Dehydroaunulenes. VI. Synthesis and Properties of 1,6,12,17-Tetraphenyl-2,4,13,15-tetrakisdehydro[22]annulene

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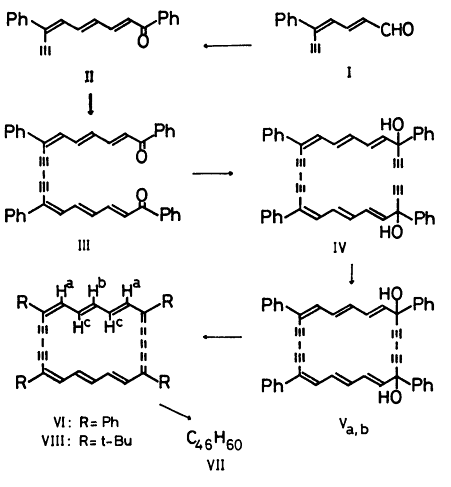
1,6,12,17-Tetraphenyl-2,4,13,15-tetrakisdehydro[22]annulene has been synthesized. The sparlingly soluble tetrakisdehydro[22]annulene was found to be conformationally stable and strongly diatropic.

As reported in previous papers of this series, interesting difference has been observed between the properties of tetra-*t*-butyl-[1] and tetraphenyltetrakisdehydro[18]annulenes.[2] The successful synthesis of tetra-*t*-butyltetrakisdehydro[22]annulene (VIII)[3] prompted us to synthesize tetraphenyltetrakisdehydro[22]annulene (VI) with the purpose to compare their properties.

The aldol condensation of 5-phenyl-2,4-heptadien-6-ynal (I)[4] with acetophenone gave II in a high yield. Oxidative coupling of II with copper(II) acetate in pyridine–methanol yielded diketone (III) as red crystals in an almost quantitative yield. Bis-ethynylation of III could be achieved by lithium acetylide–ethylenediamine complex.[5] Bis-ethynyl alcohol (IV) obtained as yellow fine crystals was oxidatively coupled under high dilution conditions to yield cyclic glycol (V) which could be separated into diastereomers. It was found that V forms containing 1 mol of ethyl acetate as a solvent of crystallization. Formation of similar adducts has been observed in some acyclic[6] and cyclic acetylene glycols.[7]



Scheme 1.

A solution of V in dichloromethane was mixed at −15 °C with a solution of tin(II) chloride dihydrate in concentrated hydrochloric acid. Tetrakisdehydro[22]annulene (VI) was obtained as unstable and sparlingly soluble black violet crystals. Full hydrogenation of VI over platinum catalyst yielded a mixture of stereoisomers of a saturated hydrocarbon, tetraphenylcyclodocosane (VII). The tetrakisdehydro[22]annulene (VI) forms air sensitive CT-complex with 2,4,7-trinitrofluorenone.

Electronic spectrum of VI consists of three main absorption bands showing characteristic feature of [4*n*+2]annulenes as illustrated in Fig. 1. The spectrum of VI was found to be closely related with that of tetra-*t*-butyltetrakisdehydro[22]annulene (VIII)[3] although VI showed remarkable bathochromic shift.

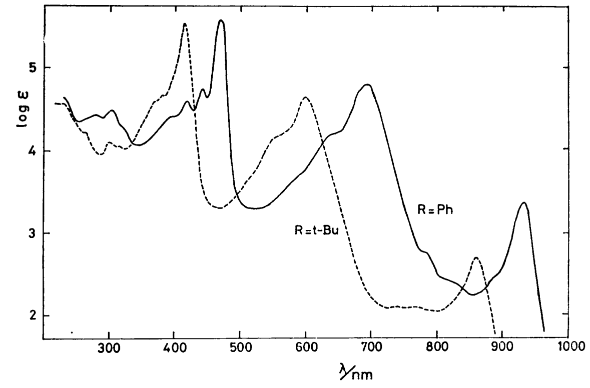


Fig. 1. Electronic spectra of tetra-*t*-butyltetrakisdehydro[22]annulene (VIII) (···) and tetraphenyltetrakisdehydro[22]annulene (VI) (—) in THF.

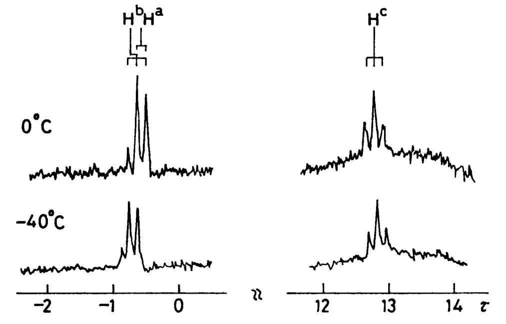


Fig. 2. 100 MH ^{1}H FT-NMR spectra of tetraphenyltetrakisdehydro[22]annulene (VI) in THF-d_8.

The ^{1}H FT-NMR spectra of VI indicate clearly that the tetrakisdehydro[22]annulene (VI) is strongly diatropic showing outer proton signals at a low-field and those of inner protons at fairly high-field (Fig. 2). The NMR parameters of VI are summarized in Table 1 together with those of VIII for comparison. The NMR spectra were essentially temperature independent indicating high conformational stability of the tetrakisdehydro[22]annulene ring. Appreciable down-field shift for both of the inner and outer proton signals of VI as compared with those of VIII seems to be attributable to deshielding effect of ring current of phenyl groups. Inversely, down-field shift of *ortho*-protons in phenyl groups reflects deshielding effect of diamagnetic ring current induced in the 22-membered ring.

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TABLE 1. 100 MHz H^1 FT-NMR PARAMETERS OF VI (in THF-d_8) AND VIII (in $CDCl_3$)
τ-Values, J in Hz.

	VI		VIII
	−40 °C	0 °C	−40 °C
H^b	−0.79 t	−0.62 t	−0.43 t
	$J=14$	$J=14$	$J=13$
H^a	−0.72 d	−0.55 d	0.09 d
	$J=14$	$J=14$	$J=13$
o-H of Ph	0.93 d	1.04 d	
	$J=8$	$J=8$	
m,*p*-H of Ph	2—2.5 m	2—2.5 m	
H^c	12.80 t	12.76 t	13.71 t
	$J=14$	$J=14$	$J=13$

It was found that VI is less stable and less soluble than the tetra-*t*-butyl analogue (VIII). Remarkable bathochromic shift of electronic spectrum of VI as compared with that of VIII indicates that phenyl groups exert larger electronic perturbation on the dehydroannulene system than *t*-butyl groups. These facts are the further support for the suitable nature of *t*-butyl group as substituent[1] in the study of aromaticity of dehydroannulene system.

Experimental

All melting and boiling points are not corrected. The IR spectra were obtained on a Hitachi EPI-2 or EPI-3G spectrometer. The electronic spectra, measured with a Hitachi-EPS-3T spectrophotometer, were recorded in nm and the ε-values were given in parentheses. Shoulder was denoted by sh. The mass spectra were obtained on a Hitachi RM-50 spectrometer. The ^{1}H NMR spectra obtained on a Varian XL-100 spectrometer were given in τ-values with respect to TMS as an internal standard, and the coupling constants (J) are recorded in Hz. Silica gel (Merck, Kiesel Gel 60) or alumina (Merck, Act. II—III) was used for column chromatography, unless otherwise stated.

1,7-Diphenyl-2,4,6-nonatrien-8-yn-1-one (II). A solution of sodium hydroxide (0.26 g, 6.6 mmol) in 50% aqueous ethanol (4 ml) was added to a stirred and ice-cooled mixture of I (1.20 g, 6.6 mmol), acetophenone (0.79 g, 6.6 mmol) and ethanol (15 ml). After the mixture had been stirred for 2 h, yellow crystals deposited were collected and washed successively with water, methanol and water to give fairly pure II: mp 92—95 °C; IR (CCl_4): 3300 (C≡CH), 1600 (C=C), 1015, 1000 (*trans* CH=CH) cm^{-1}; NMR (CCl_4): 6.38 (s, 1, C≡CH), 2.52 (m, 15, olefinic and aromatic).

Found: C, 88.49; H, 5.72%. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67%.

1,7,12,18-Tetraphenyl-2,4,6,12,14,16-octadecahexaen-8,10-diyn-1,18-dione (III). A solution of II (7.00 g, 0.025 mol) in pyridine (70 ml) and methanol (70 ml) was added over 30 min period to a solution of copper(II) acetate monohydrate (14.5 g) in pyridine (70 ml) and methanol (70 ml) at room-temperature. After being stirred for 3 h, reddish orange crystals deposited were collected and washed with water and methanol. Slightly crude III (mp 210—214 °C, 6.92 g, 99%) was dissolved in benzene and passed through a short column of alumina. Concentration of the filtrate under reduced pressure yielded pure III: red crystals; mp 213—216 °C; IR (KBr-disk): 1640 (C=O), 1590, 1580, 1565 (C=C and aromatic), 1010, 1000 (*trans* CH=CH) cm^{-1}.

Found: C, 88.98; H, 5.29%. Calcd for $C_{42}H_{30}O_2$: C, 89.05; H, 5.30%.

3,9,14,20-Tetraphenyl-4,6,8,14,16,18-docosahexaen-1,10,12,21-tetrayn-3,30-diol (IV). Lithium acetylide–ethylenediamine complex[5] (6.5 g, 0.07 mol) was added to THF (100 ml) saturated with acetylene. A solution of II (1.00 g, 1.77 mmol) in the same solvent (500 ml) was added to the mixture over 2 h-period under slow bubbling of acetylene, and saturated ammonium chloride solution (30 ml) was added to the reaction mixture under cooling in an ice-salt-bath. The aqueous layer was extracted with ether, and the extract was combined with the organic layer. The combined organic layer was washed successively with saturated ammonium chloride and sodium chloride solutions, and dried ($MgSO_4$). Brown crystalline powder obtained on concentration of the organic layer was dissolved in benzene and chromatographed on alumina (20 g). Elution with ether–benzene (1: 9—2: 8) yielded acyclic glycol, IV: yellow crystalline solid (attempts to recrystallize this material were failed); mp 84—86 °C; 0.69 g, 63%; NMR (CCl_4): 7.65 (s, 1, OH), 7.28 (s, 1, C≡CH), 4.23—3.03 (m, 5, olefinic), 2.78 (m, 6, *m*,*p*-H of phenyl), 2.48 (m, 4, *o*-H of phenyl).

Found: C, 88.84; H, 5.78%. Calcd for $C_{46}H_{34}O_2$: C, 89.29; H, 5.54%.

1,6,12,17-Tetraphenyl-8,9,11,17,19,21-cyclodocosahexaen-2,4,13,-15-tetrayn-1,6-diol (V). To a stirred and refluxing solution of copper(II) acetate monohydrate (2.5 g) in pyridine (200 ml), ether (200 ml) and methanol (100 ml) was added a solution of IV (0.95 g, 1.54 mmol) in pyridine (115 ml), ether (115 ml) and methanol (50 ml) over 7.5 h-period using a high dilution apparatus. After being refluxed for further 30 min, the reaction mixture was stirred overnight at a room-temperature. The mixture was concentrated to 1/2 volume under reduced pressure, and the concentrate was extracted with ether (300 ml). The extract was washed successively with chilled water, diluted hydrochloric acid and brine, and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave crude cyclic glycol, V (brown crystalline powder). The oxidative coupling was repeated 3 times under the same reaction conditions using the same quantity of materials. Crude (total 2.33 g, 83%), thus obtained, was dissolved in benzene (20 ml). Crystals deposited on standing the benzene solution were collected and washed with benzene–hexane to give one *diastereomer of the cyclic glycol*, V_a *(yellow tiny cubes, 0.52 g,* 18%). Recrystallization of the crystals from ethyl acetate yielded V_a containing 1 mol of the solvent: mp *ca.* 200 °C (dec); IR (KBr-disk): 3700—3100 (OH), 2190 (C≡C), 1715 (C=O), 990 (*trans* CH=CH) cm^{-1}; UV (THF): λ_{max} 254.5 (29700), 262 (29800), 280 (17200), 348 (107000), 394 (13500), 416 (17500), 441 (16800) nm; NMR (acetone-d_6): 2.0—4.1 (m, 30, olefinic and aromatic), 4.45 (s, 2, OH), 5.95 (q, 2, CH_2), 8.03 (s, 3, CH_3CO), 8.79 (t, 3, CH_3).

Found: C, 85.29; H, 5.74%. Calcd for $C_{46}H_{32}O_2 \cdot CH_3COOC_2H_5$: C, 85.20; H, 5.72%.

The mother liquor obtained on filtrating the crude V_a was chromatographed on alumina (100 g). The other diastereomer of the cyclic glycol, V_b (light brown crystalline powder, 0.68 g, 24%) was obtained on elution with ether–benzene (4: 6), which was recrystallized from benzene–hexane to give pure V_b: yellow needles; mp *ca.* 200 °C (dec); IR (KBr-disk): 3700—3100 (OH), 2190 (C≡C), 990 (*trans* CH=CH) cm^{-1}; UV(THF): λ_{max} 254.5 (27000), 262 (26300), 280 (14900), 348 (98600), 394 (12400), 416 (15900), 441 (15400) nm; NMR (acetone-d_6): 2.0—4.1 (m, 30, olefinic and aromatic), 4.42 (s, 2, OH).

Found: C, 89.57; H, 5.58%. Calcd for $C_{46}H_{32}O_2$: C, 89.34; H, 5.65%.

1,6,12,17-Tetraphenyl-2,4,13,15-tetrakisdehydro[22]annulene (VI). A solution of tin(II) chloride dihydrate (0.1 g, 4 mmol) in concentrated hydrochloric acid (2 ml) was added in one portion to a stirred and chilled (−15 °C) solution of V_b (10 mg, 0.016 mmol) in dichloromethane (80 ml). After 3 min, ice–water was added to the reaction mixture. Resulting dark green organic layer was washed successively with cold water, diluted sodium hydrogen carbonate solution and cold water, and dried (K_2CO_3). The organic layer was passed through a short column of alumina (5 g). Evaporation of the solvent under reduced pressure at low temperature yielded VI: unstable deep violet fine crystals; 8.5 mg, 90%; UV (THF): λ_{max} 290 (25800), 305.5 (29600), 400 (24200), 419 (38200), 442 (54700), 469 (363000), 682 (59500), 942 (2300) nm; NMR: see, Table 1 and Fig. 2.

Owing to unstable nature of VI, elemental analyses gave unsatisfactory results.

V_a containing 1 mol of ethyl acetate also gave VI in a high yield under the same reaction conditions.

CT-Complex of VI with 2,4,7-Trinitrofluorenone. A solution of VI in cold dichloromethane was mixed with a large excess of a solution of 2,4,7-trinitrofluorenone in the same solvent. Dark green fine needles were obtained on standing the mixture at 0 °C for 1 h. Elemental analyses gave no definite results, presumably owing to the sensitivity of the complex to atmospheric oxygen.

Catalytic Hydrogenation of VI. V_b (0.30 g, 0.049 mmol) was converted into VI according to the above procedure. Freshly obtained VI in THF (5 ml) was added to ethyl acetate (100 ml) containing platinum oxide catalyst (0.10 g), and the mixture was vigorously stirred under hydrogen atmosphere at −15 °C for 5 h. Resulting colorless solution was concentrated under reduced pressure to give colorless crystalline material (0.025 g, 84% based on V_b), which was dissolved in hexane and passed through a short column of alumina (Woelm, W200). Crystals obtained on concentration of the filtrate under reduced pressure were recrystallized from pentane–hexane to give VII: colorless rods; mp 108—117 °C; NMR (CD_2Cl_2): 2.6—3.0 (m, 20, aromatic), 7.3—7.6 (m, 4, CH), 8.1—9.0 (m, 36, CH_2).

Found: C, 89.88; H, 9.84%, M^+ 612. Calcd for $C_{46}H_{60}$: C, 90.13; H, 9.87%, Mol. wt, 612.

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