Synthesis and Properties of a New Methano-bridged Tetradehydro[22]annulenedione

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The title annulenedione **8** was synthesized starting from 1-acetyl-6-(3-oxobut-1-enyl)cyclohepta-1,3,5-triene **25** by aldol condensation with (Z)-3-methylpent-2-en-4-ynal **26** to afford the dione **27** and then by another aldol condensation of the dione **27** with the aldehyde **26**, followed by intramolecular oxidative coupling of the resulting acyclic diacetylene **28**. Examination of the ^{1}H NMR spectra indicated that compound **8** is paratropic in acidic media.

In our previous papers,[1-3] we reported syntheses of a series of methanol-bridged tetradehydroannulenes **1** and found that these compounds have high thermal and conformational stability, which is reasonably ascribed to considerable rigidity of the molecular skeleton imposed by the presence of a bridging methylene group and a 1,3-diacetylenic linkage. Their thermal stability enabled us to study the non-linear optical properties of these annulenes.[4]
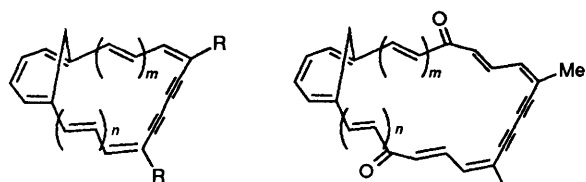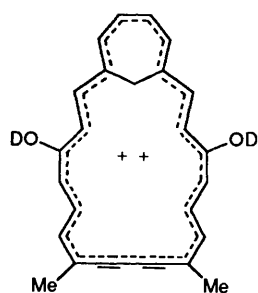

R = Me or Bu[t]
1 m = 1–6
n = 1–6

[20]- **2** m = n = 0
[24]- **3** m = n = 1
[26]- **4** m = 1, n = 2
[28]- **5** m = n = 2
[30]- **6** m = 2, n = 3
[32]- **7** m = n = 3
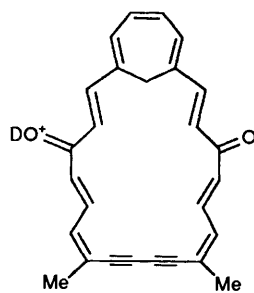
3A   **3B**

Also, we recently reported syntheses of a series of tetra-dehydromethanoannulenediones **2–7** in which the ring size was increased systematically up to 32, in order to examine their tropic properties in both neutral and acidic media.[5] We found that among them only the tetradehydromethano[24]annulene-dione **3** forms the diatropic monodeuteronated species **3A** in CF_3CO_2D and the highly diatropic dideuteronated species **3B** in D_2SO_4, although compound **3** is weakly diatropic in a neutral medium $(CDCl_3)$.[5b]

To enhance the non-linear optical properties, particularly in the appearance of the second-order hyperpolarizability, we

considered that the annulenediones **2–7** are more appropriate substances than the annulenes **1**, since the former have the two polarizable carbonyl groups as compared with the latter.[6] However, in these studies the 22-membered ring has so far not been studied,[5b] since the preparation of the tetradehy-dro[22]annulenedione **8** required a synthetic intermediate different from those used in the preparation of compounds **2–7**. In connection with our study on non-linear optical properties of the two-dimensional conjugated system,[7] we describe here the preparation and properties of the title compound **8**.
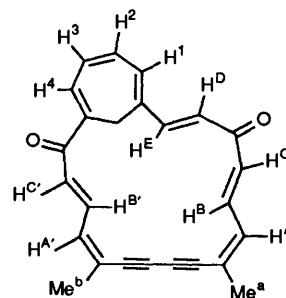

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Results and Discussion

Synthesis.—We have reported a simple general approach to the methano-bridged tetradehydroannulenediones **2–7**.[5b] The method employs aldol condensation of 1,6-diacetylcyclohepta-1,3,5-triene[8] or its vinylogous diones with (Z)-3-methylpent-2-en-4-ynal **26**,[9] followed by intramolecular oxidative coupling of the resulting acyclic diacetylenes.

We planned to apply this method to the synthesis of the title compound **8** by using the bis(methyl ketone) **25** as a key intermediate (see Scheme 3). Several attempts to prepare compound **25** were therefore made.

First, we considered that the dione **25** would be obtainable by reaction of the dicarboxylic acid **21** (Scheme 2; see later) with methyllithium. We thought that the dicarboxylic acid **21** could be prepared from 6-acetylcyclohepta-1,3,5-triene-1-car-baldehyde **14** by homologation of the formyl group, followed by oxidation of the resulting vinylogous aldehyde. Therefore we attempted direct introduction of an acetyl group into the 6-position of the aldehyde **11**,[10] the alcohol **9**[10] or its acetate **10**. The acetate **10** was obtained from the alcohol **9** in 45% yield. However, attempted Friedel–Crafts acetylation of

9 R = CH₂OH
10 R = CH₂OAc
11 R = CHO

12 R = CH₂OH
13 R = CH₂OAc
14 R = CHO
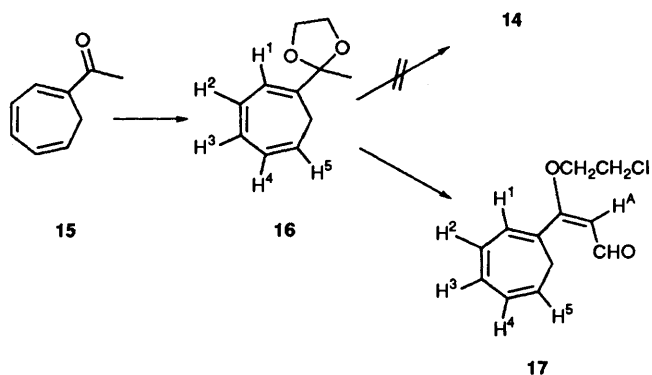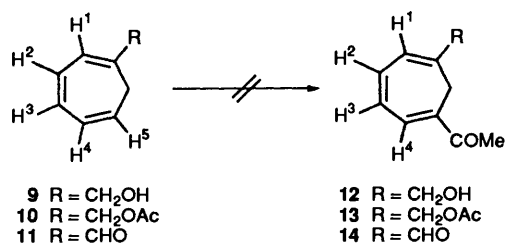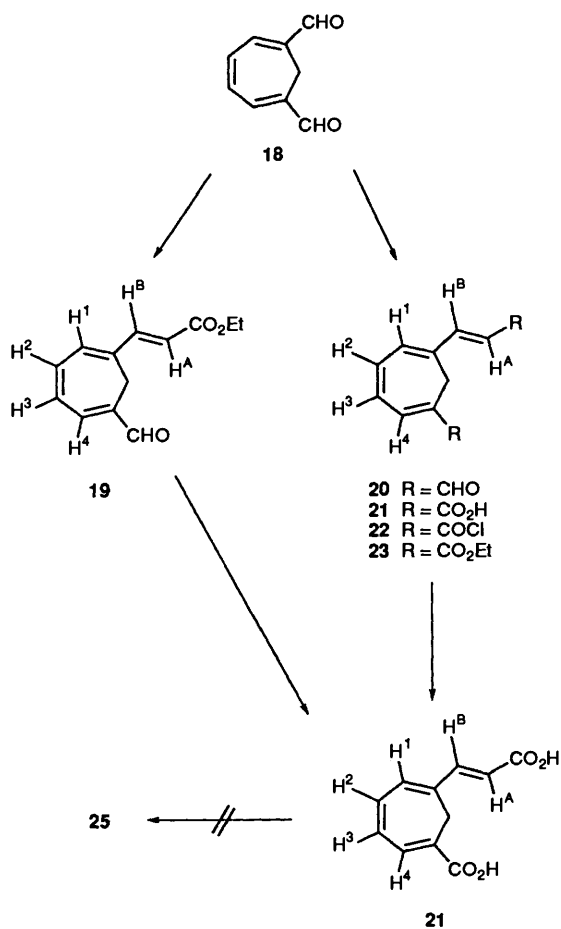
Scheme 1

Scheme 2

compounds **9–11** with acetyl chloride in the presence of aluminium chloride under the conditions used for the preparation of 1,6-diacetylcyclohepta-1,3,5-triene from 1-acetylcyclohepta-1,3,5-triene **15**,[8] did not afford the 6-acetyl derivatives **12–14** at all.

Then the ketone **15** was converted into its ketal **16** in 47%

yield by treatment with ethylene glycol (Scheme 1). Then Vilsmeier formylation of **16** was attempted in order to prepare aldehyde **14**, but the formylvinyl derivative **17** was formed in 44% yield instead of the desired aldehyde **14**. The formation of a formylvinyl group from an acetyl group under Vilsmeier conditions has been observed before in heteroaromatic compounds.[11]

Thus since attempts to introduce an acetyl group or a formyl group directly onto the cycloheptatriene ring were unsuccessful, we attempted the conversion of the substituents on the cycloheptatriene ring toward the dicarboxylic acid **21**. The dialdehyde **18**[8] was converted into the vinylogous ester **19** in 68% yield by Wittig condensation with ethoxycarbonylmethyl-enetriphenylphosphorane.[12] However, Jones oxidation[13] of compound **19** gave a low yield (26%) of the dicarboxylic acid **21**. Although attempted oxidation of the dialdehyde **20**, which was prepared from the dialdehyde **18** as reported,[14] with KMnO₄[15] was unsuccessful, Jones oxidation[13] of compound **20** afforded the crude dicarboxylic acid **21** in 60% yield. To obtain the pure dicarboxylic acid **21**, the crude material was converted into the diethyl ester **23** in 49% yield *via* the dicarboxylic acid dichloride **22**. However, several attempts to convert the dicarboxylic acid **21** into the dione **25** by reaction with methyllithium[16] under various conditions by changing temperature and solvent met without success.
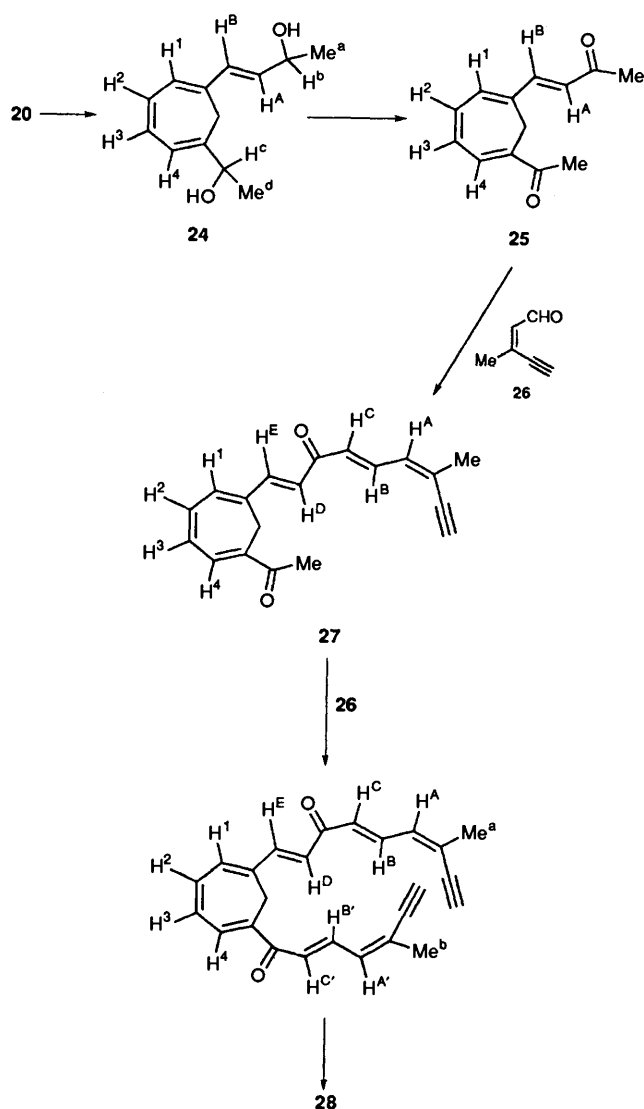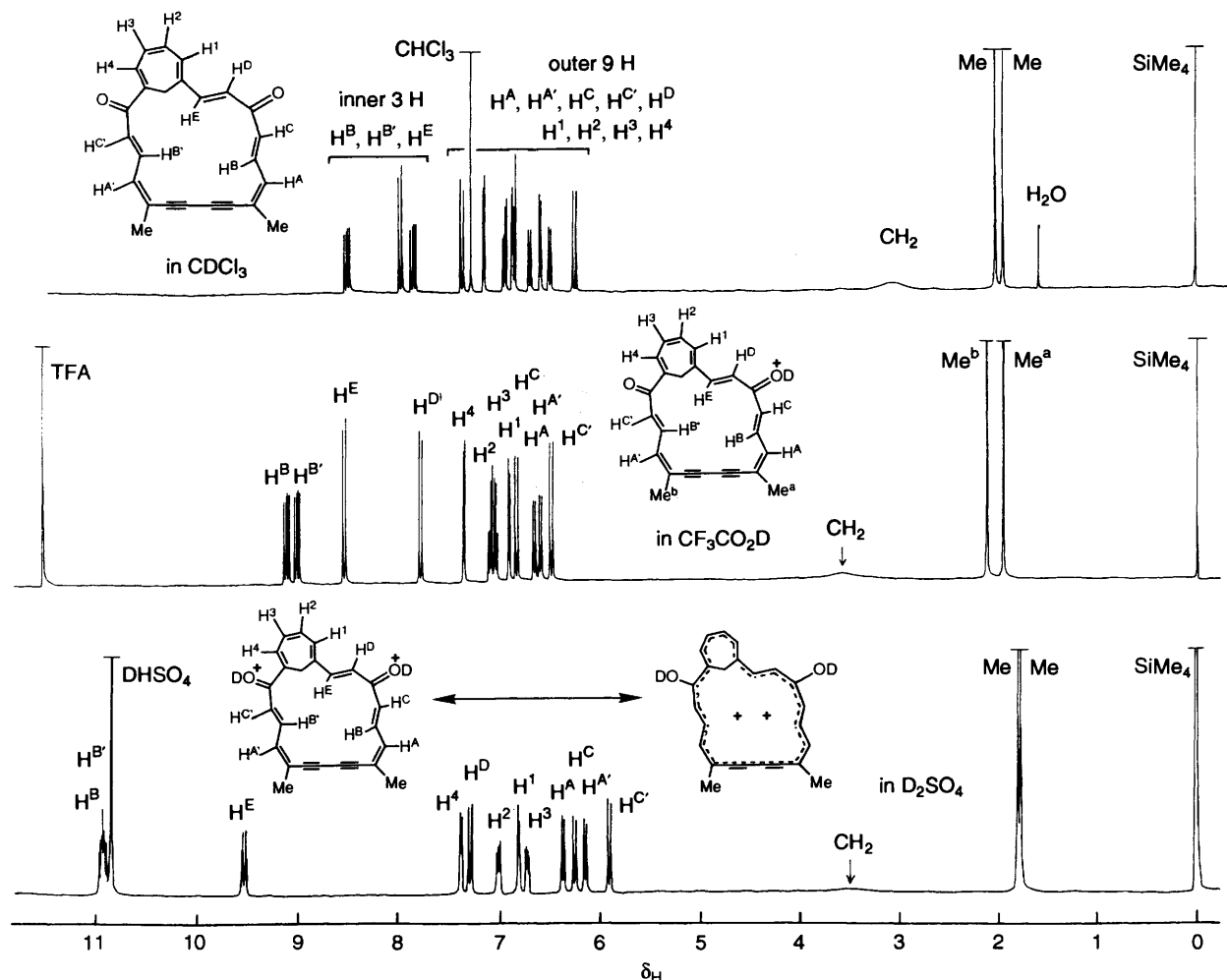

Scheme 3

Fig. 1   500 MHz ^{1}H NMR spectra of compound 8 at 26 °C. (a) In CDCl$_3$, (b) in CF$_3$CO$_2$D and (c) in D$_2$SO$_4$.

We finally succeeded in preparing the dione 25 as follows. Grignard reaction of the dialdehyde 20 with a large excess of methylmagnesium iodide gave the diol 24 as a diastereoisomeric mixture in 55% yield (Scheme 3). Oxidation of the isomeric diol 24 with Ba(MnO$_4$)$_2$[17] gave the dione 25 in 63% yield.

Aldol condensation of the dione 25 with the aldehyde 26[9] gave a single condensation product, the dione 27 in 4.4% yield. The structure of compound 27 was confirmed by NOE experiments; irradiation of the methyl protons of the remaining acetyl group enhanced the H^4 signal. Judging from the fact that the precursor diones of compounds 2–7 were prepared in high yield under the same conditions as for the preparation of dione 27, it is noted that the reactivity of the dione 25 for aldol condensation is quite low and only the less crowded acetyl group reacted selectively.

The second aldol condensation of the dione 27 with the aldehyde 26 afforded the dione 28 in 9% yield. The dione 28 proved to be very unstable towards diffused light and air, and satisfactory elemental analysis for compound 28 could not be obtained. Intramolecular oxidative coupling of compound 28 with anhydrous copper(II) acetate in pyridine–diethyl ether afforded the desired methano[22]annulenedione 8 in 24% yield. Compound 8 formed thermally relatively stable orange crystals.

Solutions of compound 8 in CDCl$_3$ and CF$_3$CO$_2$D were very stable and no spectral change was detected even after the solutions had been kept for one month at −20 °C, but the solution in D$_2$SO$_4$ was rather unstable and about one-third of compound 8 had decomposed in 3 days at −20 °C.

^{1}H NMR Spectral Studies.—The ^{1}H NMR spectra of compound 8 taken in CDCl$_3$, CF$_3$CO$_2$D and D$_2$SO$_4$ at 26 °C are shown in Fig. 1. Decoupling experiments in CDCl$_3$ clearly revealed two series of proton sequences, Me^a–H^A–H^B–H^C and Me^b–H$^{A'}$–H$^{B'}$–H$^{C'}$, although the chemical-shift assignments are interchangeable between the two series. Irradiation of the Me^a, Me^b and H^D signals enhanced the intensity of the H^A, H$^{A'}$ and H^1 signals, respectively, indicating that H^A, H$^{A'}$ and H^D were located outside the macrocyclic ring. These data afforded the geometry given by the structural formula 8 and the chemical-shift assignments given in Table 1. The spectrum in CF$_3$CO$_2$D was similarly analysed although the chemical-shift assignments for the two sequences given in Table 1 are again interchangeable. In D$_2$SO$_4$, two series of the three-olefin-proton sequences were clearly analysed but no definite assignments of the methyl signals were made.

Since the tetradehydromethano[24]annulenedione 3 showed weak diatropicity in neutral media as a 22π-electron system arising from polarization of two carbonyl groups, the tetra-dehydromethano[22]annulenedione 8 was also expected to show paratropicity as a 20π-electron system due to polarization. As can be seen from Table 1, the inner protons and the bridge methylene protons in compound 8 resonate at lower field than do the corresponding protons in the acyclic model compound 28. However, the outer protons do not resonate at higher field than do those of compound 28, although the methyl protons are at higher field. Compound 8 is therefore atropic in CDCl$_3$.

If both of the carbonyl groups of compound 8 are protonated

Table 1 ^{1}H NMR parameters of compounds **28** and **8** at 26 °C[a]

| | δ_H (J/Hz) Inner protons | | | | Outer protons | | | | | | | | | | |
Compound	H[B]	H[B']	H[E]	CH$_2$	H[A]	H[A']	H[C]	H[C']	H[D]	H[1]	H[2]	H[3]	H[4]	Me[a]	Me[b]
28[b]	7.72dd (15.0, 11.5)	7.85dd (15.5, 11.3)	7.37d[c] (15.4)	2.95s	6.46d (11.5)	6.49d (11.3)	6.85d (15.2)	6.48d (15.4)	7.35d[c] (15.4)	6.62d (6.2)	6.94dd (11.1, 6.2)	6.84dd (11.1, 6.1)	7.20d (6.1)	2.03s 2.05s	
8	8.48dd (15.1, 11.7)	7.82dd (16.0, 11.0)	7.94d (15.2)	3.06br s	6.68d (11.8)	6.47d (11.0)	6.84d (14.9)	6.23d (16.0)	7.35d (15.2)	6.57d (6.2)	6.93dd (11.1, 6.2)	6.84dd (11.1, 6.0)	7.13d (6.0)	1.94s	2.01s
8A[d]	9.12dd (15.3, 11.6)	9.01dd (15.1, 11.4)	8.53d (14.9)	3.61br s	6.65dd (11.6, 1.2)	6.59d (11.3)	6.83d (15.3)	6.48d (15.2)	7.77d (15.0)	6.91d (6.1)	7.10dd (11.2, 6.1)	7.04dd (11.1, 6.0)	7.35d (6.0)	1.95s	2.11s
8B[e]	10.93dd (15.2, 11.1)	10.91dd (14.6, 11.5)	9.53d (15.0)	3.50br s	6.35d (11.1)	6.13d (11.5)	6.23d (15.2)	5.85d (14.6)	7.28d (15.0)	6.79d (6.9)	7.00dd (11.2, 6.8)	6.71dd (11.4, 6.8)	7.37d (6.9)	1.56s 1.79s	

[a] Obtained at 500 MHz in CDCl$_3$ unless otherwise stated. [b] In addition, two singlets at δ 3.59 and 3.48 due to two acetylenic protons. [c] Mutually interchangeable. [d] In CF$_3$CO$_2$D. [e] In D$_2$SO$_4$.

8A   8A′

8B   8B′

Fig. 2 Electronic absorption spectra of compound 8, (-----) in THF, (— - — - —) in TFA and (————) in H₂SO₄
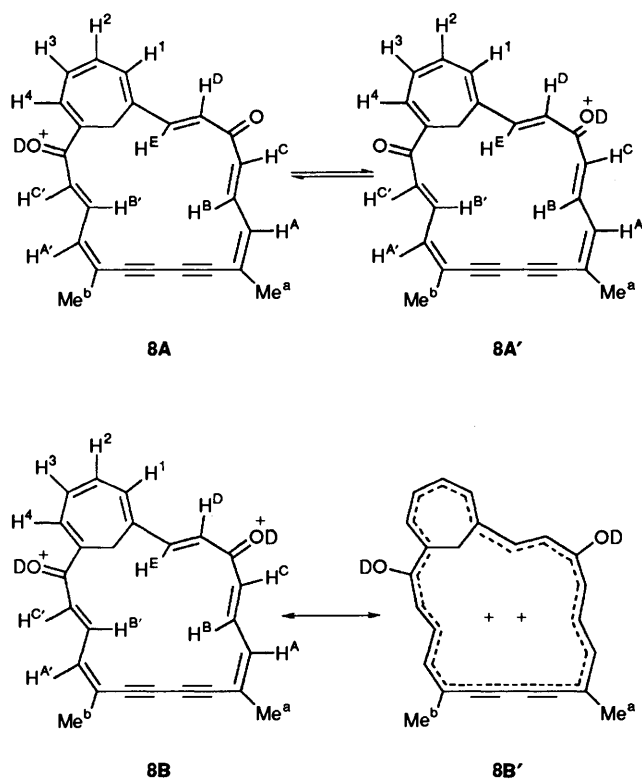
to form a dicationic species, compound 8 would be expected to show strong paratropicity. Therefore, ¹H NMR spectra of compound 8 were taken in acidic media and the data are also given in Table 1. In deuteriotrifluoroacetic acid (CF₃CO₂D), the olefinic protons show a downfield shift, by 0.07–1.19 ppm, from those in deuteriochloroform (CDCl₃) except for the Hᴬ and Hᶜ protons, which indicates that compound 8 exists probably as a rapidly equilibrating, monodeuteronated species (8A ⇌ 8A′) and that the contribution from a dication 8B is very low, if at all, as was found for compounds 2 and 4 in CF₃CO₂D.⁵ᵇ Upon changing the medium from CF₃CO₂D to D₂SO₄, the inner olefinic protons and the methylene protons move significantly downfield while the outer olefinic protons as well as the methyl protons shift upfield, indicating the formation of the highly paratropic dideuteronated species 8B where the delocalized 20π-electron structure 8B′ contributes to a great extent to the overall structure.

Another remarkable feature of the ¹H NMR spectra of dione 8 was that the methylene protons afforded a very broad signal at 26 °C in any of the solvents examined, indicating that flipping of the methano bridge was taking place on the NMR time-scale. The methylene signal decoalesced at −5 °C and appeared as an AB-quartet (δ 4.44 and 1.72 with J 12.5 Hz) at −65 °C in CDCl₃, while in CF₃CO₂D it decoalesced at 2 °C and appeared as two broad signals (δ 5.11 and 2.42) at −28 °C, the lowest temperature where the spectrum could be obtained without freezing of the sample. Measurements at low temperatures were abandoned in D₂SO₄ because of the instability of the sample and the high viscosity of the solution. The free energy of activation for the flipping of the methano bridge was calculated as 12.1 kcal mol⁻¹* at −5 °C in CDCl₃ and was roughly estimated as 12.4 kcal mol⁻¹* at 2 °C in CF₃CO₂D.

The lower homologue of dione 8, the methano[20]annulenedione 2, was found to have a higher barrier to flipping than compound 8 (ΔG‡ at 26 °C: 13.2, 14.5 and 16.8 kcal mol⁻¹
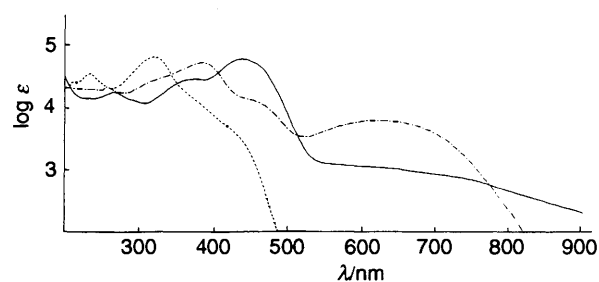
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* 1 cal = 4.184 J.

in CDCl₃, CF₃CO₂D and D₂SO₄, respectively), while all the higher homologues of compound 8 have lower barriers than compound 8.⁵ The results are reasonable because the flipping barrier should be related to the ring size in this series of compounds. The tendency for the barrier to increase with the acidity of the solvent, as observed in compound 2, is also found in the present compound though to a smaller degree.

Electronic Spectra of Compound 8.—The electronic absorption maxima of the annulenedione 8, determined in tetrahydrofuran (THF), CF₃CO₂H (TFA) and H₂SO₄, are listed in Table 2, together with those of the lower homologue (compound 2) and the symmetrical first higher one (compound 3), and the absorption spectra of compound 8 are illustrated in Fig. 2.

It is recognized that the electronic absorption spectra of annulenes[18] and of dehydroannulenes 1[1,2] have been shown to alternate, the main absorption maxima (the strongest maxima) of (4n + 2)π-electron systems being at higher wavelength than those of (4n)π-systems.[19] Table 2 shows that the difference of the main absorption maxima between the [24]annulenedione 3 (485 nm)⁵ᵇ and the [22]annulenedione 8 (436 nm) in H₂SO₄ is larger than that between the [22]annulenedione 8 and the [20]annulenedione 2 (416 nm),⁵ᵇ although this behaviour among compounds 2, 3 and 8 was not observed in THF. Thus, the main absorption maxima of the [4n]annulenediones 2 and 3 in which polarization of two carbonyl groups renders them (4n + 2)π-electron system, are of rather longer wavelength than that of the [4n + 2]annulenedione 8. Thus, it is evident that in these tetradehydromethanoannulenediones the same alternation occurs in the wavelengths of the main absorption maxima, reflecting that these annulenediones have an annulene character in H₂SO₄, as is revealed by their ¹H NMR spectra.

Also, it is evident from Table 2 and Fig. 2 that all the bands of compound 8 show a progressive large bathochromic shift on changing the solvent from THF to TFA and to H₂SO₄, and the end absorption in H₂SO₄ appears toward longer wavelength as compared with those in THF and TFA, reflecting the degree of extended conjugation of the π-electron system in the solvent, as is revealed by the ¹H NMR spectra (see above).

Experimental

M.p.s were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a Hitachi 260-50 or JASCO-7300 spectrophotometer with samples as KBr discs, unless otherwise specified, and were calibrated against polystyrene; only significant maxima are described. Electronic spectra were measured in THF solution, unless otherwise stated, with a Hitachi 220A or a Shimadzu 2200A spectrophotometer. Mass spectra 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-

Table 2 Electronic absorption maxima of compounds **2**, **3** and **8** [*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}) for compound **8** and relative extinction efficients for compounds **2** and **3**; *c*, in TFA, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})]. Strongest absorption indicated in bold type.

[20]-	2*a*	a	230 (27 000), **271 (39 100)**, 320 (18 300), 407sh (5700)
		b	308 (0.75), **416 (1.00)**, 535 (0.33)
[22]-	8	a	212 (25 800), 235 (35 000), **322 (64 200)**
		b	267 (17 600), 372 (28 400), **436 (60 400)**
		c	256 (20 000), 307sh (23 800), **383 (52 600)**, 468sh (10 900)
[24]-	3*a*	a	267sh (33 300), **283 (42 600)**, 355 (39 200)
		b	456sh (0.50), **485 (1.00)**, 614 (0.11)

a See ref. 5*b*.

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 to 2 kV). Samples for FAB-MS were prepared by dissolution of the compounds in a *m*-nitrobenzyl alcohol matrix. ^{1}H NMR spectra at ambient temperature were recorded for CDCl$_3$ solutions, unless otherwise specified, with a JEOL FX-90Q (90 MHz) or a Bruker AM-500 (500 MHz) spectrometer. Internal SiMe$_4$ was used as reference when the solvent was CDCl$_3$ or CF$_3$CO$_2$D, 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 for CDCl$_3$ solutions, unless otherwise indicated, on the AM-500 at 125.76 MHz with internal SiMe$_4$ as reference. The marks p, s, t and q denote the primary, secondary, tertiary and quaternary carbons respectively.

Ethanolic sodium ethoxide (2.17 mol dm^{-3}) was used for the aldol condensations of compounds **25** and **27** with the aldehyde **26**, and was prepared from sodium (1.50 g) and dry ethanol (25 cm^3) immediately before use. Progress of all reactions was followed by TLC on Merck precoated silica gel. Silica gel (Daiso gel 1001 W or Daiso gel 1002 W) was used for column chromatography. Compounds were preadsorbed from diethyl ether, benzene or dichloromethane solution onto the adsorbent before column chromatography. Dichloromethane used in reactions was distilled over calcium hydride before use. Dry *N,N*-dimethylformamide (DMF) was prepared by being stirred with calcium hydride overnight and then by distillation before use. Organic extracts were washed with saturated aq. sodium chloride and were dried over anhydrous sodium sulfate prior to removal of solvent. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

(*Cyclohepta*-1,3,5-*trienyl*)*methyl Acetate* **10**.—To a stirred solution of the alcohol **9**^{10} (4.80 g, 39.3 mmol) in dry dichloromethane (50 cm^3) was added dropwise a solution of acetyl chloride (9.30 g, 0.12 mol) in dry dichloromethane (40 cm^3) during 30 min at room temperature. After being stirred for 40 min at 36 °C, the mixture was poured onto water, extracted with dichloromethane, and the extract was dried. The residue obtained after removal of solvent was chromatographed on silica gel (4.2 × 11.0 cm). The fractions eluted with 30% benzene in hexane were collected and the residue obtained after removal of solvent was distilled to afford the *acetate* **10** (2.94 g, 45%) as a liquid, b.p. 79–80 °C/3 mmHg; *m/z* 104 (M$^+$ − CH$_3$CO$_2$, 100%) (C$_{10}$H$_{12}$O$_2$ requires M, 164.2); λ_{max}/nm 207 (ε/dm^3 mol^{-1} cm^{-1} 4680) and 260 (3400); ν_{max}(neat)/cm^{-1} 1730 (C=O); δ_H(90 MHz) 6.59–6.52 (2 H, m, H^2 and H^3), 6.26–6.14 (2 H, m, H^1 and H^4), 5.39 (1 H, dt, *J* 7, H^5), 4.68 (2 H, br s, CH$_2$O), 2.35 (2 H, d, *J* 7, CH$_2$) and 2.10 (3 H, s, Me) (Found: C, 73.1; H, 7.65. C$_{10}$H$_{12}$O$_2$ requires C, 73.1; H, 7.4%).

Attempted Friedel–Crafts Acetylation of Aldehyde **11**.—To a stirred suspension of finely divided, anhydrous aluminium chloride (12.1 g, 90.7 mmol) in dry dichloromethane (46 cm^3)

was added dropwise acetyl chloride (7.10 g, 90.4 mmol) during 30 min at room temperature and the mixture was then heated under reflux for 30 min. The aldehyde **11**^{10} (5.00 g, 41.6 mmol) was added dropwise during 1 h at room temperature. After being stirred for 3 h at room temperature, the mixture was cooled to −20 °C. After addition of acetic acid (4.2 cm^3) and then water (21 cm^3) at −5 °C, the mixture was poured onto ice–water and extracted with dichloromethane. The combined extracts were washed with aq. NaHCO$_3$ and dried. The residue obtained after removal of solvent was chromatographed on silica gel (4.2 × 7 cm). However, the desired compound **14** was not detected.

Attempted Friedel–Crafts acetylations of both the alcohol **9** and the acetate **10** under almost the same conditions as for the aldehyde **11** described above were also unsuccessful.

2-(*Cyclohepta*-1,3,5-*trienyl*)-2-*methyl*-1,3-*dioxolane* **16**.—A mixture of the ketone **15**^{8} (5.00 g, 0.037 mol), ethylene glycol (30 cm^3) and toluene-*p*-sulfonic acid monohydrate (70 mg) in dry benzene (50 cm^3) was refluxed for 2 h in a flask equipped with a Dean–Stark apparatus. Then the mixture was poured onto water and extracted with benzene. The combined extracts were washed with aq. NaHCO$_3$ and dried over potassium carbonate. The residue obtained after removal of solvent was chromatographed on silica gel (3.2 × 12.0 cm). The fractions eluted with hexane–benzene (4:1) were collected and the residue obtained after removal of solvent was distilled to afford the *acetal* **16** (3.10 g, 47%) as a yellow liquid, b.p. 68–70 °C/4 mmHg; *m/z* 178 (M$^+$, 29%) and 87 (100) (C$_{11}$H$_{14}$O$_2$ requires M, 178.2); λ_{max}/nm 213 (ε 5650) and 263 (3900); ν_{max}(neat)/cm^{-1} 1205 and 1045 (C–O–C); δ_H(90 MHz) 6.59–6.51 (2 H, m, H^2 and H^3), 6.32 (1 H, m, H^4), 6.15 (1 H, m, H^1), 5.44 (1 H, m, H^5), 3.97–3.76 (4 H, m, OCH$_2$CH$_2$O), 2.34 (2 H, d, *J* 7, CH$_2$) and 1.55 (3 H, s, Me) (Found: C, 73.9; H, 8.0%; C$_{11}$H$_{14}$O$_2$ requires C, 74.1; H, 7.9%).

3-(2-*Chloroethoxy*)-3-(*cyclohepta*-1,3,5-*trienyl*)*propenal* **17**.—To dry, stirred, ice-cooled DMF (6.0 cm^3) was added dropwise phosphorus trichloride oxide (2.0 cm^3, 0.022 mol) during 30 min. Then a solution of the acetal **16** (3.10 g, 0.017 mol) in dry DMF (15.0 cm^3) was added dropwise during 1 h below 10 °C and the mixture was stirred for 3 h at 70 °C. After the mixture was cooled, crushed ice and then 30% aq. sodium hydroxide (21 cm^3) were added. Then dichloromethane (25 cm^3) was added and the mixture was stirred for 1 h at room temperature. The mixture was poured onto water and extracted with dichloromethane. The combined extracts were washed with aq. NaHCO$_3$ and dried. The residue after removal of solvent was chromatographed on silica gel (3.2 × 13.0 cm). The fractions eluted with hexane–benzene (1:9) afforded the *aldehyde* **17** (1.70 g, 44%) as a yellow liquid; *m/z* 226 (M$^+$ + 2, 6%), 224 (M$^+$, 17%) and 222 (M$^+$ − 2, 100) (C$_{12}$H$_{13}$ClO$_2$ requires M, 224.6); λ_{max}/nm 214 (ε 15 000), 246 (9650) and 294 (8260); ν_{max}(neat)/cm^{-1} 1660 (C=O) and 1210 (C–O–C); δ_H(90

MHz) 9.32 (1 H, d, J 7, CHO), 6.91–6.22 (4 H, m, H^1, H^2, H^3 and H^4), 5.56 (1 H, d, J 7, H^A), 5.52 (1 H, m, H^5), 4.16 (2 H, t, J 5, OCH$_2$), 3.83 (2 H, t, J 5, CH$_2$Cl) and 2.59 (2 H, d, J 7, CH$_2$) (Found: C, 63.9; H, 5.85. $C_{12}H_{13}ClO_2$ requires C, 64.15; H, 5.8%).

Ethyl 3-(6-Formylcyclohepta-1,3,5-trienyl)propenoate **19.**—To a stirred solution of the dialdehyde **18**[8] (1.00 g, 6.80 mmol) in dry DMF (180 cm^3) was added dropwise a solution of ethoxycarbonylmethylenetriphenylphosphorane[12] (2.36 g, 6.80 mmol) in dry DMF (48 cm^3) during 3.5 h at 80 °C under argon. After being stirred for 1.5 h at 80 °C, the mixture was poured onto brine and extracted with benzene. The combined extracts were washed and dried. The residue obtained after removal of solvent was chromatographed on silica gel (4.2 × 10.0 cm). The initial fractions eluted with hexane–ether (4:1) afforded the *ester* **19** (1.01 g, 68%) as yellow needles, m.p. 40–41 °C (from hexane–benzene); m/z 218 (M$^+$, 65%) and 115 (100) (C$_{13}$H$_{14}$O$_3$ requires 218.2); λ_{max}/nm 256 (ε 33 300) and 342 (8000); ν_{max}/cm^{-1} 1705 (C=O), 1675 (C=O), 1625 (C=C) and 990 [(E)-HC=CH]; δ_H(90 MHz) 9.45 (1 H, s, CHO), 7.30 (1 H, d, J 16, H^B), 7.07–6.47 (4 H, m, H^1, H^2, H^3 and H^4), 6.45 (1 H, d, J 16, H^A), 4.20 (2 H, q, J 7, CH_2Me), 2.82 (2 H, s, CH$_2$) and 1.30 (3 H, t, J 7, CH$_2$Me) (Found: C, 71.4; H, 6.5. C$_{13}$H$_{14}$O$_3$ requires C, 71.5; H, 6.5%).

The later fractions eluted with hexane–ether (1:1) afforded the recovered aldehyde **18** (180 mg).

Ethyl 6-[(2-Ethoxycarbonyl)vinyl]cyclohepta-1,3,5-triene-1-carboxylate **23.**—To a stirred solution of the dialdehyde **20**[14] (1.00 g, 5.74 mmol) in dry acetone (60 cm^3) was added dropwise a solution of Jones reagent[13] (20 cm^3), prepared from chromium(VI) trioxide (5.3 g), conc. H$_2$SO$_4$ (4.6 cm^3) and water (20 cm^3), during 1 h at 0 °C. After being stirred for 3 h at 0 °C, the reaction was terminated by addition of isopropyl alcohol (20 cm^3). Then NaHCO$_3$ was added in small portions until the pH of the reaction mixture became 5.5. The mixture was filtered and the filtrate was concentrated under reduced pressure. To the ice-cooled concentrate was added in one portion 5% aq. sodium hydroxide (20 cm^3) so that the solution was alkaline. The solution was shaken twice with dichloromethane to remove the unchanged dialdehyde **20** and was then neutralized with conc. HCl under ice-cooling. The precipitates thus formed were collected by filtration and washed with water, to give the crude dicarboxylic acid **21** (0.71 g, 60%).

A mixture of diacid **21** (710 mg, 2.70 mmol), thionyl dichloride (27 cm^3) and a few drops of pyridine was heated under reflux for 1 h. Then the mixture was concentrated under reduced pressure. The concentrate was dried under reduced pressure and was dissolved in dry dichloromethane (25 cm^3). To the stirred solution of the crude dicarboxylic acid dichloride **22** was added dry ethanol (40 cm^3) in one portion and the solution was heated under reflux for 1 h. Then the mixture was poured onto water and extracted with benzene. The combined extracts were washed with brine and dried. The residue obtained after removal of solvent was chromatographed on silica gel (3.2 × 7.0 cm). The fractions eluted with 25–30% dichloromethane in benzene afforded the *diester* **23** (300 mg, 33%) as a yellow liquid; m/z 262 (M$^+$, 100%) (C$_{15}$H$_{18}$O$_4$ requires M, 262.3); λ_{max}/nm 246sh (ε 29 000), 252 (30 200) and 337 (9230); ν_{max}(neat)/cm^{-1} 1705 (C=O) and 990 [(E)-HC=CH]; δ_H(90 MHz) 7.38 (1 H, d, J 16, H^B), 7.32 (1 H, m, H^4), 6.87–6.76 (2 H, m, H^2 and H^3), 6.52 (1 H, d, J 16, H^A), 6.50 (1 H, m, H^1), 4.26 (2 H, q, J 7, CH_2Me), 4.24 (2 H, q, J 7, CH_2CH$_3$), 2.86 (2 H, s, CH$_2$), 1.34 (3 H, t, J 7, CH$_2$Me) and 1.31 (3 H, t, J 7, CH$_2$Me) (Found: C, 68.95; H, 7.1. C$_{15}$H$_{18}$O$_4$ requires C, 68.7; H, 6.9%).

6-(2-Carboxyvinyl)cyclohepta-1,3,5-triene-1-carboxylic Acid **21.**—To a stirred solution of the diester **23** (520 mg, 1.98 mmol)

in ethanol (1.0 cm^3)–water (2.0 cm^3) was added 20% aq. sodium hydroxide (2.0 cm^3) and the mixture was stirred for 30 min at 50 °C before being poured onto water, and was shaken with dichloromethane to remove the unchanged diester **23**. Then conc. HCl was added to the solution until it turned acidic to litmus. The precipitates thus formed were filtered off and were washed with water, to give the *dicarboxylic acid* **21** (200 mg, 49%) as a pale yellow amorphous solid, m.p. 266–267 °C (decomp.) (from MeOH); m/z 206 (M$^+$, 100%) (C$_{11}$H$_{10}$O$_4$ requires M, 206.2); λ_{max}/nm 245 (ε 30 900), 250 (32 000) and 335 (9250); ν_{max}/cm^{-1} 3100–2800 (OH), 1690–1670 (C=O) and 985 [(E)-HC=CH]; δ_H[90 MHz; (CD$_3$)$_2$SO] 7.30 (1 H, d, J 16, H^B), 7.26 (1 H, m, H^4), 6.94–6.83 (2 H, m, H^2 and H^3), 6.70 (1 H, m, H^1), 6.35 (1 H, d, J 16, H^A) and 2.75 (2 H, s, CH$_2$) (Found: C, 63.8; H, 4.9. C$_{11}$H$_{10}$O$_4$ requires C, 64.1; H, 4.9%).

Preparation of Dicarboxylic Acid **21** *From Ester* **19.**—To a stirred solution of the ester **19** (450 mg, 2.06 mmol) in dry acetone (20 cm^3) at 5 °C was added dropwise during 1 h a solution of Jones reagent (21 cm^3), prepared from chromium(VI) trioxide (5.30 g), conc. H$_2$SO$_4$ (4.6 cm^3) and water (20 cm^3). After the mixture had been stirred for 3 h at 5 °C, the reaction was terminated by addition of isopropyl alcohol (10 cm^3). Then the mixture was worked up as described above for the preparation of the crude dicarboxylic acid **21** from the dialdehyde **20**, and gave the dicarboxylic acid **21** (110 mg, 26%).

Attempted Conversion of Dicarboxylic Acid **21** *into Dione* **25.**—To a stirred solution of the dicarboxylic acid **21** (200 mg, 0.97 mmol) in dry THF (120 cm^3) was added dropwise a solution of methyllithium in ether (1.5 mol dm^{-3}; 2.59 cm^3, 3.88 mmol) by a syringe during 30 min at 0 °C. After being stirred for 3 h at 0 °C, the mixture was heated for 2 h at 50 °C. After the addition of ethyl acetate (10 cm^3), the mixture was concentrated. To the stirred, ice-cooled residue were added water and then conc. HCl. The dicarboxylic acid **21** (180 mg) was recovered by filtration.

The attempted conversion of the dicarboxylic acid dichloride **22** into the dione **25** under similar conditions to those described above was also unsuccessful.

4-[6-(1-Hydroxyethyl)cyclohepta-1,3,5-trienyl]but-3-en-2-ol **24.**—To a stirred solution of methylmagnesium iodide, prepared from iodomethane (43.8 g, 0.287 mol) and magnesium (7.00 g, 0.287 mol) in dry ether (260 cm^3), was added dropwise a solution of the dialdehyde **20**[14] (500 mg, 2.87 mmol) in dry THF (15 cm^3) during 1 h at room temperature. After the mixture has been stirred for 2 h at room temperature, aq. ammonium chloride was added under ice cooling. The mixture was extracted with benzene. The combined organic layers were washed with brine and dried. The residue obtained after removal of solvent was chromatographed on silica gel (2.2 × 5.0 cm). The fractions eluted with 10–30% ethyl acetate in dichloromethane afforded the *diol* **24** (324 mg, 55%) as pale yellow microcrystals, m.p. 111–113 °C (from hexane–THF); m/z 206 (M$^+$, 3%) and 128 (100) (C$_{13}$H$_{18}$O$_2$ requires M, 206.2); λ_{max}/nm 226 (ε 27 200), 230 (27 400) and 305 (9250); ν_{max}/cm^{-1} 3250 (OH) and 970 [(E)-HC=CH]; the ^{1}H NMR spectrum showed that compound **24** consisted of a 5:1 mixture of two diastereoisomers. The major isomer: δ_H(500 MHz) 6.55–6.49 (2 H, m, H^2 and H^3), 6.30 (1 H, d, J 15.7, H^B), 6.17–6.15 (2 H, m, H^1 and H^4), 6.10 (1 H, dd, J 15.7 and 6.5, H^A), 4.42 (1 H, quint, J 6.4, H^b), 4.34 (1 H, q, J 6.5, H^c), 2.77 (1 H, d, J 13.0, CH$_2$), 2.42 (1 H, d, J 13.0, CH$_2$), 1.72 (2 H, br s, OH), 1.36 (3 H, d, J 6.5, Me^d) and 1.33 (3 H, d, J 6.4, Me^a); the minor isomer: δ_H(500 MHz) 2.74 (1 H, d, J 13.0, CH$_2$), 2.44 (1 H, d, J 13.0, CH$_2$), 1.36 (3 H, d, J 6.4, Me) and 1.33 (3 H, d, J 6.4, Me) (Found: C, 75.5; H, 8.75. C$_{13}$H$_{18}$O$_2$ requires C, 75.7; H, 8.8%).

4-(6-Acetylcyclohepta-1,3,5,-trienyl)but-3-en-2-one **25**.—An isomeric mixture of the diol **24** (250 mg, 1.21 mmol) and $Ba(MnO_4)_2{}^{17}$ (50 g, 0.20 mol) in dry dichloromethane (150 cm³) was stirred for 10 h at room temperature. The mixture was filtered and the filtrate was concentrated. The residue was chromatographed on silica gel (2.6 × 6.5 cm). The fractions eluted with hexane–dichloromethane (1:9) afforded the *dione* **25** (155 mg, 63%) as a dark red liquid; m/z 202 (M⁺, 100%) ($C_{13}H_{14}O_2$ requires M, 202.2); λ_{max}/nm 260 (ε 24 600) and 345 (9670); ν_{max}(neat)/cm⁻¹ 1650 (C=O) and 980 [(E)-HC=CH]; δ_H(500 MHz) 7.20 (1 H, d, J 15.7, H^A), 7.17 (1 H, d, J 6.0, H⁴), 6.94 (1 H, dd, J 11.2 and 6.1, H²), 6.94 (1 H, d, J 15.7, H^B), 6.84 (1 H, dd, J 11.2 and 6.0, H³), 6.58 (1 H, d, J 6.1, H¹), 2.82 (2 H, s, CH_2), 2.39 (3 H, s, Me) and 2.34 (3 H, s, Me) (Found: C, 76.9; H, 6.9. $C_{13}H_{14}O_2$ requires C, 77.2; H, 7.0%).

1-(6-Acetylcyclohepta-1,3,5-trienyl)-7-methylnona-1,4,6-trien-8-yn-3-one **27**.—To a stirred solution of the dione **25** (584 mg, 2.89 mmol) and the aldehyde **26**⁹ (3.90 g, 41.4 mmol) in dry benzene (130 cm³) was added dropwise a mixture of ethanolic sodium ethoxide (1.0 cm³) in dry benzene (2.0 cm³) by a syringe during 1 h at 6 °C. After the mixture had been stirred for 1 h, a further quantity of ethanolic sodium ethoxide (1.0 cm³) in dry benzene (2.0 cm³) was added during 30 min three times, each at an interval of 30 min. After being stirred for a further 1 h at 6 °C, the mixture was poured onto an ice-cooled mixture of saturated aq. ammonium chloride (80 cm³) and benzene (50 cm³), and the aqueous layer was extracted with benzene. The combined organic layers were washed with aq. $NaHCO_3$ and dried. The dark red liquid obtained after removal of solvent was chromatographed on silica gel (3.8 × 4.5 cm). The fractions eluted with hexane–benzene (2:3) afforded the *dione* **27** (35 mg, 4.4%) as orange plates, m.p. 107–112 °C (decomp.) (from hexane–dichloromethane); m/z 278 (M⁺, 47%) and 115 (100) ($C_{19}H_{18}O_2$ requires M, 278.3); λ_{max}/nm 238 (ε 23 600), 313 (18 300) and 360 (17 800); ν_{max}/cm⁻¹ 3228 (C≡CH), 2085 (C≡C), 1655 (C=O), 1599 (C=C) and 990 [(E)-HC=CH]; δ_H(500 MHz) 7.83 (1 H, dd, J 15.4 and 11.3, H^B), 7.35 (1 H, d, J 15.4, H^E), 7.27 (1 H, d, J 15.4, H^D), 7.17 (1 H, d, J 6.0, H⁴), 6.95 (1 H, dd, J 11.1 and 6.2, H²), 6.83 (1 H, dd, J 11.1 and 6.0, H³), 6.60 (1 H, d, J 6.2, H¹), 6.49 (1 H, d, J 11.3, H^A), 6.47 (1 H, d, J 15.4, H^C), 3.55 (1 H, s, C≡CH), 2.86 (2 H, s, CH_2), 2.39 (3 H, COMe) and 2.05 (3 H, s, Me); δ_C 196.4 (q, C=O), 189.4 (q, C=O), 142.6 (t), 140.1 (t), 135.8 (t), 135.3 (t), 133.64 (q), 133.63 (t), 132.6 (t), 132.1 (q), 131.2 (t), 131.0 (t), 128.5 (q), 126.4 (t), 86.5 (t, ≡CH), 82.0 (q, –C≡), 25.9 (s, CH_2), 25.5 (p, Me) and 23.8 (p, Me) (Found: C, 81.7; H, 6.5. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%).

7-Methyl-1-[6-(5-methyl-1-oxohepta-2,4-dien-6-ynyl)cyclohepta-1,3,5-trienyl]nona-1,4,6-trien-8-yn-3-one **28**.—To a stirred solution of the dione **27** (150 mg, 0.539 mmol) and the aldehyde **26** (1.00 g, 10.6 mmol) in dry benzene (30 cm³) was added dropwise a mixture of ethanolic sodium ethoxide (1.0 cm³) in dry benzene (2.0 cm³) by a syringe during 10 min at 5 °C. After the mixture had been stirred for 1.5 h, a further quantity of ethanolic sodium ethoxide (0.5 cm³) in dry benzene (1.0 cm³) was added dropwise during 10 min at 5 °C. After being stirred for 1.5 h at 5 °C, the mixture was worked up as for the isolation of compound **27**. The product was chromatographed on silica gel (3.8 × 4.5 cm). The fractions eluted with hexane–benzene (1:1) afforded the dione **28** (17 mg, 8.9%) as a yellow liquid; m/z 355 (M⁺ + 1) (FAB MS) ($C_{25}H_{22}O_2$ requires M, 354.4); λ_{max}/nm 234 (ε 11 800), 326 (19 300) and 390sh (5500); ν_{max}(neat)/cm⁻¹ 3294 and 3243 (C≡CH), 2088 (C≡C), 1641 (C=O), 1598 (C=C) and 986 [(E)-HC=CH]; for ¹H NMR data see Table 1; δ_C 189.6 (q, C=O), 188.4 (q, C=O), 142.8 (t), 140.2 (t), 140.1 (t), 135.9 (t), 135.5 (t), 135.2 (t), 133.7 (q), 133.3 (q), 132.7 (t), 132.6 (t), 131.3 (t), 131.2 (t), 128.4 (q), 128.2 (q), 126.4

(t), 125.0 (t), 86.6 (t, ≡CH), 86.2 (t, ≡CH), 82.0 (q, –C≡), 81.9 (q, –C≡), 26.3 (s, CH_2), 23.84 (p, Me) and 23.81 (p, Me) (Found: C, 84.0; H, 7.2. $C_{25}H_{22}O_2$ requires C, 84.7; H, 6.3%). Attempts to improve the elemental analysis failed.

11,16-Dimethyl-12,13,14,15-tetradehydro-7,20-dihydro-1,6-methano[22]annulene-7,20-dione **8**.—A solution of compound **28** (40 mg, 0.113 mmol) in pyridine–ether (3:1; 120 cm³) was added dropwise during 3 h to a stirred solution of anhydrous copper(II) acetate (1.53 g) in pyridine–ether (3:1; 120 cm³) at 50 °C, and the mixture was stirred for 1 h at 50 °C. Then the mixture was poured onto water and extracted with benzene. The combined extracts were washed successively with 5% HCl until they turned acidic to litmus, and then with aq. $NaHCO_3$, and were dried. After removal of solvent the residue was chromatographed on silica gel (2.8 × 4.5 cm). The fractions eluted with hexane–benzene (1:4) afforded the *tetradehydro-*[22]*annulenedione* **8** (9.5 mg, 24%) as orange needles, m.p. 203 °C (decomp.) (from hexane–benzene); m/z 352 (M⁺, 22%) and 116 (100) ($C_{25}H_{20}O_2$ requires M, 352.4); for UV data see Table 2 and Fig. 2; ν_{max}/cm⁻¹ 2179 (C≡C), 1637 (C=O), 1576 (C=C) and 981 [(E)-HC=CH]; for ¹H NMR data see Table 1 and Fig. 1; δ_C 191.9 (q, C=O), 187.9 (q, C=O), 144.2 (t), 143.3 (t), 139.9 (t), 138.4 (t), 138.1 (t), 135.9 (t), 135.3 (t), 133.8 (q), 133.2 (q), 132.1 (t), 131.7 (t), 131.4 (t), 129.5 (q), 125.4 (q), 123.1 (t), 122.9 (t), 85.23 (q, –C≡), 85.20 (q, –C≡), 84.8 (q, –C≡), 81.2 (q, –C≡), 28.1 (s, CH_2), 23.6 (p, Me) and 20.8 (p, Me); $\delta_C(CF_3CO_2D)$ 198.7 (q, C=O), 196.2 (q, C=O), 157.0 (q), 154.6 (q), 149.6 (t), 142.0 (t), 141.0 (q), 140.5 (t), 140.1 (t), 138.9 (t), 138.3 (t), 137.0 (t), 136.9 (t), 136.1 (t), 135.8 (q), 130.7 (t), 125.0 (t), 121.0 (t), 90.1 (q, –C≡), 88.9 (q, –C≡), 87.3 (q, –C≡), 86.2 (q, –C≡), 29.5 (s, CH_2), 25.2 (p, Me) and 21.3 (p, Me); $\delta_C(D_2SO_4)$ 195.4 (q, C=O), 191.3 (q, C=O), 161.5, 161.4, 156.2, 149.8, 148.3, 146.5, 145.1, 143.1, 140.3, 138.5, 137.0, 135.6, 132.5, 126.2, 119.0, 92.6 (q, –C≡), 90.5 (q, –C≡), 89.2 (q, –C≡), 89.0 (q, –C≡), 28.8 (s, CH_2), 24.0 (p, Me) and 21.2 (p, Me). In D_2SO_4 only 11 olefinic CH carbon signals are detected although compound **8** has 12 olefinic CH carbons (Found: C, 85.15; H, 5.8. $C_{25}H_{20}O_2$ requires C, 85.2; H, 5.7%).

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