Delayed Fluorescence of Anthracene and Some Substituted Anthracenes

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WE have observed both monomer and dimer bands in the *P*-type delayed fluorescence spectrum of 9,10-dimethylanthracene, whether excited by direct light absorption, or by sensitisation with naphthalene (Figure 1, curve 1). At the concentration used ($5{\cdot}5 \times 10^{-5}$ M) the proportion of dimer emission in the prompt fluorescence spectrum was negligible (Figure 1, curve 2) although it has previously been observed in the prompt fluorescence spectrum at much higher concentrations.[1] The results were thus analogous to those previously reported for pyrene.[2] As the temperature was reduced, the ratio of the efficiencies of delayed fluorescence of the dimer and the monomer (θ_D/θ_M) passed through a maximum and fell to a relatively low value at $-100°$ in ethanol (Figure 2, curve 1). These results are similar to those already observed with pyrene and benz[*a*]pyrene in ethanol.[3] They may be interpreted in terms of the competition between two kinds of mechanism, in one of which the process of triplet–triplet interaction produces excited dimer and in the other excited monomer. The details of these mechanisms are still in dispute.[4] The curve obtained in dimethylformamide (Figure 2, curve 2) was similar in form, but the proportion of delayed dimer emission in this solvent was at all temperatures less than that observed in ethanol.

The triplet formation efficiency of 9,10-dimethylanthracene, and the probability factor *p* (for the ultimate formation of an excited singlet from two triplets) were determined by the method previously reported for perylene[5] (see Table) but

TABLE

Photoluminescence of substituted anthracenes at 20°

Compound	Prompt fluorescence efficiency ϕ_f	Lifetime of triplet (msec.)	Triplet formation efficiency ϕ_t	Probability factor p	Dimer emission in delayed fluorescence
Anthracene	[0·30]	9	[0·70]	0·07	At low temperature only
9,10-Dimethyl-(in ethanol)	0·89	8	0·03	0·08	At high and low temperature
9,10-Dimethyl-(in dimethylformamide)	high	4	0·02	0·08	At high and low temperature
9-Methyl-	0·33	10	0·67	0·03	At high and low temperature
9-Phenyl-	0·49	15	0·47	0·05	At high and low temperature
9,10-Diphenyl-	0·89	22	0·03	0·13	At neither

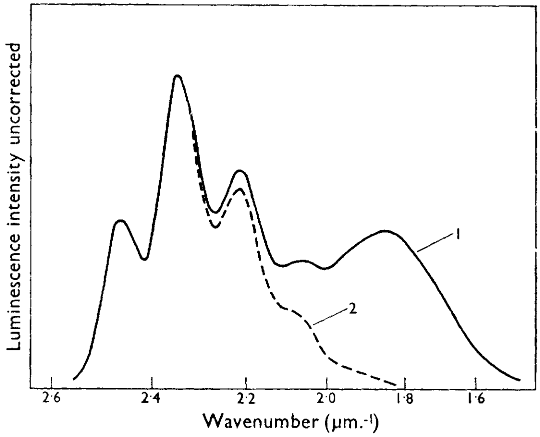

FIGURE 1. *Delayed fluorescence of* 9,10-*dimethylanthracene* ($5·5 \times 10^{-5}$M) *in ethanol at* 20° *sensitised by naphthalene* ($2·4 \times 10^{-3}$M) *to* 313 *nm radiation. Curve* 1, *delayed fluorescence; curve* 2, *prompt fluorescence at much lower sensitivity.* (*The delayed fluorescence of the naphthalene was completely quenched*).

using naphthalene as sensitiser. Both ϕ_t and p are low, and this accounts for the very low intensity of P-tspe delayed fluorescence observed by direct excitation.

We have also observed P-type delayed fluorescence from dilute ethanolic solutions of the 9-methyl-, 9-phenyl-, and 9,10-diphenyl-anthracenes. The 9-methyl and 9-phenyl derivatives showed an appreciable proportion of dimer emission at both +20° and −75°, but the diphenyl derivative gave a negligible proportion of dimer emission at either temperature. Unsubstituted anthracene was found to give appreciable dimer emission at −75°, although it shows little at +20°.[6] Preliminary determinations of ϕ_t and p (at +20°) for the substituted anthracenes are included in the Table together with the values for unsubstituted anthracene. It seems that although the substitution of the two bulky phenyl groups in the 9,10-positions inhibits the formation of excited dimer, it does not prevent the formation of singlet excited monomer from two triplets (compare the values of p in the Table). This is taken as evidence that triplet-to-triplet energy transfer can occur over distances greater than that required for excited dimer formation.

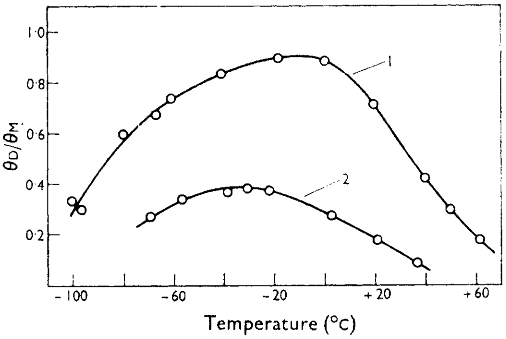

FIGURE 2. *Effect of temperature on the delayed fluorescence of the dimer. Solutions contained* $5·5 \times 10^{-5}$M-9,10-*dimethylanthracene and* $2·4 \times 10^{-3}$M-*naphthalene in* (1) *ethanol, and* (2) *dimethylformamide. Excitation was at* 313 *nm.*

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[5] C. A. Parker and T. A. Joyce, *Chem. Comm.*, 1966, 108.

[6] C. A. Parker and C. G. Hatchard, *Proc. Roy. Soc.*, 1962, *A*, **269**, 574.