binding to a strongly binding ligand. The difference $\Delta H^{\ddagger}$ for the metal ion and metal chelate catalyzed oxidation and the variation of $\Delta H^{\ddagger}$ in a particular series of metal chelate catalysts is in accord with the Franck–Condon principle.[15] As the binding between the metal ion and the chelating agent becomes stronger, the, tendency to form a mixed ligand chelate with ascorbate anion decreases. This results in less rigid bonding of the substrate in the mixed ligand chelate, which is easily deformed on electron transfer. The ease of deformation leaves the mixed ligand chelate species more or less geometrically similar before and after the electron transfer. This geometrical similarity of the oxidized and reduced ions requires very little change in hydration energy during the electron transfer, which is reflected in a lowering of $\Delta H^{\ddagger}$. A more positive value of $\Delta F^{\ddagger}$ in these cases is, however, due to a more negative entropy term. In the case of the mixed ligand chelates of weak ligands (more rigid bonding of the substrate) the unfavorable enthalpies are more than compensated for by more positive entropies, which make $\Delta F^{\ddagger}$ more negative.

---

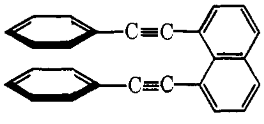
[15] W. F. Libby, *J. Chem. Phys.*, **38**, 420 (1963).

Communications to the Editor

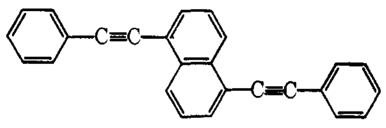
Interactions and Reactions of 1,8-Bis(phenylethynyl)naphthalene

Sir:

We wish to describe 1,8-bis(phenylethynyl)naphthalene (I), a *peri* derivative in which the acetylene groups are essentially parallel.[1]



I

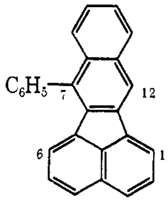


II

Compound I (mp 106°, light yellow) and 1,5-bis(phenylethynyl)naphthalene (II, mp 199°, white) were prepared[2] by treating (phenylethynyl)copper with 1,8-diiodonaphthalene and 1,5-diiodonaphthalene. I is slightly more colored than II. I exhibits acetylenic absorption at 4.48 μ and ultraviolet maxima (ethanol) at 209 (ϵ 47,800), 243 (66,300), 265 (25,800), 344 (29,300), and 365 mμ (26,800); 1-(phenylethynyl)naphthalene[3] has maxima at 256, 268, 317, and 338 mμ. The ultraviolet spectra of I and II are essentially superimposable except that the maxima of I occur at slightly longer wavelengths (1–2 mμ) and the intensity of its phenylethynyl band (265 mμ (ϵ 26,800)) is considerably less than that of II (263 mμ (ϵ 44,000)).

Compound I exhibits nuclear magnetic resonance at τ 2.52–3.08 (multiplet, 12 H) and 2.11–2.40 (multiplet, 4 H); II shows proton resonance at τ 3.15–2.83 (multiplet, 14 H) and 1.39–1.64 (doublet, 2 H). Phenyl proton signals in I (τ 2.87) are centered upfield from those in II (2.57), phenylacetylene (2.68), diphenylbutadiyne (2.67), 1,2-bis(phenylethynyl)benzene[4a] (2.71), 1-phenylnaphthalene[4b] (2.62), and 1,7-diphenylnaphthalene[4b] (2.51); shielding is apparently less than in 1,8-diphenylnaphthalene[4b] (τ 3.15) and [2.2]paracyclophane[4c] (3.63). From the moderate shielding and the absorption, the phenyl groups in I appear to be moved apart, and there may be some interaction between the acetylene groups. What is clear is that there is no marked transannular conjugation in electronically excited I.[4b] The results are also consistent with predictions that cyclobutadienes are not highly delocalized.[5]

Compound I yields 7-phenylbenzo[*k*]fluoranthene (III, mp 167°, pale yellow) when warmed to 100°, photolyzed in pentane, or exposed to aluminum chloride. Compound III does not exhibit infrared absorption for an acetylene group, resists catalytic hydrogenation, and is not oxidized by potassium permanganate. Its ultraviolet spectrum ($\lambda_{\max}^{\text{ethanol}}$ 216 (ϵ 42,300), 246 (42,900), 270 (17,700), 287 (18,000), 298 (31,200), 309 (38,400), 364 (5250), and 384 mμ (8200)) is similar throughout to that of benzo[*k*]fluoranthene[6a] and 7,12-diphenylbenzo[*k*]fluoranthene.[6b] Its nmr spectrum shows aromatic proton signals at τ 3.47 (doublet, 1 H), 2.49 (multiplet, 14 H), and 1.83 (singlet, 1 H). The naphthyl proton at C-6 is shielded by the twisted phenyl group, giving the doublet at τ 3.47; the proton singlet is that at C-12.



III

---

[1] The distance between 1,8-hydrogens in naphthalene is $\sim$2.45 Å; the transannular distances between similar carbon atoms in [2.2]paracyclophane range from 2.83 to 3.09 Å: C. J. Brown, *J. Chem. Soc.*, 3265 (1953).

[2] All new compounds have satisfactory analyses and molecular weights.

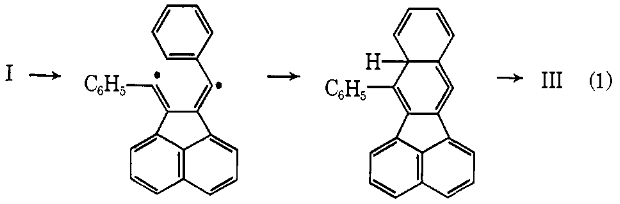
[3] S. A. Kandil and R. E. Dessy, *J. Am. Chem. Soc.*, **88**, 3027 (1966).

[4] (a) Private communication, H. W. Whitlock, Jr.; (b) H. O. House, R. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963); (c) D. C. Cram, C. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963);[4d] (d) *p*-xylene has aryl proton resonance at τ 2.95.

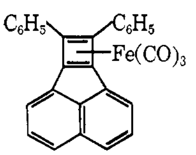
[5] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 3255 (1965).

[6] (a) M. Orchin and L. Reggel, *ibid.*, **73**, 436 (1951); (b) E. Bergmann, *ibid.*, **74**, 1075 (1952); (c) structures which are excluded will be discussed in a final manuscript.

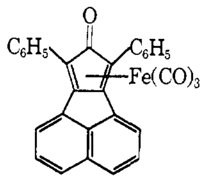
A diradical process for formation of III which allows the geometric changes necessary and involves hydrogen rearrangement is summarized in eq 1. Related concerted, dipolar, acid-catalyzed, or more complicated mechanisms can also be envisaged. The gross chemical changes in conversion of the *parallel* acetylene I to III are analogous to formation of 9-phenyldibenz[*a*,*c*]-anthracene by irradiation of the *crossed* acetylene, 2,2′-bis(phenylethynyl)biphenyl.[3,7] Cyclobutadiene and other intermediates may be involved in the present systems; however they are not yet isolable. Attempts to lock I with iron pentacarbonyl[8] as its cyclobutadiene-iron tricarbonyl (IV) gives acecycloneiron tricarbonyl (V, mp 205°, tan) and III. Compound V is identified by its keto and metal carbonyl absorptions (6.13 and 4.87, 5.02, and 5.05 μ) and its decomposition to acecyclone. The novel 1,4-transannular insertion reaction of I with iron pentacarbonyl differs from that for 1,2-bis(phenylethynyl)benzene.[9]



(1)



IV

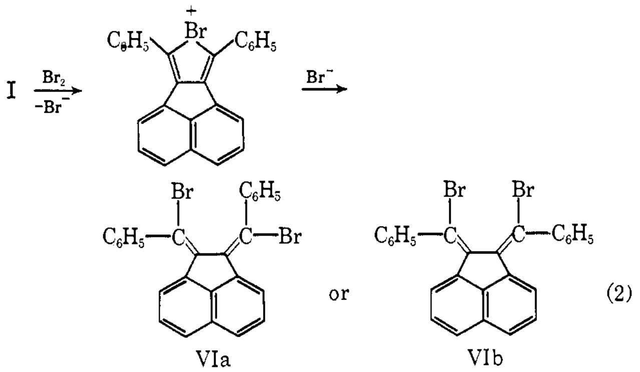


V

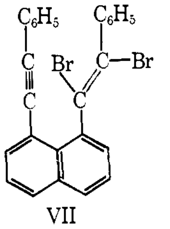
Bromination of I occurs by transannular 1,4-addition to yield 1,2-bis(α-bromobenzylidene)acenaphthene (VI, eq 2, mp 149°); adducts VII–XI and their geometric isomers were not isolated. Bromination of I is strikingly different from the collapsing domino process in conversion of 1,2-bis(phenylethynyl)benzene by bromine to 3-bromo-1-(α-bromobenzylidene)-2-phenylindene.[9]

Compound VI is white, shows no acetylenic absorption, gives a negative silver nitrate test, is oxidized by sodium dichromate to acenaphthenequinone, and, of particular interest, reacts with magnesium to give I. Its ultraviolet spectrum ($\lambda_{\max}^{\text{ethanol}}$ 210 (ϵ 41,800), 239 (65,900), and 328 mμ (13,000)) is similar to that of acenaphthylene derivatives and indicates that its exocyclic double bonds are highly twisted.[10] Structure VIa or VIb agrees with the nmr in that the phenyl groups (τ ~2.80) are not extensively shielded.

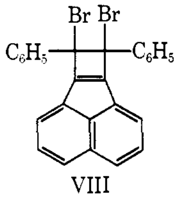
Compound VI dehydrobrominates to 7-bromo-12-phenylbenzo[*k*]fluoranthene (XII, 78%, mp 138°) when warmed or photolyzed, possibly as in eq 3. The structure of XII is confirmed from its spectra and its reaction with magnesium and hydrolysis to give III.



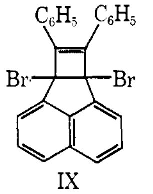
VIa VIb (2)



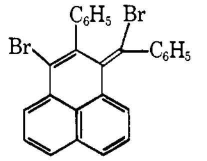
VII



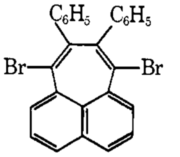
VIII



IX

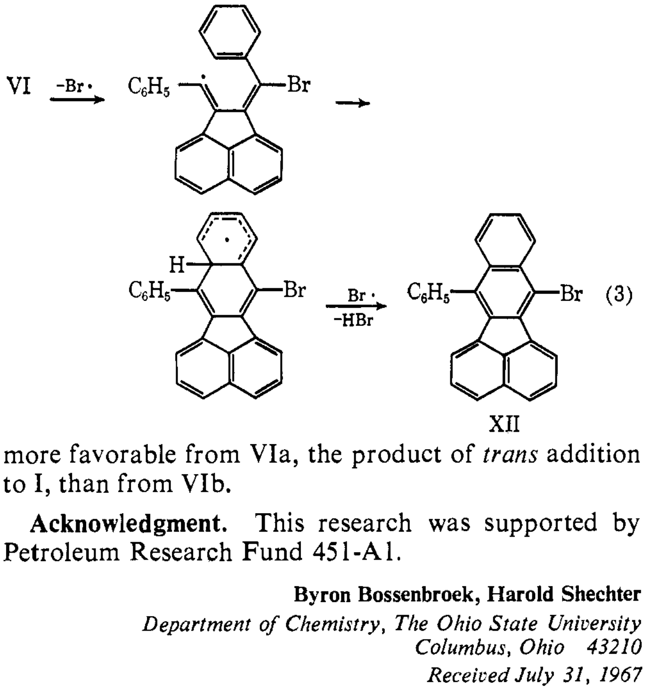


X



XI

The reactivity of VI apparently stems from its twisted exocyclic structure, and conversion to XII appears more favorable from VIa, the product of *trans* addition to I, than from VIb.



(3)

XII

Acknowledgment. This research was supported by Petroleum Research Fund 451-A1.

Byron Bossenbroek, Harold Shechter
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
Received July 31, 1967

---

[7] (a) E. H. White and A. A. F. Sieber, *Tetrahedron Letters*, 2473 (1966). (b) B. Bossenbroek, Ph.D. Thesis, The Ohio State University, 1967, independently concluded that 2,2′-bis(phenylethynyl)biphenyl photolyzes to 9-phenyldibenz[*a*,*c*]anthracene.[7a]

[8] L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3253 (1965).

[9] H. W. Whitlock, Jr., and P. E. Sandvick, *ibid.*, **88**, 4525 (1966).

[10] N. Maxim, *Bull. Soc. Chim. France*, **45**, 1137 (1929), reports that 1,2-bis(benzylidene)acenaphthene is red-orange.

The Effects of Neighboring Heteroatoms in Rearrangement to Divalent Carbon

Sir:

The abilities of the indicated groups to migrate to divalent carbon in decomposition of diazo compounds are: hydrogen > aryl > methyl.[1] Photolysis of 1-

---

[1] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961); (b) H. Phillip and J. Keating, *Tetrahedron Letters*, 523 (1961); (c) G. Kaufmann, The Ohio State University, 1963–1966.