Dehydroannulenes. IX. Effects of Substituents on the ^{1}H NMR Spectra of Tetrakisdehydro[18]- and Bisdehydro[14]annulenes

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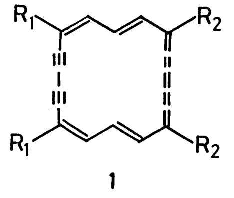
(Received May 15, 1978)

In order to obtain information on the cause of low field shift of ^{1}H NMR signals of 'acetylene-cumulene'-dehydroannulenes on introduction of substituents, the syntheses of 1,8-bisdehydro[14]- and 6,8,15,17-tetrakisdehydro[18]annulenes bearing *p*-substituted phenyl group(s) have been performed. The examination of their ^{1}H NMR spectra indicates that the low field shift of NMR signals can be regarded as a superposition of three effects, *i.e.*, 1) decrease of ring current in annulene nucleus by perturbation of substituent group(s), 2) Deshielding effect of ring current in aryl substituent(s) exerted on annulene protons, and 3) Electronic effect of *p*-substituent in phenyl group(s) transmitted to annulene ring.

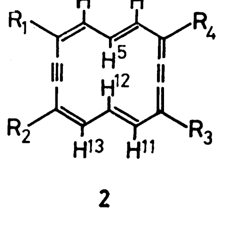
Replacement of the methyl groups in 1,5,10,14-tetramethyl-6,8,15,17-tetrakisdehydro[18]annulene (**1a**)[1] by *t*-butyl groups to give tetra-*t*-butyl derivative (**1b**)[2] resulted in appreciable down field shifts of both of the outer and inner proton signals of the annulene ring. As pointed out in previous papers of this series,[3] further down field shifts of annulene protons were observed on successive replacement of the methyl groups in **1a** or *t*-butyl groups in **1b** by phenyl groups to give **1c**[3] or **1d**[4]. Furthermore, tetraphenyltetrakisdehydro[18]annulene (**1e**)[3] exhibits both of the inner and outer proton signals at even more low field than those of **1c** or **1d**.

Preparation of tetrasubstituted 1,8-bisdehydro[14]annulenes bearing various substituents has revealed the similar substituent effects on the chemical shifts of protons in 1,8-bisdehydro[14]annulene ring. Substitution of the hydrogens at 3,7,10 and 14-positions in the parent bisdehydro[14]annulene (**2a**)[5] by *t*-butyl groups (**2b**) resulted in an appreciable down field shifts of inner protons (H^5 and H^{12}) accompanying with slight high field shifts of the outer protons (H^4, H^6, H^{11}, and H^{13}). The H^1 NMR spectra of position isomers of di-*t*-butyl-diphenyl-1,8-bisdehydro[14]annulene, (**2c**),[6] (**2d**),[7] (**2e**),[7] and the tetraphenyl derivative (**2f**)[6] exhibit also low field shift of both of the inner and outer protons in the annulene ring as compared with those of **2b**.



1

a : $R_1 = R_2 = Me$
b : $R_1 = R_2 = t\text{-}Bu$
c : $R_1 = Me$, $R_2 = Ph$
d : $R_1 = t\text{-}Bu$, $R_2 = Ph$
e : $R_1 = R_2 = Ph$
f : $R_1 = R_2 = p\text{-}MeO\text{-}Ph$

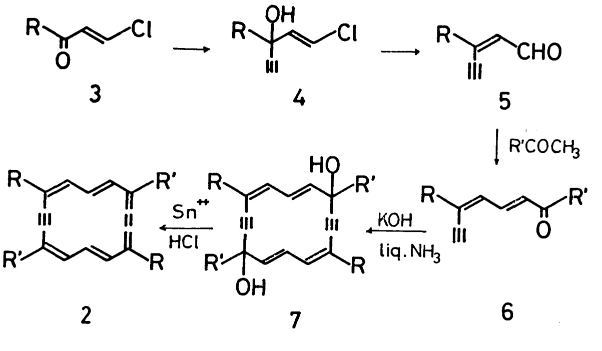


2

a : $R_1 = R_2 = R_3 = R_4 = H$
b : $R_1 = R_2 = R_3 = R_4 = t\text{-}Bu$
c : $R_1 = R_3 = t\text{-}Bu$, $R_2 = R_4 = Ph$
d : $R_1 = R_2 = t\text{-}Bu$, $R_3 = R_4 = Ph$
e : $R_1 = R_4 = t\text{-}Bu$, $R_2 = R_3 = Ph$
f : $R_1 = R_2 = R_3 = R_4 = Ph$

In order to get further insight into the effect of substituents, we have carried out the syntheses of tetrasubstituted 'acetylene-cumulene'-dehydroannulenes bearing *p*-substituted phenyl group(s).

Syntheses. 3,7,10,14-Tetrasubstituted 1,8-bisdehydro[14]annulenes (**2g**—**m**) were obtained by a similar reaction sequence used in the preparation of other analogues (**2b, c**) outlined in Scheme 1.



g : R = R' = p-MeO-Ph,
h : R = Ph, R' = p-MeO-Ph
i : R = t-Bu, R' = p-MeO-Ph,
j : R = t-Bu, R' = p-Br-Ph
k : R = t-Bu, R' = p-Cl-Ph,
l : R = t-Bu, R' = p-Me-Ph
m : R = t-Bu, R' = p-MeOOCPh

Scheme 1.

The stepwise sequence of reactions employed for the preparation of "*ortho*"- (**2d**) and "*meta*"-isomers (**2e**)[7] was adopted to the synthesis of tri-*t*-butyl (*p*-methoxycarbonylphenyl)-1,8-bisdehydro[14]annulene (**2n**) (Scheme 2). Crude product of the aldol condensation of the hydroxy aldehyde (**8**)[8] with *p*-acetyl-benzoic acid was converted into the methyl ester (**9**). The hydroxy ketone (**9**) was treated with potassium hydroxide in liquid ammonia and the product was methylated by diazomethane to give 14-membered cyclic glycol (**10**). Reductive dehydroxylation of **10** by means of tin(II) chloride dihydrate in ether saturated with hydrogen chloride yielded **2n**.

The tetrakis(*p*-methoxyphenyl)tetrakisdehydro[18]annulene (**1f**) was synthesized by the method used for the preparation of other analogous tetrakisdehydro[18]annulenes (**1a**—**e**).[1–4] The reaction sequence is outlined in Scheme 3. The diketone

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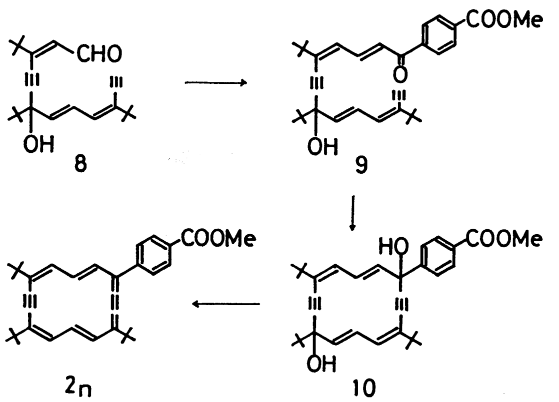
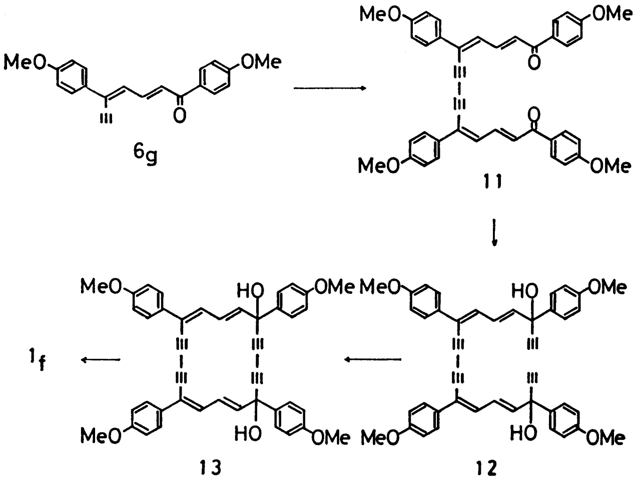
Table 1. Color of crystals, melting points and electronic spectra of **2g**—**n** and **1f**

	Color of crystals mp (°C) (dec)	Electronic spectra in THF λ_{max} in nm and (ε)
2g	deep violet >280	247.5(21600), 285(33600), 333(19200), 350(25700), 408(298000), 576(57400), 665(2270)
2h	deep violet >250	245(19300), 261*(20500), 283(27100), 330(17100), 347(24700), 395(278000), 563(52100), 665(4800)
2i	deep violet >230	240(14400), 267(16000), 316(30500), 334(20700), 367(176000), 524(60500), 625(2240)
2j	dark brick red >275	231(14620), 239(16580), 269(14250), 315(30350), 332(45160), 348*(78470), 361(191700), 514(57740), 574(879), 628(2270)
2k	dark copper red >280	229.5(13800), 237.5(16200), 267.5(14600), 332(48000), 360(196200), 512(58400), 570(540), 623(2120)
2l	dark reddish violet >280	237.5(14600), 264(13900), 330.5(41900), 361(192100), 513(54800), 571(680), 624(1580)
2m	deep violet >320	235(17300), 275.5(15200), 317(32400), 334(46100), 351(69500), 365(186000), 525(61100), 578(1560), 616(2950)
2n	reddish brown >270	234.5(11300), 255*(10300), 267.5(11600), 305*(22500), 326*(42600), 340*(77500), 354.5(161000), 491(36800), 561(695), 612(1800)
1f	deep green 169—171	282(31700), 305(30200), 329(22400), 358(23400), 381(36300), 453(288500), 670(115000), 784(3900)

* Asterisk indicates shoulder.



Scheme 2.



Scheme 3.

(**11**) obtained by the oxidative coupling of dienyne ketone (**6g**) by cupric acetate in pyridine was allowed to react with lithium acetylide-ethylenendiamine complex[9] in THF to give the acetylenic glycol (**12**). Oxidative coupling of **12** by cupric acetate in pyridine under high dilution conditions yielded the cyclic glycol (**13**), which could be converted into the tetrakis(*p*-methoxyphenyl)tetrakisdehydro[18]annulene (**1f**) on treatment with tin(II) chloride dihydrate in ether saturated with hydrogen chloride.

The color of crystals, melting points and the electronic spectral data of **2g**—**n** and **1f** are summarized in Table 1.

Discussion. The effect of alkyl groups on the chemical shifts of protons on 'acetylene-cumulene'-dehydroannulene rings is summarized in Table 2. The most remarkable change caused by the replacement of hydrogens by *t*-butyl groups (**2a**→**2b**) or methyl by *t*-butyl groups (**1a**→**1b**) is the appreciable low field shifts of inner protons signals. The essentially planar structures of tetra-*t*-butylbisdehydro[18]-[10] and [22]annulenes[11] have been proved by the X-ray structure analyses, and the almost temperature independent ^{1}H NMR spectra of this series of 'acetylene-cumulene'-dehydroannulenes indicate their high conformational stability.[1,3,14] Also the examination of molecular models of *t*-butylsubstituted derivatives reveals that they have no steric interference between the *t*-butyl group and the adjacent outer hydrogen atom. In view of the rather high diatropicity of **1** and **2**, it seemed to be reasonable to assume that the annulenes (**1** and **2**) hold essentially planar conformation in solution just as in crystalline state. Therefore, the marked low field shifts of inner protons seems to be difficult to ascribe solely to the deformation of annulene perimeter caused by introduction of substituent groups. Also the remarkable low field shifts can not be attributed to the change of electron density of the annulene ring induced by the introduction of substituent groups, becaues the ^{1}H NMR spectra of **14a**[12] and **14b**[12] bearing electron attractive acetyl

Table 2. Effects of alkyl and acyl substituents

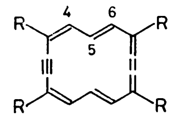
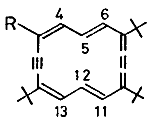
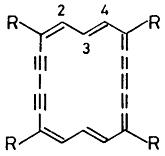
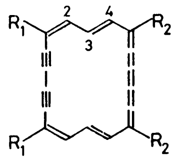
	R	Outer-H	Inner-H	Me	*t*-Bu	Solvent
 2	**a**: H[5]	$H^{4,6}$ 0.45	H^5 15.54			$CDCl_3$
	b: *t*-Bu[6]	$H^{4,6}$ 0.58	H^5 13.39		8.10	THF-d_8
 14	**a**: $COCH_3$[12]	H^6 0.05 H^4 0.48 $H^{11,13}$ 0.68, 0.66	H^5 14.16 H^{12} 13.88		8.13 8.11 8.09	$CDCl_3$
	b: COOH[12]	H^4 −0.12 H^6 0.40 $H^{11,13}$ 0.61	H^5 14.29 H^{12} 14.07		8.04 8.09	$CDCl_3$
 1	**a**: Me[1]	$H^{2,4}$ 0.34	H^3 15.24	7.42		THF-d_8
	b: *t*-Bu[2]	$H^{2,4}$ 0.02	H^3 14.92		7.98	THF-d_8

Table 3. Effects of aryl substituents on tetrakisdehydro[18]annulenes

	R_1	R_2	Outer-H	Inner-H	Aryl-H *o*-	Aryl-H *m.p*-	*t*-Bu	Me	Solvent
 1	**a**: Me	Me	$H^{2,4}$ 0.34	H^3 15.24				7.42	$CDCl_3$
	b: *t*-Bu	*t*-Bu	$H^{2,4}$ 0.04	H^3 14.89			7.98		$CDCl_3$
	c: Ph	Me	H^2 0.12 H^4 0.54	H^3 14.20	1.36	2.60		6.56	
	d: Ph	*t*-Bu	H^2 −0.40 H^4 0.01	H^3 13.90	1.13	2.37	7.93		THF-d_8
	e: Ph	Ph	$H^{2,4}$ −0.31	13.19	1.30	2.40			THF-d_8
	f: $R_1=R_2=p$-$MeOC_6H_4$		$H^{2,4}$ −0.04	H^3 13.00	1.21	*ca.* 2.7*		5.98	$CDCl_3$

* Submerged in $CHCl_3$ peak.

Table 4. ^1H NMR parameters of diaryl-di-*t*-butyl-1,8-bisdehydro[14]annulene (**2**) in THF-d_8. τ-values

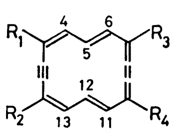
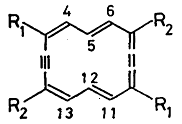
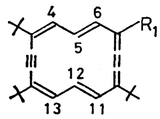
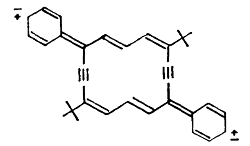
	R_1	R_2	R_3	R_4	Outer-H	Inner-H	Aryl-H *o*-	Aryl-H *m p*-	*t*-Bu	Lit
 2	**b**: *t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu	$H^{4,6}$ 0.58	H^5 14.39			8.10	6)
	c: *t*-Bu	Ph		*t*-Bu	H^6 0.16 H^4 0.49	H^5 13.45	1.39	2.39	8.05	6)
	d: *t*-Bu	*t*-Bu	Ph	Ph	$H^{4,13}$ 0.58 $H^{6,11}$ 0.26	H^5 13.51	1.37	2.38	8.10	7)
	e: *t*-Bu	Ph	*t*-Bu	Ph	$H^{4,13}$ 0.64 $H^{6,11}$ 0.17	H^5 13.65 H^{12} 13.54	1.41	2.40	8.07	7)
	i: *t*-Bu	*p*-$MeOC_6H_4$		*t*-Bu	H^6 0.27 H^4 0.58	H^5 13.40	1.47	2.81	8.05	present paper
	j: *t*-Bu	*p*-BrC_6H_4		*t*-Bu	H^6 0.04 H^4 0.39	H^5 13.45	1.50	2.22	8.07	present paper
	k: *t*-Bu	*p*-ClC_6H_4		*t*-Bu	H_6 0.14 H^4 0.44	H^5 13.48	1.35	2.33	8.05	present paper
	l: *t*-Bu	*p*-MeC_6H_4		*t*-Bu	H^6 0.22 H^4 0.53	H^5 13.46	1.52	2.57	8.07	present paper
	m: *t*-Bu	*p*-$MeOOCC_6H_4$		*t*-Bu	H^6 0.04 H^4 0.32	H^5 13.36	1.24	1.68	8.04	present paper

Table 5. ^{1}H NMR parameters of tetraaryl- and tri-*t*-butyl-*p*-methoxycarbonylphenyl-1,8-bisdehydro[14]annulenes

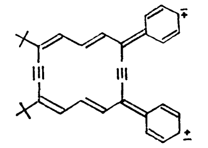
2	R_1	R_2	$H^{4,6}$	H^5	Aryl-H		OCH_3	*t*-Bu	Solvent
					o-	*m,p*-			
	**f**: Ph	Ph	0.06	12.56	1.30	2.35			THF-d_8
	g: $R_1 = R_2 =$ *p*-$MeOC_6H_4$		0.44	12.60	1.54	2.80	6.04		$CDCl_3$
	h: Ph	*p*-$MeOC_6H_4$	0.21	12.50	1.40	2.50	6.08		THF-d_8
	**n**: *p*-$MeO_2CC_6H_4$		H^6 0.25 H^4 0.55 $H^{11,13}$ 0.66	H^5 13.93 H^{12} 13.95	1.34	1.69	5.99	8.10(18H) 8.07(9H)	$CDCl_3$

or carboxyl group exhibit essentially the same NMR trend as compared with **2a** and **2b** having hydrogen or electron donating alkyl groups.

The ^{1}H NMR parameters of aryl substituted tetrakisdehydro[18]annulene derivatives are recorded in Table 3 together with those of tetramethyl and tetra-*t*-butyl derivatives (**1a** and **1b**) as references. The ^{1}H NMR parameters of bisdehydro[14]annulenes bearing two aryl groups are summarized in Table 4 together with tetra-*t*-butyl derivative (**2b**) as a reference. It is to be noted that the position isomers of di-*t*-butyldiphenylbisdehydro[14]annulenes (**2c**, **2d**, and **2e**) show quite similar ^{1}H NMR spectra. This fact indicates that decrease of ring current by the contribution of dipolar structures such as **15a** or **15b** can be ignored in the ground state of 1,8-bisdehydro[14]annulene system.[13]



15a



15b

As schematically illustrated in Fig., the magnitude of low field shifts of H^{15} and H^{16} in **2c**, **i**, **j**, **k**, **l**, and **2m** caused by the substituent group at the *p*-position of phenyl group is found to be in the same sequence with the corresponding positions ($H^{m'}$ and $H^{o'}$) in monosubstituted benzenes. This fact suggests that the perturbation of bisdehydro[14]annulene ring on benzene nucleus is not sufficiently large enough to alter the electronic state or electron density of the *p*-substituted phenyl group. Interestingly, as shown in Fig., low field shifts of outer protons of the annulene nuclei (H^4 and H^6), although in less extent being maximum values 0.19 and 0.23 ppm for H^4 and H^6, respectively, are found in the same sequence of H^{16} and $H^{o'}$. This fact indicates a transmission of the effects of *p*-substituent group to the annulene nuclei.

The ^{1}H NMR parameters of tetraaryl-1,8-bisdehydro[14]annulenes (**2f**, **g**, **h**) and tri-*t*-butyl(*p*-methoxycarbonylphenyl)-1,8-bisdehydro[14]annulene (**2n**) are recorded in Table 5. The tetraaryl derivatives (**2f**, **g**, **h**) showed inner proton signals at lower field than those for diaryl derivatives (Table 4). On the other hand, high field shifts of both of the inner and outer proton signals were observed in the monoaryl-derivative (**2n**) as compared with the diaryl derivatives (**2c**, **d**, **e**, **i**, **j**, **k**, **l**, **m**) shown in Table 4. This trend seems to indicate that the diamagnetic ring current induced in the aryl substituent(s) exerts deshielding effect on the outer and inner protons of the annulene nuclei.

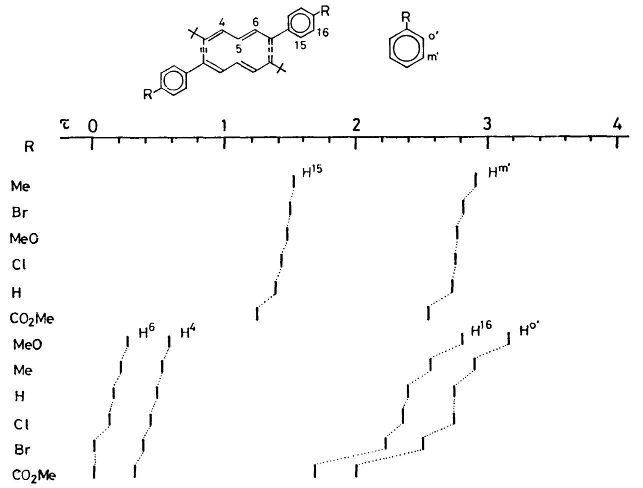


Fig. ^{1}H NMR chemical shifts of bis(*p*-substituted-phenyl)-di-*t*-butyl-1,8-bisdehydro[14]annulenes (**2c**, **i**—**m**) and corresponding monosubstuitedt benzenes.

The deshielding effect of phenyl group in di-*t*-butyldiphenyl-1,8-bisdehydro[14]annulene (**2c**) on the annulene protons has been calculated assuming coplanar conformation of the phenyl groups with the annulene ring by the Johnson-Bovey's method. The low field shifts due to the diamagnetic ring current in phenyl groups were estimated to be as follows : H^6 -0.60—-0.50; $H^4 < -0.15$; H^5 -0.15—-0.20 ppm. In view of the observed much larger down field shifts, this results seem to indicate that some other effects cooperate with the deshielding effect of aryl substituents.

It is well recognized that the signals of inner protons show remarkable shifts on minor variation of diamagnetic ring current in contrast to rather insensitive outer proton signals.[14] Because as pointed out previ-

Table 6. Preparation of heptadienyne ketones (**6h**—**m**)

6	Starting materials				Reaction		Heptadienyne ketone **6**			
	Aldehyde **5**	R′COCH$_3$	Solvent	Base	Temp (°C)	Time (h)	Color	Mp (°C)	Yield (%)	Found (Calcd), %
h	R=Ph 0.888 g 5.69 mmol	R′=*p*-MeOC$_6$H$_4$ 0.858 g 5.71 mmol	EtOH 65 ml	NaOH 0.3 g H$_2$O 2 ml	0	overnight	pale yellow	125	1.05 (63.7)	C, 83.15(83.31); H, 5.55(5.59)
i	R=*t*-Bu 5.5 g 40.4 mmol	R′=*p*-MeOC$_6$H$_4$ 6.0 g 40.4 mmol	EtOH 200 ml	NaOH 2.0 g H$_2$O 4 ml EtOH 50 ml	5	overnight	yellow	54.7— 55.7	2.1 (65.0)	C, 80.30(80.50); H, 7.36(7.51)
j	R=*t*-Bu 3.8 g 28 mmol	R′=*p*-BrC$_6$H$_4$ 5.6 g 30 mmol	EtOH 30 ml	NaOH 1.6 g H$_2$O 2 ml EtOH 10 ml	5	overnight	greenish yellow	109	4.5 (64.0)	C, 64.23(64.27); H, 5.45(5.35); Br, 25.09(25.15)
k	R=*t*-Bu 1.09 g 8 mmol	R′=*p*-ClC$_6$H$_4$ 1.16 g 7.5 mmol	EtOH 15 ml	NaOH 0.32 g H$_2$O 3 ml	0	2	pale yellow	119— 121	1.96 (96.0)	C, 75.04(74.86); H, 6.26(6.24); Cl, 13.06(13.00)
l	R=*t*-Bu 1.09 g 8 mmol	R′=*p*-MeC$_6$H$_4$ 1.07 g 8 mmol	EtOH 15 ml	NaOH 0.32 g H$_2$O 3 ml	0	3	pale yellow	93— 94	1.60 (79.0)	C, 85.70(85.67); H, 7.90(7.99)
m[a)]	R=*t*-Bu 1.27 g 9.3 mmol	R′=*p*-HOOCC$_6$H$_4$ 1.56 g 9.5 mmol	EtOH 15 ml	NaOH 1.24 g H$_2$O 36 ml	r. t.	20	yellow	109.9— 111.0	0.723 (27.0)	C, 76.91(77.00); H, 6.78(6.80)

a) The product of the aldol condensation was treated with diazomethane to give the methyl ester (**6m**).

Table 7. Prepartion of tetrasubstituted 1,8-bisdehydro[14]annulene (**2g**—**m**)

	Heptadienyne ketone **6**	Cyclic dimerization						Reductive dehydroxylation			Annulene **2**		
	g (mmol)	THF (ml)	Time[a)] (h)	KOH (g)	NH$_3$ (ml)	Temp (°C)	Time[b)] (h)	Sn^{2+} [c)] (g)	Solvent-H$^+$	Temp (°C)	Mp (°C) (dec)	Yield mg(%)	Found (Calcd), %
g	R=R′=*p*-MeOC$_6$H$_4$ 0.456 (1.43)	90	3	18.0	250	*ca.* −35	over-night	1.3	THF-Et$_2$O-HCl	−59	>280	176(58.4)	C, 83.61(83.70); H, 5.62(5.62)
h	R=Ph, R′=*p*-MeOC$_6$H$_4$ 0.448 (1.55)	60	4	16.0	250	*ca.* −35	over-night	0.6	CH$_2$Cl$_2$-HCl	−15	>250	93(22)	C, 88.30(88.53); H, 5.52(5.57)
i	R=*t*-Bu, R′=*p*-MeOC$_6$H$_4$ 0.924 (3.45)	100	4	19.0	250	−35—−40	24	2.0	Et$_2$O-HCl	−66	>230	100(11.6)	C, 85.76(86.01); H, 7.62(7.62)
j	R=*t*-Bu, R′=*p*-BrC$_6$H$_4$ 0.475 (1.50)	50	8	17.0	250	*ca.* −35	24	2.0	Et$_2$O-HCl	−58	>275	98.3(21.9)	C, 67.85(68.01); H, 5.35(5.37); Br, 26.50(26.62)
k	R=*t*-Bu, R′=*p*-ClC$_6$H$_4$ 0.50 (1.80)	60	4	15.0	400	−35—−40	5	0.5	Et$_2$O-HCl	−15	>280	140(31)	C, 79.75(79.83); H, 6.30(6.31); Cl, 13.78(13.86)
l	R=*t*-Bu, R′=*p*-MeC$_6$H$_4$ 0.50 (1.83)	60	4	15.0	400	−35—−40	5	0.5	Et$_2$O-HCl	−15	>280	130(33)	C, 91.73(91.86); H, 8.15(8.14)
m[d)]	R=*t*-Bu, R′=*p*-MeOOCC$_6$H$_4$ 0.20 (0.67)	15	8	5.0	500	−35—−40	1	1.0	CH$_2$Cl$_2$-Et$_2$O-HCl	−50	>320	98(52)	C, 81.16(81.69); H, 6.94(6.86)

a) Over this period, the THF solution of **6** was added. b) After the addition of THF solution, the mixture was stirred over this period. c) The amount of tin(II) chloride dihydrate. d) The crude cyclic glycol was treated with diazomethane to reconvert into the dimethyl ester (**7m**).

ously, steric effects of the substituent groups seem to be insufficient to explain the marked ^{1}H NMR change, a decrease of ring current as a result of perturbation of substituent(s) may be largely responsible for the marked low field shifts of the inner proton signals, although the nature of perturbation is not clear yet and the low field shift of outer protons in **1b** can not be explained in terms of decrease of ring current.[15] The diamagnetic ring current induced in aryl substituent exerts deshielding effect on both of inner and outer protons of annulene ring. Inversely, the deshielding effect of ring current induced in annulene ring is reflected in the low field shifts of *o*-protons of aryl substituent as compared with that of *m*-protons. Also the outer protons of annulene ring suffer a minor electronic effect of *p*-substituent in phenyl group as illustrated in Fig. The interesting ^{1}H NMR characteristics observed in substituted 'acetylene-cumulene'-dehydroannulenes should arise from the superposition of these various effects.

Experimental

The melting points were measured on a Mettler FP-2 apparatus and uncorrected. The IR spectra were obtained on a Hitachi EPI-G3 or a JASCO DS-402G spectrophotometer. The NMR spectra were measured on a Varian A-60D or XL-100 spectrometer, and the parameters were given in τ-values with respect to TMS used as an internal standard. The electronic spectra were obtained in THF on a Hitachi EPS-3T spectrophotometer. The adsorbents used in column chromatography are silica gel (Merck) and alumina (Merck, Act. II-III and Woelm Act. I). Evaporation of solvent was performed under reduced pressure.

2,2-Dichloroethyl p-*Methoxyphenyl Ketone.* To a stirred solution of *p*-methoxybenzoyl chloride (45.5 g, 0.266 mol) in 1,2-dichloroethane (500 ml) was added dropwise a solution of anhydrous aluminium chloride (41.0 g, 0.307 mol) in nitromethane (75 ml) under bubbling of vinyl chloride. After being stirred for 2 h, the reaction mixture was poured onto cracked ice. The organic layer was washed with sodium hydrogencarbonate solution. The crystals obtained on evaporation of the solvent were washed with ethanol to give fairly pure dichloroethyl ketone, pale yellow crystals, mp 58 °C (dec), 32.4 g, 52.2%, IR(KBr-disk): 1670 (C=O), 706 (C–Cl) cm^{-1}, NMR($\mathrm{CCl_4}$): 6.13 (3H, s, $\mathrm{CH_3}$), 6.23 (2H, d, J=6 Hz, $\mathrm{CH_2}$), 3.70 (1H, t, J=6 Hz, $\mathrm{CHCl_2}$); 3.07 (2H, d, J=10 Hz, aromatic-H), 2.08 (2H, d, J=10 Hz, aromatic-H).

Found: C, 51.58; H, 4.29; Cl, 30.02%. Calcd for $\mathrm{C_{10}H_{10}Cl_2}$: C, 51.53; H, 4.32; Cl, 30.42%.

2-Chlorovinyl p-*Methoxyphenyl Ketone (**3g**).* A solution of triethylamine (17.0 g, 0.086 mol) in ether (40 ml) was added at 5 °C to a solution of 2,2-dichloroethyl *p*-methoxyphenyl ketone (20.0 g, 0.086 mol) in the same solvent (260 ml). After being stirred for 3 h at the same temperature, the reaction mixture was kept in a refrigerator overnight. The amine hydrochloride deposited was removed by filtration. Crystalline solid obtained on concentrating the filtrate was extracted with petroleum ether (bp 35—60 °C). Evaporation of the solvent yielded pure **3g**, pale yellow crystals, mp 47 °C (dec), 17.0 g, quantitative, IR(KBr-disk): 1665 (C=O), 940 (CH=CH), 758 (C–Cl) cm^{-1}, NMR($\mathrm{CCl_4}$): 6.13 (3H, s, $\mathrm{CH_3}$), 2.66 (1H, s, vinyl-H), 2.63 (1H, s, vinyl-H), 2.99 (2H, d, J=10 Hz, aromatic-H), 2.15 (2H, d, J=10 Hz, aromatic-H).

Found: C, 61.68; H, 4.75; Cl, 17.87%. Calcd for $\mathrm{C_{10}H_9O_2Cl}$: C, 61.40; H, 4.64; Cl, 17.61%.

*1-Chloro-3-(*p*-methoxyphenyl)-1-penten-4-yn-3-ol (**4g**).* A solution of **3g** (16.9 g, 86.2 mmol) in THF (190 ml) was added to a stirred solution of lithium acetylide (prepared from lithium, 0.81 g, 0.12 g atm) in liquid ammonia (250 ml) over a period of 5 h at −60 °C. After the ammonia was allowed to evaporate, saturated ammonium chloride solution (100 ml) was added to the residue at −20 °C. The aqueous layer was extracted with ether and the extract was combined with the organic layer and dried ($\mathrm{Na_2SO_4}$). Evaporation of the solvent yielded crude **4g**, reddish brown liquid, 19.0 g. Because attempted high vacuum distillation resulted in decomposition, the crude material was subjected to a chromatography on silica gel to give fairly pure **4g**, IR(neat): 3425 (O–H), 3300 (C≡CH), 2120 (C≡C), 1608 (CH=CH), 940 (CH=CH), 734 (C–Cl) cm^{-1}, NMR($\mathrm{CCl_4}$): 7.33 (1H, s, C≡CH), 6.30 (3H, s, $\mathrm{CH_3}$), 6.63 (1H, s, OH), 4.00 (1H, d, J=13 Hz, vinyl-H), 3.51 (1H, d, J=13 Hz, vinyl-H), 3.26 (2H, d, J=9 Hz, aromatic-H), 2.59 (2H, d, J=9 Hz, aromatic-H).

*3-(*p*-Methoxyphenyl)-2-penten-4-ynal (**5g**).* A solution of **4g** (34.9 g, 0.12 mol) in THF (100 ml) was mixed with 1.5 M sulfuric acid (450 ml) and the mixture was stirred under nitrogen atmosphere for 3 days at 18 °C. The organic layer was separated and the aqueous layer, after neutralization with an aqueous sodium hydroxide solution, was extracted successively with ether and benzene. The combined organic solution was washed with brine and dried ($\mathrm{Na_2SO_4}$). Crude brown crystals obtained on concentration of the solution were recrystallized from ethanol to give pure **5g**, yellow crystals, mp 120 °C (dec), 5.5 g, 26%, IR(KBr-disk): 3210 (C≡CH), 2080 (C≡C), 1670 (C=O) cm^{-1}, NMR($\mathrm{CDCl_3}$): 6.23 (1H, s, C≡CH), 6.16 (3H, s, $\mathrm{CH_3}$), 3.23 (1H, d, J=8 Hz, vinyl-H), 3.06 (2H, d, J=10 Hz, aromatic-H), 2.26 (2H, d, J=10 Hz, aromatic-H), −0.24 (1H, d, J=8 Hz, CHO). **5g** was found to be rather unstable decomposing gradually in a dark at low temperature and gave less satisfactory elemental analysis.

Found: C, 77.05; H, 5.41%. Calcd for $\mathrm{C_{12}H_{10}O_2}$: C, 77.40; H, 5.41%.

*1,5-Bis(*p*-methoxyphenyl)-2,4-heptadien-6-yn-1-one (**6g**).* A solution of sodium hydroxide (0.5 g, 12.5 mmol) in 50% aqueous ethanol (4 ml) was added at 5 °C to a stirred solution of *p*-methoxyacetophenone (1.53 g, 0.2 mmol) and **5g** (1.90 g, 10.2 mmol) in ethanol (70 ml). After being stirred overnight, deposited crystals were collected and washed successively with water and ethanol to give **6g**, yellow crystals, mp 111—112 °C, 1.95 g, 62%, IR(KBr-disk): 3230 (C≡CH), 2100 (C≡C), 1650 (C=O) cm^{-1}, NMR($\mathrm{CDCl_3}$): 6.33 (1H, s, C≡CH), 6.18 (3H, s, $\mathrm{CH_3}$), 6.13 (3H, s, $\mathrm{CH_3}$), 3.10 (2H, d, J=9.0 Hz, aromatic-H), 3.05 (2H, d, J=9.0 Hz, aromatic-H), 2.31 (2H, d, J=9.0 Hz, aromatic-H), 2.05 (2H, d, J=9.0 Hz, aromatic-H), 2—3(3H, m, vinyl-H).

Found: C, 79.19; H, 5.70%. Calcd for $\mathrm{C_{21}H_{18}O_3}$: C, 79.22; H, 5.69%.

*Preparation of 1,5-disubstituted 2,4-Heptadien-6-yn-1-one (**6h—m**).* Because the heptadienyne ketones (**6h—m**) were prepared by the aldol condensation of methyl ketones with 3-substituted-2-penten-4-ynals (**5**, R=Ph[3]) and R=*t*-Bu[2]) under similar reaction conditions used in the synthesis of **6g**, the reaction conditions, physical properties, yields and elemental analyses are tabulated in Table 6. The IR and NMR spectra of **6h—m** were found to be consistent with the assigned structures.

*Preparation of 3,7,10,14-Tetrasubstituted 1,8-Bisdehydro[14]annulenes (**2g—m**).* The preparation of **2g—m** were performed by the previously reported procedure.7) Because the cyclic glycols (**7g**—**m**) were obtained as amorphous solids and found to be difficult to crystallize, the crude materials were subjected to the reductive dehydroxylation to give **2g**—**m**. The products were purified by chromatography on alumina (Merck or Woelm). The reaction conditions, melting points and analytical data are summarized in Table 7. The yields of **2g**—**m** were calculated on the basis of **6g**—**m**.

*1-(*p*-Methoxycarbonylphenyl)-5,8,12-tri-*t*-butyl-2,4,9,11-tetradecatetraene-6,13-diyn-1-one (**9**).* To a stirred solution of *p*-acetylbenzoic acid (0.5240 g, 3.19 mmol) in water (4 ml) containing sodium hydroxide (0.34 g, 8.5 mmol) was added under argon atmosphere at 15 °C a solution of hydroxy aldehyde9) (**8**, 0.939 g, 2.65 mmol) in methanol (30 ml). After being stirred for 44.5 h, 1 M hydrochloric acid was added to the reaction mixture, and the resulting turbid yellow mixture was extracted with ether. Yellow solid obtained on working up the extract was treated with an ethereal solution of diazomethane. Chromatography of the product on alumina (Merck, 70 g) followed by elution with hexane–benzene (1:1) and ether afforded **9**, yellow solid, 523 mg, 38%, IR(KBr-disk): 3480 (O–H), 3300 (C≡CH), 2081 (C≡C), 1727 (C=O ester), 1655 (C=O), 1585 (CH=CH) cm^{-1}, NMR(CCl_4): 8.91 (9H, s, *t*-Bu), 8.83 (9H, s, *t*-Bu), 8.77 (9H, s, *t*-Bu), 7.00 (1H, s, OH), 6.80 (1H, s, C≡CH), 6.11 (3H, s, $COCH_3$), 4.13—1.89 (10H, m, olefinic and aromatic-H).

Attempts to crystallize **9** were unsuccessful.

*3,10,14-Tri-*t*-butyl-7-(*p*-methoxycarbonylphenyl)-1,8-bisdehydro-[14]annulene (**2n**).* A solution of **9** (105.7 mg, 0.205 mmol) in THF (20 ml) was added over 6.5 h-period to a stirred suspension of powdered potassium hydroxide (4.0 g, 71.4 mmol) in liquid ammonia (300 ml) at −35—−40 °C. After the mixture had been stirred for further 15 h, ammonium chloride (4.0 g, 74.7 mmol) was added and the ammonia was allowed to evaporate. The residue was mixed with water and extracted with ether. The aqueous layer was acidified with 1 M hydrochloric acid and extracted with ether. The combined extract, after being washed successively with water and brine, and dried ($MgSO_4$), was concentrated in a small volume. An ethereal solution of diazomethane was added to the concentrate. As the purification of **10** was found to be difficult, the crude **10** in ether (10 ml) was treated with a solution of tin(II) chloride dihydrate (0.5 g) in the same solvent saturated with hydrogen chloride (10 ml) at −15 °C. After 5 min, the resulting deep reddish brown solution was poured on an aqueous solution of sodium hydrogencarbonate, and extracted with ether. The crude product obtained on working up the extract was chromatographed on alumina (Merck, 50 g). Elution with hexane–benzene (1:1) gave **2n**, reddish brown crystals, mp> 270 °C (dec), 93.2 mg, 32% based on **9**, IR (KBr-disk): 2075 (C–C≡C–C ↔ C=C=C=C=), 1714 (C=O), 1604 (CH=CH), 970 (*trans* CH–CH) cm^{-1}, mass (*m*/*e*): 480 (M^+), calcd for $C_{34}H_{40}O_2$: mol wt 480.66.

*1,5,10,14-Tetra-*p*-methoxyphenyl-2,4,10,12-tetradecatetraene-6,8-diyne-1,14-dione (**11**).* A solution of copper(II) acetate monohydrate (12.0 g) in pyridine–methanol (1:1, 200 ml) was added to a stirred solution of **6g** (5.4 g, 17 mmol) in the same solvent (200 ml) at 5 °C. The mixture was stirred overnight at a room temperature. Yellow crystals deposited were collected and washed successively with water and ethanol to give pure **11**, yellow crystals, mp 156.8 °C, 5.3 g, 98%, IR(KBr-disk): 2830 (C–H in O–CH_3), 1645 (C=O), 983 (CH=CH) cm^{-1}, NMR($CDCl_3$): 6.13 (12H, s, OCH_3), 3.10 (4H, d, *J*=9 Hz, aromatic-H), 2.86 (4H, d, *J*=9 Hz, aromatic-H), 2.33 (4H, d, *J*=9 Hz, aromatic-H), 2.03 (4H, *J*=9 Hz, aromatic-H), 1.9—2.3 (6H, m, olefinic-H).

Found: C, 79.44; H, 5.44%. Calcd for $C_{42}H_{34}O_6$: C, 79.48; H, 5.40%.

*3,7,12,16-Tetra-*p*-methoxyphenyl-4,6,12,13-octadecatetraene-1,8,-10,17-tetrayne-3,6-diol (**12**).* A solution of **11** (2.050 g, 3.23 mmol) in THF (330 ml) was added over 2 h-period at 15—17 °C to a stirred suspension of lithium acetylide-ethylenediamine complex (4.2 g, 45.5 mmol) in the same solvent (50 ml) under bubbling of acetylene. After being stirred for further 4 h, saturated aqueous solution of ammonium chloride (50 ml) was added to the reaction mixture at −15 °C. The aqueous layer was extracted with benzene and combined with the organic layer, which was worked up to give a light brown solid. The material was chromatographed on alumina (Merck, 20 g) to give slightly crude **12**, 1.980 g, which was used without further purification in the subsequent reaction.

*1,5,10,14-Tetra-*p*-methoxyphenyl-6,8,15,17-tetrakisdehydro[18]-annulene (**1f**).* To a vigorously stirred solution of copper(II) acetate monohydrate (3.7 g) in pyridine (60 ml), methanol (30 ml) and ether (180 ml) was added a solution of crude **12** (2.23 g) in pyridine (40 ml), methanol (20 ml) and ether (10 ml) over a period of 14 h at 40—45 °C. The residue obtained on evaporation of the solvent was digested with benzene. The benzene solution was washed successively with brine, sodium hydrogencarbonate solution and brine, and dried ($MgSO_4$). Evaporation of the solvent yielded brown crystalline solid, which was washed with benzene to give sufficiently pure **13**, pale yellow fine crystals, 0.514 g, 23.2% based on **11**.

A solution of tin(II) chloride dihydrate (1.0 g, 4.4 mmol) in ether saturated with hydrogen chloride (5 ml) was added at −78 °C to a stirred solution of **13** (100 mg, 0.15 mmol) in ether (20 ml) and THF (5 ml). After being stirred for 10 min at the same temperature, water (100 ml) was added to the reaction mixture. Crystals deposited were washed successively with ethanol and acetone to give fairly pure **1f**, deep green crystals, mp 169—171 °C (decomposed without fusion), 76 mg, 77%. A specimen obtained by passing repeatedly a solution of **1f** in THF through a column of alumina (Woelm) gave rather unsatisfactory elemental analysis.

Found: C, 84.38; H, 5.33%. Calcd for $C_{46}H_{34}O_4$: C, 84.90; H, 5.27%.

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