at 6.55 (m), 8.17 (s), 9.10 (m), 9.95 (s), 10.60 (m), 13.03 (s), and 13.60 (m) μ. 4-Chloro-2,3-dimethylphenol (Aldrich) was recrystallized from hexane to mp 83–84° (lit.[35] 84.5°). 2,3,6-Trimethylphenol (Aldrich) was recrystallized from hexane to mp 60–62° (lit.[36] 62°). Solvents used for spectra were dried and purified by standard methods: distillation from lithium aluminum hydride or sodium for the ethers; from calcium hydride for the polar aprotic solvents. **5** was prepared according to Pedersen's Method X,[26] in 15% yield, mp 161.5–163.5° (lit.[26] 164°).

Sodium Salt of 1-Nitroindene. A solution of 0.1 g of **1** in 5 ml of water was passed through a column (10 cm high × 1 cm diameter) of Dowex 50W-X1 resin which had been first washed with 30 ml of 1 *N* NaOH solution then 60 ml of water. Washing with 70 ml of water sufficed to remove the sodium salt from the column as judged by the color of the effluent. The water was stripped off at room temperature under vacuum, and the resulting dark yellow solid was dried at 0.2 mm pressure and room temperature. The infrared spectrum was essentially the same as that of **1**. On heating, the material darkened at *ca.* 200°, but did not melt even at 250°. A flame test showed a brilliant sodium coloration, but no potassium color through cobalt glass.

Sodium 4-Chloro-2,3-dimethylphenoxide (6). Sodium hydroxide (1.095 g, 27.4 mmol) was partially dissolved in 50 ml of methanol, then 4.184 g (26.7 mmol) of 4-chloro-2,3-dimethylphenol was added. The mixture was stirred at room temperature under a nitrogen atmosphere until homogeneous, then stripped on a rotatory evaporator. The residue was dried at 0.1 mm and room temperature for 24 hr. The material did not melt below 200°. The neutralization equivalent was 177 (calcd for C_8H_8ClNaO, 178.6).

Comparable attempts to prepare **7** gave only material of very high neutralization equivalent. Consequently, the spectra of **7** were obtained by dissolving the phenol in a solution containing excess sodium methoxide, and, if necessary, filtering quickly under nitrogen pressure.

Spectra. The electronic spectra were obtained using a Perkin-Elmer Model 202 or Beckman DK-2A spectrophotometer. All solutions were deoxygenated by passing dry nitrogen through them for several minutes before running the spectra. Concentrations of **1** and **2** were typically 1–5 × 10^{-5} *M*; those of **6** and **7**, 1–5 × 10^{-4} *M*. Nuclear magnetic resonance spectra were obtained using a Varian A-60, with tetramethylsilane as internal standard (τ 10.00). The spectral data are given in the text. Excess sodium alkoxide was used in obtaining the phenoxide spectra in protic solvents. None of the salts was sufficiently soluble in the ethers (5%) to give usable nmr spectra.

Acknowledgments. We are grateful to the Research Corporation and the Research Foundation of the State University of New York for support of this work. We wish also to thank Miss Mary Hodos for the preparation of **1**.

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(35) L. E. Hinkel, W. T. Collins, and E. E. Ayling, *J. Chem. Soc.*, **123**, 2968 (1923).

(36) G. T. Morgan and A. E. J. Pettet, *ibid.*, 418 (1934).

The Interactions and Chemistry of 1,8-Bis(phenylethynyl)-naphthalene and 1,8-Bis(1-alkynyl)naphthalenes

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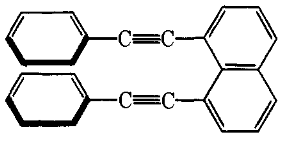
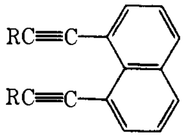
Received August 28, 1968

Abstract: The *peri*-diacetylenes, 1,8-bis(phenylethynyl)naphthalene (I) and 1,8-bis(1-alkynyl)naphthalenes (IIa–c), have been prepared from 1,8-diiodonaphthalene (III) and appropriate cuprous acetylides in pyridine. The ultraviolet absorption maxima of I are at slightly longer wavelengths than those of 1,5-bis(phenylethynyl)naphthalene (IV). The moderate nmr shielding and the absorption in I indicate that its phenyl groups may be moved apart and there may be some transannular acetylenic interaction upon its electronic excitation. Thermolysis or photolysis of I yields 7-phenylbenzo[*k*]fluoranthene (VI); reaction of I with iron pentacarbonyl gives acecycloneiron tricarbonyl (XIV). Bromination of I occurs by transannular 1,4 addition yielding 1,2-bis(α-bromobenzylidene)acenaphthene (XVI). XVI reacts with magnesium or *n*-butyllithium to give I, VI, and 7-bromo-12-phenylbenzo[*k*]fluoranthene (XXIII). Photolysis or thermolysis of XVI results in XXIII. Absorption in IIa occurs at slightly longer wavelengths than in 1,5-bis(1-propynyl)naphthalene (XXVII); transannular electronic interaction of the acetylene groups in IIa upon excitation is not large. Addition of 2 equiv each of bromine, hydrogen bromide, and hydrogen iodide to IIa occurs without net transannular structural change to yield 1,8-bis(1,2-dibromo-1-propenyl)naphthalene (XXVIII), 1,8-bis(1-bromo-1-propenyl)naphthalene (XXIXa), and 1,8-bis(1-iodo-1-propenyl)naphthalene (XXIXb), respectively. *peri*-Diacetylene I adds 2 equiv of hydrogen bromide to give the adduct $C_{26}H_{18}Br_2$.

The present research involves synthesis and study of 1,8-bis(phenylethynyl)naphthalene (I)[1] and 1,8-bis(1-alkynyl)naphthalenes (IIa–c). These *peri*-naphthalene derivatives contain near-rigid acetylene groups



I



IIa, R = CH_3
b, R = CH_3CH_2
c, R = $CH_3(CH_2)_3$

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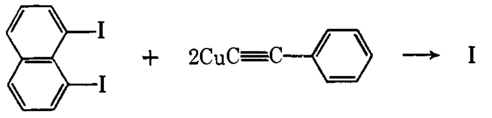
(1) (a) In the present publication the synthesis and chemistry of I reported is a summary of the Ph.D. dissertation of B. Bossenbroek, The Ohio State University, 1967. (b) Synthesis and chemistry of 1,8-bis(phenylethynyl)naphthalene (I) have been described preliminarily as a communication by B. Bossenbroek and H. Shechter, *J. Am. Chem. Soc.*, **89**, 7111 (1967). (c) Essentially simultaneously J. Ipaktschi and H. A. Staab, *Tetrahedron Letters*, 4403 (1967), submitted a communication in which syntheses, properties, and conversions of I to 7-phenylbenzo[*k*]fluoranthene (VI), 12-phenylindeno[1,2-*a*]phenylene (XI), and acecycloneiron tricarbonyl (XIV) are reported. (d) Subsequently E. Müller, J. Heiss, M. Sauerbrier, D. Streichfuss, and R. Thomas, *ibid.*, 1195 (1968), described conversion of I by platinum tetrachloride to XI, its photolysis to VI, 7-phenylazuleno[1,2-*a*]acenaphthylene (XII, tentative) and an unassigned red product, and its thermolysis to VI. (e) For further communications and publications of the rapidly expanding field of parallel acetylenes see H. A. Staab, H. Mack, and E. Wehinger, *ibid.*, 1465 (1968); H. A. Staab, A. Nissen, and J. Ipaktschi, *Angew. Chem.*, 80, 241 (1968); and R. H. Mitchell and F. Sondheimer, *Tetrahedron*, **24**, 1397 (1968).

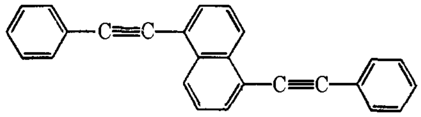
which are essentially parallel and at distances (∼2.44 Å) such that they might exhibit significant intramolecular interactions and reactions.[2] The particular objectives of study of I and IIa–c are (1) to evaluate their transannular electronic interactions, (2) to investigate their possible conversions to stabilized or pseudo cyclobutadienes and their subsequent derivatives, and (3) to characterize their various addition reactions with reagents of interest. *peri*-Diacetylene I, a white fluorescent solid (mp 105–106°), has been presently prepared (72%) from 1,8-diiodonaphthalene (III)[3] and (phenylethynyl)copper (2 equiv) in pyridine at 25–30°. Improved or new methods of synthesis of III involve (1) diazotization of


III

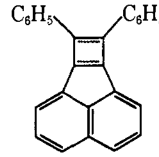
(1)

1,8-naphthalenediamine in dilute sulfuric acid and decomposition of the 1,8-naphthalenebis(diazonium) bisulfate in aqueous hydriodic acid at 25° (32%),[4] (2) reaction of 8-iodo-1-naphthyldiazonium chloride[5a] and aqueous potassium iodide (67%), and (3) decarboxylative iodination of 8-iodo-1-naphthoic acid by mercuric oxide and iodine (15%). The structure of I is indicated by its (1) elemental analysis and molecular weight, (2) infrared absorption at 4.48 μ (C≡C), and (3) ultraviolet absorption maxima in ethanol at 209 (ϵ 47,800), 243 (66,300), 265 (25,800), 344 (29,300), and 365 mμ (26,800). In hot benzene I reacts with 2,4,7-trinitrofluorenone to give a stable red-brown 1:1 molecular complex, $C_{39}H_{21}N_3O_7$ (mp 149–150°).

Synthesis of 1,5-bis(phenylethynyl)naphthalene (IV) was effected from 1,5-diiodonaphthalene and (phenylethynyl)copper in hot pyridine in order to compare its chemistry, its infrared and ultraviolet absorption, and its nuclear magnetic resonance with that of I. The 1,5-diacetylene (IV) is a fluorescent white solid (mp 198–199°) which forms a red-brown 1:2 complex ($C_{52}H_{26}N_6O_{14}$, mp 180–181°) with 2,4,7-trinitrofluorenone. Infrared absorption for C≡C in IV occurs at 4.47 μ; ultraviolet absorption maxima (ethanol) are exhibited at 208 (ϵ 46,600), 341 (33,200), and 355 mμ (26,900). The ultraviolet spectra of I and IV are thus very similar except that I absorbs at somewhat longer wavelengths and with less intensity in the 265-mμ region. Absorption at 268 mμ for 1-(phenylethynyl)naphthalene in tetrahydrofuran has been attributed to the acetylene group.[6] Analogous bands appear in the spectrum of I at 265 mμ (ϵ 26,800, 95% ethanol) in IV. From the increased wavelength and the diminished intensity of absorption in I, electronic excitation may involve transannular acetylenic conjugation. It is apparent however that the overlap of the *peri*-acetylene groups in I is not large.


IV

The nuclear magnetic resonances of I and IV are of particular interest. Resonance of I occurs at τ 2.52–3.08 (multiplet, 12 H) and 2.11–2.40 (multiplet, 4 H);[7] IV shows proton signals at τ 3.15–2.83 (multiplet, 14 H) and 1.39–1.64 (doublet, 2 H).[8] Phenyl proton resonance in I (τ 2.87) is thus centered upfield from that in IV (τ 2.57) along with those in phenylacetylene (τ 2.68), diphenylbutadiyne (τ 2.67), 1,2-bis(phenylethynyl)benzene[9a] (τ 2.71), 1-phenylnaphthalene (τ 2.62), and 1,7-diphenylnaphthalene (τ 2.51). There is apparently less shielding in I than in 1,8-diphenylnaphthalene[9b] (τ 3.15) and [2.2]paracyclophane (τ 3.63).[9c] The diminished shielding in I may arise from intramolecular acetylenic interaction such that it has some cyclobutadiene character (V). The actual phenyl proton resonance signal in I (τ 2.83) is similar to that in *cis*-stilbene[10] (τ 2.82). It is also possible that the phenylethynyl groups in I are not parallel but are pushed apart for steric reasons. As a result the phenyl protons will be less shielded. What is indeed clear from the spectral and the proton resonance properties of I is that it does not show extensive delocalized cyclobutadiene character.[11]



V

Elaboration of the chemistry of I has been a principle objective of this research. Thermolysis of I at 100° or photolysis (3×10^{-3} *M*) in pentane followed by chromatography yields pale yellow crystals of 7-phenylbenzo[*k*]fluoranthene (VI, mp 166–167°). The reaction product VI gives no infrared absorption for an acetylene group, is not oxidized by acidic or basic potassium

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(2) The chemistry and intramolecular effects in 1,8-naphthalene derivatives have been reviewed by V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

(3) This synthesis is based on the prior observations of R. D. Stephens and C. E. Castro, *J. Org. Chem.*, **28**, 2163, 3313 (1963), that diarylacetylenes are obtained by heating aryl iodides with copper arylacetylides in pyridine. It is of note in the present synthesis that in refluxing pyridine I isomerizes to VI as subsequently described.

(4) This is the preferred method of synthesis of I in this research and is an improvement of that of H. H. Hodgson and J. S. Whitehurst, *J. Chem. Soc.*, **80**, (1947).

(5) (a) 8-Iodo-1-naphthylamine was prepared from (1) 1,8-naphthalenediamine, nitrous acid (1 equiv), and hydrochloric acid and potassium iodide,[5b] and (2) Schmidt reaction[5c] of 8-iodo-1-naphthoic acid as derived from disodium 1,8-naphthalate and aqueous mercuric acetate *via* 8-(acetoxymercuri)-1-naphthoic acid[5d] and then sodium hypoiodite. (b) A modification of the method of R. Scholl, Chr. Seer, and R. Weitzenbock, *Ber.*, **43**, 2202 (1910). (c) D. Berndt, Ph.D. Dissertation, The Ohio State University, 1961. (d) A. Corbellini and V. Fossati, *Rend. Ist. Lombardo Sci.*, **69**, 264 (1936).

(6) Absorption maxima in 1-(phenylethynyl)naphthalene also occur at 256, 317, and 338 mμ: S. A. Kandil and R. E. Dessy, *J. Am. Chem. Soc.*, **88**, 3027 (1966).

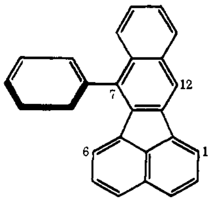
(7) The four protons centered at τ 2.25 are those *ortho* and *para* to the ethynyl groups on the naphthalene ring. α-Naphthyl protons are normally centered at τ 2.27 and β-naphthyl protons at τ 2.63. Electron withdrawal by the ethynyl groups deshields the *ortho* protons resulting in a shift from τ 2.63 to 2.25.

(8) The phenylethynyl groups deshield the *para* protons in the naphthalene ring resulting in a downfield shift to τ 1.53.

(9) (a) H. W. Whitlock, Jr., private communication: (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); (d) aryl proton resonance in *p*-xylene occurs at τ 2.95.

(10) Varian NMR Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 305.

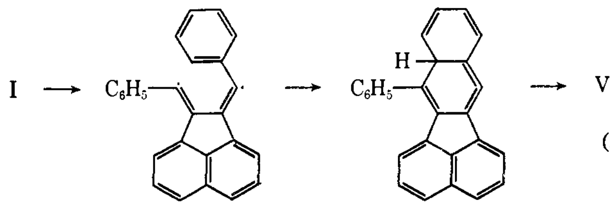
(11) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 3255 (1965), predict that cyclobutadiene is a nonconjugated, rectangular cyclodiene of singlet ground state.



VI

permanganate, and is not hydrogenated over palladium on charcoal or platinum at 25°. The fluoranthene VI forms a red-brown 1:1 molecular complex, $C_{39}H_{21}N_3O_7$ (mp 184–185°), with 2,4,7-trinitrofluorenone.

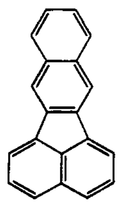
The mechanism by which I is converted to VI is not clear. Formation of VI by a diradical process which indicates the necessary changes in geometry and rearrangement of hydrogen is summarized in eq 2.[12]



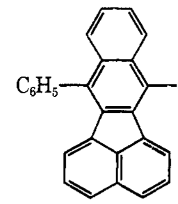
(2)

Concerted, dipolar, or more complex reaction mechanisms may be actually involved. Cyclobutadiene and other intermediates may be formed during the thermal and the photochemical processes. As yet attempts to isolate such intermediates have been unsuccessful.

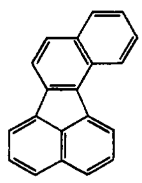
The structural assignment of VI is based primarily on the similarity of its ultraviolet spectrum with that of benzo[*k*]fluoranthene (VII)[13a] and 7,12-diphenylbenzo[*k*]fluoranthene (VIII)[13b] as indicated in Table I. The three benzo[*k*]fluoranthenes (VI–VIII) differ in the number of phenyl substituents. Because of steric requirements the phenyl groups are highly twisted from the planes of the benzofluoranthene nuclei in VI and VIII. Significant conjugation of the phenyl rings with the fluoranthene system is prevented and thus the spectra show only small substituent effects in that absorption occurs at slightly longer wavelengths for VI and VIII than for VII.[14] Spectral data for benzo[*j*]fluoranthene (IX) are included in Table I since a possible product of I is 11-phenylbenzo[*j*]fluoranthene (X).[15] Comparison shows that the absorption of VI is different from that of IX particularly in the region from 315 to 355 mμ. The absorption of X would not be changed significantly (a small substituent effect) from that of IX since coplanarity of the phenyl and the benzofluoranthene groups in X is prevented sterically.



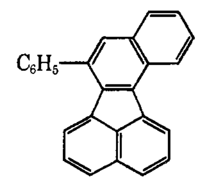
VII



VIII



IX



X

Table I. Ultraviolet Absorption of VI, VII, VIII, and IX in Ethanol

VII		VI		VIII		IX	
λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
215	36,200	216	42,300			226	38,000
240	56,200	246	42,900	252	63,000	242	39,800
269	22,900	270	17,700	270	30,200	308	24,000
282	26,200	286	18,000			318	30,200
296	46,700	298	31,200	298	42,600	332	10,950
308	56,200	309	38,400	310	61,500	349	3,620
361	7,240	364	5,250	366	7,940	365	6,600
380	13,200	384	8,200	386	15,100	376	5,360
						383	10,000

The nuclear magnetic resonance of VI is consistent with the structural assignment in that aromatic proton signals are exhibited 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.[16,17]

Cyclobutadiene is trapped by iron pentacarbonyl as cyclobutadieneiron tricarbonyl.[18] An attempt to convert I with iron pentacarbonyl to its cyclobutadieneiron tricarbonyl (XIII) results instead in insertion of carbon monoxide and coordination to give acecycloneiron tricarbonyl (XIV, tan, mp 205°) along with V. The structural assignment of XIV is based on its keto and

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[12] The chemical transformation by which the parallel acetylene I is converted to VI is analogous to irradiation of the crossed acetylene, 2,2′-bis(phenylethynyl)biphenyl to give 9-phenyldibenz[*a,c*]anthracene; E. H. White and A. A. F. Sieber, *Tetrahedron Letters*, 2473 (1966). B. Bossenbroek (Ph.D. Thesis)[1a] and E. Müller, *et al.*,[1d] also independently concluded that 9-phenyldibenz[*a,c*]anthracene is produced by photolysis of 2,2′-bis(phenylethynyl)biphenyl.

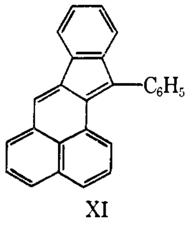
[13] (a) M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **69**, 505 (1947); and M. Orchin and L. Reggel, *ibid.*, **73**, 436 (1951); (b) E. Bergmann, *ibid.*, **74**, 1075 (1952).

[14] (a) 1-Phenylnaphthalene has an ultraviolet spectrum similar to that of naphthalene. The apparent reason for the similarity of absorption is that steric factors limit coplanarity of the phenyl and naphthalene rings. Support for this interpretation comes from the similarity of the ultraviolet absorption of 1-phenylnaphthalene (λ_{max} 225 and 288 mμ) with that of 1-cyclohexylnaphthalene (λ_{max} 224 and 283 mμ). The ultraviolet absorption of 2-phenylnaphthalene is shifted to longer wavelengths from that of 1-phenylnaphthalene because increased conjugation is sterically allowed. (b) M. Orchin and R. A. Friedel, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1951, spectra no. 198, 290, and 297.

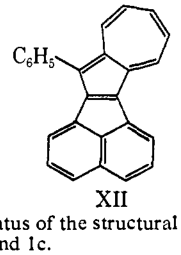
[15] (a) By extension of mechanisms proposed for photolysis of diphenylacetylene[15b] and *o*-bis(phenylethynyl)benzene,[15c] respectively. (b) G. Buchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.*, **27**, 4106 (1962). (c) E. Müller, M. Saurbrier, and J. Heiss, *Tetrahedron Letters*, 2473 (1966).[15d] (d) See also ref 1d.

[16] As will be seen, this signal is absent in an analogous product (XXIII) containing bromine rather than hydrogen at C-12.

[17] Reaction of I with catalytic amounts of aluminum chloride in ethylene dichloride occurs rapidly to give XI along with VI and XII.



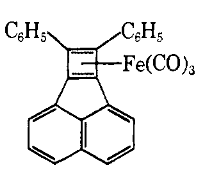
XI



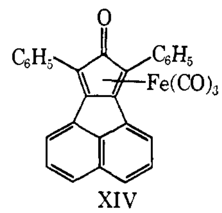
XII

Similar transformations of I and the status of the structural assignments of XI and XII are discussed in ref 1b and 1c.

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



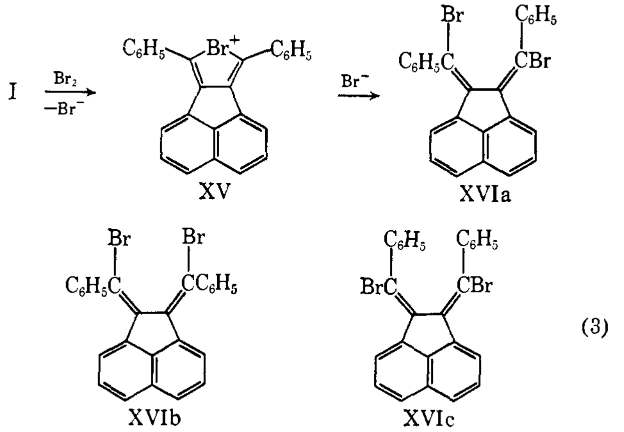
XIII



XIV

metal carbonyl infrared absorptions at 6.13 and 4.87, 5.02 and 5.05 μ,[19] and its decomposition to acecyclonone chromatography. Attempts to lock I as a cyclobutadiene with other metal derivatives are in progress.

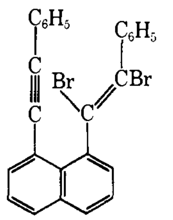
Addition of bromine (1 equiv) to I in chloroform yields 1,2-bis-(α-bromobenzylidene) acenaphthene (XVIa–c, eq 3, mp 149°) possibly by a 1,4-transannular process involving XV. Products such as XVII–XXI or their geometric isomers have not been obtained.[20] The structure of the adduct is assigned as indicated (XVI) because it is white, does not exhibit acetylenic infrared absorption,[21] does not give a positive silver nitrate test even when heated,[22] is oxidized by sodium dichromate in acetic acid to acenaphthenequinone (XXII), 1,8-naphthalic anhydride, and benzoic acid, and is debrominated by magnesium (eq 4) to I along with VI and XXIII (see subsequent discussion).



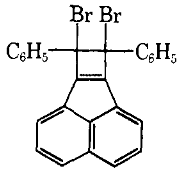
XV XVIa

XVIb XVIc

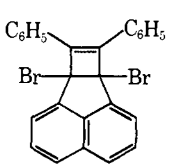
(3)



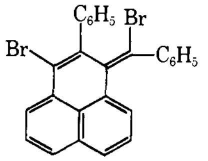
XVII



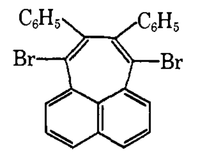
XVIII



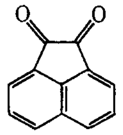
XIX



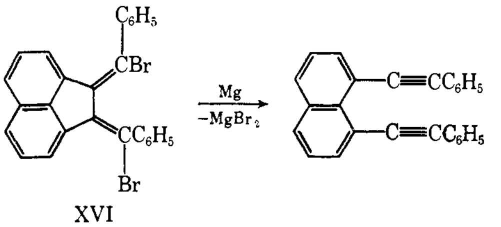
XX



XXI



XXII

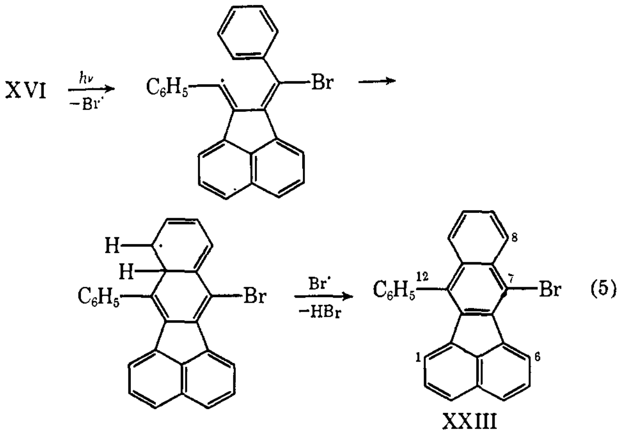


XVI

(4)

There are three possible geometric isomers of XVI (a, b, and c). In each of the isomers the exocyclic double bonds are expected to be highly twisted because of the steric requirements of the phenyl groups and the bromine atoms. The similarity of the ultraviolet spectrum of XVI [$\lambda_{\max}^{\text{ethanol}}$ 210 (ϵ 41,800), 239 (65,900), and 328 mμ (13,000)] with that of acenaphthylene [$\lambda_{\max}^{\text{ethanol}}$ 207 (ϵ 9700), 228 (46,800), and 323 mμ (9540)] and various acenaphthylene derivatives is indeed indicative of the limited conjugation and the extensive twisting of the *exo* double bonds of XVI. The nuclear magnetic resonance of the phenyl protons of the dibromide is not extensively shielded (τ $\sim$2.80) and thus XVIc is excluded as the product. There is no evidence yet which confirms or excludes XVIa or XVIb. However both the proposed mechanism for formation of XVI and its facile loss of hydrogen bromide as discussed below suggest that the stereochemistry of the dibromide is that of XVIa.

Dibromide XVI loses hydrogen bromide readily on irradiation (3500 and 5250 Å) in pentane or upon thermolysis and yields 7-bromo-12-phenylbenzo[*k*]-fluoranthene (XXIII, 78%, mp 137–138°).[23] A possible mechanism of formation of XXIII from XVI is summarized in eq 5. Both VI and XXIII are light



(5)

XXIII

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(19) (a) Metal tricarbonyl absorption of 2,5-diphenylcyclopentadienoneiron tricarbonyl occurs at 4.78, 4.93, and 4.97 μ (Nujol)[19b] and for hexatrienyliron tricarbonyl at 4.88, 5.03, and 5.07 μ (film).[19c] Iron tetracarbonyl complexes show a minimum of four bands for metal carbonyl absorption of which the first band always appears at 4.75 μ or lower.[19d] (b) F. A. Cotton and J. R. Leto, *Chem. Ind.* (London), 1592 (1958); (c) E. Weiss, *Helv. Chim. Acta*, **46**, 1588 (1963); (d) E. Weiss, *ibid.*, **46**, 288 (1863).

(20) H. W. Whitlock, Jr., and P. E. Sandvick, *J. Am. Chem. Soc.*, **88**, 4525 (1966), report that 1,2-bis(phenylethynyl)benzene reacts with bromine (1 equiv) to give 3-bromo-1-(α-bromobenzylidene)-2-phenylindene.

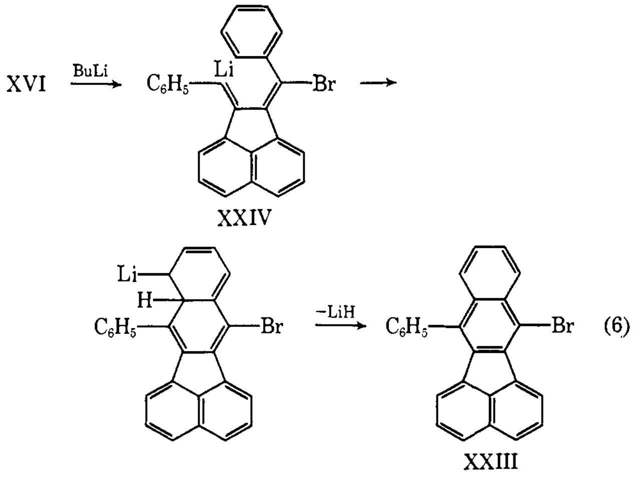
(21) Absorptions for C≡C in I, IV, and 8-nitro-1-(phenylethynyl)-naphthalene (see Experimental Section) occur at 4.48, 4.47, and 4.46 μ, respectively.

(22) (a) Immediate precipitates are given by silver nitrate with 3,4-dibromotetraphenylcyclobutene[22b] and with 3,4-dibromo-1,2-diphenylcyclobutene[22c] at room temperature. (b) H. D. Freedman and A. M. Frantz, *ibid.*, **84**, 4165 (1962); (c) A. T. Blomquist and E. A. La Lancette, *J. Org. Chem.*, **29**, 2331 (1964).

(23) In 95% ethanol and upon exposure to laboratory light for several weeks, XVI is also converted to XXIII.

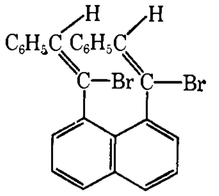
yellow. The ultraviolet absorption of XXIII [λ_{max} 216 (ϵ 31,800), 248 (43,990), 271 (12,900), 288 (11,500), 299 (28,700), 3311 (37,200), and 387 mμ (6400)] is similar to that of VI. The nuclear magnetic resonance spectrum shows doublets at τ 3.60, 1.52, and 1.22 and a multiplet at τ 2.60 (1 : 1 : 1 : 12). The doublet at τ 3.60 is assigned to the proton at C-1 and is shielded by the phenyl group attached at C-12. The doublets at τ 1.52 and 1.22 are protons at C-6 and C-8 as deshielded by bromine at C-7.[24] The structure of XXIII is confirmed upon its reaction with magnesium followed by hydrolysis to give VI in near quantitative yield.

Treatment of dibromide XVI with excess *n*-butyllithium (4.5 equiv) gives a red solution which becomes light brown after 4 hr. Acidification and chromatography yields XXIII (53%), I (18%), and VI (12%). A reasonable mechanism for formation of XXIII from XVI is illustrated in eq 6. An intermediate such as XXIV may undergo loss of bromide ion to give I and VI. The benzo[*k*]fluoranthene VI is also possibly produced by isomerization of I or exchange of XXIII with *n*-butyllithium and hydrolysis.

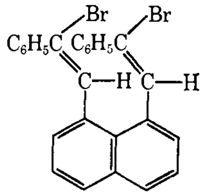


peri-Diacetylene I undergoes rapid electrophilic addition of 2 equiv of hydrogen bromide to give a white adduct, $C_{26}H_{18}Br_2$ (65%, mp 160.5°). The dihydrobromide does not give a bromide test with alcoholic silver nitrate. Its infrared spectrum does not exhibit absorption for an acetylene group, thus indicating that both carbon–carbon triple bonds have reacted with hydrogen bromide. The adduct has nuclear magnetic resonance [τ 3.07 (m, 9 H), 2.81 (s, 1 H), 2.70 (s, 2 H), 2.50 (m, 4 H), and 2.05 (m, 2 H)] consisting of five singlets and multiplets which lie totally in the aromatic region. The main signal for phenyl protons at τ 3.06 indicates that the phenyl groups are shielded. The ultraviolet absorption spectrum of the adduct in hexane [λ_{max} 210 (ϵ 38,200), 222 (43,500), and 279 mμ (23,400)] is similar to that for alkylnaphthalenes and shows no extended conjugation. The dihydrobromide is thus derived by addition of 2 equiv of hydrogen bromide to I without effecting net transannular structural change. The chemistry of the adduct is of interest however in that it loses 2 equiv of hydrogen bromide upon photolysis or upon reaction with potassium *t*-butoxide to give VI.

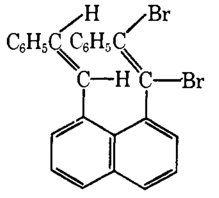
The are 14 possible geometric isomers for the dihydrobromide based on the four structural types illustrated (XXVa–d; the *trans–trans* and the *cis–trans* isomers are not shown). In all isomers the substituted phenylethylene groups are twisted approximately perpendicular to the naphthalene ring. Each of the isomers will explain the spectral, nmr, and chemical properties, but the positions of the protons and bromines on the ethylene groups cannot be assigned from the available evidence. On the basis of reaction mechanism and the structure of the product derived from addition of 2 equiv of hydrogen bromide to IIa (see subsequent discussion), it is likely that the present dihydrobromide is of structural type XXVa.



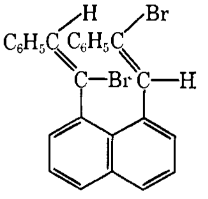
XXVa



XXVb

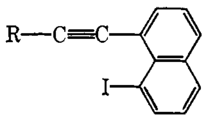


XXVc



XXVd

1,8-Bis(1-alkynyl)naphthalenes (IIa–c) are obtained (60–70%) from III and cuprous salts (>3 equiv) of propyne, 1-butyne, and 1-hexyne, respectively, in pyridine at >80° for 12 hr. With III and 2 equiv of the copper acetylides at 25° for long reaction times (72 hr), the principal products (up to 80%) are 8-iodo-1-(1-alkynyl)naphthalenes (XXVIa–c). Conversions of XXVIa–c to IIa–c by cuprous alkynes are considerably slower than for 8-iodo-1-(phenylethynyl)naphthalene and (phenylethynyl)copper. The decreased rates of formation of IIa–c as compared to I appear to arise from the greater steric requirements of the former systems.



XXVIa, R = CH_3
b, R = CH_3CH_2
c, R = $CH_3(CH_2)_3$

Diacetylenes IIa–c are more stable thermally and photochemically than is I. The 1,8-bis(1-alkynyl)-naphthalenes can be isolated and handled by usual methods. They reveal distinctive acetylene absorption (~4.48 μ) and can be readily separated and purified as monopicrates. The structures of IIa–c are indicated from analytical, mass spectral, spectroscopic, and nuclear magnetic resonance data.

1,8-Bis(1-propynyl)naphthalene (IIa, a white solid, mp 113–115°) exhibits ultraviolet absorption maxima in ethanol at 213 (ϵ 20,400), 238 (61,400), 262 (9,500), 310 (11,800), 324 (15,800), and 339 mμ (15,800). Ultraviolet absorption maxima for 1,5-bis(1-propynyl)-naphthalene (XXVII, prepared from 1-propynylcopper

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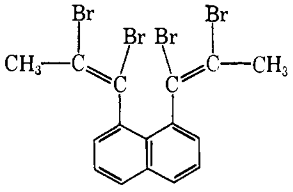
[24] Similar deshielding effects are exhibited in 1-bromonaphthalene and 2,3-dibromonaphthalene.

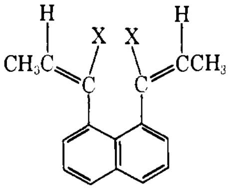
and III in refluxing pyridine, 36%, mp 148–149°) in 95% ethanol occur at 212 (ϵ 28,400), 236 (65,000), 307 (13,300), 319 (19,100), and 337 mμ (15,600). In general IIa absorbs at slightly longer wavelengths than does XXVII; the relative spectroscopic behavior of IIa and XXVII is similar to that of I and IV. Transannular electronic interaction of the acetylene groups in IIa upon excitation thus does not appear to be large.

Reaction of IIa with bromine (2 equiv) occurs rapidly to give 1,8-bis(1,2-dibromo-1-propenyl)naphthalene (XXVIII, a white solid, 98%, mp 168–170°). Efforts to obtain a dibromide from IIa by using limited quantities of bromine at various temperatures failed. The product always obtained is tetrabromide XXVIII; its stereochemistry is unknown. The structure assigned to the tetrabromide is consistent with the observations that it does not give a silver nitrate test nor absorption for an acetylene group. Proton magnetic resonance in XXVIII is exhibited at τ 7.33 (singlet, 6 methyl H) and 2.1–2.8 (multiplet, 6 naphthyl H). Ultraviolet absorption maxima for XXVIII in 95% ethanol are at 211 (ϵ 35,000), 234 (47,000), and 316 mμ (7600). The chemistry of XXVIII is consistent with the assigned structure in that reaction with zinc in acetic acid–ether yields IIa. As yet efforts to prepare a dibromide from XXVIII have been unsuccessful.



XXVIII

Addition of hydrogen bromide (2 equiv) to IIa takes place without transannular structural complication to yield 1,8-bis(1-bromo-1-propenyl)naphthalene (XXIXa, a white solid, 73%, mp 131–133°). The structure of the dihydrobromide is indicated by its analysis and molecular weight, its vinyl absorption at 6 μ, its resistance to ethanolic silver nitrate unless heated, its nuclear magnetic resonance [τ 8.53 (doublet, 6 methyl H), 3.74 (quartet, 2 vinyl H), and 2.10–2.84 (multiplet, 6 naphthyl H)], and its ultraviolet absorption maxima in ethanol at 213 (ϵ 33,600), 234 (42,000), and 317 mμ (6000). Reaction of IIa occurs with 2 equiv of hydrogen iodide to give 1,8-bis(1-iodo-1-propenyl)naphthalene (XXIXb, 65%, mp 149°, stereochemistry unknown). Electrophilic addition of 2 equiv of hydrogen iodide and hydrogen bromide to IIa are thus completely analogous.



XXIXa, X = Br
b, X = I

Experimental Section

8-Iodo-1-naphthylamine Hydrochloride. A. From 8-Iodo-1-naphthoic Acid.[5c] Sodium azide (2.5 g, 0.0385 mol) was added to a stirred suspension of 8-iodo-1-naphthoic acid[5d] (10 g, 0.0334 mol) in concentrated sulfuric acid (160 ml) and water (40 ml) at 5°. The mixture was warmed to room temperature; the gas collected (STP) indicated 89% completion of the reaction. The mixture was poured onto ice and made basic with concentrated aqueous sodium hydroxide. The aqueous solution was extracted with ether. The combined ether extracts were washed with water, dried over potassium carbonate, and filtered. Treatment of the filtrate with gaseous hydrogen chloride gave a tan precipitate of 8-iodo-1-naphthylamine hydrochloride (8.65 g, 0.0283 mol, 85%), mp 192–195° (lit.[5b] mp 186–189°).

B. From 1,8-Naphthalenediamine.[5b] A solution of 1,8-naphthalenediamine (15 g, 0.095 mol) in concentrated hydrochloric acid (36 ml) and warm water (200 ml) was filtered into water (1500 ml) and ice (300 g). Sodium nitrite (6.7 g, 0.097 mol) in water (50 ml) was added dropwise at 0–5°. After the mixture had been stored 2 hr, the solid was filtered and added to hydrochloric acid (113 g, 47%). The mixture was heated in the presence of copper bronze (1 g) at 90° until nitrogen evolution ceased. The black solid was filtered, dried, powdered, and made alkaline with cold 10% sodium hydroxide. The black solid was filtered, dried, and extracted with ether. The combined ether extracts were dried over potassium carbonate and treated with gaseous hydrogen chloride. Filtering and drying yielded 8-iodo-1-naphthylamine hydrochloride (6.75 g, 0.022 mol, 23%) as a tan solid, mp 188–189° (lit.[5b] mp 186–189°).

Diazotization of a more concentrated solution (15 g of 1,8-naphthalenediamine in 1 l. of water and 36 ml of concentrated hydrochloric acid) gave 7.75 g of iodoamine (26% yield). Replacement of hydriodic acid with aqueous potassium iodide lowered the yield to 11%. An attempt to decompose the diazonium salt under reduced pressure at room temperature resulted in a yield of only 4%.

1,8-Diiodonaphthalene (III). A. From 8-Iodo-1-naphthylamine Hydrochloride. A solution of 8-iodo-1-naphthylamine hydrochloride (16.8 g, 0.0552 mol) in water (150 ml) and concentrated hydrochloric acid (15 ml) was cooled to 0° and sodium nitrite (3.87 g, 0.0561 mol) in water (50 ml) was added in 30 min. After stirring 1 hr at 0–5°, the mixture was filtered into a stirred solution of potassium iodide (150 g, 0.9 mol) in water (200 ml). After the mixture had been stirred under reduced pressure overnight, the solid formed was filtered. Extraction of the dry solid with Skellysolve B gave a dark red solution which was concentrated and chromatographed on basic alumina. The yellow solid obtained, on crystallization from methanol–Skellysolve B, yielded III (14.0 g, 0.0368 mol, 67%), mp 109–110° (lit.[4] mp 109°).

B. From 1,8-Naphthalenediamine. A solution of recrystallized 1,8-naphthalenediamine (7.0 g, 0.0444 mol), concentrated sulfuric acid (15 ml), and water (50 ml) was prepared and ice (~125 g) then added. A solution of sodium nitrite (9 g, 0.13 mol) and water (40 ml) was then added dropwise to the mixture (<15 min) at 5°. After the mixture had been stirred less than 5 min, potassium iodide (45 g, 0.27 mol) in water (60 ml) was added as rapidly as possible while keeping the temperature below 10°. The mixture was then warmed rapidly in a water bath. Nitrogen was evolved during the early stages of heating; the mixture was finally heated for 10 min at 80°.

The reaction mixture was rapidly cooled to 20° and made strongly alkaline with 6 *N* sodium hydroxide (~60 ml). The black tarry precipitate was suction-filtered, air-dried, and thoroughly extracted with ether. The ether extracts were concentrated, diluted with carbon tetrachloride (50 ml), and chromatographed on activated alumina using carbon tetrachloride as eluent. Removal of the eluent yielded III (5.3 g, ~30%), mp 107–109°

C. From 8-Iodo-1-naphthoic Acid. A stirred solution of 8-iodo-1-naphthoic acid (10.0 g, 0.0336 mol), red mercuric oxide (10.0 g, 0.0461 mol), and iodine (10.0 g, 0.0394 mol) in cyclohexane (250 ml) was protected from light and refluxed overnight. After cooling, the solids were filtered, and the solvent was evaporated. The residue was dissolved in ether and washed with aqueous sodium bisulfite and then aqueous sodium bicarbonate. The ether solution was dried with anhydrous magnesium sulfate, decolorized with charcoal, and evaporated. The residue (4.16 g) was dissolved in Skellysolve B and chromatographed on basic alumina. Evaporation of the solvent yielded III (1.9 g, 0.005 mol, 15%), mp 108–109°.

1,8-Bis(phenylethynyl)naphthalene (I). (Phenylethynyl)copper[3] (8.7 g, 0.0529 mol) and III (10.0 g, 0.0263 mol) were dissolved in dry pyridine (250 ml) and protected from light. The system was purged with nitrogen and the mixture stirred at room temperature for 24 hr. Removal of the solvent under reduced pressure gave a tan solid which was stirred with ether (200 ml) and filtered. The filtrate was evaporated and the residue dissolved in Skellysolve B. Chromatography on basic alumina gave I (6.16 g, 0.0188 mol, 72%) as a light yellow solid. Several recrystallizations from Skellysolve B gave nearly white crystals, mp 105–106°.

Anal. Calcd for $C_{26}H_{18}$: C, 95.09; H, 4.91; mol wt, 328. Found: C, 94.78; H, 4.85; mol wt, 328.

2,4,7-Trinitrofluorenone (0.192 g, 6.1 × 10^{-4} mol) and I (0.20 g, 6.1 × 10^{-4} mol) were dissolved separately in warm benzene (15 ml) and the two hot solutions mixed. A dark red color appeared immediately and cooling yielded red-brown needles. Recrystallization from absolute ethanol gave the trinitrofluorenone complex as fine red-brown needles, mp 149–150°.

Anal. Calcd for $C_{39}H_{21}N_3O_7$: C, 72.78; H, 3.29; N, 6.53. Found: C, 72.59; H, 3.30; N, 6.69.

1,5-Diiodonaphthalene. 1,5-Naphthalenediamine (12.0 g, 0.076 mol) in glacial acetic acid (100 ml) was added dropwise to a stirred solution of sodium nitrite (12.0 g, 0.174 mol) in concentrated sulfuric acid (100 ml) at 0–5°. After stirring 15 min, the mixture was poured onto ice (100 g) and urea (1 g) was added. The mixture was added to potassium iodide (400 g, 2.4 mol) in water (400 ml) and stirred overnight at reduced pressure. The solid was filtered, dried, and extracted with carbon tetrachloride. The combined extracts were decolorized with charcoal and concentrated. Chromatography on neutral alumina yielded pale yellow needles of 1,5-diiodonaphthalene (20.6 g, 0.542 mol, 71%), mp 148.5–149° (lit.[4] mp 147°).

Anal Calcd for $C_{10}H_6I_2$: C, 31.61; H, 1.59. Found: C, 31.69; H, 1.60.

1,5-Bis(phenylethynyl)naphthalene (IV). Pure dry nitrogen was bubbled through a solution of 1,5-diiodonaphthalene (5.0 g, 0.01315 mol) in dry pyridine (100 ml) and a solution of (phenylethynyl)-copper (4.35 g, 0.0265 mol) in dry pyridine (100 ml) for 18 hr. The mixtures were combined with a large syringe and stirred at room temperature under nitrogen. After 2 days the copper salt was still visible and the mixture was heated at 110° for 12 hr. Most of the pyridine was removed under reduced pressure and the residue extracted with ether. The combined ether extracts were washed with dilute hydrochloric acid and water and dried over magnesium sulfate. Concentration gave a brown oily solid which was dissolved in Skellysolve B and chromatographed on silica gel. The first fractions gave diphenylbutadiyne (1.99 g, 0.00985 mol, 75%), mp 85–86° (lit.[25] mp 88°). The following fractions yielded a white to light yellow solid which produced a blue fluorescence in ultraviolet light. Decolorization and recrystallization from Skellysolve B resulted in white crystals of IV (0.42 g, 0.00128 mol, 10%), mp 198–199°.

Anal. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91; mol wt, 328. Found: C, 94.91; H, 5.02; mol wt, 337.

Reaction of IV with a molecular equivalent of 2,4,7-trinitrofluorenone in hot benzene gave a trinitrofluorenone complex as fine red-brown needles, mp 180–181° after recrystallization from absolute ethanol. The analysis indicated that the complex was composed of one molecule of IV and two molecules of trinitrofluorenone.

Anal. Calcd $C_{52}H_{26}N_6O_{14}$: C, 65.14; H, 2.73; N, 8.76. Found: C, 64.79; H, 2.59; N, 8.40.

8-Iodo-1-nitronaphthalene. Sodium nitrite (0.85 g, 0.0123 mol) in water (50 ml) was added dropwise at 0° to a stirred solution of 8-nitro-1-naphthylamine (2.3 g, 0.0122 mol) in 10% hydrochloric acid (50 ml). After stirring 1 hr the mixture was filtered into a stirred solution of potassium iodide (50 g, 0.3 mol) in water (100 ml). The solid formed was filtered, dried and extracted with Skellysolve B. Chromatography on neutral alumina yielded 8-iodo-1-nitronaphthalene (1.6 g, 0.00535 mol, 44%), mp 78–80° (lit.[26] mp 80°).

8-Nitro-1-(phenylethynyl)naphthalene. 8-Iodo-1-nitronaphthalene (1.6 g, 0.00535 mol) and (phenylethynyl)copper (0.88 g, 0.00535 mol) were stirred in dry pyridine (100 ml) under nitrogen for 24 hr. The solvent was removed under reduced pressure and the residue extracted with ether. Concentration gave an oil which was crystallized twice from methanol to yield a light brown solid, mp 118–120°. The solid was dissolved in carbon tetrachloride and decolorized with silica gel. Recrystallization from 95% ethanol gave yellow crystals of 8-nitro-1-(phenylethynyl)naphthalene (0.24 g, 9.2 × 10^{-4} mol, 17%), mp 120.5–121.5°; infrared absorption at 4.46 ($C{\equiv}C$) and 6.55 and 7.36 μ (NO_2).

Anal. Calcd for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13. Found: C, 79.16; H, 4.19; N, 5.13.

Photolysis of 1,8-Bis(phenylethynyl)naphthalene (I). A solution of I (1 g, 0.00305 mol) in Skellysolve B (300 ml) in a quartz tube was irradiated externally at reflux temperature for 24 hr. The light source was a medium-pressure mercury vapor lamp. A small amount of insoluble tar formed on the wall of the tube. The light brown solution was concentrated and chromatographed on neutral alumina with Skellysolve B. Crystallization yielded pale yellow cubic crystals of 7-phenylbenzo[*k*]fluoranthene (VI, 0.59 g, 0.0018 mol, 59%), mp 162–163°. In solution, VI gave a blue fluorescence in ultraviolet light. It was insoluble in concentrated sulfuric acid.

External irradiation at room temperature gave VI much more slowly. Thus I (2.0 g, 0.0061 mol) after 24 hr yielded a light yellow mixture of starting material and VI (1.6 g), mp 93–98°. Further irradiation at room temperature for 24 hr gave impure VI (1.23 g, 0.00375 mol, 62%), mp 154–156°.

Anal. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91; mol wt, 328. Found: C, 94.94; H, 5.05; mol wt, 312.

Reaction of the product with a molecular equivalent of 2,4,7-trinitrofluorenone in hot benzene yielded the trinitrofluorenone complex as fine maroon needles, mp 184–185°, after recrystallization from absolute ethanol.

Anal. Calcd for $C_{39}H_{21}N_3O_7$: C, 72.78; H, 3.29; N, 6.53. Found: C, 72.88; H, 3.30; N, 6.58.

Thermolysis of 1,8-Bis(phenylethynyl)naphthalene (I). A solution of I (2.0 g, 0.0061 mol) in diglyme was heated in the dark at 130° for 24 hr. Isolation of the reaction product as before yielded VI (1.59 g, 0.00485 mol, 80%), mp 166–167°.

Reaction of 1,8-Bis(phenylethynyl)naphthalene (I) with Aluminum Chloride. To a solution of I (0.250 g, 0.76 mol) in ethylene dichloride (25 ml) was added aluminum chloride (0.070 g). The mixture immediately became dark brown. After 1 hr, the mixture was filtered and concentrated. Chromatography of the dark red oil on silica gel with Skellysolve B yielded VI (0.040 g, 0.12 mol, 16%) and products described as XI and XII. This study was terminated because of those of ref 1c and 1d.

Reaction of 1,8-Bis(phenylethynyl)naphthalene (I) and Iron Pentacarbonyl. Iron pentacarbonyl (1.8 g, 0.0092 mol), I (2.0 g, 0.0061 mol), and diglyme were placed in a steel bomb and heated at 130° for 4 hr. The mixture was cooled and the solvent removed at 28–30° (2 mm). Extraction of the residue with Skellysolve B and chromatography on neutral alumina yielded I (1.59 g, 0.00485 mol, 79.5%), mp 166–167°. Recrystallization of the insoluble portion of the residue from acetone yielded a light tan solid identified as acecycloneiron tricarbonyl (XIV, 0.150 g, 3 × 10^{-4} mol, 5%), mp 204–205°.

Anal. Calcd for $C_{30}H_{16}FeO_4$: C, 72.60; H, 3.25; mol wt, 496. Found: C, 71.27; H, 3.80; mol wt, 492.

On standing in air XIV turned black. The residue was chromatographed on neutral alumina with carbon tetrachloride to yield blue-black crystals of acecyclone, mp 289°. Identification was confirmed by comparison with an authentic sample on thin layer chromatography and mixture melting point. The infrared absorption spectrum of the acecyclone could be superimposed on a spectrum of an authentic sample.

Reaction of 1,8-Bis(phenylethynyl)naphthalene (I) and Bromine. A solution of I (3.0 g, 0.00915 mol) in chloroform (100 ml) was stirred at room temperature while bromine (1.46 g, 0.00915 mol) in chloroform (25 ml) was added in 20 min. The mixture turned dark red immediately; stirring was continued for 15 hr. Concentration gave a dark red oil which was dissolved in Skellysolve B. On standing a dark solid formed which was dissolved in carbon tetrachloride and chromatographed on silica gel. Several recrystallizations of the resulting light brown solid from 95% ethanol gave white crystals of 1,2-bis(α-bromobenzylidene)acenaphthene (XVI, 1.5 g, 0.0031 mol, 34%), mp 148–149°. Its infrared absorption is similar to that of I except that acetylene absorption is absent. Nuclear magnetic resonance occurs at τ 2.80 (m, 12 H) and 2.25 (m, 4 H). The product gives a negative test with alcoholic silver nitrate.

Anal. Calcd for $C_{26}H_{16}Br_2$: C, 63.96; H, 3.30; Br, 32.73. Found: C, 63.66; H, 3.39; Br, 32.78.

Reaction of 1,2-Bis(α-bromobenzylidene)acenaphthene (XVI) and *n*-Butyllithium. Excess *n*-butyllithium (2.4 × 10^{-3} mol) was syringed into a solution of XVI (0.250 g, 5.1 × 10^{-4} mol) in dry ether (50 ml) at 0°. The mixture turned dark immediately. After 4 hr, the color changed to light brown, and the solution was poured on ice and dilute sulfuric acid. The ether layer was dried over magnesium sulfate and concentrated. Chromatography on silica gel with Skellysolve B yielded VI (0.020 g, 6.1 × 10^{-5} mol, 12%), I (0.03 g, 9.2 × 10^{-5} mol, 18%), and XXIII (0.110 g, 2.7 × 10^{-4} mol, 53%)

Reaction of 1,2-Bis(α-Bromobenzylidene)acenaphthene (XVI) and Magnesium. The mixture derived from reaction of XVI (0.100

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(25) A. F. Holleman, *Ber.*, 20, 3081 (1887).

(26) H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 571 (1939).

g, 3.05×10^{-4} mol) and magnesium (0.030 g, 1.23×10^{-5} g-atom) in ether (25 ml) was hydrolyzed. The product obtained on work-up and analysis by thin layer chromatography was primarily **I**; small amounts of VI and traces of XXIII were also isolated.

Oxidation of 1,2-Bis(α-bromobenzylidene)acenaphthene (XVI). Oxidation of XVI (0.025 g, 5.1×10^{-5} mol) was effected in glacial acetic acid (15 ml) with sodium dichromate dihydrate (0.026 g, 8.7×10^{-5} mol). No change was observed after stirring the mixture for 8 hr at room temperature. After having been refluxed for 2 hr, the mixture was poured onto ice and extracted with ether; the combined extracts were dried and concentrated. The infrared spectrum, which showed carbonyl absorption at 5.62, 5.75, and 5.89 μ, was compared with the spectra of 1,8-naphthalic anhydride (C=O at 5.62 and 5.73 μ), acenaphthenequinone (XXII, C=O at 5.74 μ), and benzoic acid (C=O at 5.89 μ). The quinone (XXII) was separated by silica gel chromatography and identification confirmed by its mixture melting point. Its retention time on gas chromatography was the same as an authentic sample using a 5 ft × $^1/_8$ in. column containing 5% SE 30 on 60–80 Chromosorb W.

Photolysis of 1,2-Bis(α-bromobenzylidene)acenaphthene (XVI). A solution of XVI (0.2 g, 0.41 mol) in Skellysolve B (100 ml) was placed in a quartz tube and irradiated for 16 hr at 40°. The light source had peak intensities at 3500 and 5250 Å. Concentration yielded a red oil which on chromatography on neutral alumina with Skellysolve B gave two bands. The first band was removed with 5% ether–Skellysolve B to give a yellow solid. Recrystallization from Skellysolve B–95% ethanol yielded fine pale yellow needles of 7-bromo-12-phenylbenzo[*k*]fluoranthene (XXIII, 0.132 g, 3.2×10^{-4} mol, 78%), mp 137–138°. The infrared spectrum of XXIII is very similar to that of VI.

Anal. Calcd for $C_{26}H_{15}Br$: C, 76.67; H, 3.71; Br, 19.62. Found: C, 76.66; H, 3.59; Br, 19.47.

The second band was removed with 50% ether–Skellysolve B to give a bright orange solid (20 mg), mp 200–220°. No meaningful spectral data could be obtained and investigation of the product was terminated.

Reaction of 1,8-Bis(phenylethynyl)naphthalene (I) and Hydrogen Bromide. Gaseous hydrogen bromide was bubbled through a solution of I (0.750 g, 0.00228 mol) in benzene (10 ml) at 10° for 1.5 hr. After the dark red mixture had been stirred overnight at 20–30°, the mixture was concentrated. The dark red residue was dissolved in carbon tetrachloride and chromatographed on silica gel. Four fractions were collected and analyzed by thin layer chromatography. The first two fractions were VI (0.50 g, 1.52×10^{-4} mol, 7%). The third and fourth fractions were combined and crystallized from Skellysolve B as fine white needles (0.750 g, 0.00143 mol, 63%), mp 160–160.5°, which analyzed for XXV.

Anal. Calcd for $C_{26}H_{18}Br_2$: C, 63.70; H, 3.70; Br, 32.60; mol wt, 490. Found: C, 63.78; H, 3.92; Br, 31.54; mol wt, 494.

Properties of XXV. The dihydrobromide XXV loses hydrogen bromide when heated to its melting point and gives a positive alcoholic silver nitrate test when warmed but not at room temperature. Irradiation of XXV (0.100 g, 2.04×10^{-4} mol) in Skellysolve B (150 ml) for 24 hr at 40° yields VI (0.039 g, 1.19×10^{-4} mol, 58%).

The dihydrobromide (XXV, 0.100 g, 2.04×10^{-4} mol) was heated at 50° for 3 hr with potassium *t*-butoxide (0.048 g, 4.3×10^{-4} mol). Examination of the mixture by thin layer chromatography showed partial conversion to VI. There was no evidence for additional products.

1-Propynylcopper. Cuprous chloride (20.0 g, 0.20 mol) and ammonium carbonate (30.0 g, 0.26 mol) were dissolved in water (200 ml). Concentrated ammonium hydroxide was added to dissolve the white precipitate that formed. Propyne was bubbled through the rapidly stirred dark blue solution for 1 hr. The solid that separated was filtered and washed with ammonium hydroxide until the washings were colorless and then successively with water, ethanol, and ether. Vacuum drying afforded 1-propynylcopper (10.7 g, 0.104 mol, 52%) as a yellow-orange amorphous solid.

1,8-Bis(1-propynyl)naphthalene (IIa). A solution of 1-propynylcopper (10.8 g, 0.105 mol) and 1,8-diiodonaphthalene (10.0 g, 0.0263 mol) was prepared in dry pyridine (250 ml). The mixture was purged with nitrogen and the mixture stirred at 80° for 12 hr. Removal of the solvent under reduced pressure gave a tan solid which was stirred with ether (300 ml) and filtered. After evaporation of the filtrate, the residue was dissolved in Skellysolve B and chromatographed on neutral alumina to give IIa (3.35 g, 0.0164 mol, 62%) as a light yellow solid. Recrystallization from Skellysolve B afforded near-white crystals of IIa, mp 113–115°.

Anal. Calcd for $C_{16}H_{12}$: C, 94.07; H, 5.93. Found: C, 94.08; H, 5.77.

Individual solutions of picric acid (0.115 g, 5×10^{-4} mol) and IIa (0.102 g, 5×10^{-4} mol) were prepared in warm 95% ethanol and then mixed. The solution on cooling deposited fine orange needles of the monopicrate of IIa, mp 150–152° (from 95% ethanol).

Anal. Calcd for $C_{22}H_{15}N_3O_7$: C, 60.97; H, 3.05; N, 9.69. Found: C, 60.73; H, 3.49; N, 9.48.

1,5-Bis(1-propynyl)naphthalene (XXVII). A mixture of 1-propynylcopper (5.4 g, 0.053 mol) and 1,5-diiodonaphthalene (5.0 g, 0.013 mol) in pyridine (125 ml) was purged with nitrogen and then refluxed for 48 hr. Isolation of the product as described for IIa gave XXVII (0.96 g, 0.0047 mol, 36%) as white crystals, mp 148–149°, exhibiting infrared absorption at 4.48 μ (C≡C) and nuclear magnetic resonance at τ 7.84 (s, 6 H) and 3.05–1.59 (m, 6 H).

Anal. Calcd for $C_{16}H_{12}$: C, 94.07; H, 5.93. Found: C, 93.91; H, 6.06.

1,8-Bis(1,2-dibromo-1-propenyl)naphthalene (XXVIII). A solution of IIa (0.408 g, 0.002 mol) in methylene chloride (20 ml) was stirred at −78° while bromine (0.640 g, 0.004 mol) in methylene chloride (10 ml) was rapidly added (1 min). The resulting green solution was immediately evaporated to dryness, and the tan residue dissolved in pentane and chromatographed on neutral alumina. Recrystallization of the product from Skellysolve B afforded white crystals of XXVIII (1.03 g, 0.00197 mol, 98%), mp 150–152°. The tetrabromide on stirring in ethanol or *t*-butyl alcohol increased in melting point to 168–170°. The infrared spectra in carbon tetrachloride, the ultraviolet spectra in 95% ethanol, the nuclear magnetic resonance in carbon tetrachloride, and the analyses of the products melting at 150–152 and 168–170° are identical.

Anal. Calcd for $C_{16}H_{12}Br$: C, 36.68; H, 2.31; Br, 61.01. Found: C, 36.69; H, 2.35; Br, 61.29.

Reaction of 1,8-Bis(1,2-dibromo-1-propenyl)naphthalene (XXVIII) and Zinc. A suspension of XXVIII (0.524 g, 0.001 mol) and zinc dust (0.458 g, 0.007 g-atom) in ethyl ether (20 ml) and glacial acetic acid (5 ml) was stirred 1 hr at room temperature. The mixture was diluted with water and extracted with ethyl ether. The combined ether extracts were washed with saturated sodium bicarbonate and saturated sodium chloride and dried. Evaporation of ether and recrystallization of the product yielded IIa, mp 113–115°.

Reaction of 1,8-Bis(1-propynyl)naphthalene (IIa) and Hydrogen Bromide. Gaseous hydrogen bromide was passed into a solution of IIa (0.408 g, 0.002 mol) in chloroform (15 ml) at 10°. Concentration of the mixture gave a dark red residue which was chromatographed in pentane on neutral alumina. Recrystallization of the combined fractions in Skellysolve B gave fine white needles of XXIXa (0.530 g, 0.00144 mol, 72%), mp 131–133°.

Anal. Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.83. Found: C, 52.65; H, 3.85.

Reaction of 1,8-Bis(1-propynyl)naphthalene (IIa) and Hydrogen Iodide. Reaction of IIa (0.204 g, 0.001 mol) and excess gaseous hydrogen iodide (>2 equiv) in chloroform at 20–30° and isolation of the product by chromatography on neutral alumina yielded XXIXb (0.149 g, 3.2×10^{-4} mol, 32%), mp 146–149° after repeated recrystallizations from Skellysolve B. The adduct did not exhibit acetylene absorption; ultraviolet maxima in 95% ethanol occur at 215 (ε 27,100), 237 (30,700), and 320 mμ (5500). The dihydroiodide displays nuclear magnetic resonance at τ 7.88 (doublet, 6 H), 4.02 (quartet, 2 H), and 3.62–1.7 (multiplet, 6 H).

Anal. Calcd for $C_{16}H_{14}I_2$: C, 41.76; H, 3.06. Found: C, 42.04; H, 3.58.

Reaction of 1,8-Diiodonaphthalene (III) and 1-Butynylcopper. A. (2 Equiv of 1-Butynylcopper, 20–25°). A mixture of III (5.0 g, 0.0131 mol) and 1-butynylcopper (3.5 g, 0.0298 mol) in dry, freshly distilled pyridine (160 ml) was purged thoroughly with nitrogen and then stirred for 72 hr at room temperature. The pyridine was removed at reduced pressure and the residue then extracted with ether. The filtered extract was concentrated, dissolved in Skellysolve B, and then chromatographed on acid-washed alumina. The major eluent on evaporation yielded 8-iodo-1-(1-butynyl)naphthalene (XXVIb, 0.98 g, 0.00313 mol, 24%), a yellow oil which exhibits acetylenic absorption at 4.4 μ and nuclear magnetic resonance at τ 8.8 (triplet, 3 H), 7.6 (quartet, 2 H), and 2.5 (multiplet, 6 H).

Anal. Calcd for $C_{14}H_{11}I$: C, 54.92; H, 3.62. Found: C, 54.52; H, 3.48.

Further elution of the chromatographic column and isolation of the product as above gave slightly impure 1,8-bis(1-butynyl)naphthalene (IIb, a yellow oil, 0.40 g, 0.00172 mol, 13%). The structure of IIb is assigned from its infrared spectrum (absorption at ~4.46 μ for an acetylene group), its nuclear magnetic resonance (τ at 8.8, 7.6, and 2.7 of almost proper integration), and upon its comparison with the highly purified established product.

B. (6 Equiv of 1-Butynylcopper, 70–80°). The above reaction was repeated using III (5 g, 0.0131 mol), 1-butynylcopper (9.21 g, 0.079 mol), and pyridine (180 ml) in the indicated quantities. Separation as previously described and chromatography of the products on acid-washed alumina with Skellysolve B gave XXVIb (~0.47 g, 0.00154 mol, 12%) and then IIb (a yellow oil, 1.92 g, 0.00827 mol, 63%). The diacetylene exhibits infrared absorption at 4.47 μ (C$\equiv$C), nuclear magnetic resonance at τ 8.8 (triplet, 3 H), 7.6 (quartet, 2 H), and 2.7 (multiplet, 3 H), and a parent mass spectral peak at 232.2.

Diacetylene IIb was converted to its monopicrate as follows. Solutions of picric acid (0.40 g, 0.00175 mol) and of IIb (0.4 g, 0.00173 mol) in warm 95% ethanol (8 ml) were mixed. On standing orange needles of the monopicrate of IIb precipitated (0.42 g, 9.1×10^{-4} mol, 53%), mp 133–134° (from 95% ethanol).

Anal. Calcd for $C_{24}H_{19}N_8O_7$: C, 62.47; H, 4.12; N, 9.11. Found: C, 62.31; H, 4.05; N, 9.29.

Reaction of 1,8-Diiodonaphthalene (III) and 1-Hexynylcopper. A mixture of III (5.0 g, 0.031 mol), 1-hexynylcopper[27] (11.41 g, 0.0786 mol), and dry pure pyridine (150 ml) was stirred at 80° for 24 hr in a nitrogen atmosphere. Concentration, chromatography, and purification of the products as in the previous experiments yielded impure 8-iodo-1-(1-hexynyl)naphthalene (XXVIc)[28] and 1,8-bis(1-hexynyl)naphthalene (IIc, 1.46 g, 0.00506 mol, 39%[28b]) as a light yellow oil. Nuclear magnetic resonance occurs in IIc at τ 9.0 (distorted triplet, 3 H), 8.4 (multiplet, 4 H), 7.5 (distorted triplet, 2 H), and 2.6 (multiplet, 3 H). The ratio of aliphatic to aromatic hydrogen found for IIc is 3.05, theory 3.00.

Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.15; H, 8.34.

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[27] Prepared by addition of 1-hexyne (20.5 g, 0.25 mol) in 95% ethanol (80 ml) to a solution of cuprous chloride (54.4 g, 0.55 mol), water (200 ml), and concentrated ammonium hydroxide (200 ml).

[28] (a) In reaction of III with 2 equiv of 1-hexynylcopper at room temperature for 72 hr, the principal product is XXVIc. It is difficult to separate XXVIc from III and IIc. The structure of XXVIc is assigned from its acetylenic absorption at 4.4–4.5 μ, its nearly acceptable analysis and its nuclear magnetic resonance at τ 9.1 (distorted triplet, 3.1 H), 8.5 (multiplet, 4.5 H), 7.6 (multiplet, 2 H), and 2.5 (multiplet, 6.2 H). The ratio of aliphatic to aromatic hydrogen observed in XXVIc is 1.54, theory 1.50. (b) The yield of IIc is considerably higher than reported because of the difficulty in its separation from XXVIc.

Nuclear Magnetic Resonance Studies of *ortho*-Substituted Phenols in Dimethyl Sulfoxide Solutions. Electronic Effects of *ortho* Substituents[1]

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Abstract: The relative chemical shifts of O*H* in *ortho*-substituted phenols ($\Delta\delta_o$) in dimethyl sulfoxide (DMSO) solutions are linearly related to those for *para*-substituted phenols ($\Delta\delta_p$), are apparently free of steric effects, and afford an excellent measure of electronic effects of *ortho* substituents. The strong intermolecular hydrogen bond between the phenolic OH and DMSO is apparently oriented away from a single *ortho* substituent so that proximity interactions are minimal; 2,6-disubstituted phenols do exhibit serious steric interactions even in DMSO solution. The $\Delta\delta_p$ values are linearly correlated with Hammett σ_p^- constants, and, from the equation for this line ($\sigma^- = 0.720\Delta\delta - 0.038$) *ortho*-substituent constants (σ_o^-) for 32 substituents have been assigned. The *o*-acetyl and *o*-nitro substituents do not fit this correlation because of intramolecular hydrogen bonding. The new *ortho*-substituent constants are shown to correlate successfully the reactivity data for *ortho*-substituted compounds in 29 reaction series.

A well-known observation by investigators in the field of physical organic chemistry concerns the inability of the classical Hammett σ–ρ approach[2] (eq 1) to correlate rate or equilibrium data for *ortho*-substituted benzene derivatives. Discussions of linear free energy relationships with particular emphasis upon the Hammett equation have been the subject of several recent reviews.[3]

$$\log (k/k_0) = \sigma\rho \qquad (1)$$

Although to date theoretical and empirical studies of rate and equilibrium data have been generally unsuccessful in describing the reactivities of *ortho*-substituted compounds accurately, for some time chemists have had at their disposal the knowledge of some of the various interactions which may occur between the *ortho* substituent and the reaction center (including its solvation sheath). Some of the more important phenomena which may substantially affect reaction rates of *ortho*-substituted benzene derivatives are (1) both intra- and intermolecular hydrogen bonding; (2) substituent polar interactions transmitted to the reaction center either through the σ-bond network (inductive effect[4]) or more

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[1] (a) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 10, 1967, Abstracts S89, and at the Second Conference on Linear Free Energy Relationships, University of California, Irvine, March 27–29, 1968; (b) abstracted from the Ph.D. dissertation of M. T. T., submitted to Louisiana State University, May, 1968.

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