Photo-formation and Erasure, Optical and ^{1}H Nuclear Magnetic Resonance Spectra, and Oxidation of 4a,4b-Dihydro-3,4,5,6-dibenzophenathrene

By T. KNITTEL, G. FISCHER, and E. FISCHER*
(*Department of Chemistry, The Weizmann Institute of Science, Rehovot, Israel*)

Summary The title compound has been prepared by u.v. irradiation of *cis*-1,2-di-(2-naphthyl)ethylene, and its structure proved by dehydrogenation to the dibenzophenanthrene with atomic iodine.

4a,4b-DIHYDROPHENANTHRENE (I) and its derivatives (DHP), formed photochemically from *cis*-stilbene (II) and its derivatives,[1] are hydrocarbons of particular interest: they are obtainable only photochemically, have strong absorption bands in the visible region, are light-sensitive (the system *cis*-stilbene $\rightleftharpoons$ DHP is photoreversible), and they contain two rather reactive hydrogens that can be removed by molecular oxygen,[1,2a] molecular iodine,[2b] and other oxidants to give phenanthrene and its derivatives. The ring-opening DHP → *cis* takes place both thermally and radiatively, thus affording in principle an excellent example for studies of electrocyclic reactions in the ground and excited states.

cis-1,2-Di-(2-naphthyl)ethylene (III) yields a DHP which is practically stable at 25°, even in air.[3] We now found that the quantum yield of its photo-formation exceeds that of the reverse photoreaction about twentyfold at +10° with light at 366 nm. It is therefore possible to achieve substantial photoconversion into the DHP by irradiation at this convenient wavelength. In Figure 1, curves 1 and 2a, we illustrate such a photoconversion. The absorption spectrum of the pure DHP is somewhere between curves 2a and 2b, corresponding to a molar extinction coefficient, at 423 nm, of between 6600 and 13,200. In order to prove a clear-cut correlation between (V) and the observed DHP for which structure (IV) is postulated, it was essential to oxidize (IV) quantitatively. This was also important for a more accurate assessment of the extent of photoconversion of *cis*-(III) into (IV) by measuring the known oxidation product (V), by analogy with our earlier results with the system *cis*-stilbene $\rightleftharpoons$ DHP → phenanthrene.[1]

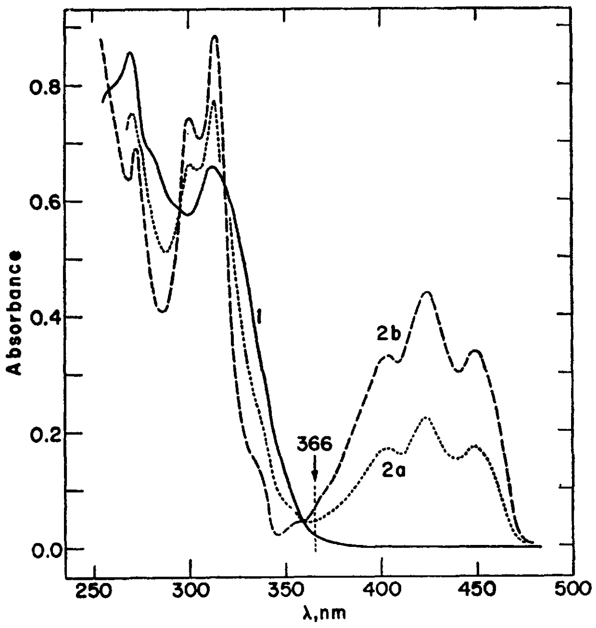


FIGURE 1. *Absorption spectra of* cis (III) (*curve* 1) *and of* (IV) *curves* 2a and 2b). *Concentration* ca. 10^{-5}M *in methylcyclohexane,* 40 mm *cells, at* +10°, *under argon. Curve* 2a *was obtained*[1] *by adding to curve* 1 *the difference between the experimental curves and after erasure of the* DHP *with light at* 436 nm. *The* DHP *was formed by irradiation at* 366 nm. *Curve* 2b *was obtained as* 2a, *but adding to curve* 1 *double the above difference. The position of the minimum at* 345 nm *indicates that this curve represents the maximal extrapolation.*[1] *The actual absorption curve of* DHP (IV) *is close to* 2b (*cf. text*).

Both molecular oxygen and molecular iodine had almost no effect on the DHP formed from (III), but atomic iodine, produced by long-wavelength irradiation of molecular iodine,[4] brought about a very efficient disappearance of the DHP. The product was spectroscopically identical[5] with (V), proving that the DHP has structure (IV). Moreover, from the extent of photoconversion into (IV), the molar extinction coefficient of (IV) could be estimated to be 12,000 ± 2000 at the 423 nm peak. The resulting complete spectrum of (IV) is close to curve 2b in Figure 1.

Preliminary measurements of quantum yields of the three photoconversions *cis*-(III) → *trans*-(III), *cis*-(III) → DHP, DHP → *cis*-(III) at 0° gave further evidence for the rather unusual properties of this particular DHP, (IV), as compared with the DHP's described earlier.[1] These yields were ϕ[*cis*-(III) → DHP] ≈ 0·1, ϕ[*cis*-(III) → *trans*-(III)] ≈ 0·3 and ϕ[DHP → *cis*-(III)] ≈ 0·005. ϕ[*cis*-(III) → DHP] falls off sharply on cooling. For comparison our values for *cis*-stilbene were[1,6] ϕ(*cis* → DHP) ≈ 0·1, ϕ(*cis* → *trans*) ≈ 0·4, and ϕ(DHP → *cis*) ≈ 0·7. The very low value of ϕ[DHP → *cis*-(III)] is particularly unusual, and makes the existence of fluorescence probable. Such fluorescence was indeed detected, and is shown in Figure 2. Its yield at −100° is 0·70. (Fluorescein served as standard,[7] excitation was at 425 nm). This is the first report of DHP emission.

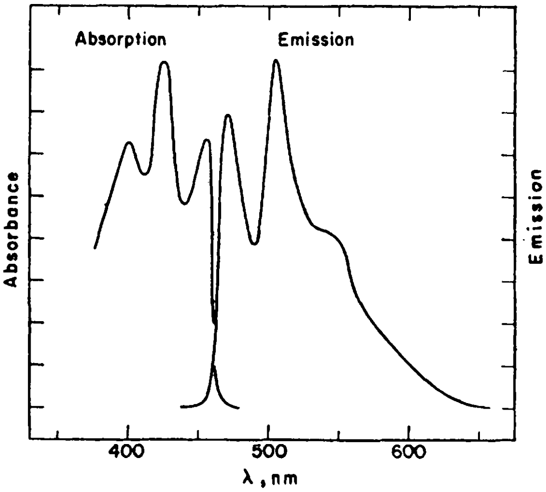


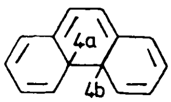
Figure 2. *Absorption and corrected emission spectra of* DHP (IV) *at* −100° *in methylcyclohexane, presented on an arbitrary scale.*

^{1}H N.m.r. spectra of (IV) were estimated from the observed (Bruker 90MC) spectra of solutions irradiated first at 366 nm to form DHP, and then at 436 nm to "erase" it. Those peaks which disappeared after "erasure" were assigned to (IV), and are given in the Table with our preliminary, and admittedly speculative, assignments. This spectrum seems to be the first one of DHP with H atoms in the 4a,4b positions.[8]

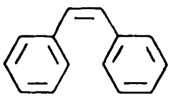
Table

δ p.p.m. (from $SiMe_4$)	Relative peak integral	Type	Assignment
4·0	1	singlet	H_a, H_a
5·9	1	singlet	H_c, H_c
6·4	2	quartet	H_d, H_d
7·0	4	multiplet	H_e, $H_{e'}$

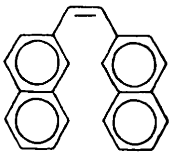
The signal at the highest field, 4·0 p.p.m., is assigned to the H_a, H_a' protons. This may be compared with the signals observed for the H_a protons in 9,10-dihydronaphthalene, (VII). Here van Tamelen *et al.* report a peak at δ 3·25 p.p.m. for the *cis*-isomer,[10] and at 2·8 p.p.m. for the *trans*-isomer.[11] The quartet at 6·4 p.p.m. is assigned to protons H_d and H_d'. These form an AB system, with a coupling constant of J 10 Hz.



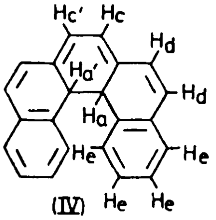
(I)



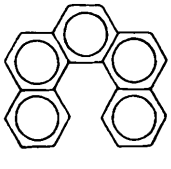
(II)



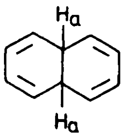
(III)



(IV)



(V)



(VII)

The optical absorption spectra and the photochemical results will be discussed in the context of the photochemistry of all the naphthylethylenes currently being investigated by us.[12]

(*Received, September* 1*st*, 1971; *Com.* 1504.)

---

[1] K. A. Muszkat and E. Fischer, *J. Chem. Soc.*, (*B*), 1967, 662.

[2] (a) A. Bromberg, K. A. Muszkat, and E. Fischer, *Chem. Comm.*, 1968, 1352; (b) H. Stegemeyer and E. Fischer, unpublished results.

[3] E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc.* (*C*), 1970, 163.

[4] G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc.* (*B*), 1968, 1156.

[5] We are indebted to Prof. H. Stegemeyer for providing us with a sample.

[6] S. Malkin and E. Fischer, *J. Phys. Chem.*, 1964, **68**, 1153.

[7] J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

[8] Our earlier ^{1}H n.m.r. measurements were performed on a DHP methylated in the 4a,4b positions.

[9] K. A. Muszkat, D. Gegiou, and E. Fischer, *Chem. Comm.*, 1965, 447.

[10] E. E. van Tamelen and B. Pappas, *J. Amer. Chem. Soc.*, 1963, **85**, 3296.

[11] E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, 1967, **89**, 151.

[12] J. Klueger, G. Fischer, E. Fischer, Ch. Goedicke, and H. Stegemeyer, *Chem. Phys. Letters* 1971, **8**, 279.