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THE IRRADIATION OF 2,2'-DI(PHENYLETHYNYL)BIPHENYL

Emil H. White and Alexander A. F. Sieber
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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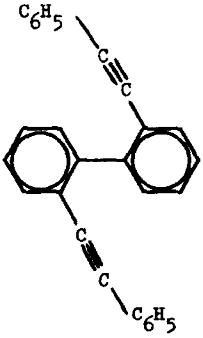
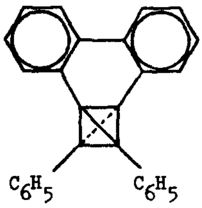
It has been reported that 2,2'-di(phenylethynyl)biphenyl (I) yields an isomeric compound (A) on irradiation (and also thermally); tetrahedrane (II) and cyclobutadiene (III) structures were considered as possibilities for the isomer (1), but no structural investigations were made.



I



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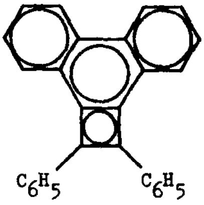
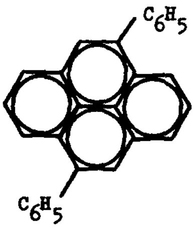


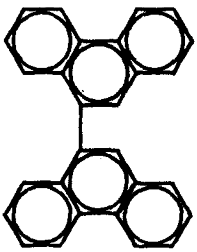
III

We have repeated the conversions and confirm the formation of isomer A, m.p. 230-231°. Under optimum conditions, degassed 10^{-5} M solutions of I (a) heated at 100° in isooctane for 20 days, or (b) irradiated with a sunlamp for 2 min. through Pyrex at 25° in ethanol possessed ultraviolet spectra very close to that of pure isomer A (Fig. 1)(2,3).

A third possible structure (IV) for the isomer was ruled out by Kandil and Dessy on the basis of the ultraviolet absorption spectrum (1,4).



IV



V

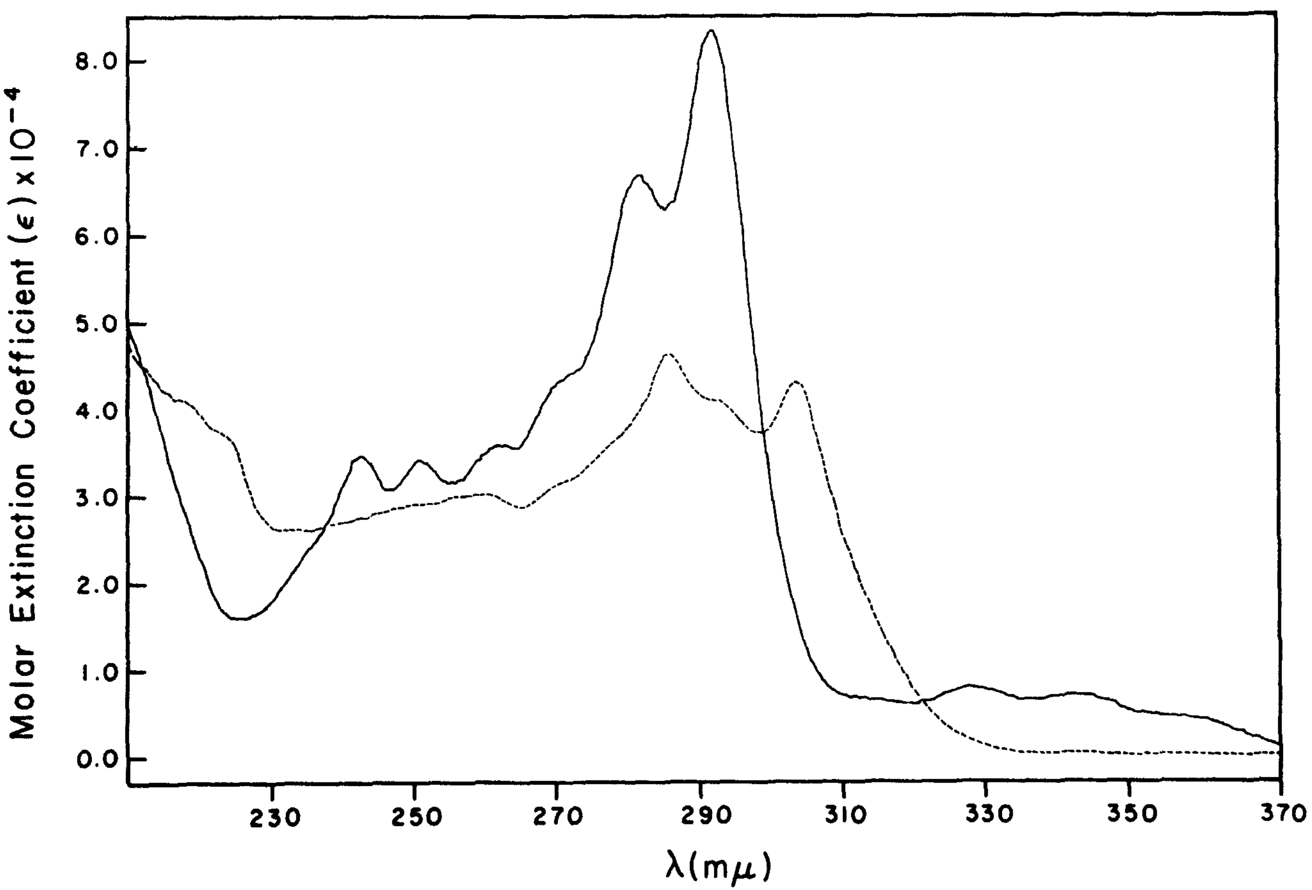
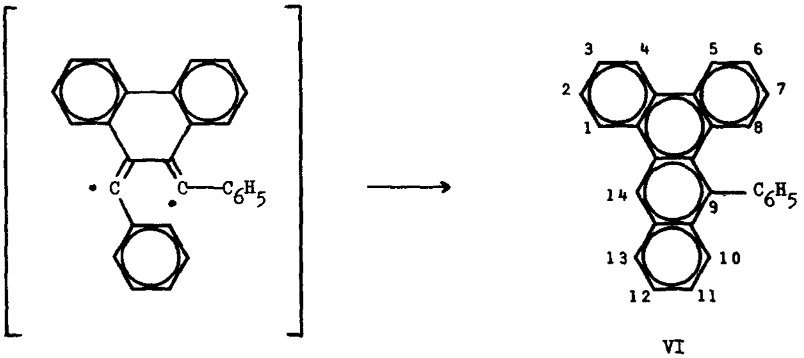


Fig. 1

Ultraviolet Absorption Spectra in methylcyclohexane; compound I (.......) and compound VI = isomer A (————).

Similarly, 9,9'-biphenanthryl (V), a compound which could in principle be derived from III (5), can be eliminated on the basis of the ultraviolet spectrum (6). Furthermore, structures II and III can probably also be eliminated from consideration in view of the absorption spectra of model biphenyls (7) and a model cyclobutadiene (8). The absorption spectrum of isomer A suggests that it is a highly conjugated aromatic compound, probably of the *cata* type (9).

A consideration of possible courses for the isomerization leads to 9-phenyl-dibenz[a,c]-anthracene (VI) as a likely possibility. The ultraviolet absorption spectrum of isomer A is actually very similar to that of dibenz[a,c] anthracene itself (7). A comparison of photoisomer A and authentic VI (3) has now been made and the two substances are, in fact, identical (10). The infrared, ultraviolet, and *nmr* spectra, the melting points, and the rfs (TLC) of the two samples were identical; the melting point of a mixture, furthermore, showed no depression. The structure of VI, establisned by Bergmann and Berlin (3), is confirmed by *nmr* spectra at 60 and 100 MHz, which show a singlet at 0.85τ (11) and multiplets centered at 1.27, 1.54 (12), 1.86, 2.47, and 3.00τ in a weight ratio of 1:1:2:1:12:1.



VI

In the hope that compounds II and III might be formed as metastable intermediates in the irradiation of I, we have carried out photolyses at low temperatures: (a) in an EPA glass at -190°, (b) in isopentane at -135° (13), and (c) in isooctane or ethanol at -70°. The reactions were followed in the ultraviolet at the temperature of the irradiations. Compound I proved stable at -190° and -135° to light from either a sunlamp or a medium pressure mercury arc. At -70°, VI was formed accompanied by side-products with spectra closely related to that of phenanthrene.

Compound I was also photolyzed in a fluorocarbon matrix (14) at -190°, -130°, and -80° with essentially the same results as in solution. After each test, the sample was heated to 100°, but in no case was evidence for a heat-labile intermediate found. Thermal decompositions of I (10^{-3}M degassed solutions in isooctane, 48 hrs. at 150°) gave over 80% of compound VI along with small amounts of the same side-products that were found in the photolyzed samples. The side-products had very similar properties, but three compounds were finally obtained in an enriched state by preparative TLC; all had melting points over 400° and ultraviolet spectra closely resembling the spectra of phenanthrene and compound V but shifted to longer wave lengths (15). No unambiguous evidence for the formation of compound V was obtained. A similar temperature dependence for photolysis has also been noted for 5,6-diphenyldibenzo[a,e]cyclooctatetraene; at room temperature the 5,11-diphenyl isomer was formed, as reported by Stiles and Burckhardt (16), whereas at -190°, the compound was essentially stable to light. At -80°, other photochemical reactions occurred which led to only end absorption in the ultraviolet spectrum (not changed by subsequent heating).

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References

(1) S. A. Kandil and R. E. Dessy, J. Am. Chem. Soc., **88**, 3027 (1966).

(2) Our spectra are slightly different from the published ones (1) (largely a matter of resolution).

(3) We thank Professor R. E. Dessy for samples of I and photoisomer A, and Professor E. Bergmann for a sample of compound VI (E. Bergmann and T. Berlin, J. Chem. Soc., 493 (1939)).

(4) The reference spectra listed (R. O. C. Norman, G. A. Thompson, and W. A. Waters, J. Chem. Soc., 175 (1958)) are apparently for the 1,6 and 1,8-diphenyl isomers and not the 4,9 (IV); however, it appears that spectra of the pyrenes are somewhat insensitive to the number and position of the phenyl substituents (R. O. C. Norman et.al., loc. cit.; K. F. Lang and H. Buffleb, Chem. Ber., **90**, 2894 (1957)).

(5) E. H. White, G. E. Maier, R. Graeve, U. Zirngibl, and E. W. Friend, J. Am. Chem. Soc., **88**, 611 (1966).

(6) We thank Professor I. T. Millar for a sample of compound V (M. A. Ali, J. G. Carey, D. Cohen, A. J. Jones, I. T. Millar and K. V. Wilson, J. Chem. Soc. 387 (1964)). Ultraviolet (C_6H_{12}):

λ_{max} 212 mμ (log ε 4.77), 224 (4.67), 248 (4.97), 255 (5.03), 276sh (4.53), 287 (4.36), and 298 (4.43).

(7) "Organic Electronic Spectral Data", Interscience Publishers, New York, N.Y.

(8) M. P. Cava, B. Hwang, and J. P. Van Meter, *J. Am. Chem. Soc.*, **85**, 4032 (1963).

(9) "Ultraviolet Spectra of Organic Compounds", R. A. Friedel and M. Orchin, John Wiley & Sons, Inc., New York, 1951.

(10) In contrast to these results is the finding that the irradiation of 1,2-di(phenylethynyl) benzene (high concentrations?) yields a dimeric compound of the azulenic type (E. Müller, M. Sauerbier, and J. Heiss, *Tetrahedron Letters*, #**22**, 2473 (1966)).

(11) P. Durand, J. Parello, and N. P. Buu-Hoi (*Bull. Soc. Chim. France*, 2438 (1963)) report τ = 1.10 for protons 9 and 14 of dibenz[a,c]anthracene.

(12) The 4,5 protons of various phenanthrenes have been reported at τ = ca 1.5 (R. C. Fahey and G. C. Graham, *J. Phys. Chem.*, **69**, 4417 (1965); L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4085 (1964).

(13) The ultraviolet spectrum of I shows unusually large changes on cooling. A strong band appears at 250 mμ (10% stronger than the 285-303 mμ multiplet-Fig. 1) and weaker bands in the latter multiplet also appear.

(14) "Dupont" fluorocarbon FCX 330.

(15) 250sh, 257, 272, 279, 288, and 300 mμ.

(16) M. Stiles and U. Burckhardt, *J. Am. Chem. Soc.*, **86**, 3396 (1964).