Crossed Photodimerisation in Solution between Donor and Acceptor Anthracenic Monomers

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SEVERAL authors have studied crossed photodimerisation between different anthracene derivatives,[1–4] including the fluorescence quenching of one of the irradiated monomers.[3] However, the competition between pure and crossed photodimerisation which might be expected to occur when the two monomers have similar singlet excitation energies does not appear to have been considered.

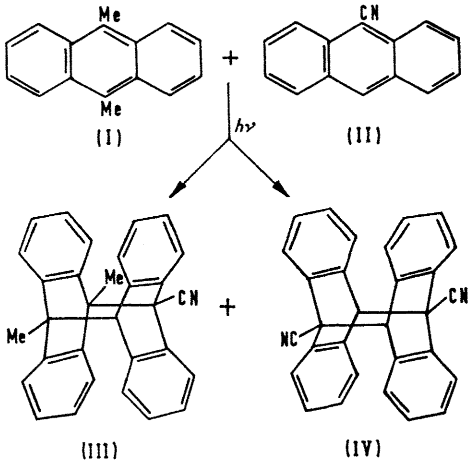
We have shown that the irradiation of a mixture of an electron donor [9,10-dimethylanthracene (I)] and an electron acceptor [9-cyanoanthracene (II)] greatly facilitates the formation of the mixed dimer.

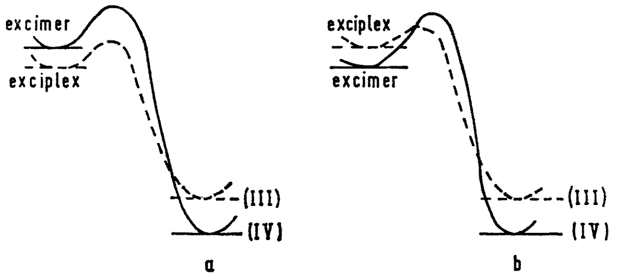
No complex in the ground state was detected in the u.v. absorption spectrum of a mixture of (I) and (II) in solution, at least at a concentration of 10^{-4} mole l.$^{-1}$. However, (I) and (II) are each known to yield excimers[5,6] and the studies of Chandross and Ferguson[7] on the fluorescent exciplexes between (II) and several donors, such as 2,3-dimethylnaphthalene, suggest the formation of an exciplex between (I) and (II).

9,10-Dimethylanthracene does not photodimerise[8] and is therefore photostable in deoxygenated solutions; this eliminates one possible photodimeric species. Only two photodimers (III) and (IV) are therefore to be expected, one of which (IV) is already known.[9]

The 0–0 S^1 levels of the two monomers are approximately the same: from the u.v. spectra in ether solution one finds 25·250 cm.$^{-1}$ for (I) (72·6 kcal.) and 25·030 cm.$^{-1}$ for (II) (72 kcal). Because of the proximity of these two levels, (difference is approximately kT) the population of (I) and (II) in the S^1 state are equal within a factor of $1/e$, when thermal equilibrium is established. Consequently, at the beginning of the irradiation, one would expect the two photodimers to be formed in a statistical ratio of (III) : (IV) of approximately 1·4 : 1.

After a half an hour irradiation (125 w mercury lamp, Pyrex) we have found that the total yield of photodimers is about 21% and that the ratio (III) : (IV) = 99·5 : 0·5 (v.p.c.) (Table 1). However (III) is not stable: it decomposes rapidly into (I) and (II) whereas (IV) is relatively stable. Irradiation at 80° only yields (IV). We conclude that (III) is the kinetically-controlled product.





FIGURE

Excimers are now accepted as intermediates in photodimerisation[6,10–12] although this has not been proved in every case.

As the formation of excimers and exciplexes in diluted

Irradiation of an equimolecular (100 × 10^{-4} M) *mixture of* 9,10-*dimethylanthracene* (I) *and* 9-*cyanoanthracene* (II)

[Crossed dimer (III)] × 10^4	[Pure dimer (IV)] × 10^4	% ratio (III) : (IV)	Solvent	ε 25°	Temp.	Exposure time, hr.
21	0·1	99·5 : 0·5	Ether	4·3	30°	0·5
87	0·6	99 : 1	Ether	,,	30	2
20	3·2	86 : 14	Ethanol	24·3	30	2
16	9	65 : 35	Methanol	32·6	30	2
56	12	83 : 17	Ether	,,	35	4·5
0	77	0 : 100	Benzene		80	9
0	70	0 : 100	Acetonitrile		82	9

solutions is collision controlled[10] we suggest that our results can be rationalized by the difference in activation energy of the step leading to the dimers from the intermediate species whatever be their relative energy levels.† The possible reaction paths are qualitatively shown in the Figure (a and b).

The yield of crossed dimer decreases on irradiation in solvents of increasing dielectric constant, whereas the yield of the pure dimer increases (Table). This is consistent with Weller's results about the solvent polarity effect on the formation of exciplexes and solvated ion pairs from electron donor and electron acceptor compounds.[13]

Thus, the formation of ion pair and crossed dimer from the exciplex are likely to compete in ethanol and methanol.

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† A. Weller has shown for 1-cyanonaphthalene and polymethylnaphthalenes that the energy levels of the exciplexes are slightly higher than that of the excimers, an argument in favour of path b. (*Acta Phys. Polon.*, 1968, **34**, 593.)

[1] D. E. Applequist, R. L. Litle, E. C. Friedrich, and R. E. Wall, *J. Amer. Chem. Soc.*, 1959, **81**, 452; D. E. Applequist and R. Searle, *ibid.*, 1964, **86**, 1389. D. E. Applequist, R. Searle, M. D. Steinhardt, E. C. Friedrich, and R. L. Litle, *J. Org. Chem.*, 1965, **30**, 2126.

[2] F. D. Greene, *Bull. Soc. chim. France*, 1960, 1356.

[3] A. S. Cherkasov and T. M. Vember, *Optika i Spektroskopiya*, 1959, **6**, 148; A. S. Cherkasov, N. F. Neznaiko and I. E. Obyknovennaya, *ibid.*, 1965, **21**, 45; T. M. Vember, *ibid.*, 1966, **20**, 347.

[4] H. Bouas-Laurent and R. Lapouyade, *Compt. rend.*, 1967, **264**, *C*, 1061.

[5] R. L. Barnes and J. B. Birks, *Proc. Roy. Soc.*, 1966, *A*, **291**, 570.

[6] B. Stevens, T. Dickinson, and R. R. Sharpe, *Nature*, 1964, **204**, 876.

[7] E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, 1967, **47**, 2557.

[8] R. Laland and R. Calas, *Bull. Soc. chim. France*, 1960, 144; R. Lapouyade, A. Castellan, and H. Bouas-Laurent, *Compt. rend.*, 1969, **268**, *C*, 217.

[9] R. Calas, R. Lalande, and P. Mauret, *Bull. Soc. chim. France*, 1960, 148.

[10] J. B. Birks, *Nature*, 1967, **214**, 1187.

[11] J. S. Bradshaw, N. Brent Nielsen, and D. P. Rees, *J. Org. Chem.*, 1968, **33**, 257.

[12] P. Wilairat and B. Selinger, *Austral. J. Chem.*, 1968, **21**, 733.

[13] A. Weller, "Organic Photochemistry; Second International Symposium, Enschede, 1968," Butterworths, London, 1968, p. 115 and unpublished work.