Intramolecular Donor–Acceptor Complexes: *N*-(Aminoalkyl)phthalimides

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The u.v. absorption spectra of *N*-(aminoalkyl)phthalimides (1)—(3) show that they form intramolecular charge-transfer complexes. Compounds (1; $n = 1$—4), (2), and (3; $n = 2$) show intramolecular charge-transfer fluorescence in solution and quantum yields of fluorescence are given. Charge-transfer fluorescence can be observed when the compounds are contained in rigid cyclohexane, acetonitrile, and ethanol matrixes at 77 K. It could not be proven whether the fluorescence is from inter- or intra-molecular complexes. Phosphorescence from the imide group is observed when an ethanol matrix is used. Intermolecular charge-transfer fluorescence from complexes of *NN*-dimethylaniline with *N*-butylphthalimide and *N*-butyl-3,4,5,6-tetrachlorophthalimide was detected in solution and in rigid matrixes at 77 K. Freezing cyclohexane and acetonitrile solutions of the amine containing the imides aids complex formation. Imides (1; $n = 0$) and (3; $n = 0$) exhibit charge-transfer absorption bands but do not fluoresce. An *X*-ray analysis of (1; $n = 0$), showed the aniline and the imide group to be nearly orthogonal to each other. The charge-transfer band is, therefore, proposed as arising from an orbital system in which the π-system of the aniline group is coupled to the *n*-orbitals of the oxygen atoms of the imide group *via* the σ-bonded framework. Compounds (4a) and (4b) do not show charge-transfer absorption or emission bands. Phosphorescence from the imide group is observed.

AROMATIC imides are known to form intermolecular charge-transfer complexes with aromatic hydrocarbons and amines.[1] Examples of intramolecular complex formation have also been found.[1,2] Recently there have been several reports of the photochemical reactions of imides in which charge-transfer processes have been proposed as playing a part.[3] There has been a very limited discussion of the photophysical aspects of these systems. We now report upon the fluorescence, phosphorescence, and absorption spectra of a number of *N*-(aminoalkyl)phthalimides.

RESULTS

Investigations were carried out on the imides (1)—(4).

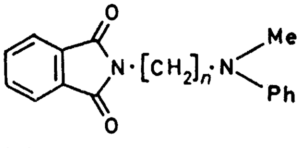
Absorption Spectra.—We have previously reported [4] that (1; $n = 0$—4) and (2) exhibit absorption bands, at $\lambda > 300$ nm, which can be attributed to excitation into a charge-transfer band. The absorption maxima of these bands, as evaluated by inspection of the spectra, are given in Table 1. Also in Table 1 are the values derived from the absorption curve of the complex, as obtained by subtracting the absorption spectrum of an equimolar mixture of *N*-butylphthalimide and *NN*-dimethylaniline (1×10^{-4}M) from the spectra of the imides (1; $n = 0$—4) and (2).[5] Compounds (1; $n = 1$—4) and (2) also show absorption bands around 295 nm (see Figure 1) which are characteristic of the *N*-alkylphthalimido-group. These bands may also contain a contribution from the *N*-alkylanilino-group. Compound (1; $n = 0$) shows absorption bands around 285 nm but not at 295 nm. *N*-Acetyl-*N*-methylphenylhydrazine shows

TABLE 1

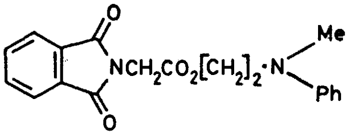
Wavelengths (nm) of maximum absorption and extinction coefficients (l mol^{-1} cm^{-1}) [a] of some *N*-(aminoalkyl)-phthalimides

	Cyclohexane		Benzene		Ethanol	
Compound	$\lambda_{max.}$	ε_M	$\lambda_{max.}$	ε_M	$\lambda_{max.}$ [b]	ε_M
(1; $n = 0$)	370	88	383	84	378 (379)	86
(1; $n = 1$)	361	67	364	62	350 (355)	64
(1; $n = 2$)	357	97	363	92	359 (360)	89
(1; $n = 3$)	*c*	16	*c*	16	*c* (360)	22
(1; $n = 4$)	*c*	8	*c*	9	*c*	10
(2)	*c*	11	*c*	15	*c* (360)	16
(3; $n = 0$)	412	65	408	62	402	40
(3; $n = 2$)	402	90	400	75		

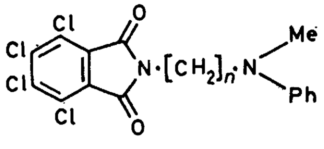
[a] ε_M is the molar extinction coefficient based on the concentration of imide. [b] The value given in parentheses was obtained from measurements of 'difference spectra.' [c] These compounds do not show a discrete $\lambda_{max.}$ (see ref. 4, Figure 1). The ε_M values are quoted for $\lambda = 400$ nm.



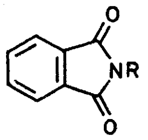
(1) n=0,1,2,3, and 4



(2)



(3) n=0,2



(4)

a; R = $[CH_2]_2{\cdot}NMe_2$

b; R = $[CH_2]_3{\cdot}NEt_2$

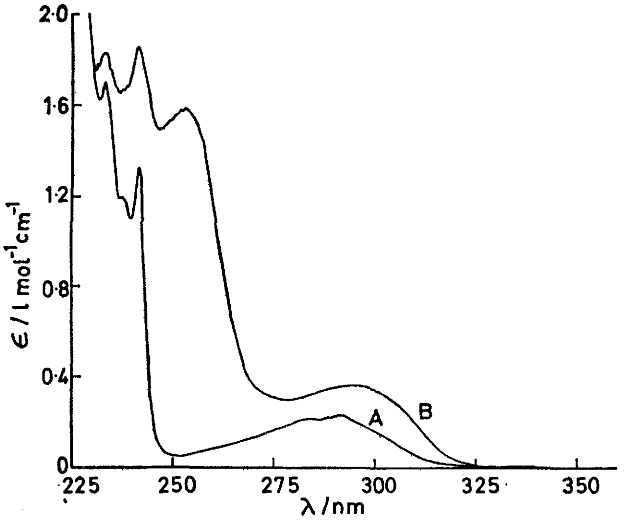


FIGURE 1 U.v. absorption spectra of (A), *N*-butylphthalimide (1×10^{-4}M in acetonitrile) and (B) (1; $n = 2$) (1×10^{-4}M in ethanol)

absorption bands around 285 nm (see Figure 2). Compounds (3; $n = 0$ and 2) have absorption bands at *ca.* 400 nm. Since the corresponding *N*-butyl-imide shows no absorption in this region the band is assigned to that of a charge-transfer transition. The absorption spectra of (4a) and (4b) are similar to that of *N*-butylphthalimide indicating that there is little tendency for these compounds to form ground state charge-transfer complexes.

For compounds which exhibit charge-transfer absorption bands, a study was made of the relationship between the intensity of the bands and the concentration of the imide. A linear dependence over a wide range of concentrations (10^{-5}M—10^{-2}M) was found, *i.e.* Beer's Law holds. This shows that the charge-transfer process is intramolecular. Another result which shows the process to be intramolecular is that complex formation between *NN*-dimethylaniline and *N*-butylphthalimide and *N*-butyl-3,4,5,6-tetrachlorophthalimide could only be detected when concentrations of the components exceeded 5×10^{-3}M.

That the anilino-group is involved in the charge-transfer processes of (1; $n = 1$—4), (2), and (3) is demonstrated by the fact that the addition of dilute hydrochloric acid to solutions of the imides causes the charge-transfer transitions to disappear.

Emission Studies.—Compounds (1; $n = 1$—4), (2), and (3; $n = 2$) exhibit fluorescence in non-polar solvents at room temperature. This fluorescence is produced on excitation into either the charge-transfer absorption band or into the phthimido absorption band at 295 nm. Quantum yields of fluorescence have been determined and are shown in Table 2. Both the $\lambda_{\text{max.}}$ of the fluorescence bands and the quantum yields are extremely solvent dependent. The fluorescence maximum moves to the red with a concomitant decrease in intensity as the solvent polarity is increased. Because of the difficulties in observing the fluorescence in solvents of widely differing polarities, it was impossible to obtain an estimate of the dipole moment of the excited charge-transfer complexes. However, the solvent sensitivity does indicate that emission is occurring from an excited state having considerable charge-transfer character.[6] Since fluorescence can be observed from solutions of concentration as low as 1×10^{-5}M, the emission is attributed to fluorescence from an intramolecular charge-transfer state. Intermolecular charge-transfer fluorescence can be observed from cyclohexane solutions of *NN*-dimethylaniline and *N*-butylphthalimide and *N*-butyl-3,4,5,6-tetrachlorophthalimide (at 510 and 560 nm respectively) when the concentration of each component exceeds 1×10^{-2}M.

TABLE 2

Wavelengths (nm) of fluorescence (1; $n = 1$—4) and (2) and (3; $n = 2$) (1×10^{-4}M)

Solvent	Compound					
	(1; $n = 1$)	(1; $n = 2$)	(1; $n = 3$)	(1; $n = 4$)	(2)	(3; ($n = 2$)
Hexane	503	513	513	503	498	
Cyclohexane [a]	508 (0.001)	513 (0.002)	523 (0.006)	508 (0.002)	501 (0.006)	558
Benzene–cyclohexane [b]	*c*	539	538	528	528	
Benzene	*c*	*c*	553 [d]	*c*	553 [d]	

[a] Values of fluorescence quantum yields are given in parentheses. [b] Mixture was in the ratio 26 : 74 v/v. [c] No emission observed. [d] Very weak emission.

Fluorescence was not observed from compounds (1; $n = 0$) (3; $n = 0$), and (4a) and (4b).

The emission spectra of (1; $n = 0$—4), (2), (3; $n = 0$—2), (4a), and (4b) in cyclohexane, ethanol and acetonitrile matrixes at 77 K were recorded and the results are shown in Table 3. It was found that rapid cooling of either cyclohexane or acetonitrile solutions of the imides (1; $n = 1$—4) led to the development of a strong yellow colour indicating that the freezing process aids complex formation.* Emission spectra from frozen cyclohexane, ethanol, and acetonitrile solutions of *NN*-dimethylaniline containing *N*-butylphthalimide and *N*-butyl-3,4,5,6-tetrachlorophthalimide were also recorded and the results are shown in Table 4.

X-*Ray Analysis of Compound* (1; $n = 0$).—In order to establish the conformation of this imide an *X*-ray analysis

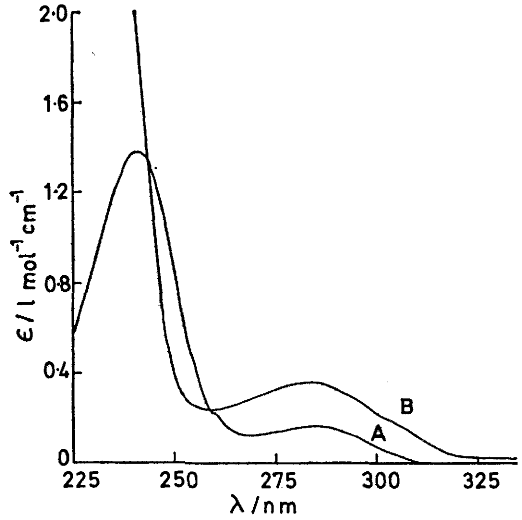


FIGURE 2 U.v. absorption spectra of (A), *N*-methyl-*N*-phenylacetohydrazide (6×10^{-5}M in ethanol) and (B), (1; $n = 0$) (6×10^{-5}M in ethanol)

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* A similar observation has recently been reported.[7] This paper has a good discussion on the importance of n–π^* and π–π^* transitions in phthalimides.

TABLE 3

Wavelengths (nm) at which the maximum intensity of fluorescence (F) and phosphorescence (P) occur for (1; $n = 0$—4), (2), and (3; $n = 2$), and (4a) and (4b) in degassed solutions at 77 K [a]

Solvent	Solute conc.	(1; $n = 0$)		(1; $n = 1$)		(1; $n = 2$)		(1; $n = 3$)		(1; $n = 4$)		(2)		(3; $n = 2$)		(4a)		(4b)	
		F	P	F	P	F	P	F	P	F	P	F	P	F	P	F	P	F	P
Cyclohexane	1×10^{-4}M	*b*	*b*	523 (390)	*b*	528 (400)		528 (400)	*b*	528 (400)	*b*	528 (400)	*b*			*b*	435 (305)	*b*	438 (301)
	5×10^{-4}M													565 (450)	*b*				
Ethanol	1×10^{-2}M	*b*	452 (336)	513 (400)	438 (314)	523 (400)	*b*	523 (400)	448 (362)	498 (314)	448 (314)	523 (350)	438 (321)			*b* *b*	445 (310)	*b*	443 (320)
	1×10^{-4}M	*b*	439 (300)	*b*	438 (300)	*b*	445 (310)	*b*	443 (310)	*b*	443 (310)	*b*	438 (300)			*b*	438 (310)	*b*	448 (300)
Acetonitrile	1×10^{-4}M	*b*	*b*	533 (400)	*b*	533 (400)	*b*	533 (400)	*b*	538 (400)	*b*	536 (400)	*b*						
	1×10^{-4}M	*b*	*b*	528 (300)	*b*	533 (370)	*b*	528 (400)	*b*	537 (400)	*b*	533 (400)	*b*	(400)		*b*	452 (310)	*b*	448 (300)

[a] Excitation wavelength shown in parentheses. [b] No detectable emission. [*N*-n-Butylphthalimide exhibits phosphorescence at 450, 460, and 470 nm in cyclohexane, ethanol and acetonitrile matrixes at 77 K.]

TABLE 4

Wavelengths (nm) at which the maximum intensity of fluorescence (F) and phosphorescence (P) for equimolar mixtures of *N*-n-butylphthalimides and *NN*-dimethylaniline occur (temperature 77 K) [a]

Solvent	Concentration of components	*N*-n-Butylphthalimide F	*N*-n-Butylphthalimide P	*N*-n-Butyl-3,4,5,6-tetrachlorophthalimde F	*N*-n-Butyl-3,4,5,6-tetrachlorophthalimde P
Cyclohexane	1×10^{-4}M	518 (400)	420 (310)		
	5×10^{-4}M			558 (450)	463 and 411 [b] (350) (300)
Ethanol	1×10^{-2}M	528 (400)	454 (326)		
	1×10^{-4}M	*c*	432 (310)		
Acetonitrile	1×10^{-2}M	533 (400)	*c*		
	1×10^{-4}M	533 (310 or 400)	438 (310)		

[a] Excitation wavelength shown in parentheses. [b] Phosphorescence from the *NN*-dimethylaniline. [c] No detectable emission.

was undertaken. From Figure 3 it can be seen that phthalimido- and anilino-groups are almost orthogonal to each other (dihedral angle = 107.3°). In Figure 4, the spatial arrangement of the molecules in the unit cell is shown. It can be seen that the anilino-group. of one molecule does *not* interact with the phthalimido-group of another molecule, *i.e.* the colour of the crystalline material is *not* due to an intermolecular complex.

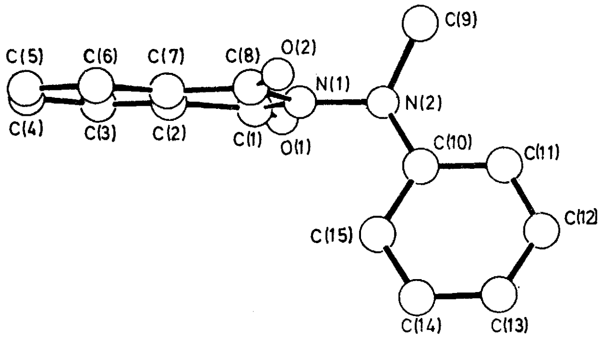


FIGURE 3 A view of (1; $n = 0$) showing the numbering of the atoms

DISCUSSION

Ground State Charge-transfer Formation.—The finding that compounds (1; $n = 1$—4), (2), and (3; $n = 2$) show absorption bands which are present in neither *N*-butylphthalimide nor *NN*-dimethylaniline is indicative of there being some association between the imide and the amine ground state. The data presented show that this association is intramolecular. It is difficult to pinpoint the real $\lambda_{\text{max.}}$ for these charge-transfer transitions since they lie on the base of other absorption peaks. The values obtained from the 'difference spectra' should be treated with some caution in view of the criticism of this technique.[5] Since the extinction coefficients quoted in Table 1 are based on the concentration of imide, they do not represent the true extinction coefficient of the charge-transfer transition. However, for compounds (1; $n = 1$—4) they do show that the compound having $n = 2$ has the greatest degree of association in the ground state. Compound (1; $n = 1$) has quite a high ε value and presumably this is because the anilino-group cannot get very far away from the imide group. That compound (2) has a higher ε value than (1; $n = 4$) can be rationalised as being due to the ester group allowing a greater flexibility of the chain in this compound than the tetramethylene chain in (1; $n = 4$).[8] The presence of charge-transfer transitions in the absorption spectra of (1; $n = 1$—4), (2), and (3; $n = 2$) shows that these compounds exist in conformations which allow a relatively close approach of the phthalimido- and anilino-groups. What the transitions do not indicate is whether there is a unique conformation for the intramolecular complex. The presence of a charge-transfer transition in the spectrum of (1; $n = 1$) shows that it is not necessary for the anilino-group to lie over the imide for the transitions to occur. Dewar and Thompson [9] have commented on the fact that the intensity of a charge-transfer transition will not of necessity be very low if there is little overlap between the highest occupied molecular orbital of the donor and the first vacant orbital of the acceptor.

It is rather surprising that (1; $n = 0$) and (3; $n = 0$) exhibit charge-transfer transitions. In the case of (1; $n = 0$), the *X*-ray analysis showed the anilino- and phthalimido-groups to be nearly orthogonal to one another. Previous n.m.r. work[10] has shown that *NN*-diacylhydrazides have, in their preferred conformation the dialkylamino- and diacylamino-groups orthogonal to each other. There is also quite a sizeable barrier to rotation. From the work of Dewar and Jennings[11] one would anticipate this barrier to rotation in (1; $n = 0$) to be even higher since the rotation process will lead to the p_π–p_π repulsions which are higher in energy than n–p_π repulsions which occur in the *NN*-diacylhydrazides. Thus it seems reasonable to suppose that, in solution, a very high proportion of the molecules of (1; $n = 0$) will be in the same conformation as in the solid. This poses the problem as to how the anilino-group manages to interact with the phthalimido-group. The answer comes from an inspection of the absorption spectrum (Figure 2). This shows a group of bands centred at 285 nm which we assign to the anilino-group. Similar bands are found in the absorption spectrum of *N'*-methylphenylacetohydrazide. This shows that the long wavelength absorption band of the anilino-group has been hypsochromatically shifted by the electron-withdrawing carbonyl group. The bands which occur at 280—310 nm in *N*-alkylphthalimides (Figure 1) are absent in (1; $n = 0$) and we propose that n–π^* have been bathochromically shifted and are giving rise to the transition at 380 nm and that the π–π^* absorption band is unaffected.[7] This shift is caused by coupling of the nitrogen p-orbital of the anilino-group with n-orbitals of the carbonyl groups *via* the σ-bonded framework. In this way a charge-transfer system can be set up which will cause a red shift in the n–π^* bands of the imide. This type of interaction has been identified as occurring in several bromo-[12] and amino-ketones.[13] The lack of fluorescence from (1; $n = 0$) is not surprising if the long wavelength band is of an $n \rightarrow \pi^*$ type, having charge-transfer character.

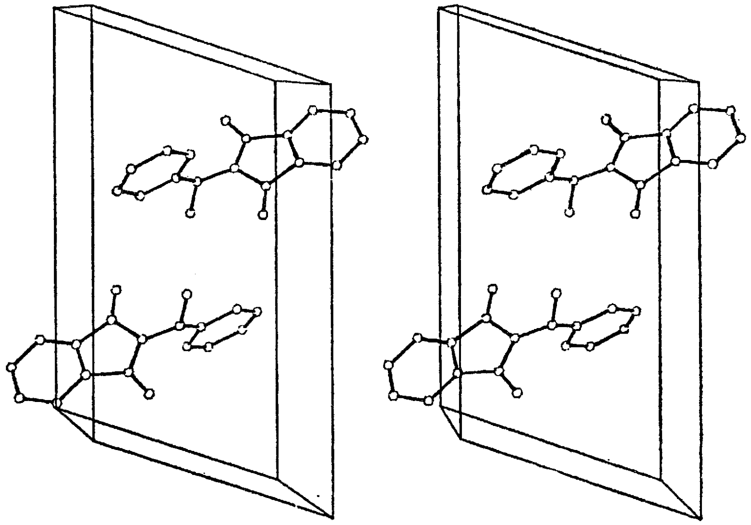
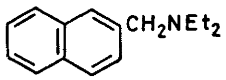


FIGURE 4 Stereoscopic view of the packing of (1; $n = 0$) view, approximately along the *c* axis

Excited Charge-transfer Complex Formation.—The fluorescence spectra of (1; $n = 1$—4), (2), and (3; $n = 2$) in fluid solution show that these compounds form excited charge-transfer complexes. Since no emission was observed from the phthalimido- or anilino-groups complex formation must be very efficient. The low quantum yields of fluorescence from the complexes may be due to either the excited complex having a number of radiationless processes (*e.g.* dissociation into radical ions, intersystem crossing)[6] available to it or else the quenching process is taking place as phthalimido- and anilino-groups start to interact but before they have attained the equilibrium conformation of the complex. This latter proposal is tantamount to saying that quenching occurs in the ' Franck–Condon ' complex.

It is interesting to note that (2) shows excited complex formation even though it contains five atoms between the phthalimido- and anilino-groups. As was noticed in the discussion on ground-state complex formation, the ester group confers flexibility on the linking chain. The fact that fluorescence could not be observed in solvents more polar than benzene is indicative of the readiness with which interaction of the phthalimido- with the anilino-group gives radical ions.

The finding that (1; $n = 1$) exhibits excited charge-transfer complex fluorescence is particularly interesting. The presence of only one methylene group prevents the molecule from adopting a conformation in which the anilino-group lies over the imide group, *i.e.* the molecule cannot adopt the most favourable conformation for excited charge-transfer formation. A similar situation arises with (5).[14] This compound exhibits exciplex fluorescence even though the amino-group can never sit over the aromatic π-system. In both (1; $n = 1$) and (5) emission from the excited complexes is very weak. This is, no doubt, a reflection of the unfavourable conformation which these complexes adopt. The binding energy of the complexes must be almost entirely due to a coulombic interaction since the conformation of the complexes does not allow a resonance energy interaction.



(5)

Compounds (1; $n = 1$—4) and (2) exhibit charge-transfer fluorescence in cyclohexane and acetonitrile matrixes at 77 K. Examination of the excitation spectra, showed that the most intense excitation band is at 400 nm. This, together with the observation that solutions of the compounds develop a strong yellow colour on freezing is indicative of the freezing process aiding complex formation. Emission from (1; $n = 0$) was not observed in these matrixes.

The type of emission observed from (1; $n = 1$—4) and (2) in ethanol matrixes at 77 K is dependent on the concentration of the imide (see Table 3). At a concentration of 1×10^{-2}M, excitation at 390 nm produces fluorescence from the complex whereas excitation at 315 nm produces phosphorescence typical of the phthalimido-group. Such an effect is not seen with cyclohexane and acetonitrile matrixes. That for ethanol matrixes, the emission spectra are excitation wavelength dependent indicates that more than one species is present in the matrix. Irradiation at 390 nm only excites the molecules in conformations having the anilino- and phthalimido-groups close enough for complex formation. Irradiation at 345 nm excites complexed molecules giving charge-transfer fluorescence and the uncomplexed molecules which have as their lowest energy excited state the triplet state of the phthalimido-group. When 1×10^{-4}M-solutions of the imides are used only phosphorescence from the phthalimido-group can be detected.

Compound (1; $n = 0$) is only emissive in an ethanol matrix and the emission is phosphorescence from the imide group. Compounds (4a) and (4b) show phosphorescence from the imide group in all three matrixes and at 1×10^{-2}M and 1×10^{-4}M concentration. That no charge-transfer fluorescence is observed attests to the weakness of the complexes formed between imides and aliphatic amines.

The finding that many of the imides exhibit excited charge-transfer complex fluorescence in ethanol and acetonitrile matrixes shows that the freezing of these solvents affects the solvating properties to such an extent that they cannot aid dissociation of the excited complexes into radical ions. The freezing of the cyclohexane and acetonitrile solutions also aids complex formation and to such an extent that no uncomplexed molecules of (1; $n = 1$—4) and (2) exist in this system. Complexing may be due to the freezing process causing crystallisation of the imides[15] or causing them to aggregate in the faults of the crystalline matrix. If either or both these reasons is correct then we cannot assume that the fluorescence is from intramolecular charge-transfer complexes. Ethanol behaves differently from the other two solvents by not aiding complex formation. We attribute this to the solvent hydrogen bonding to the anilino-group so that on freezing the imide molecules will be randomly dispersed in the matrix. Furthermore, the hydrogen bonding should decrease the efficiency of intramolecular complex formation since it will hinder the interaction of the anilino with the imide group.

The question as to whether the imides (1; $n = 1$—4) and (2) form intra- or inter-molecular complexes in the matrixes was tackled by studying intermolecular complex formation between *NN*-dimethylaniline and *N*-butylphthalimide and *N*-butyl-3,4,5,6-tetrachlorophthalimide in frozen matrixes (Table 4). When each of the components is at a concentration of 1×10^{-4}M, charge-transfer fluorescences can be observed with cyclohexane and acetonitrile matrixes. Since fluorescence from these solutions cannot be observed at room temperature it is evident that the freezing has aided complex formation. With all the systems phosphorescence can be observed indicating that the freezing does not cause total complexation. Not surprisingly ethanol does not aid complexation to anything like the same extent and weak complex fluorescence was only observable when the concentration of the components is around 1×10^{-2}M. These results show that charge-transfer fluorescence observed from (1; $n = 1$—4) and (2) in these matrixes cannot be unequivocally assigned to being either inter- or intra-molecular. However the fact that no phosphorescence is observable from these imides at a concentration of 1×10^{-4}M in cyclohexane and acetonitrile matrixes whereas it is observable from the imide–amine mixtures suggests that the fluorescence is probably intramolecular. These results serve to emphasise the hazards of using crystalline matrixes for emission studies.

From the emission studies we know that the excited charge-transfer singlet state lies at lower energy than the triplet state of the phthalimido-group. Since neither delayed fluorescence nor phosphorescence from the excited complex was observed we cannot evaluate the energy of the triplet complex nor the efficiency of its population. We can conclude from these findings that the photochemistry of compounds (1; $n = 1$—4) and (2) and (3; $n = 2$) will arise predominantly from the excited complex which in all probability will be in its singlet state.

EXPERIMENTAL

Instrumentation.—^{1}H N.m.r. were recorded for solutions in deuteriochloroform (with tetramethylsilane as internal standard) with a Varian T60 spectrometer. Mass spectra were determined with an A.E.I. MS9 instrument. I.r. spectra, for samples in Nujol, were obtained with a Perkin-Elmer 257 spectrophotometer. Fluorescence and phosphorescence spectra were recorded with a Baird Atomic Fluorispec, model SF100E and were not corrected for instrumental response. A phosphoroscope attachment was used to differentiate between fluorescence and phosphorescence. M.p.s (uncorrected) were determined with a Kofler hot-stage apparatus.

Reagents.—The cyclohexane, acetonitrile, and ethanol used for emission experiments were Merck Spectrograde (Uvasol) solvents.

Imides.—*N*-n-Butylphthalimide and *N*-n-butyl-3,4,5,6-tetrachlorophthalimide were prepared according to literature methods and their m.p.s agreed with the literature values. Imides (1; *n* = 0, *n* = 2), (4b) and *N*-(3-bromo)propylphthalimide, *N*-(4-bromo)butylphthalimide were gifts from I.C.I., Organics Division, Blackley, Manchester.

N-(N-*Methylanilino*)*methylphthalimide* (1; *n* — 1). A mixture of *N*-hydroxymethylphthalimide[16] (1.56 g) and *N*-methylaniline (1.07 g) in methanol was heated under reflux for 1 h. On cooling a yellow solid precipitated which on crystallisation gave *N*-(*N*-methylanilino)methylphthalimide as pale yellow needles (1.6 g), m.p. 92—93 °C (from ethanol) (Found: C, 72.1; H, 5.3; N, 10.3. $C_{16}H_{14}N_2O_2$ requires C, 72.2; H, 5.3; N, 10.5%), $\nu_{max.}$ 1 775 and 1 710 cm^{-1}; τ 2.1—2.65 (4 H, m, aromatic), 2.7—3.4 (5 H, m, aromatic), 4.9 (2 H, s), and 6.9 (3 H, s); *m/e* 266 (M^+), 161, 120, 106, and 77.

N-(3-N-*Methylanilino*)*propylphthalimide* (1; *n* = 3).—A mixture of decalin (15 ml), *N*-(3-bromo)propylphthalimide (2.78 g), and *N*-methylaniline was heated under nitrogen at 170 °C for 5 h. The reaction mixture was extracted with 2N-hydrochloric acid (2 × 5 ml) and the aqueous layer made basic and extracted with diethyl ether (3 × 25 ml); the ethereal solution was then dried. Removal of the ether under reduced pressure gave an oil which was distilled *in vacuo*. *N*-Methylaniline was collected and then an oil (b.p. 210 °C at 5 × 10^{-2} mmHg) which crystallised from ethanol to give *N*-(3-*N*-methylanilino)propylphthalimide as yellow plates (1.9 g), m.p. (from ethanol) 73—74 °C (Found: C, 73.4; H, 6.2; N, 9.5. $C_{18}H_{18}N_2O_2$ requires C, 73.45; H, 6.2; N, 9.5%), $\nu_{max.}$ 1 780 and 1 710 cm^{-1}; τ 2.05—2.55 (4 H, m, aromatic), 2.6—3.2 (5 H, m, aromatic), 6.2 (2 H, t, *J* 8 Hz), 6.7 (2 H, t, *J* 8 Hz), 7.0 (3 H, s), and 7.9 (2 H, quint); *m/e* 294 (M^+), 147, 120, and 77.

N-(4-N-*Methylanilino*)*butylphthalimide* (1; *n* = 4).—This compound was prepared from *N*-(4-bromo)butylphthalimide (2.92 g) and *N*-methylaniline (2.14 g) in decalin (15 ml) by the method given for (1; *n* = 3). Distillation of the reaction products gave an oil (b.p. 190 °C at 1 × 10^{-3} mmHg) which crystallised to give *N*-(4-*N*-methylanilino)butylphthalimide as pale yellow plates (1.2 g), m.p. (from ethanol) 71—72° (Found: C, 74.0; H, 6.55; N, 9.0. $C_{19}H_{20}N_2O_2$ requires C, 74.0; H, 6.5; N, 9.1%), $\nu_{max.}$ 1 776 and 1 710 cm^{-1}; τ 2.1—2.5 (4 H, m, aromatic), 2.6—3.4 (5 H, m), 6.2 (2 H, t, *J* 7 Hz), 6.7 (2 H, t, *J* 7 Hz), 7.1 (3 H, s), and 8.0—8.55 (4 H, m); *m/e* 308 (M^+), 147, 120, and 77.

2-(N-*Methylanilino*)*ethylphthaloylglycyl Acetate*.—Phthaloyloglycine was converted to its acid chloride with thionyl chloride. A benzene solution (10 ml) of the acid chloride (0.01 mol) was added dropwise to a stirred ice-cold solution of 2-*N*-methylanilinoethanol (0.01 mol) in benzene (5 ml). The mixture was stirred at room temperature for 4 h and then extracted with 2N-hydrochloric acid (25 ml). The aqueous washings were made basic and extracted with diethyl ether (3 × 15 ml) and the ethereal solution then dried. Removal of the solvent gave a solid which recrystallised to give 2-(*N*-methylanilino)ethylphthaloylglycyl acetate as yellow needles (2.0 g), m.p. (from cyclohexane) 90—92 °C (Found: C, 67.5; H, 5.3; N, 8.1. $C_{19}H_{18}N_2O_4$ requires C, 67.4; H, 5.4; N, 8.3%), $\nu_{max.}$ 1 770, 1 740, and 1 720 cm^{-1}; τ 2.1—2.6 (4 H, m), 2.7—3.6 (5 H, m), 5.7 (2 H, s), 5.8 (2 H, t, *J* 5 Hz), 6.5 (2 H, t, *J* 5 Hz), and 7.1 (3 H, s); *m/e* 338 (M^+), 161, 120, and 77.

N-(N-*Methylanilino*)-3,4,5,6-*tetrachlorophthalimide* (3; *n* = 0).—A solution of tetrachlorophthalic anhydride (2.86 g) in glacial acetic acid (25 ml) containing *N*-methyl-*N*-phenylhydrazine was heated under reflux for 1 h, after which time the product precipitated. Recrystallisation gave *N*-(*N*-methylanilino)-3,4,5,6-tetrachlorophthalimide as yellow needles (3.7 g), m.p. (from acetonitrile) 252—253 °C (Found: C, 46.2; H, 2.0; Cl, 36.5; N, 7.0. $C_{15}H_8Cl_4N_2O_2$ requires C, 46.15; H, 2.0; Cl, 36.4; N, 7.2%), $\nu_{max.}$ 1 793 and 1 740 cm^{-1}; *m/e* 388, 105, and 77.

N-(2-N-*Methylanilino*)*ethyl*-3,4,5,6-*tetrachlorophthalimide* (3; *n* = 2).—2-Bromoethylamine (1.24 g) and *N*-methylaniline (1.07 g) were heated together at 170 °C for 1 h in a nitrogen atmosphere. The residue was dissolved in diethyl ether (30 ml) and added to tetrachlorophthalic anhydride (2.86 g) in glacial acetic acid (25 ml). The ether was distilled off and the remaining solution heated under reflux for 2 h. An orange solid precipitated which was crystallised to give *N*-(2-*N*-methylanilino)ethyl-3,4,5,6-tetrachlorophthalimide as orange needles (2.8 g), m.p. (from benzene) 280—281 °C (Found: C, 48.7; H, 2.85; Cl, 33.85; N, 6.5. $C_{17}H_{12}Cl_2N_2O_2$ requires C, 48.8; H, 2.9; Cl, 34.0; N, 6.7%), $\nu_{max.}$ 1 770 and 1 710 cm^{-1}; *m/e* 416 (M^+), 120, 105, and 77.

N-(2-*Dimethylamino*)*ethylphthalimide* (4a).—A mixture of

TABLE 5

Atomic fractional co-ordinates with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
O(1)	0.748 9(5)	0.856 2(3)	0.111 6(8)
O(2)	0.796 7(4)	0.649 7(3)	0.622 3(7)
N(1)	0.728 7(5)	0.741 0(3)	0.375 1(7)
N(2)	0.568 2(5)	0.679 5(3)	0.356 9(7)
C(1)	0.809 7(6)	0.825 2(4)	0.245 4(9)
C(2)	0.981 4(6)	0.867 3(3)	0.308 1(9)
C(3)	1.115 2(7)	0.950 7(4)	0.229 5(10)
C(4)	1.259 7(8)	0.971 8(5)	0.323 7(11)
C(5)	1.270 0(8)	0.911 8(5)	0.488 4(11)
C(6)	1.136 7(7)	0.827 6(4)	0.565 2(10)
C(7)	0.994 1(6)	0.806 2(3)	0.468 0(8)
C(8)	0.835 9(6)	0.722 0(3)	0.507 7(8)
C(9)	0.571 2(7)	0.597 4(4)	0.188 7(10)
C(10)	0.434 5(6)	0.670 1(3)	0.565 0(8)
C(11)	0.275 3(6)	0.599 2(4)	0.571 1(9)
C(12)	0.141 1(8)	0.592 4(4)	0.776 0(10)
C(13)	0.163 2(8)	0.651 6(4)	0.972 5(11)
C(14)	0.317 6(7)	0.721 9(4)	0.968 3(10)
C(15)	0.454 6(7)	0.733 0(3)	0.766 3(9)
H(3)	1.106 4(7)	0.993 8(4)	0.110 2(10)
H(4)	1.358 9(8)	1.031 8(5)	0.271 9(11)
H(5)	1.376 8(8)	0.929 6(5)	0.554 3(11)
H(6)	1.143 4(7)	0.784 8(4)	0.686 9(10)
H(91)	0.688 20	0.610 00	0.075 80
H(92)	0.545 90	0.537 00	0.281 10
H(93)	0.481 60	0.587 40	0.094 10
H(11)	0.257 2(6)	0.553 6(4)	0.427 9(9)
H(12)	0.027 0(8)	0.541 8(4)	0.777 6(10)
H(13)	0.064 7(b)	0.644 3(4)	1.120 5(11)
H(14)	0.332 7(7)	0.766 4(4)	1.114 3(10)
H(15)	0.566 7(7)	0.784 7(3)	0.764 1(9)

TABLE 6

Bond lengths (Å) and angles (°) with standard deviations in parentheses

(*a*) Bond lengths

O(1)–C(1)	1.207(12)	C(4)–C(5)	1.381(18)
O(2)–C(8)	1.203(12)	C(5)–C(6)	1.387(17)
N(1)–N(2)	1.379(11)	C(6)–C(7)	1.376(14)
N(1)–C(1)	1.380(13)	C(7)–C(8)	1.474(14)
N(1)–C(8)	1.414(13)	C(10)–C(11)	1.395(14)
N(2)–C(9)	1.442(15)	C(10)–C(15)	1.394(14)
N(2)–C(10)	1.394(13)	C(11)–C(12)	1.387(16)
C(1)–C(2)	1.491(14)	C(12)–C(13)	1.347(17)
C(2)–C(3)	1.384(15)	C(13)–C(14)	1.365(16)
C(2)–C(7)	1.380(14)	C(14)–C(15)	1.385(16)
C(3)–C(4)	1.381(16)		

(*b*) Bond angles

C(1)–N(1)–N(2)	122.8(8)	C(2)–C(3)–C(4)	117.1(1.2)
C(8)–N(1)–N(2)	125.0(8)	C(3)–C(4)–C(5)	121.2(1.3)
C(8)–N(1)–C(1)	112.0(8)	C(4)–C(5)–C(6)	121.7(1.3)
C(9)–N(2)–N(1)	115.1(9)	C(5)–C(6)–C(7)	116.9(1.1)
C(10)–N(2)–N(1)	116.8(8)	C(6)–C(7)–C(2)	121.7(1.0)
C(10)–N(2)–C(9)	119.9(8)	C(6)–C(7)–C(8)	129.7(1.0)
C(2)–C(1)–N(1)	105.7(9)	C(7)–C(2)–C(3)	121.4(1.0)
N(1)–C(1)–O(1)	125.4(1.0)	N(2)–C(10)–C(11)	120.1(9)
O(1)–C(1)–C(2)	128.9(1.0)	N(2)–C(10)–C(15)	121.0(9)
C(1)–C(2)–C(7)	108.2(9)	C(11)–C(10)–C(15)	118.9(9)
C(2)–C(7)–C(8)	108.6(8)	C(10)–C(11)–C(12)	119.7(1.1)
C(7)–C(8)–N(1)	105.3(8)	C(11)–C(12)–C(13)	121.0(1.2)
C(7)–C(8)–O(2)	130.9(1.0)	C(12)–C(13)–C(14)	119.9(1.3)
N(1)–C(8)–O(2)	123.8(9)	C(13)–C(14)–C(15)	121.2(1.2)
C(1)–C(2)–C(3)	130.4(1.0)	C(14)–C(15)–C(10)	119.2(1.0)

phthalic anhydride (2.96 g) and 2-dimethylaminoethylamine (1.76 g) in glacial acetic acid (25 ml) was heated under reflux for 2 h. Removal of the solvent left an oil which on trituration with light petroleum gave a solid which on crystallisation gave *N*-(2-dimethylamino)ethylphthalimide as colourless plates (2.35 g), m.p. (from ethanol) 103.5—104.5 °C (lit.,[17] 104—105 °C), $\nu_{max.}$ 1 770 and 1 710 cm^{-1}; τ 2.1—2.5 (4 H, m), 6.2 (2 H, t, *J* 7 Hz), 7.4 (2 H, t, *J* 7 Hz), and 7.7 (6 H, s).

Crystal Data.—(1) $C_{15}H_{12}N_2O_2$, $M = 252$. Triclinic, $a = 8.370(9)$, $b = 14.425(15)$, $c = 5.704(9)$ Å, $\alpha = 96.3(1)$, $\beta = 75.2(1)$, $\gamma = 108.40(5)°$, $U = 631.5$ Å^3, $Z = 2$, $D_c = 1.33$, $D_m = 1.32$ g cm^{-3}, $F(000) = 264$. Space group $P\bar{1}$ assumed. Mo-K_α radiation $\lambda = 0.710\ 69$ Å; μ(Mo-K_α) = 0.5 cm^{-1}.

Lattice parameters were obtained from a combination of precession photographs and diffractometer co-ordinates of high angle reflections. Intensity data were collected from a crystal of dimensions 0.11 × 0.13 × 0.45 mm mounted about *c*. The intensities of reflections with $\sin\theta/\lambda < 0.6$ Å^{-1} were measured for the layers *hk*0—5 on a Stoe Weissenberg diffractometer using graphite-monochromated Mo-K_α radiation and a variable *w*-scan technique. 1 223 Reflections with $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarisation effects.

The structure was solved by the centrosymmetric direct methods routine which forms part of the SHELX-76 system (written by G. M. Sheldrick, University of Cambridge), this system was used for the subsequent analysis. All 19 non-hydrogen atoms were revealed in the *E*-map corresponding to the solution with largest *M*(abs). The methyl hydrogen atoms were located from a difference-Fourier at $R = 0.109$ and, after idealising their co-ordinates with C–H 1.00 Å and H–C–H 109.5°, were not refined further. Other hydrogen atoms were included in their calculated positions. Four reflections with large discrepancies between $F_{obs.}$ and $F_{calc.}$ were excluded from later cycles of refinement, and convergence was obtained at $R = 0.077$ ($R_w = 0.087$) for 1 219 reflections, anisotropic thermal parameters were refined only for nitrogen and oxygen atoms.

Atomic co-ordinates and their standard deviations are in Table 5, Table 6 contains bond lengths and angles involving non-hydrogen atoms. A list of observed and calculated structure factors and thermal parameters have been deposited as Supplementary Publication No. 22499 (7 pp.).*

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* For details of the Supplementary Publications scheme see Notice to Authors No. 7, *J.C.S. Perkin II*, 1978, Index issue.

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