.3 δ, 12H, m; 3.6-4.0 δ, 2H, m; 3.1-3.5 δ,
                     2H, m; 2.85 δ, 3H, s.

^{13}C NMR obtained

IR (NUJOL)   :   3040, 1600, 1500, 1280, 1190, 1110, 1050, 1030,
                 990, 950, 860, 800, 780, 750, 690 cm^{-1}.

2-NpCH$_2$CH$_2$NMePh   :   m.pt. 99-101°C

NMR (CDCl$_3$)   :   6.7-8.0 δ, 12H, m; 3.55-3.85 δ, 2H, t; 2.9-3.2 δ,
                     2H, t; 2.9 δ, 3H, s.

^{13}C NMR obtained

IR (NUJOL)   :   3040, 1600, 1510, 1230, 1210, 1190, 1100, 1000,
                 990, 900, 860, 820, 760, 750, 740, 690 cm^{-1}.

(30) 3-(1'-Naphthyl)-propionyl chloride

This compound was prepared by a method identical to 4.2.(19) starting with the naphthyl propionic acid 4.2.(10). The product was used immediately in later steps.

(31)   N,N-Diethyl-3-(1'-naphthyl)-propionamide

1 g of the acid chloride from 4.2.(30) was reacted with excess diethylamine (5 ml) as in 4.2.(24). The amide was used in 4.2.(32) unpurified.

1-NpCH$_2$CH$_2$CONEt$_2$:

NMR (CCl$_4$)	: 7.0-7.9 δ, 7H, m; 2.4-3.5 δ, 8H, m; 0.9-1.2 δ, 6H, m.
IR (Film)	: 3040, 2970, 2920, 1710, 1630, 1510, 1300, 1170, 1040, 970, 850, 800, 770 cm^{-1}.

2-NpCH$_2$CH$_2$CONEt$_2$:

NMR (CCl$_4$)	: 6.9-7.6 δ, 7H, m; 2.7-3.5 δ, 6H, m; 2.3-2.6 δ, 2H, t; 0.8-1.2 δ, 6H, m.
IR (Film)	: 3040, 2960, 1730, 1630, 1490-1410, 1265, 1215 1120, 850, 810, 740 cm^{-1}.

(32)   N,N-Diethyl-1-(3'-aminopropyl)-naphthalene

The amide prepared in 4.2.(31) was reduced with lithium aluminium hydride as described in 4.2.(27). The 1- and 2-derivatives were purified by vacuum distillation.

1-NpCH$_2$CH$_2$CH$_2$NEt$_2$: b.pt. 143°C, 0.01 mm; lit. 135-137°C, 0.7 mm[88]

NMR (CCl$_4$)	: 7.0-7.9 δ, 7H, m; 2.9-3.2 δ, 2H, t; 2.3-2.7 δ, 6H, m; 1.5-2.0 δ, 2H, quintet, 0.9-1.2 δ, 6H, t.

^{13}C NMR obtained

IR (Film)	: 3040, 2960, 2920, 2860, 2800, 1600, 1520, 1460, 1380, 1200, 1065, 800-770 cm^{-1}.

2-NpCH$_2$CH$_2$CH$_2$NEt$_2$: b.pt. 170°C, 0.1 mm

NMR (CDCl$_3$) : 7.1-7.8 δ, 7H, m; 2.3-2.8 δ, 8H, m; 1.5-2.0 δ,

2H, quintet, 0.9-1.2 δ, 6H, t.

^{13}C NMR obtained

IR (Film) : 3040, 2960, 2920, 2860, 2800, 1600, 1500, 1460,

1370, 1200, 1060, 890, 845, 810, 740 cm^{-1}.

(33)   N-Methyl-N-phenyl-3-(1'-Naphthyl)-propionamide

This compound was prepared by the method of 4.2.(25) using

naphthyl propionyl chloride prepared in 4.2.(30) and N-methylaniline.

Both derivatives were used in 4.2.(34) unpurified.

(34)   N-Methyl-N-phenyl-1-(3'-amino propyl)-naphthalene

The preparation was by reduction of the amide from 4.2.(33)

with lithium aluminium hydride as described in 4.2.(27).

1-NpCH$_2$CH$_2$CH$_2$NMePh : b.pt. 170°C, 0.01 mm

NMR (CDCl$_3$) : 6.6-8.2 δ, 12H, m; 3.35-3.6 δ, 2H, t; 3.0-3.25 δ,

2H, t; 2.95 δ, 3H, s; 1.8-2.3 δ, 2H, quintet.

IR (Film) : 3060, 2940, 2860, 1600, 1505, 1450, 1360, 1190,

1110, 1040, 990, 800, 780, 750, 690 cm^{-1}.

2-NpCH$_2$CH$_2$CH$_2$NMePh : b.pt. 185°C, 0.0005 mm

NMR (CCl$_4$) : 6.6-8.0 δ, 12H, m; 3.1-3.4 δ, 2H, t; 2.8 δ,

3H, s; 2.55-2.8 δ, 2H, t; 1.6-2.1 δ, 2H, quintet.

IR (Film) : 3040, 2920, 2850, 1600, 1500, 1450, 1365, 1190,

1030, 990, 950, 890, 850, 810, 740, 690 cm^{-1}.

C$_{20}$H$_{21}$N requires C: 87.3; H: 7.6; N: 5.1,

Found, C: 87.3; H: 7.7; N: 5.0%.

(35)   1-Naphthylacetaldehyde

To one litre of dichloromethane 80 ml of dry pyridine

was added. To this mixture 50 g of chromium trioxide was

added carefully. The dichloromethane was then distilled off

and used immediately in the reaction. 400 ml of this purified

dichloromethane was stirred well while 40 ml of dry pyridine

was added, followed by 30 g of chromium trioxide (the order

of addition is important). After the mixture had been stirring

under dry nitrogen for 20 minutes and had turned a deep red

brown with little black tarry deposit, 10 g of the alcohol from

4.2.(5) were added. A thick black tar was immediately deposited

and after stirring well for a minute the dichloromethane

solution was poured off and the flask washed out with more

(unpurified) solvent. After collecting the portions they were

washed well with hydrochloric acid to remove the excess pyridine

and then with sodium hydroxide solution. After drying and

evaporating, the product was dissolved in dry ether and filtered

through Celite. The ether was then evaporated leaving the

product in >70% yield. The 1- and 2-derivatives were obtained

as oils and used in the next preparation without purification.

They were coloured due to contamination by chromium impurities

most of which were removed in the next stage.

(36)   4-(1'-Naphthyl)-but-2-enoic acid

This preparation was carried out as in 4.2.(9) except

that in this case it was necessary to heat on a water bath and

under nitrogen for 16 hours. The product did not always pre-cipitate and was extracted into ether and purified by a base-acid work-up. The yield in this case was ∿60% and a mixture of cis and trans isomers was obtained. The compound was used directly in the next section.

(37)   4-(1'-Naphthyl)-butyric acid

The unsaturated acid prepared in 4.2.(36) was hydrogenated as in 4.2.(10). It was recrystallised from aqueous ethanol.

1-NpCH$_2$CH$_2$CH$_2$CO$_2$H	: m.pt. 103-106°C; lit. 107-108.5°C[208]
NMR (CDCl$_3$)	: 10.6 δ, 1H, b.s.; 7.1-8.1 δ, 7H, m; 3.0-3.2 δ, 2H, t; 1.9-2.6 δ, 4H, m.
IR (NUJOL)	: 3250-2500 (broad), 1700, 1600, 1330, 1280, 1220, 1205, 910, 865, 790, 770, 730 cm⁻¹.
2-NpCH$_2$CH$_2$CH$_2$CO$_2$H	: m.pt. 95-97°C; lit. 100°C [208]
NMR (CDCl$_3$)	: 11.0 δ, 1H, b.s.; 7.2-8.0 δ, 7H, m; 2.7-3.0 δ, 2H, t; 1.8-2.7 δ, 4H, m.
IR (NUJOL)	: 3250-2500 (broad), 1690, 1605, 1350, 1290, 1220, 1205, 920, 900, 860, 830, 750 cm⁻¹.

(38)   4-(1'-Naphthyl)-butyrylchloride

This compound was made by the procedure of 4.2.(19) starting with the acid obtained from 4.2.(37). The product was used immediately without purification.

(39)   N,N-Diethyl-4-(1'-Naphthyl)-butylamide

The acid chloride from 4.2.(38) was used in a procedure identical with 4.2.(24), both derivatives being used without further purification.

1-NpCH$_2$CH$_2$CH$_2$CONEt$_2$:

NMR (CCl$_4$)	: 7.2-8.2 δ, 7H, m; 2.95-3.6 δ, 6H, m; 1.95-2.5 δ, 4H, m; 0.85-1.35 δ, 6H, m.
IR (Film)	: 3040, 2960, 2920, 2860, 1645, 1480-1420, 1260, 1220, 1130, 800-770 cm^{-1}.

2-NpCH$_2$CH$_2$CH$_2$CONEt$_2$:

NMR (CCl$_4$)	: 7.1-7.8 δ, 7H, m; 2.5-3.5 δ, 6H, m; 1.6-2.5 δ, 4H, m; 0.85-1.35 δ, 6H, t.
IR (Film)	: 3040, 2960, 2920, 2860, 1645, 1480-1420, 1260, 1220, 1130, 950, 890, 850, 810, 740, 675 cm^{-1}.

(40)   N,N-Diethyl-1-(4'-aminobutyl)-naphthalene

The amide from 4.2.(39) was reduced with lithium aluminium hydride as described in 4.2.(27).

1-NpCH$_2$CH$_2$CH$_2$CH$_2$NEt$_2$: b.pt. 145-150°C, 0.0005 mm

NMR (CCl$_4$)	: 7.1-8.0 δ, 7H, m; 2.85-3.15 δ, 2H, t; 2.2-2.6 δ, 6H, m; 1.2-2.0 δ, 4H, m; 0.85-1.15 δ, 6H, t.
^{13}C NMR obtained	
IR (Film)	: 3050, 2960, 2930, 2860, 2800, 1600, 1510,

1460, 1380, 1200, 1070, 800-770 cm^{-1}.

$C_{18}H_{25}N$ requires C:84.7; H: 9.8; N: 5.5;

Found, C: 84.4; H: 9.9; N: 5.4%.

2-NpCH$_2$CH$_2$CH$_2$CH$_2$NEt$_2$: b.pt. 135-140°C, 0.0005 mm

NMR (CCl$_4$) : 7.1-7.8 δ, 7H, m; 2.2-2.9 δ, 8H, m; 1.2-

2.0 δ, 4H, m; 0.85-1.15 δ, 6H, t.

^{13}C NMR obtained

IR (Film) : 3050, 2960, 2930, 2860, 2800, 1600, 1510,

1460, 1380, 1200, 1070, 890, 850, 810,

740 cm^{-1}.

$C_{18}H_{25}N$ requires C: 84.7; H: 9.8; N: 5.5,

Found, C: 84.4; H: 9.9; N: 5.35%.

(41)   N-Methyl-N-phenyl-4-(1'-Naphthyl)-butylamide

The acid chloride from 4.2.(38) was used to prepare this
compound by a method identical to 4.2.(25). Both derivatives
were used in 4.2.(42) without further purification.

1-NpCH$_2$CH$_2$CH$_2$CONMePh :

NMR (CCl$_4$) : 6.9-8.1 δ, 12H, m; 3.2 δ, 3H, s; 2.8-3.1 δ,

2H, t; 1.8-2.3 δ, 4H, m.

IR (Film) : 3080, 3060, 3030, 2930, 2860, 1650, 1590,

1500, 1380, 1280, 1120, 1070, 1030, 800,

770, 700, 680 cm^{-1}.

2-NpCH$_2$CH$_2$CH$_2$CONMePh :

| NMR (CDCl$_3$) | : 7.0-8.1 δ, 12H, m; 3.3 δ, 3H, s; 2.6-2.9 δ, 2H, t; 1.8-2.3 δ, 4H, m. |
| IR (Film) | : 3040, 2920, 2840, 1650, 1595, 1495, 1415, 1380, 1270, 1120, 1070, 1020, 890, 850, 815, 770, 745, 700 cm^{-1}. |

(42) N-Methyl-N-phenyl-1-(4'-aminobutyl)-naphthalene

This compound was prepared by reduction of the amide from 4.2.(41) as described in 4.2.(27).

1-NpCH$_2$CH$_2$CH$_2$CH$_2$NMePh : b.pt. 180-190°C, 0.0005 mm

NMR (CCl$_4$)	: 6.6-8.0 δ, 12H, m; 2.7-3.5 δ, 4H, m; 2.8 δ, 3H, s; 1.5-2.0 δ, 4H, m.
IR (Film)	: 3050, 2930, 2860, 1600, 1500, 1360, 1180, 1120, 1070, 1030, 980, 850, 800-770, 740, 690 cm^{-1}.
	C$_{21}$H$_{23}$N requires C: 87.2; H: 8.0; N: 4.8; Found, C: 86.9; H: 8.1; N: 4.8%.

2-NpCH$_2$CH$_2$CH$_2$CH$_2$NMePh : b.pt. 175-180°C, 0.0005 mm

| NMR (CDCl$_3$) | : 6.6-8.0 δ, 12H, m; 3.15-3.45 δ, 2H, m; 2.6-3.0 δ, 2H, m; 2.85 δ, 3H, s; 1.5-2.0 δ, 4H, m. |

^{13}C NMR obtained

| IR (Film) | : 3020, 2910, 2830, 1605, 1510, 1370, 1195, 1115, 1040, 990, 855, 820, 750, 690 cm^{-1}. |
| | C$_{21}$H$_{23}$N requires C: 87.2; H: 8.0; N: 4.8; Found, C: 87.2; H: 8.05; N: 4.7%. |

(43)   1-Naphthylmethyl-N,N-diethylaminoacetate

1 equivalent (1 g) of the bromoester from 4.2.(17) was added to excess (5 ml) diethylamine in 25 ml ether at room temperature. After stirring for half an hour the product was extracted in the usual acid-base work up for amines and after evaporation of the ether the product remained in >80% yield.

1-NpCH₂OCOCH₂NEt₂ : b.pt. 130-135°C, 0.04 mm

NMR (CDCl₃)   : 7.3-8.3 δ, 7H, m; 5.6 δ, 2H, s; 3.4 δ, 2H, s; 2.5-2.8 δ, 4H, q; 0.9-1.2 δ, 6H, t.

IR (Film)   : 3050, 2970, 2940, 2880, 2830, 1740, 1600, 1510, 1460, 1380, 1350, 1270, 1210, 1160, 1080, 990, 955, 800-780 cm⁻¹.

C₁₇H₂₁NO₂ requires C: 75.3; H: 7.75; N:5.2; Found, C: 75.0; H: 7.8; N: 5.1%.

2-NpCH₂OCOCH₂NEt₂ : b.pt. 133°C, 0.003 mm

NMR (CDCl₃)   : 7.5-8.1 δ, 7H, m; 5.4 δ, 2H, s; 3.45 δ, 2H, s; 2.5-2.9 δ, 4H, q; 0.9-1.2 δ, 6H, t.

IR (Film)   : 3050, 2960, 2920, 2860, 2800, 1740, 1610, 1510, 1450, 1380, 1275, 1230-1150, 1130, 1090, 1075, 1020, 950, 850, 820, 750 cm⁻¹.

C₁₇H₂₁NO₂ requires C: 75.3; H: 7.75; N: 5.2, Found, C: 75.0; H: 7.8; N: 4.9%.

(44) 1-Naphthylmethyl-N-phenylaminoacetate

This compound was prepared by a method described in 4.2.(46) using distilled aniline instead of N-methylaniline. The product in this case was much more basic and easily extracted with acid-base work up. The 1-derivative was recrystallised from benzene-petroleum ether (60-80) (50/50) and the 2-derivative from ethanol.

1-NpCH$_2$OCOCH$_2$NHPh	: m.pt. 117-119°C

NMR (CDCl$_3$)	: 6.6-8.2 δ, 12H, m; 5.75 δ, 2H, s; 3.8-4.6 δ, 1H, broad; 4.0 δ, 2H, s.
IR (NUJOL)	: 3380, 3030, 1740, 1610, 1515, 1290, 1260, 1215, 1185, 1150, 1040, 980, 870, 860, 790, 770, 745, 695 cm^{-1}.
	C$_{19}$H$_{17}$NO$_2$ requires C: 78.35; H: 5.8; N: 4.8; Found, C: 77.9; H: 6.0; N: 5.1%.

2-NpCH$_2$OCOCH$_2$NHPh	: m.pt. 77-79°C

NMR (CDCl$_3$)	: 6.6-8.1 δ, 12H, m; 5.45 δ, 2H, s; 3.9-4.6 δ, 1H, broad; 4.0 δ, 2H, s.
IR (NUJOL)	: 3380, 3040, 1740, 1610, 1510, 1200-1120, 990, 965, 950, 910, 830, 820, 750, 690 cm^{-1}.
	C$_{19}$H$_{17}$NO$_2$ requires C: 78.35; H: 5.8; N: 4.8, Found, C: 78.2; H: 5.9; N: 4.8%.

(45) 1-Naphthylmethyl-N-tert. butylaminoacetate

The preparation of this compound was the same as in 4.2.(43) substituting tertiary butylamine instead of diethyl-amine.

1-NpCH$_2$OCOCH$_2$NH^{t}Bu : b.pt. 135°C, 0.005 mm

NMR (CDCl$_3$) : 7.3-8.2 δ, 7H, m; 5.65 δ, 2H, s; 3.45 δ, 2H,

s; 1.55 δ, 1H, s; 1.05 δ, 9H, s.

IR (Film) : 3330, 3060, 2960, 2800, 1740, 1605, 1515, 1460,

1370, 1280-1120, 990, 960, 800-780 cm^{-1}.

C$_{17}$H$_{21}$NO$_2$ requires C: 75.3; H: 7.75; N: 5.2,

Found, C: 75.25; H: 7.9; N: 5.1%.

2-NpCH$_2$OCOCH$_2$NH^{t}Bu : b.pt. 145°C, 0.002 mm

NMR (CDCl$_3$) : 7.4-8.1 δ, 7H, m; 5.4 δ, 2H, s; 3.5 δ, 2H, s;

1.65 δ, 1H, s; 1.1 δ, 9H, s.

IR (Film) : 3320, 3060, 2960, 2900, 1740, 1605, 1510,

1450, 1370, 1340, 1275-1130, 950, 890, 855,

820, 750 cm^{-1}.

C$_{17}$H$_{21}$NO$_2$ requires C: 75.3; H: 7.75; N: 5.2,

Found, C: 75.3; H: 7.7; N: 4.8%.

(46) 1-Naphthylmethyl-N-methyl-N-phenylaminoacetate

1 equivalent of the bromoester from 4.2.(17) was added
to 2 equivalents of N-methylaniline in 15 ml of tertiary butanol
and refluxed at 110°C overnight. The solvent was removed under
reduced pressure and ether added. A quick wash with weak
hydrochloric acid removed the N-methylaniline hydrochloride -
much stronger acid being necessary to complete the acid base
extraction. After evaporation of the ether the product remained
in ∿70% yield. Both derivatives were distilled in vacuo and

the 2-derivative recrystallised from ethanol.

1-NpCH$_2$OCOCH$_2$NMePh : b.pt. 170-175°C, 0.001 mm

NMR (CDCl$_3$)	: 6.6-8.2 δ, 12H, m; 5.6 δ, 2H, s; 4.1 δ, 2H, s; 3.0 δ, 3H, s.
IR (Film)	: 3040, 2920, 2880, 1740, 1600, 1500, 1360, 1250, 1170, 1110, 1030, 1010, 985, 960, 800, 790, 780, 750, 690 cm^{-1}.

C$_{20}$H$_{19}$NO$_2$ requires C: 78.7; H: 6.2; N: 4.6,

Found, C: 78.7; H: 6.2; N: 4.6%.

2-NpCH$_2$OCOCH$_2$NMePh : b.pt. 190-200°C, 0.004 mm; m.pt. 61-62.5°C

NMR (CDCl$_3$)	: 6.65-8.05 δ, 12H, m; 5.35 δ, 2H, s; 4.15 δ, 2H, s; 3.05 δ, 3H, s.
IR (NUJOL)	: 3040, 1740, 1600, 1500, 1360, 1250, 1210-1150, 1110, 1030, 1010, 985, 960, 950, 925, 890, 860, 810, 770, 760, 740, 680 cm^{-1}.

C$_{20}$H$_{19}$NO$_2$ requires C: 78.7; H: 6.2; N: 4.6;

Found, C: 78.4; H: 6.4; N: 4.6%.

(47) N,N-Diethyl-1-Naphthylmethoxyacetamide

Preparation of this compound was effected by adding 1 equivalent (~1 g) of 1-hydroxymethylnaphthalene, 4.2.(1), to 10 ml of dry dimethylsulphoxide and 1.5 equivalents of crushed potassium hydroxide pellets. The mixture was stirred for 10 minutes and then 1 equivalent of N,N-diethylbromoacetamide, 4.5.(1), was added. Stirring was continued at room temperature

for an hour after which time the mixture was added to 100 ml of water and 100 ml ether. The ether layer was well washed with water, dried and evaporated to leave the product as an oil which was used unpurified in the next stage, 4.2.(48).

1-NpCH$_2$OCH$_2$CONEt$_2$:

NMR (CDCl$_3$)	: 7.3-8.4 δ, 7H, m; 5.15 δ, 2H, s; 4.25 δ, 2H, s; 3.0-3.6 δ, 4H, m; 0.8-1.4 δ, 6H, m.
IR (Film)	: 3040, 2970, 2930, 2860, 1650, 1600, 1510, 1490-1430, 1380, 1350, 1270, 1220, 1170, 1100, 800, 780 cm^{-1}.

2-NpCH$_2$OCH$_2$CONEt$_2$:

NMR (CDCl$_3$)	: 7.3-8.1 δ, 7H, m; 4.8 δ, 2H, s; 4.2 δ, 2H, s; 3.1-3.7 δ, 4H, m; 0.9-1.4 δ, 6H, m.
IR (Film)	: 3060, 2980, 2940, 2870, 1650, 1505, 1480-1430, 1380, 1350, 1260, 1220, 1170, 1100, 1030, 850, 810, 750 cm^{-1}.

(48)   O-(1'-Naphthylmethyl)-N,N-diethyl-2-aminoethanol

The amide prepared in the previous preparation, 4.2.(47), was reduced with lithium aluminium hydride in a method identical with 4.2.(27). The product was obtained in good yield (>80%).

1-NpCH$_2$OCH$_2$CH$_2$NEt$_2$: b.pt. 135°C, 0.15 mm

NMR (CDCl$_3$)	: 7.3-8.4 δ, 7H, m; 5.0 δ, 2H, s; 3.55-3.8 δ, 2H, t; 2.4-2.85 δ, 6H, m; 0.85-1.2 δ, 6H, t.
IR (Film)	: 3040, 2960, 2930, 2860, 2800, 1595, 1505, 1450, 1370, 1200, 1160, 1090, 1060, 790, 780, 770 cm^{-1}.

$C_{17}H_{23}NO$ requires C: 79.4; H: 8.95; N: 5.45;

Found, C: 79.2; H: 9.0; N: 5.4%.

2-NpCH$_2$OCH$_2$CH$_2$NEt$_2$: b.pt. 137°C, 0.05 mm

NMR (CDCl$_3$)	: 7.5-8.1 δ, 7H, m; 4.75 δ, 2H, s; 3.5-3.75 δ, 2H, t; 2.3-2.9 δ, 6H, m; 0.85-1.2 δ, 6H, t.
IR (Film)	: 3040, 2960, 2920, 2860, 2800, 1600, 1505, 1450, 1370, 1200, 1170, 1120, 1080, 850, 810, 750 cm^{-1}.

$C_{17}H_{23}NO$ requires C: 79.4; H: 8.95; N: 5.45;

Found, C: 79.2; H: 9.0; N: 5.5%.

(49) <u>N-Methyl-N-phenyl-1-naphthylmethoxyacetamide</u>

Preparation of this compound was by a method identical with 4.2.(47) except that N-methyl-N-phenyl-bromoacetamide 4.5.(2) was used instead of the diethylamide.

1-NpCH$_2$OCH$_2$CONMePh :

NMR (CDCl$_3$)	: 7.0-8.4 δ, 12H, m; 5.1 δ, 2H, s; 4.0 δ, 2H, s; 3.35 δ, 3H, s.
IR (Film)	: 3040, 2970, 2920, 2860, 1670, 1600, 1500, 1400, 1330, 1290, 1170, 1110, 800, 790, 770, 700 cm^{-1}.

2-NpCH$_2$OCH$_2$CONMePh :

NMR (CDCl$_3$)	: 7.1-8.2 δ, 12H, m; 4.85 δ, 2H, s; 4.05 δ, 2H, s; 3.3 δ, 3H, s.
IR (Film)	: 3060, 2930, 2860, 1670, 1600, 1500, 1440, 1400, 1340, 1280, 1175, 1110, 1030, 860, 820, 775, 755, 705 cm^{-1}.

(50) O-(1'-Naphthylmethyl)-N-methyl-N-phenyl-2-aminoethanol

The amide prepared in 4.2.(49) was reduced with lithium aluminium hydride by a procedure analogous to 4.2.(27).

1-NpCH$_2$OCH$_2$CH$_2$NMePh : b.pt. 157-160°C, 0.15 mm

NMR (CDCl$_3$) : 6.5-8.2 δ, 12H, m; 5.0 δ, 2H, s; 3.3-3.85 δ, 4H, m; 2.9 δ, 3H, s.

IR (Film) : 3040, 2920, 2890, 2850, 1600, 1500, 1370, 1170, 1100, 1070, 1030, 990, 790, 775, 645, 690 cm^{-1}.

C$_{20}$H$_{21}$NO requires C: 82.5; H: 7.2; N: 4.8; Found, C: 82.4; H: 7.4; N: 4.8%.

2-NpCH$_2$OCH$_2$CH$_2$NMePh : b.pt. 180°C, 0.06 mm

NMR (CDCl$_3$) : 6.8-8.3 δ, 12H, m; 4.85 δ, 2H, s; 3.6-3.9 δ, 4H, m; 3.1 δ, 3H, s.

IR (Film) : 3060, 2960-2800, 1600, 1500, 1450, 1360, 1100, 1070, 1040, 900, 860, 820, 750, 700 cm^{-1}.

C$_{20}$H$_{21}$NO requires C: 82.5; H: 7.2; N: 4.8; Found, C: 82.5; H: 7.3; N: 4.7%.

(51) (1-Naphthylmethyl)methyl ether

This compound was prepared by the method of 4.2.(47) except that methyl iodide was used in place of the bromoacetamide.

1-NpCH$_2$OMe : b.pt. 95°C, 0.001 mm; lit. 106-107°C, 3 mm [216]

NMR (CDCl$_3$) : 7.4-8.3 δ, 7H, m; 4.95 δ, 2H, s; 3.45 δ, 3H, s.

IR (Film) : 3040, 2980, 2910, 2860, 2810, 1600, 1510, 1450, 1380, 1200, 1170, 1100, 1075, 960, 800, 790, 780 cm^{-1}.

2-NpCH₂OMe   : b.pt. 94°C, 0.001 mm

NMR (CDCl₃)   : 7.4-8.0 δ, 7H, m; 4.65 δ, 2H, s; 3.45 δ, 3H, s.

IR (Film)   : 3060, 2980, 2810-2920, 1605, 1510, 1470-1440,
                   1390, 1375, 1270, 1190, 1130, 1100, 1020, 960,
                   920, 890, 850, 810, 750 cm⁻¹.

4.3.   Anthracene Derivatives

(1)   9-Hydroxymethylanthracene

A solution of sodium borohydride (0.2 g) in water (1 ml)

and MeOH (10 ml) was slowly added to a refluxing mixture of 2 g

of 9-anthraldehyde in 50 ml of methanol. The bright yellow colour

of the solution faded to pale yellow and the mixture was then

poured into 200 ml of ice-water. The cream precipitate was filtered

off and dried to yield the product in over 70% yield. It was

recrystallised from methanol-water (80-20) yielding cream needles.

9-AnCH₂OH   : m.pt. 158-159°C; lit. 162-4°C²¹⁷

NMR (CDCl₃)   : 7.3-8.6 δ, 9H, m; 5.7 δ, 2H, s; 2.5 δ, 1H, b.s.

IR (NUJOL)   : 3400, 3040, 1620, 1350, 1275, 1050, 990, 980,
                   885, 730 cm⁻¹.

(2)   9-Chloromethylanthracene

1.5 g of 9-hydroxymethylanthracene was refluxed in 50 ml

of dry benzene and 2 equivalents of thionyl chloride for three

hours or until hydrogen chloride ceased to be evolved. The

mixture was then cooled and washed with sodium bicarbonate solution.
The benzene solution was dried and evaporated to yield the product
in 80% yield. The crude material was recrystallised from benzene-
petroleum ether (60-80) yielding bright yellow needles. '

9-AnCH$_2$Cl   : m.pt. 137-8°C; lit. 141-142.5°C[217]

NMR (CDCl$_3$)   : 7.3-8.6 δ, 9H, m; 5.6 δ, 2H, s.

IR (NUJOL)   : 3040, 1630, 1240, 1150, 1030, 1050, 940, 870,

                    850, 830, 775, 720, 680, 660 cm^{-1}.

(3)   9-Bromomethylanthracene

This compound was prepared from 9-methylanthracene by
the method of 4.2.(3). The crude product was recrystallised from
benzene/petrol (60-80), (50/50) to give bright yellow needles.

9-AnCH$_2$Br   : m.pt. 131-133°C; lit. 138-140°C[218]

NMR (CDCl$_3$)   : 7.3-8.6 δ, 9H, m; 5.55 δ, 2H, s.

IR (NUJOL)   : 3040, 1625, 1260, 1200, 1055, 960, 885, 870,

                    840, 790, 730 cm^{-1}.

(4)   9-Bromoanthracene

10 g of anthracene was refluxed in 150 ml CCl$_4$ with 2
equivalents of cupric bromide for 24 hours or until hydrogen
bromide ceased to be evolved. The resulting mixture was filtered
and the solvent evaporated to leave the crude product in >80%
yield. It was readily recrystallised from ethanol.

9-AnBr   : m.pt. 96-98°C; lit. 101°C[208]

(5)   9-(2'-Hydroxyethyl)anthracene

To a solution of butyl lithium in hexane (as supplied 21%
by weight; 5 ml used) 9-bromoanthracene (2 g) was added in 50 ml
of ether which had been dried with lithium aluminium hydride.
The mixture was stirred under dry nitrogen and the solution cooled
to 0°C. A solution of ethylene oxide, 1.2 g in 10-15 ml of ether
was added and stirring continued at 0°C for $\frac{1}{2}$ hour followed by
15 min gently refluxing. A bright yellow precipate was obtained
at this stage. Water was added carefully (50 ml) and the product
extracted from the ether layer to yield the crude product in ∿70%
yield. The product was chromatographed on alumina eluting with
benzene and after impurities has been removed, was washed off the
column by changing to ethylacetate solvent. The product was
finally recrystallised from benzene/petroleum ether (60-80)
(40/60 vv) to give pure white needles. To avoid inconvenient
side-products the reaction should be done at low substrate con-
centration.

9-AnCH₂CH₂OH   : m.pt. 107-109°C, lit; 106-108°C [219]

NMR (CDCl₃)   : 7.2-8.6 δ, 9H, m; 3.8-4.2 δ, 4H, m; 1.55 δ, 1H, s.

IR (NUJOL)   : 3250, 3030, 1620, 1150, 1035, 960, 890, 840,
                  785, 730, 680 cm⁻¹.

(6)   9-(2'-Chloroethyl)anthracene

This compound was prepared starting from 9-(2-hydroxyethyl)-
anthracene by a method described in 4.3.(2). It was recrystallised
from dry methanol.

9-AnCH$_2$CH$_2$Cl   : m.pt. 92-94°C; lit. 93-96°C [220]

NMR (CDCl$_3$)   : 7.0-8.3 δ, 9H, m; 3.65-4.3 δ, 4H, m.

IR (NUJOL)   : 3040, 1620, 1240, 1150, 950, 885, 835, 790,

            730, 685 cm^{-1}.

(7)   9-(2'-Bromoethyl)anthracene

        1 g of 9-(2'-hydroxyethyl)anthracene was added to 20 ml of

dry dimethylformamide and 1.2 g of triphenylphosphine. Bromine in

DMF was added dropwise to the solution, which was cooled in ice,

until a permanent orange colour remained. 150 ml of water was

added and the organic components extracted into benzene which was

dried and evaporated. The residue, which was a mixture of product

and triphenyl phosphine oxide, was purified by chromatography on

a silica column, eluting with benzene-ethylacetate (60/40 vv).

The phosphine oxide stuck to the column and the product was removed.

Recrystallisation was from methanol giving white needles. Yield

after chromatography, 50%.

9-AnCH$_2$CH$_2$Br   : m.pt. 98-102°C

NMR (CDCl$_3$)   : 7.1-8.3 δ, 9H, m; 3.9-4.3 δ, 2H, m; 3.4-3.8 δ, 2H, m.

IR (NUJOL)   : 3020, 1615, 1200, 1140, 1030, 1010, 875, 830,

            780, 725, 660 cm^{-1}.

MASS SPEC.   : 177 (Ar$^+$), 191, 205, 284, 286 (M$^+$).

(8)   2-(9'-Anthryl)ethyl tosylate

To 10 ml of dry pyridine 0.4 g of 9-(2'-hydroxyethyl) anthracene was added and then 1.1 equivalents of p-toluene sulphonyl chloride added to the cooled solution. The mixture was stored in a refrigerator for 24 hours. After this time the mixture was poured into 50 ml of 4% sodium bicarbonate solution and the white precipitate filtered off and dried in a vacuum. The product was used immediately in the next reaction. The yield was >80%.

(9)   9-(2'-Iodoethyl)anthracene

0.6 g of the tosylate from 4.3.(8) was converted to the iodide by a procedure identical with 4.2.(4). The product was obtained as a yellow solid in 90% yield which recrystallised from benzene petroleum ether (60-80) (50/50 vv) or from MeOH, the latter solvent being better.

9-AnCH$_2$CH$_2$I   : m.pt. 110°C; lit. 110°C[219]

NMR (CDCl$_3$)   : 7.0-8.3 δ, 9H, m; 3.8-4.3 δ, 2H, m; 3.1-3.5 δ,

2H, m. ,

IR (NUJOL)   : 3040, 1625, 1170, 1015, 890, 840, 790, 730 cm^{-1}.

(10)   9-Anthrylmethyl acetate

1 g of 9-hydroxymethyl anthracene was added to 50 ml dry benzene and 1 equivalent of dry pyridine. To the mixture 1 equivalent of acetyl chloride was added and stirring continued for $\frac{1}{2}$ hour. After this time an equal volume of dilute hydrochloric

acid was added and the product extracted from benzene as a yellow solid in >70% yield. It was recrystallised from benzene-petroleum ether (60-80) (50/50 vv) yielding yellow needles.

9-AnCH$_2$OCOCH$_3$: m.pt. 111-112°C

NMR (CCl$_4$)	: 7.2-8.5 δ, 9H, m; 6.1 δ, 2H, s; 2.0 δ, 3H, s.
IR (NUJOL)	: 3060, 1720, 1620, 1245, 1020, 960, 920, 890, 885, 780, 735 cm^{-1}.
	C$_{17}$H$_{14}$O$_2$ requires C: 81.6; H: 5.6; Found, C: 81.5; H: 5.7%.

(11)   9-Anthrylmethyl chloroacetate

This compound was made using the method of 4.3.(10) and chloroacetyl chloride instead of acetyl chloride. Recrystallisation was from benzene petroleum ether (60-80) (50/50 vv) to give yellow needles.

9-AnCH$_2$OCOCH$_2$Cl : m.pt. 146-148°C

NMR (CDCl$_3$)	: 7.2-8.6 δ, 9H, m; 6.35 δ, 2H, s; 4.05 δ, 2H, s.
IR (NUJOL)	: 3040, 1750, 1630, 1415, 1320, 1230, 1200, 1165, 970, 950, 940, 930, 885, 840, 795, 740, 730 cm^{-1}.
	C$_{17}$H$_{13}$ClO$_2$ requires C: 71.7; H: 4.6; Cl: 12.5; Found, C: 71.6; H: 4.5; Cl: 12.5%.

(12)   9-Anthrylmethyl bromoacetate

The method used was as in 4.3.(10), substituting bromoacetyl bromide for acetyl chloride. The product was recrystallised from

benzene-petroleum ether (60-80) (50/50 vv) giving bright yellow plates.

9-AnCH₂OCOCH₂Br : m.pt. 130-132°C

NMR (CDCl₃) : 7.2-8.6 δ, 9H, m; 6.35 δ, 2H, s; 3.9 δ, 2H, s.

IR (NUJOL) : 3040, 1730, 1620, 1395, 1290, 1170, 950, 940,
920, 880, 870, 830, 775, 725 cm⁻¹.

$C_{17}H_{13}BrO_2$ requires C: 61.8; H: 3.9; Br: 24.5;

Found, C: 62.1; H: 3.9; Br: 24.2%.

(13)   9-Anthrylmethyl iodoacetate

This compound was prepared as described in 4.2.(4) starting from 9-anthrylmethyl-bromoacetate and using benzene to extract the product. Recrystallisation was from dry ethanol giving yellow needles.

9-AnCH₂OCOCH₂I : m.pt. 93-95°C

NMR (CDCl₃) : 7.3-8.6 δ, 9H, m; 6.25 δ, 2H, s; 3.75 δ, 2H, s.

IR (NUJOL) : 3040, 1730, 1625, 1400, 1270, 1150, 1120, 965,
955, 930, 900, 890, 870, 845, 790, 740 cm⁻¹.

$C_{17}H_{13}IO_2$ requires C: 54.25; H: 3.5; I: 33.8;

Found, C: 54.1; H: 3.5; I: 33.5%.

(14)   9-Anthrylmethyl-N,N-diethylaminoacetate

This compound was prepared from the bromoacetate described in 4.3.(12), using benzene instead of ether as solvent, by the method of 4.2.(43).

9-AnCH$_2$OCOCH$_2$NEt$_2$: m.pt. 63-65°C

NMR (CDCl$_3$)	: 7.4-8.7 δ, 9H, m; 6.25 δ, 2H, s; 3.4 δ, 2H, s; 2.5-2.9 δ, 4H, q; 0.9-1.2 δ, 6H, s.
IR (Film)	: 2860-2980, 1735, 1460, 1380, 1180, 990, 745, 735 cm^{-1}.

$C_{21}H_{23}NO_2$ requires C: 78.5; H: 7.2; N: 4.4;

Found, C: 78.1; H: 6.8; N: 4.4%.

(15)   9-Anthrylmethyl-N-tert.butylaminoacetate

The same method as in 4.3.(14) was used but replacing diethylamine by tert.butylamine.

9-AnCH$_2$OCOCH$_2$NH^{t}Bu : m.pt. 137-138°C

NMR (CDCl$_3$)	: 7.1-8.4 δ, 9H, m; 6.05 δ, 2H, s; 3.3 δ, 2H, s; 2.15 δ, 1H, b.s.; 1.0 δ, 9H, s.
IR (NUJOL)	: 1740, 1630, 1225, 1190, 1175, 960, 900, 730 cm^{-1}.

$C_{21}H_{23}NO_2$ requires C: 78.5; H: 7.2; N: 4.4;

Found, C: 78.5; H: 7.2; N: 4.4%.

(16)   9-Anthrylmethyl-N-methyl-N-phenylaminoacetate

The method of preparation was as described in 4.2.(46) using the bromoester from 4.3.(12) as starting material and extracting the product in benzene. Recrystallisation was from benzene-petrol, (60-80), (50/50 vv).

9-AnCH$_2$OCOCH$_2$NMePh : m.pt. 110-112°C

NMR (CDCl$_3$)	: 6.4-8.4 δ, 14H, m; 6.1 δ, 2H, s; 4.0 δ, 2H, s;
	3.0 δ, 3H, s.
IR (NUJOL)	: 1740, 1605, 1260, 1190, 1175, 1120, 955, 880,
	775, 735, 720, 675 cm^{-1}.
	C$_{24}$H$_{21}$NO$_2$ requires C: 81.1; H: 5.9; N: 3.9;
	Found, C: 80.8; H: 5.95; N: 3.9%.

4.4. Pyrene derivatives

(1) 1-Hydroxymethylpyrene

This compound was prepared by reducing 1 g of pyrene carboxaldehyde with sodium borohydride in 50 ml of refluxing methanol as in 4.3.(1). When the yellow colour had faded the solution was cooled and the methanol evaporated. The residue was taken up in chloroform and washed with water. The organic layer was then dried and the chloroform evaporated to yield the product in >70% yield. Recrystallisation was from methanol.

1-PyCH$_2$OH : m.pt. 153-155°C; lit. 155°C [221]

NMR (CDCl$_3$)	: 7.8-8.4 δ, 9H, m; 5.4 δ, 2H, s; 1.95 δ, 1H, s.
IR (NUJOL)	: 3250, 3030, 1600, 1185, 1070, 1030, 1010, 900,
	850, 840, 760, 710 cm^{-1}.

(2) 1-Pyrylmethyl acetate

1 g of hydroxymethyl pyrene from 4.4.(1) was added to 30 ml of THF dried over lithium aluminium hydride, together with

1 equivalent of pyridine. The mixture was stirred at room temperature and 1 equivalent of acetyl chloride added. The stirring was continued for an hour after which time the THF was evaporated under reduced pressure. 50 ml of chloroform was added to the residue and the solution washed with an equal volume of dilute acid. After separation of the chloroform layer, drying and evaporation, the product remained in >60% yield and could be recrystallised from ethanol.

1-PyCH$_2$OCOCH$_3$: m.pt. 66-70°C

NMR (CDCl$_3$)   : 7.7-8.2 δ, 9H, m; 5.7 δ, 2H, s; 2.1 δ, 3H, s.

IR (NUJOL)   : 3050, 1725, 1600, 1250, 1060, 1040, 930,

850, 805, 760, 710 cm^{-1}.

C$_{19}$H$_{14}$O$_2$ requires C: 83.2; H: 5.1; Found,

C: 83.4; H: 5.2%.

(3)   1-Pyrylmethyl chloroacetate

The same method as in 4.4.(2) was used for this preparation substituting chloroacetyl chloride for acetyl chloride.

1-PyCH$_2$OCOCH$_2$Cl   : m.pt. 105-108°C

NMR (CDCl$_3$)   : 7.7-8.2 δ, 9H, m; 5.8 δ, 2H, s; 4.0 δ, 2H, s.

IR (NUJOL)   : 3040, 1730, 1600, 1310, 1200, 1160, 960, 940,

910, 845, 820, 710 cm^{-1}.

C$_{19}$H$_{13}$ClO$_2$ requires C: 73.9; H: 4.2; Cl: 11.5;

Found, C: 73.8; H: 4.15; Cl: 11.3%.

(4)   1-Pyrylmethyl bromoacetate

An identical procedure as in 4.4.(2) was used except that bromoacetyl bromide replaced acetyl chloride. The product was

recrystallised from ethanol to give cream needles.

1-PyCH$_2$OCOCH$_2$Br   : m.pt. 105-108°C

NMR (CDCl$_3$)   : 7.7-8.2 δ, 9H, m; 5.5 δ, 2H, s; 3.7 δ, 2H, s.

IR (NUJOL)   : 3030, 1730, 1600, 1290, 1180, 1120, 950, 930, 845, 710 cm^{-1}.

$C_{19}H_{13}BrO_2$ requires C: 64.6; H: 3.7; Br: 22.6;

Found, C: 64.6; H: 3.9; Br: 22.4%.

(5)   1-Pyrylmethyl Iodoacetate

The same method was used to prepare this derivative as that described in 4.2.(4) using the bromoacetate from 4.4.(4) as starting material and extracting the product with chloroform. Recrystallisation was from ethanol yielding cream needles.

1-PyCH$_2$OCOCH$_2$I   : m.pt. 110-112°C

NMR (CDCl$_3$)   : 7.9-8.4 δ, 9H, m; 5.9 δ, 2H, s; 3.75 δ, 2H, s.

IR (NUJOL)   : 3030, 1730, 1600, 1270, 1250, 1160, 1140, 960, 950, 845, 755, 725, 700 cm^{-1}.

$C_{19}H_{13}IO_2$ requires C: 57.0; H: 3.25;

Found, C: 57.25; H: 3.35%.

4.5.   Miscellaneous Preparations

(1)   N,N-Diethylbromoacetamide

1 equivalent (2 g) of bromoacetyl bromide in 5 ml dry benzene was added rapidly to a stirred solution of 2 equivalents of diethyl-

amine in dry benzene (30 ml). After 10 min stirring, an equal

volume of dilute hydrochloric acid was added and the product

extracted from the benzene layer with the usual work-up. Distill-

ation of the product yielded a colourless oil (>80%).

$BrCH_2CONEt_2$	: b.pt. 92-95°C, 1 mm; lit. 82°C, 0.6 mm [222]

NMR ($CDCl_3$)	: 3.95 δ, 2H, s; 3.25-3.65 δ, 4H, q; 1.15-1.4 δ,
	6H, t.
IR (Film)	: 2960, 2920, 2860, 1650, 1460, 1440, 1360, 1320,
	1310, 1280, 1215, 1130, 1100, 1020, 950, 790,
	700, 680 cm^{-1}.

(2) Bromo-N-methylacetanilide

1 equivalent (2 g) of bromoacetyl bromide was added to a

stirred solution of 1 equivalent of N-methylaniline and 1 equivalent

of dry pyridine in dry benzene (30 ml). After 10 min stirring an

equal volume of dilute hydrochloric acid was added and the product

extracted from the benzene layer as a yellow oil. Addition of

dry ether to the product and evaporation yielded pale yellow crystals.

$BrCH_2CONMePh$	: m.pt. 46-48°C; lit. 47°C [223]

NMR ($CDCl_3$)	: 7.2-7.7 δ, 5H, m; 3.7 δ, 2H, s; 3.3 δ, 3H, s.
IR (Film)	: 3060, 2960, 1670, 1600, 1500, 1430, 1380,
	1300, 1220, 1110, 1075, 1045, 770, 700, 640 cm^{-1}.

4.6. Sources of Other Compounds Used

Chapter 1

Naphthalene	BDH
1-chloro-	BDH
1-bromo-	courtesy Mrs. Szpek
1-iodo-	Koch-Light
2-chloro-	I.C.N. Pharmaceuticals
2-bromo-	BDH
1- and 2-methyl-	Koch-Light
Pyrene	BDH
9-Methylanthracene	Aldrich

Chapter 3

Aniline	Fisons
N-Methylaniline	Fisons
N,N-Dimethylaniline	Fisons
Diphenylamine	BDH
Tribenzylamine	Koch-Light
DABCO	Emanuel
Triethylamine	Emanuel
Indole	Koch-Light
Skatole	Koch-Light
Indole acetic acid	Emanuel
Gramine	Emanuel
Tryptamine hydrochl.	Emanuel
Tryptophan	Koch-Light

N-Acetyltryptophan	Cambrian
Rose Bengal	BDH
Methylene Blue	Aldrich
Ruthenium trichloride	Johnson Matthey
Eosin	BDH
Fluorescein	Fisons
DPBF	Oxford Organics
β-Carotene	Sigma
Anthracene	BDH
-carboxylic acid	Emanuel
-carboxaldehyde	Koch-Light
Acetyl-	Emanuel
9,10-dimethyl	Aldrich
1,2-benz-	Emanuel
2,3-Dimethylnaphthalene	
2,6-Dimethyl-	Aldrich
Acenaphthylene	BDH
Acenaphthene	BDH
Acridine	Hopkin and Williams
Phenazine	Koch-Light
Ergosterol	Emanuel
Fluorenone	Koch-Light

Chapter 4

1-Naphthoic acid	Koch-Light
2-Naphthoic acid	Koch-Light and Cambrian
1-Naphthyl acetic acid	Koch-Light and Emanuel

2-Naphthyl acetic acid	Cambrian
1-Naphthaldehyde	Koch-Light
2-Naphthaldehyde	Aldrich
1-Pyrene carboxaldehyde	Aldrich

INDEX OF COMPOUNDS

4·1 Benzene derivatives

1) $Ph-CH_2NEt_2$

4·2 Naphthalene derivatives (1-and 2-substd.)

1) $NpCH_2OH$

2) $-Cl$

3) $-Br$

4) $-I$

5) $Np(CH_2)_2OH$

6) $-Cl$

7) $-Br$

8) $-I$

9) $NpCH=CHCO_2H$

10) $-(CH_2)_2CO_2H$

11) $-(CH_2)_3OH$

12) $-Cl$

13) $-Br$

14) $-I$

15) $NpCH_2OCOCH_3$

16) $-CH_2Cl$

17) $-Br$

18) $-I$

19) $NpCH_2COCl$

20) $-CH_2CO_2CH_3$

21) $-(CH_2)_2Cl$

22) $-Br$

23) $-I$

24) $NpCH_2NEt_2$

25) $-NMePh$

26) $NpCH_2CONEt_2$

27) $-(CH_2)_2NEt_2$

28) $-CH_2CONMePh$

29) $-(CH_2)_2NMePh$

30) $Np(CH_2)_2COCl$

31) $-(CH_2)_2CONEt_2$

32) $-(CH_2)_3NEt_2$

33) $-(CH_2)_2CONMePh$

34) $-(CH_2)_3NMePh$

---

35) $NpCH_2CHO$

36) $-CH=CHCO_2H$

37) $-(CH_2)_3CO_2H$

38) $-COCl$

39) $-CONEt_2$

40) $-(CH_2)_4NEt_2$

41) $-(CH_2)_3CONMePh$

42) $-(CH_2)_4NMePh$

---

43) $NpCH_2OCOCH_2NEt_2$

44) $-NHPh$

45) $-NH^tBu$

46) $-NMePh$

---

47) $NpCH_2OCH_2CONEt_2$

48) $-(CH_2)_2NEt_2$

49) $-CH_2CONMePh$

50) $-(CH_2)_2NMePh$

51) $-CH_3$
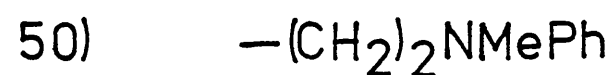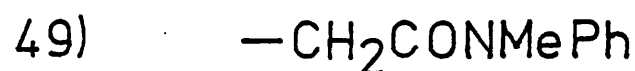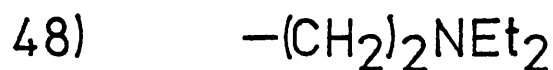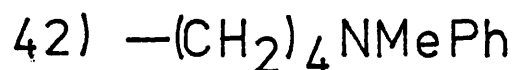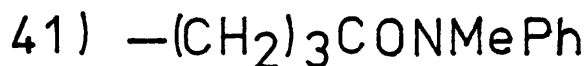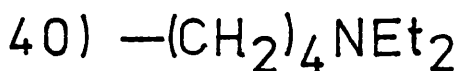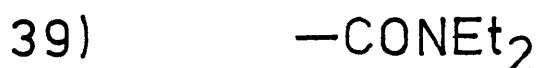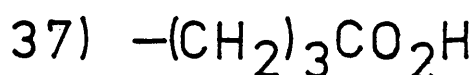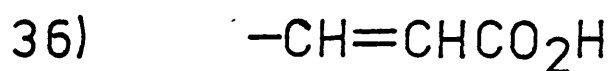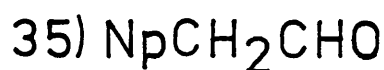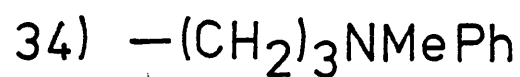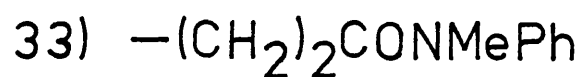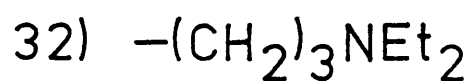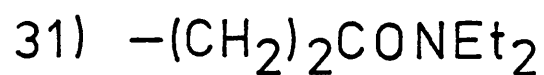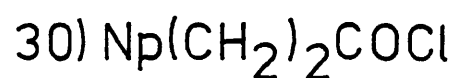
4·3 Anthracene derivatives (9 – substd.)

1) $AnCH_2OH$

2)   –Cl

3)   –Br

4) $AnBr$

5) $An(CH_2)_2OH$

6)   –Cl

7)   –Br

8)   –OTos

9)   –I

10) $AnCH_2OCOCH_3$

11)   –CH_2Cl

12)   –Br

13)   –I

14) $AnCH_2OCOCH_2NEt_2$

15)   –NH^tBu

16)   –NMePh

4·4 Pyrene derivatives (1 – substd.)

1) $PyCH_2OH$

2)   –$OCOCH_3$

3)   –CH_2Cl

4)   –Br

5)   –I

4·5 Miscellaneous.

1) $BrCH_2CONEt_2$

2) $BrCH_2CONMePh$

Appendix 1.9. Analysis of Kinetic Flash Photolysis Data

The analysis is based on the method of Linschitz and
Sarkanen.[203] It uses data taken from an oscilloscope trace of
the decay fed into a BASIC computer programme and is for FIRST
ORDER DECAYS ONLY. The programme is listed below and details
for the input of data follow, with examples from the diagram below.
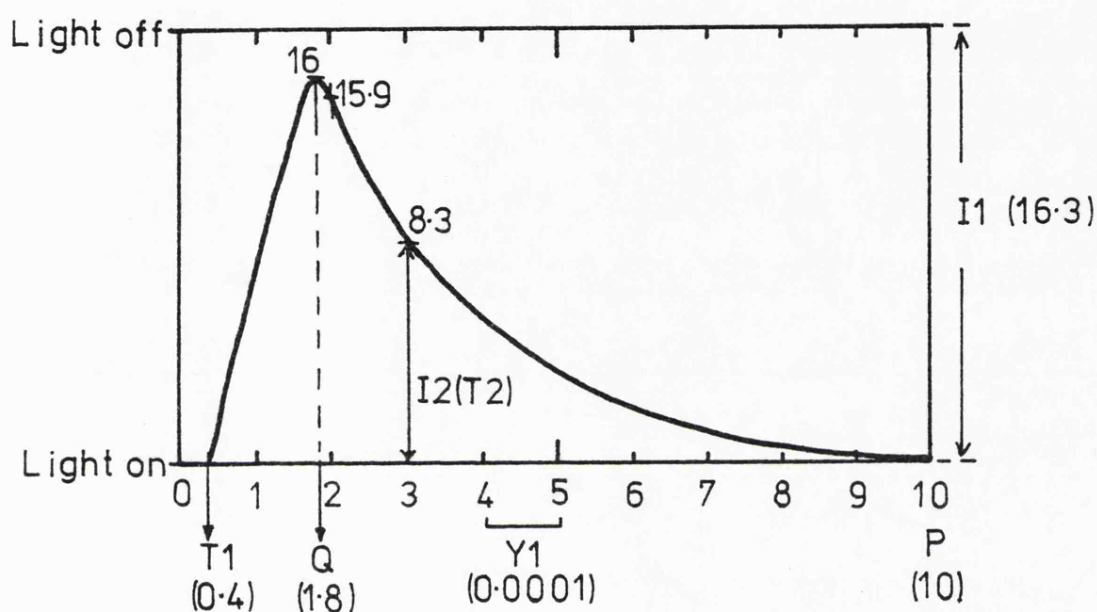
The data input requires the following:

(a)   T1 : This is the point on the time scale from which
time is to be measured (e.g. 0.4).

(b)   P : This is the maximum value of the time scale (e.g. 10).

(c)   Q : This is the point on the time scale at which the
maximum occurs for the trace (e.g. 1.8). Note: this must
not be integral. Use 1.99 or 2.01 when 2 is required, for example.

(d)   Y1 : This is the time base in secs/div.

(e)   I1 : This is the distance between the on/off levels.

(f)   I2(T2) : This is the distance from the base line to the curve measured on each major grid line after T1 together with one value measured for the maximum of the decay at time Q. If it is not possible to enter a reading a value of 0 must be used; the programme will ignore this value.

The distances can be measured from a photograph using a travelling microscope and the data assembled for each photograph (the programme will compute as many as required). Assemble the data as follows:

(i)   T1, P, Q, Y1, I1, followed by each I2(T2) value in order of ascending grid value. Using the example in the diagram there will be 11 I2(T2) values since the one for the decay maximum must be included in order. Any non-sensical values are denoted by zero. Hence the value between T1 and Q on grid line 1 is given the value zero. This may not always be present. (If T1 falls on a grid line a zero must be included for this value also.)

(ii)   Type the data into the programme in the normal way, e.g.

1 DATA 0.4, 10, 1.8, 0.0001, 16.3, 0, 16, 15.9, 8.3, etc.
Lines 1-999 may be used.

(iii)   Run the programme. It will be necessary to input the number of runs (photographs) required.

It may be convenient to use Y1 in ms/div. This will naturally alter the output but is easily converted. The slope

is the rate constant and the intercept is the $\log_e$ (OD), the
antilog of which will yield the concentration of intermediate
extrapolated to zero time. The size of the errors will indicate
the linearity of the plot.

FIRST ORDER DECAY ANALYSIS

```
1000 DIM A(11)
1001 DIM B(11)
1002 DIM C(11)
1003 DIM D(11)
1004 DIM W(11)
1005 DIM Y(11)
1006 DIM I2(11)
1010 PRINT "NUMBER OF RUNS="
1020 INPUT N
1021 LET X=1
1030 READ T1
1031 READ P
1032 READ Q
1033 READ Y1
1034 READ I1
1035 PRINT "RUN" X
1040 LET Z=1
1041 LET F=0
1050 FOR T2=0 TO P
1060 IF Q<T2 THEN 1080
1070 GOTO 1120
1080 IF Q>(T2-1) THEN 1100
1090 GOTO 1120
1100 LET T3=Q-T1
1110 GOSUB 1190
1120 LET T3=T2-T1
1130 IF T3>=0 THEN 1170
1140 IF T2=1 THEN 1150
1145 GOTO 1310
1150 READ I2(T2)
1155 IF I2(T2)=0 THEN 1157
1156 GOTO 1160
1157 LET F=F+1
1160 GOTO 1310
1170 GOSUB 1190
1180 GOTO 1300
1190 LET T4= Y1*T3
1200 LET W(Z)=T4
1210 READ I2(T2)
1220 IF I2(T2)=0 THEN 1222
1221 GOTO 1230
1222 LET F=F+1
1223 GOTO 1310
1230 LET I3=I1-I2(T2)
1240 LET I4=I1/I3
1250 LET D1=LOG(I4)/2.303
1260 LET D2=LOG(D1)
1270 LET D2=INT(D2*100)
1280 LET D2=D2/100
1285 LET Y(Z)=D2
1287 LET Z=Z+1
1290 RETURN
1300 IF T2=P THEN 1320
1310 NEXT T2
1320 GOSUB 2000
1330 IF X=N THEN 5000
1340 LET X=X+1
1350 GOTO 1030
2000 PRINT
2010 PRINT "TIME","LOG.C.D.","BEST-FIT CD.","DEVN.","% DEVN."
```

```
2020 LET Z=1
2040 LET A(0)=0
2050 LET B(0)=0
2060 LET C(0)=0
2070 LET D(0)=0
2080 LET A(Z)=W(Z)
2090 LET B(Z)=Y(Z)
2100 LET C(Z)=W(Z)*W(Z)
2110 LET D(Z)=W(Z)*Y(Z)
2120 LET A(Z)=A(Z)+A(Z-1)
2130 LET B(Z)=B(Z)+B(Z-1)
2140 LET C(Z)=C(Z)+C(Z-1)
2150 LET D(Z)=D(Z)+D(Z-1)
2160 IF Z=P+1-F THEN 2190
2170 LET Z=Z+1
2180 GOTO 2080
2190 LET R1=A(Z)/Z
2200 LET S1=B(Z)/Z
2210 LET R2=Z*R1*S1
2220 LET S2=Z*R1*R1
2230 LET R3=D(Z)-R2
2240 LET S3=C(Z)-S2
2250 LET K=R3/S3
2260 LET L=S1-(K*R1)
2270 LET Z=1
2280 LET W1=(W(Z)*K)+L
2281 LET W1=INT(W1*100)
2282 LET W1=W1/100
2290 LET Y=Y(Z)-W1
2291 LET Y=INT(Y*100)
2292 LET Y=Y/100
2300 PRINT W(Z),Y(Z),W1,Y,
2310 IF Y(Z)=0 THEN 2340
2320 LET Y=Y*100/Y(Z)
2321 LET Y=INT(Y*10)
2322 LET Y=Y/10
2325 PRINT Y
2330 GOTO 2350
2340 LET Y=0
2350 IF Z=P+1-F THEN 2370
2360 LET Z=Z+1
2365 GOTO 2280
2370 PRINT "SLOPE=",K,"INTERCEPT=",L
2380 RETURN
5000 STOP
READY
```
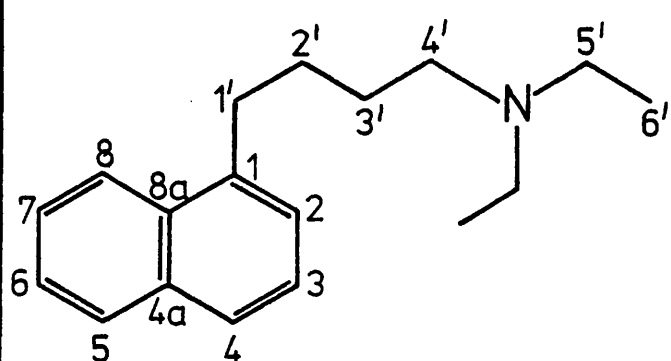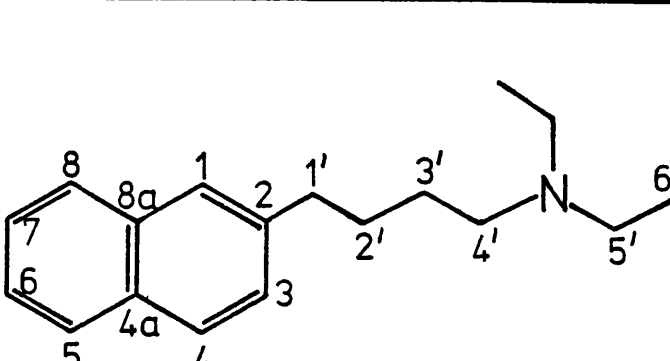
APPENDIX 3.2.6.

^{13}C NMR DATA FOR Ar(CH$_2$)NEt$_2$.

Shifts in p.p.m.   Ref: T.M.S.   Solvent: CCl$_4$

C	α1E	α2E	α3E	α4E	C	β1E	β2E	β3E	β4E
6'	11·6	11·7	11·8	11·8	6'	11·8	11·8	11·7	11·8
5'	47·0	47·0	47·0	47·0	5'	46·9	47·0	46·9	47·0
1'	56·1	30·6	31·0	33·1	1'	57·8	33·7	37·1	36·1
2'		54·0	28·3	28·9	2'		54·8	29·3	29·4
3'			53·0	27·4	3'			53·6	26·9
4'				52·9	4'				52·9
8	124·6	123·6	123·9	123·9	6	125·4	125·0	125·0	125·0
7/3	125·2	125·4	125·4	125·4	7	125·8	125·8	125·8	125·8
6	125·6	125·8	125·6	125·6	1	127·2	126·7	126·3	126·3
2	126·9	126·4	125·8	125·9	8	127·4	127·4	127·4	127·4
4	127·4	126·7	126·5	126·5	4,5	127·6	127·6	127·6	127·6
5	128·3	128·7	128·7	128·7	3		127·8	127·8	127·8
4a		132·0	132·0	132·0	4a	132·8	132·1	132·0	132·1
8a	133·8	133·9	133·9	134·0	8a	133·4	133·7	133·7	133·7
1	135·8	136·5	138·7	138·7	2	137·5	138·2	139·9	140·1

13C NMR DATA FOR NAPHTHALENE COMPOUNDS

Shifts in p.p.m.   Ref: T.M.S.   Solvent: CCl$_4$

C	αMN	C	βMN
α	19.1	β	21.4
		6	125.0
		7	125.9
		1	127.1
8	124.2	8	127.5
7,3,6	125.6	4,5	127.9
2,4	126.7	3	128.2
5	128.7	4a	132.2
8a	133.0	8a	134.1
1,4a	134.1	2	135.4
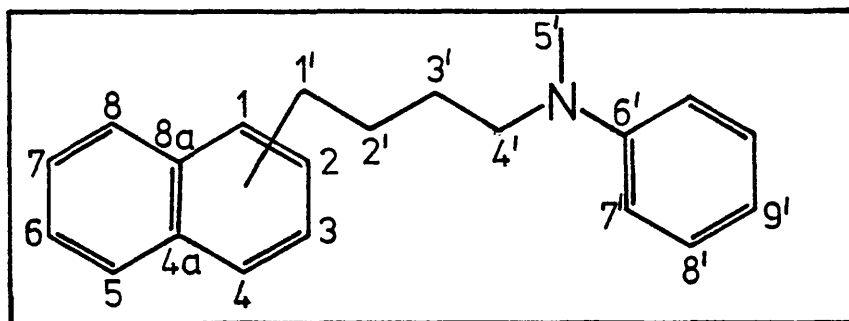
C	α2N	C	β2N	β4N
1'	30.0	1'	33.1	35.9
2'	53.9	2'	54.7	28.8
3'		3'		26.4
4'		4'		52.6
5'	38.4	5'	38.5	38.2
7'	112.3	7'	112.3	112.2
9'	116.3	9'	116.3	116.0
8	123.5	6	125.3	125.0
7,3	125.6	7	126.0	125.8
6	126.0	1	127.0	126.3
		8	127.4	127.4
2,4	126.7	4,5	127.6	127.6
5	128.9	3	128.0	127.8
8'	129.3	8'	129.3	129.1
4a	132.0	4a	132.1	132.0
8a	133.9	8a	133.7	133.6
1	136.0	2	137.3	139.7
6'	148.9	6'	148.9	149.4

Assignments from refs. 224,225.

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K.R. TRETHEWEY.   Ph.D. Thesis.   1976.

Some Excited State Charge Transfer Interactions

by Kenneth R. Trethewey

Abstract

The intramolecular excited state interactions of polycyclic aromatic hydrocarbons and halogens have been studied where the aromatic nucleus is separated from the quencher by numerous linking chains. The effects of the interactions on the various aromatic decay parameters are explained in terms of excited complex formation rather than simple heavy atom theory. Mechanisms for formation of the complexes are discussed and correlated with the different derivatives used in the study. The reactivity of the carbon-halogen bond is found to have a considerable importance on the effects observed, particularly in relation to work at low temperature and studies of the triplet yields.

The work was extended to include the interactions of a variety of amines with aromatic nuclei by means of similar series of derivatives. The geometrical requirements for excited complex formation are discussed in depth and the conclusion is reached that amine exciplexes require very loose geometries in relation to excited dimers.

Finally the excited state interactions of several photo-sensitisers with a large number of quenchers have been examined. Excited singlet state quenching is shown to be a general phenomenon and the quenching constants are reported for many aromatic hydro-carbon derivatives, amines and anions. The interactions are shown to be dependent on the ionisation potential of the quencher.

An important interaction of β-carotene and the excited singlet state of chlorophylla is reported, together with some interactions of photosensitiser triplet states.