Dehydroannulenes. IV. Synthesis and Properties of 1,14-Di-*tert*-butyl-5,10-diphenyl-6,8,15,17-tetrakisdehydro[18]annulene. Evidence for the Identity of Diacetylene and Hexapentaene Units in the 18π-Electron System

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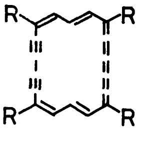
(Received August 18, 1975)

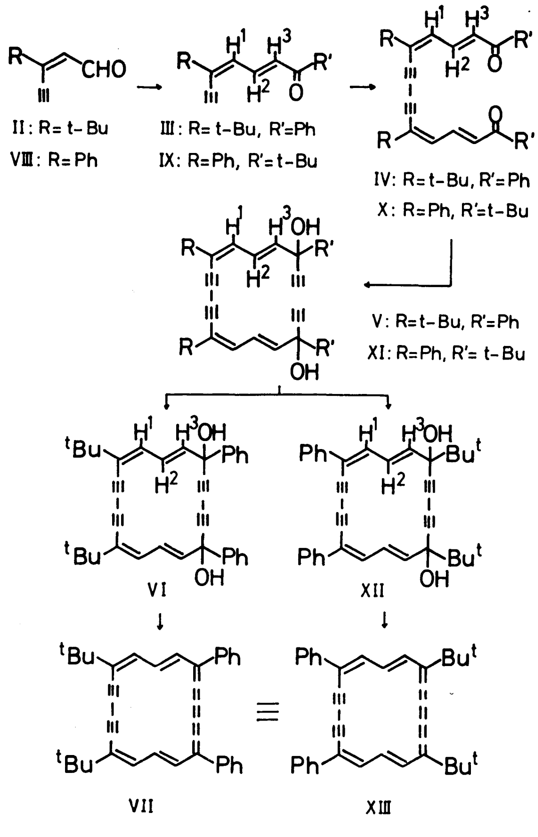
The synthesis designed to lead to isomeric di-*tert*-butyldiphenyl-tetrakisdehydro[18]annulenes (VII and XIII) have been performed. It was found that the isomeric tetrakisdehydro[18]annulenes (VII and XIII) are identical in all respects, thus providing chemical evidence for the identity of diacetylene and hexapentaene units incorporated in the aromatic 18π-electron system. Argon laster Raman spectra of VII and XIII exhibited single absorption due to stretching vibration of sp-hybridized carbon-carbon bond at 2080 cm^{-1} indicating equalized nature of acetylenic and cumulenic linkages in the aromatic dehydroannulene system.

It has been proved that tetrasubstituted tetrakisdehydro[18]annulene such as I_a, I_b, and I_c[1,2,3] sustain strong diamagnetic ring current suggesting that the acetylenic and cumulenic carbon atoms equally offer their p-electrons in the orbitals perpendicular to the molecular plane for the formation of π-molecular orbital. Furthermore, the NMR spectral pattern of the symmetrical tetrakisdehydro[18]annulenes (Ia, Ib, and Ic) indicates the equivalence of outer protons. These facts suggest the identity of diacetylene and hexapentaene units in the aromatic system just as formal signle and double bonds in benzene. It is of considerable interest to get further evidence for the identity of diacetylene and cumulene in tetrakisdehydro[18]annulene system. The syntheses of formally isomeric dimethyldiphenyltetrakisdehydro[18]annulenes have been reported in a previous paper.[2b] However, perfect agreement in their physical properties could not be obtained presumably owing to minor difference in purity and to their instability. The present paper is concerned with the syntheses of isomeric di-*tert*-butyldiphenyltetrakisdehydro[18]annulenes (VII and XIII), which can be expected to have higher stability than the dimethyldiphenyl analogue.[3]



I_a: R=Me
I_b: R=Ph
I_c: R=t-Bu

Syntheses. The aldol condensation of acetophenone with 3-*tert*-butyl-2-penten-4-ynal (II)[3] yielded dieneyne ketone (III). Oxidative coupling of III by cupric acetate in pyridine[4] gave diketone (IV) in an almost quantitative yield. The diketone (IV) was treated with lithium acetylide–ethylenediamine complex[5] in tetrahydrofuran to give acyclic glycol (V). Oxidation of V by cupric acetate in pyridine–methanol–ether under high dilution conditions resulted in 18-membered cyclic glycol (VI) in 85% yield. A solution of the cyclic glycol (VI) in ether was mixed with a solution of stannous chloride dihydrate in concentrated hydrochloric acid at a low temperature. Di-*tert*-butyldiphenyltetrakisdehydro[18]annulene (VII) was obtained in 85% yield.



Alternatively, dieneyne ketone (IX) obtained by the aldol condensation of 3-phenyl-2-penten-4-ynal (VIII)[2a] with pinacolone was oxidatively coupled to give diketone (X) in a high yield. Bis-ethynylation of the diketone (X) by lithium acetylide–ethylenediamine comples[5] yielded XI in 97% yield. Oxidative coupling of XI under high dilution conditions gave cyclic glycol (XII), an isomer of VI, in 71% yield. XII could be converted into di-*tert*-butyldiphenyltetrakisdehydro[18]-annulene (XIII) on treatment with stannous chloride in ether saturated with hydrogen chloride.

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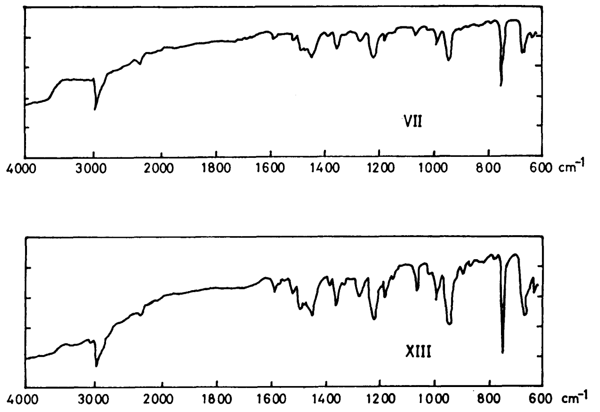

Fig. 1. IR spectra of VII and XIII (KBr-disk).

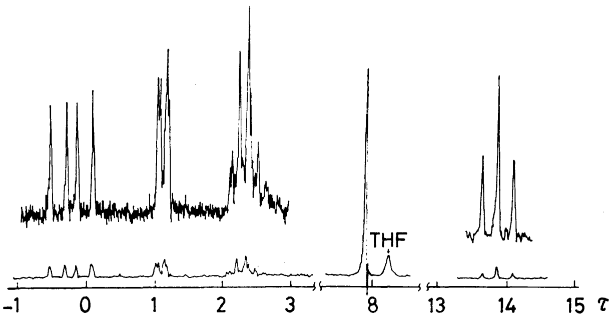

Fig. 2. 60 MHz NMR spectrum of VII in THF-d_8.

Properties. The IR spectra of di-*tert*-butyldiphenyltetrakisdehydro[18]annulenes (VII and XIII) were found to be superimposable as illustrated in Fig. 1. The NMR spectrum of VII shown in Fig. 2 indicates induction of a strong diamagnetic ring current in the tetrakisdehydro[18]annulene ring showing inner proton signal at a fairly high-field and outer proton signals at a low-field. Among two multiplets appeared at medium field, the lower field one could be assigned to *o*-protons of phenyl groups, which suffer deshielding effect of diatropicity of the annulene ring. The higher field multiplet could be reasonably ascribed to *m,p*-protons of phenyl groups, which are disposed in a less deshielding region. Down-field shift of *tert*-butyl proton signal also reflects the diatropicity of the annulene ring. The NMR parameters of VII and XIII are summarized in Table 1. As can be seen from the table, the chemical shifts and coupling constants of all signals of both tetrakisdehydro[18]annulenes (VII and XIII) were found to be identical within the experimental error, the difference of chemical shifts between the corresponding signals being τ ±0.02.

Table 1. 60 MHz NMR parameters of VII and XIII in THF-d_8

	VII		XIII	
Outer protons adjacent to phenyl	−0.40 d (14 Hz)	1H	−0.40 d (14 Hz)	1H
Outer protons adjacent to *tert*-butyl	−0.01 d (14 Hz)	1H	0.01 d (14 Hz)	1H
o-Protons of phenyl	1.13m	2H	1.15m	2H
m,p-Protons of phenyl	2.37m	3H	2.39m	3H
Protons of *tert*-butyl	7.93 s	9H	7.93 s	9H
Inner protons	13.90 t (14 Hz)	1H	13.90 t (14 Hz)	1H

The chemical shifts are given in τ-values.

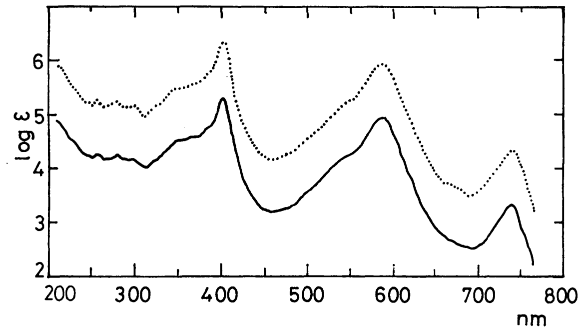

Fig. 3. Electronic spectra of VI (—) and XIII (···) in THF. The curve of XIII has displaced upward by 1.0 log ε unit increment.

Table 2. Electronic spectra of VII and XIII in THF λ_{max} in nm ($\varepsilon \times 10^{-2}$)

VII	231 sh (288),	245 sh (160),	256.5 (179),
	270 sh (153),	277.5 (176),	299 (142),
	325 sh (152),	347 sh (303),	368 sh (373),
	386 sh (616),	402 (2200),	544 sh (164),
	587 (875),	670 sh (4.80),	740 (21.7)
XIII	231 sh (285),	245 sh (162),	256.5 (177),
	270 sh (152),	277.7 (175),	299 (142),
	325 sh (151),	347 sh (303),	368 sh (374),
	386 sh (614),	402 (2190),	544 sh (164),
	587 (873),	670 sh (4.72),	740 (21.6)

Shoulder is denoted by sh.

The electronic spectra of VII and XIII are illustrated in Fig. 3, and the numerical data are recorded in Table 2. The wavelength of all absorption maxima were found to be identical in both tetrakisdehydro[18]annulenes (VII and XIII), and the absorption intensities also agreed within the experimental error being the difference between the corresponding maxima *ca.* ±1% at short wavelength region.

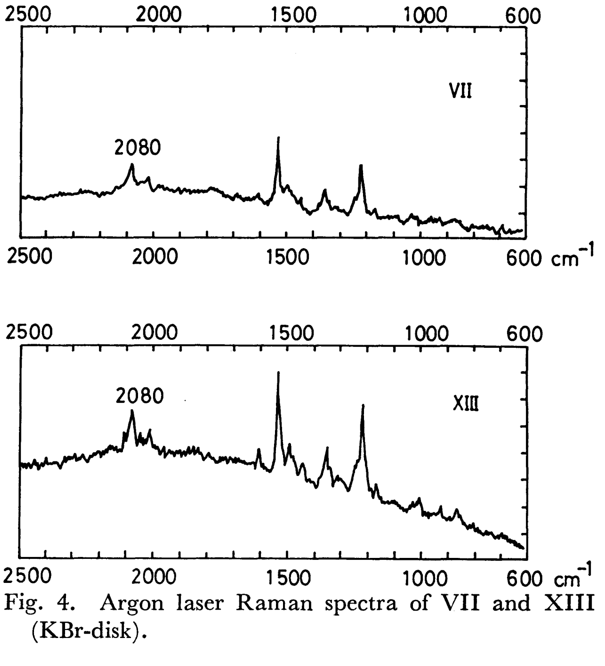

Fig. 4. Argon laser Raman spectra of VII and XIII (KBr-disk).

Argon laser Raman spectra of VII and XIII measured with KBr-disk method at a temperature of liquid nitrogen showed single absorption due to stretching vibration of sp-hybridized carbon-carbon linkage at 2080 cm^{-1} (Fig. 4), thus indicating equalized nature of the diacetylene and hexapentaene linkages incorporated in the aromatic system.

VII and XIII gave identical 1: 1 CT complexes with 2,4,7-trinitrofluorenone.

The above-stated results provide confirmative evidences for the identity of diacetylenic and cumulenic linkages in the 18π-electron system. Consequently, it can be concluded reasonably that the tetrakisdehydro-[18]annulene ring has a highly delocalized π-electron system consisting of equalized sp-hybridized carbon-carbon linkages and polyene system with minor bond-alternation.

Experimental

All melting points are uncorrected. The IR spectra were obtained on a Hitachi EPI-2 spectrometer, and strong, medium and weak bands are denoted by S, M, and W, respectively. The electronic spectra were measured with a Hitachi EPS-3T spectrophotometer using well-matched pair of quartz cells, and the wavelengths were calibrated with the spectrum of benzene vapor and a didymium glass filter. A Varian A-60 spectrometer was used for the measurements of NMR spectra, and the chemical shifts with respect to TMS as an internal standard and coupling constants are given in τ-values and Hz, respectively. The mass spectra were obtained on a Hitachi RM-50 spectrometer. Laser Raman spectra were measured on a JASCO R750 spectrometer using argon laser (514.5 nm). KBr-disk was prepared under nitrogen atmosphere and measurements were performed in a high vacuum at liquid nitrogen temperature. Merck alumina (Act. II—III) and Merck silica gel (70—325 mesh) were used in chromatography, unless otherwise stated.

Measurements of physical properties of the tetradehydro-[18]annulenes (VII and XIII) were carried out successively using freshly prepared samples.

1-Phenyl-5-tert-butyl-2,4-heptadien-6-yn-1-one (III). To a stirred solution of II[3] (12.0 g, 0.0881 mol) and acetophenone (10.57 g, 0.0881 mol) in ethanol (55 ml) was added over 15 min-period a solution of sodium hydroxide (4.5 g) in ethanol (12 ml) and water (12 ml) at $-10\sim-5$ °C. The mixture was stirred for further 3—4 hr under ice-cooling (2 °C). Crystals deposited were collected and washed successively with ethanol-water (1: 1) and water to give III, pale yellow crystals, 13.0 g, 62.1%, which were recrystallized from hexane to yield pure III, pale yellow rods, mp 82.1—83.4 °C, IR (KBr-disk): 3280 (M, $-C\equiv CH$), 1655 (S, C=O), 1600, 1580 (s, vS, aromatic C=C) cm^{-1}, NMR (CCl_4): 8.75 (s, 9H, *tert*-butyl-H), 6.40 (s, 1H, ethynyl-H), 3.43 (d, $J_{12}=11$, 1H, H^1), 3.03 (d, $J_{23}=15$, 1H, H^3), 2.50 (m, 3.5H, *m*, *p*-H of phenyl and H^2), 2.13 (m, 2.5H, *o*-H of phenyl and H^2).

Found: C, 85.93; H, 7.61%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

The ketone (III) decomposed gradually on stading at room temperature, but could be kept without change in a refrigerator.

1,14-Diphenyl-5,10-di-tert-butyl-2,4,10,12-tetradecatetraene-6,8-diyne-1,14-dione (IV). A solution of III (1.5 g, 0.0063 mol) in pyridine (6 ml) and methanol (6 ml) was added over 30 min-period to a stirred solution of cupric acetate monohydrate (3.8 g, 0.019 mol) in pyridine (24 ml) and methanol (24 ml) at room temperature. After being stirred for further 9 hr at the same temperature, the reaction mixture was poured into cold 1M sulfuric acid (300 ml), and extracted with benzene. The extracts were worked up in the usual way, and the solvent was removed under reduced pressure. Yellow amorphous solid, thus obtained, could be crystallized from hexane, 1.30 g, 97.7%. Recrystallization of the crystals from hexane containing trace of benzene gave pure IV, yellow leaflets, mp 144—146 °C, IR (KBr-disk): 1655 (S, C=O), 1580 (vS, aromatic C=C) cm^{-1}, NMR (CCl_4): 8.73 (s, 9H, *tert*-butyl-H), 3.34 (d, $J_{12}=11$, 1H, H^1), 3.04 (d, $J_{23}=15$, 1H, H^3), 2.52 (m, 3.5H, *m*,*p*-H of phenyl and H^2), 2.13 (m, 2.5H, *o*-H of phenyl and H^2).

Found: C, 85.97; H, 7.24%. Calcd for $C_{34}H_{34}O_2$: C, 86.04; H, 7.22%.

3,16-Diphenyl-7,12-di-tert-butyl-4,6,12,14-octadecatetraene-1,8,-10,17-tetrayne-3,16-diol (V). To a stirred suspension of lithium acetylide–ethylenediamine complex[5] (4.8 g) in tetrahydrofuran (260 ml) saturated with acetylene was added at room temperature over 1 hr-period a solution of IV (2.0 g, 0.00421 mol) in the same solvent (100 ml) under slow introduction of acetylene. Introduction of acetylene was stopped after 10 min, and the mixture was stirred for further 2.5 hr at the same temperature. Saturated aqueous ammonium chloride solution (30 ml) was added to the reaction mixture under cooling on an ice-bath. The mixture was extracted with ether. Dark colored oily residue obtained on concentrating the extracts *in vacuo* was chromatographed on silica gel (40 g), and eluted with benzene and benzene–ether (95: 5). V (2.2 g, *ca.* 90%) was obtained as a viscous yellow liquid on concentrating the eluates, IR (neat): 3400 (OH), 3280 ($-C\equiv CH$) cm^{-1}, NMR (CCl_4): 8.8 (s, 9H, *tert*-butyl-H), 7.5 (broad s, 1H, OH, disappeared on addition of D_2O), 7.25 (s, 1H, ethynyl-H), 4.13 (d, $J_{23}=15$, 1H, H^3), 3.62 (d, $J_{12}=11$, 1H, H^1), 2.83 (m, 4H, *m*, *p*-H of phenyl and H^2), 2.47 (m, 2H, *o*-H of phenyl).

Attempts to crystallize V were failed.

1,6-Diphenyl-10,15-di-tert-butyl-7,9,15,17-cyclooctadecatetraene-2,4,11,13-tetrayne-1,6-diol (VI). To a stirred and refluxing solution of cupric acetate monohydrate (3.6 g) in pyridine (100 ml), ether (100 ml) and methanol (50 ml) was added over 8.5 hr-period a solution of V (0.7785 g, 0.00148 mol) in pyridine (50 ml), ether (50 ml) and methanol (50 ml) using a high dilution apparatus, and stirring was continued for further 9 hr at the same temperature. The reaction mixture was then stirred at room temperature for 6 hr, and concentrated to 1/3 volume under reduced pressure on a water-bath kept at 40 °C. The concentrate was extracted with ether, and the extracts were washed thoroughly with water, diluted hydrochloric acid, aqueous sodium hydrogencarbonate solution and saturated aqueous sodium chloride solution, successively, and dried over magnesium sulfate. Brown crystalline powder obtained on concentrating the extracts was chromatographed on alumina (25 g). Elution with benzene and benzene–ether (95: 5) yielded pale yellow crystalline powder, which was crystallized from hexane to give pale yellow crystals, 0.661 g, 85.2%. Recrystallization of the crystals from hexane yielded pure cyclic glycol (VI), colorless leaflets, mp *ca.* 160 °C (dec.), IR (KBr-disk): 3390 (broad, OH) cm^{-1}, NMR ($CDCl_3$): 8.82 (s, 9H, *tert*-butyl-H), 7.47 (broad s, 1H, OH, disappeared on addition of D_2O), 4.05 (d, $J_{23}=15$, 1H, H^3), 3.52 (d, $J_{12}=11$, H^1), 2.49 (m, 6H, H^2 and phenyl-H).

Found: C, 86.99; H, 7.18%. Calcd for $C_{38}H_{36}O_2$: C, 86.98; H, 6.91%.

1,14-Diphenyl-5,10-di-tert-butyl-6,8,15,17-tetrakisdehydro[18]-annulene (VII). A solution of stannous chloride dihydrate (320 mg) in concentrated hydrochloric acid (4 ml) was added to a stirred solution of VI (150 mg, 0.286 mmol) in ether (35 ml) under nitrogen atmosphere at −12 °C (on an ice–salt-bath). After being stirred for 30 min at the same temperature, ether (30 ml) and ice–water (30 ml) were added to the deep blue violet reaction mixture. The organic layer was washed successively with water, aqueous sodium hydrogencarbonate solution and saturated sodium chloride solution, and passed through a short column of anhydrous potassium carbonate. Reddish purple powder obtained on evaporating the filtrate under reduced pressure was dissolved in hexane–ether (9: 1) and chromatographed on alumina (50 g). Elution with the same solvent yielded reddish purple crystals, 0.112 g, 80.0%. Recrystallization of the crystals from hexane–ether (3: 1) gave pure VII, reddish purple leaflets, mp 189.0—191.0 °C (dec.).

Found: C, 92.77; H, 7.05%, M^+ 490. Calcd for $C_{38}H_{34}$: C, 93.02; H, 6.98%, Mol. wt., 490.7.

CT Complex of VII with Trinitrofluorenone. A solution of 2,4,7-trinitrofluorenone (20 mg) in ether (15 ml) and methanol (15 ml) was added to a solution of VII (30 mg) in ether–methanol (1: 1, 30 ml). After being warmed to 50 °C for 5 min, the mixture was allowed to stand in a refrigerator for 30 min. Fine bluish purple crystals were collected and washed with ether and dried *in vacuo* for 1.5 hr, 34 mg, 69.4%. On attempted melting point determination, the color of the crystals faded at 240—241 °C.

Found: C, 75.87; H, 4.96; N, 5.25%. Calcd for $C_{38}H_{34}\cdot C_{13}H_5N_3O_7$: C, 76.01; H, 4.88; N, 5.21%.

2,2-Dimethyl-7-phenyl-4,6-nonadien-8-yn-3-one (IX). To a stirred solution of 3-phenyl-2-penten-4-ynal[2a] (VIII, 6.0 g, 0.0384 mol) and pinacolone (4.6 g, 0.0461 mol) in ethanol (90 ml) was added under nitrogen atmosphere over 30 min-period at −2 °C a solution of potassium hydroxide (2.16 g, 0.0384 mol) in ethanol (4 ml) and water (4 ml). The mixture was stirred for further 3.5 hr at 2 °C, and then for 15 hr at 14°C. The reaction mixture was mixed with cold diluted hydrochloric acid, and extracted with ether. The extracts, after being worked up in the usual way, were concentrated under reduced pressure. Dark colored oily residue dissolved in carbon tetrachloride–benzene (1: 9) was passed through a column of silica gel (Wakogel, 120 g). Orange yellow liquid obtained on concentrating the filtrate was dissolved in cyclohexane and passed through a column of alumina (60 g). Pale yellow liquid obtained from the filtrate was mixed with a small amount of cyclohexane–hexane (1: 1) to give pale yellow crystals, 3.8 g, 41.6%, which were recrystallized 3 times from the same solvent to give pure IX, pale yellow leaflets, mp 75.5—76.2 °C, IR (KBr-disk): 3250 (S, −C≡CH), 1675 (vS, C=O), 1600, 1575 (sh, vS, aromatic C=C) cm^{-1}, NMR (CCl_4): 8.83 (s, 9H, *tert*-butyl-H), 6.35 (s, 1H, ethynyl-H), 3.33 (d, $J_{23}=15$, 1H, H^3), 3.0 (d, $J_{12}=11$, 1H, H^1), 2.73 (m, 3H, *m,p*-H of phenyl), 2.37 m, 2.71 dd, $J_{23}=15$, $J_{12}=11$ (3H, *o*-H of phenyl and H^2).

Found: C, 85.91; H, 7.64%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

*1,14-Di-*tert*-butyl-5,10-diphenyl-2,4,10,12-tetradecatetraene-6,8-diyne-1,14-dione (X).* A solution of IX (3.5 g, 0.0147 mol) in pyridine–methanol (1: 1, 30 ml) was added at room temperature over 20 min-period to a stirred solution of cupric acetate monohydrate (8.8 g) in pyridine–methanol (1: 1, 108 ml). After being stirred for further 3 hr at the same temperature, the reaction mixture was poured into cold 1M sulfuric acid (700 ml), and extracted with ether. The extracts, after being worked up in the usual manner, were evaporated under reduced pressure to give yellowish brown powder. The material dissolved in carbon tetrachloride was passed through a column of alumina (30 g). Yellow powder obtained on concentrating the filtrate under reduced pressure was crystallized from hexane, thus yielding X, yellow crystals, 3.4 g, 98.3%, which were recrystallized from hexane–benzene (2: 1) to give analytical specimen, yellow needles, mp 154—156 °C, IR (KBr-disk): 1680 (M, C=O), 1585 (vS, aromatic C=C) cm^{-1}, NMR ($CDCl_3$): 8.8 (s, 9H, *tert*-butyl-H), 3.23 (d, $J_{23}=15$, 1H, H^3), 2.92 (d, $J_{12}=11$, 1H, H^1), 2.7 (m, 3H, *m,p*-H of phenyl), 2.4, m, 2.31, dd, $J_{12}=11$, $J_{23}=15$ (3H, *o*-H of phenyl and H^2).

Found: C, 86.00; H, 7.17%. Calcd for $C_{34}H_{34}O_2$: C, 86.04; H, 7.22%.

*3,16-Di-*tert*-butyl-7,12-diphenyl-4,6,12,14-octadecatetraene-1,8,-10,17-tetrayne-3,16-diol (XI).* Bis-ethynylation of X (2.0 g, 0.00421 mol) with lithium acetylide–ethylenediamine complex[5] (4.8 g) was carried out under the same reaction conditions as the case of preparation of V. Dark colored oily product was chromatographed on silica gel (40 g). Viscous yellow liquid obtained from benzene and benzene–ether (95: 5) eluates was mixed with hexane, and the solution was allowed to stand overnight in a refrigerator to yield pale yellow crystals, 2.15 g, 97.3%. Recrystallization of the crystals from hexane containing trace of benzene gave pure XI, pale yellow fine crystals, mp 145.5—148.5 °C, IR (KBr-disk): 3560 (M, OH), 3920 (M, −C≡CH), 1600 (W, aromatic (C=C) cm^{-1}, NMR ($CDCl_3$): 8.93 (s, 9H, *tert*-butyl-H), 7.92 (s, 1H, OH, disappeared on addition of D_2O), 7.33 (s, 1H, ethynyl-H), 3.80 (d, $J_{23}=15$, 1H, H^3), 2.77 (m, 5H, *m,p*–H of phenyl and H^2, H^1), 2.38 (m, 2H, *o*–H of phenyl).

Found: C, 86.42; H, 7.31%. Calcd for $C_{38}H_{38}O_2$: C, 86.65; H, 7.27%.

*1,6-Di-*tert*-butyl-10,15-diphenyl-7,9,15,17-cyclooctadecatetraene-2,4,11,13-tetrayne-1,6-diol (XII).* A solution of XI (1.29 g, 0.00245 mol) in pyridine–ether–methanol (1: 1: 1, 150 ml) was added over 10.5 hr-period to a stirred and refluxing solution of cupric acetate monohydrate (8.8 g) in pyridine (140 ml), ether (100 ml) and methanol (100 ml). After being refluxed under stirring for further 10 hr, a part of solvents was distilled out (bp 40—60 °C, 110 ml), and stirring under reflux was continued for further 4 hr. The reaction mixture was concentrated to 1/3 of its volume under reduced pressure at 40 °C. The concentrate was extracted with ether. The ethereal extracts were worked up in the usual way. Deep brown solid obtained on evaporating the extracts was dissolved in benzene and chromatographed on alumina (25 g). Yellow crystalline powder obtained from benzene and benzene–ether eluates was triturated with a small amount of carbon tetrachloride to give pale yellow crystals, 0.911 g, 70.8%. The crystals were recrystallized from carbon tetrachloride and carbon tetrachloride–hexane (1: 1) to give pure XII, pale yellow needles, mp 156.0—158.0 °C (dec.), IR (KBr-disk): 3400 (OH) cm^{-1}, NMR ($CDCl_3$): 8.89 (s, 9H, *tert*-butyl-H), 8.0 (broad s, 1H, OH, disappeared on addition of D_2O), 3.83 (d, $J_{23}=15$, 1H, H^3), 2.73 (m, 5H, *m,p*-H of phenyl and H^1, H^2), 2.33 (m, 2H, *o*-H of phenyl).

XII recrystallized from carbon tetrachloride or carbon tetrachloride–hexane contained tenaciously a small amount of the chloride and gave unsatisfacotry elemental analysis.

*1,14-Diphenyl-5,10-di-*tert*-butyl-6,8,15,17-tetrakisdehydro[18]-annulene (XIII).* To a stirred solution of XII (200 mg, 0.381 mmol) in ether (35 ml) cooled to −12 °C was added a mixture of stannous chloride dihydrate (400 mg) in ether (6 ml) saturated with hydrogen chloride. Deep bluish purple solution was stirred for 30 min at the same temperature, and then ether (30 ml) and ice–water (30 ml) were added successively to the reaction mixture. The organic layer was washed thoroughly with cold water, aqueous sodium hydrogencarbonate and sodium chloride solutions, successively. The organic layer, after being passed through a short column of anhydrous potassium carbonate, was concentrated to give reddish purple powder. The powder dissolved in hexane–ether (9: 1) was chromatographed on alumina (30 g), and eluted with the same solvent. Evaporation of the eluates *in vacuo* yielded reddish purple crystals, 0.126 g, 67.4%, which were recrystallized 3 times from hexane–ether (3: 1) to give analytical specimen of XIII, reddish purple leaflets, mp 189.0—191.0 °C (dec.).

Found: C, 92.60; H, 7.04%, M^+ 490. Calcd for $C_{38}H_{34}$: C, 93.02; H, 6.98%, Mol. wt., 490.7.

CT Complex of XIII with Trinitrofluorenone. A solution of XIII (30 mg) in ether–methanol (1: 1, 30 ml) was mixed with a solution of 2,4,7-trinitrofluorenone (20 mg) in the same solvent (30 ml), and the mixture was kept at 50 °C for 5 min. According to similar procedure as that for the preparation of CT complex of VII, CT complex of XIII was obtained as purple fine crystals, 39 mg, 79.6%. The color of the crystals faded at 240—240.5 °C.

Found: C, 75.82; H, 4.84; N, 5.18%. Calcd for $C_{38}H_{34}\cdot C_{13}H_5N_3O_7$: C, 76.01; H, 4.88; N, 5.21%.

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