Synthesis and Properties of Methano Bridged Tetradehydro-[18]annulene, -[20]annulene, -[22]annulene, -[24]annulene, and the Related [1,3]Cyclophanpolyenediyne Compounds

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The title annulenes (4a—d) have been synthesized by a Wittig reaction of cyclohepta-1,3,5-triene-1,6-dicarbaldehyde (1a) or its vinylogous dialdehydes (1b—d) with 3-methylpent-2-en-4-ynyltriphenylphosphonium bromide (2), followed by intramolecular oxidative coupling of the resulting acyclic compounds. They proved to be diatropic or paratropic, depending on the number of peripheral π-electrons. The related [1,3]cyclophanpolyenediynes (11), (14), (17), (19), (21), and (23) were prepared by a double Wittig reaction of 3-methylpent-2-en-4-ynal (8) and/or its vinylogous aldehydes (9) and (10), with 1,3-bis(triphenylphosphoniomethyl)benzene dibromide (7), followed by intramolecular oxidative coupling of the resulting acyclic compounds. Their properties are compared, on the basis of ¹H n.m.r. and electronic spectral results, with those of tetradehydromethanoannulenes.

Although many carbocyclic annulenes are known,[1] there are few monocyclic annulenes with a 20—30 membered ring size, such compounds usually being unstable compared with those having fewer-membered rings owing to increased vibration of the molecular perimeter along with increasing ring size. A number of multi-bridged annulenes have, however, been prepared and an extensive review of their properties has appeared.[2] Bearing these facts in mind, we aimed to provide compounds from which theoretical[3] predictions might be drawn concerning the delocalization of π-electrons in macrocyclic rings (20—30 membered rings). For this purpose, we chose the tetradehydromethanoannulenes (4a—d), which were expected to have both a rather rigid perimeter and to exhibit slight perturbation with respect to π-electron conjugation. We report here a simple, and apparently general, new synthesis of tetradehydroannulenes (4a—d),[4] which formally have a methano bridge between the 1 and 6 sites, and a 1,3-diacetylene linkage on the annulene perimeter.

Also, the related [1,3]cyclophanpolyenediynes (11), (14), (17), (19), (21) and (23) having a molecular perimeter similar to that of the tetradehydroannulenes (4a—d), have been prepared in order to examine how for cyclopolyenediynes conjugation differs for cycloheptatriene-containing as compared with benzene-containing systems.

Results and Discussion

Synthesis.—The annulenes (4a—d) were synthesized according to the reaction sequence, illustrated in the Scheme. The

starting material was cyclohepta-1,3,5-triene-1,6-dicarbaldehyde (1a),[5] which by Wittig condensation with 1.3 molar equiv. of [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide (5)[6] and lithium methoxide in N,N-dimethylformamide at 75 °C, followed by hydrolysis with dilute hydrochloric acid in tetrahydrofuran at room temperature gave the homologous vinylogue (1b). The bis-vinylogue (1c) was similarly prepared from the dicarbaldehyde (1a), employing 8 equiv. of the salt (5) and lithium ethoxide in N,N-dimethylformamide. A repeat of this reaction for the dicarbaldehyde (1b) under conditions identical with those for the preparation of (1c) from (1a), gave rise to the higher vinylogue (1d). The yields of these condensations from lower homologues were 60—85%. Although Sondheimer et al. have reported an unsuccessful result,[7] we were able to prepare 3-methylpent-2-en-4-ynyltriphenylphosphonium bromide (2) from 5-bromo-3-methylpent-3-en-1-yne[8] via 3-methylpent-2-en-4-yn-1-ol (kindly made available to us by Hofmann-La Roche, Basel) and triphenylphosphane according to the reported procedure.[9]

First, Wittig reaction of the dicarbaldehyde (1a) and the salt (2) was carried out employing ethanolic lithium ethoxide as a base in N,N-dimethylformamide; however the only material identified was a single condensation product, the carbaldehyde (6). When Wittig reactions between the dicarbaldehydes (1a—d) and the salt (2) were carried out with butyl-lithium in tetrahydrofuran at −70 to −65 °C, the corresponding acyclic compounds (3a—d), respectively, were obtained in 5—40% yields. Although the stereoisomeric products from these reactions were not followed up, *trans*-configurations for the newly


Scheme.

(1a)   (5)   (1b)   (1d)

(1c)

(6)   (3a)   (4a)   (4b)

(3b)   (3c)   (4c)

(4d)
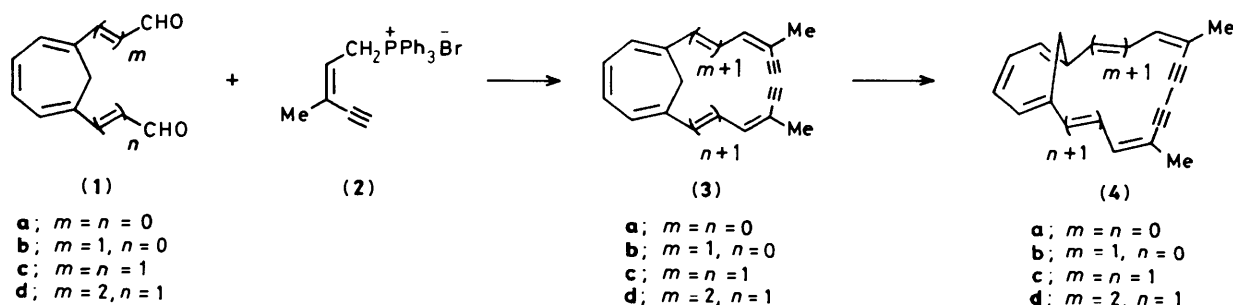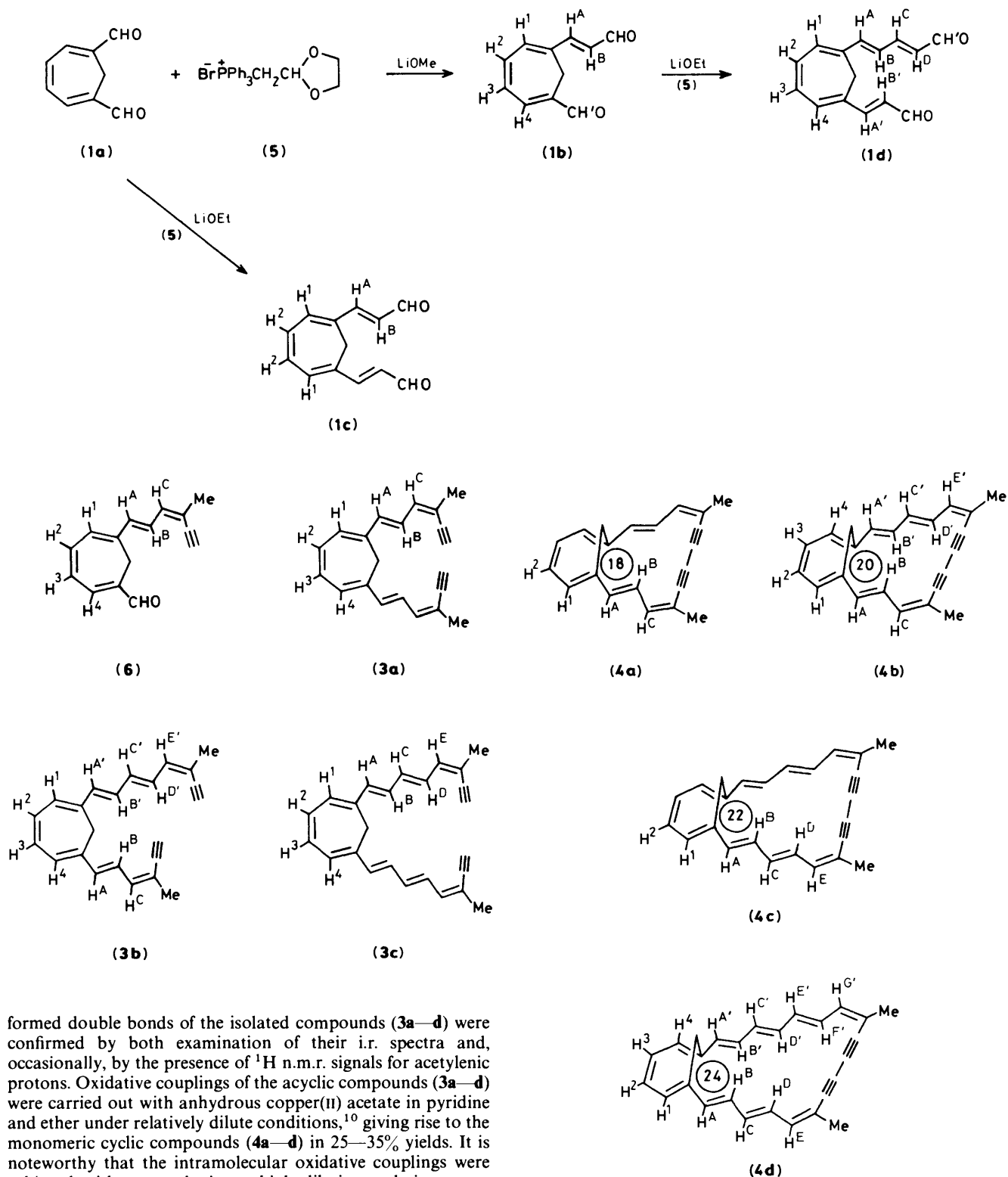
formed double bonds of the isolated compounds (3a—d) were confirmed by both examination of their i.r. spectra and, occasionally, by the presence of [1]H n.m.r. signals for acetylenic protons. Oxidative couplings of the acyclic compounds (3a—d) were carried out with anhydrous copper(II) acetate in pyridine and ether under relatively dilute conditions,[10] giving rise to the monomeric cyclic compounds (4a—d) in 25—35% yields. It is noteworthy that the intramolecular oxidative couplings were achieved without employing a high dilution technique, presumably because of the presence of 1,6-methano bridge in the acyclic polyenes (3a—d). Tetradehydromethano-[18]annulene (4a), -[20]annulene (4b), -[22]annulene (4c), and -[24]annulene (4d), so obtained, formed stable, deep coloured crystals with a metallic lustre. Further, they were thermally stable when compared with the corresponding, monocyclic annulenes and dehydroannulenes,[1] presumably as a result of the rigidity of the molecular skeleton arising from a methano bridge and a 1,3-diacetylenic linkage.

The [1,3]cyclophanpolyenediyne derivatives (11), (14), (17), (19), (21), and (23) were prepared by a double Wittig reaction between 1,3-bis(triphenylphosphoniomethyl)benzene dibromide (7),[11] with 1 or 2 molar equiv. each of the aldehyde (8)[12] and its vinylogous aldehydes (9) and (10),[13] followed by oxidative coupling of the resulting acyclic compounds. The preparation of the lowest member (11) has been reported pre-

(7)

(8)

(9)

(10)

(11)
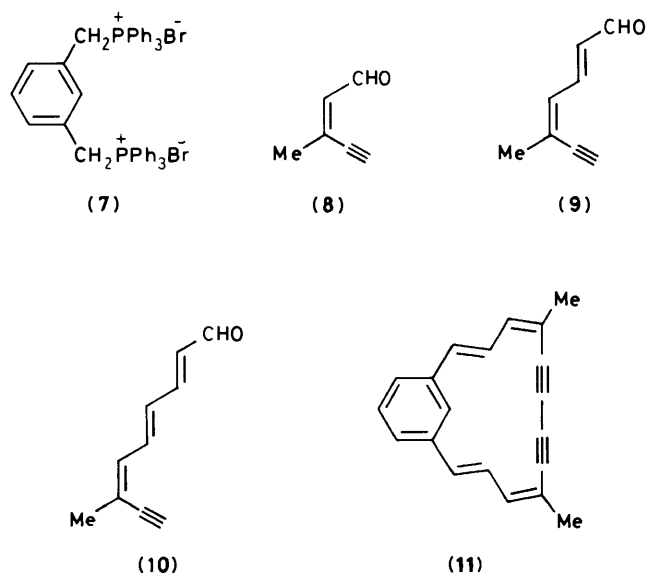
viously.[14] The reaction of the salt (7), (2Z)-3-methylpent-2-en-4-ynal (8),[12] and (2E,4Z)-5-methylhepta-2,4-dien-6-ynal (9)[13] gave the acyclic di-*trans* isomer (13) and its stereoisomers, along with compounds (12),[14] (16) (see below), and their isomers. Intramolecular oxidative coupling, as before, of compound (13) gave the monomeric cyclic compound (14) (7.6% yield). Similarly, reaction of the salt (7) and 2 molar equiv. of the aldehyde (9), gave the mono-*cis* (15) (20%) and the di-*trans* isomer (16) (31% yield). Oxidation of (15) gave the cyclic mono-*cis* isomer (17′) and the di-*trans* isomer (17) in 8.7 and 8.0% yields, respectively, while the di-*trans* isomer (16) gave only the cyclic di-*trans* isomer (17) in 11% yield. Thus a configurational change occurred during the coupling reaction, as has been reported in the synthesis of benzannulenes[14] and annulenones.[15] Reaction of the salt (7), the aldehyde (8), and (2E,4E,6Z)-7-methylnona-2,4,6-trien-8-ynal (10)[13] gave the acyclic di-*trans* isomer (18) in 22% yield, along with (12) and (20). Oxidation of (18) gave the mono-*cis* isomer (19) in 3.3% yield. The reaction of (7), (9), and (10) gave the di-*trans* isomer (20) in 38% yield, along with the acyclic compounds (16) and (22). Oxidation of (20) gave the cyclic di-*trans* isomer (15) in 1.8% yield. The reaction of (7) and (10) gave the acyclic di-*trans* isomer (22) in 9.7% yield. Oxidation of (22) gave the cyclic mono-*cis* isomer (23) (24% yield).

[1]H N.m.r. Spectra.—The [1]H n.m.r. chemical shifts of olefinic, methylene, and methyl protons of the tetradehydroannulenes (4a—d) are listed in Table 1, together with those of the corresponding acyclic compounds (3a—d). Individual assignments were made on the basis of multiplicities and coupling constants given in the Experimental section, and were further clarified by decoupling experiments where necessary. An assignment of the protons in the spectrum of (4d) was made from examination of its two-dimensional spectrum taken on a Brucker WM-360 spectrometer.

Comparison of the [1]H n.m.r. chemical shifts of the various protons of the tetradehydroannulenes (4a) and (4c) with those of the corresponding acyclic compounds (3a) and (3c), indicates that these annulenes (4a) and (4c) are diatropic, as might be expected of 18π- and 22π-electron systems, respectively. This follows from the fact that the outer protons (including methyl protons) in (4a) and (4c) resonate at lower field than the corresponding protons in (3a) and (3c), respectively, whereas the inner protons (including methylene protons) resonate at higher field.

The [1]H n.m.r. spectra of the tetradehydroannulenes (4a—d) are presented in Figure 1. It is evident that in the spectra of (4a) and (4c) the inner protons resonate at higher field than the outer protons, while in the spectra of (4b) and (4d) the inner protons resonate at lower field than the outer protons. This confirms the indicated conformations for the annulenes (4a—d) and shows that the above-described alternation of the ring currents in (4a—d) can be deduced without having to make comparisons with the corresponding acyclic models. The simplest test for the nature of the ring currents in (4a—d) is provided by the chemical shifts of the methyl and the methylene protons, since these must always be external and internal, respectively, and can readily be recognized. The alternation of the methyl and the methylene proton resonances between the [4n + 2]annulenes (4a) and (4c) (relatively low- and high-field, respectively) and the [4n]annulenes (4b) and (4d) (relatively high- and low-field, respectively) confirms the diatropicity of the former and the paratropicity of the latter. Also, comparison of the chemical-shift differences between the olefinic inner and outer protons or of the chemical shifts of the methylene protons indicates that the diatropicity falls off quite considerably in the sequence (4a) > (4c), while the paratropicity falls off in the order (4b) > (4d). Both the diamagnetic ring current effect in the [4n + 2]π-electron system and the paramagnetic ring current effect in [4n]π-electron system therefore become less as the ring size increases. Thus, although the annulenes (4a—d) have both a methano bridge and a 1,3-diacetylene unit the above-described pattern of behaviour seems to reflect an increasing flexibility of the tetradehydroannulene perimeter with an increase in ring size.

Since from the spectrum (Figure 1) of the [20]annulene (4b), the olefinic $H^{A'}$ and $H^{B'}$ protons are seen to resonate in the usual range, it seems that, in contrast to the other protons of (4b) and the olefinic protons in (4a), (4c), (4d) they are unaffected by the presence of a ring current. This agrees with the expectations resulting from an inspection of a Dreiding molecular model which predicts that for the molecular conformation indicated for (4b) the $CH^{A'}{=}CH^{B'}$ function would be out of the molecular plane.

Variable-temperature [1]H n.m.r. spectra of (4a—d) were run at 90 MHz over the range −60 to 60 °C, the results of which, summarized in Table 2, show all the spectra of (4a—d) to be essentially temperature-independent, ruling out any conformational change for (4a—d) between these temperatures. However with decreasing temperature the resonances of the inner (including methylene protons) and the outer (including methyl protons) protons of the [18]annulene (4a) and the [22]annulene (4c) move to a slightly higher and lower field, respectively, whereas the resonances of the inner and outer protons of the [20]annulene (4b) and the [24]annulene (4d) move to a slightly lower and higher field, respectively. This reflects the higher planarity at lower temperature which these annulenes (4a—d) have. Thus, it is rather surprising that the resonances of the bridged methylene protons in (4a—d) appear as a singlet between these temperatures, in contrast to those of multi-bridged annulenes,[2] in which the bridged methylene protons usually appear as two doublets even at room temperature. This phenomenon may be attributable to the rigidity of the molecular skeleton in these compounds which results from the presence of a methano bridge and a 1,3-diacetylene linkage in the molecular perimeter of each.

Judging from the tropicity of molecules carrying a 1,3-diacetylenic linkage on their molecular perimeter and by examining the lowfield shifts of the inner protons in paratropic molecules such as the tetradehydroannulenes (4a) and (4d) and 1,2,3,4-tetradehydroannulenones,[16] it would appear that some contribution arising from the local anisotropic effect of a 1,3-diacetylene linkage, cannot be neglected.[17] In order to estimate

(12)

+

(7) + (8) + (9) ⟶

(13)

+ (16)

(14)

(15)

(17')

(7) + (9) ⟶

+

(16)

(17)
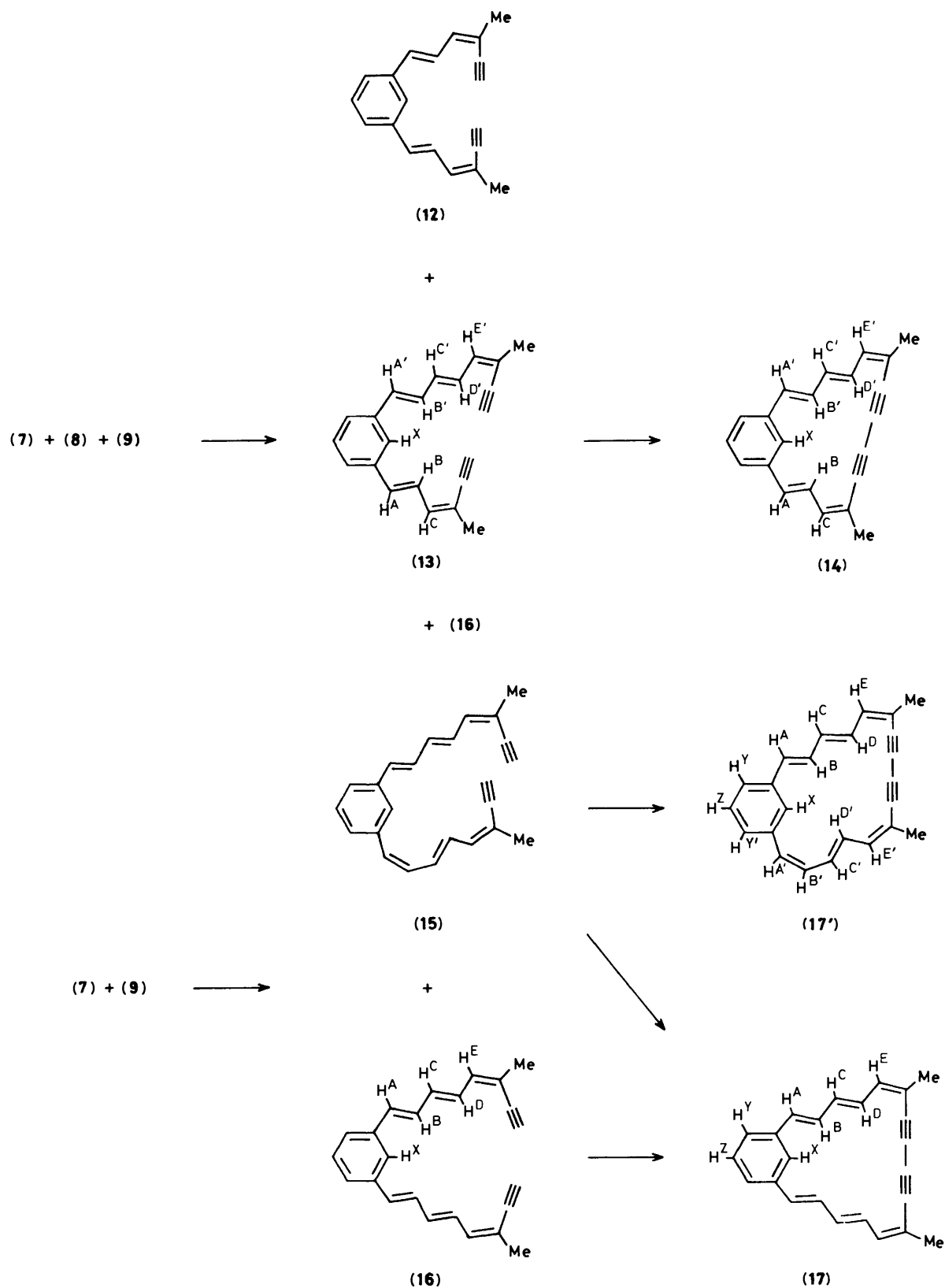
the effect in practice, the [1,3]cyclophanpolyenediyne deriv-
atives (11), (14), (17), (19), (21), and (23) were considered to be
appropriate model compounds, since they are not fully con-
jugated molecules and therefore do not induce a ring current.

The ¹H n.m.r. spectra of compounds (11), (14), (17), (19), (21),

and (23) are illustrated in Figure 2. It is observed that the inner
protons always resonate at lower field than the outer protons of
the large rings, and the degree of the lowfield shifts of the inner
protons is usually larger in the formally symmetrical derivatives
(11), (17) than the formally unsymmetrical derivatives (14), (21),

(12)

+

(7) + (8) + (10) ⟶

(18)

⟶

(19)

+ (12) + (22)

(7) + (9) + (10) ⟶

(20)

⟶

(21)

+ (16) + (22)

(7) + (10) ⟶

(22)

⟶

(23)
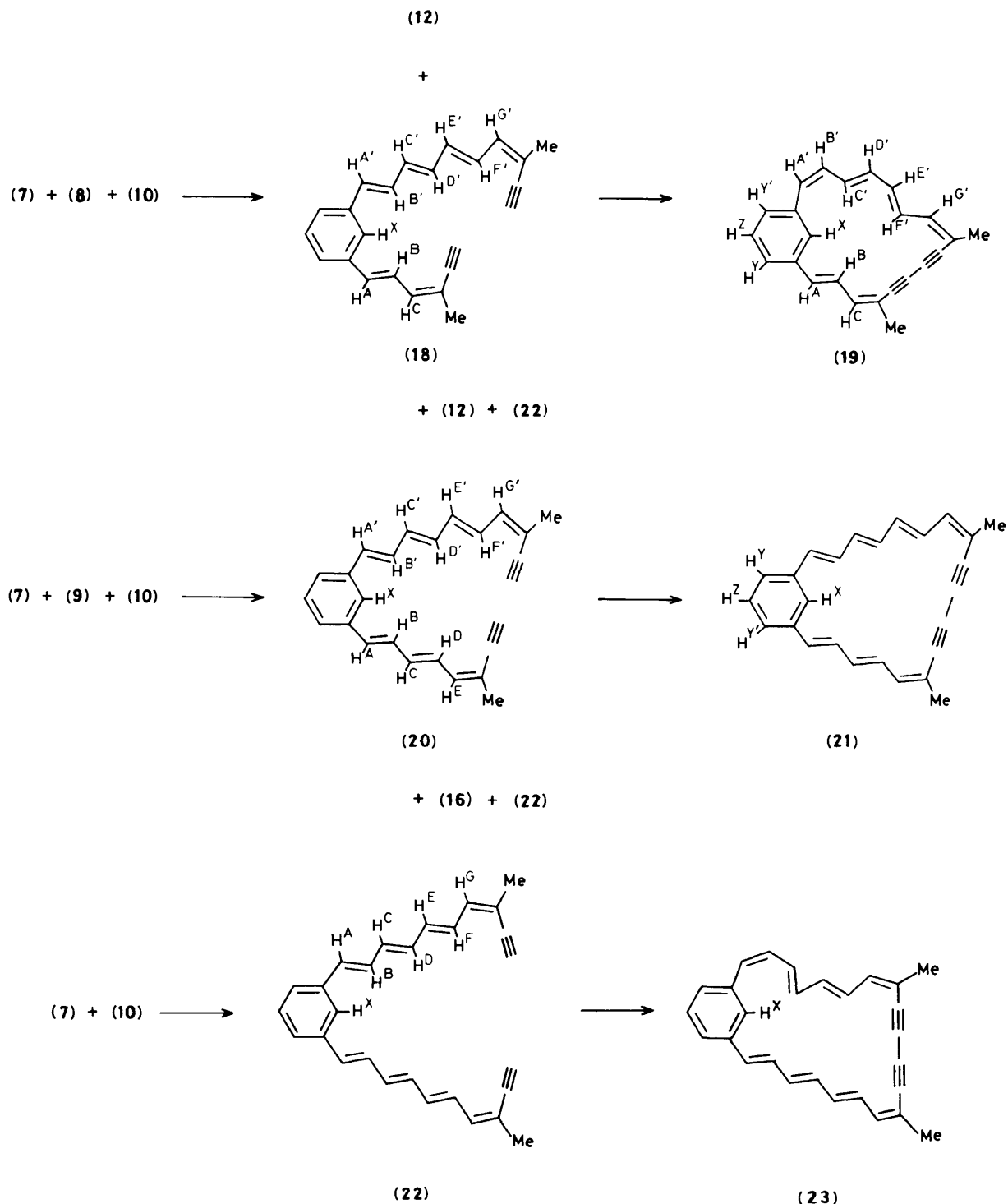
and (23). The lowfield shifts of the inner protons, particularly of the H^X protons, which are also affected by the anisotropic effect of the benzene ring, decrease with increasing ring size in the derivatives (11), (14), (17), (19), (21), and (23), i.e. as the H^X proton is further from the 1,3-diacetylene function. This observation shows that the local anisotropic effect of the 1,3-diacetylene function causes the resonances of the olefinic inner protons to shift to lower field. Accordingly, it is considered that in the spectra of the paratropic annulenes (4b) and (4d) (Figure 1) the local anisotropic effect contributes to the lowfield shifts of inner protons to some extent.

Electronic Spectra.—The electronic absorption spectra of the tetradehydroannulenes (4a—d) are illustrated in Figure 3. The spectra of the annulenes (4a) and (4c) exhibit three main bands characteristic of the $[4n + 2]\pi$-annulenes and dehydroannulenes.[1] In contrast, the spectra of the annulenes (4b) and (4d) show rather broadening absorption curves, as recognized in the spectra of the $[4n]\pi$-annulenes and dehydroannulenes.[1]

The absorption maxima of these tetradehydroannulenes (4a—d) and the [1,3]cyclophanpolyenediynes (11), (14), (17), (19), (21), and (23) are listed in Table 3, together with the absorption wavelengths of the main maxima of the tetra-

Table 1. The ^{1}H n.m.r. parameters of compounds (**3a—d**) and tetradehydroannulenes (**4a—d**) in CDCl$_3$ at 200 or 270 MHz (τ values)

Compd.	H^A	H$^{A'}$	H^B	H$^{B'}$	H^C	H$^{C'}$	H^D	H$^{D'}$	H^E	H$^{E'}$	H$^{F'}$	H$^{G'}$
(3a)	3.61		2.85		3.62							
(4a)	1.95		7.97		2.08							
(3b)	3.59	3.57	2.85	3.14	(3.58————	——3.73)		3.07		(3.58—3.73)		
(4b)	4.41	2.71	0.35	2.20	4.27	3.94		0.25		4.06		
(3c)	3.60		3.24		3.62		3.14		3.63			
(4c)	2.50		6.22		2.56		6.14		2.50			
(3d)	(3.08——)											
(4d)	4.21	4.06	1.32	1.43	4.29	4.09	1.14	1.55	4.17	4.26	0.76	3.94

Compd.	H^1	H^4	H^2	H^3	CH$_2$	Me
(3a)	(3.90————3.94)		(3.43————3.47)		7.15	8.05
(4a)	————————2.56————————				10.45	7.47
(3b)	(3.58————3.73)		(3.39————3.43)		7.24	8.04
(4b)	(4.16————4.22)		(4.01————4.11)		5.36	8.44
(3c)	(3.70————3.74)		(3.42————3.46)		7.28	8.05
(4c)	(2.97————3.01)		(2.81————2.85)		9.19	7.64
(3d)	(————————————————3.90)				7.29	8.01, 8.04
(4d)	(4.15————4.20)		(3.86————3.90)		5.88	8.36, 8.39
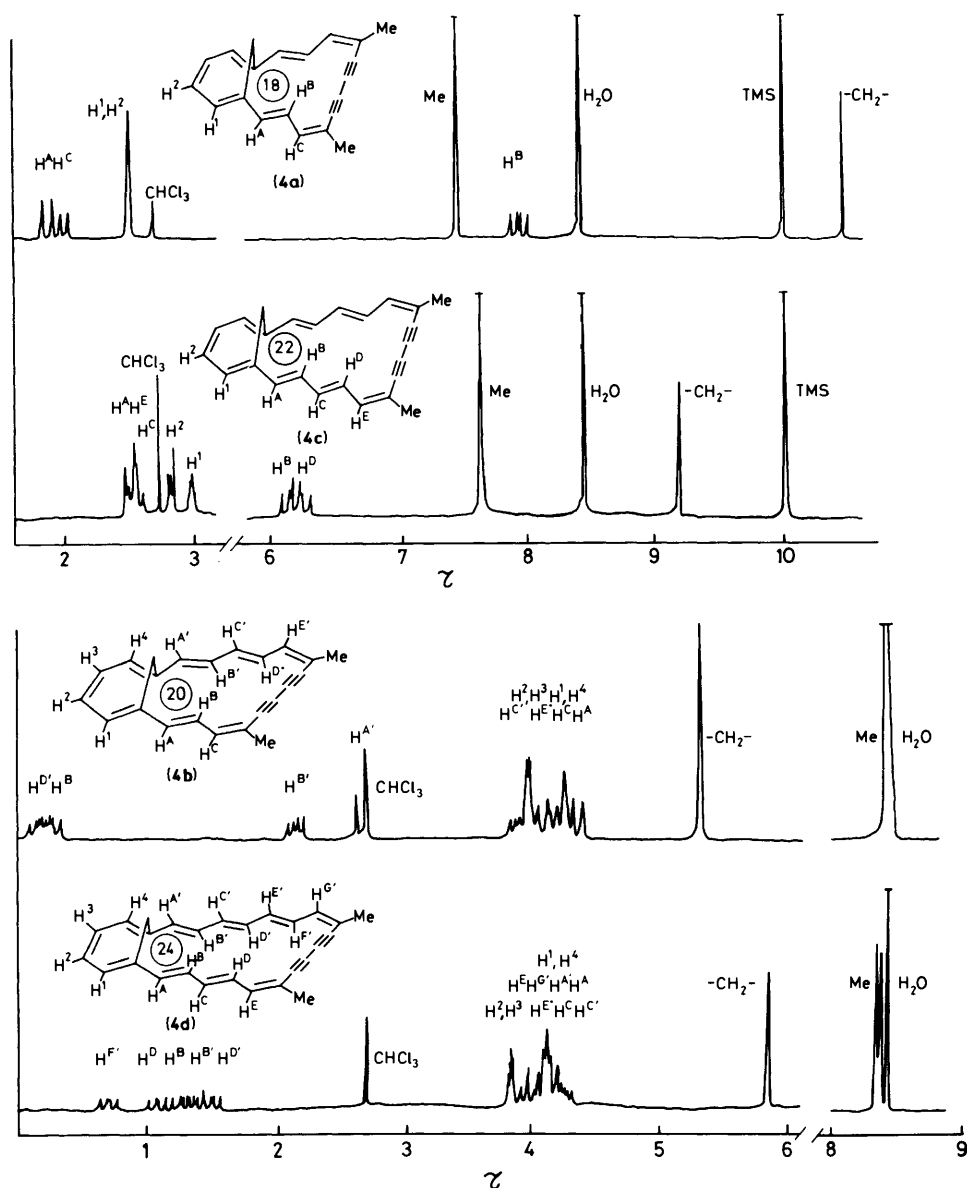
Figure 1. ^{1}H N.m.r. spectra of tetradehydroannulenes (**4a—d**) in CDCl$_3$ at 200 MHz, determined at 21 °C (τ values)
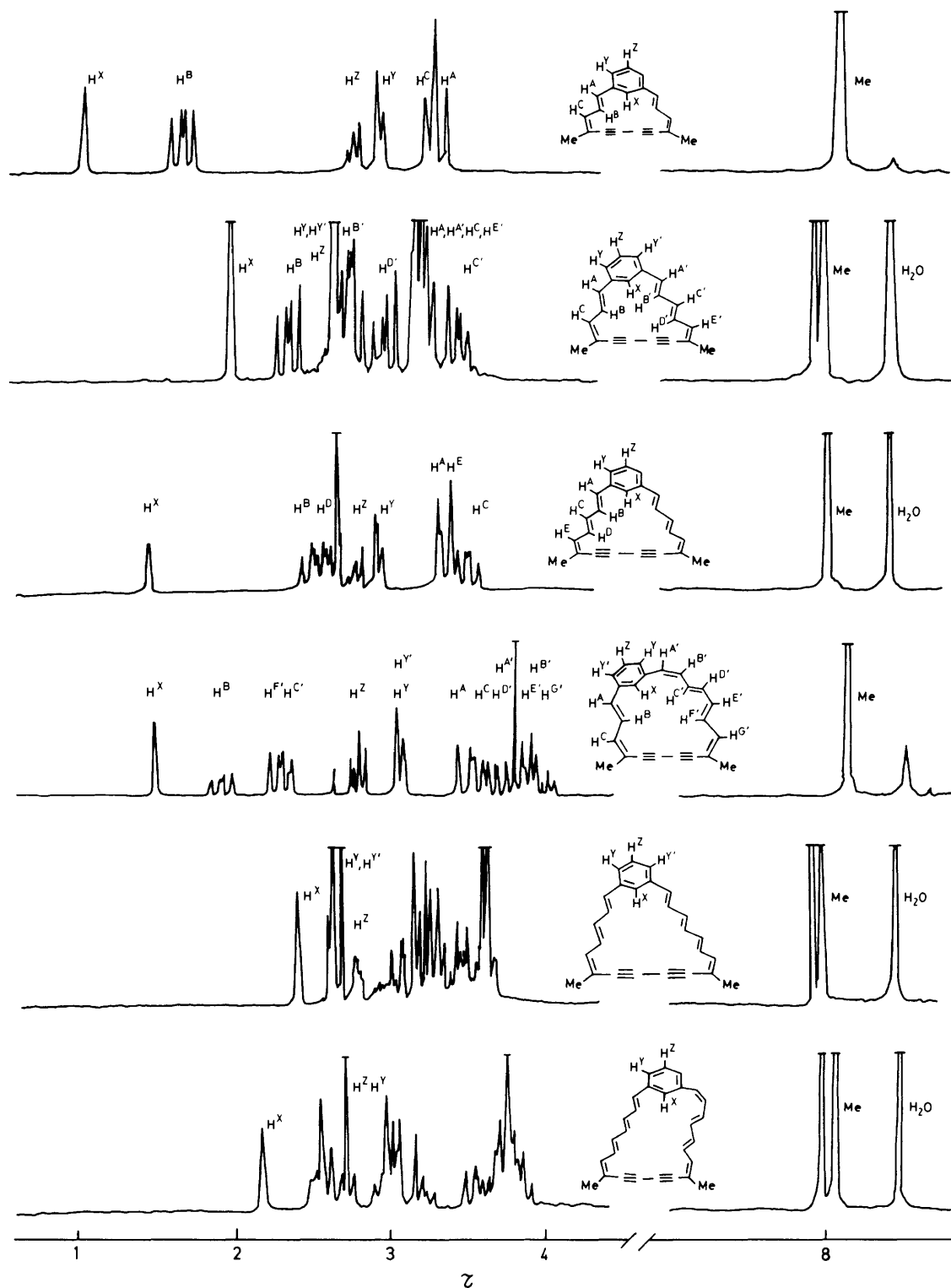
Figure 2. ¹H N.m.r. spectra of [1,3]cyclophanpolyenediynes (11), (14), (17), (19), (21), and (23) in CDCl₃ at 200 MHz, determined at 21 °C (τ values)

dehydrobenzannulene series (24), which were prepared by Sondheimer *et al.*[10] Table 3 shows that the main maxima of the (4*n* + 2)annulenes are of rather longer wavelength than those of (4*n*)annulenes in both methano bridged (4a—d) and benzannelated annulenes (24). Thus, it is evident that in these tetradehydroannulenes the same alternation occurs in the

wavelengths of the main electronic absorption maxima between (4*n* + 2) and (4*n*)systems, as has been demonstrated for monocyclic annulenes and dehydroannulenes.[18] In contrast, the main maxima of the related [1,3]cyclophanpolyenediynes exhibit an almost regular bathochromic shift as the ring size increases, a reflection of the increasing number of double bonds in the large
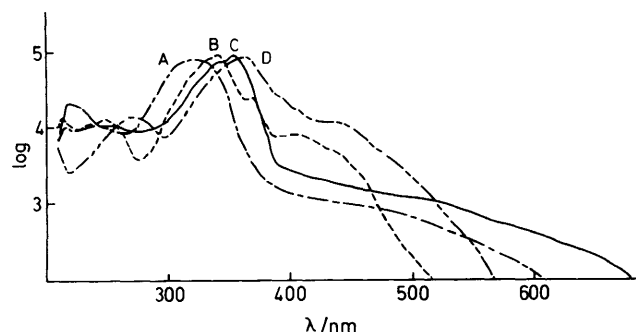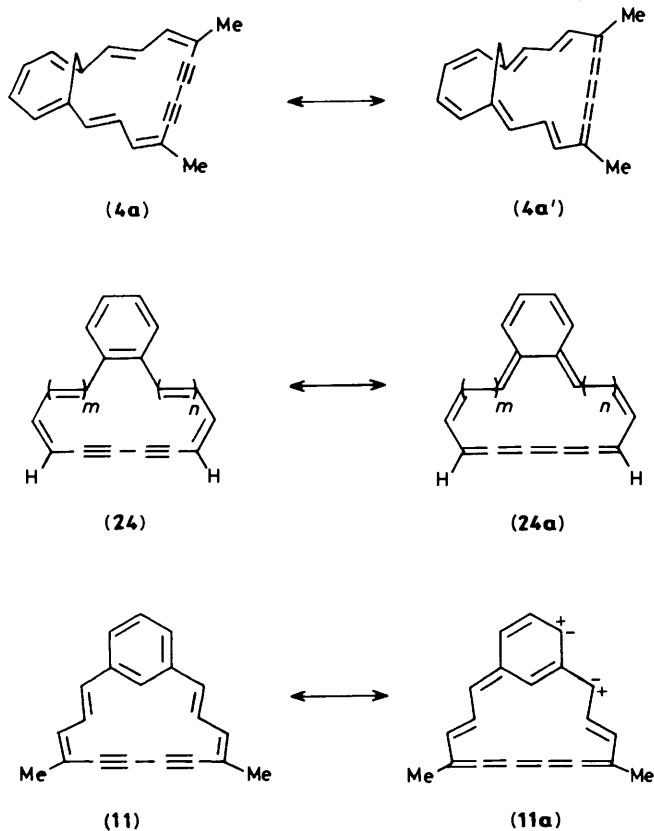
Figure 3. Electronic absorption spectra of tetradehydro-[18]annulene (4a) (B), -[20]annulene (4b) (A), -[22]annulene (4c) (D), and -[24]annulene (4d) (C) in tetrahydrofuran

ring. Thus, the behaviour of the electronic spectra of the tetradehydroannulenes (4a—d) and the benzannelated annulene series (24) is different from that of the related [1,3]cyclophanpolyenediynes (11), (14), (17), (19), (21), and (23); this indicates that the latter have no annulene character, as can be seen from their ¹H n.m.r. spectra (Figure 2).

A simple explanation for this observation may be made as follows. Thus, in the annulene system, the Kekulé structures such as (4a') and (24a) can be written, while in the [1,3]cyclophanpolyenediynes only the disadvantageous ionic structure (11a) can be written.

Experimental

M.p.s. were determined with a hot-stage apparatus and are uncorrected. I.r. spectra were taken with a Hitachi 260-50 spectrophotometer as KBr discs; only significant maxima are

described. U.v. spectra were measured in tetrahydrofuran (THF) solution and run with a Hitachi 220A spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 200 spectrometer operating at 75 eV using a direct inlet system. ¹H N.m.r. spectra were recorded as CDCl₃ solutions (unless otherwise specified) with a FX-90Q (90 MHz), a Varian XL-200 (200 MHz), a JEOL GX-270 (270 MHz) or a Brucker WM-360 (360 MHz) spectrometer, tetramethylsilane being used as an internal standard. Assignments were clarified by the use of decoupling experiments where necessary. Merck alumina (activity II—III) or Merck silica-gel was used for column chromatography. Progress of most reactions was followed by t.l.c. using Merck pre-coated silica gel. Organic extracts with benzene or dichloromethane were washed with saturated aqueous sodium chloride and dried over anhydrous sodium sulphate prior to solvent removal. Solvents were evaporated under water-pump pressure.

1-*Formyl*-6-(2-*formylvinyl*)*cyclohepta*-1,3,5-*triene* (1b).— Lithium methoxide prepared from lithium (110 mg, 0.016 g atm) in dry methanol (65 ml) was added dropwise over 3.5 h at 75 °C under nitrogen atmosphere to a stirred solution of the dialdehyde (1a) (1.80 g, 12.1 mmol) and the salt (5) (6.80 g, 15.8 mmol) in N,N-dimethylformamide (DMF) (120 ml). After being stirred for a further 30 min at 75 °C, the solution was cooled to room temperature, poured onto water, and then extracted with benzene. The extracts were washed with brine, dried, and evaporated to leave a residual red liquid which was dissolved in THF (65 ml) and mixed with 15% hydrochloric acid (HCl) (49 ml). The mixture was stirred for 1 h at room temperature after which it was separated and the aqueous layer was extracted with benzene. The combined organic layers were washed with aqueous sodium hydrogen carbonate, dried, and evaporated. The residue was chromatographed on silica gel (4.2 × 12 cm). The initial fractions eluted with 70—80% ether in hexane afforded the dialdehyde (1b) (1.17 g, 55.5%) which formed yellow *needles*, m.p. 76—77 °C, from hexane–benzene; m/z 174 (M⁺, 68%) and 115 (100); M, 174.1; λ_max. 220sh (ε5 570), 259 (18 000), and 350 nm (4 620); ν_max. 1 655, 1 640 (CHO), and 960 cm⁻¹ (*trans* C=C); τ (90 MHz) 0.39 (1 H, d, J 7 Hz, CHO), 0.47 (1 H, s, CH'O), 2.68 (1 H, d, J 15.4 Hz, Hᴬ), 2.97—3.09 (3 H, m, H¹, H², and H³), 3.07 (1 H, dd, J 15.4 and 7 Hz, Hᴮ), 3.29—3.42 (1 H, m, H⁴), and 7.13 (2 H, s, CH₂) (Found: C, 75.8; H, 5.8. C₁₁H₁₀O₂ requires C, 76.0; H, 5.9%).

The later fractions with ether afforded the dialdehyde (1c) (see below) (175 mg, 4.4%).

1,6-*Bis*(2-*formylvinyl*)*cyclohepta*-1,3,5-*triene* (1c).—Lithium ethoxide prepared from lithium (427 mg, 0.061 mol) in dry ethanol (105 ml) was added dropwise over 4.5 h at 75 °C under nitrogen to a stirred solution of the dialdehyde (1a) (1.78 g, 12.0 mmol) and the salt (5) (26.1 g, 60.7 mmol) in DMF (240 ml). After being stirred for a further 1 h at 75 °C, the mixture was cooled, poured onto water, and extracted with benzene. The extracts were washed with brine, dried and evaporated. The residue dissolved in THF (105 ml) was mixed with 15% HCl (70 ml) and the mixture stirred for 2.5 h at room temperature. It was then worked up as for the isolation of (1b). The residue was chromatographed on silica gel (4.0 × 15.5 cm). The fractions eluted with 50—80% ether in hexane afforded the dialdehyde (1c) (1.71 g, 71%) which formed yellow *needles*, m.p. 163—164 °C, from hexane–benzene; m/z 200 (M⁺, 93%) and 128 (100); M, 200.2; λ_max. 235sh (ε 8 650), 281 (53 800), and 376 nm (8 310); ν_max. 1 660 (CHO), 1 605 (C=C), and 985 cm⁻¹ (*trans* C=C); τ (90 MHz) 0.39 (2 H, d, J 7.2 Hz, CHO), 2.81 (2 H, d, J 15.6 Hz, Hᴬ), 3.24—3.44 (4 H, m, H¹ and H²), 3.58 (2 H, dd, J 15.6 and 7.2 Hz, Hᴮ), and 7.22 (2 H, s, CH₂) (Found: C, 78.0; H, 6.1. C₁₃H₁₂O₂ requires C, 78.0; H, 6.0%).

Table 2. Variable-temperature ^{1}H n.m.r. parameters for the dehydroannulenes (**4a**—**d**) at 90 MHz (τ values)

Compd.	T (°C)	H^A	H$^{A'}$	H^C	H$^{C'}$	H^E	H$^{E'}$	H^G
(**4a**)	+60	2.00		2.12				
	+25	1.96		2.10				
	−30	1.96		2.07				
	−60	1.88		2.01				
(**4b**)	+60	(3.92—4.48)	2.70	(3.92—4.48)	3.88		(3.92—4.48)	
	+25	4.41	2.73	(4.00—4.30)	3.90		(4.00—4.30)	
	−30	4.46	2.85	(3.94————4.40)			(3.94—4.40)	
	−60	(4.06—4.52)	2.90	(4.06————4.52)			(4.06—4.52)	
(**4c**)	+60	2.56		(2.50—3.10)		(2.50—3.10)		
	+25	2.53		(2.50—3.10)		(2.50—3.10)		
	−30	2.52		(2.40—3.04)		(2.40—3.04)		
	−60	2.48		(2.40—3.04)		(2.40—3.04)		
(**4d**)	+60	(3.04————4.42)		(3.84————————4.42)				
	+25	(3.83————4.46)		(3.83————————4.46)				
	−30	(3.83————4.44)		(3.83————————4.44)				
	−60	(3.84————4.50)		(3.84————————4.50)				

Compd.	T(°C)	H^B	H$^{B'}$	H^D	H$^{D'}$	H$^{F'}$	H^1	H^2	H^3	H^4	CH$_2$	Me
(**4a**)	+60	7.88						2.60			10.40	7.50
	+25	7.97						2.58			10.45	7.49
	−30	8.06						2.55			10.51	7.47
	−60	8.19						2.50			10.58	7.45
(**4b**)	+60	0.46	2.32		0.40		(3.92			4.48)	5.44	8.44
	+25	0.37	2.22		0.26		(4.00			4.30)	5.38	8.46
	−30	0.29	2.00		0.07		(3.94			4.40)	5.28	8.48
	−60	(−0.08—0.28)	1.80		(−0.08—0.28)		(4.06			4.52)	5.21	8.48
(**4c**)	+60	6.22		6.02			(2.50			3.10)	9.13	7.66
	+25	6.30		6.12			(2.50			3.10)	9.18	7.65
	−30	6.42		6.30			(2.40			3.04)	9.29	7.64
	−60	6.54		6.36			(2.40			3.04)	9.34	7.64
(**4d**)	+60	1.47	1.57	1.23	1.62	0.84	(3.84			4.42)	5.93	8.37
	+25	1.46	1.48	1.16	1.54	0.78	(3.83			4.46)	5.90	8.39
	−30	(1.20————1.63)		1.09	(1.20—1.63)	0.70	(3.83			4.44)	5.85	8.39
	−60	(0.50——————————1.50)					(3.84			4.50)	5.84	8.43

Table 3. Electronic absorption maxima of the annulenes (**4a**—**d**), the [1,3]cyclophanpolyenediynes (**11**), (**14**), (**17**), (**19**), (**21**), and (**23**), and the benzannulenes (**24**)^a in tetrahydrofuran $\lambda_{max.}$ (nm) ($\varepsilon_{max.}$)

[18]- (**4a**): 235sh (11 800), 250 (13 400), 264sh (8 150), 328sh (69 500), **343 (94 700)**, 370 (29 600), 407 (8 650), 456sh (1 480)

[20]- (**4b**): 240 (10 500), 311sh (71 700), **324 (81 400)**, 402sh (1 320), 493sh (756)

[22]- (**4c**): 252sh (9 330), 268 (14 000), 280sh (13 200), 357sh (76 600), **367 (83 900)**, 397sh (22 800), 438sh (10 900)

[24]- (**4d**): 258 (11 600), 272 (9 670), 322sh (34 100), 343 (70 300), **355 (87 100)**

(**11**)^b: 217 (13 900), 253sh (14 300), 264sh (18 400), 278 (25 400), **306 (36 600)**

(**14**): 220 (16 100), 250sh (14 200), 261sh (15 300), 289 (28 400), **316 (37 000)**

(**17**): 227sh (7 500), 254 (5 500), 267 (5 700), 289 (12 000), 304 (20 500), **330 (31 900)**

(**19**): 245 (14 500), 268sh (18 900), 287sh (32 500), 300 (49 100), 319sh (56 800) **332 (65 600)**, 363sh (9 240), 425 (2 490)

(**21**): 230 (16 500), 259sh (14 000), 279sh (18 000), 313 (39 700), 336sh (44 000) **348 (49 100)**

(**23**): 219 (15 200), 251 (20 200), 272 (24 200), 286 (23 800), 325 (51 300), **363 (62 800)**, 373sh (59 100), 449sh (4 640)

(**24**)^a [14]-:	**317 nm**
[16]-:	**297 nm**
[18]-:	**339 nm**
[20]-:	**324 nm**

^{a} In ether, see ref. 10. ^{b} See Ref. 14.

1-(2-*Formylvinyl*)-6-(4-*formylbuta*-1,3-*dienyl*)*cyclohepta*-1,3,5-*triene* (**1d**).—Lithium ethoxide prepared from lithium (854 mg, 0.122 mol) in dry ethanol (210 ml) was added dropwise over 5 h at 65 °C under nitrogen to a stirred solution of the dialdehyde (**1b**) (2.66 g, 15.3 mmol) and the salt (**5**) (52.5 g, 0.122 mol) in DMF (400 ml). After being stirred for a further 1 h at 65 °C, the mixture was worked up as for the isolation of the acetal of (**1b**). The residue was dissolved in THF (220 ml) and mixed with 15% HCl (142 ml). After being stirred for 1 h at room temperature, the mixture was extracted with dichloromethane, and the combined extracts were washed with aqueous sodium hydrogen carbonate and dried. The product was chromato-graphed on silica gel (4.5 × 15.0 cm). The initial fractions eluted with 40% ether in hexane afforded the dialdehyde (**1c**) (0.28 g, 8.0%). The following fractions eluted with 50—60% ether in hexane afforded the dialdehyde (**1d**) (2.94 g, 85%). It formed yellow *needles*, m.p. 95—96 °C, from hexane–benzene; *m/z* 226 (*M*$^+$, 100%); *M*, 226.2; $\lambda_{max.}$ 267sh (ε 13 900), 281sh (27 500), 294sh (47 500), 304 (55 900), and 399 nm (11 000); $\nu_{max.}$ 1 660 (CHO), 1 610 (C=C), 995, and 980 cm^{-1} (*trans* C=C); τ (270 MHz) 0.38 (1 H, d, *J* 7.3 Hz, CHO), 0.40 (1 H, d, *J* 7.8 Hz, CH'O), 2.78 (1 H, d, *J* 15.6 Hz, H$^{A'}$), 2.78 (1 H, dd, *J* 15.8 and 10.6 Hz, H^C), 3.14—3.48 (5 H, m, H^1, H^2, H^3, H^4, and H^B), 3.26 (1 H, d, *J* 15.2 Hz, H^A), 3.56 (1 H, dd, *J* 15.6 and 7.7 Hz, H$^{B'}$), 3.67 (1 H, dd, *J* 15.1 and 7.8 Hz, H^D), and 7.21 (2 H, s, CH$_2$) (Found: C, 79.4; H, 6.2. C$_{15}$H$_{14}$O$_2$ requires C, 79.6; H, 6.2%).

5-*Bromo*-3-*methylpent*-3-*en*-1-*yne*.—This compound was pre-pared from 3-methylpent-2-en-4-yn-1-ol, as reported;[8] it had

b.p. 45—47 °C/18 mmHg (lit., 45—50 °C/14 mmHg); $v_{max.}$(neat) 3 290 (C≡C–H), 2 100 (C≡C), 1 625 (C=C), and 640 cm⁻¹ (CBr); τ (90 MHz) 4.01 (1 H, t, J 8 Hz, olefinic H), 5.84 (2 H, d, J 8 Hz, CH₂), 6.68 (1 H, s, C≡CH), and 8.08 (3 H, s, Me).

3-Methylpent-2-en-4-ynyltriphenylphosphonium *Bromide* (2).—This compound was prepared from 5-bromo-3-methyl-pent-3-en-4-yne and triphenylphosphine, as reported;[9] it had m.p. 158—159 °C (lit., 153—154 °C); τ (90 MHz, CF₃CO₂D) 2.05—2.45 (15 H, m, ArH), 4.21—4.40 (1 H, m, olefinic H), 5.76 (2 H, dd, J 15 and 7 Hz, CH₂), 6.77 (1 H, s, C≡CH), and 8.07 (3 H, br s, Me).

1-Formyl-6-(4-methylhexa-1,3-dien-5-ynyl)cyclohepta-1,3,5-triene (6).—Lithium ethoxide prepared from lithium (325 mg, 47 mmol) in dry ethanol (71 ml) was added dropwise over 2 h at 60 °C under nitrogen to a stirred solution of the salt (2) (19.5 g, 46.3 mmol) and the dialdehyde (1a) (3.10 g, 21 mmol) in DMF (250 ml). After being stirred for a further 1.5 h at 60—65 °C, the solution was poured onto water and extracted with benzene. The extracts were washed with brine, dried and evaporated. The residual dark red liquid was passed through a short column of alumina (4.5 × 7.0 cm). The fractions eluted with hexane–ether (1 : 4) were collected and evaporated and the residue was chromatographed on alumina (4.5 × 13.5 cm). The fractions eluted with 5—10% ether in hexane afforded the aldehyde (6) (232 mg, 2.3%). It formed yellow *cubes*, m.p. 54—55 °C, from hexane–benzene; m/z 210 (M^+, 100%); M, 210.2; $\lambda_{max.}$ 229 (ε 11 500), 266sh (22 500), 278 (38 500), 287 (40 500), and 401 nm (10 300); $v_{max.}$ 3 260 (C≡C–H), 2 080 (C≡C), 1 655 (CHO), and 970 cm⁻¹ (*trans* C=C); τ (200 MHz) 0.57 (1 H, s, CHO), 2.62 (1 H, dd, J 15.5 and 11. Hz, H^B), 3.00—3.30 (3 H, m, H^1, H^2, and H^3), 3.63 (1 H, d, J 11 Hz, H^C), 3.64 (1 H, d, J 16 Hz, H^A), 3.66—3.68 (1 H, m, H^4), 6.47 (1 H, s, C≡CH), 7.13 (2 H, s, CH₂), and 8.02 (3 H, s, Me) (Found: C, 85.7; H, 6.7. C₁₅H₁₄O requires C, 85.7; H, 6.7%).

1,6-Bis(4-methylhexa-1,3-dien-5-ynyl)cyclohepta-1,3,5-triene (3a).—To a stirred suspension of the salt (2) (14.7 g, 34.8 mmol) in dry THF (120 ml) was added a solution of butyl-lithium (BuLi) (1.64 M; 21.3 ml) in hexane by a syringe over 30 min at −68 °C under argon. The mixture was stirred at −68 °C for a further 1 h, after which a solution of the dialdehyde (1a) (2.14 g, 14.5 mmol) in dry THF (150 ml) was added dropwise over 3.5 h at −65 °C and stirring was continued for a further 30 min at −65 °C. The temperature of the mixture was raised to 5 °C and the latter then stirred at this for a further 1.5 h. After quenching with ethyl acetate (20 ml) the mixture was poured onto water and extracted with benzene. After solvent removal, the residual liquid was passed through a short column of alumina (3.7 × 7.0 cm). The fractions (300 ml) eluted with ether were collected and evaporated and the residual red liquid chromatographed on alumina (3.7 × 10 cm). The fractions eluted with 5—10% ether in hexane afforded compound (3a) (247 mg, 6.3%). It formed red *needles*, m.p. 91—92 °C, from hexane–benzene; m/z 272 (M^+, 89%) and 242 (100); M, 272.3; $\lambda_{max.}$ 225 (ε 13 300), 300 (62 100), 311 (72 800), and 408 nm (7 480); $v_{max.}$ 3 280 (C≡C–H), 2 100 (C≡C), and 965 cm⁻¹ (*trans* C=C); τ (200 MHz) 2.85 (2 H, dd, J 15.5 and 10.5 Hz, H^B), 3.43—3.47 (2 H, m, H^2 and H^3), 3.61 (2 H, d, J 15 Hz, H^A), 3.62 (2 H, d, J 10.5 Hz, H^C), 3.90—3.94 (2 H, m, H^1 and H^4), 6.48 (2 H, s, C≡CH), 7.15 (2 H, s, CH₂), and 8.05 (6 H, s, Me) (Found: C, 92.8; H, 7.4. C₂₁H₂₀ requires C, 92.6; H, 7.4%).

10,15-Dimethyl-11,12,13,14-tetradehydro-1,6-methano[18]-annulene (4a).—A solution of the compound (3a) (65.5 mg, 2.39 mmol) in pyridine and dry ether (3 : 1; 20 ml) was added dropwise over 3.5 h at 49—51 °C to a stirred solution of anhydrous

copper(II) acetate (1.10 g) in pyridine and dry ether (3 : 1; 56 ml). After being stirred for a further 1 h at 49—51 °C, the mixture was poured onto water and extracted with benzene. The extracts were washed successively with 5% HCl (until it turned acidic) and aqueous sodium hydrogen carbonate and dried. The semisolid obtained after solvent removal was chromatographed on alumina (3.7 × 8.5 cm). The fractions eluted with 3% ether in hexane afforded the [18]annulene (4a) (21 mg, 32%). It formed brown *needles*, m.p. 169—170 °C, from hexane–benzene; m/z 270 (M^+, 71%) and 239 (100); M, 270.3; for u.v. data see Table 3 and Figure 3; $v_{max.}$ 2 130 (C=C) and 960 cm⁻¹ (*trans* C≡C); τ (200 MHz) 1.95 (2 H, d, J 15 Hz, H^A), 2.08 (2 H, d, J 11 Hz, H^C), 2.56 (4 H, s, H^1, and H^2), 7.47 (6 H, s, Me), 7.97 (2 H, dd, J 15 and 11 Hz, H^B), and 10.45 (2 H, s, CH₂); see also Figure 1 (Found: C, 93.0; H, 6.65. C₂₁H₁₈ requires C, 93.3; H, 6.7%).

1-(4-Methylhexa-1,3-dien-5-ynyl)-6-(6-methylocta-1,3,5-trien-7-ynyl)cyclohepta-1,3,5-triene (3b).—To a stirred suspension of the salt (2) (18.0 g, 42.6 mmol) in dry THF (150 ml) was added a solution of BuLi (2.16 M; 19.7 ml) in hexane by a syringe over 15 min at −70 °C under argon. The mixture was stirred for 1 h at 70 °C, after which a solution of the dialdehyde (1b) (2.65 g, 15.2 mmol) in dry THF (150 ml) was added over 2 h at −70 °C. The mixture was then stirred for a further 2.5 h at −70 °C after which it was worked up as for the isolation of (3a). The residual red liquid was chromatographed on alumina (3.7 × 15.0 cm) and the fractions eluted with 5% ether in hexane afforded compound (3b) (245 mg, 5.3%). It formed red *needles*, m.p. 97—98 °C (decomp.), from hexane–hexane; m/z 298 (M^+, 100%); M, 298.4; $\lambda_{max.}$ 240sh (ε 6 160), 280sh (11 500), 306sh (36 800), 318 (63 300), 330 (75 200), and 426 nm (7 800); $v_{max.}$ 3 300 (C≡C–H), 2 100 (C≡C), 1 000, and 980 cm⁻¹ (*trans* C=C); τ(200 MHz) 2.85 (1 H, dd, J 15.2 and 11 Hz, H^B), 3.07 (1 H, dd, J 14.5 and 11.1 Hz, H$^{D'}$), 3.14 (1 H, dd, J 14.5 and 11.7 Hz, H$^{B'}$), 3.39—3.43 (2 H, m, H^2 and H^3), 3.57 (1 H, d, J 15 Hz, H$^{A'}$), 3.59 (1 H, d, J 15.6 Hz, H^A) 3.58—3.73 (5 H, m, H^1, H^4, H^C, H$^{C'}$, and H$^{E'}$), 6.35 (1 H, s, C≡CH), 6.63 (1 H, s, C≡CH), 7.24 (2 H, s, CH₂), and 8.04 (6 H, s, Me) (Found: C, 92.5; H, 7.6. C₂₃H₂₂ requires C, 92.6; H, 7.4%).

10,15-Dimethyl-11,12,13,14-tetradehydro-1,6-methano[20]-annulene (4b).—A solution of compound (3b) (108 mg, 0.36 mmol) in pyridine and dry ether (3 : 1, 40 ml) was added drop-wise over 4 h at 50—52 °C to a stirred solution of anhydrous copper(II) acetate (1.70 g) in pyridine and dry ether (3 : 1; 88 ml). After being stirred for a further 30 min at 50—52 °C, the mixture was worked up as for the isolation of (4a). The product was chromatographed on alumina (3.7 × 11.5 cm). The fractions eluted with 5% ether in hexane afforded the [20]annulene (4b) (29.2 mg, 27%). It formed purple *needles*, m.p. 131—132 °C, from hexane–benzene; m/z 296 (M^+, 84%) and 265 (100); M, 296.3; for u.v. data see Table 3 and Figure 3; $v_{max.}$ 2 170 (C≡C), 990, and 970 cm⁻¹ (*trans* C=C); τ (200 MHz) 0.25 (1 H, dd, J 16 and 10 Hz, H$^{D'}$), 0.35 (1 H, dd, J 16 and 11 Hz, H^B), 2.20 (1 H, dd, J 16 and 9 Hz, H$^{B'}$), 2.71 (1 H, d, J 16 Hz, H$^{A'}$), 3.94 (1 H, dd, J 16 and 9 Hz, H$^{C'}$), 4.01—4.11 (2 H, m, H^2 and H^3), 4.06 (1 H, d, J 10 Hz, H$^{E'}$), 4.16—4.22 (2 H, m, H^1 and H^4), 4.27 (1 H, d, J 10 Hz, H^C), 4.41 (1 H, d, J 16 Hz, H^A), 5.36 (2 H, s, CH₂), and 8.44 (6 H, s, Me); see also Figure 1 (Found: C, 93.3; H, 6.75. C₂₃H₂₀ requires C, 93.2; H, 6.8%).

1,6-Bis(6-methylocta-1,3,5-trien-7-ynyl)cyclohepta-1,3,5-triene (3c).—To a stirred suspension of the salt (2) (20.7 g, 49.0 mmol) in dry THF (160 ml) was added dropwise a solution of BuLi (2.16 M; 22.7 ml) in hexane by a syringe over 20 min at −70 °C under argon. After being stirred for 1 h at −70 °C, a solution of the dialdehyde (3c) (3.50 g, 17.5 mmol) in dry THF (160 ml) was added dropwise over 3.5 h at −72 °C and stirring was continued for a further 1 h at −72 °C. The mixture was then

worked up as for the isolation of (3a). The product was chromatographed on alumina (3.7 × 11.0 cm). The fractions eluted with 10% ether in hexane afforded compound (3c) (468 mg, 8.2%). It formed red *needles*, m.p. 116—117 °C, from hexane–benzene; m/z 324 (M^+, 100%); M, 324.4; $\lambda_{max.}$ 322 (ε 4 990), 345 (4 890), 311sh (26 200), 327 (61 100), 341 (88 500), and 435 nm (6 830); $\nu_{max.}$ 3 280 (C≡CH), 2 080 (C≡C), and 985 cm^{-1} (*trans* C=C); τ (200 MHz) 3.14 (2 H, dd, J 15 and 11 Hz, H^D), 3.24 (2 H, dd, J 15 and 11 Hz, H^B), 3.42—3.46 (2 H, m, H^2 and H^3), 3.60 (2 H, d, J 15 Hz, H^A), 3.62 (2 H, dd, J 15 and 10 Hz, H^C), 3.63 (2 H, d, J 11 Hz, H^E), 3.70—3.74 (2 H, m, H^1 and H^4), 6.55 (2 H, s, C≡CH), 7.28 (2 H, s, CH$_2$), and 8.05 (6 H, s, Me) (Found: C, 92.6; H, 7.45. C$_{25}$H$_{24}$ requires C, 92.5; H, 7.5%).

12,17-*Dimethyl*-13,14,15,16-*tetradehydro*-1,6-*methano*[22]-*annulene* (4c).

—A solution of compound (3c) (237 mg, 0.73 mmol) in pyridine and dry ether (3:1; 80 ml) was added dropwise over 4 h at 49—50 °C to a stirred solution of anhydrous copper(II) acetate (4.50 g) in pyridine and dry ether (3:1; 228 ml). After being stirred for a further 30 min at 49—50 °C, the mixture was worked up as for the isolation of (4a). The product was chromatographed on alumina (3.7 × 10.0 cm). The fractions eluted with 10% ether in hexane afforded the [22]-annulene (4c) (86.4 mg, 27.7%). It formed brown *leaflets*, m.p. 196—197 °C (decomp.) from hexane–benzene; m/z 322 (M^+, 100%); M, 322.4; for u.v. data see Table 3 and Figure 3; $\nu_{max.}$ 2 160 (C≡C) and 980 cm^{-1} (*trans* C=C); τ (200 MHz) 2.50 (2 H, d, J 16 Hz, H^A), 2.50 (2 H, d, J 11 Hz, H^E), 2.56 (2 H, dd, J 16 and 11 Hz, H^C), 2.81—2.85 (2 H, m, H^2), 2.97—3.01 (2 H, m, H^1), 6.14 (2 H, dd, J 16 and 11 Hz, H^D), 6.22 (2 H, dd, J 16 and 11 Hz, H^B), 7.64 (6 H, s, Me), and 9.19 (2 H, s, CH$_2$); see also Figure 1 (Found: C, 92.8; H, 6.7. C$_{25}$H$_{22}$ requires C, 93.1; H, 6.9%).

1-(6-*Methylocta*-1,3,5-*trien*-7-*ynyl*)-6-(8-*methyldeca*-1,3,5,7-*tetraen*-9-*ynyl*)*cyclohepta*-1,3,5-*triene* (3d).

—To a stirred suspension of the salt (2) (13.3 g, 31.6 mmol) in dry THF (160 ml) was added a solution of BuLi (2.16 M; 14.6 ml) in hexane by a syringe over 30 min at −72 °C under argon. After being stirred for 1 h at −70 °C, a solution of the dialdehyde (1d) (2.55 g, 11.3 mmol) in dry THF (100 ml) was added dropwise over 4 h at −72 °C and stirring was continued for a further 1 h. The mixture was then worked up as for the isolation of (3a). The product was chromatographed on alumina (4.0 × 13.5 cm) and the fractions were eluted with 5—7% ether in hexane to afford compound (3d) (1.45 g, 37%). It formed red *plates*, m.p. 95—96 °C, from hexane–benzene; m/z 350 (M^+, 59%) and 91 (100); M, 350.4; $\lambda_{max.}$ 260 (ε 6 680), 303sh (16 400), 327sh (41 700), 342 (77 500), 356 (89 500), and 440 nm (10 400); $\nu_{max.}$ 3 280 (C≡C–H), 2 100 (C≡C), 1 000, and 985 cm^{-1} (*trans* C=C); τ (200 MHz) 3.08—3.90 (16 H, m, olefinic and 7-membered ring H), 6.64 (1 H, s, C≡CH), 6.66 (1 H, s, C≡CH), 7.29 (2 H, s, CH$_2$), 8.01 (3 H, s, Me), and 8.04 (3 H, s, Me) (Found: C, 92.3; H, 7.5. C$_{27}$H$_{26}$ requires C, 92.5; H, 7.5%).

12,17-*Dimethyl*-13,14,15,16-*tetradehydro*-1,6-*methano*[24]-*annulene* (4d).

—A solution of compound (3d) (705 mg, 2.01 mmol) in pyridine and dry ether (3:1; 240 ml) was added dropwise over 3.5 h at 49—50 °C to a stirred solution of anhydrous copper(II) acetate (11.3 g) in pyridine and dry ether (3:1; 582 ml), and stirring was continued for a further 30 min at the same temperature. The mixture was then worked up as for the isolation of (4a). The product was chromatographed on alumina (4.0 × 12.0 cm). The fractions eluted with 5% ether in hexane afforded the [24]annulene (4d) (193 mg, 27.5%). It formed purple *needles*, m.p. 195—195.5 °C; from hexane:benzene; m/z 348 (M^+, 100%); M, 348.4; for u.v. data see Table 3 and Figure 3; $\nu_{max.}$ 2 170 (C≡C), 995, and 980 cm^{-1} (*trans* C=C); τ (200 MHz) 0.76 (1 H, dd, J 15 and 11 Hz, H^F), 1.14 (1 H, dd, J

15 and 11 Hz, H^D), 1.32 (1 H, dd, J 15 and 11 Hz, H^B), 1.43 (1 H, dd, J 15 and 10 Hz, H$^{B'}$), 1.55 (1 H, dd, J 15 and 11 Hz, H$^{D'}$), 3.86—3.90 (2 H, m, H^2 and H^3), 3.94 (1 H, d, J 11 Hz, H$^{G'}$), 4.06 (1 H, d, J 16 Hz, H$^{A'}$), 4.09 (1 H, dd, J 16 and 10 Hz, H^C), 4.15—4.20 (2 H, m, H^1 and H^4), 4.17 (1 H, d, J 10 Hz, H^E), 4.21 (1 H, d, J 15 Hz, H^A), 4.26 (1 H, dd, J 15 and 11 Hz, H$^{E'}$), 4.29 (1 H, dd, J 15 and 11 Hz, H^C), 5.88 (2 H, s, CH$_2$), 8.36 (3 H, s, Me), and 8.39 (3 H, s, Me); see also Figure 1 (Found: C, 93.2; H, 6.9. C$_{27}$H$_{24}$ requires C, 93.1; H, 6.9%).

1-(4-*Methylhexa*-1,3-*dien*-5-*ynyl*)-3-(6-*methylocta*-1,3,5-*trien*-7-*ynyl*)*benzene* (13).

—Lithium ethoxide prepared from lithium (800 mg, 0.12 mol) in dry ethanol (290 ml) was added dropwise over 1.5 h at 80 °C under nitrogen to a stirred solution of the salt (7) (43.3 g, 55 mmol), the aldehyde (8) (5.20 g, 55 mmol), and the aldehyde, (9), (6.60 g, 55 mmol) in DMF (800 ml). After being stirred for a further 30 min at 80 °C, the solution was worked up as for the isolation of (6). The product was chromatographed on alumina (4.0 × 15.0 cm). The fractions eluted with hexane afforded a mixture of (12) and its stereoisomers (4.89 g, 34.4%). The following fractions eluted with 5% ether in hexane afforded compound (13) and its stereoisomers (3.41 g, 22.5%) as a red liquid, which was again chromatographed on alumina (4.0 × 10.0 cm). The fractions eluted with 5—20% ether in hexane afforded the di-*trans* isomer (13) (1.10 g, 7.32%). It formed yellow *needles*, m.p. 137—138 °C (decomp.), from hexane–benzene; m/z 284 (M^+, 90%) and 203 (100); M, 284.4; $\lambda_{max.}$ 225 (ε 10 000), 239sh (7 100), 250 (6 300), 296sh (21 800), 310sh (35 800), 327 (47 400), 343 (53 700), and 362 nm (37 500); $\nu_{max.}$ 3 280 (C≡CH), 2 090 (C≡C), 995, and 970 cm^{-1} (*trans* C=C); τ (200 MHz) 2.54 (1 H, s, H^X), 2.63—2.73 (3 H, m, ArH), 2.73 (1 H, dd, J 15.5 and 11 Hz, H^B), 3.07 (1 H, dd, J 15.5 and 11.5 Hz, H$^{B'}$), 3.17 (1 H, dd, J 15 and 11.5 Hz, H$^{D'}$), 3.41 (2 H, d, J 15 Hz, H^A and H$^{A'}$), 3.53 (1 H, d, J 11 Hz, H$^{E'}$), 3.55 (1 H, dd, J 15 and 11.5 Hz, H$^{C'}$), 3.59 (1 H, d, J 11 Hz, H^C), 6.61 (1 H, s, C≡CH), 6.63 (1 H, s, C≡CH), 7.99 (3 H, s, Me), and 8.02 (3 H, s, Me) (Found: C, 92.6; H, 7.1. C$_{22}$H$_{20}$ requires C, 92.9; H, 7.1%).

The latter fractions eluted with 5—30% ether in hexane, in the first chromatography, afforded a mixture of the compound (16) (see below) and its stereoisomers (1.94 g, 12.7%).

1,3-(4,9-*Dimethyltetradeca*-1,3,9,11,13-*pentaene*-5,7-*diyne*-1,14-*diyl*)*benzene* (14).

—A solution of the compound (13) (718 mg, 2.52 mmol) in pyridine and dry ether (3:1; 60 ml) was added dropwise over 5 h at 49—50 °C to a stirred solution of anhydrous copper(II) acetate (3.0 g) in pyridine and dry ether (3:1; 120 ml). After being stirred for a further 30 min at the same temperature, the mixture was worked up as for the isolation of (4a). The product was chromatographed on alumina (4.0 × 8.0 cm). The fractions eluted with 5% ether in hexane afforded the compound (14) (53.3 mg 7.55%). It formed orange *needles*, m.p. 116—118 °C, from hexane–benzene; m/z 282.1373 (M^+ requires 282.1406); for u.v. data see Table 3; $\nu_{max.}$ 2 170 (C≡C), 995, 975, and 965 cm^{-1} (*trans* C=C); τ (200 MHz) 2.08 (1 H, s, H^X), 2.45 (1 H, dd, J 16 and 11.5 Hz, H^B), 2.70—2.84 (3 H, m, ArH), 2.84 (1 H, dd, J 15 and 11 Hz, H$^{B'}$), 3.05 (1 H, dd, J 16 and 11 Hz, H$^{D'}$), 3.26 (1 H, d, J 11.5 Hz, H^C), 3.28 (1 H, d, J 16 Hz, H^A), 3.28 (1 H, d, J 11 Hz, H$^{E'}$), 3.32 (1 H, d, J 15 Hz, H$^{A'}$), 3.52 (1 H, dd, J 15 and 11 Hz, H$^{C'}$), 7.98 (3 H, s, Me), and 8.03 (3 H, s, Me); also see Figure 2 (Found: C, 93.2; H, 6.45. C$_{22}$H$_{18}$ requires C, 93.6; H, 6.4%).

The Isomeric 1,3-*Bis*(6-*methylocta*-1,3,5-*trien*-7-*ynyl*)*benzenes* (15), (16).

—Lithium ethoxide prepared from lithium (115 mg, 16.6 mmol) in dry ethanol (44 ml) was added dropwise over 1.5 h at 80 °C to a stirred solution of the salt (7) (6.60 g, 8.32 mmol) and the aldehyde (9) (2.00 g, 16.6 mmol) in DMF (126 ml). After being stirred for a further 30 min at 80 °C, the mixture was

worked up as for the isolation of (6). The product was chromatographed on alumina (4.5 × 11.0 cm). The fractions eluted with 6—12% ether in hexane afforded the mono-*cis* isomer (15) (523 mg, 20%). It formed yellow *cubes*, m.p. 73—74 °C (decomp.), from hexane–benzene; m/z 310 (M^+, 100%); M, 310.4; $\lambda_{max.}$ 244 (ε 9 700), 253sh (9 300), 296sh (15 200), 309sh (27 300), 331 (47 500), 347 (59 800), and 367 nm (56 200); $\nu_{max.}$ 3 280 (C≡CH), 2 080 (C≡C), 995 (*trans* C=C), and 685 cm^{-1} (*cis* C=C); τ (90 MHz) 2.58—3.00 (4 H, m, ArH), 3.16—3.84 (10 H, m, olefinic H), 6.65 (1 H, s, C≡CH), 6.68 (1 H, s, C≡CH), 8.04 (3 H, s, Me), and 8.05 (3 H, s, Me).

The following fractions eluted with 15—50% ether in hexane afforded the di-*trans* isomer (16) (812 mg, 31%). It formed orange *cubes*, m.p. 126—217 °C (decomp.), from hexane–benzene; m/z 310 (M^+, 100%); M, 310.4; $\lambda_{max.}$ 252 (ε 10 400), 297sh (18 200), 310sh (33 400), 330 (59 200), 348 (75 000), and 367 nm (72 100); $\nu_{max.}$ 3 280 (C≡CH), 2 080 (C≡C), and 995 cm^{-1} (*trans* C=C); τ (200 MHz) 2.35 (1 H, s, H^X), 2.73 (3 H, br s, ArH), 3.08 (2 H, dd, J 15.5 and 11.5 Hz, H^B), 3.17 (2 H, dd, J 14 and 11.5 Hz, H^D), 3.43 (2 H, d, J 15.5 Hz, H^A), 3.56 (2 H, dd, J 14 and 11.5 Hz, H^C), 3.60 (2 H, d, J 11.5 Hz, H^E), 6.63 (2 H, s, C≡CH), and 8.03 (6 H, s, Me) (Found: C, 92.9; H, 7.05. $C_{24}H_{22}$ requires C, 92.9; H, 7.1%).

The Isomeric 1,3-(6,11-*Dimethylhexadeca*-1,3,5,11,13,15-*hexaene*-7,9-*diyne*-1,16-*diyl*)*benzenes* (17′), (17).—A solution of the mono-*cis* isomer (15) (1.53 g, 4.91 mmol) in pyridine and dry ether (3:1; 107 ml) was added dropwise over 3.5 h at 50—52 °C to a stirred solution of anhydrous copper(II) acetate (5.9 g) in pyridine and dry ether (3:1; 233 ml). After being stirred for a further 40 min at 50—52 °C, the mixture was worked up as for the isolation of (4a). The residual red liquid was chromatographed on alumina (3.7 × 9.0 cm). The fractions eluted with 5% ether in hexane afforded the cyclic mono-*cis* isomer (17′) (131 mg, 8.7%). It formed red *plates*, m.p. 96—97 °C, from hexane; m/z 308.1560 (M^+ requires 308.1558); $\lambda_{max.}$ 231 (ε 26 400), 256 (32 400), 303 (33 400), and 337 (nm (37 900); $\nu_{max.}$ 2 160 (C≡C), 995, 975 (*trans* C=C), and 690 cm^{-1} (*cis* C=C); τ (200 MHz) 2.16 (1 H, s, H^X), 2.32 (1 H, dd, J 16 and 11 Hz, H^B), 2.57 (1 H, d, J 7 Hz, H$^{Y'}$), 2.63 (2 H, dd, J 16 and 11 Hz, H^D and H$^{D'}$), 2.74 (1 H, t, J 7 Hz, H^Z), 3.02 (1 H, d, J 7 Hz, H^Y), 3.32 (1 H, dd, J 16 and 6 Hz, H$^{C'}$), 3.43 (1 H, d, J 11 Hz, H^E), 3.57 (1 H, dd, H 10.5 and 5 Hz, H$^{B'}$), 3.66 (1 H, d, J 16 Hz, H^A), 3.69 (1 H, d, J 10.5 Hz, H$^{A'}$), 3.91 (1 H, dd, J 16 and 11 Hz, H^C), 3.94 (1 H, d, J 11 Hz, H$^{E'}$), 7.95 (3 H, s, Me), and 8.07 (3 H, s, Me).

The following fractions eluted with 10—15% ether in hexane afforded the cyclic di-*trans* isomer (17) (121 mg, 8.0%). It formed orange *needles*, m.p. 145 °C (decomp.), from hexane–benzene; m/z 308.1551 (M^+ requires 308.1539); for u.v. data see Table 3; $\nu_{max.}$ 2 160 (C≡C) and 980 cm^{-1} (*trans* C=C); τ (200 MHz) 1.55 (1 H, s, H^X), 2.59 (2 H, dd, J 15.5 and 12 Hz, H^B), 2.69 (2 H, dd, J 15.5 and 11 Hz, H^D), 2.86 (1 H, t, J 6.5 Hz, H^Z), 3.00 (2 H, d, J 6.5 Hz, H^Y), 3.42 (2 H, d, J 15.5 Hz, H^A) 3.43 (2 H, d, J 11 Hz, H^E), 3.57 (2 H, dd, J 15.5 and 11 Hz, H^C), and 8.08 (6 H, s, Me); see also Figure 2.

The di-*trans* isomer (16) (385 mg, 1.24 mmol) was oxidatively coupled under conditions identical with those used for the mono-*cis* isomer (15), and only the cyclic di-*trans* isomer (17) (41 mg, 11%) was obtained.

1-(3-*Methylhexa*-1,3-*dien*-5-*ynyl*)-3-(8-*methyldeca*-1,3,5,7-*tetraen*-9-*ynyl*)*benzene* (18).—Lithium ethoxide prepared from lithium (720 mg, 104 mmol) in dry ethanol (220 ml) was added dropwise over 1.5 h at 80 °C to a stirred solution of the salt (7) (41.0 g, 52 mmol), the aldehyde (8) 4.90 g, 52 mmol), and the aldehyde (10) (7.60 g, 52 mmol) in DMF (630 ml). After being stirred for a further 1.5 h at 80 °C, the mixture was worked up as for the isolation of (6). The product was chromatographed on

alumina (4.0 × 14.0 cm). The initial fractions eluted with 8% ether in hexane afforded a mixture of the compound (12) and its isomers (3.60 g, 26.8%). The following fractions eluted with 10—20% ether in hexane afforded compound (18) (3.53 g, 21.9%). It formed yellow *needles*, m.p. 85—86 °C (decomp.), from hexane–benzene; m/z 310.1665 (M^+, requires 310.1720); $\lambda_{max.}$ 231 (ε 10 200), 268sh (9 300), 273sh (10 000), 289sh (15 500), 302sh (22 900), 319sh (32 700), 332sh (38 000), 349 (51 400), 368 (67 700), and 389 nm (60 200); $\nu_{max.}$ 3 290 (C≡CH), 2 090 (C≡C), 1 005, and 970 cm^{-1} (*trans* C=C); τ (200 MHz) 2.58 (1 H, s, H^X), 2.65—2.75 (3 H, m, ArH), 2.75 (1 H, dd, J 15.5 and 11 Hz, H^B), 3.06—3.33 (3 H, m, H$^{B'}$, H$^{D'}$, and H$^{F'}$), 3.42 (*1 H, d, J* 15.5 Hz, H^A), 3.44 (1 H, d, J 15.5 Hz, H$^{A'}$), 3.50—3.70 (4 H, m, H^C, H$^{C'}$, H^E, and H$^{G'}$), 6.62 (1 H, s, C≡CH), 6.64 (1 H, s, –C≡CH), 8.00 (3 H, s, Me), and 8.04 (3 H, s, Me) (Found: C, 92.45; H, 7.2. $C_{24}H_{22}$ requires C, 92.85; H, 7.1%).

The later fractions eluted with 30—60% ether in hexane afforded compound (22) (see below) and its isomers (831 mg, 4.41%).

1,3-(4,9-*Dimethylhexadeca*-1,3,9,11,13,15-*hexaene*-5,7-*diyne*-1,16-*diyl*)*benzene* (19).—A solution of compound (18) (1.63 g, 5.26 mmol) in pyridine and dry ether (3:1, 114 ml) was added dropwise over 3.5 h at 51—52 °C to a stirred solution of anhydrous copper(II) acetate (6.2 g) in pyridine and dry ether (3:1; 251 ml). After being stirred for a further 30 min at 51—52 °C, the mixture was worked up as for the isolation of (4a). The product was chromatographed on alumina (3.7 × 8.0 cm). The fractions eluted with 5% ether in hexane afforded compound (19) (53 mg, 3.3%). It formed red *needles*, m.p. 137—138 °C (decomp.), from hexane–benzene; m/z 308.1564 (M^+ requires 308.1564); for u.v. data see Table 3; $\nu_{max.}$ 2 180 (C≡C), 985, 970 (*trans* C=C), and 690 cm^{-1} (*cis* C=C); τ (200 MHz) 1.49 (1 H, s, H^X), 1.91 (1 H, dd, J 16 and 11 Hz, H^B), 2.28 (1 H, dd, J 16 and 11 Hz, H$^{C'}$), 2.29 (1 H, dd, J 16 and 11 Hz, H$^{F'}$), 2.78 (1 H, t, J 7.5 Hz, H^Z), 3.04 (2 H, d, J 7.5 Hz, H^Y and H$^{Y'}$), 3.44 (1 H, d, J 16 Hz, H^A), 3.53 (1 H, d, J 11 Hz, H^C), 3.65 (1 H, dd, J 15 and 11 Hz, H$^{D'}$ or H$^{E'}$), 3.80—4.02 (4 H, m, H$^{A'}$, H$^{B'}$, H$^{D'}$ or H$^{E'}$, H$^{G'}$), and 8.06 (6 H, s, Me), and see also Figure 2.

1-(6-*Methylocta*-1,3,5-*trien*-7-*ynyl*)-3-(8-*methyldeca*-1,3,5,7-*tetraen*-9-*ynyl*)*benzene* (20).—Lithium ethoxide prepared from lithium (610 mg, 87 mmol) in dry ethanol (220 ml) was added dropwise over 1.5 h at 80 °C under nitrogen to a stirred solution of the salt (7) (33.9 g, 43 mmol), the aldehyde (9) (5.20 g, 43 mmol), and the aldehyde (10) (6.60 g, 45 mmol) in DMF (630 ml). After being stirred for a further 30 min at 80 °C, the mixture was worked up as for the isolation of (6). The product was chromatographed on alumina (4.5 × 14.0 cm). The initial fractions eluted with 2% ether in hexane afforded a mixture of compound (16) and its isomers (1.22 g, 9.85%). The following fractions eluted with 4—20% ether in hexane afforded a mixture of compound (20) and its isomers (7.23 g, 50.5%) as a red liquid, which was again chromatographed on alumina (4.5 × 10 cm). The fractions eluted with 10—15% ether in hexane afforded the di-*trans* isomer (20) (5.41 g, 38%). It formed orange *cubes*, m.p. 131—132 °C (decomp.), from hexane–benzene; m/z 336 (M^+, 56%) and 28 (100); M, 336.4; $\lambda_{max.}$ 250 (ε 11 800), 269 (10 100), 316sh (39 800), 332sh (66 000), 349 (87 900), 369 (111 800), and 390 nm (88 000); $\nu_{max.}$ 3 280 (C≡C–H), 2 090 (C≡C), and 1 000 cm^{-1} (*trans* C=C); τ (200 MHz) 2.58 (1 H, s, H^X), 2.73 (3 H, br s, ArH), 3.08 (1 H, dd, J 15.5 and 10.5 Hz, H^B), 3.18 (1 H, dd, J 15 and 11 Hz, H$^{B'}$), 3.26 (1 H, dd, J 15.5 and 11 Hz, H^D), 3.43 (1 H, d, J 15.5 Hz, H^A), 3.46 (1 H, d, J 15 Hz, H$^{A'}$), 3.48—3.70 (7 H, m, H^C, H$^{C'}$, H$^{D'}$, H^E H$^{E'}$, H$^{F'}$, and H$^{G'}$), 6.64 (2 H, s, C≡CH), and 8.04 (6 H, s, Me) (Found: C, 92.45; H, 7.1. $C_{26}H_{24}$ requires C, 92.8; H, 7.2%).

The later fractions eluted with 20—50% ether in hexane,

the first chromatography, afforded a mixture of the compound (**22**) and its isomers (977 mg, 6.37%).

1,3-(6,11-*Dimethyloctadeca*-1,3,5,11,13,15,17-*heptaene*-7,9-*diyn*-1,18-*diyl*)*benzene* (**21**).—A solution of compound (**20**) (1.70 g, 5.05 mmol) in pyridine and dry ether (3:1; 120 ml) was added dropwise over 4 h at 50 °C to a stirred solution of anhydrous copper(II) acetate (6.1 g) in pyridine and dry ether (3:1; 243 ml). After being stirred for a further 30 min at 50 °C, the mixture was worked up as for the isolation of (**4a**). The product was chromatographed on alumina (3.7 × 8.0 cm). The fractions eluted with 5% ether in hexane afforded compound (**21**) (30.5 mg, 1.8%). It formed orange *needles*, m.p. 162—164 °C, from hexane–benzene; m/z 334 (M^+, 100%); M, 334.4; for u.v. data see Table 3; $\nu_{max.}$ 2 170 (C≡C), 985, and 970 cm^{-1} (*trans* C≡C); τ (200 MHz) 2.45 (1 H, s, H^X), 2.64—2.70 (2 H, m, H^Y and H$^{Y'}$), 2.78—2.84 (1 H, m, H^Z), 2.94—3.70 (12 H, m, olefinic H), 7.93 (3 H, s, Me), and 7.99 (3 H, s, Me); see also Figure 2 (Found: C, 93.3; H, 6.6. C$_{26}$H$_{22}$ requires C, 93.4; H, 6.6%).

1,3-*Bis*(8-*methyldeca*-1,3,5,7-*tetraen*-9-*ynyl*)*benzene* (**22**).—Lithium ethoxide prepared from lithium (522 mg, 76 mmol) in dry ethanol (187 ml) was added dropwise over 2 h at 80 °C to a stirred solution of the salt (**7**) (15.0 g, 19 mmol) and the aldehyde (**10**) (5.50 g, 38 mmol) in DMF (555 ml) under nitrogen. After being stirred for a further 30 min at 80 °C, the mixture was worked up as for the isolation of (**6**). The product was chromatographed on alumina (4.5 × 11.0 cm). The fractions eluted with 20—30% ether in hexane afforded the di-*trans* isomer (**22**) (689 mg, 9.7%). It formed orange *cubes*, m.p. 134 °C (decomp.), from hexane–benzene; m/z 362 (M^+, 23%) and 18 (100); M, 362.4; $\lambda_{max.}$ 262 (ε 12 400), 271 (14 300), 315sh (26 200), 332sh (55 800), 353 (99 200), 372 (135 000), and 394 nm (148 700); $\nu_{max.}$ 3 280 (C≡CH), 2.090 (C≡C), and 995 cm^{-1} (*trans* C=C); τ (200 MHz) 2.58 (1 H, s, H^X), 2.71 (3 H, br s, ArH), 3.12 (2 H, dd, J 15 and 11 Hz, H^B), 3.25 (2 H, dd, J 14 and 10 Hz, H^D), 3.44 (2 H, d, J 15 Hz, H^A), 3.50—3.69 (8 H, m, H^C, H^E, H^F, and H^G), 6.64 (2 H, s, C≡CH), and 8.04 (6 H, s, Me) (Found: C, 92.1; H, 7.2. C$_{28}$H$_{26}$ requires C, 92.8; H, 7.2%). Attempts to improve the elemental analysis failed.

1,3-(8,13-*Dimethylicosa*-1,3,5,7,13,15,17,19-*octaene*-9,11-*diyne*-1,20-*diyl*)*benzene* (**23**).—A solution of compound (**22**) (811 mg, 2.23 mmol) in pyridine and dry ether (3:1; 54 ml) was added dropwise over 3 h at 49—50 °C. After being stirred for a further 30 min, the mixture was worked up as for the isolation of (**4a**). The product was chromatographed on alumina (3.7 × 7.5 cm). The fractions eluted with 10% ether in hexane afforded compound (**23**) (191 mg, 23.7%). It formed red *needles*, m.p. 131—132 °C, from hexane–benzene; m/z 360.1874 (M^+ requires 360.1872); for u.v. data see Table 3; $\nu_{max.}$ 2 160 (C≡C), 985, and 960 cm^{-1} (*trans* C=C); τ (200 MHz) 2.20 (1 H, s, H^X),

2.50—2.78 (3 H, m, ArH), 2.91—3.92 (14 H, m, olefinic H), 7.97 (3 H, s, Me), and 8.06 (3 H, s, Me); see also Figure 2 (Found: C, 92.8; H, 7.1. C$_{28}$H$_{24}$ requires C, 93.3; H, 6.7%). Attempts to improve the elemental analysis failed.

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