

INTRAMOLECULAR DONOR-ACCEPTOR COMPLEXES: N-(AMINOALKYL)-PHTHALIMIDES

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The formation and stability of excited intramolecular donor-acceptor complexes derived from compounds such as (1) is affected by



the ionisation potential of the donor group D, the electron affinity of the acceptor group A and the number of the methylene groups which link the two interacting groups.<sup>1</sup> It has been shown that charge transfer transitions can be observed for compounds such as (1), in which it is not possible for the D and A groups to adopt a "sandwich configuration" e.g. when  $n=1$ .<sup>1,2,3</sup> When the value of  $n$  is increased the charge transfer transition is usually most readily observable when  $n = 2$  or  $3$ .<sup>1,2,3,4</sup> The transition decreases in intensity as  $n$  is increased through four and five. The weakness of the transition for compounds having  $n = 5$  is attributed to there being a lack of association between the D and A groups. For association to occur in compounds such as (1), the energy gained by the interaction of the groups has to overcome the energy requirement for making the polymethylene chain adopt a particular conformation in which non-bonded interactions may be severe.

We report that the N-(aminoalkyl)-phthalimides (2) and the closely related compound (3)

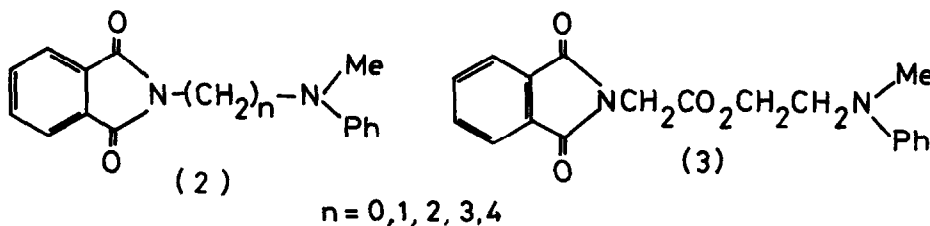
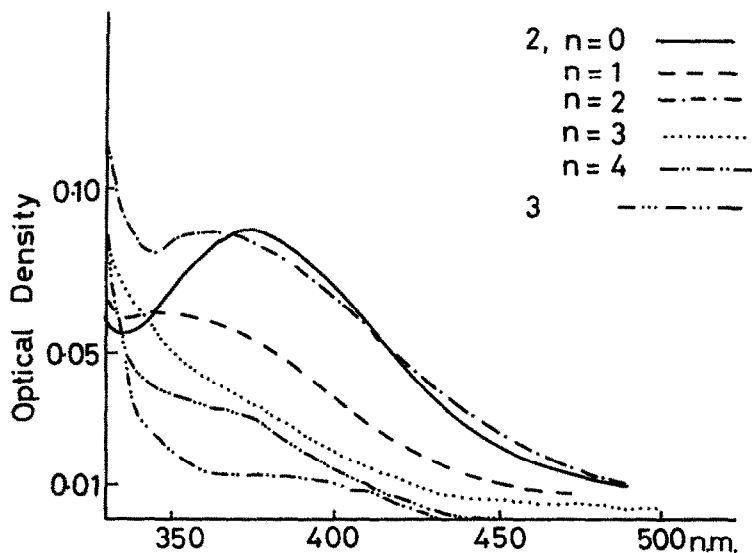


exhibit charge-transfer transitions in their ultraviolet absorption spectra (Figure 1).

That these transitions are correctly ascribed to being due to an intramolecular interaction between amine and imide groups is attested by the following observations. Compounds (2),  $n = 0$  and  $n = 2$  obey Beer's Law over a wide concentration range ( $1 \times 10^{-4}M$  to  $1 \times 10^{-2}M$ ) in ethanol and benzene solutions. A cyclohexane solution of N-n-butyl phthalimide ( $1 \times 10^{-2}M$ )

Ultraviolet Absorption Spectra of Ethanolic  
Solutions ( $1 \times 10^{-3} \text{M}$ ) of 2, n=0-4 and 3.



TABLE

Wavelength (nm) of fluorescence exhibited by (2), n = 1,2,3,4, and (3) (all  $1 \times 10^{-2} \text{M}$ ) in various solvents at 20°C

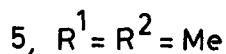
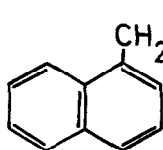
Solvent	2				3
	n = 1	n = 2	n = 3	n = 4	
Hexane	515	525	525	515	510
Cyclohexane	520 (weak)	525	535	520	513
Benzene	a	a	565 <sup>b</sup>	a	565 <sup>b</sup>

a No fluorescence observable

b Extremely weak and broad emission band.

containing *N,N*-dimethylaniline ( $1 \times 10^{-2}M$ ) has an absorption spectrum which is very similar to that produced by addition of the spectra of the two components. Use of higher concentrations of the amine leads to charge-transfer transitions ascribable to intermolecular donor-acceptor complex formation.<sup>5</sup>

It is of interest to note that the long wavelength absorption tail of 3 is of higher intensity than that for 2,  $n = 4$ . Thus, the introduction of an ester group into the methylene chain has aided the interaction of the donor and acceptor groups. We attribute this as being due to the ester group allowing the chain linking the two groups in the complex, to adopt a conformation in which there is a minimum of non-bonded interactions. In compounds (4) and (5) it has been shown<sup>6</sup> that the ester group allows the interaction of the



singlet excited state of the naphthalene group with the amino groups with the result that intramolecular exciplexes are formed. We conclude that, as for intramolecular exciplex formation, the conformational requirements of the linking chain in intramolecular donor-acceptor complexes is a factor of importance.

Another feature of note is that 2,  $n = 0$  and  $n = 1$ , show discrete charge-transfer absorption bands although their molecular framework does not allow extensive overlap between the donor and acceptor groups. This further substantiates the point made by Dewar<sup>7</sup> and de Boer<sup>1</sup> that the intensity of a charge-transfer band 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.

Compounds (2),  $n = 1, 2, 3$  and 4 and (3), exhibit fluorescence in cyclohexane solution at room temperature (Table). The emission may be ascribed as being due to charge-transfer fluorescence since excitation of the compounds in either their charge-transfer absorption bands or anhydride absorption bands, produces fluorescence. Furthermore, the position and intensity of the fluorescence bands is extremely sensitive to solvent polarity.<sup>8</sup> Fluorescence cannot be observed for any of the compounds in solvents more polar than benzene. That the wavelength of maximum emission is very similar for each of the compounds indicates that in the equilibrated excited state of the complexes,<sup>9</sup> the orientation of the donor and

acceptor groups are similar. Thus, the observation of weak fluorescence from (2),  $n = 1$  raises the question as to whether in the excited singlet state of this compound there is some relaxation of the molecular framework. The interaction of the donor and acceptor groups in the excited singlet states of (2),  $n = 3, 4$  and (3), appears to be more efficient than in the ground state. Maximum efficiency of interaction in the ground state appears to occur in (2),  $n = 2$ . Undoubtedly the enhanced susceptibility of excited states to undergo redox reactions is the reason for this observation.<sup>10</sup>

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