Inter- and Intra-molecular Donor–Acceptor Complexes Formed between Alkylphthalimides and Aromatic Hydrocarbons

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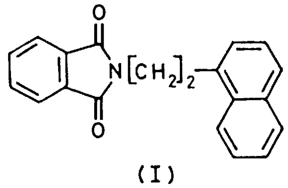
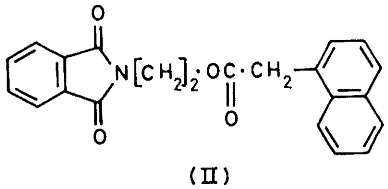
Examination of the absorption spectra and fluorescence spectra of the imides (I) and (II) show that they form intramolecular charge-transfer complexes. In rigid matrices, fluorescence from the charge-transfer complexes and also phosphorescence from the naphthalene group is observed. Any rationalisation of energy transfer in these systems must take account of the part played by the excited complexes. Intermolecular charge transfer complex formation between *N*-n-butyl-3,4,5,6-tetrachlorophthalimide and anthracene, 9-methylanthracene, and 9,10-dimethylanthracene has been observed in rigid cyclohexane matrices.

THE association of molecules in the ground state can have a profound effect upon photochemical reactions.[1,2] Thus the association of molecules precludes the necessity for molecules to undergo diffusion-controlled collision before reaction can take place and consequently the reaction of short-lived excited states such as excited singlet states can become manifest in such systems. Since many excited singlet states undergo redox reactions it is not surprising that association of potential donor and acceptor molecules in solution increases the favourability of such processes. Association between potential donor and acceptor molecules can often be facilitated by freezing solutions of donor and acceptors.[3a,b,4] In some cases the ground state association of molecules gives rise to new absorption bands--charge-transfer absorption bands. Excitation into these bands produces excited complexes which may give rise to chemical reaction or they may disssipate their energy by an emission or radiationless process which leads to no net chemical reaction. Since the energy of the lowest excited singlet state of the complex lies below the excited singlet state of either the donor or acceptor molecules the complexes may mediate in the process of intersystem crossing. This will be particularly important when the energy of the excited singlet complex lies above the triplet state of either the donor or the acceptor.



(I)

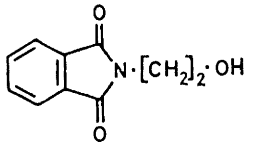


(II)

We now report the results of studies on inter- and intra-molecular complex formation between *N*-alkylphthalimides and aromatic hydrocarbons. Intramolecular complex formation by these systems is relevant to the report of Breen and Keller[4a] on intramolecular triplet energy transfer in (I). There has been one other study on intramolecular charge-transfer complex formation between imides and aromatic hydrocarbons.[4b]

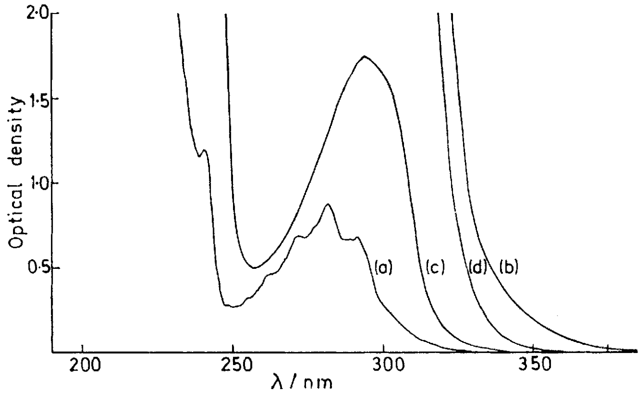
RESULTS

The imides (I) and (II) were synthesised by standard routes.



(III)

Ground State Complex Formation.—Compounds (I) and (II) do not show a discrete charge-transfer absorption band.



U.v. absorption spectra of (II) and (III) in ethanol. (a) = (II), 1×10^{-4}M; (b) = (II), 1×10^{-2}M; (c) = (III) 1×10^{-3}M; (d) = (III), 1×10^{-2}M

Comparison of the u.v. absorption spectra of (I) and (II) with (III) shows that they posssess absorption at >350 nm which is not present in either (III) or methyl 1-naphthylacetate. The intensity of the long wavelength absorption in (I) and (II) showed a linear dependence upon the concentration of the compounds and therefore the absorption is not due to intermolecular complex formation. Further support for the long wavelength absorption being due to intramolecular and not intermolecular complex formation comes from the finding that solutions containing *N*-butylphthalimide and 1-methylnaphthalene showed no new absorption bands even when their concentration is 1×10^{-2}M. Although *N*-n-butylphthalimide failed to show intermolecular complex formation with aromatic hydrocarbons, *N*-n-butylyl-3,4,5,6-tetrachlorophthalimide did form such complexes. Absorption spectra of solutions containing the imide (1×10^{-2}M) and anthracene, 9-methylanthracene, 9,10-dimethylanthracene, and 9,10-diphenylanthracene (hydrocarbon concentration 1×10^{-2}M) showed absorption at longer wavelengths than either of the components. In no case was a discrete charge-transfer band observed. The ε values for the complexes at 430 nm are 20, 64, 8, and 2 mol^{-1} cm^{-1} respectively.

Excited Complex Formation.—Compounds (I) and (II) exhibit fluorescence at 415 and 419 nm respectively when they are excited ($<$360 nm) in cyclohexane at room temperature. Fluorescence could not be detected when more polar solvents were used. Under these conditions, fluorescence from the naphthalene unit was totally quenched. The only fluorescence detected from cyclohexane and acetonitrile solutions of 1-methylnaphthalene containing *N*-n-butylphthalimide (concentration 1×10^{-2}M—1×10^{-4}M) was derived from the naphthalene.

Emission from compounds (I) and (II) contained in cyclohexane, acetonitrile, and ethanol matrices at 77 K was also observed. Charge-transfer fluorescence (see Table 1) and phosphorescence from the naphthalene group could be seen in nearly all cases. The phosphorescence was isolated by use of a phosphoroscope (a rotating cylinder). The phosphorescence spectra were distorted when the frozen matrices, cyclohexane and acetonitrile, were used and were quite normal when an ethanol glass was used.* We have previously found that frozen matrices as opposed to clear glasses often causes a distortion of the spectra. In none of the experiments was phosphorescence from the phthalimide group detected nor fluorescence from the naphthalene group. For all three matrices, excitation of (I) and (II) into the charge-transfer absorption band at 360 nm produced both charge-transfer fluorescence and phosphorescence from the naphthalene group.

TABLE 1

Wavelengths (nm) at which the maximum intensity of fluorescence (F) and phosphorescence (P) for (I) and (II) occur

			(I)		(II)	
Solvent	Solute conc.	Temp. (°C)	F	P	F	P
Cyclohexane	1×10^{-4}	293			419	
	1×10^{-4}	77			440	530, 545, 560
	5×10^{-3}	293	415			
		77	440	500, 535		
Ethanol	1×10^{-4}	77	420	490, 520, 555	440	480, 515, 555
	1×10^{-2}	77	420	488, 520, 555	440	480, 515, 555
Acetonitrile	1×10^{-4}	77	430	490, 515, 555	430	490, 520, 555
	1×10^{-2}	77	435	515 (sh), 542	452	550, 595 (sh)

TABLE 2

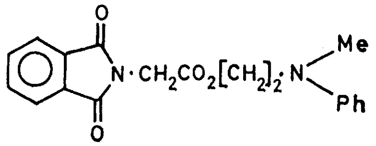
Wavelengths (nm) at which the maximum intensity of fluorescence is observed from complexes of *N*-n-butyl-3,4,5,6-tetrachlorophthalimide with anthracene in cyclohexane (each component 5×10^{-3}M).

Temp (K)	Anthracene	9-Methyl-anthracene	9,10-Dimethyl-anthracene
293	502	525	540
77	505		

Intermolecular charge-transfer fluorescence was observed from cyclohexane solutions of *N*-n-butyl-3,4,5,6-tetrachlorophthalimide containing anthracene, 9-methylanthracene, and 9,10-dimethylanthracene (see Table 2).† Use of 9,10-diphenylanthracene did not produce any charge-transfer fluorescence. It was found that charge-transfer complex formation in cyclohexane is aided by rapid cooling of the solution components. Usually the frozen solutions are highly coloured. If the matrix is softened by gentle warming and then refrozen slowly, the matrices are virtually colourless and charge-transfer fluorescence cannot be observed from such systems. A similar result is obtained if cyclohexane solutions of the components are frozen very slowly.

DISCUSSION

The u.v. absorption spectra show that (I) and (II) form intramolecular complexes in solutions at room temperature. The fluorescence spectra of (I) and (II) show that the phthalimido-group quenches the excited singlet state of naphthalene very effectively and that the quenching is accompanied by fluorescence from an excited charge-transfer complex. In the case of (II) ground state complex formation and excited complex formation occur even though the naphthalene and phthalimido-groups are separated by a fairly long chain. A similar situation arises with the imide (IV).[3a] The flexibility of the linking chain has been attributed to the presence of the ester group. Since the energy of the complex lies above the energy of the lowest triplet states of the phthalimido and naphthalene groups, the complex will play an important part in the process of intersystem crossing in (I) and (II). In view of the efficiency of fluorescence quenching in these compounds, it is likely that a substantial portion of the triplet states are populated *via* the excited complex.



(IV)

The emission spectra of (I) and (II) in rigid matrices show that the naphthalene triplet state can either be populated by excitation into the naphthalene absorption bands or into the charge-transfer absorption of the

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* The effects of rates of cooling upon the emission spectra of benzene are described in ref. 5.

† Many examples of intermolecular charge transfer complex formation between anhydrides and aromatic hydrocarbons have been reported.[6]

complex. In no cases was phosphorescence from an excited charge-transfer state observed. This would imply that the triplet charge-transfer state lies at higher energy than the naphthalene triplet state. From the u.v. spectra (see Figure) it can be seen that excitation in the 300—325 nm region leads to a substantial portion of the light being absorbed by the phthalimido-group. This group undergoes ISC with high efficiency and then undergoes triplet–triplet energy transfer to the naphthalene group.

For intermolecular charge-transfer fluorescence to be observed, relatively good electron acceptors and electron donors had to be used, *i.e.* one had to weight the factors in favour of forming relatively stable complexes. However, the absence of fluorescence from systems containing weaker donor and acceptors does not preclude the possibility of excited complexes being formed in these systems but rather that their low binding energy favours their break up into either starting materials, the triplet hydrocarbon, or products compared with emission. Thus there is the very real possibility that in the photoreactions of *N*-alkylphthalimides with dienes[7] non-emissive complexes are involved.

The reported results underline the necessity for assessing the feasibility of excited complex formation when energy-transfer studies are being made. The results of Breen and Keller[4a] must be interpreted as involving an excited singlet charge-transfer complex.

EXPERIMENTAL

Instrumentation.—This has been previously described.[3a] Solvents for emission studies were Merck Spectrograde (Uvasol).

N-2-(1-*naphthyl*)*ethylphthalimide*.—This compound was prepared according to the method of Breen and Keller.[4a]

2-(N-*Phthalimido*)*ethyl*-(1-*naphthyl*)*acetate* (II).—Phthalic anhydride (2.96 g) in glacial acetic acid (30 ml) containing 2-aminoethanol (1.22 g) was heated under reflux for 2 h. Removal of the solvent by distillation under reduced pressure left an oil which on trituration with light petroleum (b.p. 40—60 °C) followed by crystallisation gave *N*-2-hydroxyethylphthalimide (3.6 g), m.p. (from ethanol) 124—125 °C (lit.,[8] 126—127 °C). A benzene solution (10 ml) of this compound (5×10^{-3}) mol was added to 1-naphthylacetyl chloride (5×10^{-3} mol) in benzene (10 ml) containing pyridine. The mixture was stirred under an atmosphere of nitrogen for 45 h. The precipitated pyridine hydrochloride was filtered off and the filtrate concentrated to give an oil which crystallised to give 2-(*N*-phthalimido)-ethyl (1-naphthyl)acetate (38% yield), m.p. (from ethanol) 121—123.5 °C (Found: C, 73.05; H, 4.8; N, 3.95. $C_{22}H_{17}NO_4$ requires C, 73.5; H, 4.8; N, 3.9%), $\nu_{max.}$ 1 778, 1 740, 1 710, 1 600, 1 513, 1 150, 1 020, 855, 792, 785, 730, and 718 cm^{-1}, τ 2.0—2.95 (11 H, m), 5.8 (2 H, t, *J* 5 Hz), 6.15 (2 H, s), and 6.3 (2 H, t, *J* 5 Hz); *m/e* 395 (M^+), 174, 168, and 141.

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