Dehydroannulenes. VIII. Synthesis of Position Isomers of Di-*t*-butyl-diphenyl-1,8-bisdehydro[14]annulene and Dimethoxy Derivative

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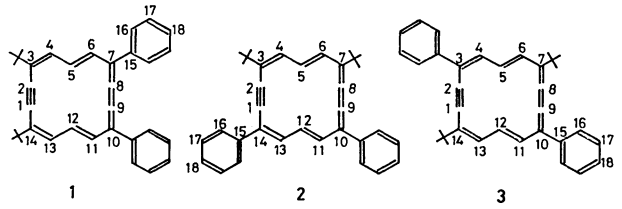
Two position isomers of di-*t*-butyl-diphenyl-1,8-bisdehydro[14]annulene corresponding to *o*- and *m*-isomers of terphenyl have been prepared by a stepwise reaction sequence, and their physical properties were compared with those of 3,10-di-*t*-butyl-7,14-diphenyl-1,8-bisdehydro[14]annulene which corresponds to the *p*-isomer of terphenyl. The marked difference in electronic spectra between *o*-, *m*-, and *p*-isomers of terphenyl could not be observed in the spectra of "*ortho*"-, "*meta*"-, and "*para*"-isomers of the [14]annulene. Dimethoxy derivative of the "*para*"-isomer, 3,10-di-*t*-butyl-6,13-dimethoxy-7,14-diphenyl-1,8-bisdehydro[14]annulene, has been synthesized.

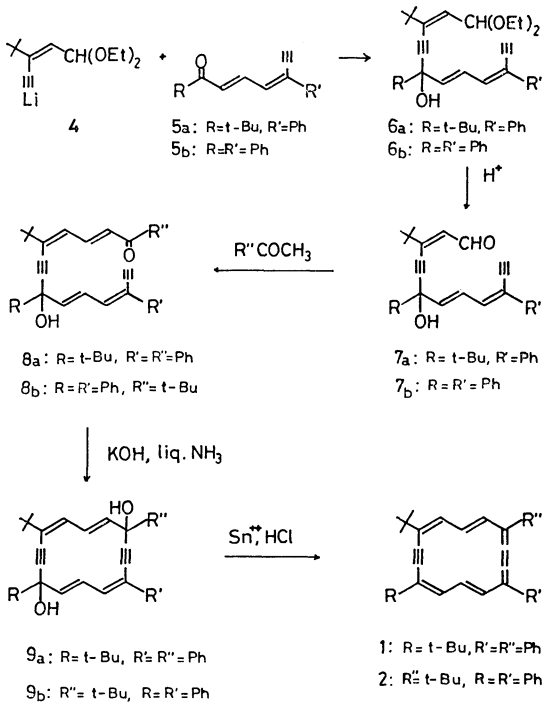
As reported in the previous papers, increase in the number of phenyl substituents on bisdehydro[14]-[1], tetrakisdehydro[18]-,[2] and tetrakisdehydro[22]annulene rings[3] caused appreciable bathochromic shifts of their electronic spectra indicating conjugative effect of π-electrons in the phenyl group on the annulene nucleus. Considering the remarkable difference in electronic spectral properties between position isomers of terphenyl,[4] we have carried out the synthesis of di-*t*-butyl-diphenyl-1,8-bisdehydro[14]annulenes (**1** and **2**) corresponding to *o*- and *m*-isomers of terphenyl.[5] The synthesis of 7,14-di-*t*-butyl-3,10-diphenyl-1,8-bisdehydro[14]annulene (**3**) which corresponds to *p*-terphenyl has been reported previously.[1]



1 2 3

Synthesis. As outlined in Scheme 1, 3-*t*-butyl-2-penten-4-ynal diethyl acetal[3b,c] was converted into lithio derivative (**4**) on treatment with phenyllithium. The reaction of the lithio derivative (**4**) with dienyne ketone (**5**) gave hydroxy acetal (**6**) in a high yield. Hydroxy aldehyde (**7**) was obtained on treatment of the acetal (**6**) in ethanol with an aqueous solution of tartaric acid. The aldol condensation of the hydroxy aldehyde (**7**) with methyl ketone yielded hydroxy ketone (**8**). A solution of the hydroxy ketone (**8**) in tetrahydrofuran was added to a suspension of finely powdered potassium hydroxide in liquid ammonia. The products were passed through a short column of alumina. Slightly crude cyclic glycol (**9**) thus obtained was subjected without further purification to the subsequent reaction. Treatment of the cyclic glycol (**9**) in ether with a solution of tin(II) chloride dihydrate in the same solvent saturated with hydrogen chloride at −15——17 °C afforded position isomers of di-*t*-butyldiphenyl-1,8-bisdehydro[14]annulene, (**1**) or (**2**).

In order to obtain further information on the effect of substituent on the electronic spectrum of 1,8-bisdehydro[14]annulene, dimethoxy derivative (**14**) of the isomer (**3**) has been prepared according to Scheme 2. The aldol condensation of 3-*t*-butyl-2-penten-4-ynal (**10**)[2b,6] with α-methoxyacetophenone (**11**)[7] gave



Scheme 1.

methoxydienyne ketone (**12**). Another geometrical isomer (**15**) can be considered for the methoxy ethynyl ketone. NMR spectroscopy of the ketone, *i.e.*, difference in chemical shift between carbon tetrachloride and deuteriobenzene solutions[8] and the NOE of H^3 or H^4 on irradiation of methyl protons in methoxyl groups, afforded no confirmative information on the discrimination between **12** and **15**. However, formation of the cyclic glycol (**13**) seemed to suggest the *trans* disposition of the methoxyl group with respect to H^3. Treatment of the methoxy ethynyl ketone (**12**) with a suspension of potassium hydroxide in liquid ammonia gave the cyclic glycol (**13**). Reductive dehydroxylation of the cyclic glycol (**13**) by tin(II) chloride dihydrate in ether saturated with hydrogen chloride yielded 3,10-di-*t*-butyl-7,14-diphenyl-6,13-dimethoxy-1,8-bisdehydro[14]annulene (**14**).

Properties. The color of crystals, melting points and ^1H NMR parameters of the position isomers of di-*t*-butyl-diphenyl-1,8-bisdehydro[14]annulene (**1** and **2**) and the dimethoxy derivative (**14**) are shown in Table 1 together with those of the other position isomer

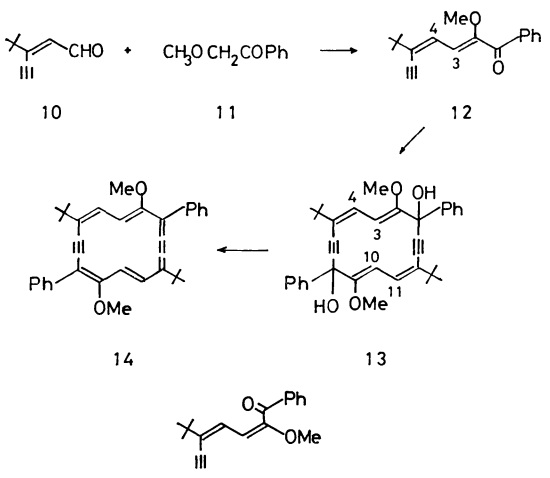
Table 1. Color of crystals, melting points and 100 MHz ^{1}H NMR parameters of **1**, **2**, **3**, and **14**

	"ortho" **1**	*"meta"* **2**	*"para"* **3**	Di-MeO- **14**
Color	deep reddish violet	reddish green	brownish violet	deep geen
Mp(°C) (dec)	248.0—249.0	200.8—202.0	284.0—284.5	281.5—282.7
Inner-H	13.51(t, J=13.5)	13.54(t, J=13.5) 13.65(t, J=13.5)	13.54(t, J=13.5)	13.76(t, J=13.5)
t-Bu	8.10(s)	8.07(s)	8.06(s)	8.15(s)
MeO				6.09(s)
m,p-H of Ph	2.38(m)	2.40(m)	2.43(m)	2.43(m)
o-H of Ph	1.37(m)	1.41(m)	1.42(m)	1.51(m)
Outer-H adjacent to *t*-Bu	0.58(d, J=13.5)	0.64(d, J=13.5)	0.56(d, J=13.5)	0.49(d, J=13.5)
Outer-H adjacent to Ph	0.26(d, J=13.5)	0.17(d, J=13.5)	0.26(d, J=13.5)	

Table 2. ^{13}C NMR parameters of **1**, **2**, **3**, and tetra-*t*-butyl analogue (**16**)[a]

tetra-*t*-Bu **16**		*"ortho"*- **1**		*"meta"*- **2**		*"para"*- **3**	
t-Bu	32.2, 37.8	*t*-Bu	32.1, 37.9	*t*-Bu	32.3, 38.0	*t*-Bu	32.3, 37.8
C^1	116.7	C^1, C^8	115.1	C^1, C^2	114.3, 116.5	C^1, C^2	114.7, 115.7
C^3	131.3	C^3, C^7, C^{15}	119.8, 133.6, 139.7	C^3, C^{10}, C^{15}	119.4, 134.4, 139.9	C^3, C^7, C^{15}	119.8, 133.7, 139.9
C^4	131.3	C^4, C^6	130.4, 130.6	C^4, C^{11}	131.5, 131.7	C^4, C^6	130.3, 130.7
C^5	129.0	C^5	132.1	C^5, C^{12}	129.4, 131.3	C^5	132.3
		C^{16}, C^{17}	128.3, 128.7	C^{16}, C^{17}	120.8, 128.8	C^{16}, C^{17}	128.0, 128.7
		C^{18}	127.3	C^{18}	127.3	C^{19}	127.3

a) The spectra were obtained on a Varian XL-100 spectrometer operated at 25.2 MHz with deuteriochloroform internal lock using TMS as an internal standard.

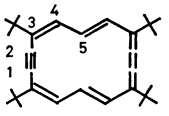


Scheme 2.

(**3**).[1]

The position isomers and the dimethoxy derivative (**1**, **2**, **3**, and **14**) were found to be strongly diatropic showing the signals of inner protons at high field and those of outer protons at low field. The close similarity of ^{1}H NMR behavior between the position isomers (**1**, **2**, and **3**) indicates that the difference of position of substituent group does not exert prominent effect on the π-electron system in the annulene nucleus at the ground state. Introduction of two methoxyl groups also exerts no essential change in NMR characteristics, although the group has both of electron attractive and donating property in the inductive and mesomeric modes. The low field shift of *ortho*-protons of phenyl groups as compared with that of *meta*- and *para*-protons can be reasonably attributed to the deshielding effect of diamagnetic ring current induced in the annulene ring. Inversely, the low field shift of outer protons of annulene ring adjacent to phenyl substituent indicates the ring current effect of benzene nucleus.

The ^{13}C NMR parameters are summarized in Table 2 together with those of tetra-*t*-butyl analogue (**16**). The assignment was made on the basis of chemical shifts, off resonance technique and the magnitude of NOE. The coupling constants are found to be J_{CH}=150—152 Hz, J_{CCH}=5 Hz and $J_{CCCH}\simeq$10 Hz. The fact that the sp-hybridized carbon atoms in the position isomers (**2** and **3**) exhibit two signals can be attributed to the difference of electron density between C^1 and C^2 which is caused by the difference of inductive effect between *t*-butyl and phenyl groups. However, it should be noted that the sp-hybridized carbon atoms in the isomer (**1**) showed only a signal in the corresponding



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region. It is also to be noted that the sp-carbon exhibits siganl at an intermediate region of acetylene and cumulene reflecting the hybrid nature of the linkage incorporated in the aromatic system.

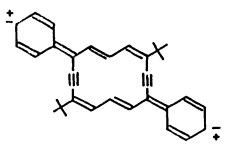
Remarkable difference in electronic spectra between the position isomers (**2** and **3**) was anticipated, because

Table 3. Electronic spectra of **1**, **2**, **3**, and **14** in THF. (λ_{max} in nm)[a]

	"*ortho*"- **1**		"*meta*"- **2**		"*para*"- **3**		di-MeO **12**	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
I	624	1800	624	1270	623	1640	637	4540
	573	538	574	352	571	590	590	698
II	507	37200	499	36430	508	52600	492	35000
	480*	18600	474*	19300	478*	1260		
III	360	215000	367	187000	357	195000	356	177000
	347*	78500	352*	87100	345*	76300	344*	8900
	331*	37600	335*	37000	332*	41100	321*	29700
	315*	22500	315*	19900	315*	27900		
IV	278	12900	275*	12800	270*	10800	264	11100
	239	14500			260	13400	253*	10900
	228*	12700			234	14300	236	10900
					226*	12300		

a) For absorption curves, see, Ref. 4. * Asterisk denotes shoulder.

the dipolar structure (**17**) may contribute in the excited state of (**3**) just as the case of *p*-terphenyl (**18**), and the contribution of such type of dipolar structure can be excluded in (**2**). However, in fact as shown in Table 3, the electronic spectra of the position isomers (**1**,**2** and **3**) and the dimethoxy derivative (**14**) showed close similarity except for the hyperchromism and bathochromic shift of the longest wavelength absorption band (I) of the dimethoxy derivative (**14**). The marked difference in electronic spectra between *p*- and *m*-terphenyls could not be observed in the spectra of the position isomers (**3** and **2**). This fact seems to be ascribable to the large difference in the stability of π-electron system between benzene nucleus and the 14-membered ring, and the general tendency that the electronic spectrum of a large conjugated system such as condensed benzenoid compound is less sensitive to the introduction of substituent group(s).



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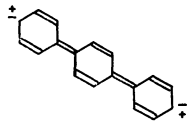

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At first sight, the intensification of the longest wavelength band (I) in **14** seemed to suggest that the direction of polarization of the longest wavelength band (I) is perpendicular to the long axis of the bisdehydro[14]annulene nucleus.[5] However, the measurements of fluorescence excitation spectra of tetra-*t*-butyl-bisdehydro[14]annulene (**16**) and the position isomer (**3**), and the theoretical calculation by PPP and RPA methods performed by Tanaka *et al.* revealed the nature of electronic transitions and the direction of polarization.[9] Namely as shown in Fig., the longest wavelength band (I) is ^1L_b species and the direction of polarization is parallel to the long axis, the medium wavelength band (II) is ^1L_a species having perpendicular polarization and the short wavelength band (III) consists of parallel polarized ^1B_b species and perpendicular polarized ^1B_a species.

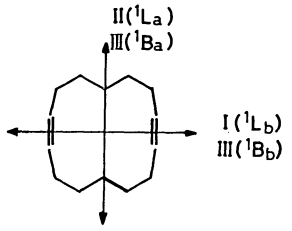

Fig. Direction of polarization of bisdehydro[14]-annulene.

Experimental

All the melting and boiling points are uncorrected. The melting points were measured an a Mettler FP-2 apparatus. The IR spectra were obtained on a Hitachi EPI-G3 or EPI-2 spectrophotometer by neat liquid film or KBr-disk method. Strong, medium, weak and broad bands were denoted by s, m, w and br, respectively. The electronic spectra were measured in THF using Hitachi EPS-3T spectrophotometer. The NMR spectra were obtained on one of the Varian spectrometerss of XL-100, A-60D, T-60 or a Hitachi R-24, and the parameters are given in τ-values with respect to TMS as an internal standard. The mass spectra were measured with a Hitachi RM-50 spectrometer (ionization potential 70 eV). The adsorbents used in the column chromatography are alumina (Merck, activity II-III or Woelm, activity I) and silica gel (Wako gel C-200). Evaporation of the solvent was performed under reduced pressure.

*3,6-Di-t-butyl-6-hydroxy-10-phenyl-2,7,9-dodecatriene-4,11-diynal Diethyl Acetal (**6a**).* 3-*t*-Butyl-2-penten-4-ynal diethyl acetal[3c] (0.9274 g, 0.00442 mol) in ether (80 ml) was mixed with 0.8 M of phenyllithium in ether (6.9 ml, 0.0055 mol) at −15——18 °C under nitrogen atmosphere to give the lithio derivative (**4**). After bing stirred for 10 min, a solution of the ketone (**5a**, 1.00 g, 0.0042 mol)[10] in ether (80 ml) was added dropwise over 1 h-period at the same temperature. After the mixture had been stirred for 1 h at 0 °C, stirring was continued overnight at room temperature. Cracked ice was added to the reaction mixture under external cooling. The organic layer was separated and the aqueous layer was extracted with ether. The combined ethereal solution was thoroughly washed with water and dried (K_2CO_3). Dark red liquid (2.1 g) obtained on evaporating the solvent was chromatographed on alumina (Merck,

100 g). The column was eluted with cyclohexane and benzene–cyclohexane (1:9) to remove a minor amount of starting material and by-product. Elution with benzene–cyclohexane (1:1) followed by benzene yielded **6a** as a pale yellow liquid, 1.21 g, 64%, IR(neat): 3425 (br, m, OH), 3300 (m, C≡CH), 1120, 1060, 960 (s, C–O–C) cm^{-1}. Further elution with ether–benzene (1:9) afforded **7** as a pale yellow viscous liquid (0.365 g, 23.2%).

*3,6-Di-t-butyl-6-hydroxy-10-phenyl-2,7,9-dodecatriene-4,11-diynal (**7a**).* A mixture of **6a** (2.9 g, 0.0065 mol), ethanol (290 ml), tartaric acid (1.5 g) and water (150 ml) was stirred for 3 h under ice-cooling and then for 2 h at 12 °C. The mixture was extracted with ether. The extract, after being washed with water and an aqueous solution of sodium hydrogencarbonate, was dried (K_2CO_3). A yellow viscous liquid (2.35 g) obtained on evaporating the solvent was dissolved in carbon tetrachloride and the solution was passed through a column of alumina (Merck, 95 g). Elution with benzene and ether–benzene (1:9) yielded a pale yellow viscous liquid (2.30 g, 95%) which was triturated with hexane to give **7a** as colorless crystals, mp 101.2—102.1 °C, 2.21 g, 91.3%, IR(KBr): 3450 (s, OH), 3280 (s, C≡CH), 1670 (s, C=O), 1580 (s, aromatic C=C) cm^{-1}, NMR(CCl_4): τ 8.90 (9H, d, *t*-Bu), 8.75 (9H, s, *t*-Bu adjacent to OH), 7.22 (1H, br s, C≡CH), 3.88 (1H, d, J=15 Hz, H^7), 8.83 (1H, d, J=8 Hz, H^8), 3.08 (1H, d, J=11 Hz, H^9), 2.75 (4H, m, *m,p*-H of Ph and H^8), 2.43 (2H, m, *o*-H of Ph), −0.16 (1H, d, J=8 Hz, CHO).

Found: C, 83.44; H, 8.10%. Calcd for $C_{26}H_{30}O_2$: C, 83.88; H, 8.07%.

*5,8-Di-t-butyl-1,12-diphenyl-8-hydroxy-2,4,9,11-tetradecatetraene-6,13-diyn-1-one (**8a**).* To a stirred solution of **7a** (1.24 g, 0.003 mol) and acetophenone (0.475 g, 0.004 mol) in ethanol (15 ml) was added at −5 °C a solution of sodium hydroxide (0.15 g, 0.38 mol) in water (1 ml) and ethanol (1 ml) under nitrogen atmosphere. After being stirred for 1 h at −5——10 °C, for 2 h at 2 °C and then for 1 h at 14 °C, the mixture was extracted with ether. A reddish liquid (1.7 g) obtained on evaporation of the ethereal extract, after being washed and dried (K_2CO_3), was dissolved in benzene–cyclohexane (1:9) and chromatographed on alumina (Merck, 70 g). Excess of acetophenone was removed on elution with benzene–cyclohexane (2:8—5:5). Further elution with benzene and ether–benzene (2:8) afforded a pale yellow viscous liquid (1.12 g, 71.2%) which crystallized on trituration with hexane to give **8a**, pale yellow needles, mp 88.5—89.5 °C, 1.09 g, 69.3%, IR(KBr): 3430 (m, OH), 3300 (m, C≡CH), 1655 (s, C=O), 1590 (s, aromatic C=C) cm^{-1}, NMR(CCl_4): 8.90 (9H, s, *t*-Bu), 8.77 (9H, s, *t*-Bu adjacent to OH), 7.15 (1H, s, disappeared on addition of D_2O), 6.67 (1H, s, C≡CH), 3.95—3.00 (6H, m, olefinic-H), 2.83—1.93 (10H, m, aromatic-H).

Found: C, 85.38; H, 7.56%. Calcd for $C_{34}H_{36}O_2$: C, 85.67; H, 7.61%.

*5,8-Di-t-butyl-1,12-diphenyl-2,4,9,11-cyclotetradecatetraene-6,13-diyn-1,8-diol (**9a**).* A solution of **8a** (0.45 g, 0.0009 mol) in THF (90 ml) was added over 8 h-period to a suspension of finely powdered potassium hydroxide (2.0 g) in liquid ammonia (280 ml) at −45——35 °C. After the mixture had been stirred for 12 h, powdered ammonium chloride (7.0 g) was added at −50——55 °C. After 15 min, the cooling bath was removed and the ammonia was allowed to evaporate. The residue was repeatedly extracted with ether. The extract was washed with saturated ammonium chloride solution and dried (K_2CO_3). The product obtained on evaporating the solvent was dissolved in ether–benzene (3:7) and passed through a column of alumina (Woelm, 10 g). Slightly crude **9a**, pale yellow fine crystals, 0.41 g, was used without further purification in the following reaction.

*3,14-Di-t-butyl-7,10-diphenyl-1,8-bisdehydro[14]annulene (**1**).* To a stirred solution of **9a** (410 mg) in ether (50 ml) was added at −12——15 °C a solution of tin(II) chloride dihydrate (500 mg) in the same solvent saturated with hydrogen chloride (10 ml). After being stirred for 3 min, cold water was added to the mixture. The organic layer was washed successively with water, aqueous sodium hydrogencarbonate solution and water, and dried (K_2CO_3). The crude product obtained on evaporating the solvent was chromatographed on alumina (Merck, 40 g) and eluted with ether–hexane (2:8). Rechromatography on alumina (Merck, 30 g) and elution with benzene afforded **1**, deep reddish violet crystals, 231 mg, 55.3% based on **8a**, which were recrystallized from ether–hexane (3:7) to give pure **1**, reddish violet plates with deep green metallic luster, mp 248.0—249.0 °C (dec).

Found: C, 92.12; H, 7.83%. Calcd for $C_{34}H_{34}$: C, 92.26; H, 7.74%.

*3-t-Butyl-6-hydroxy-6,10-diphenyl-2,7,9-dodecatriene-4,11-diynal Diethyl Acetal (**6b**).* To a stirred and cooled (ice–salt bath) solution of the lithio derivative (**4**), prepared from *t*-butyl-pentenynal diethyl acetal (2.10 g, 10 mmol) in ether (150 ml) on treatment with an ethereal phenyllithium solution (0.74 M, 18.5 ml, 13.7 mmol), was added under nitrogen atmosphere a solution of **5b** (3.00 g, 11.6 mmol)[2] in the same solvent (120 ml) over a period of 1.5 h. After being stirred for 15 min at 0 °C, and then for 14.5 h at a room temperature, the reaction mixture was poured onto ice-water. The organic layer was washed successively with cold water, cold brine and cold water, and dried (K_2CO_3). Reddish brown liquid (5.88 g) obtained on evaporation of the solvent was chromatographed on silica gel (160 g). 3-*t*-Butyl-pentenynal diethyl acetal was eluted with benzene–cyclohexane (1:1) and benzene. Further elution with ether–benzene(1:1) yielded **6b**, yellowish red powder, 4.05 g, 84.4%, IR(neat): 3380 (m, OH), 3303 (m, C≡CH), 2090 (w, C≡C), 1120, 1053, 972 (C–O–C) cm^{-1}, NMR($CDCl_3$): 2.31 (4H. m, *o*-H of Ph), 2.81 (7H, m, *m,p*-H of Ph and H^8), 4.17 (1H, d, J=7 Hz, H^2), 4.68 (1H, d, J=7 Hz, H^1), 6.32 (4H, m, CH_2), 6.47 (1H, s, C≡CH), 7.24 (1H, s, OH), 8.75 (9H, s, *t*-Bu), 8.78 (6H, t, J=7 Hz, CH_3).

The attempts to crystallize **6a** were unsuccessful.

*3-t-Butyl-6-hydroxy-6,10-diphenyl-2,7,9-dodecatriene-4,11-diynal (**7b**).* A solution of **6b** (3.03 g, 6.47 mmol) in ether (250 ml) and THF (10 ml) was added over 1 h-period to an ice-cooled aqueous solution of tartaric acid (1%, 150 ml). After being stirred for 2.5 h at 0—12 °C, the reaction mixture was poured onto ice–water and extracted with ether. The extract, after washing with brine and drying (K_2CO_3), was concentrated to give a reddish yellow solid (2.54 g), which was chromatographed on alumina and recrystallized from carbon tetrachloride and from cyclohexane to give pure **7b**, mp 84.3—85.7 °C, pale yellow plates, IR(KBr): 3325 (m, OH), 3290 (m, C≡CH), 1658 (s, C=O), 1580 (w, C=O) cm^{-1}, NMR($CDCl_3$): 8.74 (9H, s, *t*-Bu), 7.08 (1H, br, s, OH, disappeared on addition of D_2O), 6.38 (1H, s, C≡CH), 3.80 (1H, d, J=14 Hz, H^7), 3.70 (1H, d, J=8 Hz, H^8), 2.99 (1H, d, J=11 Hz, H^9), 2.61 (7H, m, *m,p*-H of Ph and H^8), 2.27 (4H, m, *o*-H of Ph), −0.16 (1H, d, J=8 Hz, H^1).

*7-t-Butyl-2,2-dimethyl-10,14-diphenyl-10-hydroxy-4,6,11,13-hexadecatetraene-8,15-diyn-3-one (**8b**).* A solution of sodium hydroxide (0.23 g, 5.75 mmol) in 50% aqueous ethanol (3.0 ml) was added under nitrogen atmosphere to an ice-cooled solution of **7b** (2.04 g, 5.18 mmol) and pinacolone (4.80 g, 47 mmol) in ethanol (25 ml). After being stirred for 2 h at 0 °C and for 24 h at a room temperature,

the reaction mixture was poured onto ice–water and extracted with ether. The extract was washed with water, brine and water, successively, and dried (K_2CO_3). A red liquid obtained on evaporation of the solvent was chromatographed on silica gel (Wako, 120 g) and eluted with cyclohexane–benzene–ether to give **8a**, a yellow solid, 1.97 g, IR(KBr): 3320 (m, OH), 3250 (m, C≡CH), 1675 (m, C=O), 1590 (s, C=C) cm^{-1}, NMR(CCl_4): 8.88 (9H, s, *t*-Bu), 8.76 (9H, s, *t*-Bu adjacent to C=O), 6.65 (1H, s, C≡CH), 3.83 (1H, d, J=16 Hz, H^{11}), 3.61 (1H, d, J=13 Hz, H^6), 3.45 (1H, d, J=15 Hz, H^4), 2.71 (8H, m, *m,p*-H of Ph and $H^{5,12}$), 2.40 (4H, m, *o*-H of Ph).

Crystallization of **8b** could not be achieved.

*1,5-Di-t-butyl-8,12-diphenyl-2,4,9,11-cyclotetradecatetraene-6,13-diyne-1,8-diol (**9b**).* A solution of **8b** (400 mg, 0.84 mmol) in THF (120 ml) was added to a stirred suspension of potassium hydroxide (3.0 g, 54 mmol) in liquid ammonia (700 ml) over a period of 22.5 h at −60——38 °C. After being stirred for further 3 h at −38——30 °C, powdered ammonium chloride was added to the reaction mixture and the ammonia was allowed to evaporate. The residue was mixed with water and extracted with ether. After being washed with a saturated solution of ammonium chloride, the extract was dried ($MgSO_4$). Removal of the solvent yielded a yellow solid, which gave IR and NMR spectra consistent with the 14-membered cyclic glycol (**9b**). The crude **9b** was used without further purification in the following reaction.

*3,7-Di-t-butyl-10,14-diphenyl-1,8-bisdehydro[14]annulene (**2**).* To a solution of crude **9b** in ether (40 ml) cooled in an ice–salt bath was added a solution of tin(II) chloride dihydrate (1.2 g) in the same solvent saturated with hydrogen chloride (15 ml). After being stirred for 15 min, ether was added to the reaction mixture, and the ethereal solution was washed successively with water and brine, and dried ($MgSO_4$). Deeply colored solid obtained on working up the extract was chromatographed on alumina (Merck, 30 g). Greenish violet crystals (8.2 mg, 20.5% based on **8b**) obtained on elution with hexane–ether were rechromatographed on alumina (Woelm) to give pure **2**, reddish green needles, mp 200.8—202.0 °C (dec).

Found: C, 92.17; H, 7.71%, mass (*m/e*): 442 (M^+). Calcd for $C_{34}H_{34}$: C, 92.26; H, 7.74%, mol wt: 442.612.

*5-t-Butyl-2-methoxy-1-phenyl-2,4-heptadien-6-yn-1-one (**12**).* To an ice-cooled solution of 3-*t*-butyl-2-penten-4-ynal (**10**, 6.7 g, 49 mmol)[2c,5] and ω-methoxyacetophenone (**11**, 7.6 g, 51 mmol)[6] in ethanol (250 ml) was added over 1 h-period a solution of sodium hydroxide (2.5 g, 83 mmol) in 50% aqueous ethanol (100 ml) under nitrogen atmosphere. After the resulting deep red solution had been stirred for 49 h at 12 °C, water was added to the mixture and extracted with ether. The extract was washed successively with water, brine and sodium hydrogencarbonate solution, and dried ($MgSO_4$). A yellow liquid obtained on evaporation of the solvent was chromatographed on alumina (Merck, 120 g). Elution with ether–hexane (1:9 to 2:8) gave **12**, a yellow liquid, 10.6 g, 80%, mass (*m/e*): 268 (M^+), Calcd for $C_{18}H_{21}O_2$: 268.348, IR(neat): 3290 (m, C≡CH), 2079 (w, C≡C), 1649 (s, C=O), 1598 (s, C=C), 1450 (s, O–CH_3), 1125 (s, C–O–C) cm^{-1}. The ^1H NMR parameters are given in Table 4. The ketone (**12**) was found to be rather unstable in neat, but can be kept for a month without appreciable decomposition in an ether solution under argon atmosphere at a room temperature. Distillation of **12** (bp 110—120 °C/ 7×10^{-5} Pa) accompanied with a remarkable decomposition.

*5,12-Di-t-butyl-1,8-diphenyl-2,9-dimethoxy-2,4,9,11-cyclotetradecatetraen-6,13-diyn-1,8-diol (**13**).* A solution of **12** (429 mg, 1.60 mmol) in THF (30 ml) was added to a suspension of potassium hydroxide (2.0 g, 56 mmol) in liquid ammonia (200 ml) over a period of 2.5 h at −64——63 °C. After stirring for 16 h at −64——30 °C, ammonium chloride was added to the reaction mixture at −60 °C, and the ammonia was allowed to evaporate. Water was added to the residue and the mixture was extracted with ether. The extract was worked up in the usual manner. Evaporation of the solvent afforded a brown liquid, which was chromatographed on alumina (Merck, 40 g). After being eluted thoroughly with cyclohexane–benzene (1:1) to remove the starting materials, the solvent was replaced by ether–benzene (1:9). Concentration of the eluate yielded a diastereomer of **13**, mp 247.9—249.1 °C (dec), colorless crystals, 68 mg, 17%. Elution with ether–benzene (1:1) gave another diastereomer of **13**, mp 265.2—266.1 °C (dec), colorless crystals, 128 mg, 30%, NMR($CDCl_3$): 8.83 (9H, s, *t*-Bu), 8.72 (1H, s, OH), 6.35 (3H, s, OCH_3), 3.46 (1H, d, J=11 Hz, H^3), 3.24 (1H, d, J=11 Hz, H^4), 2.77 (3H, m, *m,p*-H of Ph), 2.52 (2H, m, *o*-H of Ph).

Table 4. ^1H NMR parameters of **12**

	CCl_4	C_6D_6
o-H of Ph	2.20(2H, m)	2.21(2H, m)
m,p-H of Ph	2.57(3H, m)	2.87(3H, m)
H^4	3.10(1H, dd, J=0.6, 11)	2.86(1H, dd, J=0.6, 11)
H^3	3.39(1H, d, J=11)	3.06(1H, d, J=11)
OCH_3	6.28(3H, s)	6.46(3H, s)
C≡CH	6.70(1H, d, J=0.6)	7.04(1H, d, J=0.6)
t-Bu	8.80(9H, s)	8.87(9H, s)

Although the mass spectrum of the high melting isomer showed the presence of impurities, the material was subjected to the following conversion without further purification. Both of the diastereomers gave **14**.

*3,10-Di-t-butyl-6,13-dimethoxy-7,14-diphenyl-1,8-bisdehydro-[14]-annulene (**14**).* A diastereomeric mixture of crude **13** prepared from **12** (271 mg, 1.01 mmol) by the above-stated procedure was dissolved in ether (20 ml). A solution of tin(II) chloride dihydrate (1.4 g, 8.9 mmol) in ether saturated with hydrogen chloride (13 ml) was added to the stirred solution of **13** at −60 °C. After 2 min, the resulting deep reddish violet solution was poured onto ice–water, and extracted with ether. The extract, after being washed successively with water, brine, sodium hydrogencarbonate solution and water, and dried (K_2CO_3), was concentrated to give a black solid, which was chromatographed on alumina (Merck, 30 g). Elution with hexane and THF–hexane (0.5:9.5) gave **14**, green crystals, 84 mg, 33% based on **12**. Rechromatography on alumina (Woelm) followed by recrystallization from benzene–hexane (1:5) gave analytical specimen of **14**, deep green plates, mp 281.5—282.7 °C (dec).

Found: C, 85.97; H, 7.60%, mass (*m/e*): 502 (M^+). Calcd for $C_{36}H_{38}O_2$: C, 86.01; H, 7.62%, mol wt: 502.664.

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