Formation Efficiency and Energy of the Perylene Triplet

By C. A. PARKER and THELMA A. JOYCE
(*Admiralty Materials Laboratory, Holton Heath, Poole, Dorset*)

WE have previously reported the *P*-type delayed fluorescence of perylene sensitised by three donor compounds in fluid solution at room temperature.[1] Some further results obtained with 10^{-5}M-perylene in ethanol, cyclohexane, and n-hexane, using anthracene as donor, are shown in Table 1. With this concentration of perylene, the anthracene delayed fluorescence was completely quenched, indicating that the anthracene triplet was consumed almost completely by the process:

$$\text{anthracene (triplet)} + \text{perylene (singlet)} \rightarrow \text{anthracene (singlet)} + \text{perylene (triplet)}$$

Under these conditions the efficiency of sensitised delayed fluorescence of the perylene (θ) is given by an equation analogous to that for directly excited delayed fluorescence,[2] *viz.*:

$$\theta/\phi_{\mathrm{f}} = \tfrac{1}{2} p k_{\mathrm{r}} I_{\mathrm{a}} \, (\phi_{\mathrm{t}}^{\mathrm{A}} \, \tau_{\mathrm{t}}^{\mathrm{P}})^2 \qquad (1)$$

in which ϕ_{f} is the efficiency of prompt fluorescence of perylene, $\tau_{\mathrm{t}}^{\mathrm{P}}$ the lifetime of triplet perylene (equal to twice the lifetime of delayed fluorescence), I_{a} the rate of light absorption by the anthracene, $\phi_{\mathrm{t}}^{\mathrm{A}}$ the triplet formation efficiency of anthracene, k_{r} the diffusion-controlled rate constant (0·56, 0·69, and $2 \cdot 0 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$ in ethanol, cyclohexane, and n-hexane at 21°C as calculated from the viscosity), and p the probability that an encounter between perylene triplets will give rise to an excited singlet molecule. Assuming a value of 0·7 for the triplet formation efficiency of anthracene,[3] the values of p shown in column 5 of Table 1 were calculated from Equation 1.

Solutions of perylene alone gave only very weak P-type delayed fluorescence when excited by light of wavelength 436 nm (Table 2). From these data, together with the value of p from Table 1, values of the triplet formation efficiency of perylene were calculated using the equation for directly excited delayed fluorescence.[2] They are low in all three solvents and are thus consistent with the high fluorescence efficiency of perylene (0·98 in benzene[4]).

TABLE 1

Sensitised delayed fluorescence of perylene

All solutions contained 10^{-5}M-perylene and 5×10^{-5}M-anthracene. Rates of light absorption (I_a) refer to anthracene at 366 nm.

Solvent	I_a einstein l.$^{-1}$ sec.$^{-1}$	θ/ϕ_f	τ_t^P sec.	p
Ethanol	$1 \cdot 39 \times 10^{-6}$	$0 \cdot 93 \times 10^{-3}$	$4 \cdot 34 \times 10^{-3}$	0·026
n-Hexane	1·33	1·86	4·84	0·012
Cyclohexane	1·33	0·42	3·92	0·012

TABLE 2

Triplet formation efficiency of perylene

All solutions contained 10^{-5}M-perylene only. Rates of light absorption (I_a) refer to perylene at 436 nm.

Solvent	I_a	θ/ϕ_f	τ_t^P	ϕ_t^P
Ethanol	$1 \cdot 97 \times 10^{-5}$	$2 \cdot 1 \times 10^{-6}$	$4 \cdot 34 \times 10^{-3}$	0·0088
n-Hexane	2·02	12·8	4·84	0·015
Cyclohexane	2·07	2·6	3·92	0·014

The fact that the P-type delayed fluorescence of perylene is strongly sensitised by anthracene in solutions in which the anthracene triplet is strongly quenched indicates that the triplet energy of perylene is less than that of anthracene but greater than one half of the singlet energy of perylene, *i.e.*, that it lies between 1·48 μm^{-1} and 1·14 μm^{-1}. This result is consistent with the values previously reported for the triplet energy of perylene.[5,6] The low sensitivity of photomultiplier tubes in this spectral region coupled with the low triplet formation efficiency of perylene probably accounts for the fact that the $T \rightarrow S$ phosphorescence of this compound has not yet been observed.

(*Received, January 16th*, 1966; *Com.* 030.)

---

[1] C. A. Parker, C. G. Hatchard, and T. A. Joyce, *Nature*, 1965, **205**, 1282.

[2] C. A. Parker, C. G. Hatchard, and T. A. Joyce, *J. Mol. Spectroscopy*, 1964, **14**, 311.

[3] T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, 1965, **61**, 620.

[4] E. J. Bowen, *Adv. Photochem.*, 1963, **1**, 32.

[5] G. G. Hall, *Proc. Roy. Soc.*, 1952, *A*, **213**, 113.

[6] J. B. Birks and M. A. Slifkin, *Nature*, 1961, **191**, 761.