Dehydroannulenes. II. Syntheses of Diatropic Dimethyldiphenyl- and Tetraphenyl-tetrakisdehydro[18]annulenes

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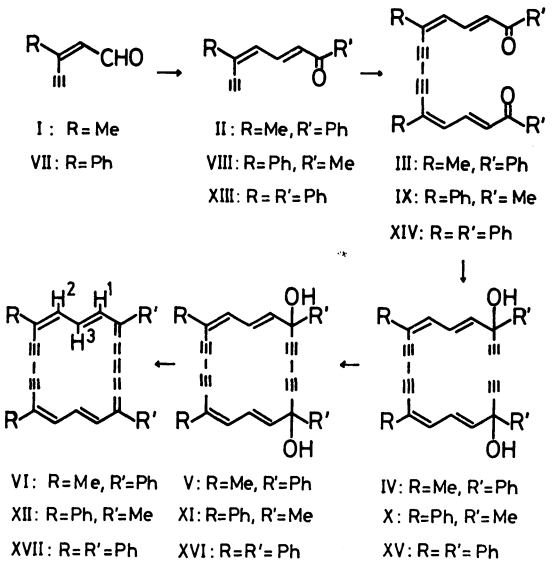
Syntheses of dimethyldiphenyl-(VI and XII) and tetraphenyltetrakisdehydro[18]annulenes (XVII) have been performed. It was found that the reaction sequence used for the synthesis of tetramethyltetrakisdehydro[18]-annulene can be used generally for the preparation of tetrakisdehydro[18]annulenes having various substituents. The annulenes (VI, XII, and XVII) were found to be strongly diatropic having high conformational stability. Remarkable stability is provided by introduction of phenyl groups accompanied with decrease in solubility of the annulene. Dimethyldiphenyl derivative was prepared by two different routes which will lead to isomers (VI and XII) with respect to the relative positions of the diacetylene and hexapentaene linkages to the substituent groups. The isomers (VI and XII) can be regarded as presumably identical, but precise agreement of NMR and UV spectra could not be attained. Bathochromic shift of UV spectra of phenyl substituted annulenes compared with tetramethyl analogue indicated that phenyl groups exert prominent perturbation on the annulene system.

As reported in the previous papers,[1] tetramethyltetrakisdehydro[18]annulene showed a strong diastropicity and a high conformational stability, but was found to be rather unstable. Therefore, the syntheses of tetradehydro[18]annulenes having various substituent groups are considerable interest from various points of view. Firstly, the preparation should offer information on the scope of validity of the reaction sequence used for the synthesis of tetramethyl derivative.[1] Secondly, it can be expected to find out substituent which stabilizes the tetradehydro[18]annulene system making possible further investigation on this type of dehydroannulenes. Finally, information on conjugative effects between the annulene ring and substituent group will be obtained from these studies.

The present paper deals with the synthesis and properties of dimethyldiphenyl- (VI, XII) and tetraphenyltetrakisdehydro[18]annulenes (XVIII).[2]

Synthesis. Synthesis of dimethyldiphenyltetrakisdehydro[18]annulene was performed according to two different route outlined in Scheme.

Dieneyne ketone (II) was obtained by the aldol condensation of 3-methyl-2-penten-4-ynal (I)[1,3] with acetophenone by the reported method[3b] with modification. Oxidative coupling of the ketone (II) by cupric acetate in pyridine–methanol[4] gave sparlingly soluble diketone (III) as yellow crystals. A solution of the diketone (III) in hot benzene was added to a suspension of lithium acetylide–ethylenediamine complex[5] in the same solvent saturated with acetylene to give acyclic glycol (IV). 18-Membered cyclic glycol (V) was obtained as a viscous yellow liquid by the oxidative coupling of IV under high dilution conditions. Treatment of the cyclic glycol (V) with stannous chloride in concentrated hydrochloric acid yielded 5,10-dimethyl-1,14-diphenyl-6,8,-15,17-tetrakisdehydro[18]annulene (VI) as black purple needles in an almost quantitative yield. Full hydrogenation of VI in ethyl acetate over platinum oxide catalyst yielded a liquid hydrocarbon corresponding to dimethyldiphenylcyclooctadecane.



β-Chlorovinyl ketone was prepared by the reported method[6] with modification, which was converted into 1-chloro-3-phenyl-1-penten-4-yn-3-ol in a high yield on treatment with sodium acetylide in liquid ammonia. Anionotropic rearrangement of the alcohol by acid treatment yielded 3-phenyl-2-penten-4-ynal (VII). NMR spectrometry reveals that the aldehyde (VII) is pure *cis*-isomer with respect to the formyl and ethynyl groups. Diene ketone (VIII) obtained by the aldol condensation of VII with acetone was oxidatively coupled by cupric acetate in pyridine[4] to give diketone (IX). Bis-ethynyl alcohol (X) prepared by the reaction of lithium acetylide–ethylenediamine complex[5] with IX yielded cyclic glycol (XI) on treatment with cupric acetate in pyridine–methanol–ether under high dilution conditions. Reduction of the crude cyclic glycol (XI) with stannous chloride dihydrate in concentrated hydrochloric acid gave 9,10-dimethyl-1,14-diphenyl-6,8,15,-17-tetrakisdehydro[18]annulene (XII) as black purple crystals.

The aldol condensation of acetophenone with VII gave diphenyldiene ketone (XIII) in a high yield. The ketone (XIII) was converted into 1,5,10,14-tetraphenyl-6,8,15,17-tetrakisdehydro[18]annulene (XVII, black purple needles) by similar reaction sequence *via* diketone (IXV), acyclic glycol (XV) and cyclic glycol (XVI).

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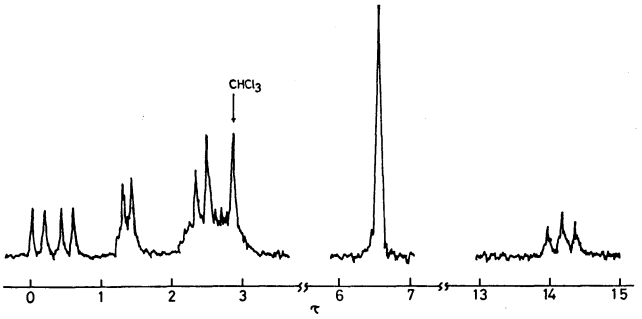

Fig. 1. 60 MHz NMR spectrum of VI in $CDCl_3$.

Properties. The NMR spectrum indicates that 1,14-dimethyl-5,10-diphenyl-6,8,15,17-tetrakisdehydro-[18]annulene (VI) is strongly diatropic exhibiting the inner proton (H^3) signal at extremely high-field (t, τ 14.20) and the outer proton (H^1 and H^2) signals at low-field (H^1, d, τ 0.12; H^2, d, τ 0.54) (Fig. 1). A low-field multiplet (τ 1.36) in the aromatic region could be assigned to *o*-protons of the phenyl groups, which suffer the deshielding effect of diamagnetic ring current of the annulene ring, and the higher-field multiplet at *ca.* τ 2.5 to the *m,p*-protons of the phenyl groups. The signal of methyl protons observed at τ 6.56 as a sharp singlet. As recorded in Table 1, VI showed essentially temperature independent NMR spectra similar to the tetramethyl analogue[1] indicating a high conformational stability of the tetrakisdehydro[18]annulene skelton. The electronic spectrum of VI illustrated in Fig. 2 showed characteristic feature of [4*n*+2]annulenes consisting of three main absorption band.

The dimethyldiphenyltetrakisdehydro[18]annulene (XII) gave an identical IR spectrum with that of VI. However, perfect coincidence of NMR and electronic spectra between VI and XII could not be attained, presumably owing to their instability, and to slight difference in their purity. In spite of the minor difference in physical property, the tetrakisdehydro[18]-annulenes (VI and XII) seemed to be an identical compound.[7]

TABLE 1. NMR PARAMETERS OF VI IN $CDCl_3$
(τ-Values, 100 MHz)

Temperature (°C)	H^1	H^2	*o*-H of phenyl	Methyl-H	H^3
−60	−0.08	0.40	1.18	6.45	14.61
−40	−0.13	0.34	1.17	6.45	14.45
−20	−0.09	0.34	1.20	6.47	14.41
− 6	−0.06	0.40	1.23	6.51	14.35
+25	0.00	0.46	1.26	6.53	14.27
+37	−0.02	0.44	1.29	6.51	14.14
+61	0.01	0.46	1.30	6.53	14.00

Tetraphenyltetrakisdehydro[18]annulene (XVIII) also showed an aromatic NMR spectrum exhibiting the inner proton (H^3) signal at τ 13.19 (t) and the outer proton (H^1 and H^2) signal at τ-0.31 (d). It is to be noted that the replacement of methyl with phenyl groups causes an appreciable down-field shift of all signals (Fig. 3).[8]

The stability of tetrasubstituted tetrakisdehydro[18]-annulenes was found to increase with the increase of phenyl substitution in the sequence of tetramethyl-<dimethyldiphenyl- (VI or XII)<tetraphenyl-derivatives (XVIII). However, as can be seen from Fig. 2, phenyl substitution caused remarkable bathochromic shift of absorption bands and intensification of the longest wavelength band indicating the perturbation of phenyl group on the annulene system. Furthermore, poor solubility of the tetraphenyl derivative (XVIII) in NMR solvents brought about experimental difficulty. In spite of the fairly effectual stabilization effect, phenyl group, aside from its interesting conjugative effect, can not be regarded as the most adequate substituent for the study of aromaticity of annulene system.

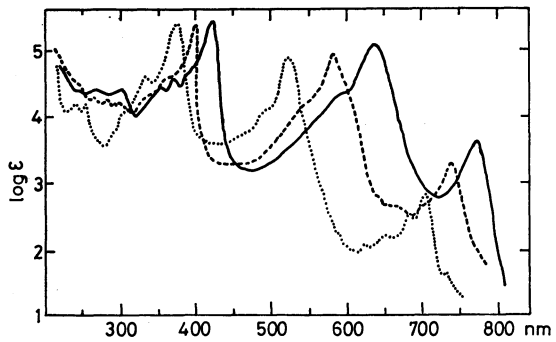

Fig. 2. Electronic spectra of tetrasubstituted tetrakisdehydro[18]annulenes. VI (---), XVII (—) and the tetramethyl analogue (···) in THF.

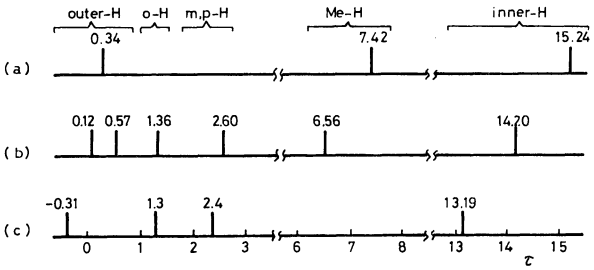

Fig. 3. Chemical shifts of tetrasubstituted tetrakisdehydro [18]annulenes. (a) tetramethyl-, (b) dimethyldiphenyl- (VI), and (c) tetraphenyl- (XVII) derivatives.

Experimental

All melting and boiling points are uncorrected. Brockmann alumina (Act. II—III) was used for chromatography. Evaporation of solvent was performed under reduced pressure in nitrogen atmosphere under shielding from light. A high dilution apparatus was used for the oxidative cyclization reaction of acyclic glycols. The IR, UV and mass spectra were obtained on a Hitachi EPI-2, a Hitachi EPS-3 and a Hitachi RMU-7HR spectrometers, respectively. Shoulder in UV spectrum is denoted by sh, and wavelength of absorption maximum is recorded in nm and ε-value is given in parentheses. NMR spectra were obtained on a Varian A-60 and JNM-4H-100 spectrometers. Chemical shift and coupling constant are given in τ-value with respect to TMS as an internal standard and in Hz, respectively.

1-Benzoyl-4-methyl-1,3-hexadien-5-yne (II). To a water-cooled and stirred mixture of I (2.04 g, 0.0217 mol)[1,3] and acetophenone (2.50 g, 0.0208 mol) was added dropwise a

mixture of 20% aqueous sodium hydroxide (8 ml) and ethanol (4 ml). After being stirred for 15 min, 1M sulfuric acid (30 ml) was added to the reaction mixture, and extracted with ether. The ethereal extracts were worked up in the usual way. The product dissolved in benzene was chromatographed on alumina, and eluted with the same solvent to give II, pale yellow rods, mp 83—87 °C (lit, 86—88 °C),[3b] 1.751 g (40%), IR (Nujol): 3230, 2090, 1655, 1590, 1575, 1360, 1280, 890, 770 cm^{-1}.

1,12-Dibenzoyl-4,9-dimethyl-1,3,9,11-dodecatetraene-5,7-diyne (III). A solution of II (2.23 g, 0.0114 mol) in benzene (50 ml) and methanol (30 ml) was added to a stirred solution of cupric acetate monohydrate (4.5 g) in pyridine (150 ml) and methanol (150 ml). The mixture containing yellow crystals was stirred overnight at room temperature. After the reaction mixture had been concentrated, the insoluble material was collected by filtration and washed throughly with water. The material thus obtained was dried and dissolved in boiling benzene. The hot benzene solution was passed through a short column of alumina. Upon cooling the filtrate, III was obtained as sparingly soluble yellow needles, mp *ca.* 150 °C (dec.), 1.33 g (60%), IR (KBr-disk): 3042, 3002, 1655, 1597, 1585, 1573, 1445, 1432, 1355, 1272, 1220, 1185, 1033, 1020, 980, 903, 853, 840, 774, 688, 658 $cm.^{-1}$

Found: C, 86.29; H, 5.88%. Calcd for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68%.

7,12-Dimethyl-3,16-diphenyl-4,6,12,14-octadecatetraene-1,8,10,17-tetrayne-3,16-diol (IV). A solution of III (1.20 g, 0.00307 mol) in hot benzene (2000 ml) was added over 1.5 hr-period to a stirred suspension of lithium acetylide–ethylenediamine complex (10 g) in the same solvent (200 ml) saturated with acetylene at 35 °C. After acetylene had been introduced for further 3.5 hr at 35—38 °C, the reaction mixture was cooled to 5—7 °C, and water (50 ml) was added. The mixture was worked up in the usual manner. The product dissolved in benzene was chromatographed on alumina (40 g). Fractions obtained by elution with benzene and ethyl acetate, which showed satisfactory IR spectra, were combined and rechromatographed on alumina (10 g). IV was obtained as an amorphous yellow solid, 0.90 g (67%), IR (KBr-disk): 3500, 3350, 3260, 3050, 3020, 2920, 2850, 2190, 2110, 1600, 1580, 1470, 1445, 1370, 1345, 1280, 1170, 1070, 1030, 1015, 1000, 970, 930, 760, 690, 670 cm^{-1}.

Attempts to crystallized this material were failed.

10,15-Dimethyl-1,6-diphenyl-7,9,15,17-cyclooctadecatetraene-2,4,11,13-tetrayne-1,6-diol (V). To a stirred and refluxing solution of cupric acetate monohydrate (1.63 g) in pyridine (2000 ml), methanol (500 ml) and ether (500 ml) was added at 70±3 °C a solution of acyclic glycol (IV, 0.90 g, 2.05mmol) in pyridine (300 ml), methanol (100 ml) and ether (100 ml) over a period of 18 hr. After being stirred for further 1.5 hr at the same temperature, the reaction mixture was concentrated to *ca.* 100 ml at 40±2 °C. The concentrate was poured into 1M hydrochloric acid (3600 ml) under ice-cooling, and extracted with benzene and ethyl acetate. Combined extracts were worked up in the usual way. The product dissolved in benzene was chromatographed on alumina (150 g). Elution with ethyl acetate–benzene gave V as partly crystallized liquid, 242 mg (26.8%), IR (neat): 3300, 2180, 1600, 1580, 1480, 1450, 1035, 970, 760, 695, 670 cm^{-1}.

This material was used directly for the following reaction.

5,10-Dimethyl-1,14-diphenyl-6,8,15,17-tetrakisdehydro[18]annulene (VI). A solution of stannous chloride dihydrate (143.4 mg, 0.0637 mmol) in concentrated hydrochloric acid (3 ml) was added to a stirred suspension of the cyclic glycol (V, 113.7 mg, 0.0258 mmol) in pentane (10 ml) and benzene (5 ml). After being stirred for 10 min, benzene (10 ml) was added to the reaction mixture. After 20 min, ether (30 ml) and water were added to the mixture, and organic layer was treated in the usual fashion. The product dissolved in benzene was chromatographed on alumina (20 g). Elution with the same solvent yielded VI, black purple needles, 102.0 mg (97%), which was recrystallized from petroleum ether–benzene to give analytical specimen of VI, decomposed at 94 °C without fusion, UV: λ_{max}^{THF} 244 (16700), 249.5 (15800), 255.5 (18400), 261 sh (15600), 270 sh (15400), 278 (17600), 298 (13800), 299 (14200), 325 sh (14800), 348 sh (29300), 354 sh (30200), 370 sh (38200), 384 sh (61400), 400 (21800), 544 sh (17900), 584 (88900), 650 sh (738), 670 (443), 715 sh (560), 742 (1930), NMR (60 MHz, $CDCl_3$): 0.12 (d, J=14, H^1), 0.54 (d, J=14, H^2), 1.36 (m, *o*-H of phenyl), 2.3—2.9 (m. *m,p*-H of phenyl), 6.56 (s, CH_3), 14.20 (t, H^3).

Found: C, 94.23; H, 5.61%. Calcd for $C_{32}H_{22}$: C, 94.54; H, 5.46%.

1,6-Dimethyl-10,15-diphenylcyclooctadecane. The annulene (VI, 16.9 mg) in ethyl acetate (15 ml) was reduced over pre-reduced platinum oxide catalyst ($PtO_2 \cdot 2H_2O$, 12.6 mg). The reduction product was chromatographed on alumina and eluted with pentane. Dimethyldiphenylcyclooctadecane was obtained as a colorless liquid, M^+ 432 (Calcd for $C_{32}H_{48}$: 432), IR (neat): 3040, 3010, 2950—2850, 1455, 1375, 1600, 1493, 757, 695 cm^{-1}.

β-Chlorovinyl Phenyl Ketone. To an ice-cooled solution of benzoyl chloride (37 g, 0.264 mol) in chloroform (80 ml) was added crashed anhydrous aluminum chloride (37 g, 0.278 mol) in a rate to keep the temperature below 10 °C. Vinyl chloride was introduced to the mixture below 20 °C until no more absorption could be observed (*ca.* 3 hr). The reaction mixture was poured onto ice (300 g).[6] The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer and extracts were worked up in the usual way. Distillation of the product under reduced pressure yielded β-chlorovinyl phenyl ketone in a high yield under elimination of hydrogen chloride, bp 134—136 °C/2395 Pa, 36.2 g (83%).

1-Chloro-3-phenyl-1-penten-4-yn-3-ol. 1) To a solution of ethynylmagnesium bromide in tetrahydrofuran (120 ml) prepared from ethyl bromide (12 g, 0.11 mol) and magnesium (2.4 g, 0.10 mol)[9] was added over 20 min-period a solution of β-chlorovinyl phenyl ketone (11.0 g, 0.066 mol) in the same solvent (15 ml). After being stirred overnight at room temperature, saturated aqueous ammonium chloride solution was added to the reaction mixture under cooling in an ice-salt bath. The aqueous layer was extracted with ether and combined with the organic layer. The organic solution was worked up in the usual manner, and the crude product was distilled under reduced pressure to give pure ethynyl alcohol, bp 118—119 °C/465.5 Pa, 8.3 g (63%). Explosive decomposition sometimes occurred at the final stage of distillation. 2) A solution of β-chlorovinyl phenyl ketone (87.1 g, 0.523 mol) in tetrahydrofuran (270 ml) was added over 40 min-period at −60 °C to a stirred solution of lithium acetylide (from lithium, 4.1 g, 0.587 mol) in liquid ammonia (600 ml). After the mixture had been stirred overnight at −60∼−30 °C, the ammonia was allowed to evaporate. Saturated ammonium chloride solution was added to the residue under strong cooling with ice-salt bath. The aqueous layer was extracted with ether, and combined with the organic layer. The product, obtained by working up the organic solution in the usual way, was distilled under reduced pressure to give pure alcohol, bp 92—97 °C/66.5 Pa, 77.5 g (77%).

3-Phenyl-2-penten-4-ynal (VII). A mixture of 1-chloro-3-phenyl-1-penten-4-yn-3-ol (77.5 g, 0.403 mol), tetrahydrofuran (300 ml) and 1M sulfuric acid (1800 ml) was stirred

under nitrogen atmosphere for 3 days at room temperature. Sodium chloride was added to the reaction mixture, and the aqueous layer was extracted with ether. The extracts combined with the organic layer was worked up in the usual way. The crude crystals deposited on concentration of the organic solution were recrystallized from carbon tetrachloride–cyclohexane (2: 1) to give pure VII, unstable crystals, mp *ca.* 65 °C, 38.2 g (61%), NMR (60 MHz, CCl_4): 6.25 (s, 1H, ethynyl H), 3.20 (d, $J=7$, 1H, olefinic H), 2.50 (m, 3H, *m, p*–H of phenyl), 2.15 (m, 2H, *o*–H of phenyl), −0.25 (d, $J=7$, formyl H). NMR spectrum indicates that VII thus prepared is pure *cis*–isomer with respect to the formyl and ethynyl groups.

Found: C, 84.39; H, 5.23%. Calcd for $C_{11}H_8O$: C, 84.54; H, 5.16%.

2,4-Dinitrophenylhydrazone: orange needles, mp 177—178 °C.

Found: C, 60.71; H, 3.59; N, 16.70%. Calcd for $C_{17}H_{12}N_4O_4$: C, 60.71; H, 3.60; N, 16.66%.

6-Phenyl-3,5-octadien-7-yn-2-one (VIII). A solution of sodium hydroxide (0.70 g, 17.5 mmol) in ethanol (4 ml) and water (4 ml) was added to an ice-cooled solution of VII (2.70 g, 17.3 mmol) in acetone (28 ml). After being stirred for 2 hr at the same temperature, the reaction mixture was neutralized with 1M hydrochloric acid and mixed with water (300 ml). The mixture was extracted with benzene. After working up in the usual way, the product dissolved in carbon tetrachloride was passed through a column of alumina. The crystals obtained from the filtrate (1.16 g, 47%) were dissolved in the same solvent and again passed through a column of alumina. Pure VIII was obtained by recrystallization from ethanol, yellow crystals, mp 70.0—72.0 °C, IR (KBr–disk): 3250, 2080, 1662, 985, 953 $cm.^{-1}$

Found: C, 85.32; H, 6.06%. Calcd for $C_{14}H_{12}O$: C, 85.68 H, 6.10%.

2,4-Dinitrophenylhydrazone: mp 180—190 °C (dec.).

Found: C, 64.13; H, 4.92; N, 14.84%. Calcd for $C_{20}H_{16}N_4O_4$: C, 63.82; H, 4.29; N, 14.89%.

6,11-Diphenyl-3,5,11,13-hexadecatetraen-7,9-diyn-2,15-dione (IX). A mixture of VIII (1.00 g, 5.10 mmol), cupric acetate monohydrate (5.0 g), pyridine (25 ml) and methanol (25 ml) was stirred for 3 hr at room temperature. The reaction mixture was poured into ice-cooled 3M hydrochloric acid (150 ml) and extracted with benzene. After washing and drying, the extracts were concentrated and chromatographed on alumina. Recrystallization of crude crystals from benzene gave pure IX, yellow crystals, mp 130—150 °C (dec.), 0.62 g (63%), IR (KBr–disk): 1663, 1643, 998, 963 cm^{-1}.

Found: C, 86.07; H, 5.70%. Calcd for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68%.

3,16-Dimethyl-7,12-diphenyl-4,6,12,14-octadecatetraene-1,8,10,17-tetrayne-3,16-diol (X). To an ice-cooled and stirred suspension of lithium acetylide–ethylenediamine complex[5] (0.5 g 5.4 mmol) in tetrahydrofuran (50 ml) was added over 10 min-period a solution of IX (300 mg, 0.77 mmol) in the same solvent (30 ml). After being stirred for 3 hr, saturated aqueous solution of ammonium chloride was added to the reaction mixture, and the aqueous layer was extracted with ether. The extracts were combined with the organic layer, and worked up in the usual way. Crude product was chromatographed on alumina, and eluted with benzene–ether. Crude X (208 mg) obtained as light brown liquid on concentrating the eluates was used without further purification for the following reaction.

1,4-Dimethyl-5,10-diphenyl-2,4,10,12-cyclooctadecatetraene-6,8,15,17-tetrayne-1,14-diol (XI). To a stirred and refluxing mixture of cupric acetate monohydrate (3.0 g, 1.5 mmol), pyridine (40 ml), methanol (20 ml) and ether (40 ml) was added over 2 hr-period a solution of crude X (208 mg) in pyridine (25 ml) and ether (25 ml). After being stirred and refluxed for further 2 hr, the reaction mixture was concentrated to *ca.* 80 ml. The concentrate was poured into 3M hydrochloric acid (200 ml) and extracted with benzene. The extracts, after being washed and dried, were concentrated to give crude cyclic glycol (XI), which was chromatographed on alumina, and eluted with benzene–ether. XI (133 mg) obtained from the eluates as light brown liquid was subjected to the further reaction.

1,14-Dimethyl-5,10-diphenyl-6,8,15,17-tetrakisdehydro[18]annulene (XII). The crude cyclic glycol (XI, 133 mg) dissolved in benzene (40 ml) was mixed under nitrogen atmosphere with a solution of stannous chloride dihydrate (0.4 g, 1.8 mmol) in concentrated hydrochloric acid (30 ml). After being stirred for 1 hr at room temperature, the reaction mixture was poured into cold water. The organic layer, after washing and drying, was concentrated, and the residue redissolved in benzene was chromatographed on alumina. Black purple crystals (63 mg, 17% based on IX) obtained from benzene eluates were recrystallized from benzene–cyclohexane, and dried *in vacuo* (0.4 Pa) for 5 hr at room temperature to give pure XII, decomposed at 94 °C without fusion, UV: λ_{max}^{THF} 244 (16600), 256 (19700), 270 sh (15300), 277.5 (17800), 292 sh (13900), 299 (14300), 324 sh (14600), 346 sh (30000), 354 sh (30800), 368 sh (38300), 385 sh (62300), 401 (212000), 542 sh (17400), 582 (85700), 666 sh (371), 715 sh (495), 742 (1790) [A maximum at 249 nm in XII which was also observed in VI disappeared on drying the crystals *in vacuo* for 5 hr.], NMR (60 MHz, $CDCl_3$): 0.05 (d, $J=14$, H^2), 0.49 (d, $J=14$, H^1), 1.35 (m, *o*–H of phenyl), 2.4 (m, *m,p*–H of phenyl), 6.54 (s, CH_3), 14.20 (t, H^3). The IR spectrum of XII (KBr–disk) was found to be perfectly identical with that of VI. Found: C, 94.46; H, 5.49%. Calcd for $C_{32}H_{22}$: C, 94.54; H, 5.46%.

CT Complex of XII with Trinitrofluorenone. A solution of XII (28 mg, 0.070 mmol) and 2,4,7-trinitrofluorenone (30 mg, 0.095 mmol) in benzene (15 ml) and methanol (15 ml) was allowed to stand in a refrigerator. Black purple crystals deposited decomposed at *ca.* 180 °C forming colorless solid. Elemental analysis indicates that the 1: 1 CT complex contains 1 mol of benzene as a solvent of crystallization.

Found: C, 76.42; H, 4.20; N, 5.16%. Calcd for $C_{32}H_{22}\cdot C_6H_6\cdot C_{13}H_5N_3O_7$: C, 76.58; H, 4.16; N, 5.25%.

1,5-Diphenyl-2,4-heptadien-6-yn-1-one (XIII). To an ice-cooled and stirred solution of phenylpentynal (VII, 2.70 g, 17.3 mmol) and acetophenone (2.08 g, 17.3 mmol) in ethanol (30 ml) was added a solution of sodium hydroxide (0.8 g, 22 mmol) in ethanol (3 ml) and water (3 ml). After 20 min, crystals deposited were collected by filtration and washed with water and ethanol. The crystals (3.70 g, 83%) were recrystallized from ethanol to give pure XIII, yellow crystals, mp 82.8—83.4 °C, IR (KBr–disk): 3240, 2070, 1653, 1016, 976 cm^{-1}.

Found: C, 88.01; H, 5.44%. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46%.

1,5,10,14-Tetraphenyl-2,4,10,12-tetradecatetraene-6,8-diyne-1,14-dione (XIV). A solution of XIII (3.70 g, 14.3 mmol) in pyridine (25 ml) was added at room temperature to a mixture of cupric acetate monohydrate (7.6 g, 38 mmol), pyridine (25 ml) and methanol (25 ml). After being stirred for 2 hr at the same temperature, the reaction mixture containing crystals was cooled in an ice-bath, and the crystals were collected and washed with methanol and water (3.2 g, 87%). The filtrate and washings were concentrated and poured into 2M hydrochloric acid, and extracted with benzene. The benzene extracts were worked up in the usual way. The residue dissolved

in benzene was passed through a column of alumina. Second crop of XIV (0.1 g) was obtained from the filtrate. Recrystallization of the crystals from benzene gave pure diketone (XIV), orange crystals, mp 159.7—160.2 °C, IR (KBr-disk): 1648, 1015, 971 cm^{-1}.

Found: C, 88.55; H, 5.00%. Calcd for $C_{38}H_{26}O_2$: C, 88.69; H, 5.09%.

3,7,12,16-Tetraphenyl-4,6,12,14-octadecatetraene-1,8,10,17-tetrayne-3,16-diol (XV). A solution of XIV (500 mg, 0.89 mmol) in tetrahydrofuran (44 ml) was added over 20 min-period to a stirred suspension of lithium acetylide-ethylenediamine complex[5] (5.6 g) in benzene (98 ml) saturated with acetylene at 15 °C, and the mixture was stirred for further 3 hr at 30—45 °C. The reaction mixture was poured onto ice-water (20 ml) and mixed with saturated sodium chloride solution (100 ml). The aqueous layer was extracted with benzene, and the extracts were combined with the organic layer. The combined organic layer was concentrated and chromatographed on alumina (8.7 g). Crude XV (352 mg) was obtained as a light brown liquid from the benzene–ether eluates.

1,5,10,14-Tetraphenyl-2,4,9,12-cyclooctadecatetraene-6,8,15,17-tetrayne-1,14-diol (XVI). Oxidative coupling of the crude XV (352 mg) by cupric acetate–pyridine–methanol–ether under similar high dilution conditions used for the preparation of XI gave crude XV (312 mg) as a viscous light brown liquid. The crude material was used for the subsequent reaction.

1,5,10,14-Tetraphenyl-6,8,15,17-tetrakisdehydro[18]annulene (XVII). The crude cyclic glycol (VI, 312 mg) was converted into XVII by the reaction with stannous chloride in concentrated hydrochloric acid under analogous conditions employed for the conversion of XI to XII. Slightly crude XVII, obtained as black purple crystals (159 mg, 31% based on XIV), was recrystallized from benzene to give pure XVII, black purple needles. XVII showed no melting point, but underwent color change at 180—190 °C, UV: λ_{max}^{THF} 245 (23300), 261 (24800), 302 (27000), 351 (26300), 373 (38000), 472 (273000), 635 (108000), 772 (4110), NMR (60 MHz, THF-d_8), −0.31 (d, $J=13$, H^1, H^2), 1.3 (m, *o*-H of phenyl), 2.4 (m, *m,p*-H of phenyl), 13.19 (t, $J=13$, H^3). XVII gave, green solutions in organic solvents.

Found: C, 94.83; H, 4.98%. Calcd for $C_{42}H_{26}$: C, 95.06; 95.06; H, 4.94%.

CT Complex of XVII with Trinitrofluorenone. A mixture of XVII (27 mg, 0.051 mmol), 2,4,7-trinitrofluorenone (22 mg, 0.070 mmol), benzene (50 ml) and methanol (25 ml) was refluxed for 3 min. CT complex deposited as black purple needles on standing the homogeneous solution in a refrigerator, which showed color change at *ca.* 240 °C without fusion.

Found: C, 77.26; H, 3.69; N, 4.83%. Calcd for $C_{42}H_{26}\cdot C_{13}H_5N_3O_7$: C, 78.09; H, 3.69; N, 4.99%.

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