

Syntheses and Properties of Dichlorodimethyltetradehydro-trideca-, -pentadeca-, -heptadeca-, and -nonadeca-fulvene, and Benzannelated Pentadecafulvene Derivatives

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Syntheses of 13-dichloromethylene-4,9-dimethyl-5,6,7,8-tetradehydrocyclotridecene (18), 15-dichloromethylene-4,9-dimethyl-5,6,7,8-tetradehydrocyclopentadecene (19), 17-dichloromethylene-6,11-dimethyl-7,8,9,10-tetradehydrocycloheptadecene (20), and 19-dichloromethylene-6,11-dimethyl-7,8,9,10-tetradehydrocyclo-nonadecene (21) are described. Examination of the ^1H n.m.r. spectra indicates that all of these fulvenes are atropic. Syntheses of benzannelated derivatives of (19), *i.e.* 7-dichloromethylene-13-methyl-14,15,16,17-tetradehydrobenzocyclopentadecene (28), 9-dichloromethylene-13-methyl-14,15,16,17-tetradehydrobenzocyclopentadecene (29), and 7-dichloromethylene-16,17,18,19-tetradehydrobenzo[*a,g*]cyclopentadecene (30) are also described. The influence of the dichloro substitution at the exocyclic bond of the fulvene, and of benzannelation on the structure of tetradehydropentadecafulvene, is discussed on the basis of the ^1H n.m.r. and u.v. spectra of these fulvenes as well as those of the corresponding diphenyl substituted derivatives.

Of the many methods available for the synthesis of the fulvene system, most involve addition of various reagents to cyclic compounds followed by an elimination or condensation reaction producing an exocyclic double bond.¹ In the preceding paper, we reported two approaches for the synthesis of dimethyldiphenyltetradehydro-trideca- [type (3; $n = 1$)], -pentadeca- [type (4; $n = 1$)], -heptadeca- [(3; $n = 2$)], and -nonadeca-fulvene [(4; $n = 2$)]. One was the direct reaction of a cyclic ketone (annulenone) with diphenylketene, and the other was the reaction of an acyclic ketone (a precursor of annulenone) with diphenylketene, followed by an intramolecular oxidative coupling of the resulting cross-conjugated acyclic polyene containing two terminal acetylene groups.² The latter method was the preferred one since the overall yields of the desired fulvenes starting from the acyclic ketones were usually better than those obtained by the former method, and the cross-conjugated acyclic polyenediynes (precursors of the desired fulvenes) served as 'open-chain' models for an examination of the tropicity of fulvenes.

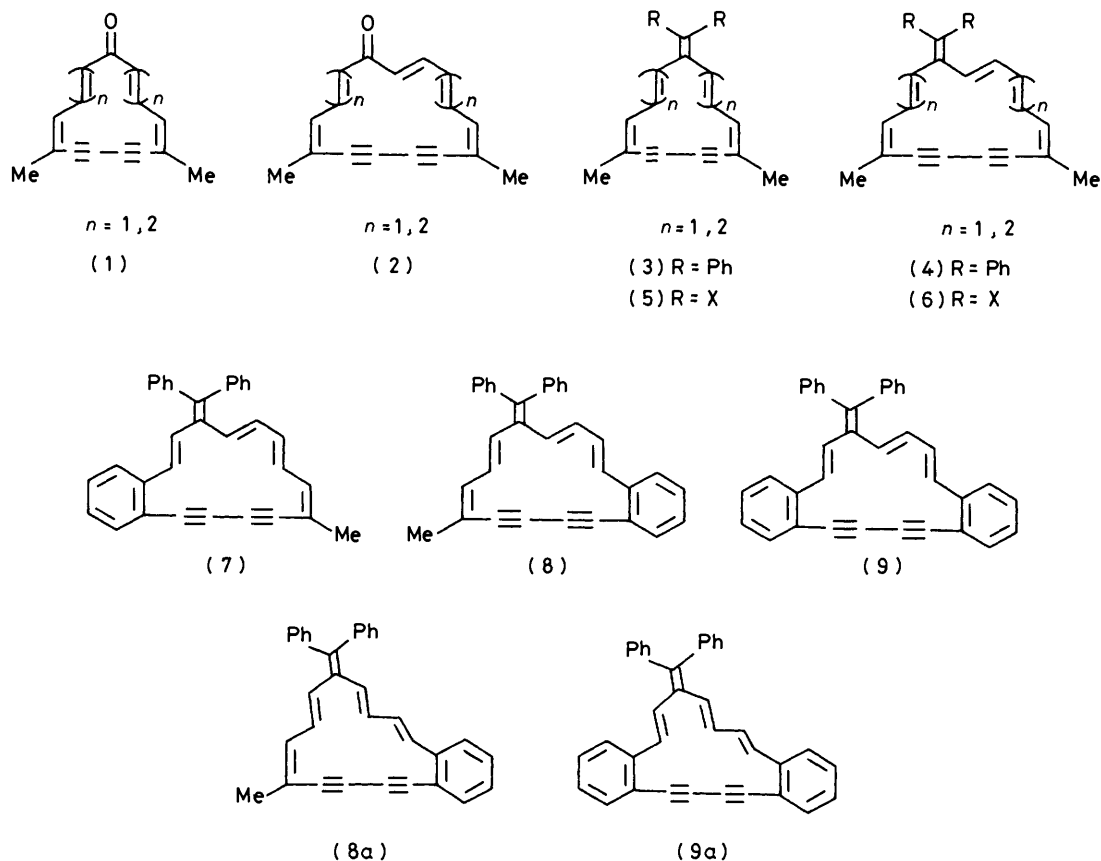
All of the dimethyldiphenyltetradehydrofulvenes (3; $n = 1,2$) and (4; $n = 1,2$) were shown to be atropic by examination of their ^1H n.m.r. spectra and by comparison of the ^1H n.m.r. spectra of their precursors with some benzannelated derivatives.² This atropicity appeared to be attributable to the absence of any contribution from a dipolar structure in the ground state of the fulvenes (3) and (4) due to the fact that the phenyl group is both electron-withdrawing and -donating and is an ambiguous substituent as far as induction is concerned. In contrast, halogen atoms exert an electron-withdrawing effect and are better electron attractors than the phenyl group. If an electronegative substituent were present at an exocyclic bond of the fulvenes (5) and (6), electron density would be pulled toward these substituents and the fulvene molecules would suffer an induced polarization in the ground state. If such polarization of an exocyclic bond occurs, fulvenes of type (5) are potentially paratropic and those of type (6) are potentially diatropic since the ring of the former contains ($4n$) π -electrons and the ring of the latter has ($4n + 2$) π -electrons, as has been shown in dehydroannulenones of types (1) and (2).^{3,4}

In view of these facts, we chose chlorine as the substituent at the exocyclic bond of the fulvene system since dichloro-

ketone is relatively easily obtained. This paper deals with the syntheses and properties of the title compounds (18)–(21). Also, from an examination of the ^1H n.m.r. spectra, it was found that the dibenzannelated fulvene (9) exists in the unlikely conformation (9a) and the monobenzannelated fulvene (8) also exists in the conformation (8a) at -30°C , although the non-benzannelated (4; $n = 1$) and the monobenzannelated fulvene (7) exist in the conformations indicated. The existence of these unexpected conformations of (8a) and (9a) prompted us to investigate the effect of benzannelation upon the molecular skeleton of dichlorodimethylpentadecafulvene (19), and we attempted the preparation of its benzannelated derivatives.

Results and Discussion

The synthesis of compounds (18)–(21) was carried out by a reaction sequence similar to that adopted for compounds (3) and (4). Reaction of the acyclic ketones (10),⁴ (11),³ (12),³ and (13)³ with dichloroketene,⁵ formed *in situ* from dichloroacetyl chloride and triethylamine, in refluxing benzene for 3–5 h afforded 7-dichloromethylene-3,11-dimethyltrideca-3,5,8,10-tetraene-1,12-diyne (14) (15%), 7-dichloromethylene-3,13-dimethylpentadeca-3,5,8,10,12-pentaene-1,14-diyne (15) (12%), 9-dichloromethylene-3,15-dimethylheptadeca-3,5,7,10,12,14-hexaene-1,16-diyne (16) (11%), and 9-dichloromethylene-3,17-dimethylnonadeca-3,5,7,10,12,14,16-heptaene-1,18-diyne (17) (14%), respectively. All of these acyclic compounds (14)–(17) were rather unstable substances. Oxidative coupling of (14)–(17) with anhydrous copper(II) acetate in pyridine and diethyl ether at 50°C ⁶ gave 13-dichloromethylene-4,9-dimethyl-5,6,7,8-tetradehydrocyclotridecene (18) (15%), 15-dichloromethylene-4,9-dimethyl-5,6,7,8-tetradehydrocyclopentadecene (19) (20%), 17-dichloromethylene-6,11-dimethyl-7,8,9,10-tetradehydrocycloheptadecene (20) (8.7%), and 19-dichloromethylene-6,11-dimethyl-7,8,9,10-tetradehydrocyclo-nonadecene (21) (27%), respectively. All of these dichlorofulvene derivatives (18)–(21) were also unstable substances. The overall yields of these fulvenes, starting from the acyclic ketones (10)–(13) were less than those of the corresponding diphenylfulvene derivatives (3) and (4). This might be attributed to instability of dichloroketene, compared with



diphenylketene,⁷ and also of the acyclic compounds (14)–(17) and the dichlorofulvene derivatives (18)–(21).

Variable-temperature ¹H n.m.r. spectra of (18)–(21) were run over the range –60 to 60 °C. The spectra of all the fulvenes (18)–(21) proved to be essentially temperature-independent, reflecting that the conformations indicated for (18)–(21), respectively, remain unchanged over this temperature range.

The ¹H n.m.r. chemical shifts of these fulvenes (18)–(21) are listed in Table 1, together with those of the corresponding acyclic compounds (14)–(17). Individual assignments were made on the basis of the multiplicities and coupling constants (Experimental section), and were assisted by use of the double resonance technique where necessary.

Comparison of the chemical shifts of the various protons of the fulvene derivatives (18)–(21) with those of the corresponding model compounds (14)–(17) (Table 1), respectively, indicates that all of these fulvenes are atropic, since no significant upfield or downfield shifts in the signals due to the outer (and methyl) and inner protons, respectively, were observed on passing from the acyclic model compounds to cyclic compounds (fulvenes) in the cases of (18) and (20), and the reverse in the cases of (19) and (21). The inner proton(s) of all of the fulvenes (18)–(21) resonate at rather low field compared with the outer protons in each case, reflecting the fact that the diacetylene moiety exerts a local anisotropic effect on the inner proton(s), as has been observed for the corresponding diphenyl series (3) and (4).² This observation also supports the supposition that these fulvenes do not possess a ring current. Therefore, it is concluded that the fulvene molecules (18)–(21) are not significantly polarized by the presence of two chlorine atoms at the exocyclic double bond in the ground state.

The preparation of the fulvenes (28)–(30) was carried out similarly to that of (18)–(21). Reaction of compounds

(22),⁸ (23),⁸ and (24)⁹ with dichloroacetone in refluxing benzene for 3–5 h gave 9-dichloromethylene-11-(*o*-ethynylphenyl)-3-methylundeca-3,5,7,10-tetraen-1-yne (25) (22%), 7-dichloromethylene-11-(*o*-ethynylphenyl)-3-methylundeca-3,5,8,10-tetraen-1-yne (26) (21%), and 3-dichloromethylene-1,7-bis(*o*-ethynylphenyl)hepta-1,4,6-triene (27) (23%), respectively. Oxidative coupling of (25)–(27), as before, afforded 7-dichloromethylene-13-methyl-14,15,16,17-tetrahydrobenzocyclopentadecene (28) (16%), 9-dichloromethylene-13-methyl-14,15,16,17-tetrahydrobenzocyclopentadecene (29) (36%), and 7-dichloromethylene-16,17,18,19-tetrahydrodibenzocyclopentadecene (30) (35%), respectively. The overall yields of these benzannulated dichlorofulvene derivatives (28)–(30) starting from the acyclic ketones (22)–(24), respectively, were less than those of the benzannulated diphenylfulvene derivatives (7)–(9) presumably for the same reason as stated above for the less satisfactory yields of (18)–(21).

The chemical shifts of the olefinic, aromatic, and methyl protons of these fulvenes (28)–(30) and those of the corresponding acyclic model compounds (25)–(27) are listed in Table 2. As can be seen from Table 2, comparison of the chemical shifts of the olefinic protons of the benzannulated fulvenes (28)–(30) with those of the corresponding acyclic compounds (25)–(27), respectively, indicates that the fulvenes (28)–(30) are atropic, since no significant upfield and downfield shifts due to the inner and outer protons of (28)–(30), respectively, are observed. The doublet (*J* 8 Hz) due to only one proton appears at low field in the spectra of both the monobenzannulated (28) and the dibenzannulated fulvene (30). This must be assigned to H⁴ of (28) and (30), since no similar resonance appears in the spectrum of (29) in which the corresponding proton is absent. The fact that this resonance appears so far downfield must be due to a large extent to a deshielding effect

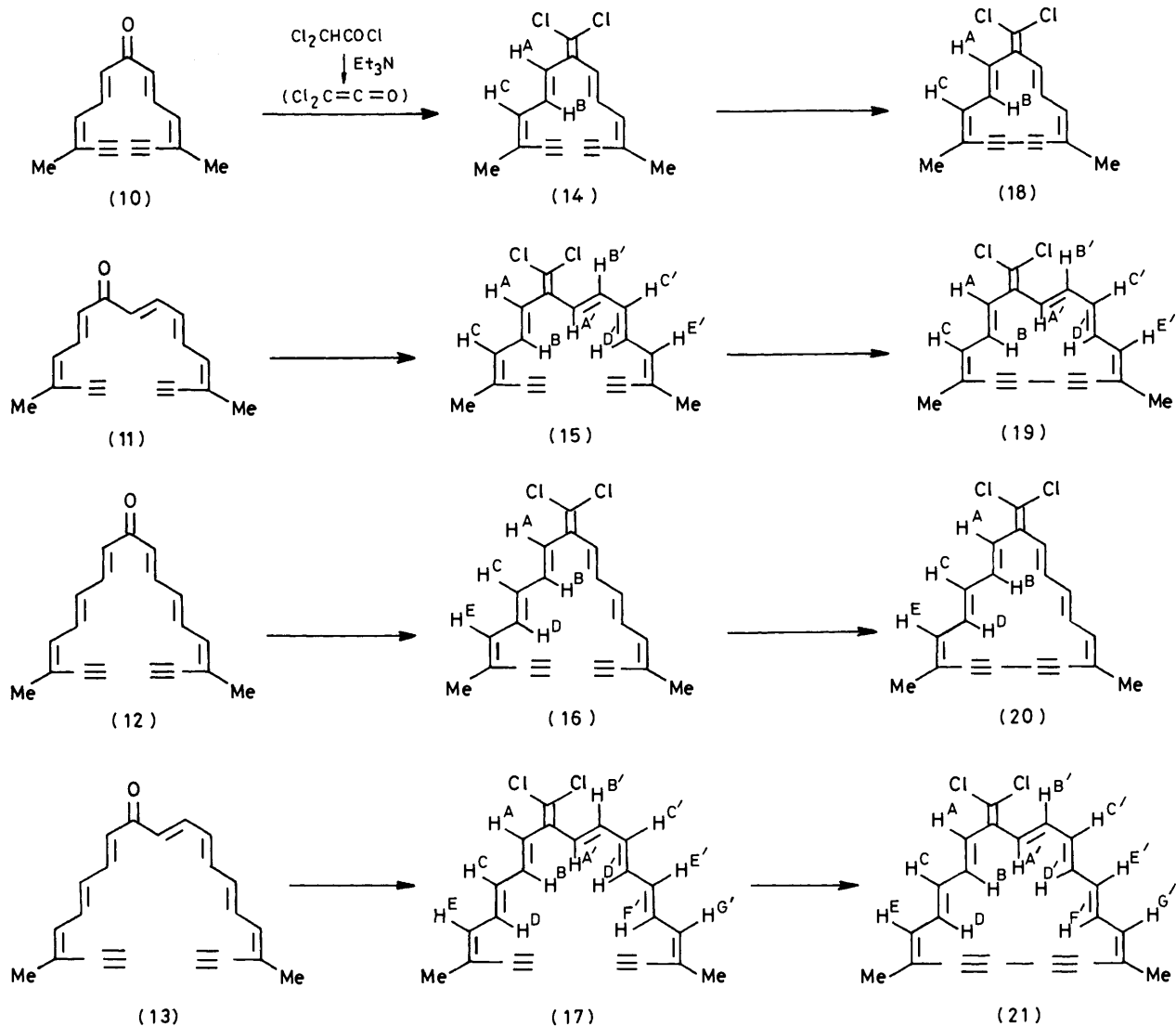


Table 1. ¹H N.m.r. parameters of compounds (14)–(21) in CDCl_3 at 200 MHz, determined at 21 °C (τ -values)

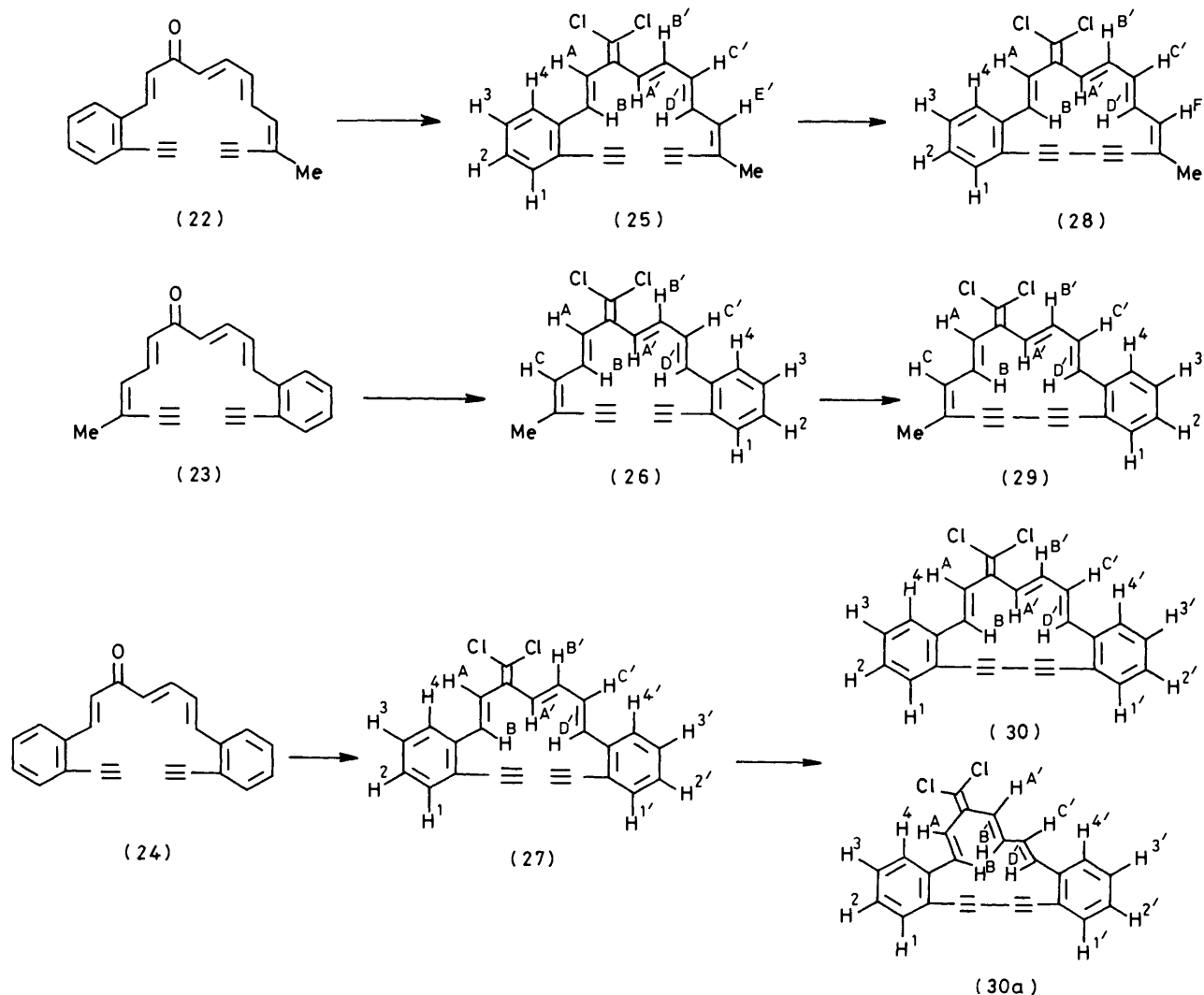
Compd.	H ^A	H ^{A'}	H ^B	H ^{B'}	H ^C	H ^{C'}	H ^D	H ^{D'}	H ^E	H ^{E'}	H ^F	H ^{F'}	H ^G	H ^{G'}	Me
(14)	3.51		3.01		3.58										8.05
(18)	3.49		2.55		3.35										8.13
(15)	3.52	3.48	3.03	3.36	3.53	3.55		3.18		3.59					7.99, 8.01
(19)	3.39	3.27	2.74	3.59	3.37	3.38		2.77		3.35					8.08
(16)	3.54		3.19		3.52		3.42		3.61						8.02
(20)	3.70		3.26		3.55		2.97		3.31						8.06
(17)	3.36—3.70		3.20	3.21	3.36								3.70		8.02
(21)	3.28					3.71	2.92	3.28		3.71	2.99		3.28—3.71		8.06, 8.09

arising from the proximity of the H^D and H^A protons in both (28) and (30).

The spectrum of the fulvene (28) shows an apparent first-order pattern which is assignable to the protons present in (28). However, the spectra of both fulvenes (29) and (30) are complex, particularly the resonances of the H^A, H^B, H^C, and H^D protons, revealing that the molecular skeletons of (29)

and (30) are mobile around the CH^{A'}—CH^{B'}—CH^{C'}—CH^{D'} moiety at room temperature, as in the case of the corresponding diphenyl-substituted derivative (8).² These puzzling patterns in the spectra led us to question the proposed structures for compounds (29) and (30).

In view of these observations, variable-temperature spectra of (28)—(30) were taken over the range -60 to 60 °C. The



spectrum of (28) proved to be essentially temperature-independent, as observed for the structurally closely related fulvene (7).² In contrast, the spectra of (29) and (30) were temperature-dependent. Although the H^A , H^B , H^C , and H^D resonances of (29) are complex multiplets over this temperature range, the corresponding bands of (30) were resolved on cooling, and an analysis of the first-order pattern indicates that (30) exists as the conformer (30a) at -60°C (Experimental section).

The observed temperature-dependency of the ^1H n.m.r. spectra of (29) and (30), and comparison with those of the corresponding diphenyl-substituted fulvenes (8) and (9), suggests that both the phenyl groups and the chlorine atoms on the exocyclic bond exert more influence upon the structure of the molecular skeleton than the oxygen atom of the tetrahydro[15]annulenone.^{2,9}

The electronic absorption maxima of the fulvenes (18)—(21) in dichloromethane are given in Table 3. Although the main maxima of the fulvenes exhibit a bathochromic shift as the ring size increases, this shift is larger between the tridecafulvene (18) (λ_{max} , 287 nm) and the pentadecafulvene (19) (λ_{max} , 308 nm) and between the heptadecafulvene (20) (λ_{max} , 315 nm) and the nonadecafulvene (21) (λ_{max} , 338 nm) than that between the pentadeca- (19) and the heptadeca-fulvene (20). Although they are not illustrated, the electronic spectra of (18) and (20) [type (5)] are similar, while those of (19) and

(21) [type (6)] differ only in the bathochromic shift of each band. This might be again considered to be due to the occurrence of the same sort of alternation in the wavelengths of the main maxima between $[4n + 2]$ and $[4n]$ systems,¹⁰ as has been observed for the corresponding diphenyl series.² Also, the longest wavelength bands of the fulvenes (18)—(21) appear at shorter wavelength than those of the corresponding diphenyl-substituted fulvenes (3) and (4), of the same ring size, reflecting the fact that the degree of extended conjugation is smaller in the dichloro series than in the diphenyl series. Also, the longest wavelength bands of the fulvenes show a shift in absorption towards longer wavelength in the sequence (19) > (28) \approx (29) > (30), *i.e.* with increasing number of fused benzene rings on the macrocyclic system, reflecting the degree of extended conjugation of the π -electron system in these fulvenes, as has been observed for the corresponding diphenyl series [$(4; n = 1)$], (7)—(9).² However, the longest wavelength bands of these fulvenes (28)—(30) are at shorter wavelength than those of the corresponding diphenyl fulvenes (7)—(9), and this difference is also observed between the diphenylfulvene [$(4; n = 1)$] and the dichlorofulvene (19).

Experimental

M.p.s were determined with a hot-stage apparatus and are uncorrected. I.r. spectra were taken on a Hitachi 260-50

Table 2. ^1H N.m.r. parameters of compounds (25)–(30) in CDCl_3 at 200 MHz, determined at 21 °C (τ -values)

Compound	H ^A	H ^{A'}	H ^B	H ^{B'}	H ^C	H ^{C'}	H ^{D'}	H ^{E'}	
(25)	3.03	3.39	2.64	3.23		3.56	3.19	3.60	
(28)	2.76	3.38	2.52	3.46		3.22	2.91	3.33	
(26)	3.38	3.48	2.96	2.98	3.51	3.23	2.76		
(29)	3.25	3.58–3.72	2.87	3.34–3.46	3.35	3.34–3.46	2.92–2.97		
(27)	2.98	3.28	2.56	2.96		3.08	2.98		
(30)	2.74	3.50–3.63	2.53	3.18–3.37		3.18–3.37	2.90–3.03		
	H ¹	H ²	H ³	H ⁴	H ^{1'}	H ^{2'}	H ^{3'}	H ^{4'}	Me
(25)	2.45	2.66	2.58	2.32					8.13
(28)	2.60	2.78	2.68	2.25					8.08
(26)	2.46	2.76	2.65	2.32					7.99
(29)	2.56			2.80					8.08
(27)	2.44	2.55	2.80	2.30	2.48	2.55	2.80	2.32	
(30)	2.56		2.77	2.25	2.56			2.77	

Table 3. Electronic absorption maxima of fulvenes in dichloromethane

$\lambda_{\text{max.}}$ (nm) ($\epsilon_{\text{max.}}$)			
(18)	(19)	(20)	(21)
269sh (16 900)	268sh (16 100)		
287 (22 600)	282sh (21 100)	291sh (29 800)	303sh (27 200)
355 (8 170)	308 (30 100)	315 (39 000)	338 (49 400)
	378sh (5 100)	390 (11 000)	391sh (11 700)
			423sh (5 980)

spectrophotometer as KBr discs. U.v. spectra were measured for solutions in dichloromethane and run with a Hitachi 220A spectrophotometer. Mass spectra were recorded with a JEOL JMS-200 spectrometer operating at 75 eV using a direct-inlet system. ^1H N.m.r. spectra were run with a Varian XL-200 (200 MHz), JEOL FX-200 (200 MHz), or FX-90Q (90 MHz) spectrometer (CDCl_3 solutions). Merck alumina (activity II-III) was used for column chromatography. Most of the reactions were followed by t.l.c. using Merck pre-coated alumina. Sodium sulphate was used as the drying agent, and solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

7-Dichloromethylene-3,11-dimethyltrideca-3,5,8,10-tetraene-1,12-diyne (14).—A solution of dichloroacetyl chloride (4.0 ml) in dry benzene (30 ml) was added dropwise during 2 h to a stirred, refluxing solution of the acyclic ketone (10)⁴ (1.30 g, 6.18 mmol) and triethylamine (8.0 ml) in dry benzene (45 ml) under nitrogen, and the mixture was stirred under reflux for a further 2.5 h. It was then chilled and poured onto water. The organic layer, combined with the benzene extracts from the aqueous layer, was washed successively with 7% hydrochloric acid, water, aqueous sodium hydrogen carbonate, and brine. Drying followed by solvent removal gave a red liquid which was passed through a short column of alumina (2 × 3 cm) and eluted with 20% ether in hexane. The liquid obtained by concentrating the eluates was chromatographed on alumina (4 × 11 cm). Fractions, eluted with 2% ether in hexane, gave the acyclic compound (14) (260 mg, 15%) as a solid. It formed yellow plates from hexane, m.p. 105–106 °C; m/z 278 (M^+ , 30%), 276 (M^+ , 50), and 191 (100); M , 277.1; $v_{\text{max.}}$ 3 300 ($\text{C}\equiv\text{CH}$), 2 090 ($\text{C}\equiv\text{C}$), and 960 cm^{-1} ($\text{trans-C}=\text{C}$); $\lambda_{\text{max.}}$ 247sh (ϵ 10 100), 256 (15 100), 265 (15 300), 299sh (21 500), 317 (29 900), and 331 nm (24 800); τ 3.01 (2 H, dd, J 16 and 11.5

Hz, H^{B}), 3.51 (2 H, d, J 16 Hz, H^{A}), 3.58 (2 H, d, J 11.5 Hz, H^{C}), 6.70 (2 H, s, $\text{C}\equiv\text{CH}$), and 8.05 (6 H, s, Me) (Found: C, 69.2; H, 5.0. $\text{C}_{16}\text{H}_{14}\text{Cl}_2$ requires C, 69.3; H, 5.1%).

13-Dichloromethylene-4,9-dimethyl-5,6,7,8-tetradecydro-cyclotridecene (18).—A solution of the acyclic compound (14) (233 mg, 0.84 mmol) in pyridine (20 ml) and dry ether (6 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (1.88 g) in pyridine (50 ml) and dry ether (17 ml) during 2 h at 50–52 °C and the solution was stirred for a further 1 h at the same temperature, and then poured onto water. The organic layer, combined with the benzene extracts from the aqueous layer, was washed with 5% hydrochloric acid until it turned acidic, then with water, aqueous sodium hydrogen carbonate, and brine. Drying followed by solvent removal gave a red liquid which was chromatographed on alumina (4 × 9 cm). Fractions, eluted with hexane, gave the tridecafulvene (18) (35 mg, 15%) as a solid. It formed pale yellow needles from hexane, m.p. 162 °C (decomp.); m/z 276 (M^+ , 35%), 774 (M^+ , 48), and 189 (100); M , 275.1; $v_{\text{max.}}$ 2 150 ($\text{C}\equiv\text{C}$) and 970 cm^{-1} ($\text{trans-C}=\text{C}$); for u.v. data see Table 3; τ 2.55 (2 H, dd, J 16 and 10 Hz, H^{B}), 3.35 (2 H, d, J 10 Hz, H^{C}), 3.49 (2 H, d, J 16 Hz, H^{A}), and 8.13 (6 H, s, Me) (Found: C, 70.0; H, 4.2. $\text{C}_{16}\text{H}_{12}\text{Cl}_2$ requires C, 69.85; H, 4.4%).

7-Dichloromethylene-3,13-dimethylpentadeca-3,5,8,10,12-pentaene-1,14-diyne (15).—A solution of dichloroacetyl chloride (3.0 ml) in dry benzene (20 ml) was added dropwise during 3 h to a stirred, refluxing solution of the acyclic ketone (11)³ (1.00 g, 4.23 mmol) and triethylamine (4.0 ml) in dry benzene (30 ml) under nitrogen, and the mixture was stirred under reflux for a further 1 h. After work-up as for the isolation of (14), the product was chromatographed on alumina (4 × 10 cm). Fractions, eluted with 3% ether in hexane, gave

the acyclic compound (15) (162 mg, 12%) as a solid. It formed yellow plates from hexane, m.p. 77–78 °C; m/z 304 (M^+ , 42%), 302 (M^+ , 64), and 153 (100); M , 303.2; v_{\max} , 3 300 ($C\equiv CH$), 2 100 ($C\equiv C$), 1 015, and 990 cm^{-1} ($trans-C=C$); λ_{\max} , 263sh (ϵ 19 900), 273 (24 900) 282sh (22 800), 328 (49 500), 343 (51 700), and 362 nm (39 100); τ 3.03 (1 H, dd, J 16.5 and 11 Hz, H^B), 3.18 (1 H, dd, J 15.5 and 11 Hz, H^D), 3.36 (1 H, dd, J 15.5 and 11 Hz, H^B), 3.48 (1 H, d, J 15.5 Hz, H^A), 3.52 (1 H, d, J 16.5 Hz, H^A), 3.53 (1 H, d, J 11 Hz, H^C), 3.55 (1 H, dd, J 15.5 and 11 Hz, H^C), 3.59 (1 H, d, J 11 Hz, H^E), 6.61 (1 H, s, $C\equiv CH$), 6.65 (1 H, s, $C\equiv CH$), 7.99 (3 H, s, Me), and 8.01 (3 H, s, Me) (Found: C, 71.4; H, 5.4. $C_{18}H_{16}Cl_2$ requires C, 71.3; H, 5.3%).

15-Dichloromethylene-4,9-dimethyl-5,6,7,8-tetradecahydro-cyclopentadecene (19).—A solution of the acyclic compound (15) (176 mg, 0.58 mmol) in pyridine (14 ml) and dry ether (4 ml) was added dropwise during 1.5 h to a stirred solution of anhydrous copper(II) acetate (1.29 g) in pyridine (40 ml) and dry ether (15 ml) at 50–52 °C, and the solution was stirred for a further 1 h at the same temperature. After work-up as for the isolation of (18), the product was chromatographed on alumina (4 × 10 cm). Fractions, eluted with 3% ether in hexane, gave the pentadecafulvene (19) (35 mg, 20%) as a solid. It formed orange cubes from hexane, m.p. 87–89 °C; m/z 302 (M^+ , 7%), 300 (M^+ , 10), and 215 (100); M , 301.2; v_{\max} , 2 160 ($C\equiv C$), 1 605 ($C=C$), and 970 cm^{-1} ($trans-C=C$); for u.v. data see Table 3; τ 2.74 (1 H, dd, J 15.5 and 11.5 Hz, H^B), 2.77 (1 H, dd, J 15.5 and 11.5 Hz, H^D), 3.27 (1 H, d, J 16 Hz, H^A), 3.35 (1 H, s, $C\equiv CH$), 3.37 (1 H, d, J 10 Hz, H^C), 3.38 (1 H, dd, J 15.5 and 4 Hz, H^C), 3.39 (1 H, d, J 16 Hz, H^A), 3.59 (1 H, dd, J 15.5 and 4 Hz, H^B), and 8.08 (6 H, s, Me) (Found: C, 71.6; H, 4.8. $C_{18}H_{14}Cl_2$ requires C, 71.8; H, 4.7%).

9-Dichloromethylene-3,15-dimethylheptadeca-3,5,7,10,12,14-hexaene-1,16-diyne (16).—A solution of dichloroacetyl chloride (4.6 ml) in dry benzene (35 ml) was added dropwise to a stirred, refluxing solution of the acyclic ketone (12)³ (1.88 g, 7.17 mmol) and triethylamine (9.3 ml) in dry benzene (52 ml) during 2 h under nitrogen, and the mixture was stirred under reflux for a further 3 h. After work-up as for the isolation of (14), the product was passed through a short column of alumina (4 × 5 cm) and eluted with 30% ether in hexane. The red liquid obtained by concentrating the eluates was chromatographed on alumina (4 × 12 cm). The fractions eluted with 8% ether in hexane gave the acyclic compound (16) (269 mg, 11%) as a solid. It formed yellow needles from hexane, m.p. 106–108 °C; m/z 330 (M^+ , 55%), 328 (M^+ , 75), and 179 (100); M , 329.2; v_{\max} , 3 290 ($C\equiv CH$), 2 090 ($C\equiv C$), 995, and 960 cm^{-1} ($trans-C=C$); λ_{\max} , 273sh (ϵ 15 100), 284 (25 100), 296 (30 300), 329 (45 100), 344 (60 300), 362 (50 400), and 425sh nm (1 570); τ 3.19 (2 H, dd, J 15 and 11 Hz, H^B), 3.42 (2 H, dd, J 15 and 11 Hz, H^D), 3.52 (2 H, dd, J 15 and 11 Hz, H^C), 3.54 (2 H, d, J 15 Hz, H^A), 3.61 (2 H, d, J 11 Hz, H^E), 6.62 (2 H, s, $C\equiv CH$), and 8.02 (6 H, s, Me) (Found: C, 72.8; H, 5.5. $C_{20}H_{18}Cl_2$ requires C, 72.95; H, 5.5%).

17-Dichloromethylene-6,11-dimethyl-7,8,9,10-tetradecahydro-cycloheptadecene (20).—A solution of the acyclic compound (16) (501 mg, 1.51 mmol) in pyridine (37 ml) and dry ether (11 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (3.4 g) in pyridine (105 ml) and dry ether (39 ml) during 2 h at 51–53 °C, and the mixture was stirred for a further 1 h at the same temperature. After work-up as for the isolation of (18), the product was chromatographed on alumina (4 × 9 cm). The fractions eluted with 5% ether in hexane gave the heptadecafulvene (20) (43 mg, 8.7%) as a solid. It formed orange needles from hexane, m.p. 222–

224 °C (decomp.); m/z 328 (M^+ , 25%), 326 (M^+ , 40), and 239 (10); M , 327.2; v_{\max} , 2 180 ($C\equiv C$) and 990 cm^{-1} ($trans-C=C$); u.v. data see Table 3; τ 2.97 (2 H, dd, J 15 and 11 Hz, H^D), 3.26 (2 H, dd, J 16 and 10.5 Hz, H^B), 3.31 (2 H, d, J 11 Hz, H^E), 3.55 (2 H, dd, J 15 and 10.5 Hz, H^C), 3.70 (2 H, d, J 16 Hz, H^A), and 8.06 (6 H, s, Me) (Found: C, 73.1; H, 5.0. $C_{20}H_{16}Cl_2$ requires C, 73.4; H, 4.9%).

9-Dichloromethylene-3,17-dimethylnonadeca-3,5,7,10,12,14,16-heptaene-1,18-diyne (17).—A solution of dichloroacetyl chloride (6.5 ml) in dry benzene (40 ml) was added dropwise during 1.5 h to a stirred, refluxing solution of the acyclic ketone (13)³ (1.95 g, 6.76 mmol) and triethylamine (13 ml) in dry benzene (70 ml) under nitrogen, and the mixture was stirred under reflux for a further 2 h. After work-up as for the isolation of (14), the product was passed through a short column of alumina (4 × 6 cm) and eluted with hexane-ether (1 : 1). The red liquid obtained by concentrating the eluates was chromatographed on alumina (4 × 12 cm). The fractions eluted with 8% ether in hexane gave the acyclic compound (17) (342 mg, 14%) as a solid. It formed orange cubes from hexane, m.p. 120–122 °C; m/z 356 (M^+ , 50%), 354 (M^+ , 75), and 179 (100); M , 355.3; v_{\max} , 3 290 ($C\equiv CH$), 2 090 ($C\equiv C$), 1 005, and 990 cm^{-1} ($trans-C=C$); λ_{\max} , 297sh (ϵ 25 600), 311 (31 500), 330sh (38 600), 347 (55 000), 366 (58 900), 389 (38 000), 423sh (5 070), and 447sh nm (2 800); τ 3.20 (1 H, dd, J 15.5 and 11.5 Hz, H^B), 3.21 (1 H, dd, J 15.5 and 11.5 Hz, H^D), 3.36–3.70 (10 H, m, H^A , H^A , H^C , H^C , H^D , H^D , H^E , H^E , H^F , and H^G), 6.62 (2 H, s, $C\equiv CH$), and 8.02 (6 H, s, Me) (Found: C, 74.2; H, 5.7. $C_{22}H_{20}Cl_2$ requires C, 74.4; H, 5.7%).

19-Dichloromethylene-6,11-dimethyl-7,8,9,10-tetradecahydro-cyclononadecene (21).—A solution of the acyclic compound (17) (191 mg, 0.54 mmol) in pyridine (14 ml) and dry ether (10 ml) was added dropwise during 1 h to a stirred solution of anhydrous copper(II) acetate (1.3 g) in pyridine (39 ml) and dry ether (15 ml) at 51–52 °C, and the solution was stirred for a further 1 h at the same temperature. After work-up as for the isolation of (18), the product was chromatographed on alumina (4 × 10 cm). Fractions, eluted with 5% ether in hexane, gave the nonadecafulvene (21) (51 mg, 27%) as a solid. It formed orange microcrystals from hexane, m.p. 135–136 °C; m/z 354 (M^+ , 30%), 352 (M^+ , 42), and 267 (100); M , 353.2; v_{\max} , 2 180 ($C\equiv C$) and 995 cm^{-1} ($trans-C=C$); u.v. data see Table 3; τ 2.92 (1 H, dd, J 15 and 11.5 Hz, H^D), 2.99 (1 H, dd, J 15 and 11.5 Hz, H^F), 3.28–3.71 (10 H, m, H^A , H^A , H^B , H^B , H^C , H^C , H^D , H^E , H^E , and H^G), 8.06 (3 H, s, Me), and 8.09 (3 H, s, Me) (Found: C, 74.8; H, 5.3. $C_{22}H_{18}Cl_2$ requires C, 74.8; H, 5.1%).

9-Dichloromethylene-11-(*o*-ethynylphenyl)-3-methylundeca-3,5,7,10-tetraen-1-yne (25).—A solution of dichloroacetyl chloride (4.0 ml) in dry benzene (26 ml) was added dropwise during 1 h to a stirred, refluxing solution of the acyclic ketone (22)⁸ (1.25 g, 4.57 mmol) and triethylamine (7.0 ml) in dry benzene (35 ml) under nitrogen, and the mixture was stirred under reflux for a further 5.5 h. After work-up as for the isolation of (14), the product was chromatographed on alumina (4 × 11 cm). Fractions, eluted with 3% ether in hexane, gave the acyclic compound (25) (337 mg, 22%) as a solid. It formed pale yellow needles from hexane, m.p. 119–120 °C; m/z 340 (M^+ , 30%), 338 (M^+ , 45), and 252 (100); M , 339.2; v_{\max} , 3 300, 3 290 ($C\equiv CH$), 2 110, 2 100 ($C\equiv C$), 1 000, 985, and 980 cm^{-1} ($trans-C=C$); λ_{\max} , 237 (ϵ 26 700), 264 (22 600), 312sh (34 100), 327 (46 400), 343 (54 200), 362 (43 500), 396 (4 000), and 421 nm (3 100); τ 2.32 (1 H, d, J 8 Hz, H^A), 2.45 (1 H, d, J 8 Hz, H^1), 2.58 (1 H, d, J 8 Hz, H^3), 2.64 (1 H, d, J 16.5 Hz,

H^B), 2.66 (1 H, d, *J* 8 Hz, H²), 3.03 (1 H, d, *J* 16.5 Hz, H^A), 3.19 (1 H, dd, *J* 15.5 and 10.5 Hz, H^D), 3.23 (1 H, dd, *J* 15.5 and 10.5 Hz, H^B), 3.39 (1 H, d, *J* 15.5 Hz, H^A), 3.56 (1 H, dd, *J* 15.5 and 10.5 Hz, H^C), 3.60 (1 H, d, *J* 10.5 Hz, H^E), 6.62 (1 H, s, C≡CH), 6.64 (1 H, s, C≡CH), and 8.13 (3 H, s, Me) (Found: C, 74.2; H, 4.5. C₂₁H₁₆Cl₂ requires C, 74.35; H, 4.75%).

7-Dichloromethylene-13-methyl-14,15,16,17-tetrahydrobenzocyclopentadecene (28).—A solution of the acyclic compound (25) (507 mg, 1.49 mmol) in pyridine (37 ml) and dry ether (11 ml) was added dropwise during 2 h to a stirred solution of anhydrous copper(II) acetate (3.4 g) in pyridine (106 ml) and dry ether (40 ml) at 50–52 °C, and the solution was stirred for a further 1 h at the same temperature. After work-up as for the isolation of (18), the product was chromatographed on alumina (4 × 11 cm). The fractions eluted with 2% ether in hexane gave the monobenzannulated fulvene (28) (79 mg, 16%) as a solid. It formed orange *needles* from hexane–benzene, m.p. 176–177 °C; *m/z* 338 (*M*⁺, 8%), 336 (*M*⁺, 10), and 255 (100); *M*, 337.2; *v*_{max}, 2 190 (C≡C) and 965 cm⁻¹ (*trans*-C=C); *λ*_{max}, 231 (ε 20 200), 293 (37 300), 318sh (30 400), and 371sh nm (13 900); τ 2.25 (1 H, d, *J* 8 Hz, H^A), 2.52 (1 H, d, *J* 16 Hz, H^B), 2.60 (1 H, d, *J* 8 Hz, H¹), 2.68 (1 H, d, *J* 8 Hz, H³), 2.76 (1 H, d, *J* 16 Hz, H^A), 2.78 (1 H, d, *J* 8 Hz, H²), 2.91 (1 H, dd, *J* 15.5 and 9.5 Hz, H^D), 3.22 (1 H, dd, *J* 15.5 and 6 Hz, H^C), 3.33 (1 H, d, *J* 9.5 Hz, H^E), 3.38 (1 H, d, *J* 15.5 Hz, H^A), 3.46 (1 H, dd, *J* 15.5 and 6 Hz, H^B), and 8.08 (3 H, s, Me) (Found: C, 75.0; H, 4.1. C₂₁H₁₄Cl₂ requires C, 74.8; H, 4.2%).

7-Dichloromethylene-11-(*o*-ethynylphenyl)-3-methylundeca-3,5,8,10-tetraen-1-yne (26).—A solution of dichloroacetyl chloride (7.0 ml) in dry benzene (45 ml) was added dropwise during 2 h to a stirred, refluxing solution of the acyclic ketone (23)⁸ (1.91 g, 6.99 mmol) and triethylamine (14.0 ml) in dry benzene (67 ml) under nitrogen, and the mixture was stirred under reflux for a further 4 h. After work-up as for the isolation of (14), the product was chromatographed on alumina (4 × 10 cm). The fractions eluted with 2% ether in hexane gave the acyclic compound (26) (499 mg, 21%) as a solid. It formed pale yellow *needles* from hexane, m.p. 98–99 °C; *m/z* 340 (*M*⁺, 12%), 338 (*M*⁺, 19), and 252 (100); *M*, 339.2; *v*_{max}, 3 290 (C≡CH), 2 090 (C≡C), 995, 990, and 970 cm⁻¹ (*trans*-C=C); *λ*_{max}, 235 (ε 16 500), 262 (21 700), 271 (21 900), 317sh (38 100), 329 (40 400), 343sh (34 500), and 372sh nm (19 900); τ 2.32 (1 H, d, *J* 7.5 Hz, H^A), 2.46 (1 H, d, *J* 8 Hz, H¹), 2.65 (1 H, d, *J* 8 Hz, H³), 2.76 (1 H, d, *J* 7.5 Hz, H²), 2.76 (1 H, d, *J* 15.5 Hz, H^D), 2.96 (1 H, dd, *J* 16 and 11.5 Hz, H^B), 2.98 (1 H, dd, *J* 15.5 and 9.5 Hz, H^B), 3.23 (1 H, dd, *J* 15.5 and 9.5 Hz, H^C), 3.38 (1 H, d, *J* 16 Hz, H^A), 3.48 (1 H, d, *J* 16 Hz, H^A), 3.51 (1 H, d, *J* 11 Hz, H^C), 6.62 (1 H, s, C≡CH), 6.65 (1 H, s, C≡CH), and 7.99 (3 H, s, Me) (Found: C, 74.4; H, 4.8. C₂₁H₁₆Cl₂ requires C, 74.4; H, 4.8%).

9-Dichloromethylene-13-methyl-14,15,16,17-tetrahydrobenzocyclopentadecene (29).—A solution of the acyclic compound (26) (216 mg, 0.64 mmol) in pyridine (15 ml) and dry ether (5 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (1.4 g) in pyridine (44 ml) and dry ether (17 ml) during 2 h at 50–52 °C, and the solution was stirred for a further 1 h at the same temperature. After work-up as for the isolation of (18), the product was chromatographed on alumina (4 × 8 cm). The fractions eluted with 2% ether in hexane gave the monobenzannulated fulvene (29) (77 mg, 36%) as a solid. It formed yellow *needles* from hexane–benzene, m.p. 134–136 °C; *m/z* 338 (*M*⁺, 20%), 336 (*M*⁺, 25), and 265 (100); *M*, 337.2; *v*_{max}, 2 190, 2 150 (C≡C)

and 970 cm⁻¹ (*trans*-C=C); *λ*_{max}, 232 (ε 30 100), 273sh (34 700), 285 (42 000), 305 (35 800), 368sh (14 000), and 394sh (10 400); τ 2.56–2.80 (4 H, m, Ar-H), 2.87 (1 H, dd, *J* 15.5 and 10.5 Hz, H^B), 2.92–2.97 (1 H, m, H^D), 3.25 (1 H, d, *J* 15.5 Hz, H^A), 3.35 (1 H, d, *J* 10.5 Hz, H^C), 3.34–3.46 (2 H, m, H^B and H^C), 3.58–3.72 (1 H, m, H^A), and 8.08 (3 H, s, Me) (Found: C, 75.0; H, 4.4. C₂₁H₁₄Cl₂ requires C, 74.8; H, 4.2%).

3-Dichloromethylene-1,7-bis(*o*-ethynylphenyl)hepta-1,4,6-triene (27).—A solution of dichloroacetyl chloride (7.5 ml) in dry benzene (46 ml) was added dropwise during 1.5 h to a stirred, refluxing solution of the acyclic ketone (24)⁹ (2.24 g, 7.25 mmol) and triethylamine (15 ml) in dry benzene (73 ml) under nitrogen, and the mixture was stirred under reflux for a further 2.5 h. After work-up as for the isolation of (14), the product was chromatographed on alumina (4 × 10 cm). The fractions eluted with 3% ether in hexane gave the acyclic compound (27) (554 mg, 23%) as a solid. It formed pale yellow *needles* from hexane–benzene, m.p. 159–160 °C; *m/z* 376 (*M*⁺, 14%), 374 (*M*⁺, 22), and 303 (100); *M*, 375.2; *v*_{max}, 3 290 (C≡CH), 2 110 (C≡C), 1 000, 985, and 980 cm⁻¹ (*trans*-C=C); *λ*_{max}, 235 (ε 40 300), 255 (33 800), 262 (33 800), 270sh (28 600), 326 (55 700), 341 (54 800), and 359sh nm (33 800); τ 2.30 (1 H, d, *J* 8 Hz, H⁴), 2.32 (1 H, d, *J* 8 Hz, H⁴), 2.44 (1 H, d, *J* 8 Hz, H¹), 2.48 (1 H, d, *J* 8 Hz, H¹), 2.56 (1 H, d, *J* 15.5 Hz, H^B), 2.55–2.80 (4 H, m, H², H², H³, and H³), 2.96 (1 H, dd, *J* 15 and 10 Hz, H^B), 2.98 (2 H, d, *J* 15.5 Hz, H^A and H^D), 3.08 (1 H, dd, *J* 15 and 10 Hz, H^C), 3.28 (1 H, d, *J* 15 Hz, H^A), 6.58 (1 H, s, C≡CH), and 6.64 (1 H, s, C≡CH) (Found: C, 77.1; H, 4.2. C₂₄H₁₆Cl₂ requires C, 76.8; H, 4.3%).

7-Dichloromethylene-16,17,18,19-tetrahydrodibenzo[a,g]-cyclopentadecene (30).—A solution of the acyclic compound (27) (98 mg, 0.26 mmol) in pyridine (7 ml) and dry ether (2 ml) was added dropwise during 2 h to a stirred solution of anhydrous copper(II) acetate (0.6 g) in pyridine (19 ml) and dry ether (7 ml) at 50–52 °C, and the solution was stirred for a further 1 h at the same temperature. After work-up as for the isolation of (18), the product was chromatographed on alumina (4 × 9 cm). Fractions, eluted with 2% ether in hexane, gave the dibenzannulated fulvene (30) (34 mg, 35%) as a solid. It formed pale yellow *needles* from hexane–benzene, m.p. 192–193 °C; *m/z* 374 (*M*⁺, 15%), 372 (*M*⁺, 25), and 302 (100); *M*, 373.2; *v*_{max}, 2 200 (C≡C), 1 000, and 980 cm⁻¹ (*trans*-C=C); *λ*_{max}, 231 (ε 39 000), 303 (56 100), and 371sh nm (13 700); τ (27 °C) 2.25 (1 H, d, *J* 8 Hz, H⁴), 2.53 (1 H, d, *J* 16 Hz, H^B), 2.56–2.77 (7 H, m, H¹, H², H³, H¹, H², H³, and H⁴), 2.74 (1 H, d, *J* 16 Hz, H^A), 2.90–3.03 (1 H, m, H^D), 3.18–3.37 (2 H, m, H^B and H^C), and 3.50–3.63 (1 H, m, H^A); τ (–60 °C) 2.24 (1 H, d, *J* 8 Hz, H⁴), 2.54 (1 H, d, *J* 16 Hz, H^B), 2.55–2.72 (7 H, m, H¹, H², H³, H¹, H², H³, and H⁴), 2.77 (1 H, d, *J* 16 Hz, H^A), 3.04 (1 H, d, *J* 16 Hz, H^D), 3.19 (1 H, dd, *J* 16 and 11 Hz, H^C), 3.31 (1 H, dd, *J* 16 and 11 Hz, H^B), and 3.58 (1 H, d, *J* 16 Hz, H^A) (Found: C, 77.0; H, 4.0. C₂₄H₁₄Cl₂ requires C, 77.2; H, 3.8%).

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