Synthesis and properties of dimethano-bridged tetradehydro[21]-, -[23]- and -[25]annulenones

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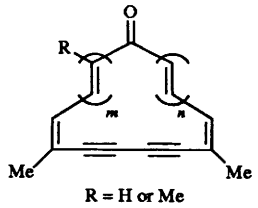
Syntheses of 7,8,9,10-tetradehydro-1,6:11,16-dimethano[21]annulen-19-one **11**, 7,8,9,10-tetradehydro-18-methyl-1,6:11,16-dimethano[21]annulen-19-one **12**, 7,8,9,10-tetradehydro-1,6:11,16-dimethano[23]annulen-19-one **13** and 7,8,9,10-tetradehydro-1,6:11,16-dimethano[25]annulen-21-one **14** are described. The influence of an introduction of two methano-bridges upon the structure and tropicity of the tetradehydro-[21]-, -[23]- and -[25]annulenone ring systems is discussed in view of the ^{1}H NMR and electronic spectra of these annulenones as well as those of the corresponding monocyclic annulenones.

Introduction

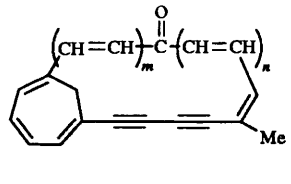
It has been confirmed that the dimethyl- or trimethyl-tetradehydroannulenones **1–7** with 13- to 25-membered rings show the alternation of the tropic nature between $(4n + 2)$ π- and $4n$π-electron systems arising from polarization of the carbonyl group.[1] However, annulenone derivatives showing the ring-current effect in which the ring size is larger than a 25-membered one are not yet known.[2] Since a cycloheptatriene ring has three conjugated double bonds and its presence in the final conjugated systems should not seriously disturb the π-electron distribution, the dimethano-bridged [21]annulenones **11** and **12** which are formally derived from the lowest member of the monocyclic annulenones, the tetradehydro[13]annulenone **1**, by replacement of two double bonds with two cycloheptatriene rings, has the same number of double bonds as the monocyclic tetradehydro[21]annulenone **5**. Thus, incorporation of cyclohepta-1,3,5-triene rings would present routes to prepare a larger π-electron systems.

In the previous paper we confirmed that the monomethano-bridged tetradehydroannulenones **8–10** have tropic nature, although their tropicity was smaller than those of the corresponding monocyclic tetradehydroannulenones **3–5** with the same number of peripherally conjugated π-electrons.[3] Therefore taking advantage of dimethano-bridging, we expected that tetradehydrodimethanoannulenones with a greater number of π-electrons than compound **7** would possibly be prepared. To test this expectation, we examined the properties of the title compounds, dimethano-bridged tetradehydro[21]- **11** and **12**, -[23]- **13** and -[25]annulenone **14**.[4]

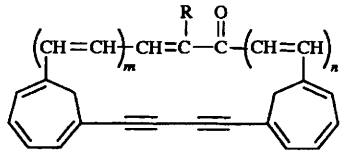


R = H or Me

[13] - **1** $m = n = 1$
[15] - **2** $m = 1, n = 2$
[17] - **3** $m = n = 2$
[19] - **4** $m = 2, n = 3$
[21] - **5** $m = n = 3$
[23] - **6** $m = 3, n = 4$
[25] - **7** $m = n = 4$



[17] - **8** $m = n = 1$
[19] - **9** $m = 1, n = 2$
[21] - **10** $m = n = 2$



[21] - **11** R = H, $m = 0, n = 1$
[21] - **12** R = Me, $m = 0, n = 1$
[23] - **13** R = H, $m = 0, n = 2$
[25] - **14** R = H, $m = 1, n = 2$

Results and discussion

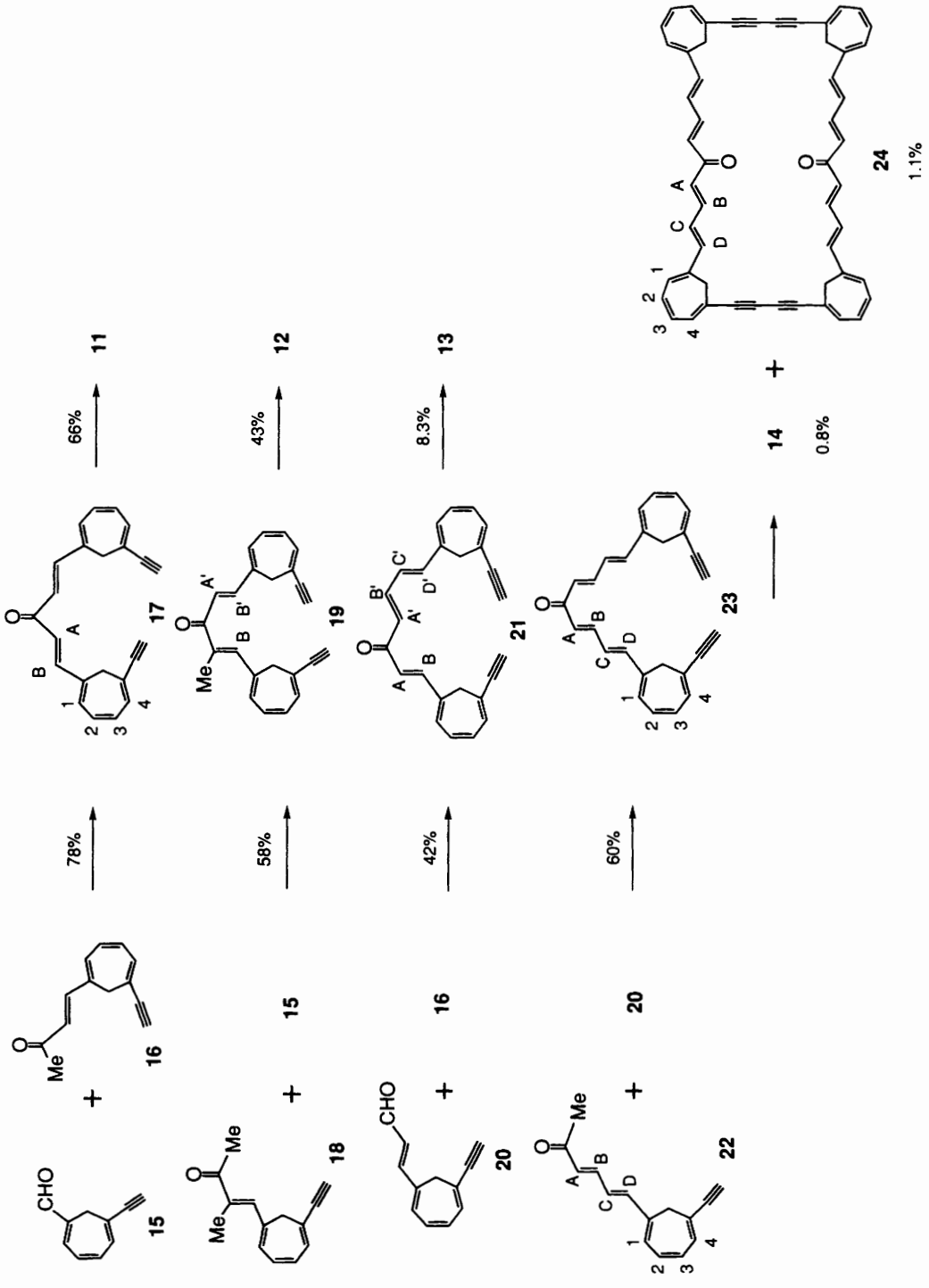
Synthesis

The syntheses of the annulenones **11–14** were carried out according to the reported procedure[5–7] as illustrated in Scheme 1, employing the construction of a ketone containing two terminal acetylene groups by aldol condensation of an appropriate aldehyde and a ketone, followed by cyclization of the resulting acyclic ketone by intramolecular oxidative coupling.[3]

Aldol condensation of the ketones **16**[3] and **18**[3] with the aldehyde **15**[3] in the presence of ethanolic sodium ethoxide in deoxygenated diethyl ether afforded the acyclic ketones **17** and **19**, respectively. Aldol condensation of the homologated aldehyde **20**[3] with the ketone **16** and with dienone **22** prepared from enal **20** and acetone afforded the acyclic ketones **21** and **23**, respectively. Oxidative coupling of ketones **17**, **19** and **21** with anhydrous copper(II) acetate in pyridine–diethyl ether at 50 °C[6,8] afforded the dimethano-bridged annulenones **11**, **12** and **13**, respectively. Oxidative coupling of the ketone **23** required high-dilution conditions and afforded the monomeric dimethano-bridged tetradehydro[25]annulenone **14** in 0.8% yield, accompanied by formation of the dimeric product **24** in 1.1% yield. For the dimer **24** IR, ^{1}H NMR and ^{13}C NMR spectral data as well as the elemental analysis were consistent with the structure, although the FAB MS spectrum did not give the $(M + 1)^+$ peak.

The poor yields of the dimethano-bridged [23]- **13** and [25]-annulenone **14** from the acyclic ketones **21** and **23** respectively discouraged us from preparing the larger-membered annulenones.

Dissolution of the annulenones **11–14** in trifluoroacetic acid (TFA) or deuteriotrifluoroacetic acid gave the corresponding



Scheme 1

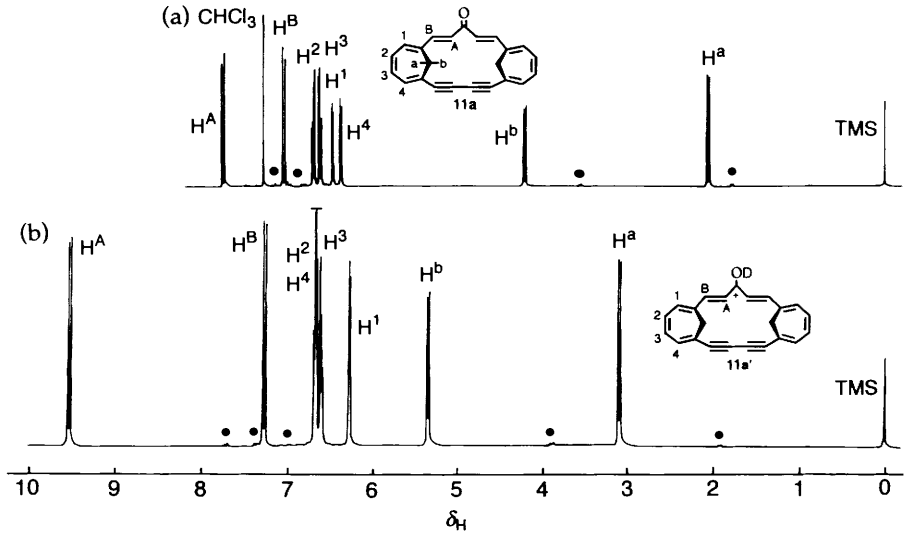
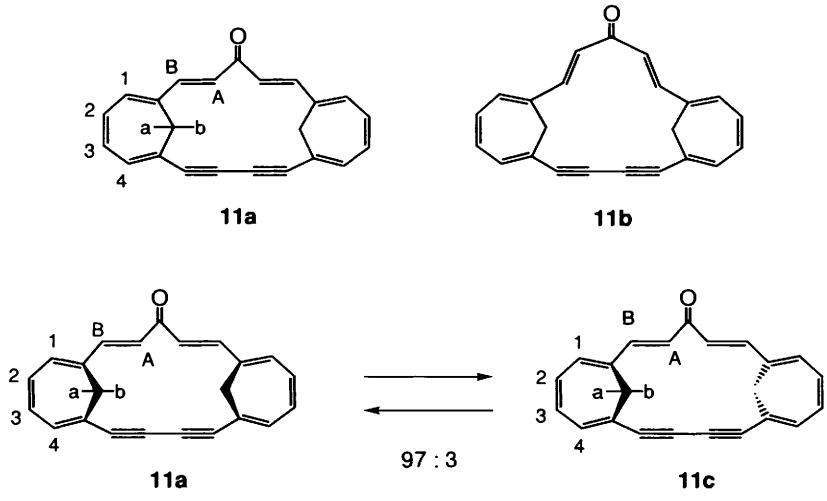


Fig. 1 500 MHz ^1H NMR spectra of compound **11** at 26 °C (a) in $CDCl_3$ and (b) in CF_3CO_2D. Peaks marked • are due to the minor isomer.



protonated or deuteronated carbonyl species **11'**–**14'**: compound **11'** was dark brown, **12'** dark green, **13'** dark blue-green and **14'** dark blue-violet. Quenching of compound **11'** with aq. sodium hydrogen carbonate resulted in regeneration of compound **11**. However, compounds **12'**–**14'** changed irreversively upon quenching, and ketones **12**–**14** were not recovered (see below).

^1H NMR spectra and geometrical determination

The ^1H NMR spectra of compounds **11**, **12**, **13** and **14** in $CDCl_3$ and in CF_3CO_2D are shown in Figs. 1, 2, 3 and 4, respectively. The ^1H NMR spectrum of compound **11** in $CDCl_3$ at 26 °C reveals that the compound exists as an equilibrium mixture of two isomers in the ratio 97:3 [Fig. 1(a)]. As for the major isomer the methylene protons appear as a pair of doublets, suggesting that the molecule is symmetric (C_s or C_2) and the flipping of the methano-bridges through the average plane of the macrocyclic ring is slow on the NMR time-scale but the relative disposition of the two methano bridges, *syn* or *anti*, is not determined from the data. The CH=CH moieties gave a vicinal coupling constant of 15.7 Hz, indicating the (*E*) configuration. Therefore the candidates for the geometry are **11a** and **11b**.

The homonuclear chemical-shift correlation spectroscopy (CH-COSY) spectrum revealed that the CH=CH protons of the major isomer affording the doublet signals at δ 7.73 and 7.03 are connected to the carbons resonating at δ_C 130.7 and 138.7, respectively. Since the carbon chemical shifts reflect the electron densities more directly than do the proton chemical shifts, the carbon signal at lower field is reasonably assigned to carbons located β to the carbonyl group, C^B. Therefore the proton signal at δ 7.03 is assigned to H^B, and the one at δ 7.73 to H^A. The H^A signal shows an intensity nuclear overhauser enhancement (NOE) upon irradiation of the low-field methylene proton H^b at δ 4.20, which indicates that H^A should be close to H^b. These facts show that the two-dimensional structure **11a** should be assigned to the major isomer. The H^B signal shows NOE upon irradiation of the doublet at δ 6.46, which is thus assigned to H^1.

The relative disposition of the methano bridges is unknown but the *syn* orientation can be assigned to the major isomer **11a**, provided that the major isomer in solution is the same as that in the crystalline state, as described below.

Although no clear information on the structure of the minor isomer is obtained because of its low population, it is most reasonable to assume that it is the isomer which differs in the relative disposition of the methano bridges from the major isomer, *i.e.* the *anti*-isomer **11c**.

Interconversion between these isomers was slow on the NMR time-scale at 26 °C as judged from the sharp NMR signals. Elevation of the temperature, however, caused broadening of the signals. When measured in [$^2H_8$]toluene, the signals due to the minor isomer began to broaden around 70 °C and

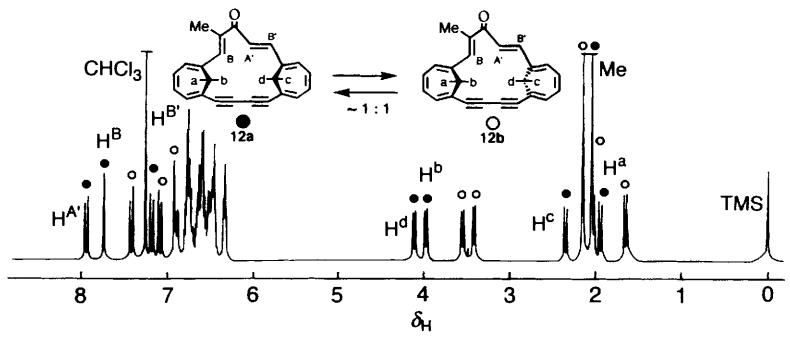


Fig. 2 400 MHz ^{1}H NMR spectrum of compound **12** at 26 °C in $CDCl_3$. Peaks marked • are due to isomer **12a** and those marked ◦ are due to isomer **12b**.

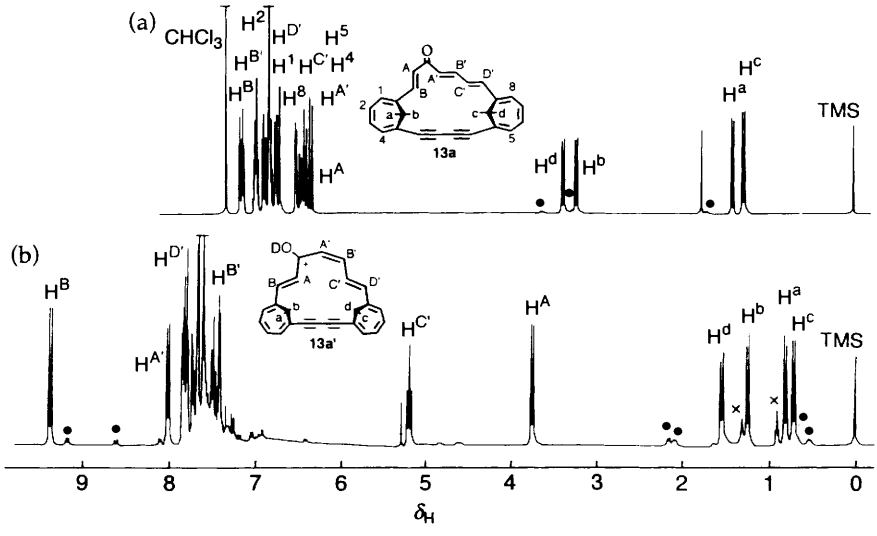
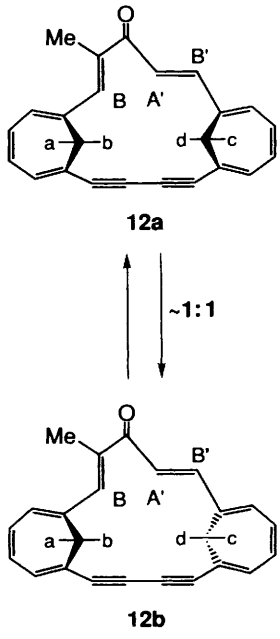


Fig. 3 500 MHz ^{1}H NMR spectra of compound **13** (a) in $CDCl_3$ at −30 °C and (b) in CF_3CO_2D at 26 °C. Peaks marked • are due to the minor isomer. Peaks marked × are due to impurities.

disappeared around 100 °C because of the coalescence with the signals due to the major isomer, while the broadening of the major isomer signals occurred above 90 °C. At 115 °C the methylene proton signals appeared as a pair of broad doublets. These observations indicate that the equilibrium between isomers **11a** and **11c** is attained at 26 °C and that the interconversion takes place on the NMR time-scale at higher temperatures, although no quantitative estimation of the rate constants can be made.

Compound **12** also exists in $CDCl_3$ as an equilibrium mixture of two isomers in the ratio ~1:1 (Fig. 2). Decoupling, NOE and qualitative saturation-transfer experiments revealed the geometries as isomers **12a** and **12b** which differ only in the relative disposition of the methano bridges and are slowly interconverting on the NMR time-scale at 26 °C. The *syn* disposition of the methano bridges is tentatively assigned to isomer **12a** showing the larger paratropicity, as discussed later. No quantitative studies on the interconversion barriers between the isomers could be made because of the instability of the compound in solution.

Compound **13** gave the methylene proton signals as four broad peaks at 26 °C, suggesting the occurrence of some rate processes. At −30 °C the spectrum gave two sets of sharp signals, indicating the presence of two isomers in the ratio



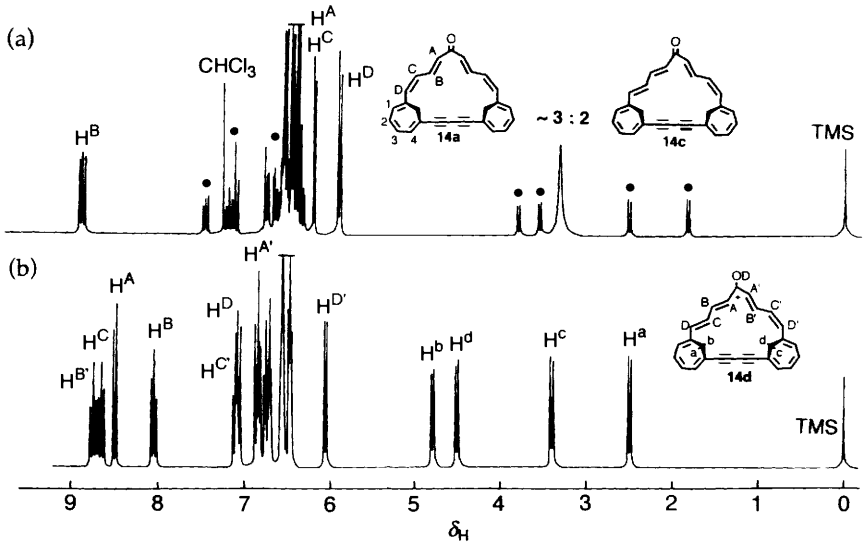
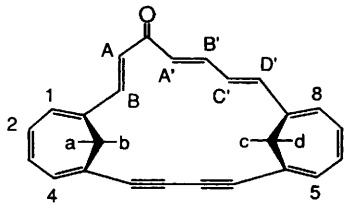
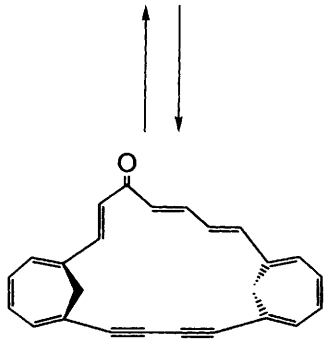


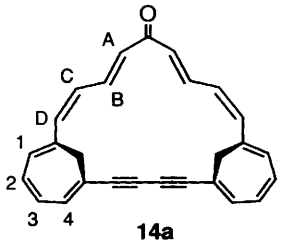
Fig. 4 400 MHz ^{1}H NMR spectra of compound **14** at 26 °C (a) in $CDCl_3$ and (b) in CF_3CO_2D. Peaks marked • are due to the minor isomer.



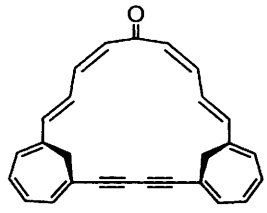
13a



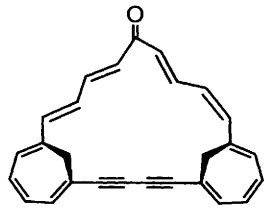
13b



14a



14b



14c

~95:5, as shown in Fig. 3(a). Decoupling and NOE experiments at −30 °C revealed the geometry of the major isomer as being structure **13a**, the *syn* disposition of the methano bridges being tentatively assumed. Only three doublets, at δ 1.70, 3.24 and 3.62, presumably ascribed to the methylene protons, were identified for the minor isomer. Although no information on the structure of the minor isomer was obtained because of the significant overlap of the signals with those of the major isomer, the *anti*-isomer **13b** may be most probable.

The ^{1}H NMR spectrum of compound **14** at 26 °C indicated that the compound exists as two isomers in the ratio ~3:2, as is seen from Fig. 4(a). The methylene proton signal of the major isomer appeared as one broad singlet, while that of the minor isomer appeared as two pairs of sharp doublets. This indicates the following: the major isomer has a symmetric structure and the flipping of the methano bridges is fast on the NMR time-scale, while the minor isomer has an unsymmetric structure and the flipping is slow. Analysis of the olefinic proton signals of the major isomer revealed that the CH=CH–CH=CH moiety is (*E*,*Z*). This suggests the geometry **14a** or **14b**, the former being more probable from inspection of molecular models. An unsymmetric structure such as **14c** may be tentatively assigned to the minor isomer. Here again the *syn* arrangement of the methano bridges may be assumed for both isomers.

X-Ray crystallographic analysis of compound 11

As compound **11** afforded good crystals suitable for X-ray crystallography, its structure determination was performed. The crystal contains two independent molecules of **11** in a unit cell [Fig. 5(a)], but their structures are quite similar and the perspective drawing of one of them is shown in Fig. 5(b). The crystal structure reveals that the compound adopts the conformation with C_s symmetry, in which the two methano-bridges are on the same side of the macrocyclic ring, *i.e. syn*, and the two *trans* double bonds are connected to the carbonyl group in a *s-cis* fashion, as represented by structure **11a**.

Tropic properties of compounds 11–14

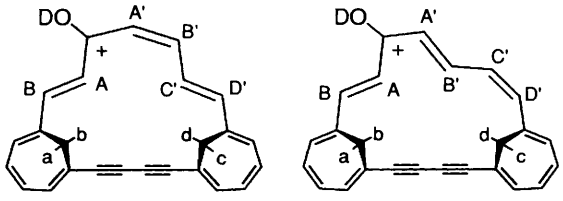
The magnitude of the tropic properties of the annulenones may be judged by the chemical shifts of various protons in the molecules relative to those of the corresponding acyclic precursors chosen as the respective reference compounds.

The major isomer **11a** of compound **11** showed the downfield shifts of the inner olefinic proton H^A (0.93 ppm) and the methylene protons (0.38 ppm on the average) and the upfield

shifts of the outer olefinic proton H^B (0.41 ppm) relative to the corresponding protons of the reference compound **17** (see Experimental section for detailed chemical-shift data). This clearly indicates that the isomer **11a** shows significant paratropicity, as expected for the potential 20π-electron system which would arise from the polarization of the carbonyl group. As can be seen from Fig. 1(b), the paratropicity is significantly enhanced in CF_3CO_2D where the carbonyl of compound **11a** is deuteronated to afford a 20π-electron cationic species **11a'**; the inner protons showed large downfield shifts, while the outer protons showed slight downfield shifts because the intrinsic downfield shifts due to the electron-density effect of the cationic species outweighed the tropic effect.

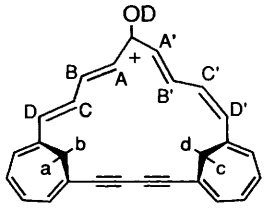
On the other hand, the minor isomer **11c** is almost atropic, even in CF_3CO_2D, as seen from Fig. 1. The large difference in paratropicity between isomers **11a** and **11c** may be ascribed to the difference in planarity of the peripheral π-system; the *syn*-isomer shows better planarity and higher tropicity, as was observed in dimethano[14]annulene.[9]

Among the isomers of compound **12**, **12a** is clearly paratropic and **12b** is atropic as judged from the chemical shifts in $CDCl_3$. This compound was quite unstable in CF_3CO_2D and no meaningful NMR data were obtained.



13a' **13b'**

The ^1H NMR data of compound **13** at −30 °C indicated that the major isomer **13a** is only slightly diatropic and the minor isomer **13b** may be atropic; judgements were made solely from the methylene chemical shifts because the olefin-proton region of the reference compound **21** can not be fully analysed. Compound **13** is unstable in CF_3CO_2D and the ^1H NMR spectrum indicated the presence of considerable amounts of decomposition products [Fig. 3(b)]. The coupling constants of the olefinic proton signals suggest the presence of a (*Z*)-CH=CH moiety, and the presence of two olefinic protons in the upfield region of δ 5.4–3.8 suggests that these protons are inside the ring. These findings indicate that the cationic species has a different geometry from the major isomer of the neutral species found in $CDCl_3$, and that the geometry of the cation is either **13a'** or **13b'**. Although differentiation between the two is difficult, structure **13a'** is tentatively assigned. Considerably larger upfield shifts of the inner protons as well as of the methylene protons (δ 1.6–0.8) suggest a large diatropicity for this cationic species. Isomerization of the double bond upon changing the solvent from $CDCl_3$ to CF_3CO_2D has been observed for the dimethyl- or trimethyl-tetradehydro-[15]-**2**,[10] -[19]-annulenone **4**[11] and methano-bridged [19]annulenone **9**.[3]



14c'

The major isomer **14a** of compound **14** is paratropic judging from the appearance of the inner olefinic (δ 8.89) and methylene (δ 3.32) protons at lower field than the corresponding protons in the reference compound **23** (δ 7.39 and 2.74, respectively). The minor isomer **14c** is also paratropic though to a lesser extent than **14a**. As is seen from Fig. 4(b), compound **14** is found to exist as a single species **14c'** in CF_3CO_2D. The methylene proton signals shift downfield by *ca.* 0.5 ppm on the average upon changing the solvent from $CDCl_3$ to CF_3CO_2D, suggesting a small increase in paratropicity.

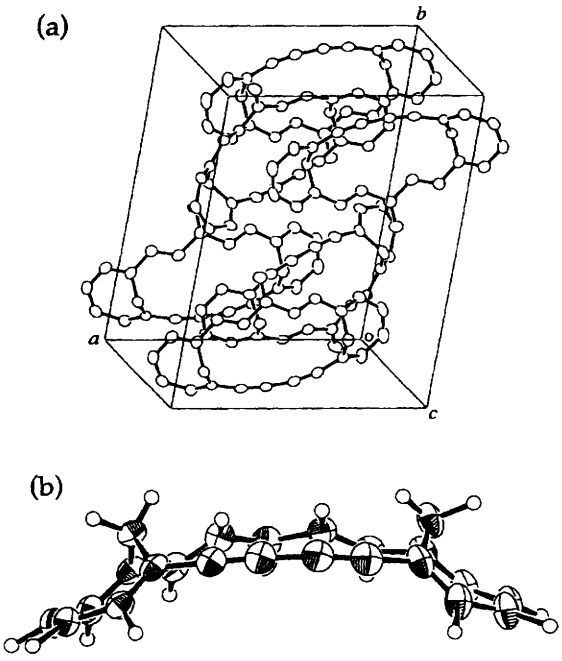


Fig. 5 The unit-cell packing diagram (a) and the ORTEP drawing (b) of compound **11**

If we compare the degree of paratropicity in the dimethano[21]annulenones **11a** (and **12a**) with the corresponding monomethano derivative **10** and the monocyclic one **5**[12] and of the dimethano[25]annulenone **14a** with compound **7**,[1b] respectively, the monocyclic annulenones **5** and **7** show the largest paratropicity while the respective dimethano-bridged counterparts, **11a** (**12a**) and **14a** show the least paratropicity under both the neutral (in $CDCl_3$) and acidic conditions (in CF_3CO_2D), judging from the chemical shifts of the inner and outer olefinic signals.

A similar comparison was also made for the diatropicity from the dimethano-bridged [23]annulenone **13** and its monocyclic counterpart **6**,[1b] revealing the larger diatropicity in monocycle **6** than in tricycle **13**. Therefore the tropicity of the [21]-, [23]- and [25]-annulenones decreases in the order: monocyclic > monomethano-bridged > dimethano-bridged. This suggests that the methano-bridging significantly perturbs the planarity of the monocyclic annulenones **1**–**7**, owing to the presence of the methano bridges.

Electronic spectra of compounds 11–14

The absorption spectra of compounds **11**–**14** in tetrahydrofuran (THF) and the spectra of compounds **11**, **13** and **14** in TFA are illustrated in Figs. 6 and 7 respectively.

It is evident from Figs. 6 and 7 that all the bands of annulenones **11**, **13** and **14** show an appreciable bathochromic shift upon changing the solvent from THF to TFA, demonstrating the more extended conjugation of their π-electron systems than those in THF. A similar trend was also observed for the annulenedione **24** (see Experimental section).

Fig. 6 shows that the spectra of compounds **11**, **12** and **14** are

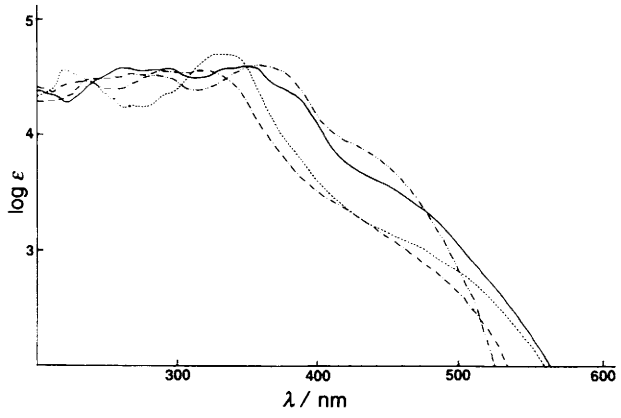


Fig. 6 Electronic absorption spectra of [21]- **11** (- - - -), [21]- **12** (– · – · –). [23]- **13** (– · · – · · –) and [25]annulenone **14** (——) in THF

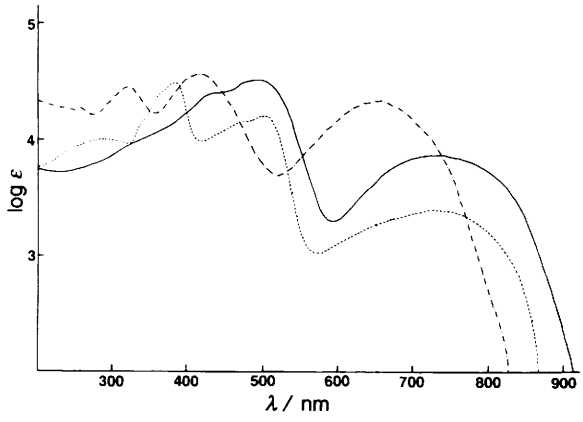


Fig. 7 Electronic absorption spectra of [21]- **11** (- - - -), [23]- **13** (– · · – · · –) and [25]annulenone **14** (——) in TFA

similar in shape as expected, and their spectra exhibit some broadening of the absorption curves, as compared with the spectrum of compound **13**, revealing that compounds **11**, **12** and **14** are the [4*n* + 1]annulenones, as has been observed in the monocyclic tetradehydroannulenone series **1**–**7**.[6,7]

This behaviour is much more marked in Fig. 7 which shows the absorption spectra of compounds **11**, **13** and **14** in TFA. The spectra of compounds **11** and **14** showed rather broad curves as compared with that of compound **13**, demonstrating that compounds **11** and **14** are [4*n*]π-electron systems. Also, the end absorptions of compounds **11** and **14** tailed to a longer wavelength than did that of compound **13**, an effect recently shown for the spectra of [4*n*]annulenes.[13]

As has been observed for the annulenes and dehydroannulenes, the occurrence of alternation between the main maxima of (4*n* – 2) and 4*n* systems is known.[14] However, it is not possible to use the main maxima of compounds **11**–**14** and **11'**–**14'** for comparison with regard to the current discussion, since the conformations are very different among compounds **11**–**14**.

Experimental

Mps were determined on a hot-stage apparatus and are uncorrected. IR spectra were taken with a JASCO-7300 spectrophotometer on samples as KBr discs; only significant maxima are described. Electronic (UV/VIS) spectra were measured in THF or TFA solution with 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 for samples in a *m*-nitrobenzyl alcohol matrix on a JEOL JMS-AX 505W high-resolution double-focusing mass spectrometer equipped with a D 5000 data system. ^{1}H NMR spectra at ambient temperature were recorded for $CDCl_3$ solutions, unless otherwise specified, with a JEOL GX-400 (400 MHz) or a Bruker AM-500 (500 MHz) spectrometer. Internal $SiMe_4$ (TMS) was used as reference. *J* Values are given in Hz. ^{13}C NMR spectra were recorded for $CDCl_3$ solutions, unless otherwise indicated, on the GX-400 or the AM-500 at 100.40 or 125.76 MHz, respectively, with internal TMS as reference.

Freshly deoxygenated diethyl ether and acetone were used to minimize oxidation of the compounds employed for aldol condensation and were prepared by passage through a short column of basic alumina (ICN, activity I), followed by flushing with argon, immediately before use. 0.36 mol dm^{-3} Ethanolic sodium ethoxide was used for the aldol condensations and was prepared from sodium (250 mg) and dry ethanol (30 cm^3) immediately before use. Progress of all reactions was followed by TLC on Merck pre-coated silica gel. Alumina (Merck, activity II–III) and silica gel (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. Preparative TLC (PLC) was carried out on 20 × 20 cm alumina plates (Merck, 0.5 or 2 mm thick). Organic extracts were washed with saturated aq. sodium chloride and dried over anhydrous sodium sulfate prior to removal of solvent. Solvents were evaporated off under water-pump pressure. Ether refers to diethyl ether.

1,5-Bis-(6-ethynylcyclohepta-1,3,5-trienyl)penta-1,4-dien-3-one 17. Typical procedure for preparation of bisethynyl ketones

An ethanolic sodium ethoxide solution (1.95 cm^3) was added in small portions to a stirred solution of the ketone **16**[3] (315 mg, 1.71 mmol) and the aldehyde **15**[3] (450 mg, 3.12 mmol) in deoxygenated ether (20 cm^3) at 5–10 °C, and the solution was stirred for 2 h at 5–10 °C. Then the reaction was terminated by addition of 2 mol dm^{-3} H_2SO_4 (2.0 cm^3). The mixture was poured onto water and extracted with benzene. The combined extracts were washed with aq. $NaHCO_3$ and dried. The residue obtained after removal of the solvent was chromatographed on alumina (3.2 × 5.5 cm). The initial fractions eluted with 20% ether in hexane afforded the unchanged aldehyde **15** (156 mg recovery). The later fractions eluted with hexane–ether (3:2) afforded the *ketone* **17** (412 mg, 78%) as orange needles, mp 99–102 °C (decomp.) (from hexane–dichloromethane); *m*/*z* 310 (M^+, 61%) and 128 (100) ($C_{23}H_{18}O$ requires M, 310.3); λ_{max}(THF)/nm 210 (ε/dm^3 mol^{-1} cm^{-1} 19 100), 243 (37 700) 295sh (13 900) and 388 (21 900); ν_{max}/cm^{-1} 3246 and 3219 (C≡CH), 2083 (C≡C), 1659 (C=O), 1607 and 1569 (C=C) and 975 [(*E*)-HC=CH]; δ_H(500 MHz) 7.441 (2 H, d, *J* 15.6, H^B), 6.800 (2 H, d, *J* 15.6, H^A), 6.732 (2 H, dd, *J* 11.0 and 6.0, H^2), 6.670 (2 H, dd, *J* 10.9 and 6.0, H^3), 6.623 (2 H, d, *J* 6.0, H^4), 6.573 (2 H, d, *J* 6.0, H^1), 2.940 (2 H, s, C≡CH) and 2.753 (4 H, s, CH_2); δ_C(125.76 MHz) 188.96 (q, C=O), 143.58 (t), 132.80 (t), 132.59 (t), 131.99 (t), 131.66 (t), 129.83 (q), 126.45 (t), 114.54 (q), 85.45 (q, –C≡), 75.43 (t, ≡CH) and 33.01 (s, CH_2) (Found: C, 89.3; H, 6.0. $C_{23}H_{18}O$ requires C, 89.0; H, 5.85%).

1,5-Bis-(6-ethynylcyclohepta-1,3,5-trienyl)-2-methylpenta-1,4-dien-3-one 19

Aldol condensation of the ketone **18**[3] (234 mg, 1.18 mmol) and the aldehyde **15**[3] (274 mg, 1.90 mmol) followed by chromatography on alumina (4.2 × 6.7 cm) with hexane–ether (7:3) as the eluent afforded the unchanged aldehyde **15** (100 mg recovery). The later fractions eluted with hexane–ether (3:2) afforded the *ketone* **19** (220 mg, 58%) as yellow cubes, mp 85–87 °C (decomp.) (from hexane–ether); *m*/*z* 324 (M^+, 18%) and 115 (100) ($C_{24}H_{20}O$ requires M, 324.4); λ_{max}(THF)/nm 238

(ε 30 900), 241 (31 900) and 372.5 (15 400); ν_{max}/cm^{-1} 3233 (C≡CH), 2084 (C≡C), 1630 (C=O), 1604, 1593, 1564 (C=C) and 975 [(*E*)-HC=CH]; δ_H(400 MHz) 7.394 (1 H, d, *J* 15.3, H$^{B'}$), 7.138 (1 H, s, H^B), 6.935 (1 H, d, *J* 15.3, H$^{A'}$), 6.77–6.57 (6 H, m, 7-membered ring H), 6.557 (1 H, d, *J* 5.9, 7-membered ring H), 6.469 (1 H, d, *J* 6.2, 7-membered ring H), 2.992 (1 H, s, C≡CH), 2.899 (1 H, s, C≡CH), 2.774 (2 H, s, CH_2), 2.748 (2 H, s, CH_2) and 2.189 (3 H, s, Me); δ_C(100.40 MHz) 192.66 (q, C=O), 143.69 (t), 139.10 (t), 139.03 (q), 133.18 (t), 132.39 (t), 132.03 (t), 131.79 (t), 131.75 (t), 131.65 (t), 130.84 (t), 130.39 (t), 129.99 (q), 129.87 (q), 122.84 (t), 114.28 (q), 113.40 (q), 85.65 (q, –C≡), 85.60 (q, –C≡), 75.56 (t, ≡CH), 75.36 (t, ≡CH), 36.54 (s, CH_2), 33.51 (s, CH_2) and 14.24 (p, CH_3) (Found: C, 88.8; H, 6.3. $C_{24}H_{20}O$ requires C, 88.9; H, 6.2%).

1,7-Bis-(6-ethynylcyclohepta-1,3,5-trienyl)hepta-1,4,6-trien-3-one 21

Aldol condensation of the aldehyde **20**[3] (500 mg, 2.94 mmol) and the ketone **16**[3] (750 mg, 4.07 mmol) followed by chromatography on alumina (3.8 × 5.0 cm) with hexane–ether (7:3) as the eluent afforded the *ketone* **21** (415 mg, 42%) as yellow needles, mp 117–121 °C (decomp.) (from hexane–dichloromethane); *m*/*z* 336 (M$^+$, 4%) and 57 (100) ($C_{25}H_{20}O$ requires M, 336.4); λ_{max}(THF)/nm 244 (ε 32 900), 278sh (26 500) and 407 (34 000); ν_{max}/cm^{-1} 3292 and 3219 (C≡CH), 2084 (C≡C), 1654 and 1640 (C=O), 1600 (C=C) and 996 [(*E*)-HC=CH]; δ_H(500 MHz) 7.46–7.40 (2 H, m, H^B and H$^{B'}$), 6.81–6.56 (11 H, m), 6.394 (1 H, d, *J* 6.2), 2.938 (1 H, s, C≡CH), 2.903 (1 H, s, C≡CH) and 2.742 (4 H, s, CH_2); δ_C(125.76 MHz) 188.75 (q, C=O), 143.42 (t), 143.14 (t), 142.20 (t), 132.82 (t), 132.77 (t), 132.60 (t), 131.96 (t), 131.87 (t), 131.69 (t), 131.00 (q), 130.86 (t), 129.89 (q), 129.79 (t), 129.63 (t), 128.46 (t), 126.39 (t), 114.56 (q), 113.86 (q), 85.55 (q, –C≡), 85.45 (q, –C≡), 75.42 (t, ≡CH), 75.06 (t, ≡CH), 33.02 (s, CH_2) and 32.78 (s, CH_2) (Found: C, 89.0; H, 6.1. $C_{25}H_{20}O$ requires C, 89.25; H, 6.0%).

6-(6-Ethynylcyclohepta-1,3,5-trienyl)hexa-3,5-dien-2-one 22

Aq. NaOH (1.25 mol dm^{-3}; 4.6 cm^3) was added in one portion to a stirred solution of the aldehyde **20**[3] (260 mg, 1.53 mmol) in deoxygenated acetone (20 cm^3) at room temperature under argon. The solution was stirred for a further 1 h at room temperature. The reaction was terminated by addition of 5% aq. acetic acid (100 cm^3). Then the mixture was poured onto water and extracted with benzene. The extracts were washed with aq. $NaHCO_3$ and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.8 × 6.0 cm). The fractions eluted with 5% benzene in hexane afforded the *ketone* **22** (213 mg, 66%) as yellow needles, mp < 15 °C (from hexane–benzene); *m*/*z* 210 (M$^+$, 73%) and 152 (100) ($C_{15}H_{14}O$ requires M, 210.2); λ_{max}(THF)/nm 228 (ε 10 900), 274sh (27 500), 284 (33 600) and 372 (18 600); ν_{max}/cm^{-1} 3285 (C≡CH), 2085 (C≡C), 1661 (C=O), 1592 (C=C) and 992 [(*E*)-HC=CH]; δ_H(500 MHz) 7.220 (1 H, ddd, *J* 15.5, 8.6 and 1.6, H^B), 6.75–6.57 (5 H, m, H^C, H^D, H^2, H^3, and H^1 or H^4), 6.377 (1 H, d, *J* 6.2, H^4 or H^1), 6.268 (1 H, d, *J* 15.4, H^A), 2.890 (1 H, s, C≡CH), 2.724 (2 H, s, CH_2) and 2.293 (3 H, s, Me); δ_C(125.76 MHz) 198.26 (q, C=O), 143.35 (t), 141.88 (t), 132.67 (t), 131.78 (t), 130.90 (t), 130.78 (t), 129.68 (q), 128.32 (t), 128.06 (t), 113.89 (q), 85.43 (q, –C≡), 75.10 (t, ≡CH), 32.78 (s, CH_2) and 27.43 (p, CH_3) (Found: C, 85.8; H, 6.8. $C_{15}H_{14}O$ requires C, 85.7; H, 6.7%).

1,9-Bis-(6-ethynylcyclohepta-1,3,5-trienyl)nona-1,3,6,8-tetraen-5-one 23

Aldol condensation of the ketone **22** (540 mg, 2.57 mmol) and the aldehyde **20**[3] (400 mg, 2.35 mmol) followed by chromatography on alumina (3.2 × 4.0 cm) with hexane–ether (1:4) as the eluent afforded the *ketone* **23** (508 mg, 60%) as red needles, mp 125–130 °C (decomp.) (from hexane–benzene); *m*/*z* 363 [(M + 1)$^+$, 34%] and 154 (100) (FAB-MS) ($C_{27}H_{22}O$ requires M, 362.4); λ_{max}(THF)/nm 260.5 (ε 15 000), 275sh (14 200), 286sh (12 600) and 418 (20 800); ν_{max}/cm^{-1} 3286 and 3216 (C≡CH), 2081 (C≡C), 1648 and 1639 (C=O), 1603 (C=C) and 995 [(*E*)-HC=CH]; δ_H(500 MHz) 7.390 (2 H, m, H^B), 6.80–6.58 (10 H, m, H^C H^D, H^2, H^3 and H^4), 6.556 (2 H, d, *J* 15.2, H^A), 6.388 (2 H, d, *J* 6.2, H^1), 2.901 (2 H, s, C≡CH) and 2.740 (4 H, s, CH_2); δ_C(125.76 MHz) 188.67 (q, C=O), 142.94 (t), 142.09 (t), 132.76 (t), 131.87 (t), 131.02 (q), 130.83 (t), 129.73 (t), 129.51 (t), 128.51 (t), 113.85 (q), 85.54 (q, –C≡), 75.04 (t, ≡CH) and 32.79 (s, CH_2) (Found: C, 89.6; H, 6.3. $C_{27}H_{22}O$ requires C, 89.5; H, 6.1%).

7,8,9,10-Tetradehydro-1,6:11,16-dimethano[21]annulen-19-one 11. Typical procedure of the intramolecular oxidative coupling of diethynyl ketones

A solution of the ketone **17** (330 mg, 1.06 mmol) in pyridine–ether (3:1; 64 cm^3) was added dropwise during 2 h to a stirred solution of anhydrous copper(II) acetate (1.70 g) in pyridine–ether (3:1; 60 cm^3) at 50 °C. After being stirred for a further 30 min at 50 °C, the solution was cooled, poured onto 1 mol dm^{-3} HCl (500 cm^3) and extracted with benzene. The combined extracts were washed successively with 2 mol dm^{-3} HCl and aq. $NaHCO_3$ and dried. The residue obtained after removal of the solvent was chromatographed on alumina (3.2 × 7.0 cm). The fractions eluted with hexane–ether (2:3) afforded *compound* **11** (214 mg, 66%) as red needles, mp 185–187 °C (decomp.) (from hexane–dichloromethane); *m*/*z* 308 (M$^+$, 100%) ($C_{23}H_{16}O$ requires M, 308.3); λ_{max}(THF)/nm 218 (ε 37 000), 235sh (30 500), 292sh (22 700), 328 (50 200) and 338sh (49 300), and see Fig. 6; λ_{max}(TFA)/nm 267sh (ε 2500), 287 (4800), 306 (10 300), 333sh (12 400), 360sh (23 900), 380 (29 700), 462sh (13 300), 499 (15 400), 752 (2600), 879 (2600) and 892 (2500), and see Fig. 7; ν_{max}/cm^{-1} 2166 (C≡C), 1664 (C=O), 1598 (C=C) and 976 [(*E*)-HC=CH]; NMR data showed the presence of two isomers in the ratio 97:3. The major isomer **11a**: δ_H(500 MHz) 7.733 (2 H, d, *J* 15.7, H^A), 7.028 (2 H, d, *J* 15.7, H^B), 6.689 (2 H, dd, *J* 11.1 and 5.9, H^2), 6.610 (2 H, dd, *J* 11.1 and 5.9, H^3), 6.463 (2 H, d, *J* 5.9, H^1), 6.370 (2 H, d, *J* 5.9, H^4), 4.200 (2 H, d, *J* 12.4, H^b) and 2.049 (2 H, d, *J* 12.5, H^a), and see Fig. 1(a); δ_C(125.76 MHz) 188.07 (q, C=O), 138.71 (t), 132.31 (t), 131.41 (t), 130.72 (t), 130.56 (t), 129.30 (q), 129.12 (t), 113.33 (q), 86.58 (q, –C≡), 73.58 (q, –C≡) and 35.32 (s, CH_2); δ_H(500 MHz; CF_3CO_2D) 9.532 (2 H, d, *J* 15.5, H^A), 7.271 (2 H, d, *J* 15.5, H^B), 6.679 (2 H, dd, *J* 11.2 and 6.0, H^2), 6.679 (2 H, d, *J* 6.0, H^4), 6.606 (2 H, dd, *J* 11.2 and 6.0, H^3), 6.279 (2 H, d, *J* 6.0, H^1), 5.344 (2 H, d, *J* 13.0, H^b) and 3.093 (2 H, d, *J* 13.0, H^a), and see Fig. 1(b); δ_C(125.76 MHz; CF_3CO_2D) 191.90 (q, C=O), 151.93 (t), 141.26 (t), 138.91 (t), 134.38 (t), 133.68 (q), 131.63 (t), 128.04 (t), 119.47 (q), 86.72 (q, –C≡), 77.47 (q, –C≡) and 38.21 (s, CH_2).

The minor isomer **11c**: δ_H 7.141 (2 H, d, *J* 15.9, H^A or H^B), 6.970 (2 H, d, *J* 15.9, H^B or H^A) 6.832 (2 H, dd, *J* 11.3 and 5.8, H^3 or H^2), 6.775 (2 H, dd, *J* 11.3 and 5.8, H^2 or H^3), 6.567 (2 H, d, *J* 5.8, H^4 or H^1), 6.534 (2 H, d, *J* 5.8, H^1 or H^4), 3.549 (2 H, d, *J* 12.8, H^b) and 1.769 (2 H, d, *J* 12.8, H^a); δ_H(500 MHz; CF_3CO_2D) signals due to H^1–H^4 were not clearly identified. δ_H 7.71 (2 H, d, *J* 16, H^A or H^B), 7.38 (2 H, d, *J* 16, H^B or H^A), 3.88 (2 H, d, *J* 13, H^b) and 1.90 (2 H, d, *J* 13, H^a) (Found: C, 89.4; H, 5.4. $C_{23}H_{16}O$ requires C, 89.6; H, 5.2%).

7,8,9,10-Tetradehydro-18-methyl-1,6:11,16-dimethano[21]-annulen-19-one 12

Oxidative coupling of the ketone **19** afforded *compound* **12** in 43% yield as red cubes, mp 174–177 °C (decomp.) (from hexane–ether); *m*/*z* 322 (M$^+$, 100%) ($C_{24}H_{18}O$ requires M, 322.4); λ_{max}(THF)/nm 236.5 (ε 31 300), 251.5 (31 700), 267 (34 000), 289 (35 200) and 318 (36 400), and see Fig. 6; λ_{max}(TFA)/nm 255.5 (ε 19 500), 258.0 (18 200) and 283.5

(14 900); ν_{max}/cm^{-1} 2163 (C≡C), 1650 (C=O), 1582 (C=C) and 968 [(*E*)-HC=CH]; The ^{1}H NMR spectrum of compound **12** in $CDCl_3$ showed that it consists of two isomers in the ratio ~ 1 : 1. The isomer **12a**: δ_H(400 MHz) 7.946 (1 H, d, *J* 15.2, H$^{A'}$), 7.741 (1 H, s, H^B), 7.183 (1 H, d, *J* 15.5, H$^{B'}$), 6.906–6.318 (8 H, m), 4.110 (1 H, d, *J* 12.9, H^d), 3.972 (1 H, d, *J* 12.0, H^b), 2.349 (1 H, d, *J* 12.9, H^c), 2.050 (3 H, s, Me) and 2.032 (1 H, d, *J* 12.0, H^a).

The isomer **12b**: δ_H 7.424 (1 H, d, *J* 15.2, H$^{A'}$), 7.087 (1 H, d, *J* 15.5, H$^{B'}$), 6.926 (1 H, s, H^B), 6.906–6.318 (8 H, m), 3.554 (1 H, d, *J* 12.9, H^d), 3.417 (1 H, d, *J* 11.7, H^b), 2.153 (3 H, s, Me), 1.943 (1 H, d, *J* 12.9, H^c) and 1.654 (1 H, d, *J* 11.7, H^a), and see Fig. 2: δ_C(100.40 MHz) 192.74 (q, C=O), 191.24 (q, C=O), 143.63 (t), 142.39 (t), 139.76 (t), 139.03 (t), 138.69 (q), 138.49 (q), 132.46 (t), 132.31 (t), 132.20 (t), 132.17 (t), 131.92 (q), 131.81 (t), 131.76 (t), 131.56 (t), 130.23 (q), 130.03 (t), 129.85 (t), 129.82 (t), 129.45 (t), 129.08 (t), 128.66 (q), 126.62 (q), 126.26 (t), 125.88 (t), 125.34 (t), 125.17 (t), 123.52 (t), 121.77 (t), 113.59 (q), 113.11 (q), 109.93 (q), 109.47 (q), 90.56 (q), 90.15 (q), 89.51 (q), 88.98 (q), 76.45 (q), 76.14 (q), 73.11 (q), 72.80 (q), 43.08 (s, CH_2), 42.99 (s, CH_2), 35.98 (s, CH_2), 35.82 (s, CH_2), 13.36 (p, CH_3) and 13.30 (p, CH_3). The ^{1}H NMR spectrum of compound **12** in CF_3CO_2D could not be analysed owing to overlap of the signals with those of the decomposition products (Found: C, 89.2; H, 5.8. $C_{24}H_{18}O$ requires C, 89.4; H, 5.6%).

7,8,9,10-Tetradehydro-1,6:11,16-dimethano[23]annulen-19-one 13

Oxidative coupling of the ketone **21** gave a dark red liquid, which was chromatographed on alumina (3.8 × 4.0 cm). The fractions eluted with benzene were collected and concentrated. The residue was further purified by PLC (dichloromethane as developer). The fast moving, third band afforded *compound* **13** (34 mg, 8.3%) as red needles, mp 130–132 °C (decomp.) (from hexane–benzene); *m*/*z* 334 (M$^+$, 75%) and 289 (100) ($C_{25}H_{18}O$ requires M, 334.3); λ_{max}(THF)/nm 231.5 (ε 29 200), 281.5 (32 400), 295sh (30 600), 357 (40 000) and 439sh (6800), and see Fig. 6; λ_{max}(TFA)/nm 317.5 (ε 28 000), 412 (35 700), 650 (22 000), 868 (180) and 894.5 (620), and see Fig. 7; ν_{max}/cm^{-1} 2161 (C≡C), 1665 and 1646 (C=O), 1597 (C=C), 993 [(*E*)-HC=CH] and 697 [(*Z*)-H=CH]; The ^{1}H NMR spectrum of compound **13** at −30 °C in $CDCl_3$ showed the presence of two isomers in ~ 95:5 ratio. The major isomer **13a**: δ_H(500 MHz; −30 °C) 7.115 (1 H, d, *J* 16.1, H^B), 7.108 (1 H, dd, *J* 14.9 and 11.0, H$^{B'}$), 6.951 (1 H, dd, *J* 11.0 and 6.2, H^2), 6.942 (1 H, dd, *J* ~ 11 and ~ 6, 7-membered ring H), 6.849 (1 H, dd, *J* 11.0 and 6.2, 7-membered ring H), 6.81–6.76 (3 H, m, 7-membered ring H), 6.716 (1 H, d, *J* 6.0, H^1), 6.684 (1 H, d, *J* 15.6, H$^{D'}$), 6.482 (1 H, d, *J* 6.1, H^8, H^4 or H^5), 6.413 (1 H, dd, *J* 15.6 and 11.1, H$^{C'}$), 6.375 (1 H, d, *J* 14.9, H$^{A'}$), 6.309 (1 H, d, *J* 16.1, H^A), 3.354 (1 H, *J* 12.6, H^d), 3.204 (1 H, d, *J* 12.5, H^b), 1.400 (1 H, d, *J* 12.7, H^a) and 1.274 (1 H, d, *J* 12.6, H^c), and see Fig. 3(a); δ_C(125.76 MHz; −30 °C) 189.87 (q, C=O), 141.38 (t), 138.40 (t), 137.40 (t), 134.60 (t), 133.64 (t), 133.27 (t), 133.08 (t), 132.70 (t), 132.40 (t), 131.40 (t), 130.15 (t), 129.76 (t), 128.49 (t), 127.95 (q), 127.45 (t), 126.40 (q), 110.43 (q), 109.71 (q), 84.48 (q, –C≡), 83.22 (q, –C≡), 71.69 (q, –C≡), 71.31 (q, –C≡), 33.50 (s, CH_2) and 31.84 (s, CH_2).

The species **13a'**: δ_H(500 MHz; CF_3CO_2D) 9.307 (1 H, d, *J* 14.4, H^B), 7.944 (1 H, d, *J* 11.4, H$^{A'}$), 7.753 (1 H, d, *J* 14.3, H$^{D'}$), 7.78–7.36 (8 H, m, 7-membered ring H), 7.431 (1 H, t, *J* 12.2, H$^{B'}$), 5.313 (1 H, t, *J* 13.3, H$^{C'}$), 3.887 (1 H, d, *J* 14.4, H^A), 1.611 (1 H, d, *J* 12, H^d), 1.299 (1 H, d, *J* 12, H^b), 0.914 (1 H, d, *J* 12, H^a) and 0.776 (1 H, d, *J* 12, H^c), and see Fig. 3(b); δ_C(125.76 MHz; CF_3CO_2D) 185.46 (q, C=O), 161.16 (t), 154.26 (t), 149.94 (t), 143.85 (t), 143.46 (t), 139.01 (t), 137.11 (t), 135.72 (t), 133.98 (q), 133.79 (t), 133.45 (t), 132.51 (t), 130.99 (t), 129.98 (t), 128.02 (q), 116.53 (q), 115.82 (q), 113.97 (t), 93.67 (q, –C≡), 92.98 (q, –C≡), 81.10 (q, –C≡), 78.20 (q, –C≡), 34.92 (s, CH_2) and 34.75 (s, CH_2) (Found: C, 89.5; H, 5.5. $C_{25}H_{18}O$ requires C, 89.8; H, 5.4%).

7,8,9,10-Tetradehydro-1,6:11,16-dimethano[25]annulen-21-one 14 and 7,8,9,10,32,33,34,35-octadehydro-21,46-dihydro-1,6:11,16:26,31:36,41-tetramethano[50]annulene-21,46-dione 24

This reaction was performed using a high-dilution apparatus. A solution of the ketone **23** (1.44 g, 3.98 mmol) in a mixture of pyridine (140 cm^3) and ether (48 cm^3) was added dropwise during 6 h to a refluxing, stirred solution of copper(II) acetate monohydrate (14.6 g) in a mixture of pyridine (310 cm^3) and ether (278 cm^3) at 60 °C. After being refluxed and stirred for a further 1.5 h at 60 °C, the mixture was worked up as for the isolation of compound **11**. The product was chromatographed on alumina (3.2 × 6.5 cm). The initial fractions eluted with benzene afforded compound **14** (12 mg, 0.8%) as orange needles, mp 180–184 °C (decomp.) (from hexane–dichloromethane); *m*/*z* 360 (M$^+$, 90%) and 119 (100) ($C_{27}H_{20}O$ requires M, 360.4); λ_{max}(THF)/nm 259 (ε 38 600), 282 (37 000), 292 (37 900), 337sh (37 800), 350 (40 000), 372sh (26 400) and 416sh (6700), and see Fig. 6; λ_{max}(TFA)/nm 440sh (ε 23 000), 495 (31 000) and 755 (12 600), and see Fig. 7; ν_{max}/cm^{-1} 2183 (C≡C), 1647 (C=O), 1588 (C=C), 989 and 983 [(*E*)-HC=CH] (Found: C, 89.4; H, 5.7. $C_{27}H_{20}O$ requires C, 90.0; H, 5.6%). Attempts to improve the elemental analysis failed. The ^{1}H NMR spectrum of compound **14** in $CDCl_3$ showed that it consisted of two isomers in ~ 3:2 ratio. The major isomer **14a**: δ_H(400 MHz) 8.891 (2 H, dd, *J* 15.5 and 11.4, H^B), 6.60–6.45 (6 H, H^2, H^3 and H^1 or H^4), 6.430 (2 H, d, *J* 15.5, H^A), 6.388 (2 H, t, *J* 11.1, H^C), 6.213 (2 H, d, *J* 6.1, H^4 or H^1), 5.918 (2 H, d, *J* 11.1, H^D) and 3.319 (4 H, s, CH_2).

The minor isomer **14c**: δ_H 7.466 (1 H, dd, *J* 14.7 and 11.2), 7.219 (1 H, dd, *J* 14.6 and 11.6), 7.156 (1 H, dd, *J* 14.6 and 11.0), 7.104 (1 H, d, *J* 15.0), 3.797 (1 H, d, *J* 12.6), 3.550 (1 H, d, *J* 13.6), 2.505 (1 H, d, *J* 13.6) and 1.824 (1 H, d, *J* 12.6). The other signals are obscured by overlap with the major isomer signals; and see Fig. 4(a).

The species **14c'**: δ_H(400 MHz; CF_3CO_2D) 8.743 (1 H, dd, *J* 14.1 and 12.8, H$^{B'}$), 8.650 (1 H, dd, *J* 14.3 and 12.2, H^C), 8.496 (1 H, d, *J* 14.1, H^A), 8.045 (1 H, dd, *J* 13.7 and 12.0, H^B), 7.096 (1 H, t, *J* 12.0, H$^{C'}$), 7.062 (1 H, d, *J* 15.0, H^D), 6.853 (1 H, d, *J* 14.5, H$^{A'}$), 6.85–6.45 (8 H, m, 7-membered ring H), 6.056 (1 H, d, *J* 11.1, H$^{D'}$), 4.791 (1 H, d, *J* 12.8, H^b), 4.508 (1 H, d, *J* 14.1, H^d), 3.402 (1 H, d, *J* 14.1, H^c) and 2.484 (1 H, d, *J* 12.8, H^a), and see Fig. 4(b); δ_C(100.40 MHz; CF_3CO_2D) 188.60 (q, C=O), 163.00 (q), 161.25 (q), 159.75 (q), 158.71 (q), 143.40 (t), 139.59 (t), 138.59 (t), 138.39 (t), 137.19 (t), 134.95 (t), 134.62 (t), 134.31 (t), 133.34 (t), 132.66 (t), 132.44 (t), 128.45 (t), 123.03 (t), 121.56 (t), 119.99 (t), 118.83 (t), 87.39 (q, –C≡), 87.26 (q, –C≡), 76.42 (q, –C≡), 74.76 (q, –C≡), 39.22 (s, CH_2) and 36.30 (s, CH_2).

The later fractions eluted with benzene–dichloromethane (7:3) afforded the dimeric products of compound **23** as a red solid. This solid was subjected to PLC (dichloromethane as developer). The fast moving, second band afforded the geometrical isomer of compound **24** (9 mg, 0.6%) as red microcrystals, mp 149–152 °C (decomp.) (from hexane–benzene); *m*/*z* 723 [(M + 3)$^+$, 2%] and 460 (15%) (FAB-MS) ($C_{54}H_{40}O_2$ requires M, 720.4); λ_{max}(THF)/nm 253 (ε 47 300), 284sh (41 300) and 399 (38 100); ν_{max}/cm^{-1} 2174 (C≡C), 1639 (C=O), 1601 (C=C), 997 [(*E*)-HC=CH] and 742 [(*Z*)-HC=CH]. Analytical and NMR spectral data could not be obtained because of a shortage of material.

The fast moving, third band afforded *compound* **24** (29 mg, 1.1%) as orange microcrystals, mp 170–178 °C (decomp.) (from hexane–benzene); *m*/*z* 138 (100), 154 (95), 307 (40) and 460 (5%) (FAB-MS) ($C_{54}H_{40}O_2$ requires M, 720.4); λ_{max}(THF)/nm 262.5 (ε 40 100), 307sh (34 000), 361.5 (32 800) and 406 (34 900); λ_{max}(TFA)/nm 259 (ε 41 300), 334 (26 000), 387 (23 300), 462

Table 1 Crystal data of compound **11** and parameters for data collection, structure determination and refinement

Empirical formula	$C_{23}H_{16}O$
Formula weight	308.38
Crystal dimension (mm)	0.1, 0.15, 0.95
Crystal system	triclinic
Space group	$P\bar{1}$ (#2)
a (Å)	13.160(3)
b (Å)	15.942(3)
c (Å)	7.918(2)
α (°)	97.41(2)
β (°)	92.39(2)
γ (°)	93.50(2)
V (Å^3)	1642.3(6)
Z	4
D_c (g cm^{-1})	1.247
$F(000)$	648
μ(Mo-$K\alpha$) (cm^{-1})	0.75
Temp. (°C)	22 ± 1
Scan width (°)	1.42 ± 0.30 tan θ
$2\theta_{max}$ (°)	55.0
No. of reflections measured	
Total	5349
Unique	5018
No. of refinement variables	428
Final R; R_w	0.063; 0.045

(22 200) and 658 (36 300); ν_{max}/cm^{-1} 2174 (C≡C), 1641 (C=O), 1601 (C=C) and 994 [(*E*)-HC=CH]; δ_H(500 MHz) 7.328 (4 H, dd, *J* 15.2 and 9.8, H^B), 6.76–6.65 (16 H, m, H^C, H^D, H^2 or H^3, H^1 or H^4), 6.576 (4 H, dd, *J* 11.2 and 6.2, H^3 or H^2), 6.491 (4 H, d, *J* 15.2, H^A), 6.342 (4 H, d, *J* 6.4, H^4 or H^1) and 2.760 (8 H, s, CH_2); δ_C(125.76 MHz) 188.47 (q, C=O), 142.74 (t), 141.89 (t), 134.58 (t), 132.48 (t), 131.03 (q), 130.68 (t), 129.93 (t), 129.78 (t), 128.87 (t), 113.39 (q), 84.48 (q, –C≡), 72.43 (q, –C≡) and 32.61 (s, CH_2); δ_H(500 MHz; CF_3CO_2D) 7.946 (4 H, dd, *J* 14.0 and 11.8, H^B), 7.194 (4 H, d, *J* 14.6, H^D), 6.965 (4 H, dd, *J* 14.5 and 11.8, H^C), 6.95–6.84 (12 H, m, H^1 or H^4, and H^2 and H^3), 6.758 (4 H, d, *J* 6.0, H^4 or H^1), 6.566 (4 H, d, *J* 14.0, H^A) and 2.900 (8 H, s, CH_2) (Found: C, 89.9; H, 5.8. $C_{27}H_{20}O$ requires C, 90.0; H, 5.6%).

X-Ray crystallography

Crystals of compound **11** were grown from dichloromethane–hexane. The crystal data and parameters for data collection, structural determination and refinement are summarized in Table 1. Diffraction data were collected on a Rigaku AFC7R diffractometer and calculations were performed using the teXsan program.[15] The structure was solved by direct methods followed by full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic. Reflection data with $|F_o| > 3\sigma(F_o)$ were used. The function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$ where $\omega = [\sigma^2(F_o)]^{-1}$.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

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* For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

References

1 (*a*) P. J. Garratt, *Aromaticity*, Wiley, New York, 1986, p. 173; (*b*) J. Ojima, K. Wada and M. Terasaki, *J. Chem. Soc., Perkin Trans. 1*, 1982, 51.
2 T. M. Cresp and M. V. Sargent, *Top. Curr. Chem.*, 1975, **57**, 111; A. T. Balaban, M. Banciu and V. Ciorba, *Annulenes, Benzo-, Hetero-, Homo-Derivatives, and their Valence Isomers*, CRC Press, Florida, 1987, vol. 3, p. 81.
3 H. Higuchi, S. Kiyoto, C. Sakon, N. Hiraiwa, K. Asano, S. Kondo, J. Ojima and G. Yamamoto, *Bull. Chem. Soc. Jpn.*, in the press.
4 Part of this work has been reported in preliminary form; H. Higuchi, S. Kiyoto, C. Sakon, N. Hiraiwa, K. Asano, J. Ojima, K. Inoue and G. Yamamoto, *Chem. Lett.*, 1994, 2291.
5 P. D. Howes, E. LeGoff and F. Sondheimer, *Tetrahedron Lett.*, 1972, 3695.
6 T. M. Cresp, J. Ojima and F. Sondheimer, *J. Org. Chem.*, 1977, **42**, 2130.
7 J. Ojima, Y. Shiroishi, K. Wada and F. Sondheimer, *J. Org. Chem.*, 1980, **45**, 3564.
8 N. Darby, T. M. Cresp and F. Sondheimer, *J. Org. Chem.*, 1977, **42**, 1960.
9 E. Vogel, J. Sombrock and W. Wagemann, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 564.
10 G. Yamamoto, H. Higuchi, H. Yamamoto and J. Ojima, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2388.
11 G. Yamamoto, H. Higuchi, H. Yamamoto and J. Ojima, *Tetrahedron Lett.*, 1991, **32**, 5129; *J. Chem. Soc., Perkin Trans. 2*, 1982, 479.
12 J. Ojima, Y. Nakagawa, K. Wada and M. Terasaki, *J. Chem. Soc., Perkin Trans. 1*, 1982, 43.
13 J. Anthony, C. B. Knobler and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 406.
14 See P. J. Garratt and K. Grohmann, in Houben-Weyl, *Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1972, vol. V, Id, pp. 533–535.
15 teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 and 1992).

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