Nitrogen-substituted Phthalimides: Fluorescence, Phosphorescence, and the Mechanism of Photocyclization

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From u.v. absorption and fluorescence measurements it is suggested that N-(dialkylaminomethyl)phthalimides fluoresce(weakly) from the second excited singlet state ($\pi.\pi^*$). and that the lowest energy singlet state ($n.\pi^*$) is non-fluorescent. Phosphorescence occurs from the lowest triplet state at 77 K. and in ethanol solution this state is unambiguously assigned a ($\pi.\pi^*$) configuration. The second triplet state ($n.\pi^*$) is quite close in energy to the first. The luminescence results point to the operation of an initial electron transfer step in the photochemical cyclization reaction of these phthalimides.

IN recent years there have been quite a number of reports of the photochemistry of N-substituted phthalimides.[1] Many of the photoreactions resemble those which are typical of ketone (n,π^*) excited states, such as intermolecular photoreduction (1) or intramolecular hydrogen abstraction and cyclization. Our contribution has included a study of the photocyclization (2) of the Mannich base N-(dibenzylaminomethyl)phthalimide.[2]

We are particularly interested in the mechanism of this photocyclization, as well as in its synthetic potential, because the excited states of phthalimides are not well characterised. For aromatic ketones, hydrogen abstraction photoreactions are normally fast and efficient when the lowest excited triplet state is (n,π^*), but slower and usually much less efficient when the lowest triplet state is (π,π^*). If the mechanism of hydrogen transfer consists of electron followed by proton transfer (rather than direct hydrogen atom transfer), then the electronic

nature of the lowest triplet state does not greatly influence the rate of the primary step nor the overall efficiency.[3] For aromatic esters and amides, which in contrast to ketones always have a lowest energy (π,π^*) state, an electron transfer mechanism is necessary if the quantum yield is to be reasonable.[4] With this in mind, we set out to identify the low-lying excited states of our N-substituted phthalimides.

RESULTS AND DISCUSSION

Absorption Spectra.—Early studies of the u.v. absorption spectra of phthalimides have concentrated on the effect of ring substituents on the strong $\pi \longrightarrow \pi^*$ absorption bands.[5] Phthalimide itself [6] and N-hydroxy-phthalimide [7] are reported to show a weak, long-wavelength $n \longrightarrow \pi^*$ absorption band ($\lambda_{max.}$ *ca.* 360 nm). We could find no distinct absorption maximum in this region for phthalimide or for our substituted phthalimides (1), but there is an extended long-wavelength

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[1] For leading references, see Y. Sato, H. Nakai, T. Mizoguchi, Y. Hatanaka, and Y. Kanaoka, *J. Amer. Chem. Soc.,* 1976, **98,** 2349; H. J. Roth and D. Schwarz, *Arch. Pharm.,* 1976, **309,** 52.

[2] J. D. Coyle and G. L. Newport, *Tetrahedron Letters,* 1977, 899.

[3] P. J. Wagner and D. A. Ersfeld, *J. Amer. Chem. Soc.,* 1976, **98,** 4515 and references therein.

[4] J. D. Coyle and D. H. Kingston, *J.C.S. Perkin II,* 1976, 1475; *Tetrahedron Letters,* 1976, 4525.

[5] See, for example, A. Arcoria and G. Scarlata, *Ann. Chim. (Italy),* 1964, **54,** 128.

[6] H. J. Roth and G. Hundeshagen, *Arch. Pharm.,* 1976, **309,** 58.

[7] W. R. Roderick and W. G. Brown, *J. Amer. Chem. Soc.,* 1957, **79,** 5196.

' shoulder ' (Figure 1) to the more intense $\pi \longrightarrow \pi^*$ band (which has maxima at 292 and 300 nm). This shoulder may be attributed to $n \longrightarrow \pi^*$ absorption, especially
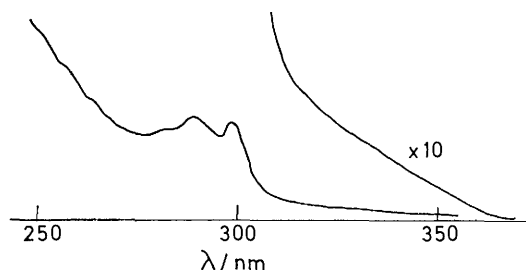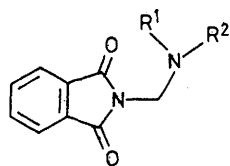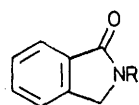

FIGURE 1 U.v. absorption spectrum of imide (1c) in cyclohexane

since there is no such feature in the spectra of related amides (2); $n \longrightarrow \pi^*$ absorption at long wavelength would not be expected for these amides.
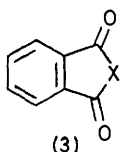

a; $R^1 = R^2 = CH_3$

b; $R^1 = R^2 = Pr^n$

c; $R^1 = R^2 = CH_2Ph$

d; $R^1 = CH_3, R^2 = Ph$

e; $R^1,R^2 = [CH_2]_4$

f; $R^1, R^2 = [CH_2]_2NMe[CH_2]_2$

g; $R^1, R^2 = [CH_2]_2O[CH_2]_2$

(1)

(2) a; R = H

b; R = CH_2N(CH_2Ph)_2

(3)

A recent survey [8] of the absorption spectra of compounds (3; $X = CH_2$, O, S, or NH) led to a similar conclusion, that there is no clear evidence for a distinct $n \longrightarrow \pi^*$ absorption maximum for phthalimide. However, our data do suggest that the lowest singlet state of the imides may be (n,π^*) in character. An alternative assignment of the absorption shoulder to a weak charge-transfer transition seems less likely to be correct, in part because a similar band would probably then be expected to appear in the spectrum of amide (2b). This conclusion is reinforced by the observation that imide (1d) *does* show a distinct charge-transfer absorption band in a non-polar solvent, $\lambda_{max.}$ (cyclohexane) 360 nm. A solution of (1d) is slightly yellow, and the colour intensity is markedly enhanced on cooling. These properties are not exhibited by the other imides, and the appearance of this distinct charge-transfer absorption

(and fluorescence, see later) is probably a feature of compounds in which one of the substituents on the nitrogen is an aryl group. (Other imides with an N-phenyl group show the charge-transfer properties.[9]) The N-(arylaminoalkyl)imides represent another group of compounds which indicate that intramolecular charge-transfer can occur even when geometrical constraints restrict the close approach of the donor and acceptor groups.[10]

Fluorescence.—Fluorescence of phthalimides, especially those with amino-substituents in the ring,[11] has been reported, though N-methylphthalimide is said to be non-fluorescent.[12] All the phthalimides (1a—g) used in the present study exhibit weak structureless fluorescence (Table 1) with a wavelength of maximum emission at

TABLE 1

Fluorescence of phthalimides in ethanol

Compound	Quantum yield [a] ϕ_f	Lifetime [b] τ_f/ns
N-Propylphthalimide	0.008	3
(1a)	0.016	3.7
(1b)	0.013	3.7$_5$
(1c)	0.017	3.7$_5$
(1d)	0.004	2.9
(1e)	0.003	2.4
(1f)	0.004	3.0
(1g)	0.003	2.7

[a] Relative to aniline in ethanol. [b] ± 0.25 ns

ca. 322 nm. The amide (2b) also shows very weak fluorescence ($\lambda_{max.}$ *ca.* 327 nm, $\phi_f < 0.005$).

The fluorescence of the imides shows strong concentration quenching, although no excimer emission was

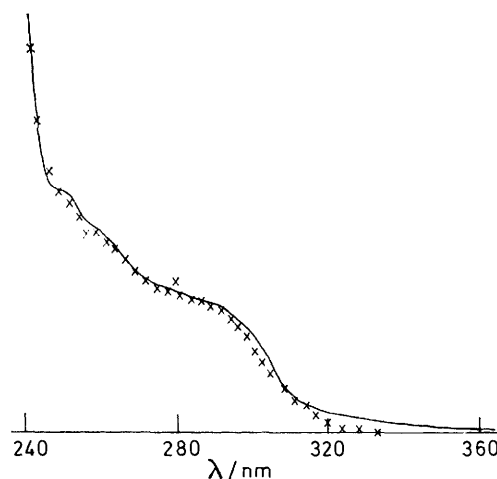FIGURE 2 Absorption spectrum (—) and corrected fluorescence excitation spectrum (xxx) of imide (1c) in ethanol (normalised at 235 nm; $O.D_{290}$ 0.013)

detected; the data in Table 1 were obtained using solutions sufficiently dilute (10^{-4}—10^{-5}M) for this effect to be negligible (*cf.* warnings about such effects on the reliability of fluorescence data [13]). The fluorescence

[8] V. Galasso and G. C. Pappalardo, *J.C.S. Perkin II*, 1976, 574.

[9] R. S. Davidson and A. Lewis, *Tetrahedron Letters*, 1974, 611; R. S. Davidson, unpublished results.

[10] R. S. Davidson and K. R. Trethewey, *J.C.S. Chem. Comm.*, 1976, 827.

[11] See, for example, A. N. Sevchenko, L. G. Pikulik and M. Y. Kostko, *Doklady Akad. Nauk S.S.S.R.*, 1965, **162**, 57 (*Soviet Physics Doklady*, 1965, **10**, 432).

[12] D. E. Breen and R. A. Keller, *J. Amer. Chem. Soc.*, 1968, **90**, 1935.

[13] J. B. Birks, *J. Luminescence*, 1974, **9**, 311.

spectrum also shows a rather small Stokes shift. These properties are characteristic of emission from (π,π^*) excited states. However, the fluorescence is not directly related to the long wavelength shoulder in the absorption spectrum (which stretches beyond 350 nm), but rather

charge-transfer fluorescence ($\lambda_{max.}$ ca. 520 nm), and the excitation spectrum matches the charge-transfer absorption band ($\lambda_{max.}$ ca. 360 nm). The other imides show no long wavelength fluorescence of this kind, even on cooling. At 'best,' imide (1c) shows a band at

TABLE 2

Phosphorescence of phthalimides

| Solvent	Ethanol			Methylcyclohexane			Bromocyclohexane	
Compound	τ_p/s [a]	0-0/nm [b]	Polarisation [c]	τ_p/s [a]	0-0/nm [b]	Polarisation [c]	τ_p/s [a]	0-0/nm [b]
(1a)	0.97	410	o-o-p	0.54	412	Mix	0.13	415
(1b)	0.99	412	o-o-p	0.55	415	Mix	0.22	410
(1c)	1.02	410	o-o-p	0.54	414	Mix	0.20	418
(1d)	2.02							
(1e)	0.91	410	o-o-p	0.42	417	Mix	0.18	417
(1f)	1.07	412	o-o-p	0.62	422	Mix	0.21	415
(1g)	1.11	410	o-o-p	0.52	420	Mix	0.16	415
(2a)	1.07			1.13			0.37	
(2b)	1.16	382	o-o-p	1.06	383	o-o-p		
N-Propylphthalimide [d]	1.04		i-p	1.05		i-p	0.84	

[a] Phosphorescence lifetime. [b] Approximate position of the 0-0 vibrational band. [c] Orientation of polarisation: o-o-p = substantially ($>70\%$) out-of-plane; i-p = substantially in-plane; mix = mixed polarisation (in the range 60 : 40—40 : 60). [d] Ref. 12 reports that N-methylphthalimide phosphoresces strongly at 77 K, with τ_p 0.70 s. We find that in ethanol at 77 K, τ_p is 1.02 s.

to the $\pi \longrightarrow \pi^*$ band centred at ca. 292 nm. The fluorescence excitation spectrum (Figure 2) appears to confirm this relationship, since the long wavelength part of the absorption spectrum (above ca. 310 nm) is absent from the excitation spectrum.

A possible conclusion is that the weakly fluorescing (π,π^*) state is S_2, the second singlet, and that there is a lower energy (n,π^*) singlet. It is increasingly recognised that fluorescence can occur from a second singlet, either

ca. 515 nm whose intensity represents a signal : noise ratio of 2 : 1, and this would not have been noticed without a very careful search.

Phosphorescence.—The phthalimides (1a—g) phosphoresce quite strongly at 77 K, and the data are given in Table 2 together with those for amides (2a and b) and for N-propylphthalimide. The wavelength of maximum emission is at ca. 420 nm for amide (2b), and at ca. 440 nm for imides (1).

(1)

(2)
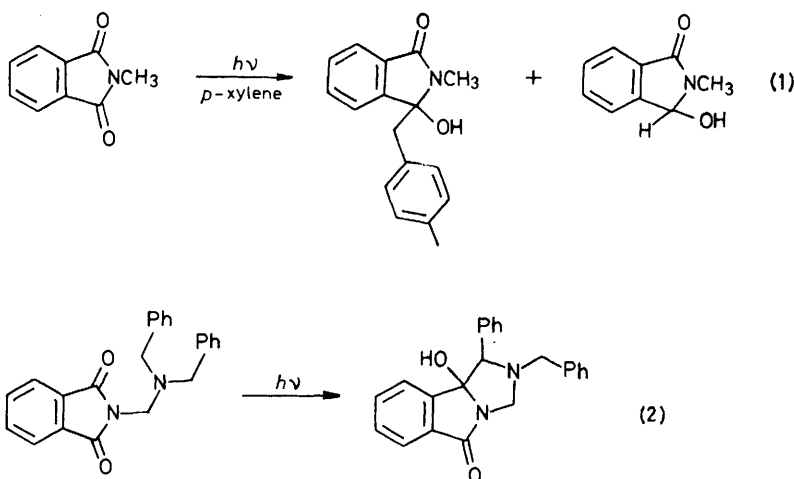
to the exclusion of S_1 fluorescence (as with azulenes [14] or thioketones [15]) or accompanying S_1 fluorescence which is usually more intense (as with fluoranthene [16] or [18]-annulene [17]). If the assignment is correct, the present systems are like the thioketones in that S_1 fluorescence is not observed, but differ from them in that the S_2-S_1 energy gap is not as large.

The N-phenylimide (1d) also shows intramolecular

The criteria [18] we use to distinguish between (n,π^*) and (π,π^*) triplet states in phosphorescence are given in Table 3. Using these criteria, the emitting states of the phthalimides can be confidently assigned as $^3(\pi,\pi^*)$ in ethanol at 77 K. There is little vibrational fine structure in the emission spectrum, the lifetime is long and is reduced considerably in a brominated solvent (which

[14] G. Eber, F. Grüneis, S. Schneider, and F.Dörr, *Chem. Phys. Letters*, 1974, **29**, 397.

[15] M. Mahaney and J. R. Huber, *Chem. Phys.*, 1975, **9**, 371.

[16] D. L. Philen and R. M. Hedges, *Chem. Phys. Letters*, 1976, **43**, 358.

[17] U. P. Wild, H. J. Griesser, and Vo Dinh Tuan, *Chem. Phys. Letters*, 1976, **41**, 450.

[18] R. S. Becker, ' Theory and Interpretation of Fluorescence and Phosphorescence ', Wiley, New York, 1969, p. 156; for comments on these criteria, see E. T. Harrigan and N. Hirota, *Mol. Phys.*, 1976, **31**, 681.

also increases the intensity of phosphorescence), and the polarisation is mainly out-of-plane. The two amides (2) show similar phosphorescence properties to those of

TABLE 3

Criteria for distinguishing between $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states on the basis of phosphorescence data

	$^3(n, \pi^*)$	$^3(\pi, \pi^*)$
Vibrational fine structure	Prominent	Often absent
Lifetime at 77 K	<0.05 s	>1 s
Heavy atom effect on lifetime	Little effect	Large decrease in τ_p
Singlet–triplet splitting	≤3 000 cm^{-1}	>3 000 cm^{-1}
Polarisation	Mainly in-plane	Mainly out-of-plane

the imides in ethanol, and these amides are expected to have lowest triplet (π,π^*) states. The shorter lifetimes and ' mixed ' polarisation for the imides in hydrocarbon solvent suggest that the triplet (n,π^*) state is very close
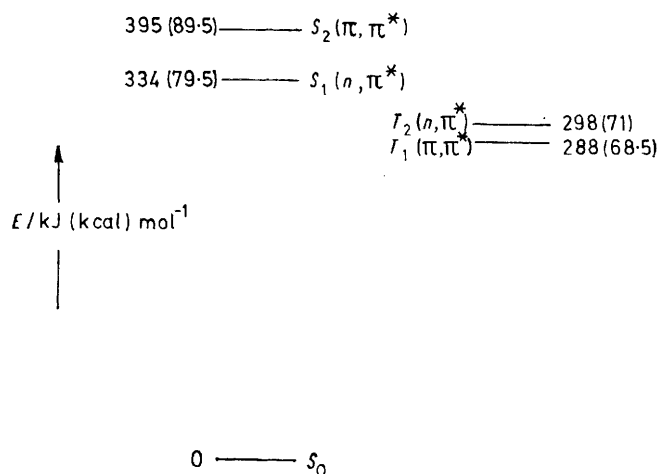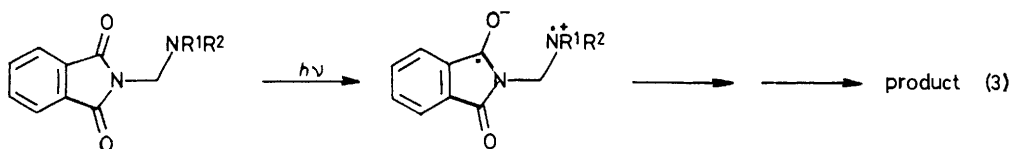

FIGURE 3 Schematic state diagram for phthalimides (1) in ethanol

to the $^3(\pi,\pi^*)$ state in energy (this behaviour is not found for the amide). The less polar solvent lowers the imide (n,π^*) excited state energy and so brings the triplets even closer together than they are in ethanol.

The suggestion that the triplet states are close in energy would also be in accord with the existence of a lowest (n,π^*) singlet state (see the energy diagram in Figure 3), because the singlet–triplet splitting is normally much smaller for an (n,π^*) configuration than for a (π,π^*) configuration.

* It could be argued that thermal population of a higher energy $^3(n,\pi^*)$ state might be responsible for reaction in ethanol at room temperature without the photochemical process making a significant contribution to the lifetime in ethanol at 77 K. However, phosphorescence results in hydrocarbon solvent ought to reflect changes in $^3(n, \pi^*)$ lifetimes, and whilst the results in methylcyclohexane at 77 K do reflect these lifetimes (the observed values are much shorter than those in ethanol) there is no variation of lifetime with chemical structure for imides (1a—c).

This energy diagram for phthalimides is in accord with work [12] on the properties of compounds (4), where it is found that singlet energy transfer occurs from the naphthalene unit [E_S 415 (99) kJ (kcal) mol^{-1}] to the phthalimide unit, whilst triplet energy transfer occurs in the reverse direction from phthalimide to naphthalene [E_T 255 (61) kJ (kcal) mol^{-1}]. N-Propylphthalimide
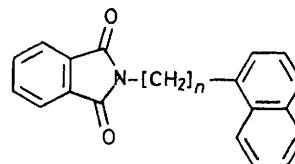
(4) $n = 0 — 3$

shows rather different phosphorescence properties, with the polarisation mainly in-plane and the lifetime affected to a much smaller extent by the heavy-atom solvent. However, the lifetime is still long, and it is not possible to be confident that the emitting state is $^3(n,\pi^*)$.

Mechanism.—The luminescence results are of value in distinguishing between hydrogen abstraction and electron transfer as the primary step in the excited state reaction. If an intramolecular hydrogen-abstraction process is one of the major routes open to an excited state, the lifetime of the state is influenced by the strength of the C–H bond at the position of abstraction. Under these circumstances the lifetime should decrease as this bond changes from primary [imide (1a)] to secondary [imide (1b)] to benzylic [imide (1c)], as it does for related changes in phenyl ketones [19] or benzoate esters.[20] There is no such change in the singlet (Table 1) or triplet (Table 2) lifetimes.* On the assumption that the pattern of triplet state behaviour is the same at room temperature as it is at 77 K, and insofar as the emitting states can be identified with the reacting states, it seems that the photochemical reaction involves electron transfer as the primary step (3).

The observed reaction is quite efficient, and there are indications that the primary step is very fast. A simple quenching experiment with penta-1,3-diene shows that the reaction is not appreciably affected by 1.3M-diene, and if a triplet state is responsible for reaction its lifetime must be <10^{-10} s (assuming that a diffusion-controlled energy transfer process would occur with a rate constant of *ca.* 5 × 10^9 l mol^{-1} s^{-1}). Flash photolysis studies indicate that two intermediate species may

[19] P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, 1972, **94**, 7495.

[20] J. A. Barltrop and J. D. Coyle, *J. Chem. Soc.* (*B*), 1971, 251.

be formed sequentially, but at present the results cannot be fully interpreted.

EXPERIMENTAL

The *N*-substituted phthalimides (1) were prepared by methods similar to those described by Reichert.[21] Phthal-imidine (2a) was prepared by reduction of phthalimide with tin and hydrochloric acid.[22] The *N*-substituted phthalimidine (2b) was obtained from (2a) by a Mannich reaction, which required a longer reaction time than for phthalimide.

Absorption spectra were recorded on a Pye–Unicam SP 800 spectrometer and also, together with fluorescence spectra, using a Perkin-Elmer MPF4 instrument with Hitachi S10 photomultiplier. For fluorescence the concentrations chosen were such that the spectra were independent of concentration in that range. Lifetimes were determined using conventional single-photon counting techniques. The fluorescence excitation spectra were corrected against Rhodamine B in ethanol, and the monochromators for fluorescence excitation and absorption were balanced using phenanthrene in ethanol. Phosphorescence measurements were made using the Perkin-Elmer MPF4 instrument with S10 photomultiplier. A steady-state method was used to obtain spectra and polarisation data; the spectra were fully corrected, and the 0–0 bands were assigned by curve-fitting averaged over 7 runs. A pulsed flash-lamp was used for phosphorescence lifetimes; the values quoted are the average of 7 readings, and the spectral decay was found to be exponential over at least two half-lives. For all the luminescence measurements the solutions were thoroughly degassed by several freeze–pump–thaw cycles.

[21] B. Reichert, ' Die Mannich-Reaktion ', Springer Verlag, Berlin, 1959, p. 104.
[22] C. Graebe, *Annalen*, 1888, **247**, 288.