Synthesis and Properties of a Bisdehydro[14]annuleno[c]furan and an Ortho-Annelated Tetrakisdehydro[14]annuleno[14]annulene

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A bisdehydro[14]annuleno[c]furan and a tetrakisdehydro[14]annuleno[14]annulene have been synthesized; their properties and effects of annelation on annulene rings are discussed on the basis of ^{1}H NMR and electronic spectra. Attempts to synthesize the related [14]annuleno[16]annuleno[14]annulene are also described.

We have already reported on a series of annelated $[4n+2]$annulenes fused with naphthalene or benzene, and clarified the effect of annelation on π-electron delocalization of the 'acetylene-cumulene' dehydroannulene ring.[1] The 'acetylene-cumulene' dehydroannulenes possess essentially a similar geometry. Therefore, the difference between the induced diamagnetic ring currents on the annulene moieties, which can be regarded as being an approximate measure of the diatropicity, clearly indicated the effect of annelation.

We have also reported on the preparation of $[4n+2]$annuleno$[4n'+2]$annulenes **1** consisting of two of the same or different size diatropic 'acetylene-cumulene' dehydroannulenes; their NMR spectral properties suggested that they comprise a fused system of two diatropic moieties having a $C_{sp}-C_{sp}$ linkage as the common bond.[2] Thus, tetra-*t*-butyltrisdehydro[14]annuleno[14]annulene **1a**[3] consisting of two bisdehydro[14]annulenes **2**[4] was concluded to be a highly delocalized system on the basis of spectroscopic[5] and X-ray analyses.[6]

On the other hand, tetramethyltetrakisdehydro[14]annuleno[14]annulene **3** synthesized by Cresp and Sondheimer showed a marked decrease in the diatropicity compared with that of monocyclic bisdehydro[14]annulene **4**.[7] For annulenoannulene **1**, like naphthalene, three stable Kekulé structures can be written, whereas only one Kekulé structure is stable in the case of **3**. In addition, although a steric hindrance between the outer protons H^b of **3** may contribute to a weakening of the ring current, the inner and outer protons of **1** apparently show no steric effect.

In order to clarify the effect of the different modes of annelation between **1a** and **3**, we were interested in preparing *ortho*-fused annulenoannulene, 3,7,10-tri-*t*-butyl-1,8,17,19-tetrakisdehydro-16,21-dimethyl[14]annuleno[14]annulene **5**, an isoannelated annulene system and a tricyclic annulene system. We considered that we might expect to estimate the resonance energy of 'acetylene-cumulene' bisdehydro[14]annulenes **2** and **5** by using the ^{1}H NMR chemical shifts of the inner and outer protons, since the fusion of a diatropic ring with a $[4n+2]$annulene exerts characteristic effects on both rings corresponding to their relative stabilities.[8]

The 6,10,13-tri-*t*-butyl-4,11-bisdehydro[14]annuleno[c]furan **6**, a 14π-electron analog of isobenzofuran, seemed to be a key intermediate for the preparation of **5**. Furthermore, the measurement of diatropicity in **6** provides important information concerning the isoannelation effect. The aromaticity of the 6π-electron system decreases in the order benzene > naphthalene > furan. Thus, the annelation of one benzene ring on the annulene rings causes a decrease in the diatropicity more than does that of one naphthalene. However, **6** can be regarded as being a macrocyclic analog of isobenzofuran, and isoannelation of the furan ring in **6** may decrease the diatropicity of the bisdehydro[14]annulene ring more than does the annelation of benzene.

Tricyclic annulenoannulenoannulenes have a novel π-electron system containing three macrocyclic conjugated rings; the tropicity of the central ring is of special interest in connection with the effect of double annelation. Although tricyclic annulenoannulenoannulenes can be expected to be unstable molecules, the tricyclic annulene system is one of the most challenging problems in annulene chemistry.

In this paper we describe the details concerning the synthesis and properties of **6**,[9a] **5**,[9b] and attempts to prepare the tetramethyl derivative **7** of a tetrakisdehydro[14]annuleno[16]annuleno[14]annulene (Chart 1).

Results and Discussion

Synthesis. The synthesis of the bisdehydro[14]annuleno[c]furan **6** was carried out by the reaction sequence outlined in Scheme 1. 4-Hydroxymethyl-3-furancarbaldehyde (**8**), which was derived from 3,4-furandimethanol,[10] was converted into its tetrahydropyranyl ether **9** in the usual way. The Wittig-Horner reaction of **9** with $LiCCl_2P(O)(OEt)_2$[11] afforded the *gem*-dichloroolefin **10** in 74% yield. Treatment of the olefin **10** with butyllithium in diethyl ether–tetrahydrofuran (THF) at −90 °C afforded the corresponding

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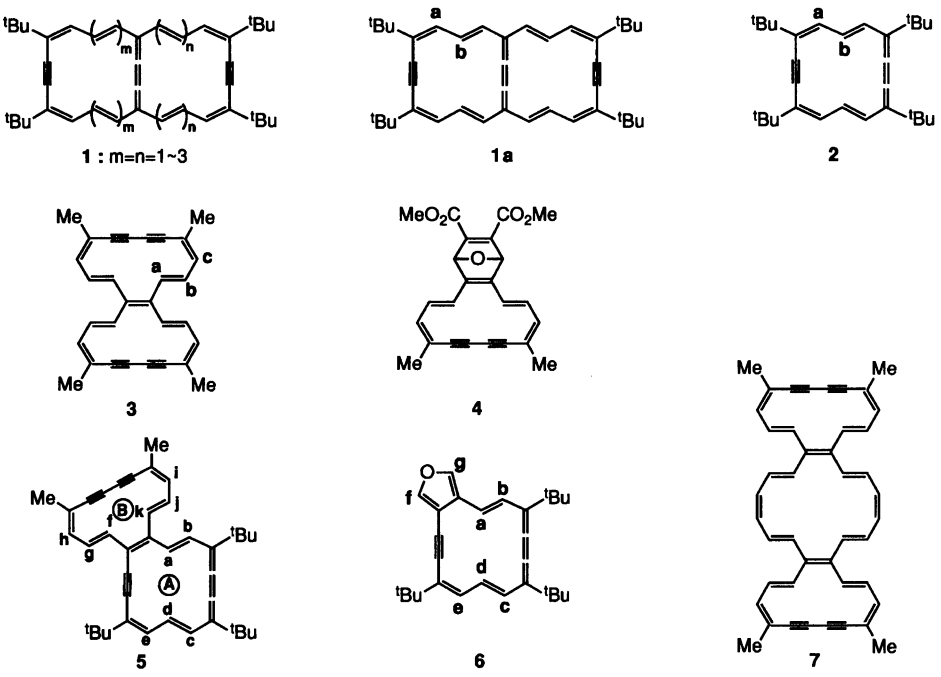
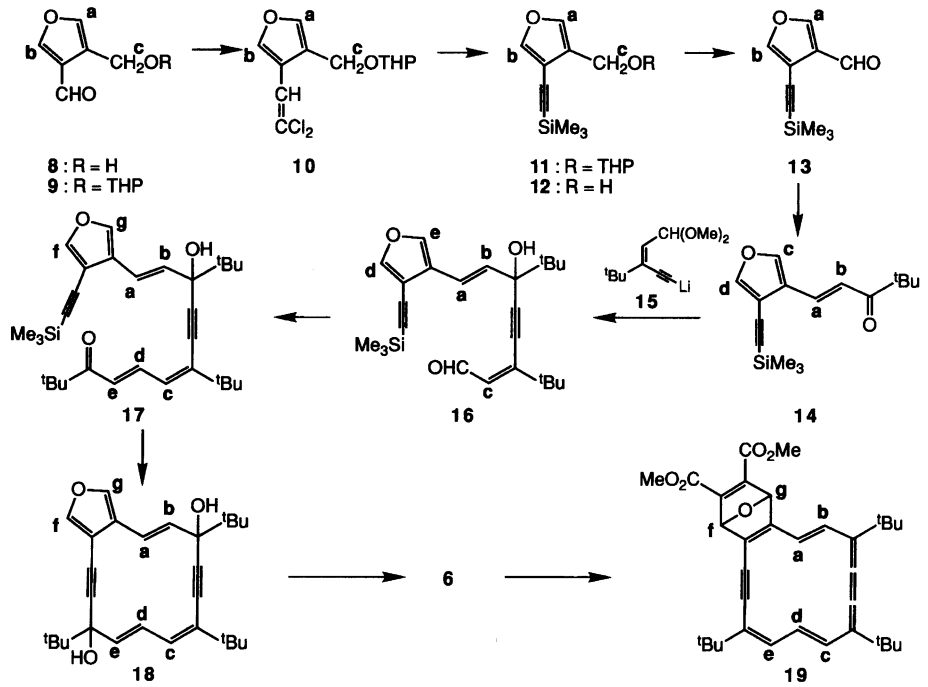


Chart 1.



Scheme 1.

lithium alkynide, which was converted directly into the trimethylsilyl derivative **11** by a reaction with Me_3SiCl. Removal of the tetrahydropyranyl protecting group of **11** was carried out using pyridinium *p*-toluenesulfonate[12] in MeOH to give the trimethylsilylethynyl alcohol **12** in 71% yield. Oxidation of the alcohol **12** with $Ba(MnO_4)_2$[13] in CH_2Cl_2 afforded the aldehyde **13** in 78% yield. The reaction of **13** with the carbanion derived from *t*-$BuCOCH_2P(O)(OEt)_2$[14] afforded the ketone **14** in 91% yield. The reaction of **14** with the lithio derivative **15** of 3-*t*-butylpentenynal dimethyl acetal[15] gave the dimethyl acetal of **16**, which was hydrolyzed without purification by aqueous acetic acid to afford the hydroxy aldehyde **16** in 97% yield (based on **14**). The Wittig–Horner reaction of **16** with *t*-$BuCOCH_2P(O)(OEt)_2$ gave the ketone **17** in 73% yield. The cyclization of **17** with KOH in liquid ammonia resulted in the formation of a diastereomeric mixture of the cyclic diol **18** in 79% yield. The dehydroxylation of **18** to the [14]annuleno[c]furan **6** could not be achieved un-

der the conditions as reported,[1] due to the instability of **6**. After several attempted experiments, it was found that the conversion could be realized under limited conditions: To a solution of the diol **18** in diethyl ether was added a mixture of tin(II) chloride and a small amount of diethyl ether saturated with HCl; the reaction mixture was neutralized by bubbling gaseous ammonia into the reaction mixture at −60 °C. The bisdehydro[14]annuleno[*c*]furan **6** was obtained as an unstable red solid, which easily isomerized to an unidentifiable [14]annulene derivative. The electronic spectrum of the isomerized product was similar to those of bisdehydro[14]annulene derivatives (see later), whereas the ^{1}H NMR spectrum showed extremely broad signals, even at low temperature. The structure of compound **6** was confirmed by the Diels–Alder reaction with diethyl acetylenedicarboxylate. The adduct **19** was obtained as stable red crystals.

The instability and enhanced reactivity of **6** as a diene seemed to suggest the possibility of conversion of **18** into a bisdehydro[14]annulene ring system. Actually, **18** could be transformed into bisdehydro[14]annulene derivatives with the isomerization of the furan system, as shown in Scheme 2. Thus, the development of a red color was observed when a solution of **18** in MeOH containing a small amount of HCl was kept for 2 h at 0 °C. The product was chromatographed on alumina to give the *trans*-dimethyldihydrofuran derivative **20a** and the *cis*-isomer **20b**. A similar reaction occurred when **18** was dissolved in acetic acid at room temperature. After being stirred overnight, the reaction mixture was worked up and the product was isolated by chromatography on alumina. A *cis* and *trans* mixture of the diacetoxy derivative **21** was obtained as a rather unstable red solid. Determinations of the *cis* and *trans* geometries of both **20** and **21** were made from comparisons of their ^{1}H NMR spectra with those of 2,5-dihydrofuran.[16] The formation of **20** and **21** from **18** can be explained by assuming the formation of a rearranged intermediate **22** under acidic conditions. It is considered that the formation of a highly stabilized 14π-electron system is the driving force of the transformation. The properties of compound **6** together with those of closely related compounds **19**, **20**, and **21** are discussed in a later section.

The synthesis of the tetrakisdehydro[14]annuleno[14]annulene **5** was carried out by the reaction sequence outlined in Scheme 3. Treatment of **18** or the dimethoxy annulene derivative **20** with aqueous HCl in THF resulted in the formation of a mixture of dialdehyde **23** and the dihydroxyfuran derivative **24**. The dialdehyde **23** could also be isolated by the dehydration of **24**. A Wittig–Horner reaction of a mixture of **23** and **24** with carbanion derived from trimethyl phosphonoacetate afforded the diester **25** in 43% yield (based on **18**). The reduction of **25** with diisobutylaluminum hydride (DIBAH) gave the diol **26** in 83% yield. The diol **26** was oxidized with $Ba(MnO_4)_2$ to afford the dialdehyde **27** in 81% yield. A Grignard reaction of **27** with a magnesium derivative of 3-bromo-1-butyne afforded the diol **28**, which was converted into the bicyclic diol **29** by oxidative coupling with copper(II) acetate in *N*,*N*-dimethylformamide (DMF). The crude **29** was treated successively with methanesulfonyl chloride in the presence of triethylamine, and then with DBU afforded the desired tetrakisdehydro[14]annuleno[14]annulene **5** in 10% yield (based on **27**). A small amount of dark-purple crystalline solid was obtained as a by-product, to which the structure of monodehydrated compound **31** was assigned on the basis of the ^{1}H NMR spectral data. The reaction of **31** with methanesulfonyl chloride-triethylamine, followed by a treatment with DBU, yielded **5** in 51% yield.

The tetrakisdehydro[14]annuleno[14]annulene **5** was found to be unstable against light and atmospheric oxygen, and gradually decomposed during evaporation in vacuo. Therefore, compound **5** was isolated by column chromatography at −30 °C, followed by concentration at low temperature and crystallization at −78 °C. The annulenoannulene **5** was obtained as dark reddish-brown cystals. The properties of **5** are discussed in a later section.

The successful results for preparing annulenes **5** and **6** encouraged us to synthesize a tricyclic system made up of three fused conjugated rings, annulenoannulenoannulene, since a system in which all three rings are macrocycles is not yet known.[17]

We initially planned to synthesize the tricyclic [14]annuleno[16]annuleno[14]annulene **32** (Chart 2), which might be formed by the reductive coupling of the dialdehyde **27**. However, we predicted that compound **32** would be unstable, because the tetrakisdehydro[14]annuleno[14]annulene **5** (as described above) proved to be thermally unstable and sensitive to light and air.

In contrast to **5**, **3** has been reported to be rather stable.[7] Therefore, we changed the target molecule to another tricyclic [14]annuleno[16]annuleno[14]annulene **7** (Chart 1) consisting of two bisdehydro[14]annulene and a [16]annulene parts. The tricyclic annulene **7** would be expected to be more stable than **32**. We thus attempted to prepare the *ortho*-fused tricyclic conju-

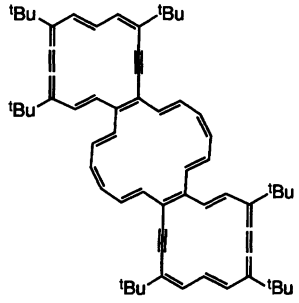


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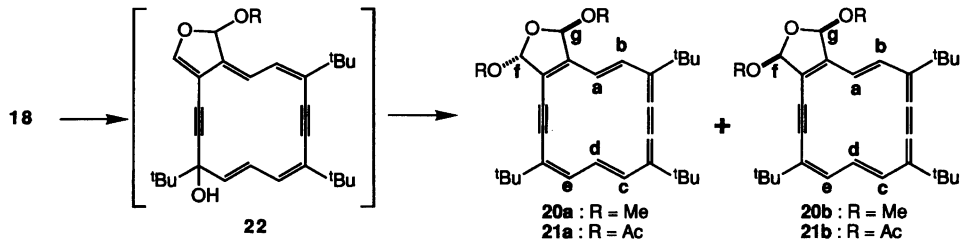
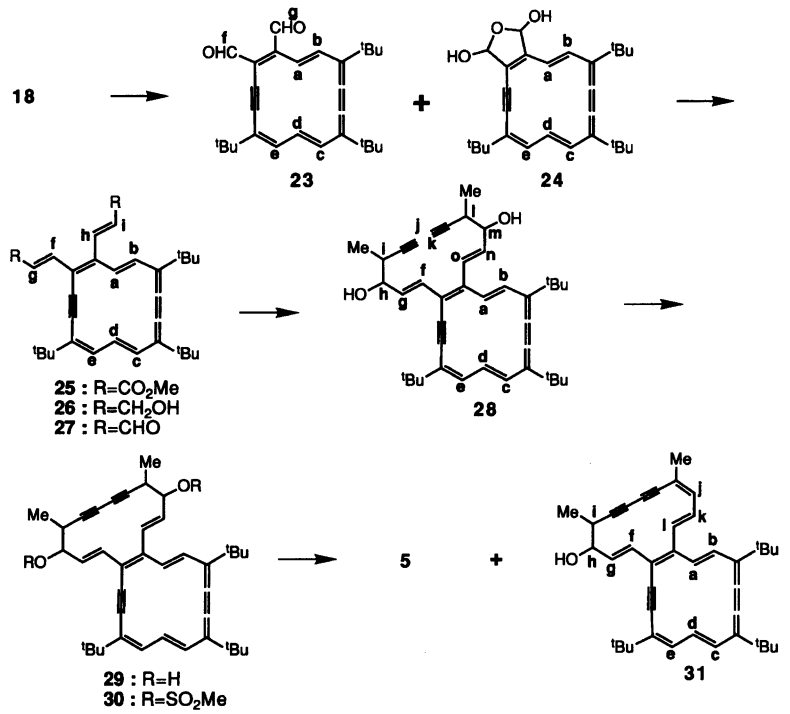
Chart 2.



Scheme 2.



Scheme 3.

gated π-electron system **7**.

We considered it possible that compound **7** might be obtainable from a reductive coupling of the known dialdehyde **33**, which had been used as an intermediate for preparing the [14]annuleno[14]annulene **3** by Cresp and Sondheimer,[7] or by a Wittig condensation of the dialdehyde **33** with the related bisphosphonium salt **34** (Chart 3).

Cresp and Sondheimer prepared the dialdehyde **33** from 8,10-bisdehydro-7,12-dimethyl[14]annuleno[*c*]furan (**35**) using 3-step reactions (oxidation of **35** with $Pb(OAc)_4$, hydrolysis, and the Wittig–Horner reaction).[7b] They prepared compound **35**[7b] from 3,4-furandicarbaldehyde (**36**)[10] according to a similar reaction sequence to that used to obtain compound **5** from compound **27**, as shown in Scheme 3. However, we could prepare compound **35** as follows.

The Wittig condensation of **36**[10] with (3-methyl-2-penten-4-ynyl)triphenylphosphonium bromide (**37**)[18] using butyllithium in THF afforded the diacetylenic compound **38** in 35% yield. An intramolecular oxidative coupling of **38** with anhydrous copper(II) acetate in pyridine and diethyl ether under relatively dilute conditions yielded the cyclic compound **35** in 45% yield. The conversion from compound **35** to the dialdehyde **33** was carried out according to the reported procedure.[7]

We then attempted an intermolecular reductive coupling of the dialdehyde **33** using a low-valent titanium reagent to obtain the objective compound **7**. The coupling of **33** was carried out in the presence of $TiCl_3$ and $LiAlH_4$ in refluxing 1,2-dimethoxyethane (DME).[19] However, this coupling did not give compound **7**, but did give a small amount of material having a higher molecular weight than that of **7**, together with polymeric products, suggesting the occurrence of hydrogenation of the unsaturated bonds of the precursor **33** and/or the coupling products during the reaction. Also, since we had already learned that several fully conjugated dialdehydes are insufferable against the reaction conditions employing $TiCl_3$ and $LiAlH_4$ at 70 °C in DME,[20] the failure to obtain compound **7** from the dialdehyde **33** might be ascribed to the same reason.

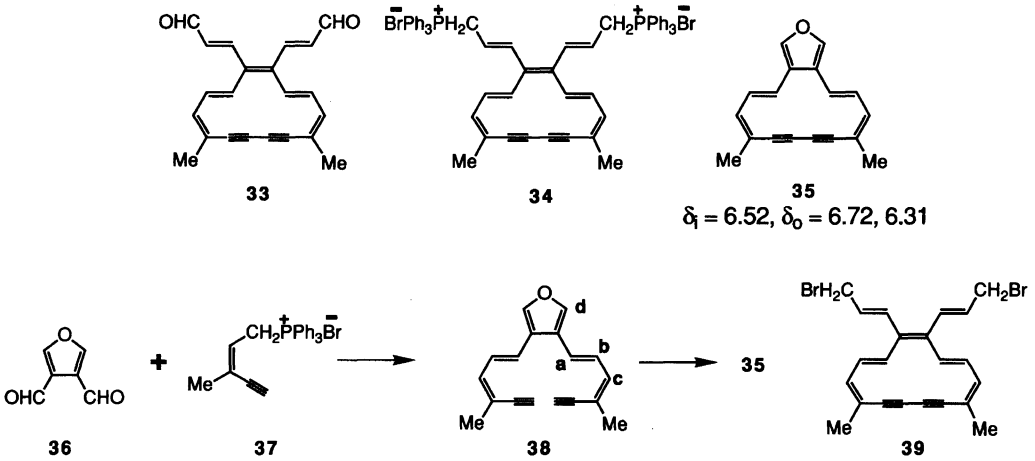


Chart 3.

Thus, since the reaction conditions used in the reductive coupling proved to be severe for the formation of compound **7**, we attempted a Wittig reaction between compound **33** and the related bisphosphonium salt **34**. The salt **34** was prepared by the reaction of the dibromide **39** with triphenylphosphine in ethyl acetate in 83% yield. The dibromide **39** was prepared from the corresponding diol, a precursor of the dialdehyde **33**, by a treatment with phosphorus tribromide in THF in 62% yield.

A Wittig reaction of compound **33** with salt **34** was carried out in the presence of ethanolic lithium ethoxide in *N*,*N*-dimethylformamide (DMF) at −40 °C. However, only an unidentified pale-yellow liquid was obtained with polymeric products, and the desired compound **7** was not detected. For the formation of **7**, although the Wittig reaction of **33** with **34** is required to produce (*Z*)-olefin, (*E*)-olefin might be formed in the first step of the Wittig reaction.

^{1}H NMR and Electronic Spectra of Annulenes 5 and 6. The ^{1}H NMR spectrum of **6** and those of compounds **19** and **20a** are illustrated in Figs. 1 and 2, respectively; their ^{1}H NMR parameters are listed in Table 1 together with those of **21b**. The assignments of the protons are based on the multiplicities and coupling constants, and are further clarified based on decoupling and NOE experiments when necessary. As can be seen from Figs. 1 and 2, the [14]annuleno[*c*]furan **6** and compounds **19** and **20a** are diatropic, as expected for 18π-electron and 14π-electron systems, respectively, since the olefinic inner H^a and H^d protons resonate at a high field, whereas the outer H^b, H^c, and H^e protons resonate at a low field. The difference in the chemical shifts between the olefinic outer (δ_o) and the inner (δ_i), $\Delta\delta=\delta_o-\delta_i$, can be regarded as being an approximate measure of the magnitude of the ring current; the $\Delta\delta$-values are also listed in Table 1. As shown in Table 1, a marked decrease in the $\Delta\delta$-value for bisdehydro[14]annuleno[*c*]furan **6**, as compared with those of the bisdehydro[14]annulene derivatives **19**, **20a**, **21b**, and **2** (see later), is observed. Also, a comparison of the coupling constants of the olefinic protons between **6** and **19** (and **20a**, **21b**) suggests that **6** is much less diatropic than **19**, **20**, and **21**. This is consistent with the result obtained for bisdehydrobenzo- **40**[21] and bisdehydronaphtho[14]annulenes **41** (Chart 4),[22] The decreasing diatropicity was found to be in the order **41**>**40**>**6**.

The instability and reduction of diatropicity of **6** exhibit the characteristic feature of an isoannelated system, such as isobenzofuran. It should be noted that the isoannelated annulene **6** shows an appreciable diatropicity in contrast to the hardly detectable diatropicity of another bisdehydro[14]annuleno[*c*]furan **35**.[7b,23] The tendency of 'acetylene-cumulene' dehydroannulene to form a highly stabilized π-electron system should be the cause of distinct diatropicity of compound **6**.

The interpretation obtained from an examination of the ^{1}H NMR spectra was supported by an observation of the electronic absorption spectra. The electronic spectrum of compound **6** is shown in Fig. 3 together with those of related compounds, **2**, **35**,[23] and **40**.[21] Of these, the spectrum of **6** is qualitative because compound **6** is unstable and quantitative data could not be obtained. The spectrum of compound **6** does not show the longest wavelength band among the three characteristic bands observed in the spectra of the 'acetylene-cumulene' [4*n*+2]annulenes.[1] Thus, the spectrum of **6** is quite similar to that of benzo[14]annulene **40** instead of the [14]annulene **2**. Furthermore, the spectrum of **6** is rather similar to that of the dimethylbisdehydro[14]-annulene **35**, except for the bathochromic shift of each band. These results show that the electronic structure of **6** is different from that of **2**, and that the extent of the π-electron conjugation of **6** is also much less compared with those of **2** and **40**. Thus, the results obtained from an examination of the electronic spectra are in agreement with the interpretation based on the ^{1}H NMR spectra.

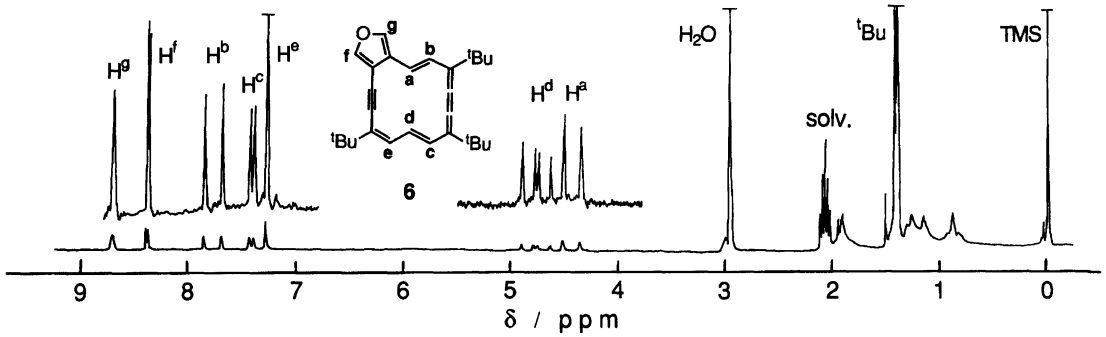


Fig. 1. ^{1}H NMR spectrum of the bisdehydro[14]annuleno[*c*]furan **6** in acetone-d_6 at 0 °C (δ-values, TMS as an internal standard).

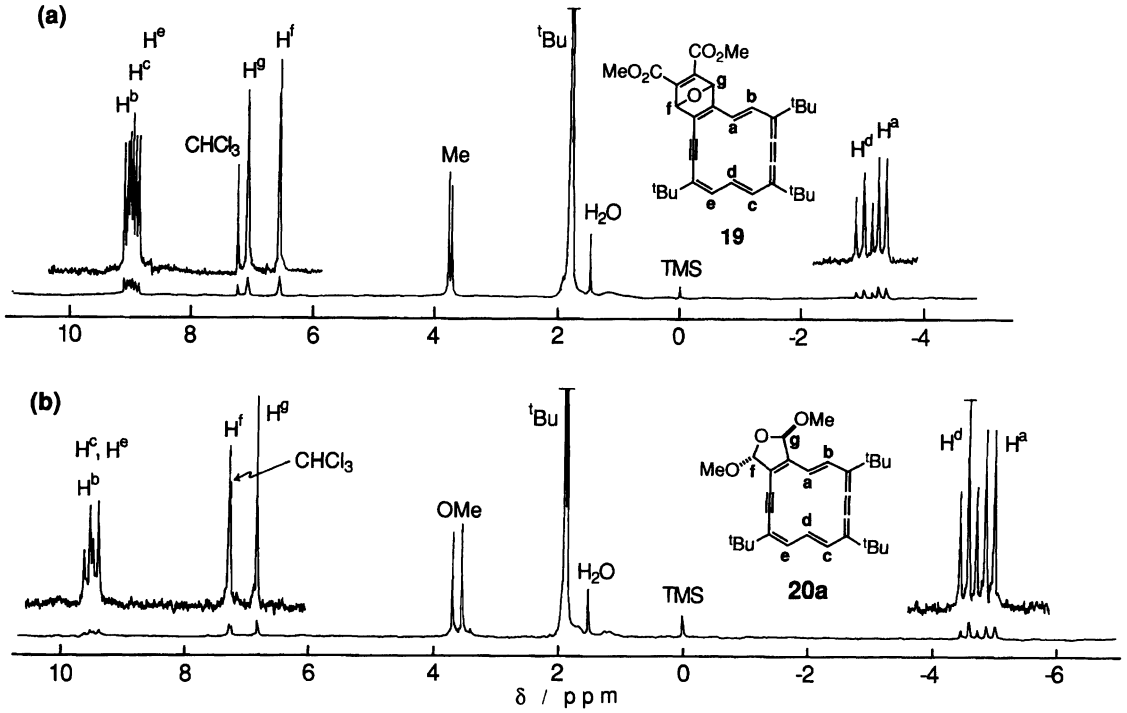
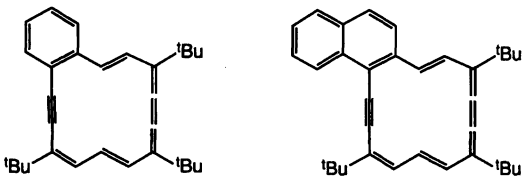


Fig. 2. ^{1}H NMR spectra of the bisdehydro[14]annulene derivatives **19** (a) and **20a** (b) in $CDCl_3$ (δ-values, TMS as an internal standard).



40

$\Delta\delta = 7.49–8.16$

41

$\Delta\delta = 10.54–11.10$

Chart 4.

The ^{1}H NMR spectrum of **5** is shown in Fig. 4. As can be seen from Fig. 4, **5** is diatropic since the olefinic inner protons resonate at an extremely high field, whereas the olefinic outer protons resonate at a low field.

The ^{1}H NMR parameters of **5** are summarized in Table 2. As shown in Table 2, strong diatropicity was observed in the A-ring (tri-*t*-butylbisdehydro[14]annulene moiety), being comparable with that of the monocyclic bisdehydro[14]annulene **2** ($\Delta\delta = 13.81$). On the contrary, a marked suppression of the diatropicity of the B-ring (dimethylbisdehydro[14]annulene moiety) was observed as being comparable with that of 11,13-bisdehydro-10,15-dimethylnaphtho[1,2-*a*][14]annulene (**42**) (Chart 5).[24]

It has been demonstrated that the magnitude of the suppression of the diatropicity of the annulene moiety annelated with benzenoids or annulenes is proportional to the resonance energy of the benzenoid or annulene system. It has also been shown that a less diatropic annulene ring suffers more suppression upon fusion with benzenoid or another annulene, as compared with a more strongly diatropic annulene moiety.[2] The $\Delta\delta$-values of **5** show that the B-ring has a considerably lo-

Table 1. ^{1}H NMR Data of Compounds **6**, **19**, **20a**, and **21b** (δ-Values; Coupling Constants in Hz).

Compound	Inner protons		Outer protons							
	H^a	H^d	H^b	H^c	H^e	H^f	H^g	OCH_3	*t*-Bu	$\Delta\delta$
6[a]	4.35 d (16.5)	4.69 dd (15.0, 11.0)	7.87 d (16.5)	7.40 d (15.0)	7.34 d (11.5)	8.47 d (1.5)	8.80 d (1.5)		1.41 s, 1.40 s	2.71—3.52
19[b]	−3.30 dd (13.0, 1.0)	−2.99 dd (14.0, 12.5)	9.03 d (13.0)	8.98 d (12.5)	8.94 d (14.0)	6.57 d (1.5)	7.09 dd (1.5, 1.0)	3.80 s, 3.74 s	1.83 s, 1.81 s, 1.78 s	11.97—12.33
20a[b]	−4.91 d (14.0)	−4.57 t (13.5)	9.53 d (14.0)	9.44 d (13.5)	9.42 d (13.5)	6.83 s	7.27 s	3.70 s, 3.56 s	1.91 s, 1.87 s	14.01—14.44
21b[b]	−4.92 d (14.0)	−4.58 t (13.5)	9.53 d (14.0)	9.45 d (13.5)	9.45 d (13.5)	7.16 s	7.57 s	3.53 s, 3.42 s	1.92 s, 1.91 s, 1.88 s	14.03—14.45

a) In acetone-d_6 at −40 °C. b) In $CDCl_3$ at room temperature.

Table 2. ^{1}H NMR Data of the Tetrakisdehydro[14]annuleno[14]annulene 5 in CS_2 at −60 °C (δ-Values; J in Hz)

	Inner protons		Outer protons				*t*-Bu	Me	$\Delta\delta$
	H^a	H^d	H^b	H^e	H^c				
A ring	−2.99 d (14.0)	−3.25 dd (13.5, 12.0)	9.80 d (14.0)	8.94 d (12.0)	8.92 d (13.5)		1.89 s 1.83 s 1.80 s		12.34
	H^f	H^k	H^j	H^g	H^i	H^h			
B ring	5.15 d (16.0)	5.28 d (15.5)	8.50 dd (15.5, 8.5)	7.81 dd (16.0, 7.5)	7.35 d (8.5)	7.26 d (7.5)		2.51 s 2.47 s	2.52

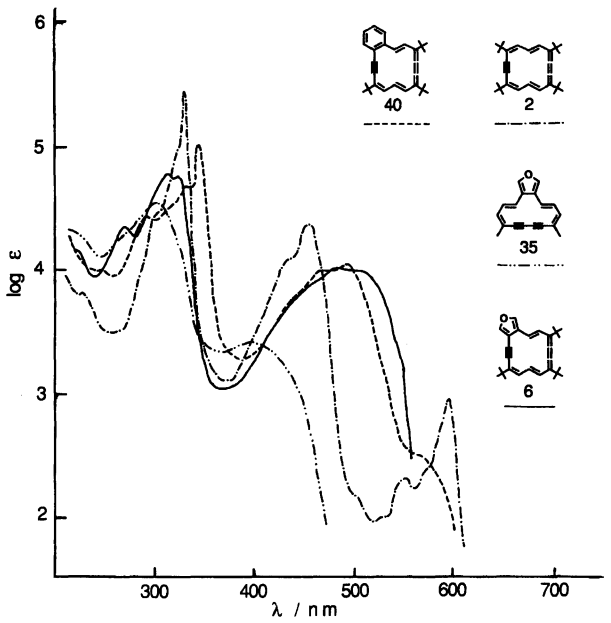


Fig. 3. Electronic absorption spectra of compounds **6** (in pentane), **2** (in THF),[a] **35** (in diethyl ether),[b] and **40** (in THF).[c] a) Taken from Ref. 4. b) Taken from Ref. 23. c) Taken from Ref. 21.

calized structure, as compared with the rather delocalized A-ring. The coupling constants (J_{ab}, J_{cd}, and J_{de}) indicate that the A-ring should be highly delocalized, whereas the coupling constants (J_{fg}, J_{gh}, J_{ij}, and J_{jk}) reflect a marked bond alternation of the B-ring. Furthermore, the steric repulsion between H^b and H^j in **5** seems to be an important factor, which may twist the B-ring, thus reducing the diatropicity. Therefore, the marked decrease in the diatropicity of **3** relative to **4** may be attributable to the small resonance energy, and probably to a steric repulsion between the outer protons in **3**.

The $\Delta\delta$-values of **42** show a marked decrease in the diatropicity of the annulene ring. The steric repulsion between $H^{b'}$ and H^d may play an important role in the reduction of the diatropicity, since the naphthalene ring is rigid and planar. The geometry of $H^{b'}$ and H^d in **42** is similar to that of H^b and H^j in **5**. Although it is difficult to estimate the extent of the steric factor, the loss of planarity of **42** seems to be nearly the same as that of **5**. The diatropicity of the B-ring of **5** is slightly larger than that of **42** (Chart 5). Therefore, the bisdehydro[14]-annulene **2** and naphthalene (fused at 1,2-positions) exerts nearly the same effect on the dimethylbisdehydro-[14]annulene ring. The relationship between the resonance energies and ring current in [4*n*+2]annulenes has been reported by Haddon[25] and Aihara.[26] The small $\Delta\delta$-values of the dimethylbisdehydro[14]annulene moiety in both **5** and **42** seem to indicate a fairly large resonance energy of the bisdehydro[14]annulene **2**, being comparable with that of a naphthalene ring (the annelation of naphthalene seems to have an effect which is consistent with the energy required to convert naph-

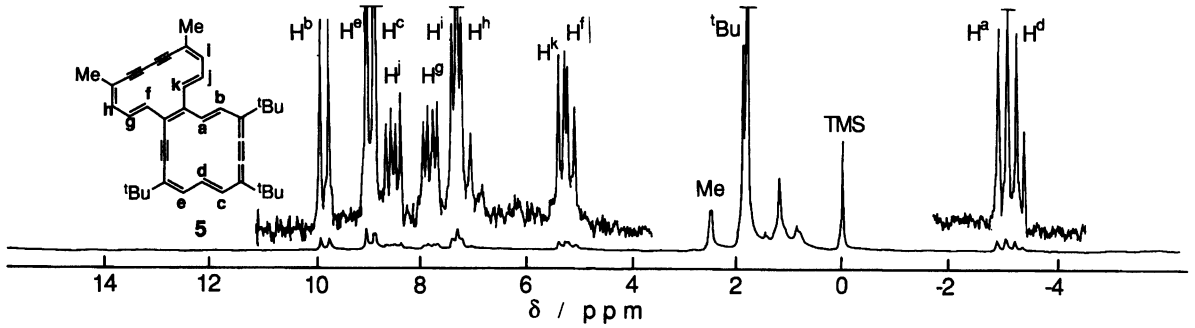
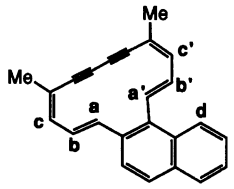


Fig. 4. ^{1}H NMR spectrum of tetrakisdehydro[14]annuleno[14]annulene **5** in CS_2 at −60 °C.



42

$\Delta\delta\ (\delta_c - \delta_a) = 1.97$

$\Delta\delta\ (\delta_c - \delta_{a'}) = 1.80$

Chart 5.

thalene into dihydronaphthalene).[27]

Although it is premature to deduce any conclusion from the above-mentioned results, it seems that the difference in the mode of fusion is not the main cause of the marked difference in the diatropicity between **3** and **1a**.

The electronic absorption spectra of compounds **5** and **1a**[3] are illustrated in Fig. 5. The spectrum of **5** shows very broad absorptions, in contrast to the spectrum of **1a**, which shows a typical absorption curve corresponding to the 'acetylene-cumulene' dehydroannulenes. Although the 'acetylene-cumulene' bisdehydro[14]annulene moiety in **5** exhibits a strong diatropicity which is stronger than that of the naphtho[14]annulene **41**, the electronic spectrum changes to very broad one unlike the spectrum of naphtho[14]annulene.[22] Therefore, the *ortho*-fused annulenoannulene, as a whole, may make a new π-electron system corresponding to the electronic structures of each ring.

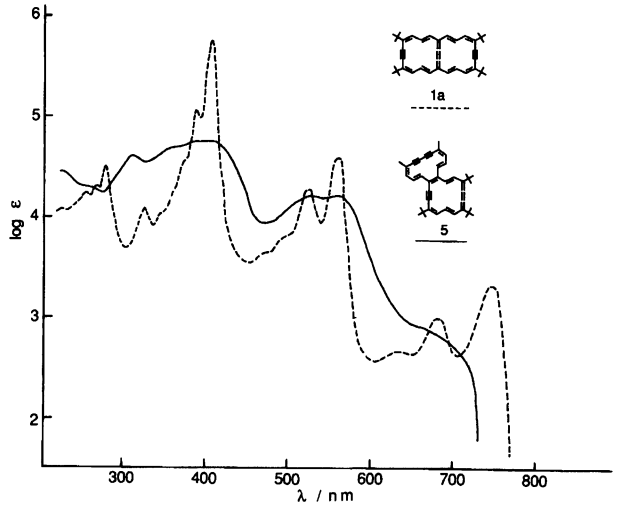


Fig. 5. Electronic absorption spectra of compounds **5** (in pentane) and **1a** (in THF).[a] a) Taken from Ref. 3.

Experimental

All of the experiments were performed under a nitrogen or argon atmosphere, except for the preparation of compound **35**. The melting points were determined on a Mettler FP-2 apparatus and are uncorrected. IR spectra were measured on a Hitachi EPI-G3, a Hitachi EPI-2, or a Hitachi 260-50 spectrophotometer as KBr disks, unless otherwise stated; only significant maxima are reported. Electronic spectra were determined on a Hitachi EPS-3T or a Hitachi 220A spectrophotometer (sh=shoulder). ^{1}H NMR spectra were measured on a Varian XL-100 (100 MHz), a JEOL FX-100 (100 MHz), a Varian A-60D (60 MHz), or a JEOL FX-90Q (90 MHz) spectrometer, and refer in δ-values with TMS as an internal standard. The coupling contants (J) are given in Hz. The assignments were assisted by decoupling and NOE experiments where necessary. Mass spectra were recorded with a Hitachi RM-50 or a JEOL JMS-O1SG-2 spectrometer operating at 75 eV using a direct inlet system or a JMS-D spectrometer equipped with a field-desorption system. Silica gel (Merck 60 or Daiso gel 1001W) and alumina (Merck, activity II—III) were used for column chromatography. Dichloromethane (CH_2Cl_2) was distilled over calcium hydride before use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen before use. The reactions were followed by TLC aluminum sheets precoated with Merck silica gel F_{254} or Merck aluminum oxid GF_{254}. Organic extracts were dried over anhydrous sodium sulfate or magnesium sulfate prior to removal of the solvent. Ether refers to diethyl ether.

4-Hydroxymethyl-3-furancarbaldehyde (8). To a solution of 3,4-furandimethanol[10] (28.2 g, 0.22 mol) in dry CH_2Cl_2 (940 cm^3) was added $Ba(MnO_4)_2$[13] (141 g, 0.54 mol) with stirring. After stirring overnight at room temperature, $Ba(MnO_4)_2$ was filtered off and collected; the product was further extracted from the precipitates with CH_2Cl_2 using a Soxhlet apparatus. The filtrate and the extract were combined and concentrated. The residue was chromatographed on a short column of alumina. The fractions eluted with ether–CH_2Cl_2 afforded the alcohol **8** (24.7

g, 89%) as a colorless solid; IR 3100 (OH) and 1660 cm^{-1} (CHO); ^1H NMR (60 MHz, CCl_4) δ=10.18 (1H, s, CHO), 8.36 (1H, d, J=2 Hz, H^b), 7.73 (1H, m, H^a), 4.95 (2H, s, CH_2), and 3.65 (1H, br s, OH).

4-Tetrahydropyranyloxymethyl-3-furancarbaldehyde (9). To a solution of alcohol **8** (3.0 g, 24 mmol) in dry benzene (100 cm^3) was added dihydropyran (2.1 g, 25 mmol) and *p*-toluenesulfonic acid monohydrate (5 mg); the mixture was then stirred for 2 h at room temperature. Then, a further quantity of dihydropyran (0.2 g) was added and the mixture was stirred for 1 h. To the mixture was added anhydrous K_2CO_3 (3.0 g) and the mixture was stirred for 2 h. The mixture was then passed through a short column of K_2CO_3 and the eluates were concentrated under reduced pressure. The residue was chromatographed on alumina (100 g). The fractions eluted with ether–benzene (1 : 1) were collected and concentrated. The residue was distilled to afford the aldehyde **9** (4.1 g, 82%) as a colorless liquid. Bp 80—93 °C/293—333×10^{-4} Pa (1 mmHg=133 Pa); Mass m/z 210 (M^+); IR (neat) 2730 (CHO), 1688 (C=O), 1538 (furan), 1135 (C–O–C), and 1032 cm^{-1} (C–O–C); ^1H NMR (60 MHz, CCl_4) δ=10.02 (1H, s, CHO), 8.11 (1H, d, J=1.5 Hz, H^b), 7.53 (1H, m, H^a), 4.94 (1H, dd, J=13.5 and 1.3 Hz, H^c), 4.75 (1H, br, –CH of tetrahydropyranyl ring), 4.68 (1H, dd, J=13.5 and 1.3 Hz, H^c), 4.2—3.3 (2H, m, $-OCH_2$ of tetrahydropyranyl ring), and 2.0—1.3 (6H, m, $(CH_2)_3$ of tetrahydropyranyl ring).

Found: C, 62.86; H, 6.91%. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71%.

3-(2,2-Dichloroethenyl)-4-(tetrahydropyranyloxymethyl)furan (10). To a solution of $CCl_3P(O)(OEt)_2$[11] (24.9 g, 97 mmol) in a mixture of dry ether (87 cm^3) and dry THF (68 cm^3) was added by a syringe a solution of butyllithium (1.14 mol dm^{-3}; 69 cm^3, 79 mmol) in dry ether during 10 min at −100 °C with stirring. Then, a solution of the aldehyde **9** (8.54 g, 41 mmol) in ether (10 cm^3) was added during 2 h and the temperature was allowed to rise to room temperature, and stirring was continued overnight at room temperature. The mixture was then cooled to −50 °C, and distilled water (50 cm^3) was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed and dried. The residue after removal of the solvent was chromatographed on silica gel (200 g). The fractions eluted with hexane were collected and concentrated. The residue was distilled to afford the olefin **10** (13.4 g, 74%) as a pale-yellow liquid. Bp 115—125 °C/199×10^{-3} Pa; Mass m/z 276 (M^+); IR (neat) 1625 (C=C) and 1533 cm^{-1} (furan); ^1H NMR (100 MHz, CCl_4) δ=7.93 (1H, m, H^a), 7.35 (1H, m, H^b), 6.74 (1H, s, –CH=), 4.60 (1H, br, –CH of tetrahydropyranyl ring), 4.55 (1H, d, J=12.5 Hz, H^c), 4.35 (1H, d, J=12.5 Hz, H^c), 4.1—3.3 (2H, m, $-OCH_2$ of tetrahydropyranyl ring), and 1.9—1.3 (6H, m, $(CH_2)_3$ of tetrahydropyranyl ring).

Found: C, 52.15; H, 5.08; Cl, 25.93%. Calcd for $C_{12}H_{14}Cl_2O_3$: C, 52.00; H, 5.09; Cl, 25.59%.

3-(Tetrahydropyranyloxymethyl)-4-(trimethylsilylethynyl)furan (11) and 3-Hydroxymethyl-4-(trimethylsilylethynyl)furan (12). To a stirred solution of the olefin **10** (7.25 g, 26 mmol) in dry ether (70 cm^3) and dry THF (70 cm^3) was added by a syringe butyllithium (1.23 mol dm^{-3}; 43 cm^3, 53 mmol) in ether during 25 min at −95 °C. After stirring for 1 h at −70 °C, the mixture was cooled to −95 °C; then, Me_3SiCl (4.27 g, 39 mmol) was added dropwise to the mixture over a period of 5 min. After the mixture was allowed to rise to −40 °C, distilled water (18 cm^3) was added. After separation, the aqueous layer was extracted with ether. The combined organic layer was washed and dried. Removal of the solvent afforded the trimethylsilylethynyl derivative **11** as a yellow liquid. The liquid was dissolved in dry MeOH (200 cm^3). To the solution was added pyridinium *p*-toluenesulfonate[12] (5 mg); the mixture was stirred overnight at room temperature. It was then concentrated under reduced pressure. The residue was chromatographed on silica gel (100 g). The fractions eluted with benzene–ether (9 : 1) were collected and concentrated. The residue was distilled to afford the alcohol **12** (3.61 g, 71%, based on **10**) as a colorless liquid. Bp 70—80 °C/199×10^{-3} Pa; Mass m/z 194 (M^+); IR (neat) 3450 (OH), 2170 (–C≡C–), and 1253 cm^{-1} (C–O–C); ^1H NMR (60 MHz, CCl_4) δ=7.53 (1H, d, J=1.9 Hz, H^b), 7.31 (1H, m, H^a), 4.50 (2H, d, J=1.1 Hz, H^c), 2.18 (1H, br s, OH), and 0.22 (9H, s, $SiMe_3$).

Found: C, 61.69; H, 7.31%. Calcd for $C_{10}H_{14}O_2Si$: C, 61.81; H, 7.26%.

4-Trimethylsilylethynyl-3-furancarbaldehyde (13). A solution of alcohol **12** (3.44 g, 17.7 mmol) in dry CH_2Cl_2 (200 cm^3) was stirred with $Ba(MnO_4)_2$ (30.0 g, 0.117 mol) for 24 h at room temperature. The mixture was worked up as for the isolation of compound **8**. The product was chromatographed on silica gel (100 g). The fractions eluted with benzene–ether (95 : 5) were collected and concentrated. The residue was distilled to afford the aldehyde **13** (2.66 g, 78%) as a colorless liquid. Bp 52—56 °C/106—146×10^{-3} Pa. The liquid crystallized as colorless needles upon standing, mp 71.0—71.6 °C; Mass m/z 192 (M^+); IR (neat) 3140 (furan), 2160 (–C≡C–), 1708, 1695 (C=O), 1572 and 1538 cm^{-1} (furan); ^1H NMR (60 MHz, CCl_4) δ=9.91 (1H, s, CHO), 7.97 (1H, d, J=1.7 Hz, H^b), 7.64 (1H, d, J=1.7 Hz, H^a), and 0.25 (9H, s, $SiMe_3$).

Found: C, 62.50; H, 6.32%. Calcd for $C_{10}H_{12}O_2Si$: C, 62.47; H, 6.29%.

4,4-Dimethyl-1-(4-trimethylsilyethynyl-3-furanyl)-1-penten-3-one (14). To a stirred suspension of NaH (0.602 g, 60% in oil, 15.0 mmol) in 1,2-dimethoxyethane (DME) (50 cm^3) was added a solution of *t*-$BuCOCH_2P(O)(OEt)_2$ (3.9 g, 16.5 mmol) in DME (60 cm^3) over a period of 10 min; the mixture was then heated at 42 °C for 20 min with stirring. To the stirred solution was added dropwise a solution of the aldehyde **13** (1.73 g, 9.01 mmol) in DME (35 cm^3) at 5—8 °C, and the mixture was stirred for 2 h at room temperature. Then saturated aqueous NH_4Cl (50 cm^3) was added dropwise under ice-cooling and ether was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed and dried. The residue after removal of the solvent was chromatographed on silica gel (100 g). The fractions eluted with hexane–benzene (1 : 4) afforded the ketone **14** (2.26 g, 91%) as a solid. It formed colorless microcrystals, mp 73.2—75.2 °C, from hexane; Mass m/z 274 (M^+); IR 3130 (furan), 2160 (–C≡C–), 1682 (C=O), 1255 (C–Si), and 992 cm^{-1} ((*E*)-HC=CH); ^1H NMR (100 MHz, $CDCl_3$) δ=7.64 (1H, d, J=1.5 Hz, H^c or H^d), 7.64 (1H, J=16.0 Hz, H^b), 7.56 (1H, J=1.5 Hz, H^c or H^d), 7.51 (1H, J=16.0 Hz, H^a), 1.21 (9H, s, *t*-Bu), and 0.26 (9H, s, $SiMe_3$).

Found: C, 70.09; H, 8.10%. Calcd for $C_{16}H_{22}O_2Si$: C, 70.02; H, 8.08%.

3,6-Di-*t*-butyl-6-hydroxy-8-(4-trimethylsilylethynyl-3-furanyl)-2,7-octadien-4-ynal (16). To a solution of 3-*t*-butyl-2-penten-4-ynal dimethyl acetal[15] (4.65 g, 25.5 mmol) in dry THF (100 cm^3) was added by a syringe butyllithium in hexane (1.5 mol dm^{-3}; 17 cm^3, 25.5 mmol) at −60 °C with stirring. After stirring for 30 min at −12 °C, a solution of the ketone **14** (4.6 g, 16.8 mmol) in dry THF (100 cm^3) was added over a period of 1 h with stirring, and the mixture was allowed to rise to 10 °C. Then, distilled water (100 cm^3) was added under ice-cooling. After the usual work up, crude acetal of aldehyde **16** was obtained as a red liquid. After this liquid was dissolved in 1, 4-dioxane (30 cm^3), the solution was added dropwise to a mixture of acetic acid (150 cm^3) and water (15 cm^3); the mixture was stirred for 4 h at room temperature. After a mixture of benzene (100 cm^3) and distilled water (200 cm^3) was added, the reaction mixture was extracted with benzene. The extracts were washed successively with aqueous $NaHCO_3$ and brine, and dried. The residue after removal of the solvent was chromatographed on silica gel (100 g). The fractions eluted with benzene–ether (4:1) afforded the aldehyde **16** (6.7 g, 97%) as pale-yellow needles, mp 120.8—121.2 °C, from hexane; Mass *m/z* 410 (M^+); IR 3485 (OH), 2170 (–C≡C–), 1678 (C=O), 1251 (C–Si), 985 and 968 cm^{-1} ((*E*)-HC=CH); ^{1}H NMR (100 MHz, $CDCl_3$) δ=10.13 (1H, d, *J*=7.7 Hz, CHO), 7.60 (1H, d, *J*=1.5 Hz, H^d or H^e), 7.36 (1H, d, *J*=1.5 Hz, H^d or H^e), 6.89 (1H, d, *J*=16 Hz, H^a or H^b), 6.69 (1H, d, *J*=16 Hz, H^a or H^b), 6.23 (1H, d, *J*=7.7 Hz, H^c), 2.09 (1H, s, OH), 1.24 (9H, s, *t*-Bu), 1.12 (9H, s, *t*-Bu), and 0.12 (9H, s, $SiMe_3$).

Found: C, 73.23; H, 8.39%. Calcd for $C_{25}H_{34}O_3$: C, 73.13; H, 8.35%.

7,10-Di-*t*-butyl-10-hydroxy-2,2-dimethyl-12-(4-trimethylsilylethylnyl-3-furanyl)-4,6,11-dodecatrien-8-yn-3-one (17). To a suspension of NaH (0.731 g, 60% in oil, 18.3 mmol) in DME (100 cm^3) was added dropwise over a period of 40 min a solution of t-$BuCOCH_2P(O)(OEt)_2$ (4.6 g, 19.5 mmol) in DME (100 cm^3) with stirring at 13—17 °C. To the solution was added dropwise over a period of 30 min a solution of the aldehyde **16** (5.4 g, 13.2 mmol) in DME (100 cm^3) with stirring at −9—5 °C. After stirring for 1 h at 28 °C, the mixture was stirred overnight at room temperature. Then, to complete the reaction, stirring was continued for an additional 2 h at 30 °C. Saturated aqueous NH_4Cl (100 cm^3) and then water (110 cm^3) were added dropwise under ice-cooling. After the organic layer was separated, the aqueous layer was extracted with ether. The combined organic layer was washed and dried. The residue after removal of the solvent was chromatographed on silica gel (100 g). The fractions eluted with benzene–ether (9:1) afforded the ketone **17** (6.4 g, 73%) as an amorphous solid; Mass *m/z* 492 (M^+); IR 3050 (OH), 2160 (–C≡C–), 1675 (C=O), 1590 (furan), 1252 (Si–C), 985 and 970 cm^{-1} ((*E*)-HC=CH); ^{1}H NMR (100 MHz, $CDCl_3$) δ=7.87 (1H, dd, *J*=15.0 and 11.5 Hz, H^d), 7.58 (2H, m, H^f and H^g), 6.92 (1H, d, *J*=16.0 Hz, H^a or H^b), 6.84 (1H, d, *J*=16.0 Hz, H^a or H^b), 6.63 (1H, d, *J*=15.0 Hz, H^e), 6.45 (1H, d, *J*=11.5 Hz, H^c), 2.37 (1H, br s, OH), 1.22 (9H, s, *t*-Bu), 1.17 (9H, s, *t*-Bu), 1.15 (9H, s, *t*-Bu), and 0.22 (9H, s, $SiMe_3$).

6,9,13-Tri-*t*-butyl-7,14-bisdehydro-6,13-dihydro-6,13-[14]annuleno[*c*]furandiol (18). To a stirred suspension of a finely divided KOH (2.0 g) in liquid ammonia (600 cm^3) was added dropwise over a period of 17 h a solution of the ketone **17** (497 mg, 1.01 mmol) in dry THF (40 cm^3) using a high-dilution apparatus at −40—−26 °C. After stirring for 5 h at −40 °C, NH_4Cl (10.0 g) was added in small portions. After evaporating ammonia, water (100 cm^3) was added at −15 °C. After the addition of ether (100 cm^3), the organic layer was separated. The aqueous layer was extracted with ether. The combined organic layer was washed and dried. The residue after removing the solvent was chromatographed on alumina (100 g). The early fractions eluted with 5% ether in benzene afforded one diastereomer (13 mg, 4%) of the diol **18** as a yellow solid, mp 136—136.9 °C, from ether–pentane; IR 3550, 3460 (OH), 2220, 2200 (–C≡C–), 1627 (C=C), 1537 (furan C=C), 965 ((*E*)-HC=CH) and 875 cm^{-1} (furan); ^{1}H NMR (100 MHz, $CDCl_3$) δ=7.42 (1H, d, *J*=1.5 Hz, H^g), 7.24 (1H, d, *J*=1.5 Hz, H^f), 7.17 (1H, dd, *J*=15.0 and 10.5 Hz, H^d), 6.67 (1H, d, *J*=16.5 Hz, H^a), 6.48 (1H, d, *J*=16.5 Hz, H^b), 6.36 (1H, d, *J*=10.5 Hz, H^c), 6.04 (1H, d, *J*=15.0 Hz, H^e), 2.73 (1H, br s, OH), 2.43 (1H, br s, OH), 1.19 (9H, s, *t*-Bu), 1.06 (9H, s, *t*-Bu), and 1.03 (9H, s, *t*-Bu).

The later fractions eluted with ether–benzene (1:1) afforded another diastereomer (316 mg, 75%) of the diol **18** as pale-yellow plates, mp 153.0—154.5 °C, from ether–pentane; Mass *m/z* 420 (M^+); IR 3585, 3490 (OH), 2230, 2200 (–C≡C–), 1632 (C=C), 1540 (furan C=C), and 963 cm^{-1} ((*E*)-HC=CH); ^{1}H NMR (100 MHz, $CDCl_3$) δ=7.55 (2H, m, H^f and H^g), 7.48 (1H, dd, *J*=15.4 and 10.8 Hz, H^d), 7.11 (1H, d, *J*=16.2 Hz, H^a), 6.39 (1H, d, *J*=10.8 Hz, H^c), 6.31 (1H, d, *J*=16.2 Hz, H^b), 6.01 (1H, d, *J*=15.4 Hz, H^e), 2.05 (1H, br s, OH), 2.01 (1H, br s, OH), 1.20 (9H, s, *t*-Bu), 1.11 (9H, s, *t*-Bu), and 1.10 (9H, s, *t*-Bu).

Found: C, 80.07; H, 8.74%. Calcd for $C_{28}H_{36}O_3$: C, 79.96; H, 8.63%.

6,10,13-Tri-*t*-butyl-4,11-bisdehydro[14]annuleno-[*c*]furan (6). To a stirred solution of the cyclic diol **18** (100 mg, 0.238 mmol) in dry ether (40 cm^3) was added in one portion a mixture of tin(II) chloride (200 mg) and ether (3.0 cm^3) saturated with gaseous HCl at −60 °C; the mixture was stirred for 20 min at −60 °C. Then, gaseous ammonia was bubbled into the mixture for 15 min; the ice-cooled water and ether were added to the mixture. After the organic layer was separated, the aqueous layer was extracted with ether. The combined organic layer was washed and dried. Evaporation of the solvent was carried out under reduced pressure at low temperature. The residue was then chromatographed on alumina at 0 °C. The fractions eluted with 10% CH_2Cl_2 in pentane were collected and removal of the solvent was carried out at low temperature. Concentration left the annulene **6** as a red solid which proved to be thermally unstable, and its quantity was not weighted. UV (pentane) 270, 313, 324, 485, and 508 nm and see Fig. 3; ^{1}H NMR see Table 1 and Fig. 1.

Dimethyl 7,11,14-Tri-*t*-butyl-5,12-bisdehydro-1,4-epoxy-1,4-dihydro-2,3-benzo[*a*][14]annulenedicarboxylate (19). To a stirred solution of the annulene **6** (ca. 90 mg, 0.24 mmol) in hexane (10 cm^3) was added in one portion a solution of dimethyl acetylenedicarboxylate (34 mg, 0.24 mmol) in hexane (10 cm^3); the mixture was stirred overnight at room temperature. The orange crystals

which precipitated were collected to afford the adduct **19** (31.6 mg), and the filtrate was concentrated. The residue was chromatographed on silica gel. The fractions eluted with 5% ether in benzene afforded a second crop (7.5 mg) of **19**. The total yield of **19** was ca. 31%. Red microcrystals, mp 210 °C (decomp), from ether–MeOH; Mass *m/z* 528 (M^+); IR 2090, 2010 (–C≡C– and –C=C–C=C–), 1745 (C=O), 997 and 958 cm^{-1} ((*E*)-HC=CH); UV (THF) 246.5 (sh, ε 12300), 257 (12700), 321.5 (79500), 422 (11000), 448 (18300), 542 (318), and 593 nm (525); ^1H NMR see Table 1 and Fig. 2.

Found: C, 77.16; H, 7.65%. Calcd for $C_{34}H_{40}O_5$: C, 77.24; H, 7.63%.

6,10,13-Tri-*t*-butyl-4,11-bisdehydro-1,3-dihydro-1,3-dimethoxy[14]annuleno[*c*]furan (20). To a stirred solution of the cyclic diol **18** (133 mg, 0.317 mmol) in dry MeOH (135 cm^3) was added dropwise ether (1.3 cm^3) saturated with gaseous HCl at −14 °C; the mixture was stirred for 30 min at −14 °C and for an additional 2 h at room temperature. Then, ether (130 cm^3) was added at −10 °C and the reaction mixture was poured onto ice-water (200 cm^3). After the organic layer was separated, the aqueous layer was extracted with ether. The combined organic layer was washed successively with aqueous $NaHCO_3$ and brine, and then dried. The residue after removing the solvent was chromatographed on alumina (200 g). The early fractions eluted with 20% benzene in hexane afforded the *trans* isomer **20a** (82 mg, 58%) of the dimethoxy annulene derivative as red crystals, mp 175.0—175.5 °C, from methyl acetate–MeOH; Mass *m/z* 448 (M^+); IR 2025 (–C≡C– and –C=C=C=C–), 1101, 1082 (C–O–C), 987 and 958 cm^{-1} ((E)-HC=CH); UV (THF) 305 (sh, ε 34200), 331 (233000), 434 (12500), 454 (24400), 524 (248), 545 (365), and 589 nm (1390); ^1H NMR see Table 1 and Fig. 2.

The later fractions eluted with hexane–ether (3:2) afforded the *cis* isomer **20b** (36.4 mg, 26%) of the dimethoxy annulene derivative as red prisms, mp 150.0—151.5 °C, from ether–MeOH; Mass *m/z* 448 (M^+); IR 2030 (–C≡C– and –C=C=C=C–), 1105, 1087 (C–O–C), 978 and 960 cm^{-1} ((*E*)-HC=CH); UV (THF) 306 (ε 30900), 331 (228000), 434 (12500), 455 (24100), 524 (249), 546 (367), and 589 nm (1400); ^1H NMR (100 MHz, $CDCl_3$) δ=9.53 (1H, d, J=14.0 Hz, H^b), 9.45 (2H, d, J=13.5 Hz, H^c and H^e), 7.57 (1H, d, J=1.5 Hz, H^g), 7.16 (1H, d, J=1.5 Hz, H^f), 4.53 (3H, s, OCH_3), 4.42 (3H, s, OCH_3), 1.92 (9H, s, *t*-Bu), 1.91 (9H, s, *t*-Bu), 1.88 (9H, s, *t*-Bu), −4.58 (1H, t, J=13.5 Hz, H^d), and −4.92 (1H, d, J=14.0 Hz, H^a).

Found: C, 79.84; H, 9.02%. Calcd for $C_{30}H_{40}O_3$: C, 80.31; H, 8.99%.

1,3-Diacetoxy-6,10,13-tri-*t*-butyl-4,11-bisdehydro-1,3-dihydro[14]annuleno[*c*]furan (21). A solution of the diol **18** (50.1 mg, 0.119 mmol) in acetic acid (100 cm^3) was stirred overnight at room temperature. The mixture was poured onto ice-water (100 cm^3) and extracted with ether. The extracts were washed successively with saturated aqueous $NaHCO_3$ and brine, and then dried. The residue after removing the solvent was chromatographed on alumina (20 g). The fractions eluted with 5% ether in benzene afforded a mixture of the *cis*- and *trans*-isomers **21** (21 mg, 35%) of the diacetoxy annulene derivative as a red solid. The *trans* isomer **21a** was separated by triturating the mixture with ethyl acetate. The *trans* isomer **21a**; Mass *m/z* 504 (M^+); IR 1745 cm^{-1} (C=O); UV (THF) 306sh, 331, 434sh, 445, 524, 545, and 590 nm; ^1H NMR (100 MHz, $CDCl_3$) δ=9.47 (2H, d, J=13.2 Hz, H^c and H^e), 9.39 (1H, d, J=14.5 Hz, H^b), 8.55 (1H, s, H^g), 8.05 (1H, s, H^f), 3.53 (3H, s, $COCH_3$), 3.42 (3H, s, $COCH_3$), 1.92 (9H, s, *t*-Bu), 1.88 (9H, s, *t*-Bu), 1.87 (9H, s, *t*-Bu), −4.65 (1H, t, J=13.2 Hz, H^d), and −5.01 (1H, d, J=14.5 Hz, H^a).

The *cis* isomer **21b**; ^1H NMR see Table 1.

5,9,12-Tri-*t*-butyl-3,10-bisdehydro-1,2-[14]annulenedicarbaldehyde (23) and 6,10,13-Tri-*t*-butyl-4,11-bisdehydro-1,3-dihydro[14]annuleno[*c*]furan-1,3-diol (24). The *trans* isomer **20a** (86 mg, 0.19 mmol) of the dimethoxy annulene derivative was dissolved in THF (80 cm^3). To the solution was added 2 mol dm^{-3} aqueous HCl (20 cm^3); the mixture was stirred for 11 h at room temperature. Then, the mixture was poured onto ice-water (300 cm^3) and extracted with ether. The extracts were washed with aqueous $NaHCO_3$ and dried. Removal of the solvent left a mixture of the dialdehyde **23** and the dihydroxyfuran derivative **24** as a red solid. The solid was dissolved in pentane–CH_2Cl_2 (1:1; 10 cm^3) and was chromatographed on silica gel (50 g). The fractions eluted with CH_2Cl_2 afforded the dialdehyde **23** (67 mg, 88%) as a deep-red solid; Mass *m/z* 402 (M^+); IR 2090 (–C≡C– and –C=C=C=C–), 1685, 1668 (C=O), and 968 cm^{-1} ((*E*)-HC=CH); UV (THF) 277 sh, 297, 332 sh, 358, 496, 549 sh, 520, and 624 nm; ^1H NMR (100 MHz, pyridine-d_5) δ=11.78 (1H, d, J=1.9 Hz, CH^gO), 11.25 (1H, s, CH^fO), 10.36 (1H, d, J=13.7 Hz, H^b), 9.57 (1H, d, J=14.2 Hz, H^c), 9.52 (1H, d, J=12.7 Hz, H^e), 1.94 (9H, s, *t*-Bu), 1.91 (9H, s, *t*-Bu), 1.90 (9H, s, *t*-Bu), −3.64 (1H, dd, J=14.2 and 12.7 Hz, H^d), and −3.94 (1H, dd, J=13.7 and 1.9 Hz, H^a).

The later fractions eluted with ether–CH_2Cl_2 afforded a mixture of the *cis* and *trans* isomers of the dihydroxyfuran derivative **24** (10 mg); UV (THF) 330.5, 454, and 590 nm; ^1H NMR (100 MHz, $CDCl_3$, −10 °C) δ=9.52 (1H, d, J=14.5 Hz, H^b), 9.44 (2H, d, J=13.5 Hz, H^c and H^e), 7.3 (2H, m, –CH), 4.9 (2H, br s, OH, disappeared by addition of D_2O), 1.91 (9H, s, *t*-Bu), 1.87 (18H, s, *t*-Bu), −4.59 (1H, t, J=13.5 Hz, H^d of the *cis*- or *trans*-isomer), −4.64 (1H, t, J=13.5 Hz, H^d of the *cis*- or *trans*-isomer), −4.96 (1H, d, J=14.5 Hz, H^a of the *cis*- or *trans*-isomer), and −4.99 (1H, d, J=14.5 Hz, H^a of the *cis*- or *trans*-isomer).

A result almost similar to that described above was obtained for a reaction using the *cis* isomer **20b** of the dimethoxy annulene derivative.

5,9,12-Tri-*t*-butyl-3,10-bisdehydro-1,2-bis[(2-methoxycarbonyl)vinyl][14]annulene (25). To a stirred solution of the cyclic diol **18** (300 mg, 0.713 mmol) in THF (240 cm^3) was added dropwise during a period of 30 min 2 mol dm^{-3} aqueous HCl (60 cm^3); the mixture was stirred for 4 h at room temperature. Then, the mixture was poured onto ice-water (300 cm^3). After the addition of ether, the organic layer was separated. The aqueous layer was extracted with ether. The combined organic layer was washed with aqueous $NaHCO_3$ and dried. The residue after removing the solvent was chromatographed on silica gel (30 g). The fractions eluted with benzene–ether (1:1) afforded a mixture of **23** and **24** as a deep-purple solid. To an ice-cooled, stirred suspension of NaH (115 mg, 60% in oil, 2.87 mmol) in dry DME (60 cm^3) was added during a period of 10 min $MeO_2CCH_2P(O)(OMe)_2$ (573 mg, 3.15 mmol) in dry DME

(15 cm^3); the mixture was stirred for 1 h at room temperature. To the mixture was added a mixture of **23** and **24**, which were obtained from the diol **18** (300 mg, 0.713 mmol), as just described above, in dry DME (15 cm^3) under ice-cooling; the reaction mixture was stirred for 1.5 h at room temperature. Saturated aqueous NH_4Cl (50 cm^3) was then added under ice-cooling. After the addition of water (30 cm^3) and ether (30 cm^3), the aqueous layer was extracted with ether. The combined organic layer was washed and dried. The residue after removing the solvent was chromatgraphed on silica gel (50 g). The fractions eluted with benzene–ether (4:1) afforded the diester **25** (157 mg, 43%, based on **18**). It formed brown microcrystals, mp 198 °C (decomp), from ether; Mass m/z 514 (M^+); IR 2090, 2020 (–C≡C– and –C=C=C=C–), 1718, 1712 (C=O), 1612 (C=C), 982 and 970 cm^{-1} ((*E*)-HC=CH); UV (THF) 285 (ε 15600), 317 (25600), 365 (91300), 504 (21900), 584 (sh, 1440), and 636 nm (2330); ^{1}H NMR (90 MHz, $CDCl_3$) δ=9.37 (1H, d, J=14.0 Hz, H^b), 9.22 (2H, d, J=13.5 Hz, H^e), 8.96 (1H, d, J=16.0 Hz, H^f), 8.64 (1H, d, J=15.0 Hz, H^h), 7.42 (1H, d, J=15.0 Hz, H^i), 6.47 (1H, d, J=16.0 Hz, H^g), 3.99 (3H, s, CO_2CH_3), 3.91 (3H, s, CO_2CH_3), 1.91 (9H, s, *t*-Bu), 1.86 (9H, s, *t*-Bu), 1.85 (9H, s, *t*-Bu), −3.55 (1H, t, J=13.5 Hz, H^d), and −3.68 (1H, d, J=14.0 Hz, H^a).

Found: C, 78.99; H, 8.23%. Calcd for $C_{34}H_{42}O_4$: C, 79.34; H, 8.23%.

5,9,12-Tri-*t*-butyl-3,10-bisdehydro-1,2-bis(3-hydroxy-1-propenyl)[14]annulene (26). To a stirred solution of the diester **25** (300 mg, 0.583 mmol) in dry benzene (30 cm^3) was added during 7 min DIBAH (0.85 mol dm^{-3}; 4.5 cm^3, 3.83 mmol) in toluene at 6 °C. After stirring for 25 min under ice-cooling, MeOH (5 cm^3) was cautiously added over a period of 5 min; the mixture was stirred for 15 min. The mixture was then poured onto 1 mol dm^{-3} aqueous HCl and the aqueous layer was extracted with ether. The combined organic layer was washed with 1 mol dm^{-3} aqueous HCl and dried. Evaporation of the solvent afforded the diol **26** (221 mg, 83%) as a solid. It formed reddish-green needles, mp 170 °C (decomp), from ether; Mass m/z 458 (M^+); IR 3240 (OH), 2030 (–C≡C– and –C=C=C=C–), and 966 cm^{-1} ((*E*)-HC=CH); UV (THF) 228 (ε 12700), 263 (10500), 335 (sh, 37800), 350 (76400), 456 (sh, 12300), 485 (25300), 574 (356), and 623 nm (1100); ^{1}H NMR (100 MHz, acetone-d_6) δ=9.53 (1H, d, J=14.0 Hz, H^b), 9.36 (2H, d, J=13.5 Hz, H^c and H^e), 7.76 (1H, d, J=15.5 Hz, H^h), 7.74 (1H, d, J=16.0 Hz, H^f), 7.49 (1H, dt, J=15.5 and 5.0 Hz, H^i), 6.40 (1H, dt, J=16.0 and 5.0 Hz, H^g), 4.69—4.50 (4H, m, CH_2), 4.26 (1H, t, J=5.5 Hz, OH), 4.06 (1H, t, J=5.5 Hz, OH), 1.89 (9H, s, *t*-Bu), 1.87 (9H, s, *t*-Bu), 1.85 (9H, s, *t*-Bu), −3.14 (1H, t, J=13.5 Hz, H^d), and −3.62 (1H, d, J=14.0 Hz, H^a).

Found: C, 83.59; H, 9.27%. Calcd for $C_{32}H_{42}O_2$: C, 83.79; H, 9.23%.

5,9,12-Tri-*t*-butyl-3,10-bisdehydro-1,2-bis(3-oxo-1-propenyl)[14]annulene (27). To a solution of the diol **26** (100 mg, 0.218 mmol) in dry CH_2Cl_2 (50 cm^3) was added $Ba(MnO_4)_2$ (1.0 g); the mixture was stirred for 2.5 h at room temperature. The mixture was filtered through a Hyflo Super-Cel and the inorganic material was washed with CH_2Cl_2. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel (30 g). The fractions eluted with benzene–ether (9:1) afforded the dialdehyde **27** (80.6 mg, 81%) as a solid. It formed reddish-brown microcrystals, mp 220 °C (decomp), from ether–pentane; Mass m/z 454 (M^+); IR 2080, 2025 (–C≡C– and –C=C=C=C–), 1685 (C=O), 970 and 955 cm^{-1} ((*E*)-HC=CH); UV (THF)) 234 (sh, ε 10000), 273 (sh, 13500), 288 (17000), 321 (26400), 373 (73500), 514 (20500), 588 (sh, 2130), and 645 nm (2580); ^{1}H NMR (90 MHz, $CDCl_3$) δ=10.18 (1H, d, J=7.5 Hz, $CH^gC\underline{H}O$), 9.98 (1H, d, J=7.5 Hz, $CH^iC\underline{H}O$), 9.39 (1H, d, J=14.0 Hz, H^b), 9.28 (2H, d, J=13.5 Hz, H^c and H^e), 8.87 (1H, d, J=16.0 Hz, H^f), 8.47 (1H, d, J=15.0 Hz, H^h), 7.69 (1H, dd, J=15.0 and 7.5 Hz, H^i), 6.82 (1H, dd, J=16.0 and 7.5 Hz, H^g), 1.90 (9H, s, *t*-Bu), 1.88 (9H, s, *t*-Bu), 1.86 (9H, s, *t*-Bu), −3.45 (1H, t, J=13.5 Hz, H^d), and −3.61 (1H, d, J=14.0 Hz, H^a).

Found: C, 81.88; H, 8.26%. Calcd for $C_{32}H_{38}O_2$: C, 81.72; H, 8.43%.

5,9,12-Tri-*t*-butyl-3,10-bisdehydro-1,2-bis(3-hydroxy-4-methyl-1-hexen-5-ynyl)[14]annulene (28). To a stirred mixture of magnesium (109 mg, 4.49 mmol) and mercury(II) chloride (9 mg) in dry ether (4.0 cm^3) was added a solution of 3-bromo-1-butyne (148 mg, 1.10 mmol) in dry ether (1.0 cm^3); the mixture was stirred until the reaction of magnesium with 3-bromo-1-butyne began. Then, a solution of 3-bromo-1-butyne (439 mg, 3.31 mmol) in dry ether (3.0 cm^3) was added over a period of 1 min, and the mixture was stirred for 2 h under ice-cooling. A solution of the dialdehyde **27** (100 mg, 0.22 mmol) in dry THF (15 cm^3) was then added over a period of 10 min at −30 °C, and the mixture was stirred for 15 min at 0 °C. Then, saturated aqueous NH_4Cl (25 cm^3) was added. The aqueous layer was extracted with ether. The combined organic layer was washed and dried. The residue after removing the solvent was chromatographed on silica gel (30 g). The fractions eluted with benzene–ether (7:3) afforded the diol **28** (99 mg) as a gum; Mass m/z 562 (M^+); IR 3350 (OH), 3310 (–C≡CH), 2120 (–C≡C–), 2025 (–C≡C– and –C=C=C=C–), and 960 cm^{-1} ((E)-HC=CH); UV (THF) 228, 265, 336 sh, 351, 457 sh, 486, 575, and 623 nm; ^{1}H NMR (90 MHz, $CDCl_3$) δ=9.38 (1H, d, J=14.0 Hz, H^b), 9.19 (2H, d, J=13.5 Hz, H^c and H^e), 7.80 (1H, d, J=15.5 Hz, H^o), 7.77 (1H, d, J=16.0 Hz, H^f), 7.41 (1H, dd, J=15.5 and 6.0 Hz, H^n), 6.27 (1H, dd, J=16.0 and 6.0 Hz, H^g), 4.57 (2H, m, H^h and H^m), 3.08—2.81 (2H, m, H^i and H^l), 2.56 (2H, br s, OH), 2.29 (1H, d, J=2.0 Hz, ≡CH^j or ≡CH^k), 2.25 (1H, J=2.0 Hz, ≡CH^j or ≡CH^k), 1.87 (9H, s, *t*-Bu), 1.86 (9H, s, *t*-Bu), 1.84 (9H, s, *t*-Bu), 1.48 (3H, d, J=7.0 Hz, Me), 1.39 (3H, d, J=7.0 Hz, Me), −3.73 (1H, d, J=14.0 Hz, H^a), and −3.65 (1H, t, J=13.5 Hz, H^d).

15,19,23-Tri-*t*-butyl-5,7,13,20-tetrakisdehydro-3,4,9,10-tetrahydro-4,9-dimethyl[14]annuleno[14]-annulene-3,10-diol (29). To a solution of copper-(II) acetate monohydrate (5.0 g) in *N*,*N*-dimethylformamide (DMF) (100 cm^3) was added dropwise over a period of 2.5 h a solution of the diol **28** (90 mg) in DMF (20 cm^3) at 65 °C using a high-dilution apparatus; the mixture was stirred for an additional 5.5 h at 65 °C. The mixture was then poured onto water (300 cm^3) and ether (300 cm^3). The aqueous layer was extracted with ether. The combined organic layer was washed and dried. Evaporation of the solvent gave the cyclic diol **29** (85 mg) as a red gum.

3,7,10-Tri-*t*-butyl-1,8,17,19-tetrakisdehydro-16,21-dimethyl[14]annuleno[14]annulene (5) and 15,18, 22-

Tri-*t*-butyl-5,7,16,23-tetrakisdehydro-3,4-dihydro-4,9-dimethyl[14]annuleno[14]annulen-3-ol (31). To an ice-cooled, stirred solution of the cyclic diol **29** (85 mg) in dry THF (12 cm^3) was added dropwise a solution of methanesulfonyl chloride (68 mg, 0.577 mmol) in dry THF (1.5 cm^3) at 3 °C. Then, a solution of triethylamine (75 mg, 0.741 mmol) in dry THF (1.5 cm^3) was added at 3 °C, and the mixture was stirred for 1 h. The mixture was allowed to stand for 1 h under ice-cooling until the precipitates were formed. Then, only the solution from the mixture was taken up by a syringe. To the solution was added over a period of 7 min a solution of DBU (931 mg, 6.12 mmol) in dry THF (3 cm^3) at 3 °C; the mixture was stirred for 3 h under ice-cooling. The mixture was then poured onto ice–water (100 cm^3) and ether (100 cm^3). The aqueous layer was extracted with ether. The combined organic layer was washed and dried. Evaporation of the solvent was carried out under reduced pressure at low temperature. The residue was chromatographed on alumina (50 g) at −30 °C. The fractions eluted with pentane–CH_2Cl_2 (4:1) afforded the [14]annuleno[14]annulene **5** (12.3 mg, 10%, based on **27**), which proved to be unstable for air; Mass m/z 524 (M^+); UV (pentane) 230 (sh, ε 27000), 263 (sh, 19000), 297 (sh, 24000), 312 (40000), 358 (sh, 46000), 389 (54000), 407 (54000), 528 (16000), 559 (16000), and 676 nm (690) and see Fig. 5; ^{1}H NMR see Table 2 and Fig. 4.

The later fractions eluted with CH_2Cl_2 afforded the [14]annulene derivative **31** (9.9 mg, 8.3%, based on **27**) as a dark purple solid, mp 135 °C (decomp); Mass m/z 542 (M^+) (field-desorption method); IR 3450 (OH), 2220 (–C≡C–), 2135, 2030 (–C≡C– and –C=C=C=C–), and 959 cm^{-1} ((*E*)-HC=CH); ^{1}H NMR (90 MHz, $CDCl_3$) δ=9.40 (1H, d, J=13.5 Hz, H^b), 9.14 (1H, d, J=15.0 Hz, H^l), 9.09 (2H, d, J=13.5 Hz, H^c and H^e), 7.77 (1H, d, J=16.0 Hz, H^f), 7.74 (1H, dd, J=15.0 and 7.0 Hz, H^k), 6.66 (1H, d, J=7.0 Hz, H^j), 6.26 (1H, dd, J=16.1 and 5.0 Hz, H^g), 4.92—4.84 (1H, m, H^h), 3.09 (1H, m, H^i), 2.27 (1H, br s, OH), 2.01 (3H, s, Me), 1.83 (9H, s, *t*-Bu), 1.81 (18H, s, *t*-Bu), 1.37 (3H, d, J=7.0 Hz, Me), −3.20 (1H, t, J=13.5 Hz, H^d), and −3.27 (1H, d, J=13.5 Hz, H^a).

The [14]Annuleno[14]annulene 5 from Compound 31. To an ice-cooled, stirred solution of **31** (5 mg) in dry THF (3.0 cm^3) was added a solution of methanesulfonyl chloride (24 mg, 0.21 mmol) in dry THF (0.5 cm^3); and then a solution of triethylamine (28 mg, 0.28 mmol) in dry THF (0.5 cm^3). The mixture was stirred for 1.5 h under ice-cooling. Then, a solution of methanesulfonyl chloride (20 mg, 0.17 mmol) in dry THF (0.5 cm^3) was added. After stirring for 30 min a solution of triethylamine (32 mg, 0.32 mmol) in dry THF (0.5 cm^3) was added. After stirring for an additional 3 h, the mixture was allowed to stand until precipitates formed. Then, only the solution was taken up by a syringe from the mixture. To the solution was added a solution of DBU (607 mg, 3.99 mmol) in dry THF (3.0 cm^3) over a period of 6 min; the mixture was then stirred for 3 h under ice-cooling. The mixture was poured onto ice–water (50 cm^3). The aqueous layer was extracted with ether. The combined organic layer was washed and dried. The residue after removing the solvent at low temperature was chromatographed on alumina (10 g) at −40 °C. The fractions eluted with pentane–CH_2Cl_2 (9:1) afforded [14]annuleno[14]annulene **5** (2.46 mg, 51%).

3,4-Bis(4-methyl-1,3-hexadien-5-ynyl)furan (38). To a stirred suspension of the salt **37**[18] (10.9 g, 25.8 mmol) in dry THF (170 cm^3) was added a solution of butyllithium (1.53 mol dm^{-3}; 16.9 cm^3, 25.8 mmol) in hexane by a syringe at −60 °C. The mixture was stirred at −60 °C for 20 min, after which a solution of 3,4-furandicarbaldehyde (**36**)[10] (800 mg, 6.44 mmol) in dry THF (50 cm^3) was added dropwise over a period of 2 h at −60 °C; stirring was continued for an additional 30 min at −60 °C. After the addition of ethyl acetate (20 cm^3) the mixture was poured onto water and extracted with benzene. The extracts were washed with brine, dried, and evaporated. The residual dark-red liquid was chromatographed on alumina (3.2×17.0 cm). The fractions eluted with hexane–ether (3:2) afforded compound **38** (559 mg, 35%). It formed yellow needles, mp 82—82.5 °C, from hexane–benzene; MS m/z 248 (M^+); IR 3270 (–C≡CH), 2080 (–C≡C–), 1165 (C–O–C), and 965 cm^{-1} ((E)-HC=CH); UV (THF) 285 (ε 37000) and 311 nm (38300); ^{1}H NMR (90 MHz, $CDCl_3$) δ=7.52 (2H, s, H^d), 6.98 (2H, dd, J=14.5 and 11 Hz, H^b), 6.43 (2H, d, J=14.5 Hz, H^a), 6.37 (2H, d, J=11 Hz, H^c), 3.30 (2H, s, C≡CH), and 1.96 (6H, s, Me).

Found: C, 86.96; H, 6.41%. Calcd for $C_{18}H_{16}O$: 87.06; H, 6.50%.

8,10-Bisdehydro-7,12-dimethyl[14]annuleno[*c*]furan (35). A solution of the compound **38** (69 mg, 0.28 mmol) in pyridine–ether (3:1; 20 cm^3) was added dropwise over a period of 1 h at 50 °C to a stirred solution of anhydrous copper(II) acetate (1.0 g) in pyridine–ether (3:1; 28 cm^3). After being stirred for an additional 1 h at 50 °C, the mixture was poured onto water and extracted with benzene. The extracts were washed successively with 5% aqueous HCl until they turned acidic and aqueous $NaHCO_3$, and dried. The semisolid obtained after removing the solvent was chromatographed on alumina (4.2×9.0 cm). The fractions eluted with hexane–ether (1:1) afforded the cyclic compound **35** (31 mg, 45%). It formed yellow needles, mp 106—108 °C (decomp) (lit,[7b] mp 123—125 °C (decomp)), from hexane–benzene.

An Attempt to Prepare the Tricyclic Compound 7 by Reductive Coupling of the Dialdehyde 33. $LiAlH_4$ (55 mg, 1.5 mmol) was added in one portion to $TiCl_3$ (0.40 g, 2.56 mmol) in dry DME (30 cm^3); the mixture was refluxed for 30 min. To the refluxing mixture was added dropwise a solution of the dialdehyde **33** (250 mg, 0.80 mmol) in dry DME (30 cm^3) over a period of 4 h with stirring; stirring was continued for an additional 1 h under reflux. The mixture was then passed through a Hyflo Super-Cel, and the precipitates formed were washed with DME. The filtrate and washings were combined and concentrated. The concentrate was chromatographed on alumina (30 g). A yellow liquid (10 mg) was obtained from the fractions eluted with hexane–benzene (1:1). The mass spectrum of the liquid showed many peaks at higher molecular weights than that of the compound **7** (mol wt 564.7).

1,2-Bis(3-bromo-1-propenyl)-7,9-bisdehydro-6,11-dimethyl[14]annulene (39). To a stirred solution of the corresponding diol (0.70 g, 2 mmol) for the compound **33**,[7b] in dry THF (30 cm^3) was added dropwise a solution of phosphorus tribromide (0.50 g, 1.8 mmol) in dry ether (10 cm^3) for 30 min at 0 °C. The mixture was then poured onto water and extracted with ether. The extracts were washed with aqueous $NaHCO_3$ and dried. After removing the solvent,

the residue was passed through a short column of silica gel (5 g) with hexane–benzene (1 : 1). The dibromide **39** (0.60 g, 62%) was obtained as a dark-red solid.

7,9-Bisdehydro-6,11-dimethyl-1,2-bis(3-triphenylphosphonio-1-propenyl)[14]annulene Dibromide (34). To a stirred solution of the dibromide **39** (0.60 g, 1.34 mmol) in ethyl acetate (10 cm^3) was added dropwise for 10 min a solution of triphenylphosphine (0.70 g, 2.68 mmol) in ethyl acetate (20 cm^3) at 0 °C. After stirring for an additional 2 h at 0 °C, stirring was continued for 16 h at room temperature. The precipitates formed were collected by filtration and washed with ether, giving the bisphosphonium salt **34** (1.1 g, 83%). It formed black microcrystals, mp 180 °C (decomp), from ethyl acetate.

Found: C, 71.90; H, 5.20; Br, 16.50%. Calcd for $C_{58}H_{50}Br_2P_2$: C, 72.30; H, 5.11; Br, 16.38%.

An Attempt to Prepare the Tricyclic Compound 7 by Wittig Reaction between the Dialdehyde 33 and the Bisphosphonium Salt 34. Lithium ethoxide prepared from lithium (0.015 g, 2.1 mmol) in dry EtOH (5 cm^3) was added dropwise over a period of 26 h to a mixture of the bisphosphonium salt **34** (0.97 g, 1 mmol) and the dialdehyde **33** (0.32 g, 1 mmol) in dry DMF (150 cm^3) at −40 °C. The mixture was then poured onto water and extracted with CH_2Cl_2. The combined extracts were washed successively with 3 mol dm^{-3} aqueous HCl and aqueous $NaHCO_3$, and dried. After removing the solvent, the residue was chromatographed on silica gel (20 g). However, the desired compound **7** was not detected.

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