

## 4 + 4 Photoaddition: Crossed Dimers of Anthracenes and Tetracene; the Pure Dimer of 9,10-Dimethylanthracene

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**Summary** Photoadducts of 9,10-dimethylanthracene, 9,10-dimethoxyanthracene, and anthracene to tetracene are described; 9,10-dimethylanthracene, previously thought to be photostable in the absence of oxygen, has been photodimerized.

In a study of the delayed fluorescence of tetracene ( $10^{-8}$  M) sensitized by anthracene ( $10^{-5}$  M) in ethanolic solutions, Parker<sup>1</sup> observed a rapid decrease of intensity of emission

When nitrogen was bubbled through a mixture of dimethylanthracene and tetracene, fair amounts of 9,10-dimethylanthracene photoperoxide were produced [n.m.r.  $\delta$  2.13 p.p.m. (methyl protons), see Table, and we have checked that tetracene sensitizes photoperoxidation of (Ib)].<sup>2†</sup>

In experiments designed to produce dimethylanthracene photoperoxide without tetracene, we surprisingly isolated *inter alia* the photodimer of dimethylanthracene (IV).

TABLE

DMA	Monomer concentrations		U.v. lamp	Exposure time	Degassing procedure	Photoproducts		Crossed dimers m.p. (dec.)
	DMA	T				Crossed dimers DMA-T	Photo-oxide DMA-O <sub>2</sub>	
3.33 × 10 <sup>-2</sup> M	3.33 × 10 <sup>-3</sup> M		500 w	0.5 h	fr-th 10 <sup>-4</sup> Torr.	80%		310°
DMA 2 × 10 <sup>-2</sup> M	T 2 × 10 <sup>-3</sup> M		125 w	22 h	bubbling N <sub>2</sub>	DMA-T 50%	DMA-O <sub>2</sub> 58%	
DMeOA 3 × 10 <sup>-2</sup> M	T 0.3 × 10 <sup>-2</sup> M		125 w ¶	117 h	bubbling N <sub>2</sub>	DMeOA-T 30%		250°
A 5 × 10 <sup>-2</sup> M	T 0.5 × 10 <sup>-2</sup> M		500 w filter NaNO <sub>2</sub>	8.5 h	fr-th 10 <sup>-2</sup> Torr	A-T § 75%		350°

Conditions: temperature: 25–28°; solvent: ether; source: Philips SP 500 or HPK 125; filter: Pyrex (¶ glass filter Sovirel AUV absorbing light under 350 nm; fr-th: freeze and thaw; A: anthracene; DMA: 9,10-dimethylanthracene; DMeOA: 9,10-dimethoxyanthracene; DMA-O<sub>2</sub>: 9,10-dimethylanthracene photo-peroxide; T: tetracene.

which he tentatively assigned to the formation of a crossed dimer between anthracene (A) and tetracene (T).

We report evidence supporting Parker's interpretation. Irradiation of more concentrated solutions of mixtures of anthracene (Ia) or two meso-derivatives of anthracene (Ib, Ic) and tetracene (II) actually led to the crossed dimers (IIIa, b, c).

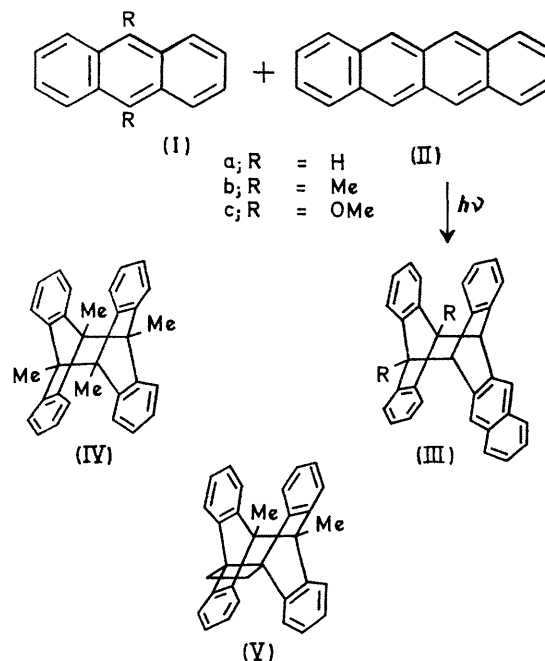
Experimental conditions and results are summarized in the Table. Tetracene is only slightly soluble in ether and was maintained in suspension with a magnetic stirrer. Irradiations were stopped when tetracene was totally transformed into photo-products, *i.e.* on decolorisation of the medium.

Structural assignments of compounds (III) are supported by elemental analyses for (IIIa, b), and the u.v. spectra are in close agreement with a spectrum calculated from the sum of the  $\epsilon_{\max}$  for one 2,3-dimethylnaphthalene + three *o*-xylenes. The mass spectrum (AEI-MS 12) for (IIIc) shows a molecular ion peak at *m/e* 466 and monomer peaks at 238 and 228. In the n.m.r. spectra<sup>†</sup> chemical shifts due to aliphatic protons appeared for (IIIb) at  $\delta$  4.12 (singlet, 2H) and 2.22 p.p.m. (singlet, 6H), and for (IIIc) at  $\delta$  4.45 (singlet 2H) and 3.57 p.p.m. (singlet 6H).

Thermal decomposition of compounds (III) in boiling benzene or cyclohexane yields mixtures of (Ia) and (Ib) or (Ic) and (II) detected by u.v. absorption spectra.

† N.m.r. spectra were recorded with a Varian A 60, at *ca.* 30° in CDCl<sub>3</sub>, with Me<sub>4</sub>Si as internal standard.

‡ The photoperoxidation of dimethylanthracene is probably sensitized by the T<sub>1</sub> triplet state of tetracene (*cf.* B. Stevens and B. E. Algar, *Chem. Phys. Letters*, 1967, 1, 58). The high inter-system crossing efficiency in tetracene may be due to the presence of a T<sub>2</sub> state close to the S<sub>1</sub> state.<sup>2</sup>



Further attempts in degassed solutions (benzene, cyclohexane, ether), gave good yields of (IV). A typical irradiation of dimethylantracene ( $4 \times 10^{-3}$  M) in ether at 25° in Pyrex with a 500 w high-pressure mercury lamp yielded 80% of (IV), after 8 h. The photodimer (IV) decomposes instantaneously and quantitatively at 150—155° into the monomer. The i.r. spectrum of (IV) contains strong  $\nu(\text{CH}_3)$  bands and typical absorptions at 1470, 1450, and 1390  $\text{cm}^{-1}$ . The n.m.r. spectrum shows a singlet at  $\delta$  1.99 p.p.m. (12 H) corresponding to the methyl groups, which appear at 3.08 p.p.m. in the monomer.

As expected from steric hindrance, (IV) rapidly decomposes into the monomer at room temperature. We noticed that compound (V)<sup>3</sup> shows the same thermal instability.

§ The i.r. spectrum (KBr pellet) of (IIIc) is distinct from those of dianthracene and ditetracene.

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<sup>2</sup> R. Astier, A. Bokobza, and Y. Meyer, *J. Chem. Phys.*, 1969, **52**, 5174.

<sup>3</sup> F. H. C. Stewart, *Austral. J. Chem.*, 1968, **21**, 1107.

<sup>4</sup> (a) R. Lalande and R. Calas, *Bull. Soc. chim. France*, 1960, 144 and refs. therein; (b) J. B. Birks and J. B. Aladekomo, *Photochem. and Photobiol.*, 1963, **2**, 415; (c) T. M. Vember, V. G. Mitina, and A. S. Cherkasov, *Teor. i eksp. Khim.*, 1968, 373; (d) R. Lapouyade, A. Castellan, and H. Bouas-Laurent, *Compt. rend.*, 1969, **268**, C, 217.

<sup>5</sup> R. Lapouyade, A. Castellan, and H. Bouas-Laurent, *Tetrahedron Letters*, 1969, 3537.

<sup>6</sup> H. Bouas-Laurent and R. Lapouyade, *Compt. rend.*, 1967, 264, C, 1061.

Previous reports that dimethylantracene did not photodimerise described experiments with too dilute solutions or low-output sources.<sup>4</sup>

The very easy synthesis of these new photo-products (III) may be due to preferential exciplex formation, as was probably the case with benzo[*a*]anthracene<sup>5</sup> and other crossed dimerizations.<sup>6</sup>

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