Syntheses and Properties of Methano-Bridged Dichlorodidehydro-[16]-, -[20]- and -[24]-annulenediones

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Bisethynylation of the vinylogous dialdehydes of cyclohepta-1,3,5-triene-1,6-dicarbaldehyde with ethynylmagnesium bromide followed by oxidation of the resulted diols afforded the diacetylenic diketones. Intramolecular oxidative coupling of these diketones under the Glaser conditions unexpectedly afforded three annulenediones with a 1,4-dichlorobutatriene moiety. The unusual structures were confirmed by X-ray crystallographic analysis of 10,13-dichloro-11,12-didehydro-1,6-methano[16]annulene-9,14-dione. These annulenediones exhibited strong diatropicity in D_2SO_4 due to the dicationic 14π-, 18π- and 22π-electron species and their diatropicities were shown to increase with increasing ring size.

Although several annulenediones are known, those with a ring larger than a 20-membered one are few.[1] In our previous paper, we reported successful syntheses of a series of methano-bridged tetradehydroannulenediones 1 and showed that among them only the [24]annulenedione (1; $m = n = 1$) exhibited diatropicity in D_2SO_4, suggesting the formation of the corresponding dicationic species.[2] In order to examine the tropic nature of a series of annulenediones in which the number of double bonds is increased systematically we planned to prepare a series of another type of tetradehydroannulenedione, compounds 2, since it was expected that both a methano-bridge and a diacetylenic linkage would contribute to keeping the annulenedione perimeter rigid.[3-5] However, during our initial attempt to prepare the tetradehydromethano[20]annulenedione (2; $m = n = 1$), we encountered the unexpected formation of a didehydromethano[20]annulenedione 4 containing a 1,4-dichlorobutatriene moiety, and of a strongly diatropic dicationic species 4A therefrom in D_2SO_4.

These interesting findings prompted us to attempt the preparation of higher and lower homologues of compound 4 and to study their tropicities systematically while keeping possible changes in stereochemistry to a minimum. In practice, we could obtain only the formally symmetrical, $(4n)$-membered didehydroannulenediones 3–5, and not the unsymmetrical $(4n + 2)$-membered ones.† The annulenediones 3–5 prepared in this study showed diatropicity for the $[4n + 2]$ π-electron system arising from polarization of two carbonyl groups. It should be pointed out that the didehydromethano[24]annulenedione 5 is the largest membered annulenedione to show the ring current effect, and the species 5A is the most highly diatropic, dicationic species formed from the annulenediones so far obtained.[1,6] Furthermore, it was found that the diatropicity of the dicationic species 3A–5A (see later, Fig. 3) increased with increasing ring size. This is unprecedented and will be discussed in detail.

1 $m = 0-3, n = 0-3$ 2

[16] - 3 $m = n = 1$
[20] - 4 $m = n = 2$
[24] - 5 $m = n = 3$
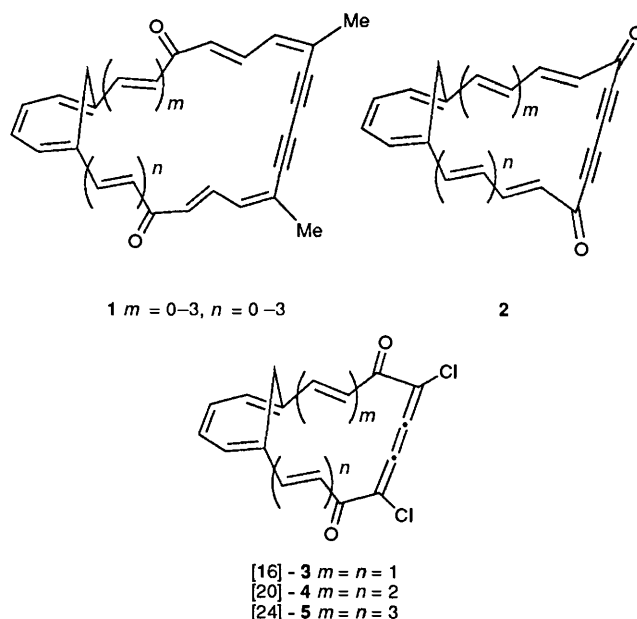
Results and Discussion

Synthesis.—Our initial attempt to obtain the tetradehydro-methano[20]annulenedione 2 ($m = n = 1$) began with the dialdehyde 10 which was prepared from cyclohepta-1,3,5-triene-1,6-dicarbaldehyde 6[7] by an interative sequence of Wittig condensations with an 8.0 molar equiv. excess of [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide, followed by immediate hydrolysis of the resulting bisacetal, according to the previously reported method.[3-5] In the case of the dialdehyde 10, the product was a mixture of the all-E isomer 10a and the mono-Z isomer 10b,[4] which had occasionally been observed in homologation of a lower homologue by Wittig condensation.[5] Bisethynylation of a mixture of di-aldehydes 10a and 10b with a large excess of ethynylmagnesium bromide in tetrahydrofuran (THF)[8] afforded the corresponding diacetylenic diol 19 (see Scheme 1) which comprised the $(E,E),(E,Z)$-isomer 19a and the $(E,Z),(E,Z)$-isomer 19b. When

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† Among the unsymmetrical diketones 25, 27, 29 and 31 studied only the diketone 25 gave supposed cyclization products, although the yields were quite low. Further studies on the structural determination of the products are in progress.
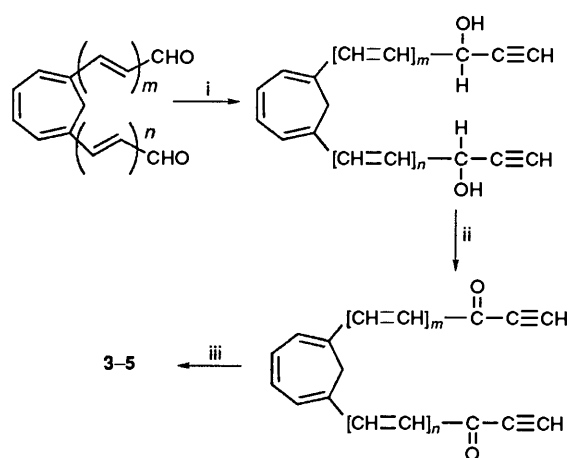
6 $m = n = 0$	15 $m = n = 0$	24 $m = n = 0$
7 $m = 1, n = 0$	16 $m = 1, n = 0$	25 $m = 1, n = 0$
8 $m = n = 1$	17 $m = n = 1$	26 $m = n = 1$
9 $m = 2, n = 1$	18 $m = 2, n = 1$	27 $m = 2, n = 1$
10 $m = n = 2$	19 $m = n = 2$	28 $m = n = 2$
11 $m = 3, n = 2$	20 $m = 3, n = 2$	29 $m = 3, n = 2$
12 $m = n = 3$	21 $m = n = 3$	30 $m = n = 3$
13 $m = 4, n = 3$	22 $m = 4, n = 3$	31 $m = 4, n = 3$
14 $m = n = 4$	23 $m = n = 4$	32 $m = n = 4$

Scheme 1 *Reagents and conditions:* i, HC≡CMgBr, THF; ii, Ba-(MnO₄)₂, CH₂Cl₂; iii, O₂, CuCl, NH₄Cl, conc. HCl, aq. EtOH–benzene, 60 °C

we carried out the bisethynylation using the pure all-*E* dialdehyde **10a**, the product was only the $(E,E),(E,Z)$-diol **19a**. Oxidation of the diol **19a** with $Ba(MnO_4)_2$[9] in dichloromethane yielded the $(E,E),(E,Z)$-diketone **28a**. However, similar oxidation of the diol **19b** yielded a mixture of the $(E,E),(E,Z)$-diketone **28a** and the $(E,E),(E,E)$-diketone **28b**. Thus, it was noted that all the olefin configurations in diol **19a** were retained during oxidation to afford the diketone **28a**, but that those in diol **19b** were not, suggesting that compound **28a** is more stable than its isomer **28b**. Attempted oxidative couplings of the acyclic diacetylenic diol **19a** or the diacetylenic diketone **28a** under Eglinton's conditions[10] using anhydrous copper(II) acetate in a mixture of pyridine and diethyl ether resulted in decomposition of the substrate (**19a** or **28a**), and neither the desired cyclic diol nor the tetrahydro[20]annulenedione (**2**; $m = n = 1$) could be obtained at all, probably owing to instability of these substrates in the basic medium, pyridine. We then attempted the coupling of compound **28** under acidic conditions.


10a   **10b**
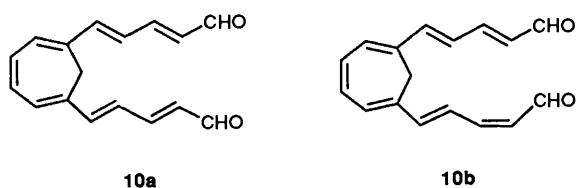
An intramolecular oxidative coupling of the acyclic diketone **28a** was attempted under Glaser conditions[11] by bubbling oxygen through a mixture of the diacetylene **28a**, copper(I) chloride and ammonium chloride in aq. ethanol–benzene with conc. hydrochloric acid at 60 °C. Chromatography of the product on silica gel afforded dark purple needles (10% yield) which decomposed at 156–161 °C on attempted determination of the m.p. The product was identified as the dichlorodidehydro[20]annulenedione **4** containing a butatriene moiety and two chlorine atoms rather than the expected structure **2** ($m = n = 1$) from the following spectral data and the elemental

analysis. The molecular-ion peak in the mass spectrum appeared at m/z 368 with the isotope peaks expected for two chlorine atoms. The IR spectrum (KBr disc) showed a strong carbonyl absorption at 1655 cm^{-1} and a weak absorption ascribable to the butatriene moiety at 2040 cm^{-1}. In the ^{13}C NMR spectrum ($CDCl_3$; 125 MHz) the quaternary carbon signals ascribable to the terminal and central carbons of the butatriene moiety appeared at δ_C 121.1 and 158.8, respectively. The coupling pattern of the olefinic protons in the ^1H NMR spectrum (see below) clearly pointed to the geometry shown by the formula **4**. Thus, it was noted that the Z-HC=CH moiety of compound **28a** isomerized to *E* during the Glaser coupling to form compound **4**. The reason for this as well as the detailed mechanism of the formation of compound **4** is uncertain, but configurational isomerization of a double bond during the intramolecular oxidative couplings has been observed in the formation of the tetradehydromethano[30]annulenedione **1** ($m = 3$, $n = 2$),[2] methanothia-[19]- and -[23]-annulene,[5] tetradehydro[15]annulenone[12] and tetradehydrotribenz[14]-annulene.[13] An inclination to formation of a less strained ring upon cyclization may be partly responsible. However, the diketone **28b** with two E-HC=CH moieties did not form compound **4** by the Glaser coupling under the same conditions as did the diketone **28a**. As discussed in the next section, the [20]annulenedione **4** formed a highly delocalized dicationic species in D_2SO_4.

These findings made us give up our initial objective of preparing the tetradehydroannulenediones of type **2** and instead to try to obtain the analogues of compound **4**. Thus, a series of the acyclic precursors, the diacetylenic diketones **24–32** in which the number of double bonds is increased systematically, were prepared according to the reaction sequence illustrated in Scheme 1. As described above for the preparations of the diketones **28a** and **28b**, the starting materials were the dialdehydes **6–14** and successive homologations of the dialdehyde **6**[7] to the vinylogous dialdehydes **7–14** were carried out according to the previously reported method.[3–5] When a geometrically isomeric mixture was formed in the preparation of the dialdehydes **7–14** as for the dialdehyde **10**, the Z-isomer was converted into the corresponding E-isomer by treatment with iodine. Bisethynylation of the all-*E* dialdehydes **7–14**[3–5] with a large excess of ethynylmagnesium bromide in tetrahydrofuran (THF)[8] afforded the corresponding diacetylenic diols **15–23** in 36–64% yield. These diols **15–23** were thermally unstable and sensitive to diffused light and air. Therefore, much effort was devoted to obtaining satisfactory spectral data and elemental analyses of these diols.

The diols **15–23** have two chiral carbon atoms and thus are capable of existing as two diastereoisomers. In the lowest homologue of the series, compound **15**, two diastereoisomers, R^*R^* (racemic) and RS (*meso*), were separately isolated and the stereochemistry was unambiguously assigned: The R^*R^* diastereoisomer gave the methylene proton signal as a singlet while the RS isomer's was an AB-quartet because of the geometrical symmetry. For the higher homologues **16–23** no effort was made to isolate the separate diastereoisomers and the characterizations were made for isomeric mixtures. In compounds **16**, **18** and **20**, two diastereoisomers existed in ~ 5:2, 5:1 and 1:1 ratios, respectively, as revealed by the presence of two sets of methylene proton signals, usually AB-quartets and for one isomer of **20** an apparent singlet. Compound **17** existed as a ~ 1:1 mixture of R^*R^* and RS isomers, whose methylene signal appeared as a singlet and an AB-quartet, respectively. As the number of side-chain CH=CH groups increased, the difference in chemical shifts between the isomers decreased. In compounds **18** and **20**, the difference between the isomers was observed only in the methylene proton signals. In compounds **21–23**, no difference between the isomers
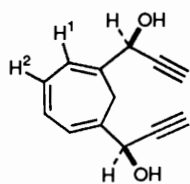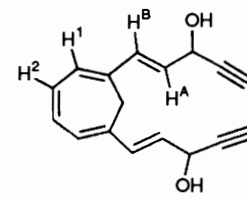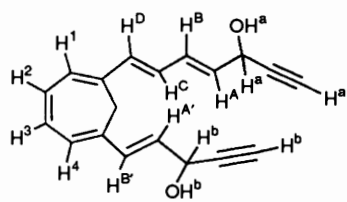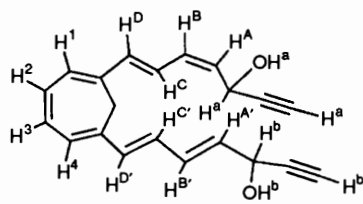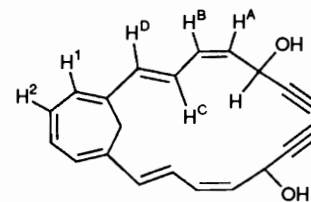
15a
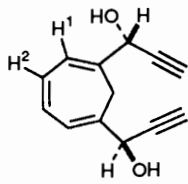
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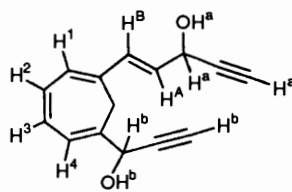
16

17

18

19a

19b
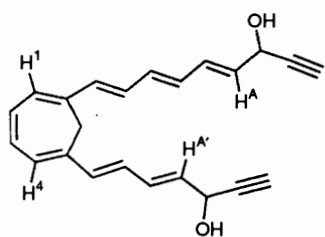
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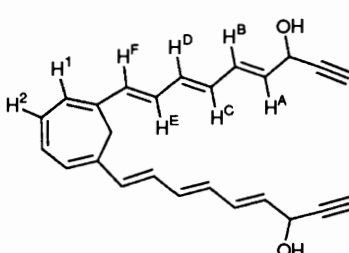
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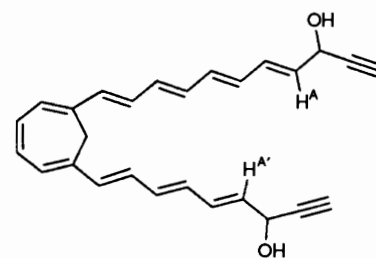
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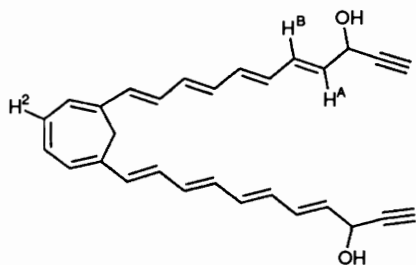
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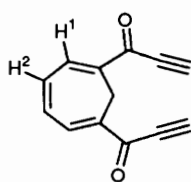
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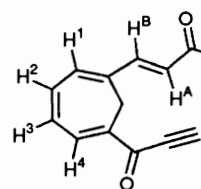
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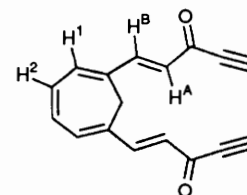
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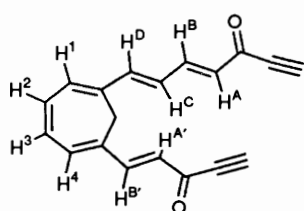
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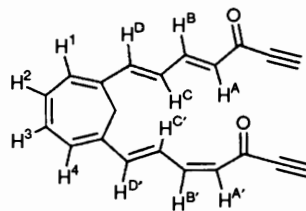
28a
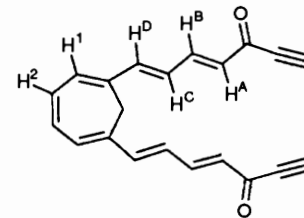
28b
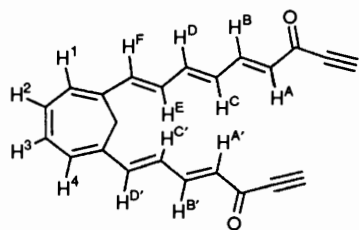
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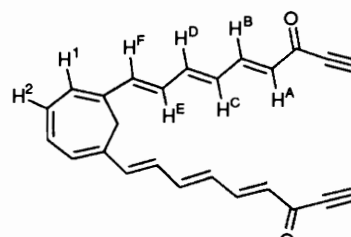
30

was detected at all and thus it is not clear whether these compounds exist as a single diastereoisomer or as a mixture of diastereoisomers.

In compounds **16–18**, the side-chain CH=CH groups were of *E* configuration as revealed by the J_{vic}-values of ~15 Hz. Compound **19** behaved unusually and one of the CH=CH groups adjacent to the CHOH moieties had the *Z* configuration as mentioned above. In compounds **20–23**, the CH=CH groups adjacent to the CHOH moieties were concluded to be all in the *E* configuration. As for the other CH=CH groups no definite assignment of configuration could be made because of overlap of the signals, and the *E* configuration was tentatively assigned.

31

32
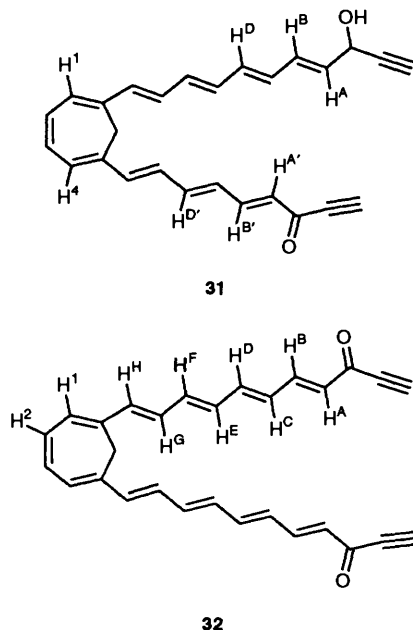
The diols **15–23** were then converted into the diacetylenic diketones **24–32** in 48–68% yield by oxidation with Ba-(MnO$_4$)$_2$[9] in dichloromethane. The ¹H NMR spectral and structural assignments of the diketones **24–32** were made on the basis of decoupling experiments. The olefin protons α to the carbonyl groups appeared at the highest field of the olefin region and those at the β positions gave their signals at the lowest field, and the other olefin protons appeared in between. The olefinic proton signals of all the diketones except for compound **31** were unambiguously analysed as given in the Experimental section, and the *E*-configuration was assigned to all the CH=CH groups except for compound **28a**. The diketones **24–32** were relatively stable compounds.

Attempts to cyclize these diketones **24–32** under Glaser conditions were made similarly as for the preparation of the [20]annulenedione **4**. Glaser couplings of the formally symmetrical precursors **26** and **30** with the CH=CH groups of the same number at positions 1 and 6 of the cycloheptatriene ring afforded the corresponding, (4n)-membered, [16]- **3** and [24]-annulenedione **5**, but those of the formally unsymmetrical precursors **25**,* **27**, **29** and **31** with the CH=CH groups of different numbers did not produce the desired (4n + 2)-membered annulenediones. In the coupling of the diketone **29**, Hay coupling using 1,4-diaminobutane[14] was also attempted, but no desired [22]annulenedione was detected. The desired products may have sterically unfavourable structures. The
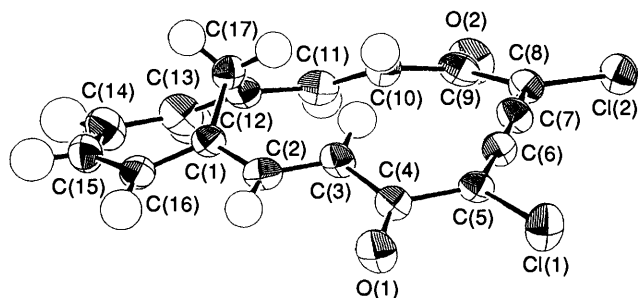

Fig. 1 An ORTEP drawing of compound **3**

coupling of the lowest member **24** did not afford the corresponding annulenedione, presumably due to a sterically unfavourable structure. Also, attempted coupling of the highest member **32** did not afford the corresponding annulenedione and compound **32** was recovered unchanged. The low solubility of substrate **32** in the reaction solvents (benzene and ethanol) may have prohibited the formation of the desired product.

Dichlorodidehydromethano-[16]annulenedione **3**, -[20]annulenedione **4** and -[24]annulenedione **5**, so obtained, formed thermally relatively stable, dark red, black-purple and dark green crystals, respectively.

X-Ray Structure Analysis of Compound **3**.—The formation of the annulenedione structure with a 1,4-dichlorobutatriene moiety seemed quite unusual, and thus X-ray crystallographic analysis was performed for compound **3** in order to confirm this unique structure, because only compound **3** afforded single crystals suitable for X-ray analysis.

The perspective drawing of the molecular structure of **3** is shown in Fig. 1.

The structural data clearly show that the compound has the structure supported by the spectroscopic studies mentioned above. The molecule is significantly distorted from the expected C_s structure presumably because of the ring strain and/or the transannular repulsion. No unusual bond lengths or angles were found except for the C4–C5 and C8–C9 bond lengths [1.500(6) and 1.514(7) Å, respectively] which are somewhat longer than the normal length of an sp²–sp² single bond. The peripheral π-system is fairly planar, although the inter-ring dihedral angles of the C9–C10, C13–C14 and C15–C16 bonds deviate from planarity by ~30°. The butatriene moiety deviates only slightly from linearity.

The ¹H NMR Spectra of Compounds **3–5**.—The ¹H NMR spectra of the dichlorodidehydroannulenediones **3–5** both in CDCl$_3$ (Fig. 2) and in D$_2$SO$_4$ (Fig. 3), were easily analysed by means of the decoupling experiments and the data are listed in Table 1 together with those of the corresponding acyclic precursors **26**, **28b** and **30**. The data of compound **28b** rather than those of its isomer **28a** were used as the more appropriate model for comparison with compound **4**, although compound **4** could not be obtained from dione **28b**.

As can be seen from Table 1, the outer protons in compounds **3–5** resonate at lower field than the corresponding protons in the acyclic model compounds **26**, **28b** and **30**, respectively, whereas the inner olefinic protons as well as the bridged methylene protons resonate at higher field. The chemical-shift differences $\Delta\delta^{AB}$ between H^A and H^B protons in compound **3**, and $\Delta\delta^{BC}$ between H^B and H^C protons in compounds **4** and **5** as the representatives of the outer and inner olefinic protons, respectively, are also shown, which are regarded as an approximate measure of the magnitude of the induced ring current. The $\Delta\delta^{AB}$- and $\Delta\delta^{BC}$-values are 1.2–1.7 ppm, and are therefore similar among compounds **3–5**. The chemical shifts of the

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* Among the unsymmetrical diketones **25**, **27**, **29** and **31** studied only the diketone **25** gave supposed cyclization products, although the yields were quite low. Further studies on the structureal determination of the products are in progress.
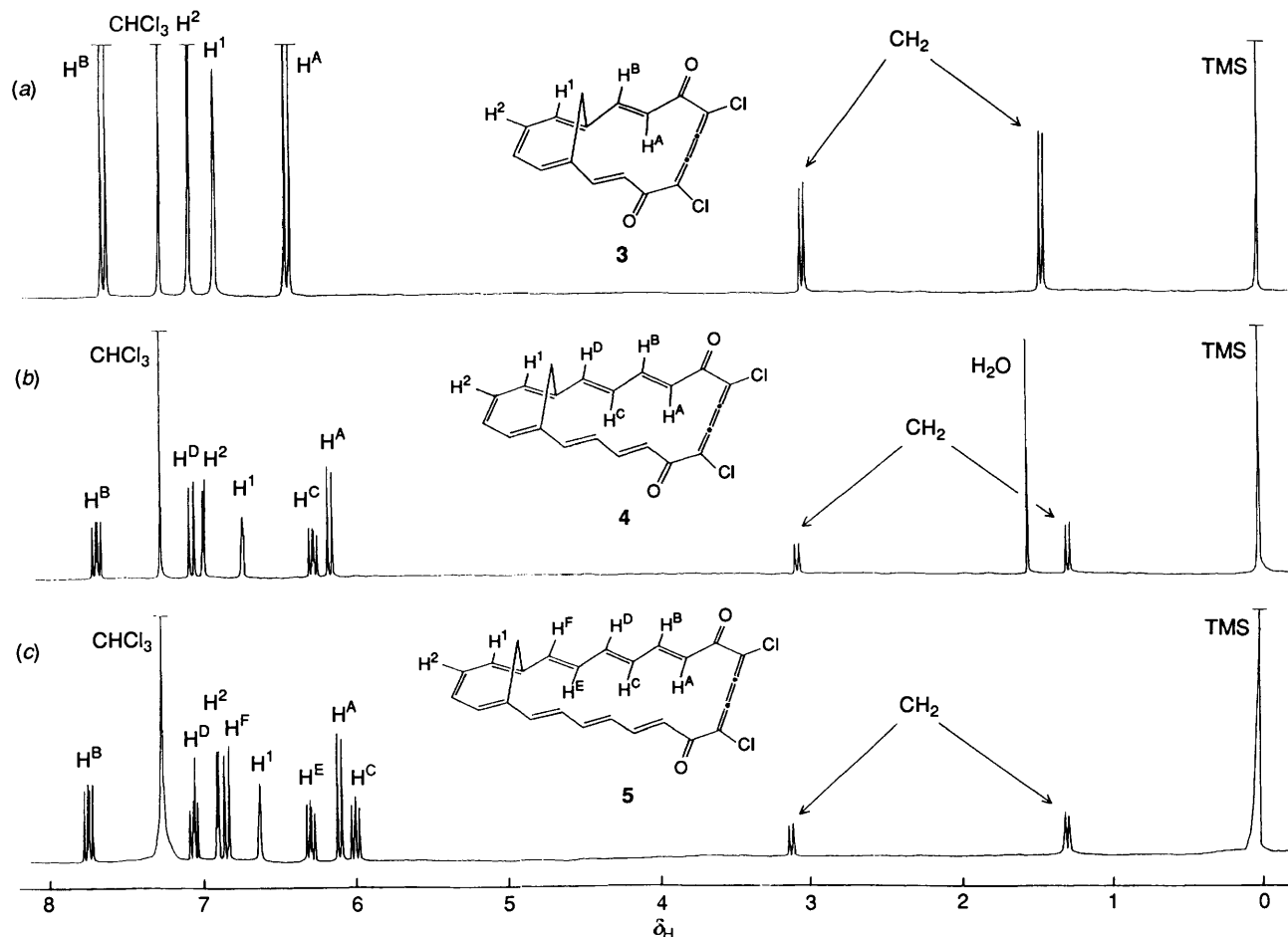
Fig. 2   500 MHz ^{1}H NMR spectra of compounds **3** (a), **4** (b) and **5** (c) in CDCl$_3$ at 26 °C

bridged methylene protons are also very similar among these compounds and their average positions are ~ 0.5 ppm upfield of those of the acyclic precursors **26**, **28** and **30**. These spectral data indicate that compounds **3–5** are diatropic in CDCl$_3$, although diatropicity is expected of 14π-, 18π- and 22π-electron systems, respectively, arising from polarization of the two carbonyl groups.

Dissolution of compound **3–5** in D$_2$SO$_4$ afforded a dark green solution, a dark green-brown solution, and a dark violet solution, respectively, suggesting the formation of the corresponding dicationic species **3A–5A**. In particular, the solution of dication **5A** was very stable and remained unchanged for several months at − 10 °C, although the solution in CDCl$_3$ was less stable and underwent considerable decomposition after several days at − 10 °C. The ^{1}H NMR spectral data of cations **3A–5A** are also given in Table 1 and the spectra are shown in Fig. 3. In species **3A–5A** the inner protons H^A, H^C and H^E as well as the bridged methylene protons appear at an extremely high field of δ − 1 to − 6.5, while the outer protons appear at a very low field of δ 9–12, indicating the induction of very strong diamagnetic ring current due to the dicationic species **3A–5A** to which the extensively delocalized 14π- **3B**, 18π- **4B** and 22π-electron structure **5B** contribute to a great extent. In addition, $\Delta\delta^{AB}$ or $\Delta\delta^{BC}$ increases in the order **3A** (11.8 ppm) < **4A** (13.7 ppm) < **5A** (16.3 ppm) with increasing ring size. Furthermore, the resonance of the bridged methylene protons, which are located inside the macrocycles, move to higher field on going from dication **3A** to **5A**, showing the increasing diamagnetic ring currents as the ring size increases.

These findings are remarkable in two respects. (i) As theoretically predicted,[15] such a large diatropicity as observed

in species **5A** for a 22π-electron system has never been observed, not even in diprotonated annulenediones 1[2] and protonated annulenones,[16] but also in neutral annulenes, such as the carbocyclic 'acetylene-cumulene' tetradehydroannulenes 33[17] and the tetradehydromethanoannulenes 34.[3,4]

(ii) The diatropicity increases with increasing ring size. This observation is also unprecedented. It has so far been recognized that the diatropicity decreases as the ring size increases in peripherally conjugated systems such as compounds 33[17] and 34.[3,4,18]

Haddon pointed out that the ring-current effect increases with increasing ring size if the macrocycles have no bond alternation and are highly delocalized.[19] As can be seen from Table 1, the species **3A–5A** may be the cases predicted by Haddon, since the bond alternation in dications **3A–5A** is considerably less as compared with that of compounds **3–5**, judging from the vicinal coupling constants (J) of the olefinic protons.

Thus, the fact that the diatropicities increase with increasing ring size in dications **3A–5A** may not be so surprising if we accept Haddon's prediction.

^{13}C NMR Spectra of Compounds 3–5.—The ^{13}C NMR spectral data of compounds **3–5** in CDCl$_3$ and in D$_2$SO$_4$ are compiled in Table 2. For compound **3** in CDCl$_3$, carbons carrying hydrogen atom(s) were unambiguously assigned by CH-COSY spectra. Among the quaternary carbon signals, the signal at δ 129.7 was assigned to the bridgehead carbon because it appeared as a complex multiplet due to $^2J_{CH}$ and higher couplings in a ^{1}H-non-decoupled spectrum. The signals at δ 121.3 and 160.3 were assigned to the sp^2- and sp-hybridized carbons,
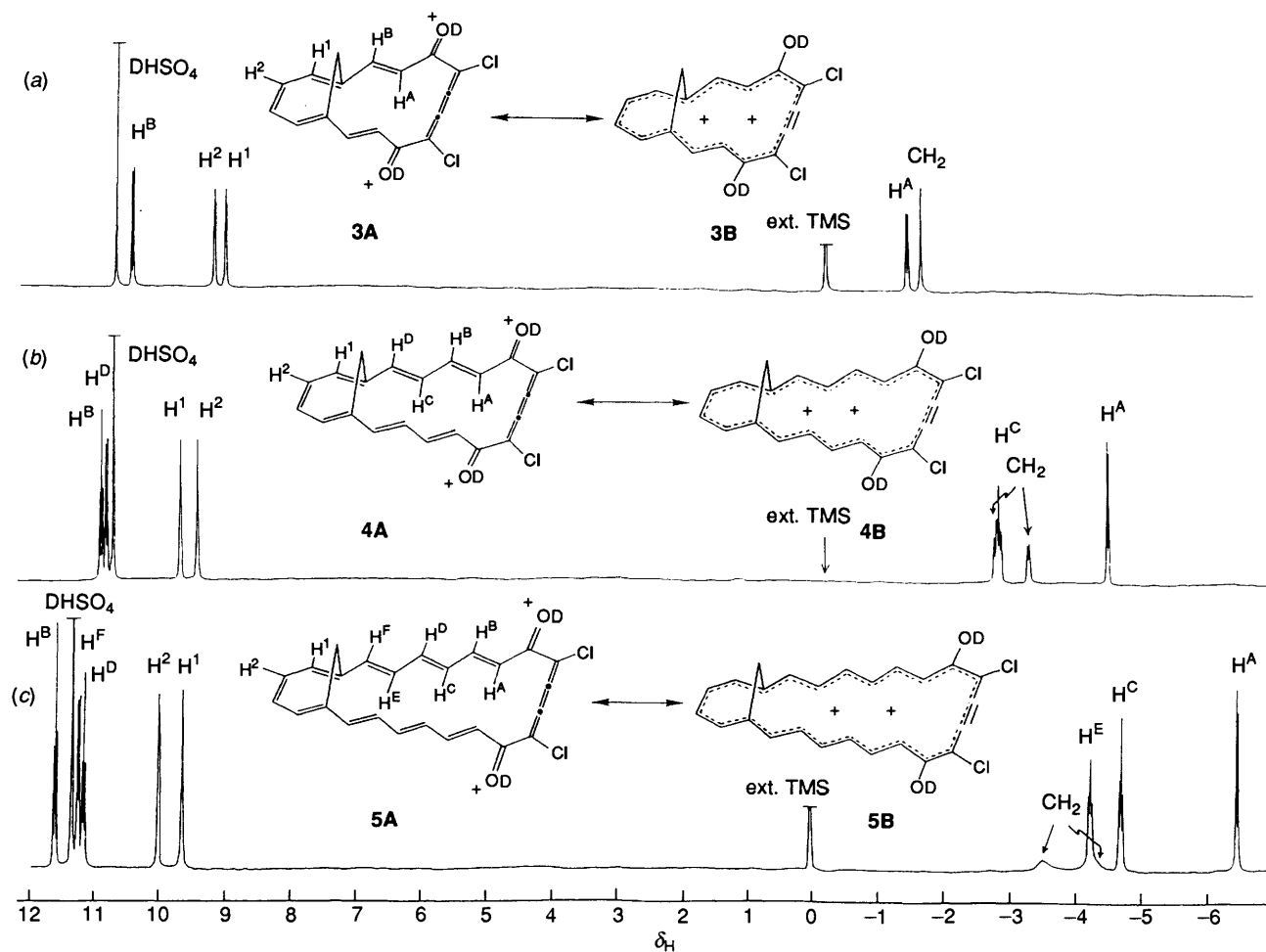
Fig. 3   500 MHz ^{1}H NMR spectra of species 3A (a), 4A (b) and 5A (c) in D_2SO_4 at 26 °C

respectively, of the butatriene moiety, in accordance with the data of various butatriene derivatives hitherto reported.[20] Both signals appeared as singlets in a ^{1}H-non-decoupled spectrum. The signal at δ 180.9, assigned to the carbonyl carbons, appeared as a double doublet with spacings of 5.8 and 4.5 Hz in a ^{1}H-non-decoupled spectrum due to $^2J_{CH}$ and $^3J_{CH}$ couplings.

As ^{1}H-non-decoupled and CH-COSY spectra could not be obtained for compounds 4 and 5 because of their low solubility and the instability of these compounds in $CDCl_3$, the spectral assignments were made in analogy with those for 3 and some ambiguity remained, as shown in Table 2.

The ^{13}C peak assignments of compounds 3–5 in D_2SO_4 were made on the basis of ^{1}H-non-decoupled and selectively decoupled spectra. Chemical shifts of quaternary carbons significantly depend on the ring size in D_2SO_4, in sharp contrast with those in $CDCl_3$. The signal assigned to the sp carbon of the butatriene moiety appeared as a singlet in the ^{1}H-non-decoupled spectrum, while that of the sp^2 carbon appeared as a doublet with a spacing of ~2.5 Hz, probably due to $^3J_{CH}$.

The methylene carbon signal shifts upfield upon changing the solvent from $CDCl_3$ to D_2SO_4 and the magnitude of the shift increases with ring size. This upfield shift can reasonably be ascribed to the ring-current effect in these highly diatropic species.

It is generally accepted that the ring-current effect on ^{13}C chemical shifts is often obscured by other factors but has a similar magnitude to that on ^{1}H chemical shifts.[21] In the present compounds, the average upfield shift of the methylene protons upon the change of solvent from $CDCl_3$ to D_2SO_4 was

3.7, 5.1 and 6.1 ppm for compounds 3, 4 and 5 (Table 1), respectively, and that of the methylene carbon was 5.7, 7.3 and 9.0 ppm (Table 2) and they are excellently parallel.

While the olefinic carbons shift downfield upon the solvent change, due to delocalization of the positive charge, the sp carbons of the butatriene moiety, as well as the carbonyl carbons, shift upfield and the magnitude of the shift is again parallel to the diatropicity of the species.

Flipping of the Methylene Bridge—Dynamic NMR Study.— In the ^{1}H NMR spectra of 3–5 in $CDCl_3$ at ambient temperature, the methylene proton signal appeared as a sharp AB quartet indicating that the flipping of the methylene bridge was slow on the NMR timescale. The methylene signal of compound 5 at 60 °C was somewhat broadened, suggesting that the flipping slowly occurred at this temperature. Although a detailed lineshape analysis could not be made because of the extremely low solubility and the thermal instability of the compound, the free energy of activation for the flipping was estimated to be far higher than 16 kcal mol^{-1}.* Compounds 3 and 4 are inferred to have higher flipping barriers than compound 5 because the ring sizes are smaller and the strain at the transition state for flipping would therefore be larger.

In D_2SO_4 the dicationic species 5A showed two broad peaks for the methylene protons at 26 °C, indicating that flipping was taking place on the NMR timescale. Spectra were obtained at several temperatures between 26 and 60 °C and lineshape

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* 1 cal = 4.184 J.

Table 1 ¹H NMR parameters of compounds **3–5**, **26**, **28b** and **30** at 26 °C[a]

Compound	δ_H(J/Hz) Inner protons			CH$_2$		Outer protons							$\Delta\delta^{AB}$/ppm ($\Delta\delta^{BC}$/ppm)
	H^A	H^C	H^E	H^a	H^b	H^B	H^D	H^F	H^1	H^4	H^2	H^3	
26[b]	6.53			2.77		7.58			6.73		6.85		
3	6.43d (15.5)			1.44d, 3.02d (13.7)	(13.7)	7.63d (15.5)			6.90m		7.07m		1.20
3A[c]	−1.23d (14.5)			−1.44s		10.58d (14.5)			9.17m		9.34m		11.81
28b[b]		6.71		2.78		7.57	6.84			6.53		6.74	
4	6.15d (14.6)	6.27dd (15.4, 11.5)		1.27d, 3.06d (13.4)	(13.4)	7.68dd (14.5, 11.5)	7.06d (15.4)		6.72m		6.98m		(1.41)
4A[c]	−4.39d (13.2)	−2.74t (13.3)		−2.68d, −3.17d (14.2)	(14.2)	11.00t (12.7)	10.92d (14.0)		9.52m		9.77m		(13.74)
30[b]	6.31	6.54	6.69	2.76		7.55	6.83	6.62	6.45		6.68		
5	6.10d (14.6)	6.00dd (14.6, 11.6)	6.29dd (15.6, 11.0)	1.29d, 3.12d (13.7)	(13.7)	7.74dd (14.6, 11.6)	7.05dd (14.5, 11.1)	6.84d (15.3)	6.62m		6.90m		(1.74)
5A[c]	−6.48d (13.3)	−4.73t (12.9)	−4.25t (13.1)	−4.30br s, −3.5br s		11.58t (13.0)	11.13t (12.6)	11.21d (13.6)	9.62m		9.98m		(16.31)

[a] Obtained in CDCl$_3$ at 500 MHz unless otherwise stated. [b] Data for the acetylenic protons are omitted (see Experimental section). [c] In D$_2$SO$_4$.

3   3A   3B

4   4A   4B

5   5A   5B

33   34
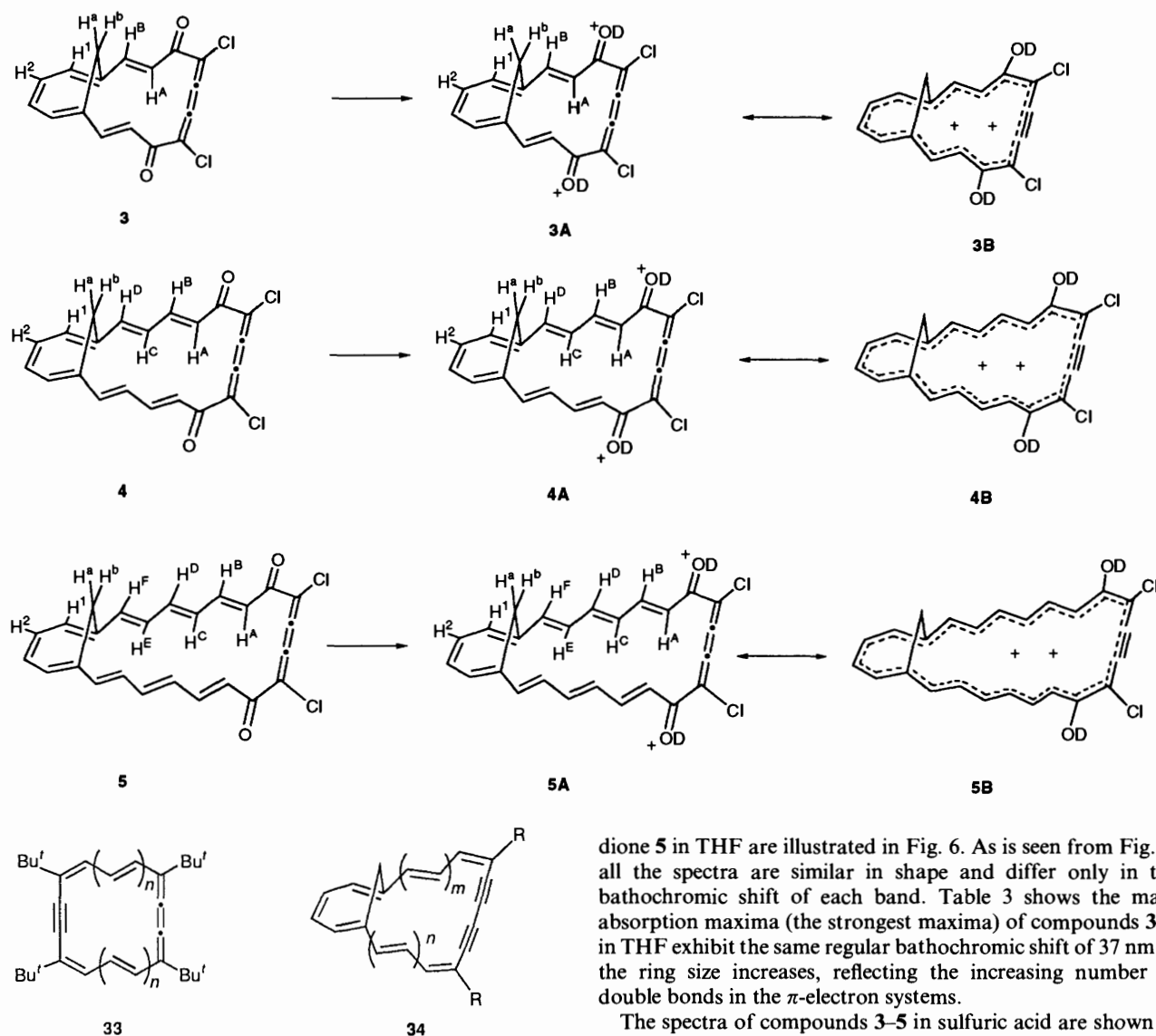
analysis* was performed to obtain the rate constants for the flipping (Fig. 4). The free energy of activation was calculated to be ~ 14.2 kcal mol⁻¹ over this temperature range.

The species 4A showed a sharp AB-quartet signal for the methylene protons at 26 °C but the lineshape broadening was observed at higher temperatures (Fig. 5). Lineshape analysis* afforded rough values of 80 and 30 s⁻¹ at 78 and 65 °C, respectively, which correspond to $\Delta G^{\ddagger}$ 17.6 kcal mol⁻¹. This value is higher than that for dication 5A, which would be reasonable judging from the smaller ring size of dication 4A.

The species 3A showed a singlet for the methylene protons at 26 °C. This was ascribed to accidental coincidence of the chemical shifts of the intrinsically diastereotopic protons rather than to rapid flipping.

The lower energy barrier to flipping in D_2SO_4 than in $CDCl_3$ observed in compound 5 may suggest a higher planarity of the molecular skeleton in the dicationic species 5A than in the neutral diketone.

The Electronic Spectra of Compounds 3–5.—The electronic absorption maxima of the annulenediones 3–5, determined in both THF and sulfuric acid, are listed in Table 3, and the absorption spectra of the [16]- 3, [20]- 4 and [24]-annulene-

* The calculated spectra were obtained by the DNMR3 program.[22]

dione 5 in THF are illustrated in Fig. 6. As is seen from Fig. 6, all the spectra are similar in shape and differ only in the bathochromic shift of each band. Table 3 shows the main absorption maxima (the strongest maxima) of compounds 3–5 in THF exhibit the same regular bathochromic shift of 37 nm as the ring size increases, reflecting the increasing number of double bonds in the π-electron systems.

The spectra of compounds 3–5 in sulfuric acid are shown in Fig. 7. It is evident from Table 3 and Fig. 7 that all the bands of compounds 3–5 show a very large bathochromic shift (130–300 nm) in every case on changing the solvent from THF to H_2SO_4, reflecting the extended conjugation of the respective π-electron system in H_2SO_4. In addition, it is noteworthy that the longest wavelength bands of compounds 4 (792 nm) and 5 (887 nm) in H_2SO_4 appear at much longer wavelengths than those of the tetradehydro-[20]- (1; $m = n = 0$) (535 nm)[2] and -[24]-annulenedione (1; $m = n = 1$) (614 nm)[2] with the same respective ring size, indicating that the diprotonated species of the former are much more highly delocalized π-electron systems than are those of the latter. Furthermore the shapes of absorption curves are rather similar to those of [4n + 2]π-tetradehydroannulenes 33,[17] as compared with the spectra in THF, reflecting the fact that compounds 3–5 are strongly diatropic as are compounds 33, as revealed by their ¹H NMR spectral data in D_2SO_4.

Experimental

Table 2 ^{13}C NMR data of compounds 3–5[a]
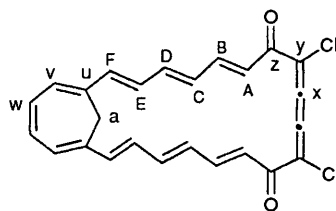
	3			4			5		
	CDCl$_3$	D$_2$SO$_4$	Δδ	CDCl$_3$	D$_2$SO$_4$	Δδ	CDCl$_3$	D$_2$SO$_4$	Δδ
a	26.90	21.17	−5.73	26.49	19.16	−7.33	26.74	17.77	−8.97
x	160.28	147.10	−13.18	158.78	135.16	−23.62	158.41	126.26	−32.15
y	121.30	127.55	6.25	121.09	123.14	2.05	121.00	118.81	−2.19
z	180.90	178.20	−2.70	179.97	170.10	−9.87	179.56	165.52	−14.04
A	122.27	124.70	2.43	126.22	129.59	3.37	124.27	127.10	2.83
B	145.09	166.03	20.94	144.07	152.38[b]	8.31	144.64	147.17	2.53
C				127.38	139.81	12.43	129.16[b]	146.23	17.07
D				142.84	163.10[b]	20.26	142.45[c]	151.32	8.87
E							130.52[b]	140.07	9.55
F							138.07[c]	158.30	20.23
u	129.71	141.38	11.67	129.80	138.54	8.74	129.91	133.94	4.03
v	135.61	152.44	16.83	131.98	149.66	17.68	131.58[d]	148.05	16.47
w	133.59	146.14	12.55	132.27	144.24	11.97	132.21[d]	142.26	10.05

[a] Measured at 26 °C. [b,c,d] Signal pairs are mutually interchangeable in each group.
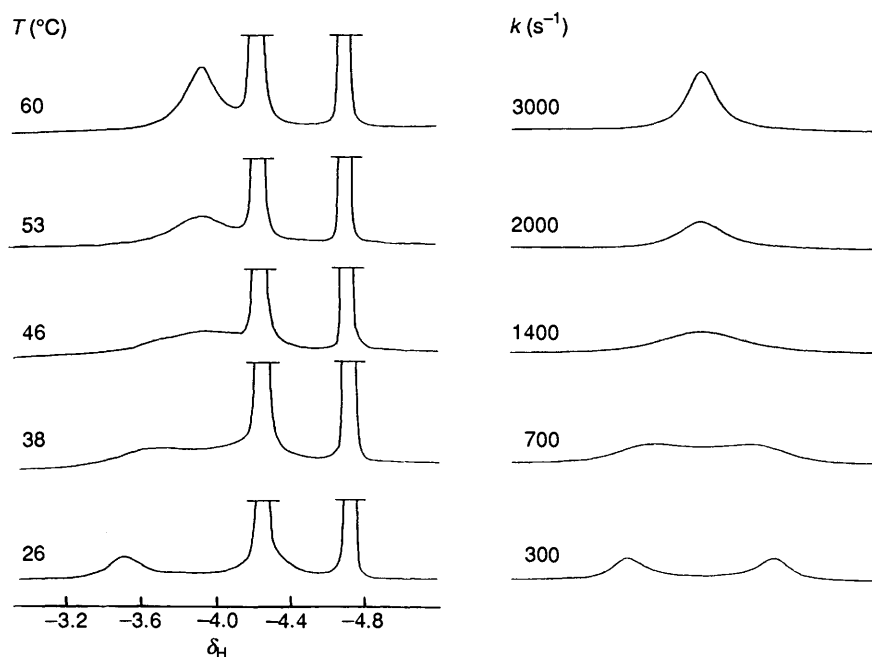
Fig. 4 Temperature-dependent ^1H NMR spectra of species **5A** in D$_2$SO$_4$. On the left are the observed spectra at various temperatures (°C) and on the right are the calculated spectra with the best-fit rate constants (s^{-1}).

were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system. Fast-atom bombardment mass spectra (FAB-MS) were obtained on a JEOL JMS-AX 505W high-resolution double-focusing mass spectrometer equipped with a D 5000 data system. Ions were generated by bombardment of the target matrix with a neutral xenon atom beam (derived from a Xe$^+$ ion beam accelerated at 2 kV). Samples for FAB-MS were prepared by dissolving the compounds in a m-nitrobenzyl alcohol matrix. ^1H NMR spectra at ambient temperature were recorded as CDCl$_3$ solutions, unless otherwise specified, with a Bruker AM-500 spectrometer at 500.14 MHz. Internal SiMe$_4$ (TMS) was used as a reference when the solvent was CDCl$_3$, while external

SiMe$_4$ was used when the solvent was D$_2$SO$_4$. J-Values are given in Hz. ^{13}C NMR spectra were recorded as CDCl$_3$ solution, unless otherwise indicated, on the AM-500 at 125.76 MHz with internal SiMe$_4$ as reference.

All preparations of the diols 16–23 were carried out in the same manner as that described in detail for the representative compound 15 where ethynylmagnesium bromide was used in 10 molar equiv. excess over the starting dialdehydes 6–14. THF used in these reactions was refluxed over potassium hydroxide pellets and distilled before use. The preparations of the diketones 25–32 were carried out in the same manner as that for the representative compound 24 where activated Ba(MnO$_4$)$_2$[9] was used in 10 molar equiv. excess over the diols 15–23.

Table 3 Electronic absorption maxima of compounds 3–5 [a, in THF, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}); b, in H$_2$SO$_4$, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})]. Strongest absorptions are indicated in bold type

|		
3	a	263sh (25 300), **271 (26 500)**, 340 (23 000), 450sh (4300)
	b	286 (20 800), 330 (17 300), **412 (79 700)**, 448 (36 600), 571 (4900), 685 (16 000)
4	a	**308 (60 300)**, 349 (36 600), 502 (6100)
	b	280 (6900), 310 (8400), 330 (10 200), 395 (20 500), 440sh (48 200), **469 (52 400)**, 480sh (49 400), 521 (40 400), 660 (2400), 700 (3600), 792 (26 500)
5	a	**345 (103 500)**, 532 (10 900)
	b	230 (11 100), 270 (7900), 305sh (7400), 320 (8400), 372 (1100), 452sh (49 300), **505 (76 500)**, 540 (75 200), 590 (67 400), 789 (7100), 815 (8400), 887 (22 300)
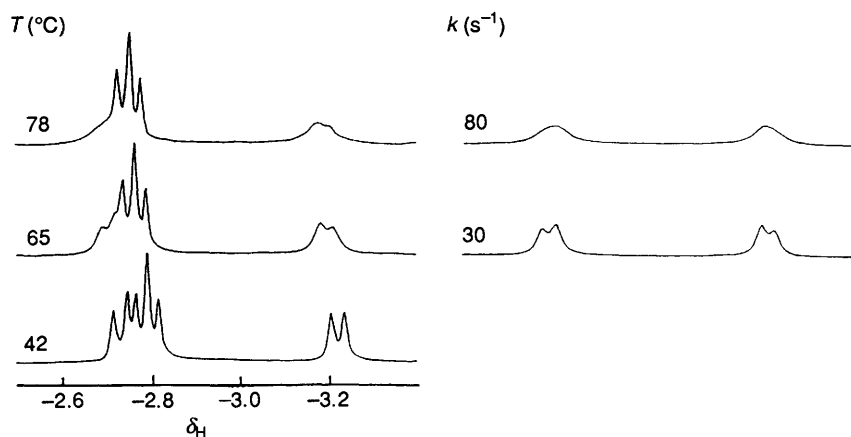
Fig. 5 Temperature-dependent ^{1}H NMR spectra of species **4A** in D$_2$SO$_4$. On the left are the observed spectra at various temperatures (°C) and on the right are the calculated spectra with the best-fit rate constants (s^{-1}).
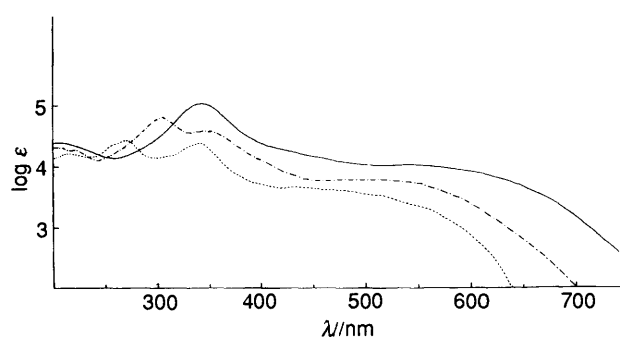
Fig. 6 Electronic absorption spectra of [16]- **3** (------), [20]- **4** (—·—·—·—) and [24]-annulenedione **5** (————) in THF

Fig. 7 Electronic absorption spectra of [16]- **3** (------), [20]- **4** (—·—·—·—) and [24]-annulenedione **5** (————) in H$_2$SO$_4$

Dichloromethane used in these reactions was refluxed over calcium hydride and distilled before use. Attempted Glaser couplings for the diketones **24–32** were carried out in almost the same manner as that for compound **3**.

Progress of all reactions was followed by TLC on Merck precoated silica gel. Merck alumina (activity II–III) and silica gel (Daiso gel 1001 W or Daiso gel 1002 W) were used for column chromatography. Compounds were preadsorbed from diethyl ether, benzene or dichloromethane solution onto the absorbent before column chromatography. Organic extracts were washed with saturated aq. sodium chloride and dried over anhydrous sodium sulfate prior to removal of solvent. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

Isomeric 1,6-Bis(1-hydroxyprop-2-ynyl)cyclohepta-1,3,5-trienes **15a** *and* **15b**.—To an ice-cooled, stirred solution of ethynylmagnesium bromide in THF (1100 cm^3), prepared from gaseous acetylene, magnesium (25.0 g, 1.03 mol) and bromoethane (123 g, 1.13 mol),[8] was added dropwise during 40 min a solution of the dialdehyde **6**[3] (1.50 g, 10.1 mmol) in THF

(200 cm^3) and the mixture was stirred for 1 h at room temperature. Then saturated aq. ammonium chloride (1800 cm^3) was added to the ice-cooled mixture and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed and dried. The dark red liquid obtained after removal of solvent was chromatographed on silica gel (4.2 × 5.0 cm). The initial fractions eluted with benzene–dichloromethane (2:3) afforded the RS-*isomer* **15a** (378 mg, 19%) of the diacetylenic diol as needles, m.p. 88–89 °C (from hexane–dichloromethane); m/z 200 (M$^+$, 18%) and 153 (100), λ_{max}/nm 210 (ε/dm^3 mol^{-1} cm^{-1} 15 500) and 273 (4850); v_{max}/cm^{-1} 3350 (OH), 3300 (C≡CH) and 2140 C≡C); δ_H 6.57 (2 H, m, H^2), 6.33 (2 H, m, H^1), 5.03 (2 H, dd, J 5.6 and 2.0, C*H*OH), 3.12 and 2.39 (2 H, AB-q, J 13.6, CH$_2$), 3.08 (2 H, d, J 5.7, OH) and 2.63 (2 H, d, J 2.2, ≡CH); δ_C 134.2 (q), 130.3 (t), 124.0 (t), 82.6 (q, –C≡), 74.5 (t, ≡CH), 65.6 (t, CHOH) and 28.2 (s, CH$_2$) (Found: C, 78.0; H, 5.9. C$_{13}$H$_{12}$O$_2$ requires C, 78.0; H, 6.0%).

The later fractions, eluted with 10% ethyl acetate in dichloromethane, afforded the R^*R^*-*isomer* **15b** (416 mg, 21%) as a pale yellow liquid; m/z 200.0845 (C$_{13}$H$_{12}$O$_2$ requires M, 200.0835); λ_{max}/nm 210 (14 000) and 274 (4300); v_{max}(neat)/cm^{-1}

3300 (OH), 3260 (C≡CH) and 2110 C≡C); δ_H 6.58 (2 H, m, H^2), 6.40 (2 H, m, H^1), 5.05 (2 H, d, J 2.2, CHOH), 3.49 (2 H, br s, OH), 2.70 (2 H, s, CH$_2$) and 2.63 (2 H, d, J 2.2, ≡CH); δ_C 134.0 (q), 130.3 (t), 123.9 (t), 82.5 (q, –C≡), 74.8 (t, ≡CH), 65.4 (t, CHOH) and 29.1 (s, CH$_2$) (Found: C, 77.45; H, 6.6%). Attempts to improve the elemental analysis failed.

1,6-Bis(1-oxoprop-2-ynyl)cyclohepta-1,3,5-triene 24.—A mixture of the RS-isomer 15a (615 mg, 3.07 mmol) and Ba(MnO$_4$)$_2$ (7.0 g, 27.3 mmol) in dry dichloromethane (500 cm^3) was stirred for 4.5 h at room temperature. Then the mixture was filtered through Celite by suction and the inorganic material was washed with dichloromethane. The combined filtrate and washings were concentrated under reduced pressure. The residue obtained after removal of solvent was chromatographed on silica gel (4.2 × 7.0 cm). The fractions eluted with 20–30% dichloromethane in benzene afforded the diketone 24 (520 mg, 86%) as yellow needles, m.p. 158–160 °C (decomp.) (from hexane–dichloromethane); m/z 196 (M$^+$, 90%) and 115 (100) (C$_{13}$H$_8$O$_2$ requires M, 196.1); λ_{max}/nm 258 (14 200) and 334 (5930); v_{max}/cm^{-1} 3290 (C≡CH), 2080 (C≡C) and 1630 and 1620 (C=O); δ_H 7.59 (2 H, m, H^1), 7.05 (2 H, m, H^2), 3.28 (2 H, s, ≡CH) and 3.19 (2 H, s, CH$_2$); δ_C 175.3 (q, C=O), 138.3 (t), 134.63 (q), 134.57 (t), 79.8 (q, –C≡), 79.7 (t, ≡CH) and 20.9 (s, CH$_2$) (Found: C, 79.5; H, 4.3. C$_{13}$H$_8$O$_2$ requires C, 79.6; H, 4.1%).

A mixture of the R*R*-isomer 15b (430 mg, 2.15 mmol) and Ba(MnO$_4$)$_2$[9] (4.00 g, 15.6 mmol) in dry dichloromethane (300 cm^3) was stirred for 2.5 h at room temperature. The mixture was worked up as described above. The product was chromatographed on silica gel (4.2 × 3.5 cm). The fractions eluted with 30% dichloromethane in benzene afforded the diketone 24 (300 mg, 71%).

Attempted Glaser coupling of the diketone 24 under the conditions reported for the preparation of compound 3 described below did not afford the corresponding [12]annulenedione.

1-(3-Hydroxypent-1-en-4-ynyl)-6-(1-hydroxyprop-2-ynyl)cyclohepta-1,3,5-triene 16.—To an ice-cooled, stirred solution of ethynylmagnesium bromide in THF (1350 cm^3), prepared from gaseous acetylene, magnesium (30.0 g, 1.23 mol) and bromoethane (147 g, 1.35 mol), was added dropwise during 1 h a solution of the dialdehyde 7[3] (1.50 g, 8.61 mmol) in THF (100 cm$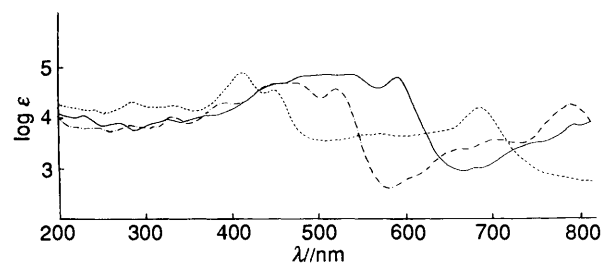^3$) and the mixture was stirred for 30 min at room temperature before being worked up as for the isolation of compound 15 except for the use of benzene as the extraction solvent. The product was chromatographed on silica gel (4.2 × 6.0 cm). The fractions eluted with benzene–dichloromethane (1 : 9) afforded the diol 16 (1.04 g, 53%) as pale yellow needles, m.p. 98–100 °C (from hexane–dichloromethane); m/z 226 (M$^+$, 7%) and 115 (100) (C$_{15}$H$_{14}$O$_2$ requires M, 226.3); λ_{max}/nm 227 (26 400), 231 (27 500) and 306 (7520); v_{max}/cm^{-1} 3300 (OH), 3280 (C≡CH), 2120 C≡C) and 1007 and 957 [(E)-HC=CH] (Found: C, 79.9; H, 6.2. C$_{15}$H$_{14}$O$_2$ requires C, 79.6; H, 6.2%). The ^{1}H NMR spectrum of compound 16 showed it to be a ~ 5:2 mixture of two diastereoisomers. The major isomer: δ_H 6.61 (1 H, dd, J 11.2 and 5.8, H^2), 6.56 (1 H, dd, J 11.2 and 5.7, H^3), 6.51 (1 H, d, J 15.6, H^B), 6.40 (1 H, d, J 6.1, H^4), 6.24 (1 H, d, J 5.8, H^1), 6.18 (1 H, dd, J 15.6 and 6.1, H^A), 5.00 (1 H, br s, CH^aOH), 4.91 (1 H, br s, CH^bOH), 2.71 and 2.66 (2 H, AB-q, J 13.3, CH$_2$), 2.617 (1 H, d, J 2.2, ≡CH^b), 2.610 (1 H, d, J 2.2, ≡CH^a), 2.395 (1 H, br d, J 6, OH^b) and 2.385 (1 H, br d, J 6, OH^a); δ_C 133.1 (q), 132.9 (t), 131.22 (q), 130.9 (t), 130.0 (t), 128.8 (t), 128.0 (t), 123.7 (t), 82.9 (q, –C≡), 81.9 (q, –C≡), 74.7 (t, ≡CH), 74.5 (t, ≡CH), 65.4 (t, CHOH), 62.7 (t, CHOH) and 27.8 (s, CH$_2$). The minor isomer: δ_H 6.61 (1 H, dd, J 11.2 and 5.8, H^2), 6.56 (1 H, dd, J 11.2 and 5.7, H^3), 6.50 (1 H, d, J 15.6, H^B), 6.39 (1

H, d, J 6.1, H^4), 6.24 (1 H, d, J 5.8, H^1), 6.18 (1 H, dd, J 15.5 and 6.3, H^A), 5.00 (1 H, br s, CH^aOH), 4.91 (1 H, br s, CH^bOH), 2.72 and 2.67 (2 H, AB-q, J 13.3, CH$_2$), 2.62 (1 H, d, J 2.2, ≡CH^b), 2.61 (1 H, d, J 2.2, ≡CH^a), 2.395 (1 H, br d, J 6, OH^b) and 2.385 (1 H, br d, J 6, OH^a); δ_C 132.93 (q), 132.91 (t), 131.3 (q), 130.9 (t), 130.0 (t), 128.8 (t), 128.0 (t), 123.8 (t), 82.9 (q, –C≡), 81.8 (q, –C≡), 74.8 (t, ≡CH), 74.5 (t, ≡CH), 65.4 (t, CHOH), 62.8 (t, CHOH) and 27.7 (s, CH$_2$).

1-(3-Oxopent-1-en-4-ynyl)-6-(1-oxoprop-2-ynyl)cyclohepta-1,3,5-triene 25.—A mixture of the diol 16 (958 mg, 4.23 mmol) and Ba(MnO$_4$)$_2$ (10.0 g, 39.0 mmol) in dry dichloromethane (700 cm^3) was stirred for 3.5 h at room temperature before being worked up as for the isolation of compound 24. The product was chromatographed on silica gel (4.2 × 4.5 cm). The fractions eluted with benzene–dichloromethane (1 : 1) afforded the diketone 25 (792 mg, 84%) as yellow needles, m.p. 146–155 °C (decomp.) (from hexane–dichloromethane); m/z 222 (M$^+$, 56%) and 115 (100) (C$_{15}$H$_{10}$O$_2$ requires M, 222.2); λ_{max}/nm 224 (14 200), 283 (27 300) and 375 (10 200); v_{max}/cm^{-1} 3212 (C≡CH), 2100 (C≡C), 1618 (C=O) and 973 [(E)-HC=CH]; δ_H 7.62 (1 H, d, J 6.1, H^4), 7.51 (1 H, d, J 15.7, H^B), 7.02 (1 H, dd, J 11.1 and 6.1, H^2), 6.94 (1 H, dd, J 11.1 and 6.1, H^3), 6.92 (1 H, d, J 15.7, H^A), 6.69 (1 H, d, J 6.1, H^1), 3.254 (1 H, s, ≡CH), 3.252 (1 H, s, ≡CH) and 2.91 (2 H, s, CH$_2$); δ_C 177.3 (q, C=O), 175.5 (q, C=O), 148.0 (t), 138.8 (t), 135.9 (t), 134.1 (t), 132.7 (q), 132.3 (q), 132.0 (t), 129.6 (t), 80.4 (q, –C≡), 79.7 (q, –C≡), 79.3 (t, ≡CH), 79.0 (t, ≡CH) and 24.5 (s, CH$_2$) (Found: C, 81.1; H, 4.6. C$_{15}$H$_{10}$O$_2$ requires C, 81.1; H, 4.5%).

Glaser coupling of the diketone 25 under the conditions reported for the preparation of compound 3 described below afforded supposed cyclization products in low yields.†

1,6-Bis(3-hydroxypent-1-en-4-ynyl)cyclohepta-1,3,5-triene 17.—To an ice-cooled, stirred solution of ethynylmagnesium bromide in THF (800 cm^3), prepared from gaseous acetylene, magnesium (17.4 g, 0.71 mol) and bromoethane (85 g, 0.78 mol),[8] was added dropwise during 2 h a solution of the dialdehyde 8[3] (1.00 g, 4.99 mmol) in THF (150 cm^3) and the mixture was stirred for 30 min at room temperature before being worked up as for the isolation of compound 15. The product was chromatographed on silica gel (4.2 × 7.5 cm). The fractions eluted with 80–90% dichloromethane in benzene afforded the diol 17 (512 mg, 41%) as pale orange needles, m.p. 96–107 °C (decomp.) (from hexane–dichloromethane); m/z 252 (M$^+$, 73%) and 165 (100) (C$_{17}$H$_{16}$O$_2$ requires M, 252.3); λ_{max}/nm 210sh (8300), 242sh (42 800), 249 (48 300) and 338 (7200); v_{max}/cm^{-1} 3300 (OH), 3260 (C≡CH), 2130 (C≡C) and 1010 and 970 [(E)-HC=CH]. Compound 17 was a ~1:1 mixture of the R*R* and RS diastereoisomers, but the chemical-shift differences between the isomers were observed for the CH$_2$ and OH protons, and CH^A and CHOH carbons: δ_H 6.65 (m, H^2), 6.57 (d, J 15.6, H^B), 6.31 (m, H^1), 6.13 (dd, J 15.6 and 6.2, H^A), 5.01 (br t, J 6.2, CHOH), 2.61 (d, J 2.2, ≡CH), 2.59 and 2.53 (AB-q, J 13.1, CH$_2$ of RS isomer), 2.56 (s, CH$_2$ of R*R* isomer), 2.46 (d, J 6.6, OH of one isomer) and 2.45 (d, J 6.6, OH of the other isomer); δ_C 133.4 (t), 130.7 (t), 129.8 (q), 128.4 (t), 127.51, 127.48 (t, CH^A), 82.8 (q, –C≡), 74.7 (t, ≡CH), 62.76, 62.73 (t, CHOH) and 27.1 (s, CH$_2$) (Found: C, 80.95; H, 6.45. C$_{17}$H$_{16}$O$_2$ requires C, 80.9; H, 6.4%).

1,6-Bis(3-oxopent-1-en-4-ynyl)cyclohepta-1,3,5-triene 26.—A mixture of the isomeric diol 17 (328 mg, 1.30 mmol) and

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† Among the unsymmetrical diketones 25, 27, 29 and 31 studied only the diketone 25 gave supposed cyclization products, although the yields were quite low. Further studies on the structural determination of the products are in progress.

Ba(MnO$_4$)$_2$ (3.0 g, 11.7 mmol) in dry dichloromethane (200 cm^3) was stirred for 6 h at room temperature before being worked up as for the isolation of compound **24**. The product was chromatographed on silica gel (4.2 × 6.5 cm). The fractions eluted with 40–60% benzene in hexane afforded the *diketone* **26** (200 mg, 62%) as yellow needles, m.p. 160–167 °C (decomp.) (from hexane–dichloromethane); *m/z* 248 (M$^+$, 100%) (C$_{17}$H$_{12}$O$_2$ requires M, 248.2); λ_{max}/nm 233 (17 100), 303 (51 900) and 396 (11 900); ν_{max}/cm^{-1} 3200 (C≡CH), 2105 (C≡C), 1630 (C=O) and 985 [(*E*)-HC=CH]; δ_H 7.58 (2 H, d, *J* 15.8, H^B), 6.85 (2 H, m, H^2), 6.73 (2 H, m, H^1), 6.53 (2 H, d, *J* 15.8, H^A), 3.28 (2 H, s, ≡CH) and 2.77 (2 H, s, CH$_2$); δ_C 177.0 (q, C=O), 149.0 (t), 135.8 (t), 133.4 (t), 130.6 (q), 127.8 (t), 80.2 (q, –C≡), 79.3 (t, ≡CH) and 26.9 (s, CH$_2$) (Found: C, 82.0; H, 4.9. C$_{17}$H$_{12}$O$_2$ requires C, 82.2; H, 4.9%).

10,13-*Dichloro*-11,12-*didehydro*-1,6-*methano*[16]*annulene*-9, 14-*dione* **3**.—A solution of the diketone **26** (161 mg, 0.648 mmol) in ethanol–benzene (3:1; 156 cm^3) was added dropwise to a stirred solution of copper(I) chloride (44.3 g, 0.448 mol), ammonium chloride (71 g), water (197 cm^3) and conc. HCl (0.81 cm^3) at 60 °C. After the mixture had been stirred for 10 min, a further quantity of benzene–ethanol (1:1; 123 cm^3) was added. The mixture was stirred for a further 2 h at 60 °C while a stream of oxygen was bubbled into the mixture. Then the mixture was cooled, poured onto water, and extracted with benzene. The combined organic layers were washed successively with 5% HCl, brine and aq. sodium hydrogen carbonate, and were then dried and concentrated. The residue obtained after removal of solvent was chromatographed on silica gel (3.6 × 6.5 cm). The fractions eluted with hexane–benzene (2:3) afforded the *didehydro*[16]*annulenedione* **3** (34 mg, 17%) as dark red needles, m.p. 129–135 °C (decomp.) (from hexane–dichloromethane); *m/z* 318 (M$^+$ + 1, 32%), 316 (M$^+$ − 1, 50) and 189 (100) (C$_{17}$H$_{10}$Cl$_2$O$_2$ requires M, 317.2); for UV data see Table 3, Figs. 6 and 7; ν_{max}/cm^{-1} 2040 (–C=C=C=C–), 1665 (C=O), 990 and 960 ([*E*]-HC=CH]; for ^{1}H NMR data see Table 1, Figs. 2 and 3; for ^{13}C NMR data see Table 2 (Found: C, 64.4; H, 3.5. C$_{17}$H$_{10}$Cl$_2$O$_2$ requires C, 64.4; H, 3.2%).

1-(5-*Hydroxyhepta*-1,3-*dien*-6-*ynyl*)-6-(3-*hydroxypent*-1-*en*-4-*ynyl*)*cyclohepta*-1,3,5-*triene* **18**.—To an ice-cooled, stirred solution of ethynylmagnesium bromide in THF (600 cm^3), prepared from gaseous acetylene, magnesium (14 g) and bromoethane (69.5 g), was added dropwise during 30 min a solution of the dialdehyde **9**^{3} (0.95 g, 4.2 mmol) in THF (100 cm^3) and the mixture was stirred for 2 h at room temperature before being worked up as for the isolation of compound **15**. The product was chromatographed on silica gel (3.8 × 6.0 cm). The fractions eluted with 5% ethyl acetate in dichloromethane afforded the *diol* **18** (358 mg, 43%) as pale yellow microcrystals, m.p. 117–126 °C (decomp.) (from hexane–dichloromethane); *m/z* 278 (M$^+$, 20%) and 165 (100) (C$_{19}$H$_{18}$O$_2$ requires M, 278.3); λ_{max}/nm 224sh (10 600), 251sh (28 600), 262 (51 300), 270 (60 200) and 360 (10 000); ν_{max}/cm^{-1} 3300 (OH), 3270 (C≡CH), 2110 (C≡C) and 990 [(*E*)-HC=CH]. Although compound **18** was a 5:1 mixture of two diastereoisomers, the difference in chemical shifts between the diasereoisomers was observed only for the methylene protons, and CH^A, CH$^{A'}$ and CHOH carbons: δ_H 6.63–6.59 (3 H, m, H^2, H^3 and H^C), 6.57 (1 H, d, *J* 15.3, H$^{B'}$), 6.53 (1 H, dd, *J* 14.8 and 10.6, H^B), 6.44 (1 H, d, *J* 15.1, H^D), 6.32 (1 H, d, *J* 5.3, H^1 or H^4), 6.30 (1 H, d, *J* 5.2, H^4 or H^1), 6.12 (1 H, dd, *J* 15.6 and 6.1, H$^{A'}$), 5.95 (1 H, dd, *J* 14.7 and 6.1, H^A), 5.03 (1 H, br m, C*H*^{b}OH), 4.97 (1 H, br m, C*H*^{a}OH), 2.66 and 2.59 (2 H, AB-q, *J* 13.0, CH$_2$ of the major isomer), 2.64 and 2.60 (AB-q, *J* 13.0, CH$_2$ of the minor isomer), 2.65 (1 H, d, *J* 2.2, ≡CH^b), 2.60 (1 H, d, *J* 2.2, ≡CH^a), 1.96 (1 H, d, *J* 6.3, OH^b) and 1.92 (1 H, d, *J* 6.4, OH^a) (the chemical shifts with integrals of

protons given refer to the major isomer); δ_C 135.7 (t), 133.4 and 132.7 (t, CH^A and CH$^{A'}$ of the major isomer), 133.3 and 132.7 (t, CH^A and CH$^{A'}$ of the minor isomer), 131.6 (t), 131.3 (q), 130.9 (t), 130.4 (t), 130.1 (q), 128.7 (t), 128.1 (t), 127.4 (t), 127.1 (t), 82.70 (q, –C≡), 82.66 (q, –C≡), 74.6 (t, ≡CH), 74.5 (t, ≡CH), 62.74 and 62.49 (t, CHOH of the major isomer), 62.71 and 62.48 (t, CHOH of the minor isomer) and 27.1 (s, CH$_2$) (Found: C, 81.7; H, 6.6. C$_{19}$H$_{18}$O$_2$ requires C, 82.0; H, 6.5%).

1-(5-*Oxohepta*-1,3-*dien*-6-*ynyl*)-6-(3-*oxopent*-1-*en*-4-*ynyl*)*cyclohepta*-1,3,5-*triene* **27**.—A mixture of the isomeric diol **18** (370 mg) and Ba(MnO$_4$)$_2$ (8.00 g) in dichloromethane (300 cm^3) was stirred for 6 h at room temperature before being worked up as for the isolation of compound **24**. The product was chromatographed on silica gel (3.8 × 6.0 cm). The fractions eluted with dichloromethane afforded the *diketone* **27** (239 mg, 65%) as orange needles, m.p. 134–137 °C (decomp.) (from hexane–THF); *m/z* 274 (M$^+$, 26%) and 115 (100) (C$_{19}$H$_{14}$O$_2$ requires M, 274.3); λ_{max}/nm 230 (12 400), 320 (46 500) and 415 (12 400); ν_{max}/cm^{-1} 3200 (C≡CH), 2110 (C≡C), 1620 (C=O), 1000 and 980 [(*E*)-HC=CH]; δ_H 7.59 (1 H, d, *J* 15.8, H$^{B'}$), 7.56 (1 H, dd, *J* 15.3 and 10.4, H^B), 6.84–6.72 (5 H, m, H^C, H^D, H^1, H^2 and H^3), 6.54 (1 H, d, *J* 7.3, H^4), 6.52 (1 H, d, *J* 15.8, H$^{A'}$), 6.42 (1 H, d, *J* 15.3, H^A), 3.28 (1 H, s, ≡CH), 3.26 (1 H, s, ≡CH) and 2.77 (2 H, s, CH$_2$) (Found: C, 83.4; H, 5.4. C$_{19}$H$_{14}$O$_2$ requires C, 83.2; H, 5.15%).

Attempted Glaser coupling of the diketone **27** under the conditions reported for the preparation of compound **3** did not afford the corresponding [18]annulenedione.

Isomeric 1,6-*Bis*(5-*hydroxyhepta*-1,3-*dien*-6-*ynyl*)*cyclohepta*-1,3,5-*trienes* **19a** *and* **19b**.—(a) *Bisethynylation of a mixture of dialdehydes* **10a** *and* **10b**. To an ice-cooled solution of ethynyl-magnesium bromide in THF (500 cm^3), prepared from gaseous acetylene, magnesium (15 g) and bromoethane (79 g), was added dropwise during 30 min a solution of an isomeric mixture of the dialdehydes **10a** and **10b**^{4} (1.20 g, 475 mmol) in THF (100 cm^3), and the mixture was stirred for 2 h at room temperature before being worked up as for the isolation of compound **15**. The product was chromatographed on alumina (2.2 × 7.5 cm). The initial fractions eluted with 30–50% dichloromethane in benzene afforded the (E,Z),(E,Z)-*isomer* **19b** (326 mg, 25%) as orange needles, m.p. 111–113 °C (decomp.) (from hexane–dichloromethane); *m/z* 304 (M$^+$, 63%) and 165 (100) (C$_{21}$H$_{20}$O$_2$ requires M, 304.4); λ_{max}/nm 278 (76 400), 288 (91 300) and 385 (9000); ν_{max}/cm^{-1} 3300 (OH), 3270 (C≡CH), 2120 (C≡C), 1010 and 1000 [(*E*)-HC=CH] and 650 [(*Z*)-HC=CH]; δ_H 6.90 (2 H, dd, *J* 15.1 and 11.3, H^C), 6.63 (2 H, m, H^2), 6.47 (2 H, d, *J* 15.1, H^D), 6.34 (2 H, m, H^1), 6.25 (2 H, dd, *J* 11.3 and 10.0, H^B), 5.65 (2 H, dd, *J* 10.0 and 8.5, H^A), 5.44 (2 H, m, C*H*OH), 3.28 and 2.06 (2 H, AB-q, *J* 13.1, CH$_2$), 3.09 (2 H, d, *J* 5.3, OH) and 2.58 (2 H, d, *J* 2.2, ≡CH). The appearance of the methylene proton signal as an AB-quartet suggests that isomer **19b** consists solely of the *RS*-diastereo-isomer at the two asymmetric carbon atoms (Found: C, 82.6; H, 6.6. C$_{21}$H$_{20}$O$_2$ requires C, 82.9; H, 6.6%).

The later fractions, eluted with 20–40% acetone in benzene, afforded the (E,E),(E,Z)-*isomer* **19a** (297 mg, 21%) as yellow plates, m.p. 145–148 °C (decomp.) (from hexane–THF); *m/z* 304 (M$^+$, 100%) (C$_{21}$H$_{20}$O$_2$ requires M, 304.3); λ_{max}/nm 276 (71 100), 286 (90 900) and 383 (10 300); ν_{max}/cm^{-1} 3300 (OH), 3250 (C≡CH), 2100 (C≡C), 1000, 980 [(*E*)-HC=CH] and 660 [(*Z*)-HC=CH]; δ_H 6.87 (1 H, dd, *J* 15.2 and 11.5, H^C), 6.74 (1 H, dd, 15.2 and 10.7, H$^{C'}$), 6.65 (2 H, m, H^2 and H^3), 6.63 (1 H, dd, *J* 14.9 and 10.7, H$^{B'}$), 6.47 (1 H, d, *J* 15.2, H$^{D'}$), 6.45 (1 H, d, *J* 15.2, H^D), 6.33 (2 H, m, H^1 and H^4), 6.22 (1 H, t, *J* 11.5, H^B), 6.12 (1 H, dd, *J* 14.9 and 5.9, H$^{A'}$), 5.62 (1 H, dd, *J* 10.4 and 8.2, H^A), 5.34 (1 H, br s, C*H*^{a}OH), 5.03 (1 H, br s, CH^{b}OH), 2.87

and 2.40 (2 H, AB-q, J 13.0, CH_2), 2.62 (1 H, d, J 2.1, $\equiv CH^b$), 2.62 (1 H, d, J 2.2, $\equiv CH^a$), 2.40 (1 H, br d, J 4.9, OH^a) and 2.34 (1 H, br d, J 6.0, $\cdot OH^b$). Compound 19a consists of only one diastereoisomer at the two asymmetric carbon atoms (Found: C, 82.7; H, 6.7%).

(b) *Bisethynylation of dialdehyde* 10a. To an ice-cooled, stirred solution of ethynylmagnesium bromide in THF (600 cm³), prepared from gaseous acetylene, magnesium (15.0 g) and bromoethane (74.3 g), was added dropwise during 1.5 h a solution of the dialdehyde 10a[4] (1.16 g, 4.59 mmol) in THF (100 cm³) and the mixture was stirred for 1 h at room temperature before being worked up as for the isolation of compound 16. The product was chromatographed on silica gel (4.2 × 7.5 cm). The fractions eluted with 5–10% ethyl acetate in dichloromethane afforded the (*E,E*),(*E,Z*)-isomer 19a (556 mg, 40%).

Attempted Eglinton Coupling of Diol 19a.—A solution of the diol 19a (190 mg, 0.624 mmol) in a mixture of pyridine–ether (3:1; 480 cm³) was added dropwise during 6 h to a stirred solution of anhydrous copper(II) acetate (5.00 g) in a mixture of pyridine–ether (3:1; 240 cm³) at 50 °C, and the mixture was stirred for a further 30 min at the same temperature. Then the mixture was poured onto water and extracted with chloroform. The combined extracts were washed successively with 7% HCl until they turned acidic to litmus, and then with aq. sodium hydrogen carbonate, and were dried and concentrated. The residue was chromatographed on alumina (2.2 × 5.0 cm). However, the corresponding cyclic compound could not be obtained from any eluate.

Isomeric 1,6-*Bis*(5-*oxohepta*-1,3-*dien*-6-*ynyl*)*cyclohepta*-1,3, 5-*trienes* 28a *and* 28b.—(a) *Oxidation of diol* 19b. A mixture of the (*E,Z*),(*E,Z*)-diol 19b (1.00 g, 3.28 mmol) and $Ba(MnO_4)_2$ (20 g) in dichloromethane (200 cm³) was stirred for 5 h at room temperature before being worked up as for the isolation of compound 24. The product was chromatographed on silica gel (3.2 × 10.0 cm). The initial fractions, eluted with 40% dichloromethane in benzene, afforded the (E,Z),(E,E)-*isomer* 28a (75 mg, 7.6%) as dark red needles, m.p. 138–143 °C (decomp.) (from hexane–dichloromethane); m/z 300 (M^+ 55%) and 53 (100) ($C_{21}H_{16}O_2$ requires M, 300.3); λ_{max}/nm 244 (19 600), 290 (15 600), 349 (63 000) and 437 (10 400); ν_{max}/cm^{-1} 3250 and 3200 (C≡CH), 2080 and 2070 (C≡C), 1630 and 1620 (C=O), 990 [(*E*)-HC=CH] and 690 and 670 [(*Z*)-HC=CH]; δ_H 8.15 (1 H, dd, J 15.5 and 11.9, H^C), 7.56 (1 H, dd, J 15.2 and 11.1, H^B), 7.18 (1 H, dd, J 15.3 and 11.0, H^C), 6.81 (1 H, d, J 15.3, H^D), 6.74 (2 H, m, H^2 and H^3), 6.73 (1 H, d, J 15.5, $H^{D'}$), 6.68 (1 H, d, J 15.1, H^A), 6.67 (1 H, dd, J 11.9 and 10.8, $H^{B'}$), 6.51 (2 H, m, H^1 and H^4), 6.21 (1 H, d, J 10.8, $H^{A'}$), 3.214 (1 H, s, ≡CH), 3.210 (1 H, s, ≡CH) and 2.79 (2 H, s, CH_2) (Found: C, 83.8; H, 5.3. $C_{21}H_{16}O_2$ requires C, 84.0; H, 5.4%).

The later fractions, eluted with benzene–dichloromethane (1:1), afforded the (E,E),(E,E)-*isomer* 28b (389 mg, 40%) as orange needles, m.p. 161–165 °C (decomp.) (from hexane–dichloromethane); m/z 300 (M^+, 63%) and 53 (100) ($C_{21}H_{16}O_2$ requires M, 300.3); λ_{max}/nm 240 (17 700), 284sh (17 300), 341 (72 100) and 432 (15 900); ν_{max}/cm^{-1} 3200 (C≡CH), 2090 (C≡C), 1620 (C=O), 990 [(*E*)-HC=CH] and 690 [(*Z*)-HC=CH]; δ_H 7.57 (2 H, dd, J 15.3 and 10.9, H^B), 6.84 (2 H, d, J 15.2, H^D), 6.74 (2 H, m, H^2), 6.71 (2 H, dd, J 15.2 and 11.0, H^C), 6.53 (2 H, m, H^1), 6.36 (2 H, d, J 15.3, H^A), 3.26 (2 H, s, ≡CH) and 2.78 (2 H, s, CH_2) (Found: C, 83.7; H, 5.5%).

(b) *Oxidation of Diol* 19a. A mixture of the diol 19a (0.50 g) and $Ba(MnO_4)_2$ (10.0 g) in dichloromethane (250 cm³) was stirred for 5.5 h at room temperature and then was worked up as for the isolation of compound 24. The product was chromatographed on silica gel (4.2 × 6.0 cm). The fractions

eluted with 30% dichloromethane in benzene afforded the (*E,Z*),(*E,E*)-diketone 28a (420 mg, 85%).

12,15-*Dichloro*-13,14-*didehydro*-1,6-*methano*[20]*annulene*-11,16-*dione* 4.—A solution of the diketone 28a (125 mg, 0.416 mmol) in ethanol–benzene (3:1; 50 cm³) was added dropwise to a stirred solution of copper(I) chloride (27.5 g), ammonium chloride (44 g), water (122 cm³) and conc. HCl (0.3 cm³) at 60–65 °C. After the mixture had been stirred for 10 min, a further quantity of benzene–ethanol (1:1; 76 cm³) was added, and the mixture was stirred for a further 1.5 h at 60 °C while being bubbled with oxygen. Then the mixture was worked up as for the isolation of compound 3. The product was chromatographed on silica gel (3.2 × 10 cm). The fractions eluted with 10% dichloromethane in benzene afforded the *didehydro*-[20]*annuledione* 4 (15 mg, 9.8%) as black-purple needles, m.p. 156–161 °C (decomp.) (from hexane–THF); m/z 370 (M^+ + 1, 42%), 368 (M^+ − 1, 68) and 115 (100) ($C_{21}H_{14}Cl_2O_2$ requires M, 368.3); for UV data see Table 3, Figs. 6 and 7; ν_{max}/cm^{-1} 2040 (–C≡C=C=C–), 1655 (C=O) and 1010 and 990 [(*E*)-HC=CH]; for ¹H NMR data see Table 1, Figs. 2, 3 and 5; for ¹³C NMR data see Table 2 (Found: C, 68.6; H, 4.1. $C_{21}H_{14}Cl_2O_2$ requires C, 68.5; H, 3.8%).

Attempted Eglinton coupling of the diketone 28a as for the diol 19a did not afford the corresponding [20]annulenedione 2 ($m = n = 1$). Also, attempted Glaser coupling of the diketone 28b as for the diketone 28a did not afford the corresponding [20]annulenedione 4.

1-(5-*Hydroxyhepta*-1,3-*dien*-6-*ynyl*)-6-(7-*hydroxynona*-1,3,5-*trien*-8-*ynyl*)*cyclohepta*-1,3,5-*triene* 20.—To an ice-cooled solution of ethynylmagnesium bromide in THF (620 cm³), prepared from gaseous acetylene, magnesium (8.70 g) and bromoethane (43.0 g), was added dropwise during 40 min a solution of the dialdehyde 11[4] (700 mg, 2.52 mmol) in THF (200 cm³) and the mixture was stirred for 30 min at room temperature before being worked up as for the isolation of compound 16. The product was chromatographed on silica gel (4.2 × 5.0 cm). The fractions eluted with benzene–dichloromethane (3:7) afforded the *diol* 20 (532 mg, 64%) as orange needles, m.p. 113–121 °C (decomp.) (from hexane–dichloromethane); m/z 330 (M^+, 39%) and 165 (100) ($C_{23}H_{22}O_2$ requires M, 330.4); λ_{max}/nm 253sh (13 600), 294 (76 300), 305 (89 200) and 400 (12 500); ν_{max}/cm^{-1} 3300 (OH), 3250 (C≡CH), 2100 (C≡C) and 990 [(*E*)-HC=CH]. Although compound 20 is a ~1:1 mixture of two diastereoisomers, the chemical-shift difference between the isomers is observed only in the methylene protons: δ_H 6.66–6.33 (10 H, m), 6.31 (2 H, m, H^1 and H^4), 5.92 (1 H, dd, J 14.4 and 6.1, H^A or $H^{A'}$), 5.87 (1 H, dd, J 15.1 and 6.1, $H^{A'}$ or H^A), 4.99 (1 H, m, C*H*OH), 4.97 (1 H, m, C*H*OH), 2.69 and 2.66 (AB-q, J 13.1, CH_2 of one isomer), 2.67 (s, CH_2 of other isomer), 2.63 (1 H, d, J 2.2, ≡CH), 2.61 (1 H, d, J 2.2, ≡CH), 1.93 (1 H, d, J 6.4, OH) and 1.90 (1 H, d, J 6.5, OH); δ_C 136.0 (t), 135.2 (t), 135.1 (t), 132.8 (t), 132.5 (t), 131.84 (t), 131.77 (q), 131.21 (t), 131.19 (q), 131.0 (t), 130.7 (t), 130.4 (t), 128.7 (t), 128.5 (t), 128.3 (t), 127.1 (t), 82.66 (q, –C≡), 82.63 (q, –C≡), 74.56 (t, ≡CH), 74.48 (t, ≡CH), 62.49 (t, CHOH), 62.48 (t, CHOH) and 27.2 (s, CH_2) (Found: C, 83.3; H, 6.8. $C_{23}H_{22}O_2$ requires C, 83.6; H, 6.7%).

1-(5-*Oxohepta*-1,3-*dien*-6-*ynyl*)-6-(7-*oxonona*-1,3,5-*trien*-8-*ynyl*)*cyclohepta*-1,3,5-*triene* 29.—A mixture of the diol 20 (400 mg) and $Ba(MnO_4)_2$ (6.0 g) in dichloromethane (200 cm³) was stirred for 2.5 h at room temperature before being worked up as for the isolation of compound 24. The product was chromatographed on silica gel (4.2 × 4.0 cm). The fractions eluted with 30% dichloromethane in benzene afforded the *diketone* 29 (225 mg, 57%) as red needles, m.p. 128–132 °C

(decomp.) (from hexane–benzene); m/z 326 (M$^+$, 58%) and 165 (100) ($C_{23}H_{18}O_2$ requires M, 326.3); λ_{max}/nm 250 (12 700), 300sh (18 100), 360 (62 900) and 445 (17 700); ν_{max}/cm^{-1} 3250 (C≡CH), 3200 (C≡CH), 2090 (C≡C), 1625 (C=O) and 1005 [(E)-HC=CH]; δ_H 7.58 (1 H, dd, J 15.3 and 10.9, H$^{B'}$), 7.54 (1 H, dd, J 15.2 and 11.3, H^B), 6.85 (1 H, d, J 15.3, H$^{D'}$), 6.82 (1 H, dd, J 14.5 and 10.7, H^D), 6.75–6.67 (4 H, m, H^2, H^3, H$^{C'}$ and H^E), 6.61 (1 H, d, J 15.1, H^F), 6.55 (1 H, dd, J 14.5 and 11.3, H^C), 6.52 (1 H, br d, J 5.6, H^1 or H^4), 6.46 (1 H, br d, J 6.1, H^1 or H^4), 6.37 (1 H, d, J 15.3, H$^{A'}$), 6.33 (1 H, d, J 15.3, H^A), 3.26 (1 H, s, ≡CH), 3.25 (1 H, s, ≡CH) and 2.77 (2 H, s, CH$_2$) (Found: C, 84.6; H, 5.7. $C_{23}H_{18}O_2$ requires C, 84.6; H, 5.6%).

Attempted Hay Coupling of Diketone 29.[14]—A solution of the diketone 29 (400 mg, 1.23 mmol) in acetone (30 cm^3) was added dropwise during 4 h to a stirred solution of copper(I) chloride (180 mg, 1.85 mmol) and 1,4-diaminobutane (0.28 cm^3, 1.85 mmol) in acetone (150 cm^3) at 40 °C. The mixture was stirred for 3 h at 40 °C while being bubbled with oxygen. The product was worked up as for the isolation of compound 3 except for the use of dichloromethane as the extraction solvent. The product was chromatographed on silica gel. However, no desired [22]annulenedione was detected.

Also, attempted Glaser coupling of the diketone 29 as for the preparation of compound 3 did not afford the corresponding [22]annulenedione.

1,6-Bis(7-hydroxynona-1,3,5-trien-8-ynyl)cyclohepta-1,3,5-triene 21.—To an ice-cooled solution of ethynylmagnesium bromide in THF (600 cm^3), prepared from gaseous acetylene, magnesium (15.0 g) and bromoethane (74.3 g), was added dropwise during 2 h a solution of the dialdehyde 12[4] (1.00 g, 3.28 mmol) in THF (200 cm^3) and the mixture was stirred for 30 min at room temperature before being worked up as for the isolation of compound 15. The product was chromatographed on silica gel (4.2 × 6.0 cm). The fractions eluted with dichloromethane afforded the *diol* 21 (531 mg, 45%) as orange needles, m.p. 138–146 °C (decomp.) (from hexane–dichloromethane); m/z 356 (M$^+$, 100%) ($C_{25}H_{24}O_2$ requires M, 356.4); λ_{max}/nm 294sh (50 700), 306 (98 400), 318 (110 200) and 418 (13 000); ν_{max}/cm^{-1} 3300 (OH), 3270 (C≡CH), 2100 (C≡C) and 990 [(E)-HC=CH]; δ_H 6.63 (2 H, dd, J 15.2 and 9.7, H^E), 6.59 (2 H, m, H^2), 6.52 (2 H, ddd, J 15.1, 10.1 and 1.1, H^B), 6.418 (2 H, d, J 15.3, H^F), 6.416 (2 H, dd, J 14.8 and 9.7, H^D), 6.36 (2 H, dd, J 14.8 and 9.8, H^C), 6.31 (2 H, m, H^1), 5.87 (2 H, dd, J 15.0 and 6.1, H^A), 4.97 (2 H, br t, J 6.2, C*H*OH), 2.68 (2 H, s, CH$_2$), 2.61 (2 H, d, J 2.2, ≡CH) and 1.97 (2 H, d, J 6.4, OH); δ_C 135.3 (t), 135.2 (t), 132.6 (t), 131.8 (t), 131.6 (q), 130.9 (t), 130.5 (t), 128.6 (t), 128.4 (t), 82.7 (q, –C≡), 74.5 (t, ≡CH), 62.5 (t, CHOH) and 27.3 (s, CH$_2$) (Found: C, 83.9; H, 6.85. $C_{25}H_{24}O_2$ requires C, 84.2; H, 6.8%).

1,6-Bis(7-oxonona-1,3,5-trien-8-ynyl)cyclohepta-1,3,5-triene 30.—A mixture of the diol 21 (0.30 g) and Ba(MnO$_4$)$_2$ (5.0 g) in dichloromethane–THF (9:1; 200 cm^3) was stirred for 6 h at room temperature before being worked up as for the isolation of compound 24. The product was chromatographed on silica gel (4.2 × 5.0 cm). The fractions eluted with 10% dichloromethane in benzene afforded the *diketone* 30 (202 mg, 68%) as purple needles, m.p. 138–142 °C (decomp.) (from hexane–dichloromethane); m/z 352 (M$^+$, 100%) ($C_{25}H_{20}O_2$ requires M, 352.4); λ_{max}/nm 250 (30 800), 373 (94 300) and 463 (21 600); ν_{max}/cm^{-1} 3170 (C≡CH), 2080 (C≡C), 1610 (C=O) and 1000 [(E)-HC=CH]; δ_H 7.55 (2 H, dd, J 15.3 and 11.3, H^B), 6.83 (2 H, dd, J 14.6 and 10.4, H^D), 6.69 (2 H, dd, J 14.4 and 9.6, H^E), 6.68 (2 H, m, H^2), 6.62 (2 H, d, J 15.1, H^F), 6.54 (2 H, dd, J 14.6 and 11.3, H^C), 6.45 (2 H, m, H^1), 6.31 (2 H, d, J 15.3, H^A), 3.25 (2 H, s, ≡CH) and 2.76 (2 H, s, CH$_2$); δ_C 177.0 (q, C=O), 148.6 (q), 143.7 (t), 139.7 (t),

131.6 (t), 131.5 (t), 130.8 (t), 130.8 (t), 130.6 (t), 127.9 (t), 80.3 (q, –C≡), 78.8 (t, ≡CH) and 27.2 (s, CH$_2$) (Found: C, 85.2; H, 5.6. $C_{25}H_{20}O_2$ requires C, 85.2; H, 5.7%).

14,17-Dichloro-15,16-didehydro-1,6-methano[24]annulene-13,18-dione 5.—A solution of the diketone 30 (283 mg, 0.803 mmol) in ethanol–benzene (3:1; 416 cm^3) was added dropwise during 30 min to a stirred solution of copper(I) chloride (47 g), ammonium chloride (75 g), water (208 cm^3) and conc. HCl (0.85 cm^3) at 60–65 °C. After the mixture had been stirred for 10 min, a further quantity of benzene–ethanol (1:1; 129 cm^3) was added and the mixture was stirred for a further 2 h at 60 °C while being bubbled with oxygen. Then the mixture was worked up as for the isolation of compound 3 except for the use of dichloromethane as the extraction solvent. The product was chromatographed on silica gel (4.2 × 6 cm). The fractions eluted with 30% dichloromethane in benzene afforded the *didehydro-[24]annulenedione* 5 (34 mg, 10%) as dark green needles, m.p. 232–236 °C (decomp.) (from hexane–dichloromethane); m/z 422 (M$^+$ + 1, 0.6%), 420 (M$^+$ − 1, 0.6%) and 84 (100) ($C_{25}H_{18}Cl_2O_2$ requires M, 421.3); for UV data see Table 3, Figs. 6 and 7; ν_{max}/cm^{-1} 2040 (–C=C=C=C–), 1640 (C=O) and 1000 and 950 [(E)-HC=CH]; for ^{1}H NMR data see Table 1, Figs. 2–4; for ^{13}C NMR data see Table 2 (Found: C, 71.05; H, 4.4. $C_{25}H_{18}Cl_2O_2$ requires C, 71.3; H, 4.3%).

1-(7-Hydroxynona-1,3,5-trien-8-ynyl)-6-(9-hydroxyundeca-1,3,5,7-tetraen-10-ynyl)cyclohepta-1,3,5-triene 22.—To an ice-cooled solution of ethynylmagnesium bromide in THF (600 cm^3), prepared from gaseous acetylene, magnesium (20.0 g) and bromoethane (98.3 g), was added dropwise during 2.5 h a solution of the dialdehyde 13[4] (1.10 g, 3.33 mmol) in THF (350 cm^3) and the mixture was stirred for 30 min at room temperature before being worked up as for the isolation of compound 15. The product was chromatographed on silica gel (4.2 × 6.0 cm). The fractions eluted with 5% ethyl acetate in dichloromethane afforded the *diol* 22 (641 mg, 50%) as orange microcrystals, m.p. 102–112 °C (decomp.) (from hexane–dichloromethane); m/z 382 (M$^+$, 61%) and 91 (100) ($C_{27}H_{26}O_2$ requires M, 382.4); λ_{max}/nm 310sh (50 200), 322 (71 000), 336 (78 900) and 421sh (14 000); ν_{max}/cm^{-1} 3350 (OH), 3270 (C≡CH), 2100 (C≡C) and 990 [(E)-HC=CH]; δ_H 6.70–6.30 (16 H, m), 5.86 (1 H, dd, J 15.1 and 6.2, H^A or H$^{A'}$), 5.84 (1 H, dd, J 15.1 and 6.2, H$^{A'}$ or H^A), 4.97 (2 H, m, C*H*OH), 2.69 (2 H, s, CH$_2$), 2.62 (1 H, d, J 2.2, ≡CH), 2.61 (1 H, d, J 2.2, ≡CH), 1.90 (1 H, d, J 6.7, OH) and 1.89 (1 H, d, J 6.7, OH) (Found: C, 84.5; H, 6.8. $C_{27}H_{26}O_2$ requires C, 84.8; H, 6.85%).

1-(7-Oxonona-1,3,5-trien-8-ynyl)-6-(9-oxoundeca-1,3,5,7-tetraen-10-ynyl)cyclohepta-1,3,5-triene 31.—A mixture of the diol 22 (200 mg, 0.52 mmol) and Ba(MnO$_4$)$_2$ (10.0 g) in dichloromethane (400 cm^3) was stirred for 6.5 h at room temperature before being worked up as for the isolation of compound 24. The product was chromatographed on silica gel (4.2 × 5.0 cm). The fractions eluted with 20% dichloromethane in benzene afforded the *diketone* 31 (97 mg, 49%) as dark red needles, m.p. 131–138 °C (decomp.) (from hexane–dichloromethane); m/z 379 (M$^+$ + 1) (FAB method) ($C_{27}H_{22}O_2$ requires M, 378.4); λ_{max}/nm 276 (14 400), 385 (86 200) and 468 (22 700); ν_{max}/cm^{-1} 3200 (C≡CH), 2100 (C≡C), 1620 (C=O) and 1010 [(E)-HC=CH]; δ_H 7.55 (1 H, dd, J 15.2 and 11.3, H^B or H$^{B'}$), 7.54 (1 H, dd, J 15.2 and 11.3, H$^{B'}$ or H^B), 6.84 (1 H, dd, J 14.7 and 10.3, H^D or H$^{D'}$), 6.80 (1 H, dd, J 14.6 and 11.1, H$^{D'}$ or H^D), 6.72–6.46 (10 H, m), 6.44 (1 H, br d, J 5.7, H^1 or H^4), 6.41 (1 H, br d, J 5.9, H^4 or H^1), 6.30 (1 H, d, J 15.3, H^A or H$^{A'}$), 6.28 (1 H, d, J 15.3, H$^{A'}$ or H^A), 3.25 (1 H, s, ≡CH), 3.24 (1 H, s, ≡CH) and 2.75 (2 H, s, CH$_2$) (Found: C, 85.4; H, 6.05. $C_{27}H_{22}O_2$ requires C, 85.7; H, 5.9%).

Table 4 Experimental details of X-ray crystal analysis of compound 3

(a) Crystal data

Empirical formula	$C_{17}H_{10}Cl_2O_2$
Relative formula mass	317.17
Crystal colour, Habit	brown, prismatic
Crystal dimensions (mm)	0.25 × 0.25 × 0.25
Crystal system	orthorhombic
No. of reflections used for unit-cell determination (2θ-range)	25(18–25°)
Omega scan peak-width at half-height	0.43
Lattice parameters:	$a = 7.430(6)$ Å
	$b = 16.970(5)$ Å
	$c = 10.946(2)$ Å
	$V = 1380(2)$ Å³
Space group	$Pna2_1$ (No. 33)
Z-value	4
D_{calc}	1.526 g cm⁻³
F_{000}	648
μ(Mo-Kα)	4.69 cm⁻¹

(b) Intensity measurements

Diffractomer	Rigaku AFC-5R
Radiation	Mo-Kα ($\lambda = 0.710\,69$ Å)
Temperature	23 °C
Attenuators	Ni foil (factors: 3.6, 12.7, 45.1)
Take-off angle	6.0°
Detector aperture	6.0 mm × 6.0 mm
Crystal-to-detector distance	25.8 cm
Scan type	2θ–ω
Scan rate	8.0°/min (in omega) (2 rescans)
Scan width	$(1.31 + 0.30 \tan θ)°$
$2θ_{max}$	55.1°
No. of reflections measured	Total 1868
Correction	Lorentz-polarization effect Absorption (trans. factors: 0.80–1.09)

(c) Structure solution and refinement

Structure solution	Patterson method
Refinement	Full-matrix least-squares
Function minimized	$\Sigma\omega(|F_o| - |F_c|)^2$
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p-factor	0.01
Anomalous dispersion	All non-hydrogen
No. of observations [$F_o > 3.0\sigma(F_o)$]	1044
No. of variables	189
Reflection/Parameter ratio	5.52
Residuals: R; R_ω	0.034; 0.026
Goodness-of-fit indicator (GOF)	1.54
Max. shift/error in final diff. map	0.20
Maximum peak in final diff. map	0.20 e Å⁻³
Minimum peak in final diff. map	−0.20 e Å⁻³

Attempted Glaser coupling of the diketone **31** as for the preparation of compound **3** did not afford the corresponding [26]annulenedione.

1,6-*Bis*(9-*hydroxyundeca*-1,3,5,7-*tetraen*-10-*ynyl*)*cyclohepta*-1,3,5-*triene* **23**.—To an ice-cooled solution of ethynylmagnesium bromide in THF (600 cm³), prepared from gaseous acetylene, magnesium (13.9 g) and bromoethane (68.3 g), was added dropwise during 1 h a solution of the dialdehyde **14**⁴ (1.50 g, 4.2 mmol) in THF (100 cm³) and the mixture was stirred for 1 h at room temperature before being worked up as for the isolation of compound **15**. The product was chromatographed on silica gel (4.2 × 4.0 cm). The fractions eluted with 90–100% dichloromethane in benzene afforded the *diol* **23** (625 mg, 36%) as brown needles, m.p. 162–168 °C (decomp.) (from hexane–dichloromethane); m/z 408 (M⁺, 67%) and 78 (100) ($C_{29}H_{28}O_2$ requires M, 408.5); λ_{max}/nm 247 (7100), 318sh (53 000), 331 (93 800), 346 (100 900) and 438 (13 400); ν_{max}/cm⁻¹ 3300 (OH), 3250 (C≡CH), 2100 (C≡C) and 980 [(E)-HC=CH]; δ_H 6.63 (2 H, m), 6.58 (2 H, m, H²), 6.51 (2 H, dd, J 14.9 and 10.4, Hᴮ), 6.43–6.31 (12 H, m), 5.84 (2 H, dd, J 15.2 and 6.0, Hᴬ), 4.97 (2 H, brt, J 5.5, CHOH), 2.69 (2 H, s, CH₂), 2.61 (2 H, d, J 2.1, ≡CH) and 1.90 (2 H, dd, J 6.4 and 0.9, OH) (Found: C, 85.1; H, 6.8. $C_{29}H_{28}O_2$ requires C, 85.3; H, 6.9%).

1,6-*Bis*(9-*oxoundeca*-1,3,5,7-*tetraen*-10-*ynyl*)*cyclohepta*-1,3,5-*triene* **32**.—A mixture of the diol **23** (600 mg, 1.47 mmol) and Ba(MnO₄)₂ (5.0 g) in dichloromethane (200 cm³) was stirred for 5 h at room temperature before being worked up as for the isolation of compound **24**. The product was chromatographed on silica gel (2.8 × 5.0 cm). The fractions eluted with dichloromethane afforded the *diketone* **32** (308 mg, 52%) as dark purple needles, m.p. 75–77 °C (decomp.) (from hexane–dichloromethane); m/z 405 (M⁺ + 1) (FAB method) ($C_{29}H_{24}O_2$ requires M, 404.4); λ_{max}/nm 278 (14 100), 396 (65 200) and 480sh (17 600); ν_{max}/cm⁻¹ 3200 (C≡CH), 2090 (C≡C), 1620 (C=O) and 1000 [(E)-HC=CH]; δ_H 7.54 (2 H, dd, J 15.3 and 11.4, Hᴮ), 6.80 (2 H, dd, J 14.4 and 11.3, Hᴰ), 6.68 (2 H, dd, J 14.8 and 10.7, Hᴳ), 6.63 (2 H, m, H²), 6.61 (2 H, dd, J 14.4 and 10.7, Hᶠ), 6.54 (2 H, d, J 14.9, Hᴴ), 6.48 (4 H, dd, J 14.4 and 11.3, Hᶜ and Hᴱ), 6.40 (2 H, m, H¹), 6.27 (2 H, d, J 15.2, Hᴬ), 3.24 (2 H, s, ≡CH) and 2.74 (2 H, s, CH₂) (Found: C, 86.3; H, 6.0. $C_{29}H_{24}O_2$ requires C, 86.1; H, 6.0%).

Attempted Glaser coupling of the diketone **32** under the conditions reported for the preparation of compound **3** did not afford the corresponding [28]annulenedione, but the diketone **32** was recovered unchanged.

X-Ray Structure Determination for Compound **3**.—An orange prismatic crystal of compound **3** grown from dichloromethane was mounted in a Lindemann capillary tube under N₂. All measurements were made on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo-Kα radiation.

The cell constants and orientation matrix were obtained from least-squares refinement of the setting angles for 25 carefully centred reflections (2θ = 18.1–24.8°). Intensity data were collected by the 2θ–ω scan technique. Systematic absences (0 k l); h + l ≠ 2n, (h 0 l); h ≠ 2n for total data set and the successful solution and refinement of the structure indicated that space group was $Pna2_1$ (No. 33). The intensities of three standard reflections monitored after every 150 reflections showed 2.5% reduction during data collection. The data were corrected for the decay, Lorentz and polarization effects and absorption using the program DIFABS.²³ Full details of the crystal data and intensity measurements are compiled in Table 4.

The phase derived from the Cl atoms was located in Patterson maps. All remaining non-hydrogen atoms were found by the successive difference Fourier syntheses and least-squares refinements. All non-hydrogen atoms were refined aniso-tropically. All hydrogen atoms were included at calculated positions, but their parameters were not refined. The final cycle of full-matrix least-squares refinements converged with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.034$ and $R_\omega = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2]^{1/2} = 0.026$ for 1044 observed reflections [$I > 3.0\sigma(I)$] and 189 variable parameters. The details of structure solution and refinement are shown in Table 4.*

Neutral atom-scattering factors were taken from Cromer and Waber.²⁴ Anomalous dispersion effects were included in F_{calc}; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Waber.²⁵ All calculations were performed on a VAX station 3100 using the TEXSAN²⁶ crystallographic software package.

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