Synthesis and Properties of Two Annelated Annulenes

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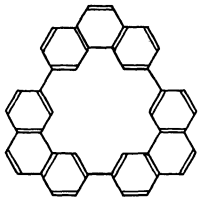
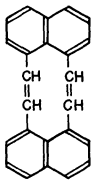
Two annelated tridehydro[18]annulenes, trinaphtho[1,9,8,7-*abc*: 1′,9′,8′,7′-*ghi*:1″,9″,8″,7″-*mno*]- and tribenzo [*a,g,m*]-5,11,17-tridehydro[18]annulenes (VI and VII), were synthesized by the Castro reaction of cuprous salts of 1-ethynyl-7-iodonaphthalene (IX) and 4-[*o*-iodophenyl]-3-buten-1-yne (XIV), respectively. The UV spectra of these annelated annulenes revealed an extended delocalization of π-electrons around the inner eighteen membered ring. However, from the chemical shifts of the inner protons (H_A and H_B) it is concluded that both VI and VII are non-aromatic compounds.

The molecular orbital theory of cyclic conjugated systems by Hückel predicted that systems containing $(4n+2)$ π-electrons would display an aromatic character. This rule has been substantially confirmed by many investigations of various nonbenzenoid conjugated systems, particularly by elegant works on annulenes and dehydroannulenes.[1] Thus it was thought to be of interest to prepare annelated annulenes in order to realize the effect of annelation on aromaticity of annulene and dehydroannulene. Recently some planar and non-planar annelated annulenes (I—V)[2] were synthesized, but no direct evidence for the presence of the aromatic character was found in the compounds except for an anion of dibenzocyclononatetraene (IV)[2d] and derivatives (V)[2e] of [18]annulene containing heterocycles.



I



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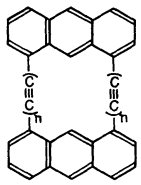
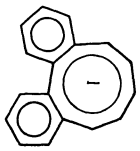
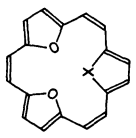


III, n=2,4

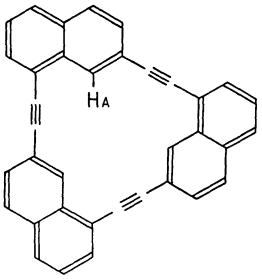


IV

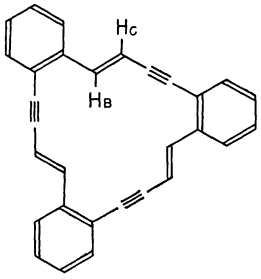


V, x=0,s

We have attempted to get better understanding of the effect of annelation on aromaticity. The present paper reports the results of a study of two planar annelated derivatives of aromatic 1,7,13-tridehydro[18]-annulene,[3] trinaphtho[1,9,8,7-*abc*: 1′,9′,8′,7′-*ghi*: 1″,9″, 8″,7″-*mno*]- and tribenzo[*a,g,m*]-5,11,17-tridehydro-[18]annulenes (VI and VII), to which Kekulé type structures of the inner eighteen membered ring systems can be assigned. The chemical shift of the inner protons (H_A and H_B) can provide significant information with regard to the diamagnetic ring current around the ring systems, *viz.*, the existence of aromatic character.



VI



VII

Results and Discussion

Synthesis 1-Acetyl-7-iodonaphthalene (VIII) was obtained by the acetylation of β-iodonaphthalene according to the Harnik method[4] in 18.5% yield. Ketone VIII was treated with phosphorus pentachloride in phosphorus oxychloride, followed by dehydrochlorination of the resulting chloride mixture with alcoholic potassium hydroxide to give 49% yield of 1-ethynyl-7-iodonaphthalene (IX). The Castro reaction[5] of dry cuprous salt of IX in pyridine afforded a cyclic acetylene compound in 8.0% yield. This compound was found to be fairly stable and can be kept without any change for a long time. The structure of VI was assigned to it based on the following. The lack of absorption due to the terminal ethynyl group in the IR- and NMR-

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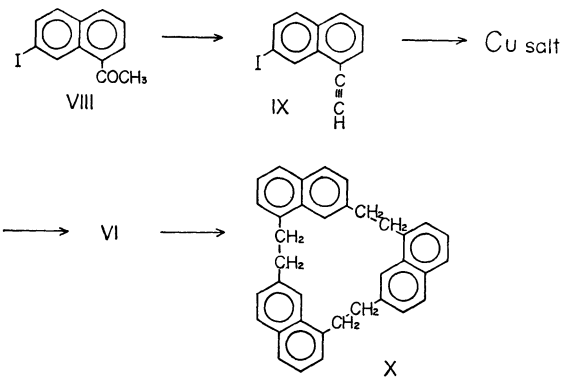
1) F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963); *Proc. Roy. Soc., Ser.* A, **297**, 173 (1967); F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, *Spec. Publs. Chem. Soc.*, No. 21 (1967), p. 75; E. Vogel, *Chimia*, **22**, 21 (1968).

2) a) H. A. Staab and H. Bräunling, *Tetrahedron Lett.*, **1965**, 45; H. A. Staab, H. Bräunling, and K. Schneider, *Chem. Ber.*, **101**, 879 (1968). b) R. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 530 (1968). c) S. Akiyama, S. Misumi, and M. Nakagawa, This Bulletin, **33**, 1293 (1960), **35**, 1829 (1962). d) P. J. Garratt and K. A. Knapp, *Chem. Commun.*, **1970**, 1215. e) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, London (1969); G. M. Badger, G. E. Lewis, and U. P. Singh, *Aust. J. Chem.*, **19**, 257, 1461 (1966); G. M. Badger, J. A. Elix, and G. E. Lewis, *ibid.*, **19**, 1221 (1966).

3) F. Sondheimer, Y. Amiel, and Y. Gaoni, *J. Amer. Chem. Soc.*, **81**, 1771 (1959), **84**, 270 (1962); L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *ibid.*, **84**, 4307 (1962); I. C. Calder, P. J. Garratt, H. C. Longuet-Higgins, F. Sondheimer, and R. Wolovsky, *J. Chem. Soc., C*, **1967**, 1041.

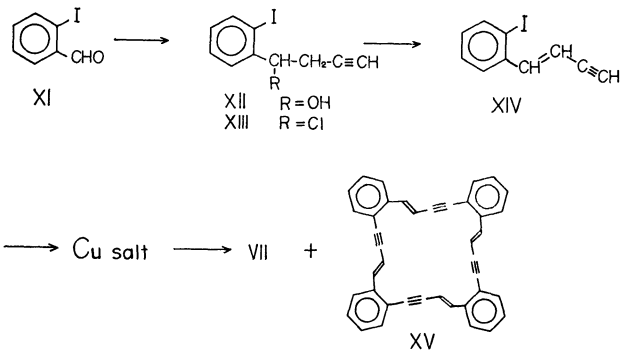
4) M. Harnik and E. V. Jensen, *Israel J. Chem.*, **3**, 13 (1965).

5) R. D. Stephens and C. E. Castro, *J. Org. Chem.*, **28**, 3313 (1963); C. E. Castro, E. J. Gaughan, and D. C. Owsley, *ibid.*, **31**, 4071 (1966); C. E. Castro, R. Havlin, V. K. Honwad, A. Malte, and S. Mojé, *J. Amer. Chem. Soc.*, **91**, 6464 (1969).



spectra suggests the cyclic structure of VI. Furthermore, the elemental analysis of VI and molecular weight determination of its hydrogenated product (X) which is satisfactorily soluble for vapour pressure osmometry established the formation of VI by trimolecular Castro reaction of IX.

An acetylenic alcohol (XII) was prepared by Reformatsky-type reaction of *o*-iodobenzaldehyde (XI)[6] with propargyl bromide using aluminum[7] in an excellent yield of around 80%. The normal Reformatsky reaction as well as the Grignard reaction afforded lower yields of XII. Chloride XIII, obtained by treatment of XII with phosphorus oxychloride, was dehydrochlorinated with methanolic potassium hydroxide. Chromatography of the reaction product on alumina gave *o*-iodophenylbutenyne (XIV) in an overall yield of 30% based on XII. The Castro reaction of cuprous salt of the butenyne XIV gave a cyclic trimer VII of fairly stable and bright yellow needles in 13.0% yield and a small amount of cyclic tetramer XV. Structures of trimer VII and tetramer XV were confirmed by elemental analysis, IR and NMR spectra and molecular weight determination.



Electronic Spectra The electronic spectra of VI and VII as well as those of diphenylbutenyne (XVI) and 1,7,13-tridehydro[18]annulene (XVII)[3] as reference substances are shown in Fig. 1. The spectrum of a cyclic trimer (I) of phenanthrene shows the maxima at the same wavelengths as those of biphenanthryl and

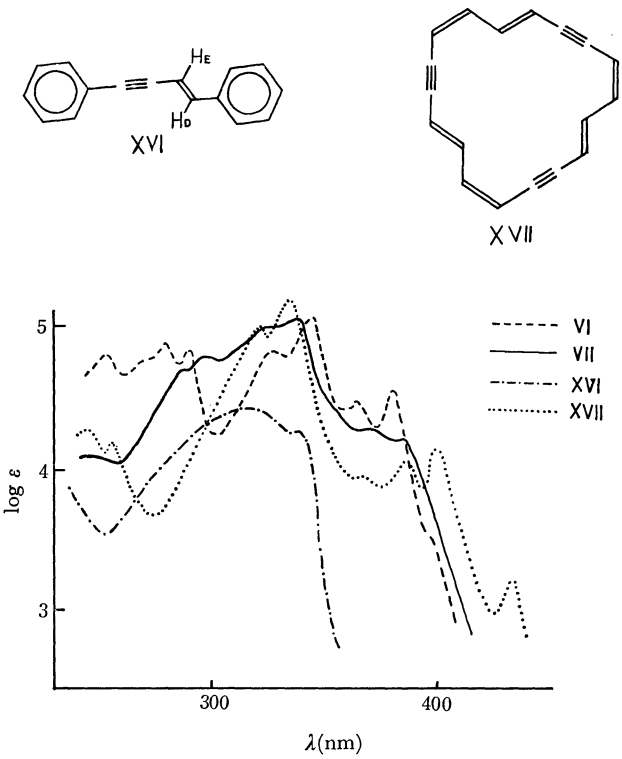


Fig. 1. The electronic spectra of VI, VII, XVI (in THF) and XVII (in isooctane).

terphenanthryl, whereas the maxima at the longest wavelength of VI and VII exhibit distinct red-shift as compared with those of tetramer XV and XVI. The absorption curve of VI is similar to that of XVII except for the lack of the maximum at near 430 nm, whereas VII shows broad and structureless absorption in contrast to VI and XVII. Thus, a comparison of these spectra suggests that both VI and VII are intermediates between I and XVII in respect of the delocalization of π-electrons. The fact that the by-product XV showed broad absorption curve and hypsochromic and hypochromic shifts of the maxima as compared with VII indicates a nonplanar structure of XV in agreement with a presumption from a skeletal molecular model.

Table 1. Chemical shifts (τ) and coupling constants (J) of inner protons of VI, VII, and XVII as well as those of olefinic protons of XV and XVI in $CDCl_3$

	VI	VII	XV	XVI	XVII[3]
τ	1.51[a]	3.36	3.51	3.69	2.44
		2.87	2.56	3.04	8.26
J		16.2	16.2	16.2	15.6 Hz

a) in $AsCl_3$ solution

NMR Spectra. The NMR spectra of VI, VII, and XVI are given in Table 1. The spectrum of VI shows two peaks, a singlet at τ 1.51 and a multiplet at τ 1.85—2.55, with an area ratio 1:5 and no other peak at a higher field. The peak at τ 1.51 is assigned to the proton H_A of naphthalene nuclei on account of its being singlet and of its area ratio to the other aromatic protons at τ 1.85—2.55. The position of the proton H_A is at a

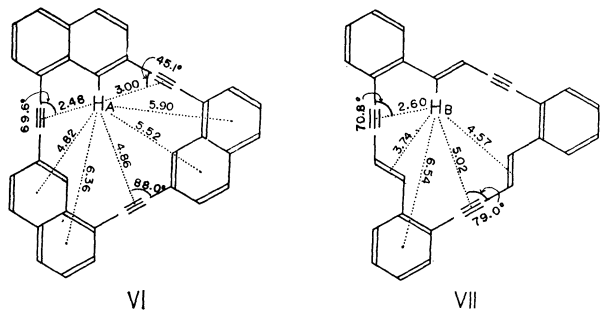
6) W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, **1941**, 487.

7) P. Läuger, M. Prost, and R. Charlier, *Helv. Chim. Acta*, **42**, 2379 (1959); K. Eiter and H. Oediger, *Ann. Chem.*, **682**, 62 (1965); F. Sondheimer, Y. Amiel, and Y. Gaoni, *J. Amer. Chem. Soc.*, **84**, 270 (1962).

lower field than that of α-proton (τ 2.19)[8] of naphthalene.

Two plausible elucidations may be given. First, the effect of diamagnetically induced ring current around the inner eighteen membered ring system is considered. If the magnitude of the ring current were not large, it would be overcome by the magnetic anisotropy of the triple bonds and other two naphthalene nuclei. As a result, the proton H_A may be observed at a slightly lower field than α-proton of naphthalene. Secondly, such a small shift of the proton H_A to the lower field would be only caused by the magnetic anisotropy of the triple bonds and naphthalene nuclei. In order to solve this problem, the magnitude of the magnetic anisotropies should be estimated. An estimate of the extent to which the shift of the proton H_A of VI is affected by both π-electron systems was performed according to the following McConnell equation[9] by using the distances and angles shown in Fig. 2.

$$\Delta\sigma = \Delta x \sum_{i=1}^{n} \frac{1}{3R^3}(1-3\cos^2\theta) \qquad (1)$$



For three triple bonds ($\Delta\chi = -11.8\times10^{-6}$ cm^3/mol),[10] the total shielding effect was calculated to be −0.20 ppm from equation (1). The shielding effect of two naphthalene nuclei, in which the shielding contribution of each naphthalene was approximated as a sum of ring currents of two benzene rings according to theoretical predictions,[11] was calculated to be −0.71 ppm by use of Johnson–Bovey table.[12] A total value −0.91 ppm due to both shielding effects was consequently found to be in good agreement with the observed shift, −0.68 ppm, from α-proton of naphthalene.[8] Similarly, the shift of proton H_B of VII from proton H_D of XVI was calculated as in VI, and the whole effect, −0.50 ppm, of double bonds, triple bonds, and benzene nuclei was found to be reasonable as compared with the observed shift −0.17 ppm. Table 1 also shows the equal coupling constant of olefinic protons in VII, XV, and XVI.

Consequently, a considerable delocalization of π-electrons in VI and VII was revealed in the electronic absorption spectra as aforementioned. However, it can be concluded that the results obtained from NMR spectra support the second elucidation stated above and provide no positive evidence for the presence of diamagnetically induced ring current in the eighteen membered ring systems of both VI and VII, and that both the annelated annulenes are non-aromatic.

Experimental

All melting points are uncorrected. The electronic spectra were taken on a Hitachi EPS-3T, the infrared spectra on a Jasco DS-402G, the NMR spectra on a Hitachi R-20, the mass spectra on a Hitachi RMU-7 and the molecular weight on a Knauer vapour pressure osmometer.

1-Ethynyl-7-iodonaphthalene (IX). A mixture of 1-acetyl-7-iodonaphthalene[4] (10.0 g, 33.8 mmol) and phosphorus pentachloride (10.4 g, 50 mmol) in phosphorus oxychloride (100 m*l*) was refluxed with stirring for 1 hr. After the reaction was over, phosphorus oxychloride was evaporated under reduced pressure and the residue was dried in a desiccator over potassium hydroxide overnight. To the crude chloride thus obtained was added 40 g of powdered potassium hydroxide and ethanol (100 m*l*). The mixture was stirred under gentle reflux for 30 min. The residual solid obtained by evaporation of ethanol in vacuum was triturated with benzene. The benzene extract was washed with water and dried over sodium sulfate. After the solvent was removed *in vacuo*, the residue (14.02 g) was chromatographed on alumina (300 g) with benzene-petroleum ether (1:9) to give yellow oil of IX, 4.60 g (49.0% yield). NMR ($CDCl_3$): τ 1.34 (s, proton at C_8), 2.1—2.9 (m, other arom. protons), 6.60 (s, ≡CH).

Mercuric Salt of IX: A solution of potassium mercuri-iodide[13] was obtained by adding 10% aq. sodium hydroxide (0.6 m*l*) to a mixture of mercuric chloride (0.275 g, 1.05 mmol) and potassium iodide (0.695 g, 4.2 mmol) in water (0.7 m*l*). To this was added a solution of IX (0.292 g, 1.05 mmol) in 6 m*l* of ethanol with stirring to yield white precipitate of mercuric salt. After it had been filtered immediately and washed with 50% aq. ethanol, the precipitate was recrystallized from benzene to afford 0.266 g (67.0%) of mercuric salt, colorless fine needles, mp 263.5—264.7°C (decomp.).

Found: C, 38.20; H, 1.63%. Calcd for $C_{24}H_{12}I_2Hg$: C, 38.19; H, 1.60%.

Trinaphtho[1,9,8,7-abc: 1′,9′,8′,7′-ghi: 1″,9″,8″,7″-mno]-5,11,17-tridehydro[18]annulene (VI). To a solution of Ilosvay's reagent[14] was added a solution of iodonaphthylacetylene (IX) (4.60 g, 16.5 mmol) in 80 m*l* of ethanol to give immediately yellow precipitate of cuprous salt. The cuprous salt obtained by filtration was washed with water, ethanol, and ether, successively, and dried *in vacuo* at 40°C, 3.52 g (62.5%).

The cuprous salt (1.73 g, 5.08 mmol) in dry pyridine (50 m*l*) was heated with stirring at 120°C under nitrogen for 8 hr. After cooling, the reaction mixture was poured into water (150 m*l*) and extracted with ether. The extract was washed with dil. hydrochloric acid, 5% aq. sodium bicarbonate, and water, successively, and dried over magnesium sulfate. After the solvent had been evaporated, the residue was chro-

8) F. A. Bovey, "NMR Data Table for Organic Compounds," Vol. 1, John Wiley & Sons, Inc., New York (1967), p. 265.

9) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

10) S. Castellano and J. Lorenc, *J. Phys. Chem.*, **69**, 3552 (1965); J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4813 (1966).

11) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed., Pergamon Press, London (1969), p. 96; N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443, (1962).

12) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

13) J. R. Johnson and W. L. McEwen, *J. Amer. Chem. Soc.*, **48**, 469 (1926); B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, **1951**, 893.

14) The reagent is obtained from cupric sulfate, aq. ammonia and hydroxylamine hydrochloride.

matographed on alumina with benzene. The residual solid (0.18 g) obtained from 4—6th fractions was recrystallized from benzene to afford 61 mg (8.0% yield) of VI, pale yellow needles, decomp. over 360°C.

Found: C, 95.72; H, 4.08%. Calcd for $C_{36}H_{18}$; C, 95.97; H, 4.03%. IR (KBr disk): 1610, 1585, 888, 831, 827 cm^{-1}. UV (in THF); λ_{max} (ε), 254 (59100), 266* (50200), 279 (78200), 290 (65600), 327 (69000), 342 (122000), 360 (25400), 365 (29000), 380 (33800), 396* nm (3410) (* inflection).

Reduction of VI. The acetylenic compound VI (40.3 mg, 9.0×10^{-2} mmol) and 10% palladium-on-charcoal (143 mg) in benzene (70 m*l*) were shaken with hydrogen at 50°C for 10 hr. After cease of hydrogen absorption, the catalyst was filtered and the solvent was evaporated under reduced pressure. The residue was recrystallized from petroleum ether to yield colorless needles of reduction product (X), mp 286—286.5°C, 38.8 mg (93.5%).

Found: C, 92.92; H, 6.54%. Calcd for $C_{36}H_{30}$: C, 93.46; H, 6.54%. Mol wt: Found; 477 (vapour pressure osmometry), 462 (mass spectrum). Calcd for $C_{36}H_{30}$; 462.6. IR (KBr disk): 830 (s), 748 (s) cm^{-1}. UV (in THF): λ_{max} (ε), 228 (193000), 278 (20600), 287 (22600), 316* (1580), 323 nm (1540) (* inflection).

o-Iodophenyl Propargyl Carbinol (XII). To aluminum metal plate (1.1 g, 40.7 mg atom), activated on heating with small pieces of mercuric chloride and iodine, was added a solution of propargyl bromide (7.2 g, 60 mmol) in dry tetrahydrofuran (10 m*l*) with stirring at room temperature. After consumption of aluminum metal, *o*-iodobenzaldehyde[5] (XI) (13.9 g, 60 mmol) in dry tetrahydrofuran (20 ml) was added dropwise to the solution at −60°C with stirring and the mixture was stirred at 0°C for 1 hr. After addition of saturated aqueous ammonium chloride (50 m*l*), the aqueous layer was separated and extracted twice with ether. The combined organic solution was washed, dried over magnesium sulfate and the solvent was removed under reduced pressure. A solution of the residue (15.64 g) in benzene-petroleum ether (1:1) was passed through a short column of alumina (30 g) and eluted with the same solvent. The effluent was concentrated to yield reddish brown oil of crude carbinol XII, 12.84 g (78.8%).

NMR ($CDCl_3$): τ 2.1—3.3 (m, 4H, arom.), 5.02 (quart., 1H, tert.), 6.96 (broad s, 1H, OH), 7.0—7.9 (m, 2H, $-CH_2-$), 7.95 (t, 1H, ≡CH).

4-[o-Iodophenyl]-3-buten-1-yne (XIV). To a cold solution of the carbinol XII (6.8 g, 25 mmol) in dry pyridine (30 m*l*) was added dropwise a mixture of dry pyridine (20 m*l*) and phosphorus oxychloride (20 m*l*) with stirring. The mixture was stirred below 5°C for 20 min, then carefully poured onto 300 g of ice and extracted with benzene. The extract was washed with water, dried and concentrated *in vacuo*. The oily residue was passed through a short column of alumina (15 g) with benzene-petroleum ether (1:1). The effluent was evaporated under reduced pressure to yield reddish brown oil of *o*-iodophenyl propargyl chloride (XIII), 3.26 g.

A mixture of the crude chloride XIII (3.26 g) and powdered potassium hydroxide (1.68 g, 30 mmol) in methanol (7 m*l*) was stirred at 50°C for 40 min. The reaction mixture was poured into 140 m*l* of water and extracted with benzene. The extract was washed with water, dried over magnesium sulfate and concentrated *in vacuo*. The residue (2.10 g) was dissolved in benzene-petroleum ether (3:17) and passed through a short column of alumina. The effluent was evaporated under reduced pressure to give unstable XIV as pale yellow oil, 1.77 g, 28.0% yield based on the carbinol XII (34.3% yield in the other run).

NMR ($CDCl_3$): τ 2.1—3.4 (m, 4H, arom.), 2.84 (d, 1H, olefin. H_1 at C_4), 4.10 (double d, 1H, olefin. H_2 at C_3), 6.94 (d, 1H, ≡CH), $J_{H_1,H_2}=15.6$ Hz.

Mercuric Salt of XIV: Mercuric salt of XIV was obtained according to the same method as IX and recrystallized from benzene, colorless needles, mp 227—232°C (decomp.).

Found: C, 34.06; H, 1.75%. Calcd for $C_{20}H_{12}I_2Hg$: C, 33.99; H, 1.71%.

Tribenzo[a,g,m]-5,11,17-tridehydro[18]annulene (VII). Well dried cuprous salt (10.0 g, 31.5 mmol) of XIV, obtained in a yield of 77% according to the same method as for IX, was heated in dry pyridine (350 m*l*) with stirring under nitrogen. The mixture was heated up to 120°C and the stirring at this temperature was continued for 8 hr. After cooling, the mixture was poured into 1.5 *l* of water and extracted with benzene. The extract was washed with dil. hydrochloric acid, 5% aq. sodium bicarbonate and water, successively, and dried over magnesium sulfate. The solvent was removed *in vacuo* to give 3.81 g of residue. The residue was chromatographed on alumina (250 g) with benzene-petroleum ether (1:1). The column was eluted with benzene-petroleum ether (the ratios 1:1 for 20 fractions and 7:3 for the successive 10 fractions of each 50 m*l*). The solid, obtained from 5—8th fractions, was recrystallized from benzene to give colorless prisms of the cyclic tetramer XV, 0.124 g (2.4% yield), decomp. over 260°C.

Found: C, 95.00; H, 4.93%. Calcd for $C_{40}H_{24}$: C, 95.21; H, 4.79%. Mol wt: Found; 509 (vapour pressure osmometry). Calcd for $C_{40}H_{24}$; 504.6. IR (KBr disk): 950 (s), 750 (s), 675 (s), 526 (m), 503 (m), 485 cm^{-1} (m). UV (in THF): λ_{max} (ε), 252 (36200), 292.5 (71700), 312.5 nm (70900).

The combined effluent of 14—30th fractions was evaporated *in vacuo* and the residue was recrystallized from benzene to afford yellow needles of the cyclic trimer VII, 0.527 g (13.0% yield), decomp. over 275°C.

Found: C, 95.37; H, 4.59%. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79%. Mol wt: Found; 372 (vapour pressure osmometry). Calcd for $C_{30}H_{18}$; 378.5. IR (KBr disk): 950 (s), 750 (s), 745 (s), 515 (m), 498 cm^{-1} (m). UV in (THF): λ_{max} (ε), 241.5 (12300), 251* (12000), 287* (45500), 297.7 (58900), 325 (103000), 337 (114000), 366 (19800), 384 nm (15800) (* inflection).

1,4-Diphenylbutenyne (XVI). Butenyne XVI was prepared by the Castro reaction of the cuprous salt of 4-phenyl-3-buten-1-yne, obtained according to Eiter,[7] with iodobenzene, mp 96.7—97.8°C (lit,[15] mp 95°C).

15) V. Grignard and Tcheoufaki, *C. R. Acad. Sci., Paris*, **188**, 1533 (1929); *Rec. Trav. Chim. Pay-Bas*, **48**, 903 (1929).