

## Photo-dimerization of 9-Phenylanthracene

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**Summary** Contrary to literature reports, 9-phenylanthracene gives a photo-dimer, but only when irradiated with piperylene.

CONJUGATED dienes are known to quench efficiently the excited singlet states of aromatic hydrocarbons.<sup>1,2</sup> One would expect that any chemical reaction initiated from the singlet state of an aromatic hydrocarbon should be reduced in efficiency when irradiated in the presence of a diene quencher. We have observed, however, a case of enhancement of reactivity of a photochemical reaction (dimerization of anthracene) known to proceed from the excited singlet state;<sup>3</sup> and, in fact, we have thus been able to prepare a hitherto unknown photo-dimer from 9-phenylanthracene, (I).<sup>4</sup>

A benzene solution 0.01 M in (I) and 0.5 M in piperylene, degassed and sealed in Pyrex tubes, was irradiated with a 200 w Hanovia medium-pressure mercury lamp for 1 week. The white crystalline solid deposited at the bottom of the tubes was collected and washed with hexane (yield: up to 80%). The solid melted at 189–193° with decomposition; and upon solidification, it gave a re-melting point of 151–153°, which was not further depressed on addition of (I). The mass spectrum of the solid is identical with that of (I).† However, molecular-weight determination‡ clearly showed that the solid is a dimer (Calc. for

dimer: 508; found:  $491 \pm 5\%$ ). Its u.v. spectrum (absence of significant absorption at wavelengths >290 nm) suggests that dimerization has also taken place at the 9,10-positions of (I). Although at present we cannot definitely assign the relative position of the two phenyl groups, considering the size of the groups, it is safe to assume that they are *anti* to each other.

The presence of piperylene is apparently necessary for formation of the dimer. Irradiation of a similar sample of (I) in benzene, but without the diene, for the same period, did not lead to disappearance of (I). Experiments designed to determine the exact role of piperylene in catalysing formation of the dimer and its relation to singlet quenching processes are in progress.

That (I) forms a stable product from the excited singlet state when irradiated in the presence of piperylene complicates its use as a donor in transferring energy from the second triplet state to the diene.§ Preliminary results did indicate that its relative triplet yield, as determined by the quantum yield of *cis-trans*-isomerization of piperylenes, decreases with increase of the diene concentration. However, when irradiated in the presence of other acceptors, *e.g.* stilbene and methylstilbene, the anthracene is photo-stable and behaves as a normal  $T_2$ -donor.<sup>8</sup>

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† Anthracene photo-dimers are known to fragment easily, giving mass spectra similar to those of the parent anthracenes (see ref. 5).

‡ Performed on a Perkin-Elmer-Hitachi M.W. Apparatus, based on vapour-pressure depression, with benzene as a solvent.

§ The intersystem crossing efficiency of (I) in paraffin (0.35)<sup>6</sup> is of comparable magnitude to those of known  $T_2$ -donors (*e.g.* 0.90 for 9,10-dibromoanthracene and 0.48 for 9,10-dichloroanthracene).<sup>7</sup>

<sup>1</sup> L. M. Stephenson, D. G. Whitten, and G. S. Hammond, in "The Chemistry of Ionization and Excitation," Taylor and Francis, London, 1967, p. 35.

<sup>2</sup> B. S. Solomon, C. Steel, and A. Weller, *Chem. Comm.*, 1969, 927.

<sup>3</sup> See *e.g.*, E. J. Bowen, *Adv. Photochem.*, 1963, **1**, 36.

<sup>4</sup> Reported to be photo-stable: R. Calas and R. Lalande, *Bull. Soc. chim. France*, 1959, 766; H. Bouas-Laurent, R. Lapouyade, and J. Faugere, *Compt. rend.*, 1967, **265**, C, 506.

<sup>5</sup> O. L. Chapman and K. Lee, *J. Org. Chem.*, 1969, **34**, 4166.

<sup>6</sup> A. R. Horrocks, T. Medinger, and F. Wilkinson, *Photochem. Photobiol.*, 1967, **6**, 21.

<sup>7</sup> R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, 1969, **91**, 1492.

<sup>8</sup> Unpublished results of R. O. Campbell, K. Lau, and R. S. H. Liu.