Synthesis and Properties of Tetramethyloctadehydrodihydro-[26]-, -[28]-, -[30]-, -[32]- and [34]-annulenediones

Hiroyuki Higuchi,[a] Shiro Kondo,[a] Yuichi Watanabe,[a] Jūro Ojima*,[a] and Gaku Yamamoto*,[b]
[a] Department of Chemistry, Faculty of Science, Toyama University, Gofuku, Toyama 930, Japan
[b] Department of Chemistry, Graduate School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Title annulenediones **5–9** were synthesized by intermolecular oxidative coupling of 6-methylocta-3,5-dien-7-yn-2-one **13** or its vinylogous ketones **14** and **15** to afford the diones **17–21** and then by an aldol condensation of these diones **17–21** with (Z)-3-methylpent-2-en-4-ynal **10**, followed by intramolecular oxidative coupling of the resulting acyclic diacetylenes **22–26**. The properties of the title compounds **5–9** are discussed on the basis of ^{1}H NMR and electronic spectra.

In previous papers, we have confirmed the alternation of the tropic nature between $[4n + 2]\pi$- and $[4n]\pi$-electron systems arising from polarization of a carbonyl group in dimethyl- or trimethyl-tetradehydroannulenones **1** with 13- to 25-membered rings.[1,2] On the other hand, although several monocyclic annulenediones with an additional carbonyl group are known,[3] there are few with a 20–30-membered ring. The only known example, the tetra-tert-butyloctadehydrodihydro-[26]annulenedione, was prepared in a study of annulenoannulenes,[4] but its properties were not studied in detail. Judging from the fact that annulenones showed a much smaller degree of dia- or para-tropicity than did the corresponding carbocyclic annulenes,[5] annulenediones were expected to show an even smaller tropicity than do annulenones. However, the dimethylhexadehydrodi-hydro[16]annulenedione **2** prepared by Lombardo and Sond-heimer proved to be clearly diatropic.[6] As for the methano-bridged annulenediones we reported the syntheses of a series of annulenediones **3** and showed that the [22]annulenedione (**3**; $m = 1$, $n = 0$)[7] and the [24]annulenedione (**3**; $m = n = 1$)[8] exhibit paratropicity and diatropicity, respectively, in D_2SO_4, suggesting the formation of the dicationic species. Also, we recently reported the preparation of a series of methano-bridged annulenediones **4** containing a 1,4-dichlorobutatriene moiety and the formation of strongly diatropic dicationic species therefrom in D_2SO_4.[9]

This, and the availability of 6-methylocta-3,5-dien-7-yn-2-one **13**[1a,10] and its vinylogues **14** and **15**[1b,2] in connection with studies to search for two-dimensional, π-electron-conjugated compounds with nonlinear optical behaviour,[11] prompted us to prepare the monocyclic annulenediones **5–9**. As described in detail below, careful examination of the ^{1}H NMR spectra of diones **5–9** in $CDCl_3$ revealed that these compounds were almost atropic in this solvent. However, the octadehydrodi-hydro[26]annulenediones **5A** and **5B** exhibited strong para-tropicity in D_2SO_4, reflecting the formation of the correspond-ing dideuteronated species **27** and **28** respectively, while the octadehydrodihydro[28]annulenediones **6A** and **6B** formed the dideuteronated species **29** and **30** in D_2SO_4 respectively, which exhibited strong diatropicity;[12] these are the largest mono-cyclic, dideuteronated annulenedione species to show the ring-current effect and the species **27** and **28** are the first examples of the monocyclic dicationic, paratropic species obtained so far.[3]

Results and Discussion

Synthesis.—The octadehydrodihydroannulenediones **5–9** were synthesized according to the reaction sequence illustrated

in Scheme 1. The starting material was (Z)-3-methylpent-2-en-4-ynal **10**.[1a,10] Successive homologations of the aldehyde **10** to the vinylogous aldehydes **11** and **12** were carried out according to the previously reported method.[2,13] Aldol condensations of the aldehydes **10–12** with acetone in the presence of aq. ethanolic sodium hydroxide afforded the corresponding methyl ketones **13–15**, respectively, as reported previously.[1,2]

3,11-Dimethyltrideca-3,5,8,10-tetraene-1,12-diyn-7-one **16** was the precursor of the tetradehydro[13]annulenone **1** (R = H; $m = n = 1$) and was prepared by aldol condensation of the methyl ketone **13** with the aldehyde **10**.[1a] We initially considered that the octadehydrodihydro[26]annulenedione **5** would be obtainable by dimerization of compound **16** by using Eglinton's method[14] at low temperature, because the formation of compound **1** (R = H; $m = n = 1$) proceeded when com-pound **16** was heated at 50 °C to bring the two terminal acetylene groups close together.[1a] However, oxidative coupling of compound **16** at low temperature gave only a small amount of the desired compound **5**, accompanied by formation of the tetradehydro[13]annulenone **1** (R = H; $m = n = 1$). There-fore we prepared the title compounds **5–9** by the stepwise reaction sequence as illustrated in Scheme 1.

The intermolecular oxidative couplings or cross-couplings using the methyl ketones **13–15** afforded the tetramethyl diones **17–21** in 30–78% yield. Of these, the dione **17** was a known compound.[10] Aldol condensation of the diones **17–21** with the aldehyde **10** in the presence of conc. ethanolic sodium ethoxide in benzene proceeded successfully, and afforded the corresponding acyclic diones **22–26** in 47–73% yield. Oxi-dative coupling of compounds **22–26** was carried out with copper(II) acetate monohydrate in pyridine and methanol (the Eglinton method)[14] under high-dilution conditions with diethyl ether as an entraining solvent,[10] and gave rise to the monomeric cyclic compounds **5–9** in 11–45% yield. In the couplings of compounds **22**, **25** and **26** tetrahydrofuran (THF) was used as a co-solvent owing to the low solubility of these compounds in pyridine (see Experimental section). It is noteworthy that the intramolecular oxidative couplings in the preparation of compounds **5–9** proceeded in less satisfactory yield than in the case of the preparation of the methano-bridged annulenediones **3**,[7,8] presumably because of the lower thermal stability of compounds **22–26** compared with the corresponding acyclic precursors of compounds **3**. Recrystallization of the unsym-metrical dione **25** from THF gave crystals containing solvent of crystallization in a molar ratio of 1:1, as evidenced by ^{1}H and ^{13}C NMR spectra and elemental analysis (see Experimental section).
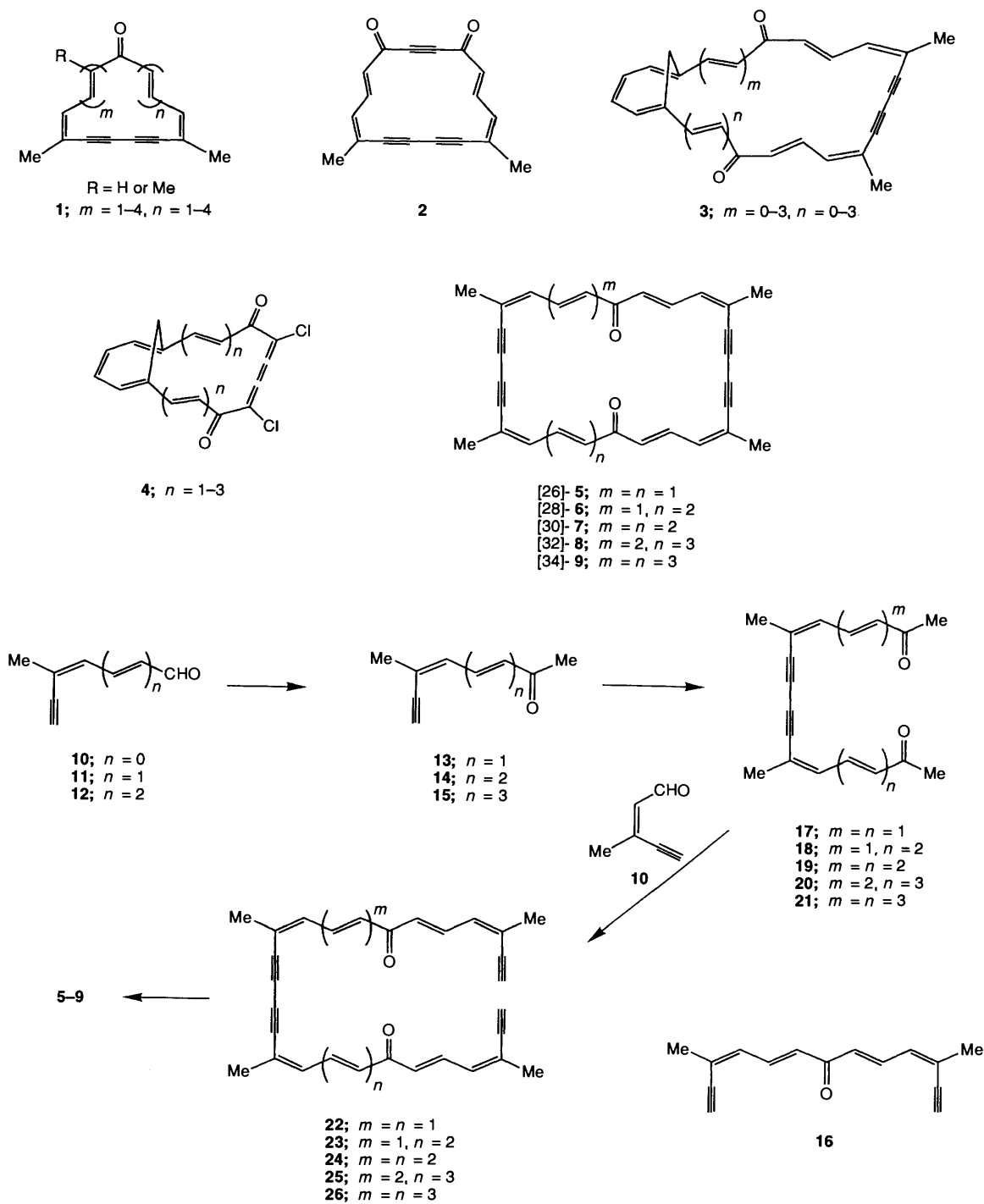
Scheme 1

Structures of these annulenediones are discussed in the next section. Both the first and the second aldol condensation always gave the products with E-configuration for the newly formed double bonds, as shown in their structural formulae. However, in the formation of the octadehydrodihydro-[26]- 5, -[28]- 6, -[30]- 7 and -[34]annulenedione 9, partial configurational isomerization of a double bond occurred during the intramolecular oxidative coupling and two geometric isomers were obtained for compounds 5–7 (see below). It should be noted that the isolated yield of the isomers does not necessarily correspond to the relative thermodynamic stability of the isomers. A similar isomerization has been observed in the preparation of methano-bridged annulenediones 3[8] and 4,[9]

methanothiaannulenes,[15] tetradehydro[15]annulenone[16] and tetradehydrotribenzo[14]annulenone.[17]

The octadehydrodihydro-[26]annulenedione 5, -[28]annulenedione 6, -[30]annulenedione 7, -[32]annulenedione 8 and -[34]annulenedione 9, thus obtained, formed thermally relatively stable, yellow, yellow, orange, red or dark red crystals, respectively.

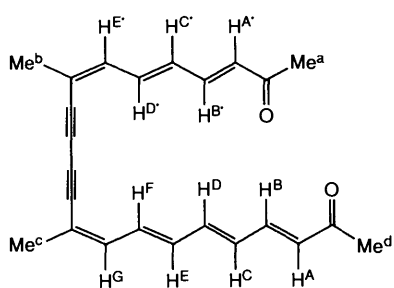*Structural and Chemical-shift Assignments.*—Chemical-shift assignments of the olefinic protons in the annulenediones 5–9 and their precursors 22–26 were made as follows. Broad doublet signals were assigned to the terminal protons of the polyenone chain adjacent to methyl groups, because the broadening was
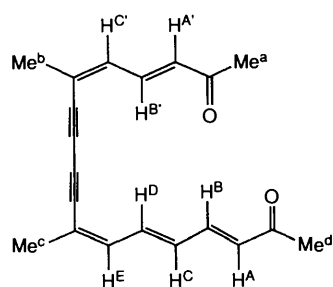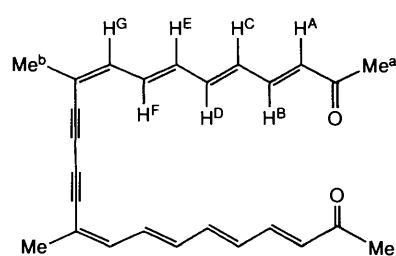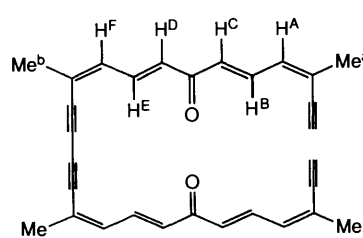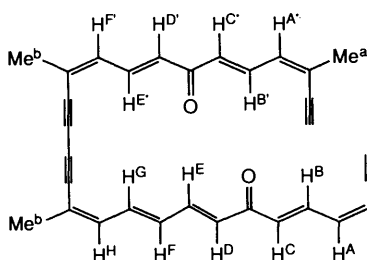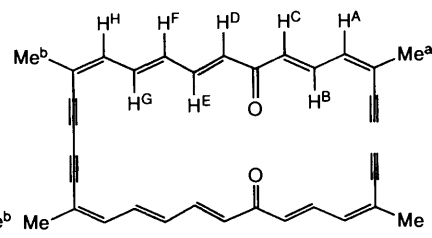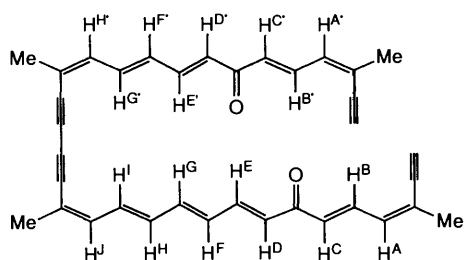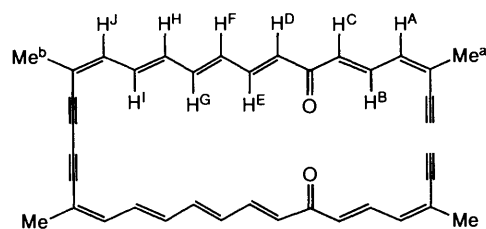
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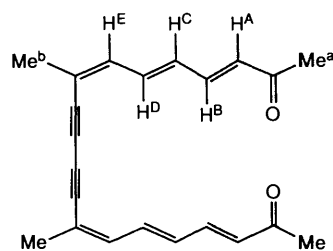
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21

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26

due to allylic coupling to methyl protons as revealed by decoupling experiments, while sharp doublets were assigned to the protons adjacent to carbonyl groups. Then the proton sequence along the polyene moiety was determined by successive decoupling experiments. When an ambiguous assignment was possible, the spectral data were compared with those for the closely related, lower homologue; for example, between compounds 17 and 18, and between compounds 22 and 23.

In all of the annulenediones examined in the present study, all the CH=CH bonds were found to be E and all the =CH–CH= bonds were found to be s-*trans* from the relevant coupling constants.

The major isomer 5A of the [26]annulenedione 5 showed one singlet for the methyl protons and only three olefinic signals, indicating a highly symmetrical structure. Irradiation of the methyl signal enhanced the intensity of the H^A signal due to a

nuclear Overhauser effect (NOE), indicating that H^A was located outside the ring. Therefore both structure and chemical shifts were unambiguously assigned as shown by formula 5A and in Table 1. The minor isomer 5B showed six olefinic signals and two singlets for the methyl protons. Irradiation of Me^a enhanced the H^A signal while that of Me^b enhanced the H^E signal, indicating that H^A and H^E are outside the ring. Therefore two structures, 5B and 5C, were compatible with the spectral data and structure 5B was tentatively assigned because it seemed to be less strained from molecular model considerations.
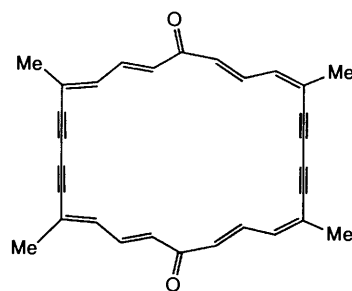
In both isomers of the [28]annulenedione 6, three sets of signals for the Me–C=CH–CH=CH–C=O sequence and one set for Me–C=CH–CH=CH–CH=CH–CO were unambiguously analysed. In the major isomer 6A, irradiation of any of the methyl signals enhanced the signal due to the proton β to the methyl
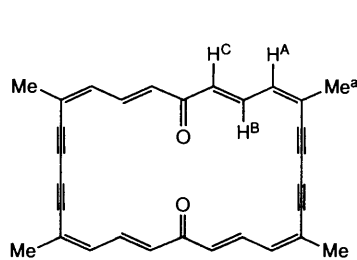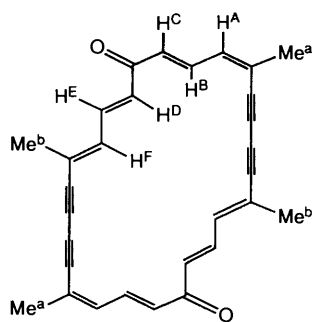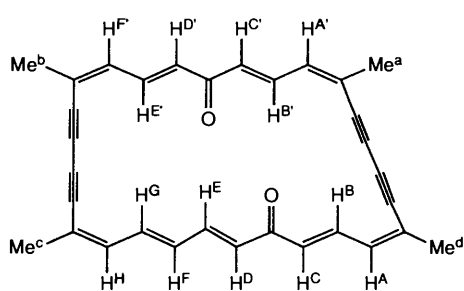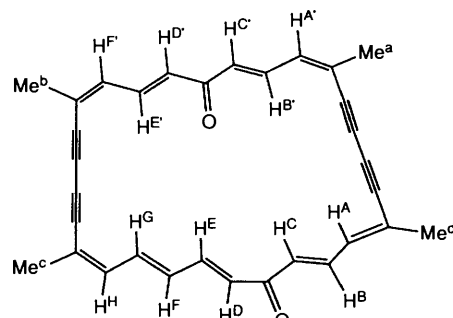
5A   **5B**   **5C**

6A   **6B**
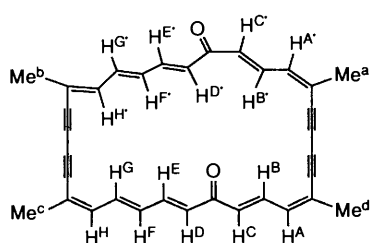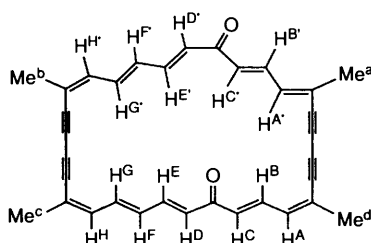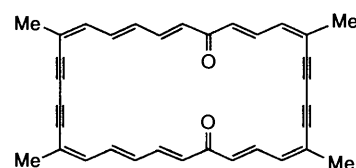
7A   **7B**   **7C**
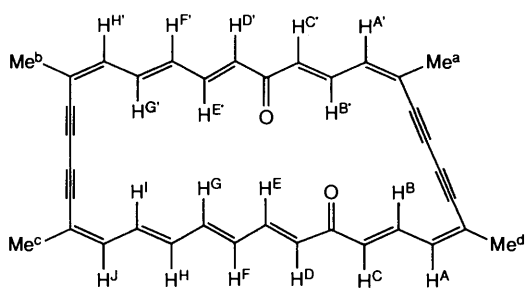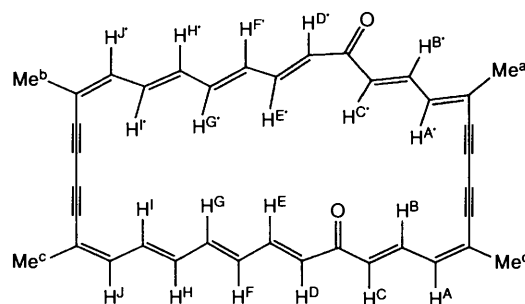
8   **9**

(Me^a ⟶ H$^{A'}$, Me^b ⟶ H$^{F'}$, Me^c ⟶ H^H and Me^d ⟶ H^A), clearly indicating the structure **6A**, although the chemical-shift assignments for the three sets of moieties Me–C=CH–CH=CH– CO are mutually interchangeable. In the minor isomer **6B**, irradiation of the four methyl signals enhanced three β-proton signals and one γ-proton signal (Me^a ⟶ H$^{A'}$, Me^b ⟶ H$^{F'}$, Me^c ⟶ H^H and Me^d ⟶ H^B). Three isomeric geometries which differ in the location of the (E)-MeC=CH moiety are compatible with the NOE data and structure **6B** is the most probable. The chemical-shift assignments for the two proton sequences, Me^a–H$^{A'}$–H$^{B'}$–H$^{C'}$ and Me^b–H$^{F'}$–H$^{E'}$–H$^{D'}$ are interchangeable.

Both isomers of the [30]annulenedione **7** proved to have unsymmetrical structures. Structure **7A** for the major isomer and the chemical shifts of the protons were unambiguously assigned on the basis of the following NOE enhancements: Me^a ⟶ H$^{A'}$, Me^b ⟶ H$^{G'}$, Me^c ⟶ H^H, Me^d ⟶ H^A and H$^{D'}$ ⟶ H$^{B'}$ and H^E. Similarly, structure **7B** was assigned to the minor isomer: Me^a ⟶ H$^{B'}$, Me^b ⟶ H$^{H'}$, Me^c ⟶ H^H, Me^d ⟶ H^A and H$^{C'}$ ⟶ H$^{E'}$. It is noteworthy that the symmetrical isomer **7C** was not detected, although the reason for this is not certain.

Only one isomer was isolated for compound **8**, which was only slightly soluble in CDCl$_3$, and NOE experiments could

Table 1 ^{1}H NMR chemical-shift data of compounds 22–26 and 5–9 at 26 °C (500 MHz; δ-values)[a]

Compd.	Solvent	Inner olefinic protons	Outer olefinic protons	Me protons
22	CDCl3			2.08, 2.03
5A	CDCl3	8.19	6.51, 6.29	1.98
	CF3CO2D	10.09	6.46, 6.10	2.02
	D2SO4	11.93	5.87, 5.20	1.62
5B	CDCl3	7.85, 7.24, 7.12	7.51, 6.52, 6.18	2.05, 2.02
	D2SO4	11.74, 10.15, 9.97	7.09, 6.00, 5.63	1.68, 1.57
23	CDCl3			2.08 (Me), 2.03 (3 × Me)
6A	CDCl3	7.68, 7.62, 7.60, 7.43, 7.07	6.65, 6.64, 6.60, 6.60, 6.51, 6.47, 6.46, 6.45, 6.45	2.08, 2.07, 2.04, 2.01
	CF3CO2D	7.05, 7.02, 6.78, 6.76, 6.32	7.47–7.17 (9 H)	2.54, 2.50, 2.50, 2.46
	D2SO4	5.31, 5.17, 5.08, 4.99, 4.47	8.05–7.82 (9 H)	2.72, 2.69, 2.60, 2.55
6B	CDCl3	7.70, 7.61, 7.28, 6.96, 6.90, 6.77	7.57, 6.70, 6.61, 6.60, 6.59, 6.52, 6.51, 6.33	2.14, 2.10, 2.05, 2.03
	D2SO4	4.57, 4.46, 4.46, 3.84, 3.28, 3.28	9.04, 8.02, 7.92–7.72 (5 H), 7.51	2.78, 2.69, 2.69, 2.66
24	CDCl3			2.04, 2.03
7A	CDCl3	7.98, 7.66, 7.60, 7.40, 7.24, 7.04, 7.00	7.37, 6.79, 6.55, 6.49, 6.47, 6.43, 6.39, 6.36, 6.20	2.09, 2.08, 1.92, 1.91
7B	CDCl3	8.17, 7.75, 7.62, 7.41, 7.29, 7.23, 7.12	7.51, 6.58, 6.47, 6.41, 6.41, 6.39, 6.33, 6.32, 6.22	2.04, 2.01, 1.99, 1.97
25	CDCl3			2.03 (4 × Me)
8	CDCl3	7.68, 7.68, 7.45, 7.43, 7.04, 6.87, 6.81	6.61, 6.58, 6.57, 6.54, 6.50, 6.48, 6.47, 6.45, 6.45, 6.44, 6.40	2.07, 2.04, 2.04, 2.01
26	CDCl3			2.04, 2.02
9	CDCl3	8.08, 7.68, 7.41, 7.11, 7.10, 7.10, 7.01, 6.99, 6.91	7.53, 6.57, 6.47–6.29 (4 H), 6.44, 6.42, 6.35, 6.31, 6.22	2.02, 2.01, 1.99, 1.98

[a] See Experimental section for detailed data and individual assignments. For the acyclic compounds 22–26, only the data for the methyl signals are shown.

not be made, although decoupling experiments revealed the sequence of protons. Tentative structural and chemical-shift assignments were made as shown. Here again the chemical-shift assignments for the groups Me[a]–H[A']–H[B']–H[C'] and Me[d]–H[A]–H[B]–H[C] are interchangeable.

In compound 9, NOE experiments (Me[a] ⟶ H[B'], Me[b] ⟶ H[J'], Me[c] ⟶ H[J] and Me[d] ⟶ H[A]) indicated that the structure of this compound was represented by formula 9, although complete chemical-shift assignments were not possible.

Tropicity of the Annulenediones.—The ^{1}H NMR chemical shifts of the annulenediones 5–9 and the respective acyclic precursors 22–26 are listed in Table 1. The ^{1}H NMR spectra of the isomeric octadehydrodihydro[26]annulenediones 5A and 5B are shown in Figs. 1 and 2, respectively and those of octadehydrodihydro[28]annulenediones 6A and 6B are shown in Figs. 3 and 4, respectively.

The [26]annulenedione 5 was expected to show paratropicity as a 24π-electron system due to polarization of the two carbonyl groups. For isomer 5A in CDCl3 the inner (H[B]) proton is at a lower field than the corresponding H[B] proton of the acyclic compound 22 and the outer H[C] proton and the methyl protons are at a slightly higher field. This suggests that isomer 5A is at most weakly paratropic in CDCl3. Compound 5B is almost atropic because the methyl signals show no significant shift from those in compound 22.

If both of the carbonyl groups are protonated to form a dicationic species, compounds 5A and 5B would be expected to show clear paratropicity. Thus, ^{1}H NMR spectra of compounds 5A and 5B were taken in acidic media and the data are also given in Table 1.

When dissolved in D2SO4, both isomers 5A and 5B showed large downfield shifts of the inner protons by 2.7–3.9 ppm and upfield shifts of the outer olefinic protons and the methyl protons by 0.4–1.1 ppm. This must be a reflection of the induction of a paramagnetic ring current indicating the presence of the dicationic species 27 and 28 where the highly delocalized 24π-electron species 27a and 28a contribute to a great extent. In

less acidic CF3CO2D, compound 5A showed a smaller degree of downfield shift of the inner protons and only a slight upfield shift of the outer protons from the positions in CDCl3 and no significant shift of the methyl signal, reflecting very small paratropicity in this solvent. The protonation was probably quite insufficient. Measurements of NMR spectra of compound 5B in CF3CO2D were abandoned because only a small amount of compound 5B was obtained in the synthesis.

27   27a

28   28a
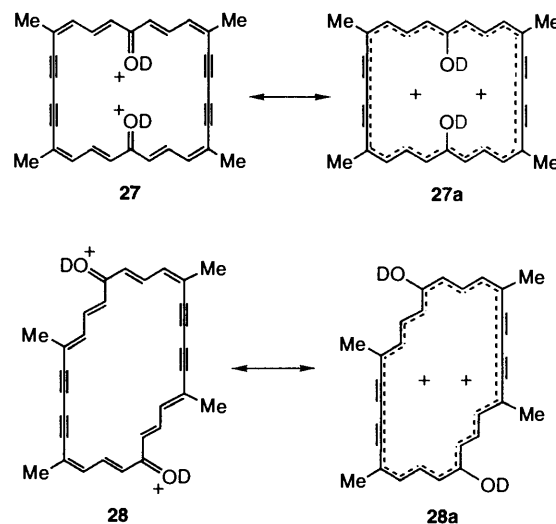
The octadehydrodihydro[28]annulenediones 6A and 6B were expected to show diatropicity as a 26π-electron system due to polarization of the carbonyl groups. However, the proton chemical shifts of the [28]annulenediones 6A and 6B measured in CDCl3 (Table 1) indicates that both isomers are atropic, since neither the downfield shift of the olefinic outer protons and the methyl protons nor the upfield shift of the olefinic inner protons are seen.

Fig. 1 500 MHz ¹H NMR spectra of compound **5A** at 26 °C. (a) in CDCl₃ and (b) in D₂SO₄ measured immediately after dissolution.

Fig. 2 500 MHz ¹H NMR spectra of compound **5B** at 26 °C. (a) in CDCl₃ and (b) in D₂SO₄ measured immediately after dissolution.

Fig. 3 500 MHz ¹H NMR spectra of compound **6A** at 26 °C. (a) in CDCl₃ and (b) in D₂SO₄ measured immediately after dissolution.

Although the [28]annulenediones **6A** and **6B** are atropic under neutral conditions (CDCl₃), these compounds are clearly diatropic in acidic media, as is seen from Table 1 and Figs. 3 and 4.
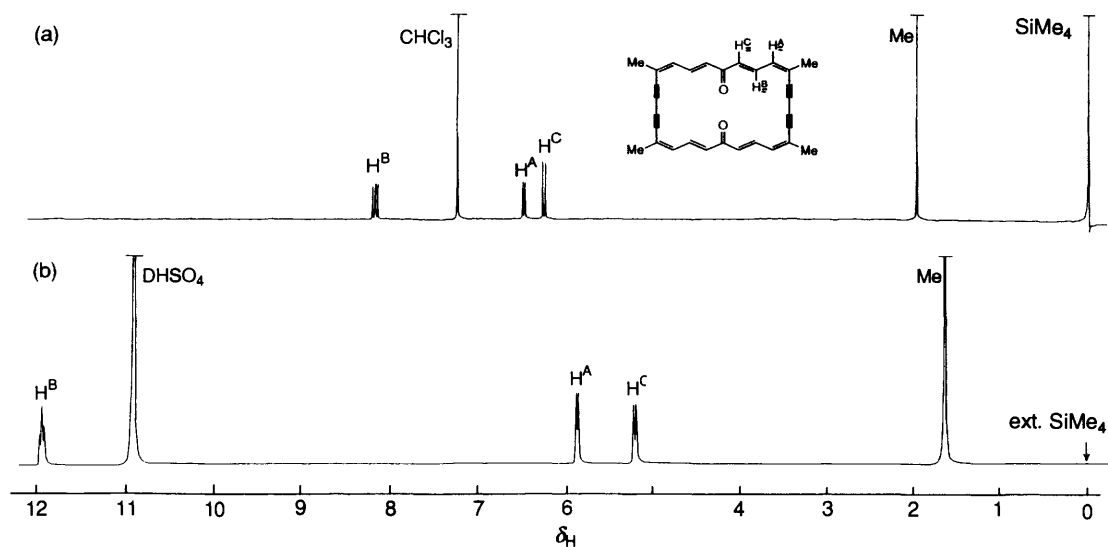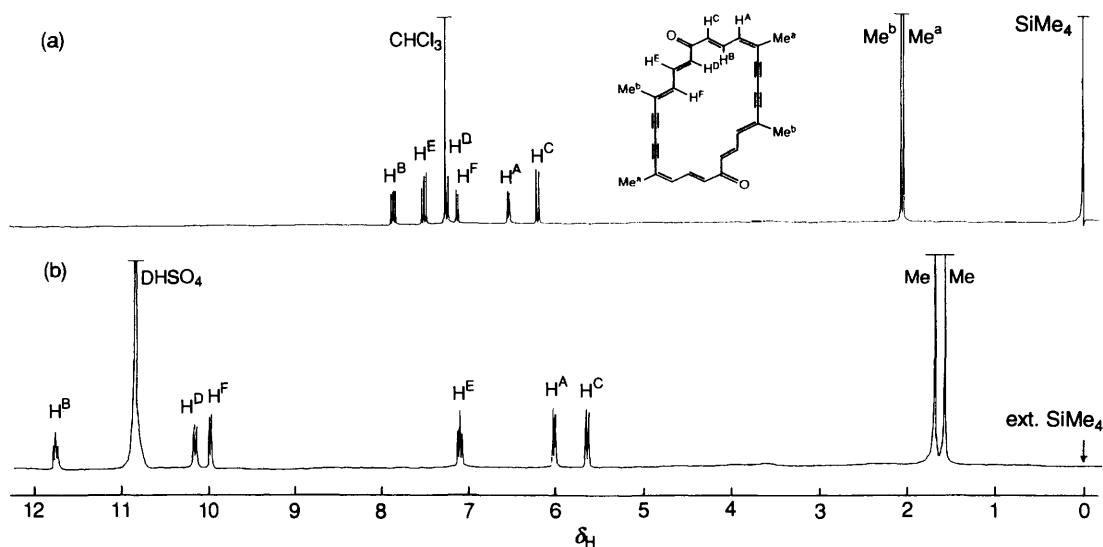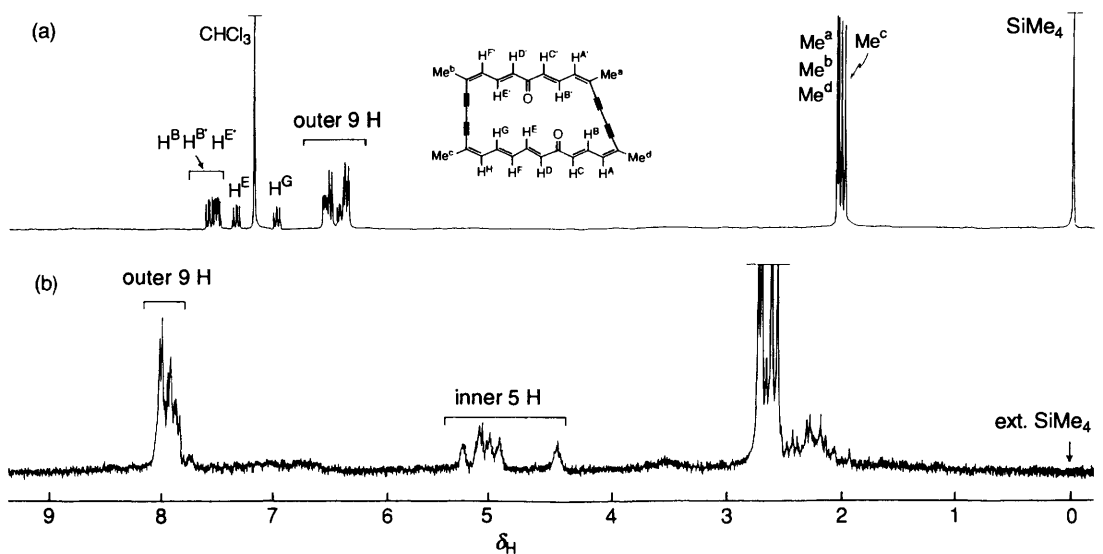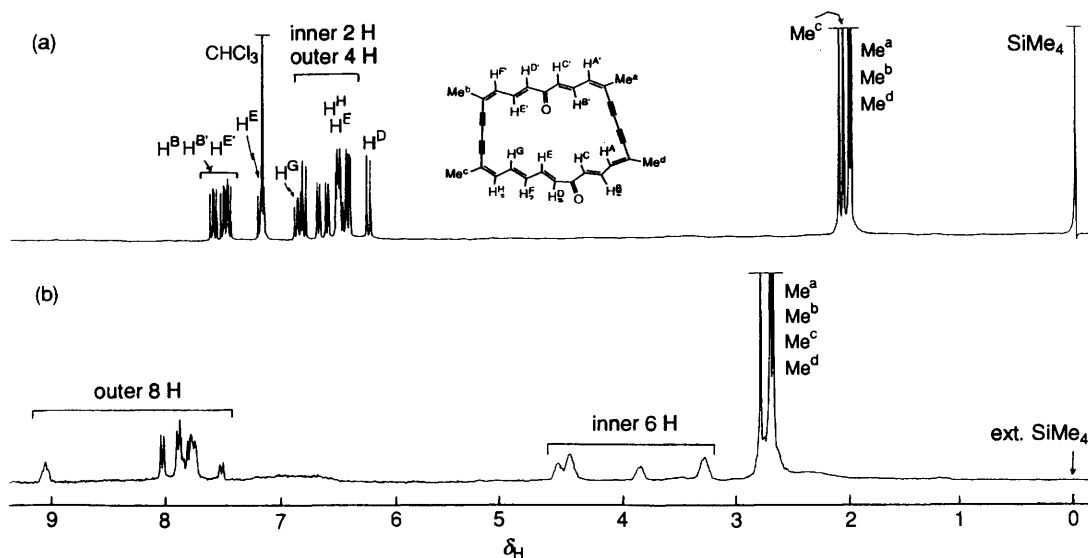
Fig. 4 500 MHz ^{1}H NMR spectra of compound **6B** at 26 °C. (a) in CDCl$_3$ and (b) in D$_2$SO$_4$ measured immediately after dissolution.

Both isomers **6A** and **6B** were rather unstable in D$_2$SO$_4$ and signals due to decomposition products grew gradually in the ^{1}H NMR spectra at ambient temperature as shown in Figs. 3 and 4. Upon a change of solvent from CDCl$_3$ to D$_2$SO$_4$, both isomers **6A** and **6B** showed significant upfield shifts of the inner olefinic proton signals and downfield shifts of the outer olefinic and methyl signals, indicating the induction of large diatropicity in D$_2$SO$_4$ and reflecting the formation of dicationic species **29** and **30**, to which isomers **29a** and **30a** contribute greatly. Compound **6A** in CF$_3$CO$_2$D showed considerable diatropicity, though to a lesser extent than in D$_2$SO$_4$. This is in contrast with the behaviour of compound **5A** which showed only slight paratropicity in CF$_3$CO$_2$D. Compound **6A** may have higher basicity than its homologue **5A**.
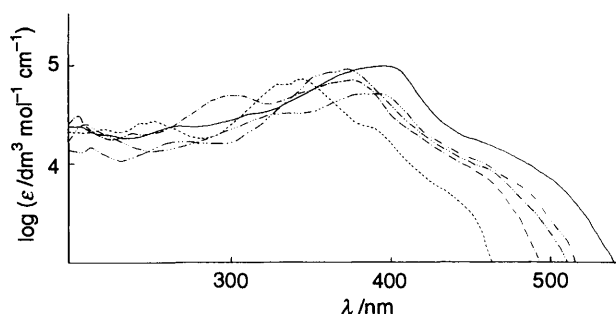
Fig. 5 Electronic absorption spectra of [26]- **5A** (– – – –), [28]-**6A** (— · — · — · —), [30]- **7A** (— · · — · · —), [32]- **8** (— — — — —) and [34]-annulenedione **9** (————) in THF

from the annulenediones **7–9** were unsuccessful due to rapid decomposition of the diones **7–9** in D$_2$SO$_4$.

Electronic Spectra of Compounds **5–9**.—The electronic absorption maxima of the annulenediones **5–9**, determined in both THF and sulfuric acid, are listed in Table 2, and the absorption spectra of the octadehydrodihydro[26]- **5**, -[28]- **6**, -[30]- **7**, -[32]- **8** and -[34]-annulenedione **9** in THF are illustrated in Fig. 5. As can be seen from Fig. 5, the spectra are similar in shape and differ only in the extinction wavelengths of each band.

It is recognized that the electronic spectra of annulenes[18] and the dehydroannulenones **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 $(4n)$ systems.[19] However, Table 2 shows that the main absorption maxima of compounds **5–9** in THF exhibit a bathochromic shift as the ring size increases, and alternation of the maxima is not exhibited, reflecting the fact that compounds **5–9** have little annulene character, as is revealed by their ^{1}H NMR spectra (see above).

Also, it is evident from Table 2 that all the bands of compounds **5** and **6** show a very large bathochromic shift (100–200 nm) on changing the solvent from THF to H$_2$SO$_4$, reflecting the degree of extended conjugation of the respective π-electron system.

In summary, this study confirmed that the octadehydrodihydro[26]- **5** and -[28]-annulenedione **6** in D$_2$SO$_4$ existed as the respective dicationic species which are significantly paratropic and diatropic, respectively. This is the first confirmation of the

29   **29a**

30   **30a**

The simplest test for the nature of the ring currents in the annulenediones **5–9** is provided by the chemical shifts of the methyl protons, since these must always be outside the ring and can readily be recognized. As is seen from Table 1, in compound **5A** the methyl protons appear at a slightly higher field than those of the acyclic model compound **22**, indicating that isomer **5A** is at most weakly paratropic in CDCl$_3$. However, the methyl protons of compounds **5B** and **6–9** resonate at almost the same field as those of the corresponding acyclic model compounds **22–26**, indicating that the annulenediones **5B** and **6–9** are atropic under neutral conditions (CDCl$_3$).

Attempts to obtain the corresponding dideuteronated species

Table 2 Electronic absorption maxima of compounds 5–9 [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

5A	a	216 (22 500), 259 (26 300), 337sh (67 700), **347 (74 300)**, 394sh (21 700)
	b	273 (13 000), 320 (10 500), 396sh (22 800), 425sh (27 800), **483 (75 900)**, 494sh (73 500)
5B	a	253 (30 000), 330sh (70 000), **345 (77 000)**, 392sh (26 500), 447sh (4 800)
6A	a	241 (20 700), 304 (49 300), 370sh (67 500), **378 (70 100)**, 427sh (17 500), 455sh (8 770)
	b	416sh (32 300), 497sh (57 200), **527 (120 000)**, 656sh (11 100)
6B	a	241 (20 400), 295sh (47 300), 302 (49 400), 366sh (68 000), **377 (72 800)**, 427sh (19 600)
7	a	284 (22 400), 360sh (73 100), **374 (81 300)**, 464sh (6 400)
8	a	323sh (53 500), 337sh (56 300), 388sh (88 400), **393 (89 300)**
9	a	217 (24 200), 310sh (30 900), 379sh (89 200), **396 (96 100)**, 475sh (12 200)

alternation of the tropic nature between $(4n + 2)\pi$- and $4n\pi$-electron systems in monocyclic annulenediones.

Experimental

M.p.s were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a Hitachi 260-50 or a JASCO-7300 spectrophotometer for samples as KBr discs and were calibrated against polystyrene; only significant maxima are described. Electronic spectra were measured in THF solution, unless otherwise specified, with a Hitachi 220A or a Shimadzu 2200A spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV and using a direct-inlet system, or with a JMS-D spectrometer equipped with a field-desorption system unless otherwise stated. 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 dissolution of the compounds in a m-nitrobenzyl alcohol matrix. ^{1}H NMR spectra at ambient temperature were recorded on samples as CDCl$_3$ solutions, unless otherwise specified, with a Bruker AM-500 spectrometer at 500.14 MHz. Internal SiMe$_4$ was used as a 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 on samples as CDCl$_3$ solutions on the AM-500 at 125.76 MHz with internal SiMe$_4$ as a reference. The designations p, t and q denote the primary, tertiary and quaternary carbons respectively.

Ethanolic sodium ethoxide (2.15 mol dm^{-3}) was used for the aldol condensations of the compounds 17–21 with the aldehyde 10 and was prepared from sodium (1.00 g) and dry ethanol (20 cm^3) immediately before use. Preparations of the acyclic diones 22–26 were carried out under argon and those of annulenediones 5–9 were performed using a high-dilution apparatus. Merck alumina (activity II–III) and silica gel (Merck 60, Daiso gel 1001 W or Daiso gel 1002 W) were used for column chromatography. Compounds were pre-adsorbed from diethyl ether, benzene or dichloromethane solution onto the adsorbent before column chromatography. Gel-permeation chromatography was performed on an LC-908 Liquid Chromatograph from Japan Analytical Industry Co., Ltd, using a series of JAIGEL 1H and 2H columns and chloroform as eluent. Progress of all reactions was followed by TLC on Merck pre-coated silica gel. 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.

3,11,16,24-*Tetramethylhexacosa*-3,5,8,10,16,18,21,23-*octaene*-1,12,14,25-*tetrayne*-7,20-*dione* **22**.—To a stirred solution of the dione 17^{10} (0.60 g, 2.4 mmol) and the aldehyde 10^{1a,10} (3.0 g, 32 mmol) in dry benzene (90 cm^3) at 4 °C was added dropwise by a

syringe during 20 min a mixture of ethanolic sodium ethoxide (1.5 cm^3) in dry benzene (1.5 cm^3). After being stirred for 2 h at 4 °C, the mixture was poured onto an ice-cooled mixture of saturated aq. ammonium chloride (300 cm^3) and benzene (180 cm^3), and the aqueous layer 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 (3.2 × 11.5 cm). The fractions eluted with 10% dichloromethane in benzene afforded the dione 22 (732 mg, 73%) as yellow needles, m.p. 104–106 °C (decomp.) (from hexane–THF); m/z 419 (M$^+$ + 1) (FAB method) (C$_{30}$H$_{26}$O$_2$ requires M, 418.5); λ_{max}/nm 258 (ε/dm^3 mol^{-1} cm^{-1} 26 000), 360 (41 800) and 387 (44 300); ν_{max}/cm^{-1} 3280 (C≡CH), 2190, 2090 (C≡C), 1660, 1645 (C=O), 1600 (C=C) and 990 [(E)-HC=CH]; δ_H 7.69 (2 H, dd, J 15.4 and 11.2, H^B), 7.65 (2 H, dd, J 15.2 and 11.5, H^E), 6.57 (2 H, d, J 11.5, H^F), 6.50 (2 H, d, J 11.4, H^A), 6.50 (2 H, d, J 15.4, H^D), 6.49 (2 H, d, J 15.5, H^C), 3.49 (2 H, s, C≡CH), 2.08 (6 H, s, Me^b) and 2.03 (6 H, s, Me^a) (Found: C, 85.9; H, 6.4. C$_{30}$H$_{26}$O$_2$ requires C, 86.1; H, 6.3%).

Isomeric 6,7,8,9,19,20,21,22-*Octadehydro*-5,10,18,23-*tetramethyl*-1,14-*dihydro*[26]*annulene*-1,14-*diones* **5A** *and* **5B**.—A solution of compound 22 (1.13 g, 2.7 mmol) in a mixture of ether (100 cm^3) and THF (80 cm^3) was added dropwise during 6 h to a stirred and refluxing solution of copper(II) acetate monohydrate (2.11 g) in a mixture of pyridine (60 cm^3), ether (180 cm^3) and methanol (120 cm^3) at 43 °C. After being refluxed and stirred for further 2 h, the mixture was poured onto water and extracted with dichloromethane. The combined extracts were washed successively with 3 mol dm^{-3} aq. HCl until they turned acidic to litmus, and then with aq. sodium hydrogen carbonate, and were dried and concentrated. The residue was chromatographed on silica gel (3.2 × 8.0 cm). The initial fractions eluted with 20–30% dichloromethane in benzene afforded one isomer (5A) of the *octadehydrodihydro*[26]-*annulenedione* (506 mg, 45%) as yellow microcrystals, m.p. 172–174 °C (decomp.) (from hexane–THF); m/z 416 (M$^+$, 47%) and 207 (100) (C$_{30}$H$_{24}$O$_2$ requires M, 416.4); for UV data see Table 2 and Fig. 5; ν_{max}/cm^{-1} 2190 (C≡C), 1670 (C=O), 1600 (C=C) and 1000 [(E)-HC=CH]; δ_H 8.19 (4 H, dd, J 15.0 and 11.8, H^B), 6.51 (4 H, d, J 11.8, H^A), 6.29 (4 H, d, J 15.0, H^C) and 1.98 (12 H, s, Me); δ_H(CF$_3$CO$_2$D) 10.09 (4 H, br s, H^B), 6.46 (4 H, d, J 11.7, H^A), 6.10 (4 H, d, J 14.8, H^C) and 2.02 (12 H, s, Me); δ_H(D$_2$SO$_4$) 11.93 (4 H, dd, J 14.9 and 11.8, H^B), 5.87 (4 H, d, J 11.8, H^A), 5.20 (4 H, d, J 14.9, H^C) and 1.62 (12 H, s, Me) and see Fig. 1; δ_C 188.0 (q, C=O), 140.5 (t), 138.6 (t), 130.1 (t), 128.0 (q), 83.6 (q, –C≡), 82.4 (q, –C≡) and 22.7 (p, Me) (Found: C, 86.25; H, 6.0. C$_{30}$H$_{24}$O$_2$ requires C, 86.5; H, 5.8%).

The later fractions eluted with 40–50% dichloromethane in benzene afforded the other isomer (5B) of the *octadehydrodihydro*[26]*annulenedione* (113 mg, 10%) as brown needles, m.p. 176–178 °C (decomp.) (from benzene–dichloromethane); m/z 416 (M$^+$, 14%) and 178 (100) (C$_{30}$H$_{24}$O$_2$ requires M, 416.4); for UV data see Table 2; ν_{max}/cm^{-1} 2175 (C≡C), 1630 (C=O), 1590 (C=C) and 980 and 970 [(E)-HC=CH]; δ_H 7.85 (2 H, dd, J 16.1 and 11.2, H^B), 7.51 (2 H, dd, J 14.6 and 12.0, H^E), 7.24 (2 H,

d, J 14.6, H^D), 7.12 (2 H, d, J 12.0, H^F), 6.52 (2 H, d, J 11.2, H^A), 6.18 (2 H, d, J 16.1, H^C), 2.05 (6 H, d, J 1.2, Me^b) and 2.02 (6 H, s, Me^a); δ_H(D$_2$SO$_4$) 11.74 (2 H, t, J 13.0, H^B), 10.15 (2 H, d, J 14.3, H^D), 9.97 (2 H, d, J 11.6, H^F), 7.09 (2 H, t, J 13.0, H^E), 6.00 (2 H, d, J 11.5, H^A), 5.63 (2 H, d, J 14.6, H^C), 1.68 (6 H, s, Me) and 1.57 (6 H, s, Me) and see Fig. 2; δ_C 189.3 (q, C=O), 140.2 (t), 138.6 (t), 138.3 (t), 136.0 (t), 133.5 (t), 128.3 (q), 126.7 (q), 125.8 (t), 88.5 (q, –C≡), 88.5 (q, –C≡), 82.9 (q, –C≡), 81.9 (q, –C≡), 23.1 (p, Me) and 17.2 (p, Me) (Found: C, 86.2; H, 6.0%).

Octadehydrodihydro[26]*annulenedione* **5A** *from Ketone* **16**.—A solution of the ketone **16**[1a] (5.00 g, 0.024 mol) in methanol (41 cm^3) was added dropwise during 1.5 h to a stirred solution of copper(II) acetate monohydrate (11.7 g) in pyridine–methanol (1:1; 236 cm^3) at 5 °C. After being stirred for 4.5 h at ambient temperature, the mixture was worked up as for the isolation of compound **5**. The product was chromatographed on silica gel (2.5 × 6.0 cm). The early fractions eluted with hexane–benzene (1:9) afforded the tetradehydro[13]annulenone **1**[1a] (R = H; m = n = 1) (218 mg). The later fractions eluted with 10% dichloromethane in benzene afforded the octadehydrodihydro[26]annulenedione **5A** (280 mg, 5.6%).

8,13-*Dimethyloctadeca*-3,5,7,13,15-*pentaene*-9,11-*diyne*-2,17-*dione* **18**.—A solution of the dienyne ketone **13**[1b] (8.70 g, 64.8 mmol) and the trienyne ketone **14**[1b] (10.40 g, 64.8 mmol) in a mixture of pyridine (300 cm^3) and ether (100 cm^3) was added dropwise during 3.5 h to a stirred solution of anhydrous copper(II) acetate (118 g) in a mixture of pyridine (900 cm^3) and ether (300 cm^3) at 50 °C. After being stirred for 3 h at 50 °C, the mixture was worked up as for the isolation of compound **5** except for the use of benzene as the extraction solvent. The product was chromatographed on silica gel (3.8 × 11.0 cm). The fractions eluted with benzene–dichloromethane (1:1) afforded the *dione* **18** (5.60 g, 30%) as yellow needles, m.p. 132–134 °C (from MeOH); m/z 292 (M$^+$, 63%) and 249 (100) (C$_{20}$H$_{20}$O$_2$ requires M, 292.3); λ_{max}/nm 226 (ε 15 000), 267 (19 900), 313 (33 400), 365sh (37 100), 376 (38 400) and 401sh (27 700); ν_{max}/cm^{-1} 2170 (C≡C), 1670 and 1650 (C=O), 1590 (C=C), 1010 and 990 [(E)-HC=CH]; δ_H 7.52 (1 H, dd, J 15.6 and 11.4, H$^{B'}$), 7.24 (1 H, dd, J 15.6 and 11.2, H^B), 7.06 (1 H, dd, J 14.8 and 11.5, H^D), 6.52 (1 H, d, J 11.3, H^E), 6.51 (1 H, d, J 11.3, H$^{C'}$), 6.42 (1 H, dd, J 14.9 and 11.8, H^C), 6.20 (1 H, d, J 15.6, H$^{A'}$), 6.18 (1 H, d, J 15.6, H^A), 2.34 (3 H, s, Me^a), 2.30 (3 H, s, Me^d), 2.08 (3 H, s, Me^b) and 2.04 (3 H, s, Me^c) (Found: C, 82.2; H, 6.9. C$_{20}$H$_{20}$O$_2$ requires C, 82.15; H, 6.9%).

3,13,18,26-*Tetramethyloctacosa*-3,5,8,10,12,18,20,23,25-*nonaene*-1,14,16,27-*tetrayne*-7,22-*dione* **23**.—To a stirred solution of the dione **18** (1.00 g, 3.42 mmol) and the aldehyde **10** (3.20 g, 34.2 mmol) in dry benzene (130 cm^3) at 5 °C was added dropwise by a syringe during 1 h a mixture of ethanolic sodium ethoxide (4.7 cm^3) in dry benzene (4.0 cm^3). After being stirred for 3 h at 5 °C, the mixture was worked up as for the isolation of compound **22**. The product was chromatographed on silica gel (3.8 × 8.0 cm). The fractions eluted with 25% dichloromethane in benzene afforded the *dione* **23** (880 mg, 58%) as red needles, m.p. 130–132 °C (decomp.) (from hexane–THF); m/z 445 (M$^+$ + 1) (FAB method) (C$_{32}$H$_{28}$O$_2$ requires M, 444.5); λ_{max}/nm 257 (ε 27 800), 360 (48 500), 406 (50 300) and 436sh (36 400); ν_{max}/cm^{-1} 3260 (C≡CH), 2160 and 2090 (C≡C), 1650 and 1640 (C=O), 1600 (C=C) and 990 [(E)-HC=CH]; δ_H 7.69 (1 H, dd, J 15.4 and 11.2, H$^{B'}$), 7.68 (1 H, dd, J 15.7 and 11.0, H^B), 7.67 (1 H, dd, J 15.2 and 11.5, H$^{E'}$), 7.40 (1 H, dd, J 15.2 and 11.3, H^E), 7.09 (1 H, dd, J 14.9 and 11.5, H$^{G'}$), 6.57–6.45 (9 H, m, H^A, H$^{A'}$, H^C, H$^{C'}$, H^D, H$^{D'}$, H^F, H$^{F'}$ and H^H), 3.50 (1 H, s, C≡CH), 3.48 (1 H, s, C≡CH), 2.08 (3 H, s, Me^a) and 2.03 (9 H, s, Me^b); δ_C 189.4 (q, C=O), 189.1 (q, C=O), 142.6 (t), 139.9 (t), 139.6 (t), 139.4 (t),

139.2 (t), 138.7 (t), 137.6 (t), 135.7 (t), 135.6 (t), 132.6 (t), 129.8 (t), 129.7 (t), 129.6 (t), 129.2 (t), 128.6 (q), 128.2 (q), 127.9 (q), 122.8 (q), 86.3 (t, ≡CH), 86.2 (t, ≡CH), 84.1 (q, –C≡), 82.9 (q, – C≡), 82.6 (q, –C≡), 82.02 (q, –C≡), 81.98 (q, –C≡), 81.6 (q, –C≡), 23.9 (p, Me), 23.9 (p, Me), 23.6 (9, Me) and 23.0 (p, Me) (Found: C, 86.1; H, 6.4. C$_{32}$H$_{28}$O$_2$ requires C, 86.45; H, 6.35%).

Isomeric 6,7,8,9,19,20,21,22-*Octadehydro*-5,10,18,23-*tetramethyl*-1,14-*dihydro*[28]*annulene*-1,14-*diones* **6A** *and* **6B**.—A solution of compound **23** (2.70 g, 6.06 mmol) in a mixture of pyridine (130 cm^3), methanol (60 cm^3) and ether (60 cm^3) was added dropwise during 8 h to a refluxing and stirred solution of copper(II) acetate monohydrate (16.2 g) in a mixture of pyridine (390 cm^3), methanol (156 cm^3) and ether (400 cm^3) at 60 °C. After being refluxed and stirred for a further 30 min, the mixture was worked up as for the isolation of compound **5**. The product was chromatographed on silica gel (4.2 × 8.0 cm). The fractions eluted with 40–60% dichloromethane in benzene afforded the *major isomer* **6A** (368 mg, 14%) of the *octadehydrodihydro*[28]*annulenedione* as yellow microcrystals, m.p. 156–163 °C (decomp.) (from hexane–dichloromethane); m/z 442 (M$^+$, 93%) and 189 (100) (C$_{32}$H$_{26}$O$_2$ requires M, 442.5); for UV data see Table 2 and Fig. 5; ν_{max}/cm^{-1} 2180 (C≡C), 1660 (C=O), 1600 (C=C) and 1005 and 995 [(E)-HC=CH]; δ_H 7.68 (1 H, dd, J 15.0 and 11.6, H$^{E'}$), 7.62 (1 H, dd, J 15.0 and 11.6, H^B), 7.60 (1 H, dd, J 15.0 and 11.7, H$^{B'}$), 7.43 (1 H, dd, J 15.0 and 11.5, H^E), 7.07 (1 H, dd, J 14.8 and 11.6, H^G), 6.65 (1 H, d, J 11.6, H$^{F'}$), 6.64 (1 H, d, J 11.6, H^H), 6.60 (2 H, d, J 11.6, H^A and H$^{A'}$), 6.51 (1 H, dd, J 14.8 and 11.5, H^F), 6.47 (1 H, d, J 15.0, H$^{D'}$), 6.46 (1 H, d, 15.0, H^C), 6.452 (1 H, d, J 15.0, H$^{C'}$), 6.447 (1 H, d, J 15.0, H^D), 2.08 (3 H, s, Me^d), 2.07 (3 H, s, Me^a), 2.04 (3 H, s, Me^b) and 2.01 (3 H, s, Me^c); δ_H(CF$_3$CO$_2$D) 7.47–7.17 (9 H, m, outer H), 7.05 (1 H, t, J 13, inner H), 7.02 (1 H, t, J 13, inner H), 6.78 (1 H, t, J 13, inner H), 6.76 (1 H, t, J 13, inner H), 6.32 (1 H, t, J 13, inner H), 2.54 (3 H, s, Me), 2.50 (6 H, s, Me) and 2.46 (3 H, s, Me); δ_H(D$_2$SO$_4$) 8.05–7.82 (9 H, m, outer H), 5.31 (1 H, br, inner H), 5.17 (1 H, br, inner H), 5.08 (1 H, br, inner H), 4.99 (1 H, br, inner H), 4.47 (1 H, br, inner H), 2.72 (3 H, s, Me), 2.69 (3 H, s, Me), 2.60 (3 H, s, Me) and 2.55 (3 H, s, Me) and see Fig. 3; δ_C 188.7 (q, C=O), 187.7 (q, C=O), 144.7 (t), 140.7 (t), 140.0 (t), 139.7 (t), 139.39 (t), 139.37 (t), 138.28 (t), 138.26 (t), 138.0 (t), 131.1 (t), 130.9 (t), 130.8 (t), 129.9 (t), 128.3 (t), 127.84 (q), 127.83 (q), 127.6 (q), 123.3 (q), 84.0 (q, –C≡), 83.4 (q, –C≡), 83.2 (q, –C≡), 83.1 (q, –C≡), 82.6 (q, –C≡), 82.4 (q, –C≡), 82.3 (q, –C≡), 81.9 (q, –C≡), 23.65 (p, Me), 23.57 (p, Me), 22.5 (p, Me) and 22.1 (p, Me) (Found: C, 86.55; H, 6.0. C$_{32}$H$_{26}$O$_2$ requires C, 86.85; H, 5.9%).

The later fractions eluted with 65% dichloromethane in benzene afforded the minor isomer **6B** (12 mg, 0.4%) as orange microcrystals, m.p. 196–199 °C (decomp.) (from hexane–dichloromethane); m/z 442.1958 (M$^+$) (C$_{32}$H$_{26}$O$_2$ requires M, 442.1983); for UV data see Table 2; ν_{max}/cm^{-1} 2170 (C≡C), 1630 (C=O), 1590 (C=C) and 1000 [(E)-HC=CH]; δ_H 7.70 (1 H, dd, J 14.9 and 11.8, H$^{E'}$), 7.61 (1 H, dd, J 14.8 and 11.9, H$^{B'}$), 7.57 (1 H, dd, J 14.6 and 12.0, H^B), 7.28 (1 H, dd, J 16.0 and 11.1, H^E), 6.96 (1 H, dd, J 14.8 and 11.7, H^G), 6.90 (1 H, d, J 14.6, H^C), 6.77 (1 H, d, J 12.0, H^A), 6.70 (1 H, d, J 12.1, H$^{F'}$), 6.61 (1 H, d, J 11.6, H$^{A'}$), 6.60 (1 H, d, J 11.5, H^H), 6.59 (1 H, dd, J 14.6 and 11.1, H^F), 6.52 (1 H, d, J 14.9, H$^{D'}$), 6.51 (1 H, d, J 14.9, H$^{C'}$), 6.33 (1 H, d, J 15.9, H^D), 2.14 (3 H, s, Me^a), 2.10 (3 H, s, Me^c), 2.05 (3 H, s, Me^b) and 2.03 (3 H, s, Me^d); δ_H(D$_2$SO$_4$) 9.04 (1 H, t, J 12.3, outer H), 8.02 (1 H, d, J ~ 12, outer H), 7.92–7.72 (5 H, m, outer H), 7.51 (1 H, d, J 14, outer H), 4.57 (1 H, br, inner H), 4.46 (2 H, br, inner H), 3.84 (1 H, br, inner H, 3.28 (2 H, br, inner H), 2.78 (3 H, s, Me), 2.69 (6 H, s, Me) and 2.66 (3 H, s, Me) and see Fig. 4; δ_C 189.5 (q, C=O), 188.0 (q, C=O), 143.7 (t), 141.4 (t), 140.9 (t), 139.7 (t), 138.72 (t), 138.68 (t), 138.46 (t), 136.8 (t), 135.3 (t), 133.5 (t), 132.8 (t), 130.0 (t), 129.7 (t), 129.4 (q), 129.0 (q), 126.9 (t), 125.8 (q), 123.3 (q), 90.1 (q, –C≡), 84.3 (q, –C≡), 83.5 (q, –C≡), 83.4 (q, –C≡),

83.1 (q, –C≡), 82.9 (q, –C≡), 82.1 (q, –C≡), 76.2 (q, –C≡), 24.3 (p, Me), 23.7 (p, Me), 22.5 (p, Me) and 16.3 (p, Me).

8,13-*Dimethylicosa*-3,5,7,13,15,17-*hexaene*-2,19-*dione* **19**.—A solution of the trienyne ketone **14**[1b] (690 mg, 4.3 mmol) in methanol (25 cm^3) was added dropwise during 5 min to a stirred solution of copper(II) acetate monohydrate (10.3 g) in a mixture of pyridine (40 cm^3) and methanol (40 cm^3) at room temperature. After being stirred for 4 h at 35 °C, the mixture was worked up as for the isolation of compound **18**. The product was chromatographed on alumina (3.2 × 5.0 cm). The fractions eluted with 10–20% dichloromethane in benzene afforded the *dione* **19** (533 mg, 78%) as yellow cubes, m.p. 172–174 °C (decomp.) (from THF); m/z 318 (M$^+$, 53%) and 217 (100) (C$_{22}$H$_{22}$O$_2$ requires M, 318.4); λ_{max}/nm 239 (ε 11 900), 285sh (17 100), 321sh (31 300), 331 (34 100), 373 (32 200), 387 (32 000) and 420sh (24 200); v_{max}/cm^{-1} 2170 and 2100 (C≡C), 1660 and 1640 (C=O), 1605 (C=C) and 1000 and 960 [(*E*)-HC=CH]; δ_H 7.24 (2 H, dd, *J* 15.5 and 11.3, H^B), 7.06 (2 H, dd, *J* 14.7 and 11.4, H^D), 6.51 (2 H, d, *J* 11.6, H^E), 6.42 (2 H, dd, *J* 15.0 and 11.3, H^C), 6.19 (2 H, d, *J* 15.6, H^A), 2.30 (6 H, s, Me^a) and 2.04 (6 H, s, Me^b) (Found: C, 83.2; H, 7.2. C$_{22}$H$_{22}$O$_2$ requires C, 83.0; H, 7.0%).

3,13,18,28-*Tetramethyltriaconta*-3,5,8,10,12,18,20,22,25,27-*decaene*-1,14,16,29-*tetrayne*-7,24-*dione* **24**.—To a stirred solution of the dione **19** (110 mg, 0.35 mmol) and the aldehyde **10** (366 mg, 3.89 mmol) in dry benzene (20 cm^3) at 6 °C was added dropwise during 20 min a mixture of ethanolic sodium ethoxide (0.23 cm^3) in dry benzene (0.27 cm^3). After being stirred for 4 h at 6 °C, the mixture was worked up as for the isolation of compound **22**. The product was chromatographed on silica gel (3.2 × 8.0 cm). The fractions eluted with 30% dichloromethane in benzene afforded the dione **24** (117 mg, 72%) as red cubes, m.p. 106–109 °C (decomp.) (from hexane–THF); m/z 470 (M$^+$) (field desorption method) (C$_{34}$H$_{30}$O$_2$ requires M, 470.5; λ_{max}/nm 258 (ε 26 500), 372 (51 700) and 415 (54 100); v_{max}/cm^{-1} 3250 (C≡CH), 2180 and 2080 (C≡C), 1660 and 1640 (C=O) and 1000 [(*E*)-HC=CH]; δ_H 7.69 (2 H, dd, *J* 15.2 and 11.4, H^B), 7.39 (2 H, dd, *J* 15.2 and 11.3, H^E), 7.09 (2 H, dd, *J* 14.7 and 11.4, H^G), 6.52 (2 H, d, *J* ~ 10, H^H), 6.49 (2 H, d, *J* ~ 16, H^D), 6.47 (2 H, dd, *J* ~ 15 and ~ 11, H^F), 6.46 (2 H, d, *J* ~ 11, H^A), 6.46 (2 H, d, *J* ~ 16, H^C), 3.48 (2 H, s, C≡CH), 2.04 (6 H, s, Me^b) and 2.03 (6 H, s, Me^a) (Found: C, 86.5; H, 6.7. C$_{34}$H$_{30}$O$_2$ requires C, 86.8; H, 6.4%).

Isomeric 6,7,8,9,21,22,23,24-*Octadehydro*-5,10,20,25-*tetramethyl*-1,14-*dihydro*[30]*annulene*-1,14-*diones* **7A** *and* **7B**.—A solution of compound **24** (254 mg, 0.54 mmol) in a mixture of ether (100 cm^3) and THF (50 cm^3) was added dropwise during 11 h to a stirred and refluxing solution of copper(II) acetate monohydrate (1.10 g) in a mixture of pyridine (50 cm^3), methanol (70 cm^3) and ether (120 cm^3) at 50 °C. After being refluxed and stirred for 1 h, the mixture was worked up as for the isolation of compound **5**. The product was chromatographed on alumina (3.2 × 9 cm). The fractions eluted with 10% dichloromethane in benzene afforded the *octadehydrodihydro*[30]*annulenedione* **7** (43 mg, 17%) as orange microcrystals, m.p. 204–206 °C (decomp.) (from benzene–THF); m/z 469 (M$^+$, 15%) and 55 (100) (C$_{34}$H$_{28}$O$_2$ requires M, 468.5); for UV data see Table 2 and Fig. 5; v_{max}/cm^{-1} 2190 (C=C), 1640 (C=O), 1605 (C=C) and 1000 [(*E*)-HC=CH] (Found: C, 86.9; H, 6.3. C$_{34}$H$_{28}$O$_2$ requires C, 87.15; H, 6.0%). The ^{1}H NMR data showed that compound **7** consisted of two isomers in the ratio 4:3. The structural and chemical-shift assignments were made after separation of the isomeric mixture using gel-permeation chromatography. The major isomer **7A**: δ_H 7.98 (1 H, dd, *J* 14.9 and 11.9, H^B), 7.66 (1 H, dd, *J* 15.0 and 11.3, H$^{B'}$),

7.60 (1 H, dd, *J* 16.0 and 11.2, H^E), 7.40 (1 H, dd, *J* 14.1 and 11.5, H^G), 7.37 (1 H, dd, *J* 14.3 and 11.7, H$^{E'}$), 7.24 (1 H, d, *J* 14.7, H$^{D'}$), 7.04 (1 H, d, *J* 11.7, H$^{H'}$), 7.00 (1 H, dd, *J* 14.5 and 11.6, H$^{F'}$), 6.79 (1 H, dd, *J* 14.5 and 11.9, H$^{G'}$), 6.55 (1 H, d, *J* 11.5, H^H), 6.49 (1 H, d, *J* 11.9, H^A), 6.47 (1 H, dd, *J* 14.1 and 11.2, H^F), 6.43 (1 H, d, *J* 11.1, H$^{A'}$), 6.39 (1 H, d, *J* 14.9, H^C), 6.36 (1 H, d, *J* 15.1, H$^{C'}$), 6.20 (1 H, d, *J* 16.0, H^D), 2.09 (3 H, s, Me^d), 2.08 (3 H, s, Me^a), 1.92 (3 H, s, Me^c) and 1.91 (3 H, s, Me^b); δ_C 189.2 (q, C=O), 188.5 (q, C=O), 145.1 (t), 142.09 (t), 142.07 (t), 141.7 (t), 140.1 (q), 139.7 (t), 139.4 (t), 138.0 (t), 137.7 (t), 137.0 (t), 135.3 (t), 135.2 (t), 134.7 (t), 130.3 (q), 130.0 (t), 129.5 (t), 129.4 (q), 128.8 (t), 128.4 (t), 126.7 (t), 125.2 (t), 124.7 (q), 121.2 (t), 91.4 (q, –C≡), 84.7 (q, –C≡), 83.9 (q, –C≡), 83.9 (q, –C≡), 83.7 (q, –C≡), 83.3 (q, –C≡)), 82.9 (q, –C≡), 75.7 (q, –C≡), 24.9 (p, Me), 23.9 (p, Me), 21.5 (p, Me) and 16.1 (p, Me). The minor isomer **7B**: δ_H 8.17 (1 H, dd, *J* 14.9 and 11.8, H^B), 7.75 (1 H, dd, *J* 14.9 and 11.7, H^E), 7.62 (1 H, dd, *J* 15.8 and 11.1, H$^{E'}$), 7.51 (1 H, dd, *J* 14.6 and 12.2, H$^{B'}$), 7.41 (1 H, dd, *J* 14.8 and 11.7, H^G), 7.29 (1 H, dd, *J* 14.7 and 11.4, H$^{G'}$), 7.23 (1 H, d, *J* 14.6, H$^{C'}$), 7.12 (1 H, d, *J* 12.4, H$^{A'}$), 6.58 (1 H, d, *J* 11.7, H^A), 6.47 (1 H, d, *J* 11.7, H^H), 6.412 (1 H, d, *J* 11.3, H$^{H'}$), 6.405 (1 H, dd, *J* 14.5 and 10.2, H^F), 6.39 (1 H, dd, *J* 14.7 and 11.0, H^F), 6.33 (1 H, d, *J* 15.0, H^C), 6.32 (1 H, d, *J* 14.9, H^D), 6.22 (1 H, d, *J* 15.9, H$^{D'}$), 2.04 (3 H, s, Me^b), 2.01 (3 H, s, Me^c), 1.99 (3 H, s, Me^a) and 1.97 (3 H, s, Me^d); δ_C 189.0 (q, C=O), 188.4 (q, C=O), 144.3, 142.1, 141.3, 141.2, 139.9, 138.7, 138.5, 138.2, 137.5, 136.1, 134.1, 130.8, 129.39, 129.36, 128.3, 128.3, 126.6, 125.6, 124.1, 122.6, 89.8 (q, –C≡), 84.1 (q, –C≡), 83.9 (q, –C≡). 83.7 (q, –C≡), 83.4 (q, –C≡), 82.3 (q, –C≡), 82.0 (q, –C≡), 76.6 (q, –C≡), 24.2 (p, Me), 22.9 (p, Me), 22.0 (p, Me) and 16.7 (p, Me).

10,15-*Dimethyldocosa*-3,5,7,9,15,17,19-*heptaene*-11,13-*diyne*-2,21-*dione* **20**.—A solution of the trienyne ketone **14**[1b] (570 mg, 3.5 mmol) and the tetraenyne ketone **15**[2] (660 mg, 3.5 mmol) in methanol (30 cm^3) was added dropwise during 20 min to a stirred solution of copper(II) acetate monohydrate (7.0 g) in a mixture of pyridine (45 cm^3) and methanol (45 cm^3) at room temperature. After being stirred at room temperature overnight, the mixture was worked up as for the isolation of compound **5**. The product was chromatographed on alumina (3.2 × 5.5 cm). The fractions eluted with benzene–dichloromethane (3:2) afforded the *dione* **20** (822 mg, 68%) as orange cubes, m.p. 184–186 °C (decomp.) (from hexane–THF); m/z 344 (M$^+$, 41%) and 95 (100) (C$_{24}$H$_{24}$O$_2$ requires M, 344.4); λ_{max}/nm 249 (ε 13 900), 286sh (19 800), 329sh (39 500), 345 (50 400), 400 (45 400) and 434sh (30 100); v_{max}/cm^{-1} 2170 and 2100 (C≡C), 1660 (C=O), 1600 (C≡C) and 1000 and 960 [(*E*)-HC=CH]; δ_H 7.24 (1 H, dd, *J* 15.4 and 10.6, H$^{B'}$), 7.19 (1 H, dd, *J* 15.4 and 11.1, H^B), 7.07 (1 H, dd, *J* 14.8 and 11.6, H$^{D'}$), 6.87 (1 H, dd, *J* 14.8 and 11.5, H^F), 6.75 (1 H, dd, *J* 14.8 and 11.2, H^D), 6.50 (1 H, d, *J* 11.5, H$^{E'}$), 6.49 (1 H, d, *J* 11.3, H^G), 6.44–6.38 (3 H, m, H^C, H^E and H$^{C'}$), 6.19 (1 H, d, *J* 15.4, H$^{A'}$), 6.17 (1 H, d, *J* 15.4, H^A), 2.30 (3 H, s, Me^a or Me^d), 2.29 (3 H, s, Me^d or Me^a), 2.03 (3 H, s, Me^c) and 2.02 (3 H, s, Me^b) (Found: C, 83.4; H, 7.1. C$_{24}$H$_{24}$O$_2$ requires C, 83.7; H, 7.0%).

3,15,20,30-*Tetramethyldotriaconta*-3,5,8,10,12,14,20,22,24,-27,29-*undecaene*-1,16,18,31-*tetrayne*-7,26-*dione* **25**.—To a stirred solution of the dione **20** (540 mg, 1.56 mmol) and the aldehyde **10** (1.47 g, 15.6 mmol) in dry benzene (140 cm^3) at 5 °C was added dropwise during 1 h a mixture of ethanolic sodium ethoxide (2.1 cm^3) in dry benzene (2.1 cm^3). After being stirred for 1.5 h at 5 °C, the mixture was worked up as for the isolation of compound **22** except for the use of dichloromethane as the extraction solvent. The product was chromatographed on silica gel (3.6 × 6.5 cm). The fractions eluted with hexane–benzene (1:9) afforded the *dione* **25** (467 mg, 60%). Recrystallization from hexane–THF afforded red needles, m.p. 80–

81 °C (decomp.), which contained one molecule of THF per molecule of dione 25; m/z 497 (M^+ + 1) (FAB method) ($C_{36}H_{32}O_2$ requires M, 496.6); λ_{max}/nm 265 (ε 30 400), 322sh (38 600), 381 (63 400) and 426 (58 300); v_{max}/cm^{-1} 3290 and 3234 (C≡CH), 2176 and 2087 (C≡C), 1641 (C=O), 1605 (C=C) and 1001 [(E)-HC=CH]; δ_H 7.69 (1 H, dd, J 15.4 and 11.3, $H^{B'}$), 7.68 (1 H, dd, J 15.4 and 11.5, H^B), 7.40 (1 H, dd, J 15.1 and 11.3, $H^{E'}$), 7.35 (1 H, dd, J 15.1 and 11.4, H^E), 7.10 (1 H, dd, J 14.8 and 11.4, $H^{G'}$), 6.88 (1 H, dd, J 14.8 and 11.4, H^G), 6.78 (1 H, dd, J 14.5 and 11.3, H^I), 6.52–6.39 (11 H, m, H^A, $H^{A'}$, H^C, $H^{C'}$, H^D, $H^{D'}$, H^F, $H^{F'}$, H^H, $H^{H'}$ and H^J), 3.75 (4 H, m, OCH$_2$ of THF), 3.488 (1 H, s, C≡CH), 3.484 (1 H, s, C≡CH), 2.03 (12 H, br s, Me) and 1.85 (4 H, m, CH$_2$CH$_2$O of THF); δ_C 189.12 (q, C=O), 189.06 (q, C=O), 142.7 (t), 142.6 (t), 141.5 (t), 139.7 (t), 139.6 (t), 139.5 (t), 138.9 (t), 138.8 (t), 135.8 (t), 135.7 (t), 134.7 (t), 133.9 (t), 132.4 (t), 132.2 (t), 129.7 (t), 129.7 (t), 129.3 (t), 128.8 (t), 128.3 (q), 128.2 (q), 123.1 (q), 120.8 (q), 86.3 (t, ≡CH), 86.2 (t, ≡CH), 84.2 (q, –C≡), 83.4 (q, –C≡), 82.03 (q, –C≡), 82.01 (q, –C≡), 81.8 (q, –C≡), 81.2 (q, –C≡), 68.0 (s, CH$_2$CH$_2$O of THF), 25.6 (s, CH$_2$-CH$_2$O of THF), 23.9 (p, Me), 23.8 (p, Me), 23.04 (p, Me) and 22.95 (p, Me) (Found: C, 84.2; H, 7.2. $C_{36}H_{32}O_2$·C_4H_8O requires C, 84.5; H, 7.1%).

6,7,8,9,21,22,23,24-*Octadehydro*-5,10,20,25-*tetramethyl*-1,14-*dihydro*[32]*annulene*-1,14-*dione* 8.—To a stirred and refluxing solution of copper(II) acetate monohydrate (6.00 g) in a mixture of pyridine (162 cm^3), methanol (46 cm^3) and ether (162 cm^3) at 50 °C was added dropwise during 9 h a solution of compound 25 (780 mg, 1.50 mmol) in a mixture of pyridine (80 cm^3), methanol (6 cm^3), ether (80 cm^3) and THF (25 cm^3). After being refluxed and stirred for 1 h, the mixture was worked up as for the isolation of compound 5. The product was chromatographed on silica gel (4.2 × 7.0 cm). The fractions eluted with hexane–dichlorometh-ane (1:4) afforded the *octadehydrodihydro*[32]*annulenedione* 8 (106 mg, 11%) as red needles, m.p. 178–180 °C (decomp.) (from hexane–THF); m/z 495 (M^+ + 1) (FAB method) ($C_{36}H_{30}O_2$ requires M, 494.6); for UV data see Table 2 and Fig. 5; v_{max}/cm^{-1} 2177 (C≡C), 1657 (C=O), 1605 (C=C) and 1003 [(E)-HC=CH]; δ_H 7.683 (1 H, dd, J 15.3 and 11.6, $H^{B'}$), 7.680 (1 H, dd, J 15.0 and 11.9, H^B), 7.45 (1 H, dd, J 14.9 and 11.5, H^E), 7.43 (1 H, dd, J 14.9 and 11.6, $H^{E'}$), 7.04 (1 H, dd, J 14.7 and 11.4, $H^{G'}$), 6.87 (1 H, dd, J 15.0 and 11.6, H^I), 6.81 (1 H, dd, J 14.7 and 11.7, H^G), 6.61 (1 H, d, J 11.6, $H^{A'}$), 6.576 (1 H, d, J 11.9, H^A), 6.573 (1 H, d, J 11.6, H^J), 6.54 (1 H, d, J 11.6, $H^{H'}$), 6.50 (1 H, dd, J 14.8 and 11.4, $H^{F'}$), 6.48 (1 H, dd, J 15.3 and 11.3, H^F), 6.47 (1 H, dd, J 15.9 and 11.3, H^H), 6.452 (1 H, d, J 14.9, $H^{D'}$), 6.452 (1 H, d, J 15.3, $H^{C'}$), 6.44 (1 H, d, J 15.0, H^C), 6.40 (1 H, d, J 14.9, H^D), 2.07 (3 H, s, Me^d), 2.043 (3 H, s, Me^b), 2.039 (3 H, s, Me^a) and 2.01 (3 H, s, Me^c); δ_C 188.5 (q, C=O), 187.2 (q, C=O), 144.5 (t), 144.2 (t), 142.7 (t), 139.6 (t), 139.49 (t), 139.46 (t), 139.2 (t), 139.1 (t), 138.18 (t), 138.14 (t), 136.3 (t), 132.43 (t), 132.37 (t), 130.9 (t), 130.41 (t), 130.37 (t), 130.32 (t), 127.7 (q), 127.6 (q), 127.4 (t), 122.9 (q), 121.4 (q), 84.1 (q, –C≡), 83.5 (q, –C≡), 83.4 (q, –C≡), 83.2 (q, –C≡), 82.5 (q, –C≡), 82.1 (q, –C≡), 81.9 (q, –C≡), 81.6 (q, –C≡), 23.7 (p, Me), 23.3 (p, Me), 22.8 (p, Me) and 22.4 (p, Me) (Found: C, 87.2; H, 6.4. $C_{36}H_{30}O_2$ requires C, 87.4; H, 6.1%).

10,15-*Dimethyltetracosa*-3,5,7,9,15,17,19,21-*octaene*-11,13-*diyne*-2,23-*dione* 21.—A solution of the tetraenyne ketone 15[2] (361 mg, 1.94 mmol) in methanol (5 cm^3) was added dropwise during 10 min to a stirred solution of copper(II) acetate monohydrate (775 mg) in a mixture of pyridine (8 cm^3) and methanol (8 cm^3) at room temperature. After being stirred for 30 h at room temperature, the mixture was worked up as for the isolation of compound 5. The product was chromatographed on alumina (3.2 × 5.0 cm). The fractions eluted with benzene–dichloromethane (1:1) afforded the *dione* 21 (197 mg, 55%) as red needles, m.p. 213–215 °C (decomp.) (from THF); m/z 370

(M^+, 17%) and 95 (100) ($C_{26}H_{26}O_2$ requires M, 370.7); λ_{max}/nm 263 (ε 15 100), 357sh (49 200), 359 (62 400), 405 (50 600) and 452sh (30 700); v_{max}/cm^{-1} 2286 (C≡C), 1672 and 1647 (C=O), 1610 and 1597 (C≡C) and 1005 and 965 [(E)-HC=CH]; δ_H 7.18 (2 H, dd, J 15.5 and 11.2, H^B), 6.87 (2 H, dd, J 14.8 and 11.4, H^F), 6.74 (2 H, dd, J 14.7 and 11.3, H^D), 6.48 (2 H, d, J 11.3, H^G), 6.40 (4 H, dd, J 14.7 and 11.3, H^C and H^E), 6.17 (2 H, d, J 15.5, H^A), 2.29 (6 H, s, Me^a) and 2.02 (6 H, s, Me^b) (Found: C, 84.1; H, 6.9. $C_{26}H_{26}O_2$ requires C, 84.3; H, 7.1%).

3,15,20,32-*Tetramethyltetratriaconta*-3,5,8,10,12,14,20,22,24, 26,29,31-*dodecaene*-1,16,18,33-*tetrayne*-7,28-*dione* 26.—To a stirred solution of the dione 21 (260 mg, 0.70 mmol) and the aldehyde 10 (660 mg, 7.0 mmol) in dry toluene (40 cm^3) at 2 °C was added dropwise during 1 h a mixture of ethanolic sodium ethoxide (1.2 cm^3) in dry toluene (1.2 cm^3). After being stirred for 4.5 h at 2 °C, the mixture was worked up as for the isolation of compound 25. The product was chromatographed on silica gel (2.6 × 9.5 cm). The fractions eluted with 30% dichloro-methane in benzene afforded the *dione* 26 (172 mg, 47%) as dark red microcrystals, m.p. 139–141 °C (decomp.) (from hexane–THF); m/z 523 (M^+ + 1) (FAB method) ($C_{38}H_{34}O_2$ requires M, 522.6); λ_{max}/nm 265 (ε 25 500), 391 (67 000) and 435 (61 400); v_{max}/cm^{-1} 3250 (C≡CH), 2180 and 2080 (C≡C), 1650 and 1640 (C=O), 1600 (C=C) and 1000 [(E)-HC=CH]; δ_H 7.68 (2 H, dd, J 15.3 and 11.3, H^B), 7.34 (2 H, dd, J 15.1 and 11.4, H^E), 6.88 (2 H, dd, J 14.8 and 11.4, H^G), 6.76 (2 H, dd, J 14.5 and 11.3, H^I), 6.50–6.39 (12 H, m, H^A, H^C, H^D, H^F, H^H and H^J), 3.48 (2 H, s, C≡CH), 2.04 (6 H, s, Me^a) and 2.02 (6 H, s, Me^b) (Found: C, 87.4; H, 6.6. $C_{38}H_{34}O_2$ requires C, 87.3; H, 6.6%).

6,7,8,9,23,24,25,26-*Octadehydro*-5,10,22,27-*tetramethyl*-1,14-*dihydro*[34]*annulene*-1,14-*dione* 9.—A solution of compound 26 (637 mg, 1.22 mmol) in a mixture of pyridine (130 cm^3), methanol (26 cm^3), ether (65 cm^3) and THF (60 cm^3) was added dropwise during 10 h to a stirred and refluxed solution of copper(II) acetate monohydrate (4.87 g) in a mixture of pyridine (260 cm^3), methanol (26 cm^3) and ether (200 cm^3) at 60 °C. After being refluxed and stirred for 1 h, the mixture was worked up as for the isolation of compound 5. The product was chromatographed on alumina (3.2 × 4.0 cm). The fractions eluted with 5% dichloromethane in benzene afforded the *octadehydrodihydro*[34]*annulenedione* 9 (77 mg, 12%) as dark red microcrystals, m.p. 164–165 °C (decomp.) (from hexane–dichloromethane); m/z 521 (M^+ + 1) (FAB method) ($C_{38}H_{32}O_2$ requires M, 520.6); for UV data see Table 2 and Fig. 5; v_{max}/cm^{-1} 2170 (C≡C), 1660 and 1640 (C=O), 1600 (C=C) and 1000 [(E)-HC=CH]; δ_H 8.08 (1 H, dd, J 15.0 and 11.7, H^B), 7.68 (1 H, dd, J 14.8 and 11.8, H^E), 7.53 (1 H, dd, J 14.5 and 12.2, $H^{B'}$), 7.41 (1 H, dd, J 15.9 and 11.0, $H^{E'}$), 7.11 (1 H, d, J 14.6, $H^{C'}$), 7.10 (1 H, d, J 12.2, $H^{A'}$), 7.10 (1 H, dd, J 14.6 and 11.5, H^G, H^I, $H^{G'}$ or $H^{I'}$), 7.01 (1 H, dd, J 14.6 and 11.8, H^G, H^I, $H^{G'}$ or $H^{I'}$), 6.99 (1 H, dd, J 14.6 and 11.6, H^G, H^I, $H^{G'}$ or $H^{I'}$), 6.91 (1 H, dd, J 14.6 and 11.3, H^G, H^I, $H^{G'}$ or $H^{I'}$), 6.57 (1 H, d, J 11.9, H^A), 6.47–6.29 (4 H, m, H^F, H^H, $H^{F'}$ and $H^{H'}$), 6.44 (1 H, d, J 11.5, H^J or $H^{J'}$), 6.42 (1 H, d, J 11.5, $H^{J'}$ or H^J), 6.35 (1 H, d, J 15.1, H^C), 6.31 (1 H, d, J 14.8, H^D), 6.22 (1 H, d, J 15.9, $H^{D'}$), 2.02 (3 H, s, Me^b or Me^c), 2.01 (3 H, s, Me^a), 1.99 (3 H, s, Me^c or Me^b) and 1.98 (3 H, s, Me^d); δ_C 189.0 (q, C=O), 188.4 (q, C=O), 144.3 (t), 144.2 (t), 142.1 (t), 140.9 (t), 140.1 (t), 139.6 (t), 139.5 (t), 138.9 (t), 138.4 (t), 136.4 (t), 136.1 (t), 134.9 (t), 134.1 (t), 133.9 (t), 133.8 (t), 132.6 (t), 130.7 (t), 129.7 (t), 129.1 (q), 127.7 (t), 126.5 (q), 125.4 (t), 121.8 (q), 120.5 (q), 89.4 (q, –C≡), 84.3 (q, –C≡), 84.0 (q, –C≡), 83.6 (q, –C≡), 83.0 (q, –C≡), 82.0 (q, –C≡), 81.6 (q, –C≡), 23.7 (p, Me), 22.8 (p, Me), 22.2 (p, Me) and 16.8 (p, Me); one acetylenic carbon signal is missing probably due to overlap with the CDCl$_3$ signal (Found: C, 87.0; H, 6.3.

$C_{38}H_{32}O_2$ requires C, 87.7; H, 6.2%). Attempts to improve the elemental analysis failed.

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