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

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Syntheses of 4,9-dimethyl-13-diphenylmethylene-5,6,7,8-tetradehydrocyclotridecene (7), 4,9-dimethyl-15-diphenylmethylene-5,6,7,8-tetradehydrocyclopentadecene (8), 6,11-dimethyl-17-diphenylmethylene-7,8,9,10-tetradehydrocycloheptadecene (9), and 6,11-dimethyl-19-diphenylmethylene-7,8,9,10-tetradehydrocyclononadecene (10) are described. Although examination of the ^{1}H n.m.r. spectra suggested that all of the fulvenes (7)—(10) are atropic, the benzannelated derivatives of pentadecafulvene (8), *i.e.* 13-methyl-7-diphenylmethylene-14,15,16,17-tetradehydrobenzocyclopentadecene (25), 13-methyl-9-diphenylmethylene-14,15,16,17-tetradehydrobenzocyclopentadecene (26) and 7-diphenylmethylene-16,17,18,19-tetradehydrodibenzo[*a*,*g*]cyclopentadecene (27) were prepared in order to examine the tropicity of (8) more closely. Comparison of the ^{1}H n.m.r. spectra of these benzannelated fulvenes (25)—(27) with that of (8) reveals that the nonbenzannelated fulvene (8) is atropic. The influence of benzannelation upon the structure of the molecular skeleton of the tetradehydropentadecafulvene system is also discussed.

Syntheses of a series of paratropic dimethyltetradehydro-[13]- (1) [1] and dimethyltetradehydro[17]-annulenones (3),[2] and the diatropic dimethyltetradehydro[15]- (2) [2] and dimethyltetradehydro[19]-annulenones (4) [2] as well as their α-methyl [3] and α-ethyl substituted derivatives [4] have been described previously. Higher analogues of these annulenones, *i.e.* [21]-,[5] [23]-,[6] and [25]-annulenone,[6] could also be synthesized, but only with difficulty. In view of the convenient and relatively easy preparation of compounds (1)—(4) they appeared to be desirable starting compounds for syntheses of cross-conjugated π-electron systems. In fact the synthesis of heptatrideca-,[7] heptapentadeca-,[8] heptaheptadeca-,[8] and heptanonadeca-fulvalene [9] derivatives through the reaction of 8-oxoheptafulvene with the annulenones (1)—(4) has been achieved previously. We were interested in another cross-conjugated π-electron system [(5) and (6)], fulvene, which might be derived from the annulenones (1)—(4).

If polarization of an exocyclic bond does not occur, the fulvenes of type (5) are potentially diatropic, and those of type (6) are potentially paratropic since the former contains cross-conjugated $(4n + 2)$π-electrons and the latter $(4n)$π-electrons. We chose the phenyl group as the substituent at the ω,ω-positions of the fulvenes [(5; R = Ph) and (6; R = Ph)] since it is known to stabilize large-membered conjugated π-electron systems.[10]

This paper deals with syntheses and properties of the title compounds (7)—(10),[11] which are the largest ring monocyclic fulvene derivatives obtained,[12] and further examines the properties of (8) by comparing them with its benzannelated derivatives (25)—(27).[13]

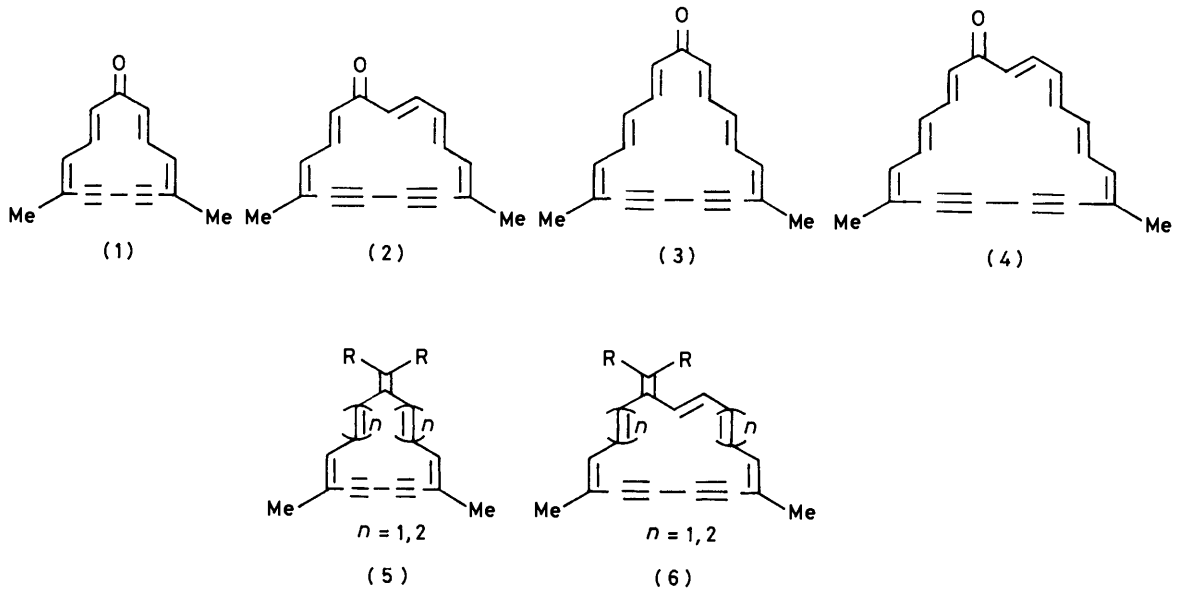
Results and Discussion

To obtain the tridecafulvene (7) we first attempted mixed reductive coupling of the annulenone (1) with benzophenone employing $TiCl_3$–Li in dimethoxyethane according to McMurry's method.[14] However, all the attempts were unsuccessful. The successful synthesis of heptafulvalene derivatives using an addition reaction of a ketene (8-oxoheptafulvene) [7,8] with annulenones prompted us to attempt the reaction of annulenones with diphenylketene, which is easily obtainable.[15]

Syntheses of the fulvenes (7)—(10) were first carried out by reaction between diphenylketene and the cyclic ketones (annulenones) (1)—(4). Diphenylketene was generated from triethylamine and diphenylacetyl chloride, which was prepared from diphenylacetic acid and excess of thionyl chloride immediately before use. Thus, the reaction of tetradehydro-[13]- (1),[1] tetradehydro[15]- (2),[2] tetradehydro[17]- (3),[2] and tetradehydro[19]-annulenone (4) [2] with diphenylketene in dry diethyl ether and/or dry benzene gave dimethyldiphenyltetradehydrotridecafulvene (7) (32%), dimethyldiphenyltetradehydropentadecafulvene (8) (51%), dimethyldiphenyltetradehydroheptadecafulvene (9) (62%), and dimethyldiphenyltetradehydrononadecafulvene (10) (35%), respectively. All of these fulvenes (7)—(10) were obtained as red crystals and proved to be very stable.

The ^{1}H n.m.r. spectra of the fulvenes (7)—(10) were taken at 200 MHz (see below). However, since very large upfield and downfield shifts of the signals due to the olefinic protons were not observed in these spectra, model compounds were necessary to examine tropicities of the fulvenes. We considered that the corresponding acyclic compounds (11)—(14), respectively, would be the most appropriate for this. Thus, we prepared the acyclic model compounds (11)—(14) from the acyclic ketones (15)—(18) [which are the precursors of annulenones (1)—(4), respectively] by almost the same procedure as that used for the synthesis of the fulvenes (7)—(10).

The reaction of the acyclic ketones (15),[1] (16),[2] (17),[2] and (18) [2] with diphenylketene afforded 3,11-dimethyl-7-diphenylmethylenetrideca-3,5,8,10-tetraene-1,12-diyne (11) (36%), 3,13-dimethyl-7-diphenylmethylenepentadeca-3,5,8,10,12-pentaene-1,14-diyne (12) (35%), 3,15-dimethyl-9-diphenylmethyleneheptadeca-3,5,7,10,12,14-hexaene-1,16-diyne (13) (22%), and 3,17-dimethyl-9-diphenylmethylenenonadeca-3,5,7,10,12,14,16-heptaene-1,18-diyne (14) (18%), respectively. Oxidative coupling of the acyclic compounds (11)—(14) with anhydrous copper(II) acetate in pyridine and diethyl ether at 50 °C [16] furnished the corresponding monomeric cyclic compounds, which proved to be identical with the above-described fulvenes (7)—(10), respectively. The acyclic compounds (11)—(14) are rather unstable substances. Thus, the desired fulvenes (7)—(10) could be obtained by two different synthetic



approaches, and the second route by the sequence (15) ⟶ (11) ⟶ (7) was preferred since the overall yields were superior to those obtained by the first route [*e.g.* (15) ⟶ (1) ⟶ (7)].

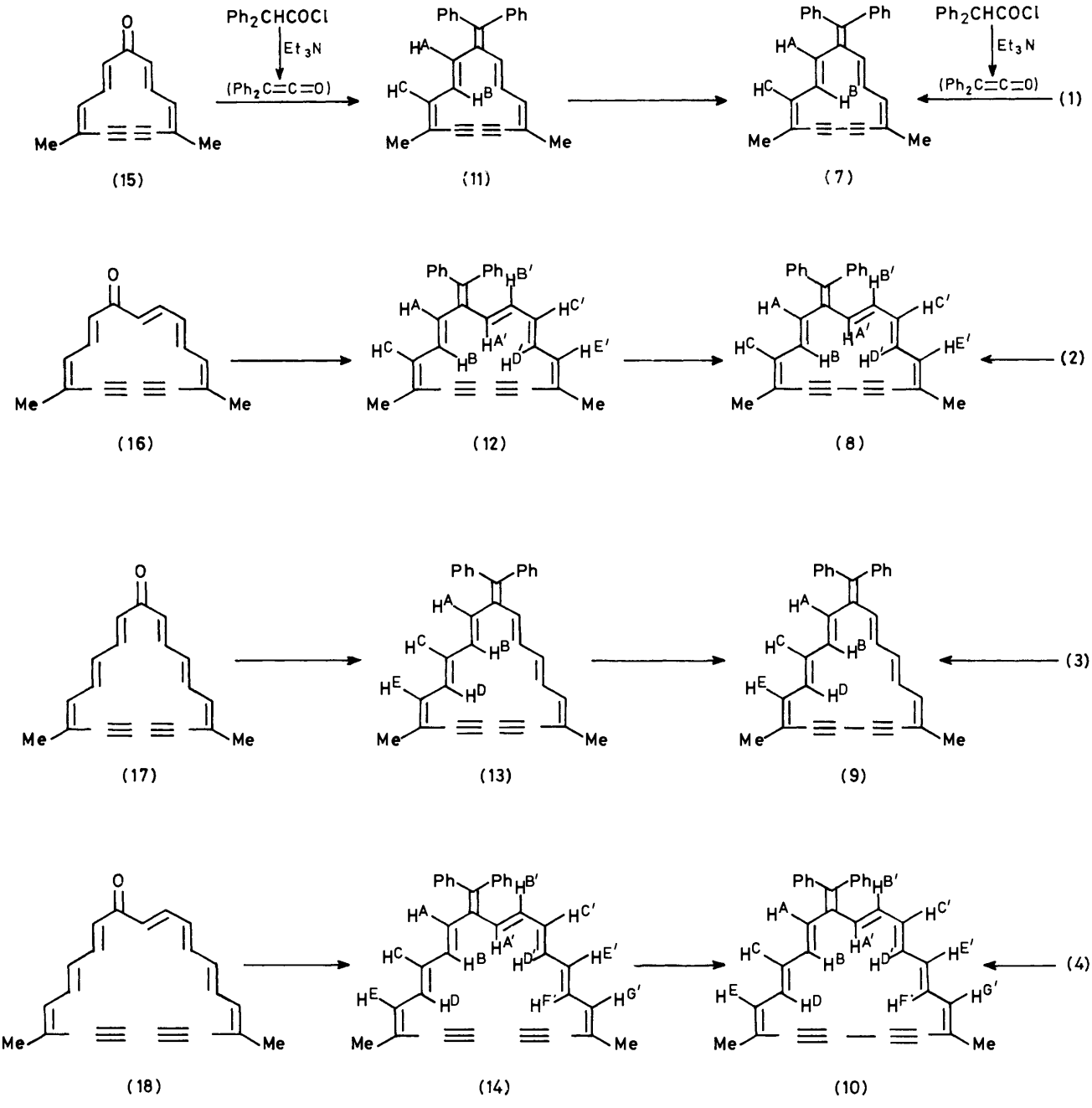
Variable-temperature ^{1}H n.m.r. spectra of compounds (7)—(10) thus obtained were run over the range −60 to 60 °C, and the spectra of all of the fulvenes (7)—(10) proved to be essentially temperature-independent, revealing that the conformations indicated remain unchanged over this temperature range, in contrast to the cases of some of the benzannelated derivatives (see below).

The chemical shifts of the olefinic, aromatic, and methyl protons of (7)—(10) are listed in Table 1, together with those of the corresponding acyclic model compounds (11)—(14). Individual assignments were made on the basis of the multiplicities and coupling constants (Experimental section), and were assisted by the use of the double resonance technique where necessary.

As can be seen from Table 1, in the spectra of the pentadecafulvene (8) and the nonadecafulvene (10), compared with those of the tridecafulvene (7) and the heptadecafulvene (9), the high- and low-field shifts of the resonances of the outer and inner protons, respectively, are as expected for the potentially paratropic fulvenes (8) and (10). However, if the tropicity of the pentadecafulvene (8) is assessed from the differences in chemical shifts between its protons and those of the corresponding acyclic model compound (12) (Table 1), the pentadecafulvene (8) is seen to be atropic since no significant upfield shift for outer protons $H^{A'}$, H^{C}, and $H^{E'}$ is observed, although a downfield shift for the inner protons $H^{A'}$, H^{B}, and $H^{D'}$ (Δ −0.79 to −0.99) and an upfield shift for the outer protons $H^{B'}$ and $H^{C'}$ (Δ +0.25 to +0.84) and the methyl protons (Δ +0.13) are observed. Similar behaviour is seen when the proton signals of the nonadecafulvene (10) are compared with those of the corresponding acyclic compound (14). Thus, the fulvenes (8) and (10) appear to be atropic, although further studies will be required to establish their tropicities fully (see below). Both the chemical shifts of the protons of the trideca- (7) and the heptadeca-fulvene (9), and comparison of the chemical shifts, as before, with those of the acyclic model compounds (11) and (13), respectively, show that the fulvenes (7) and (9) are clearly atropic.

To finally establish the tropicity of (8) we examined the ^{1}H n.m.r. spectra of its benzannelated derivatives. It is well known that increasing annelation (with one or more benzene rings) of a large-membered conjugated π-electron system usually causes progressive reduction of the tropicity of the macrocyclic system if the position of the benzene rings excludes a contribution from an equivalent Kekulé structure.[17] Thus, the synthesis of the benzannelated fulvenes (25)—(27) was carried out, in moderate yields. Reaction of the acyclic ketones (19),[18] (20),[18] and (21) [3c] with diphenylketene in dry benzene for 20—25 h at room temperature gave 11-(*o*-ethynylphenyl)-3-methyl-9-diphenylmethyleneundeca-3,5,7,10-tetraen-1-yne (22) (38%), 11-(*o*-ethynylphenyl)-3-methyl-7-diphenylmethyleneundeca-3,5,8,10-tetraen-1-yne (23) (34%), and 1,7-bis(*o*-ethynylphenyl)-3-diphenylmethylenehepta-1,4,6-triene (24) (54%), respectively. Oxidative coupling of (22), (23), and (24) with anhydrous copper(II) acetate, as before, afforded 13-methyl-7-diphenylmethylene-14,15,16,17-tetradehydrobenzocyclopentadecane (25) (65%), 13-methyl-9-diphenylmethylene-14,15,16,17-tetradehydrobenzocyclopentadecane (26) (46%), and 7-diphenylmethylene-16,17,18,19-tetradehydrodibenzo[*a*,*g*]cyclopentadecene (27) (68%), respectively.

The chemical shifts of the protons of these fulvenes (25)—(27) are also listed in Table 1. As can be seen from Table 1, comparison of the chemical shifts of the protons of the benzannelated fulvenes (25)—(27) with those of the corresponding acyclic model compounds (22)—(24), respectively, indicates that the fulvenes (25)—(27) are atropic, since no significant upfield and downfield shifts of the signals due to their outer and inner protons, respectively, are observed. [This is seen from the spectra of (25)—(27) at room temperature which were illustrated previously.[13]] In the spectra of (25)—(27), compared with that of the nonbenzannelated fulvene (8), no upfield and downfield shifts of the resonances of the outer and inner protons, respectively, are observed. However, as exemplified in the spectrum of the monobenzannelated fulvene (25), the inner H^{B} and outer $H^{B'}$, $H^{C'}$, and $H^{E'}$ protons resonate in almost the same region as those of the nonbenzannelated fulvene (8). For the inner proton, this tendency appears even in the spectra of the benzannelated fulvenes (26) and (27). Thus, decreases in both upfield and downfield shifts of the signals due to the outer and inner protons, respectively, are not clearly observed on passing from the nonbenzannelated (8), to monobenzannelated (25) and (26), to the dibenzannelated fulvene (27). Since a decrease in tropicity with benzannelation was found to occur for the



corresponding 14π-electron, diatropic tetradehydro[15]annulenone series,[3a,17b] which should have a geometry similar to that of the fulvene system, this observation together with a comparison of the chemical shifts of the protons of (8) with those of the corresponding acyclic model compound (12), as described above, leads us to believe that the appearance of the resonances of the outer and inner protons at high field and low field respectively, in the spectrum of (8) does not reflect a paramagnetic ring current induced in the 16π-electron, cross-conjugated system of (8); the ^{1}H n.m.r. spectral pattern of (8) must be a reflection of local anisotropies due to the two phenyl and the diacetylene moieties. Thus, it is concluded that the fulvene (8) is not paratropic, but atropic.

In addition, in rather surprising contrast to the cases of (8), (25), and (26), the dibenzannelated fulvene does not exist in the conformation (27), but in the more unlikely conformation (27a) at room temperature. This follows from the fact that the value of $J_{B'C'}$ is 10 Hz, indicating an *s-trans* relationship of the $CH^{B'}-CH^{C'}$ bond. In view of this result, variable-temperature spectra of (25)—(27) were run over the range −60 to 60 °C; the spectra of (25) and (27) proved to be essentially temperature-independent, while the spectrum of (26) is temperature-dependent. Although the $H^{A'}$, $H^{B'}$, and $H^{C'}$ resonances of (26) were an unresolved multiplet at 28 °C (and above), these bands were resolved on cooling, and analysis of the first-order pattern indicated that the fulvene exists in the conformation (26a) at −30 °C. Further cooling resulted in increased separation of the $H^{B'}$ and $H^{C'}$ bands (see Experimental section).

Since the benzannelated derivatives were found to exist in the same conformation as that of nonbenzannelated annulenone in both the α-methyl- and the α′-methyl-substituted tetradehydro[15]annulenone series as well as the unsubstituted one,[3c] and the corresponding dibenzannelated tetradehydro-[15]annulenone was shown to exist in the conformation (28),[17b] the unlikely conformation (27a) must be due to the effect of

Table 1. ^{1}H N.m.r. parameters of compounds (7)—(14) and (22)—(27) (in $CDCl_3$) at 200 MHz, determined at 21 °C (τ values)

	H^A	$H^{A'}$	H^B	$H^{B'}$	H^C	$H^{C'}$	H^D	$H^{D'}$	H^E	$H^{E'}$	$H^{F'}$	$H^{G'}$	ArH	Me
(11)	3.62		2.92		3.68								2.65—2.86	8.07
(7)	3.73		2.95		3.32								2.60—2.84	8.10
(12)	3.65	3.63	3.03 [a]	3.31 [a]	3.67	3.68		3.33 [a]		3.67			2.69—2.88	8.07
(8)	3.61	2.64	2.24	4.15	3.60	3.93		2.40		3.57			2.7—2.9	8.20
Δ[(8) − (12)]	−0.04	−0.99	−0.79	+0.84	−0.07	+0.25		−0.93		−0.10				+0.13
(13)	3.62		3.26		3.65		3.36		3.63				2.59—2.85	8.03
(9)	3.89		3.37—3.60		3.37—3.60		3.37—3.60		3.29				2.65—2.80	8.06
(14)	3.20											3.75	2.60—2.86	8.06
(10)	3.44—3.88	3.30	2.89	3.44		3.88	2.62	3.12	3.44		[b]	3.88	2.60—2.86	8.13, 8.15
(22)	3.13	3.54	2.57	3.10		3.64		3.26		3.64			2.47—2.84	8.06
(25)	3.00	2.60—2.94	2.25	4.11		3.69		2.60—2.94		3.52			2.60—2.94	8.16
(23)	3.52	3.61	2.95	3.02—3.24	3.63	3.02—3.24		2.89					2.37—2.82	8.05
(26)	3.36—3.56		2.47	3.36		3.56		2.61—2.86					2.61—2.86	8.15
(24)	3.11	3.44	2.51	2.86—3.22		2.86—3.22		2.36—2.84					2.36—2.84	
(27)	3.00	3.32	2.38	3.59		3.33		3.09					2.60—2.91	

[a] Assignments may be reversed in each group (see Experimental section). [b] The $H^{F'}$ proton signal of (10) is hidden by those of the phenyl protons.

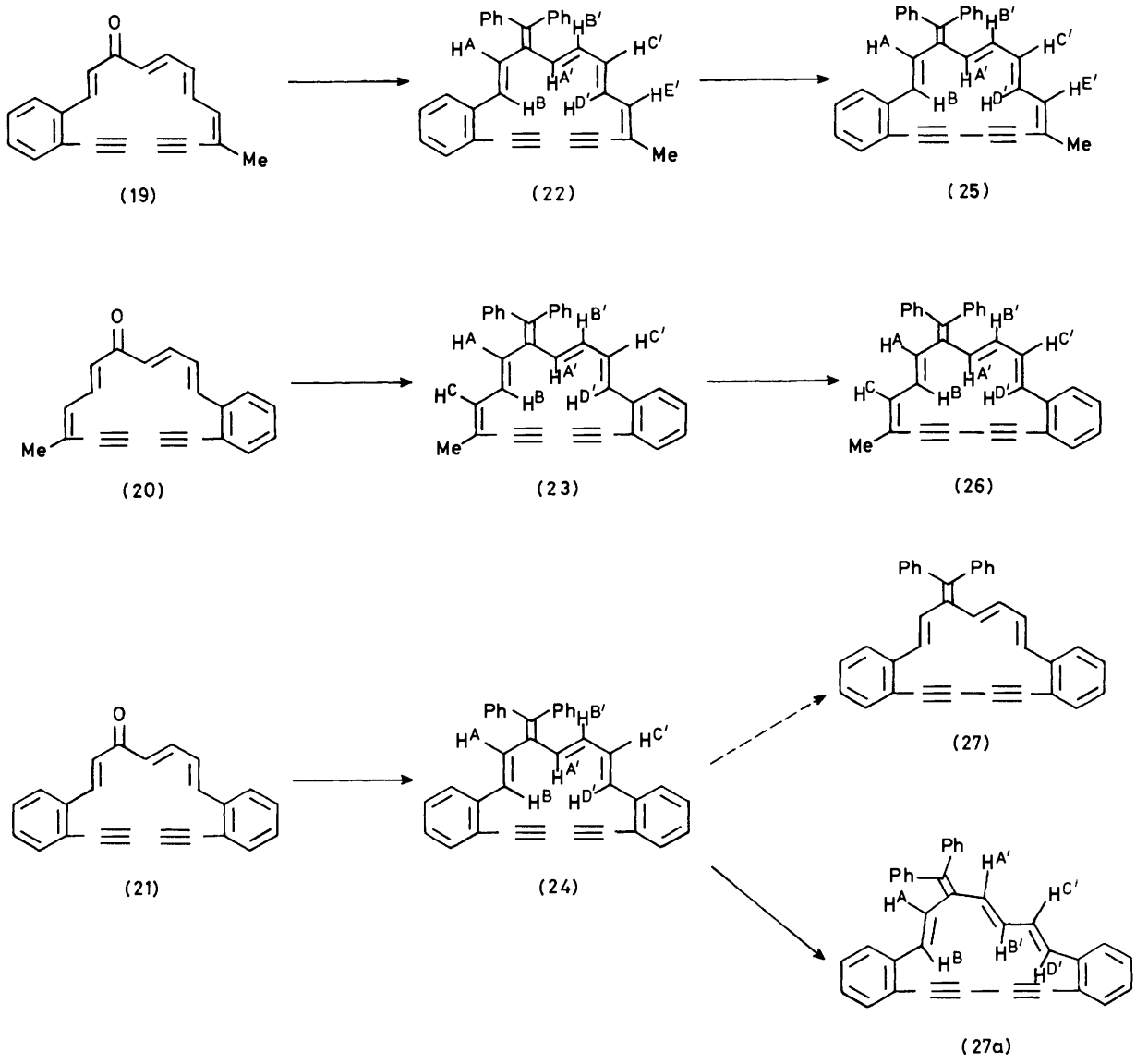


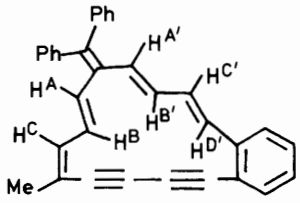
Table 2. Electronic absorption maxima of fulvenes in dichloromethane

$\lambda_{max.}$ (nm) ($\varepsilon_{max.}$)			
(7)	(8)	(9)	(10)
		278sh (25 200)	
267 (31 500)	275 (24 600)	292 (27 800)	305 (25 200)
308 (21 700)	332 (25 300)	343 (24 200)	363 (37 600)
405 (23 500)	410sh (11 400)	437 (17 800)	442sh (9 800)

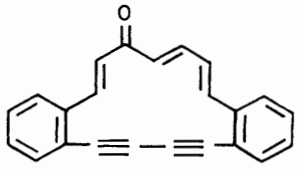
changing from the oxygen atom of the annulenone to the bulky phenyl group at the exocyclic bond of the fulvene.

The electronic absorption maxima of the fulvenes (7)—(10) in dichloromethane are given in Table 2; the spectra were illustrated previously.[11] Although the main maxima of the fulvenes exhibit a bathochromic shift as the ring size increases, this shift is larger between the trideca- (7) ($\lambda_{max.}$ 308 nm) and the pentadeca-fulvene (8) ($\lambda_{max.}$ 332 nm) and between the heptadeca- (9) ($\lambda_{max.}$ 343 nm) and the nonadeca-fulvene (10) ($\lambda_{max.}$ 363 nm) than between the pentadeca- (8) and the heptadeca-fulvene (9). Also, it is seen from the absorption curves that the spectra of (7) and (9) {type (5): [4*n* + 2]-fulvene} are similar, and those of (8) and (10) {type (6): [4*n*]fulvene} differ only in the bathochromic shift of each band. This must be due to the occurrence of the same sort of alternation between the maxima of [4*n* + 2] and [4*n*] systems as has been observed for monocyclic annulenes, dehydroannulenes,[19] and dehydroannulenones.[2]

Although the electronic spectra of the fulvenes (25)—(27) are not illustrated, the longest wavelength bands of (8) and (25)—(27) move towards longer wavelength in the sequence (8) > (25) ≃ (26) > (27), *i.e.* with increasing number of fused benzene ring(s) on the macrocyclic system; this shows the degree of extended conjugation of the π-electron system in



(26a)



(28)

tetradehydropentadecafulvene, as has been observed in the corresponding tetradehydro[15]annulenone series.[3c]

We attempted the reductive coupling of the annulenone (1) itself and of the annulenones (1) and (2) by $TiCl_3$–$LiAlH_4$ or $TiCl_3$–K (McMurry's method),[20] TiCl–Mg(Hg) (Corey's method),[21] or $TiCl_4$–Zn (Mukaiyama's method),[22] to give the tridecatridecafulvalene or tridecapentadecafulvalene, and also the condensation reaction of malononitrile with annulenone (1) or (2) according to the procedure of Oda *et al.*[23] to give dicyanofulvenes. However, these were all unsuccessful.

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 unless otherwise stated; only significant maxima are described. U.v. spectra were measured for solutions in dichloromethane and run on a Hitachi 220A spectrophotometer. Mass spectra were recorded with a JEOL JMS-200 spectrometer operating at 75 eV using a direct-inlet system, and the field desorption spectra were taken with a JEOL-01-FG2 spectrometer. ^{1}H N.m.r. spectra were run on a Varian XL-200 (200 MHz) or JEOL FX-200 (200 MHz) or FX-90Q (90 MHz) spectrometer ($CDCl_3$ solution). Merck alumina (activity II-III) and silica gel (Wako gel C-200) were used for column chromatography and preparative t.l.c. was carried out on 20 × 20 cm alumina plates (Merck, 0.5 or 2 mm thick). The progress of most reactions was followed by t.l.c. using Merck pre-coated alumina. Sodium sulphate was used as drying agent, and solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

4,9-*Dimethyl*-13-*diphenylmethylene*-5,6,7,8-*tetradehydrocyclotridecene* (7) *from Annulenone* (1).—A mixture of diphenylacetic acid (1.5 g) and thionyl chloride (15 ml) was heated under reflux for 3 h at 90—100 °C (bath temp.). After evaporating the excess of thionyl chloride under reduced pressure, the diphenylacetyl chloride thus obtained was dissolved in dry ether (15 ml). The solution was added dropwise during 20 min to a solution of triethylamine (2 ml) in dry ether (10 ml) with stirring at room temperature under nitrogen. After stirring for a further 15 min, a solution of the [13]annulenone (1) [1] (100 mg, 0.48 mmol) in dry ether–dry benzene (1 : 1, 10 ml) was added during 20 min and stirring was continued overnight at the same temperature. Then the reaction mixture was passed through a short column of alumina (2 × 2 cm) to remove inorganic materials and eluted with hexane–ether (1 : 1). The residual dark red liquid obtained by concentrating the eluates was chromatographed on alumina (3 × 5 cm). Fractions, eluted with hexane, gave the tridecafulvene (7) (111 mg, 32%) as a solid. Recrystallization from hexane afforded red *needles*, m.p. 174—175 °C; *m/z* 358 (M^+, 100%); *M* 358.4; $\nu_{max.}$ 2 150 (C≡C), 1 605 (C=C), and 980 cm^{-1} (*trans*-C=C); for u.v. data see Table 2 and see ref. 11; τ 2.60—2.66 (6 H, m, ArH), 2.70—2.84 (4 H, m, ArH), 2.95 (2 H, dd, *J* 16 and 11 Hz, H^B), 3.32 (2 H, d, *J* 10 Hz, H^C), 3.73 (2 H, d, *J* 16 Hz, H^A), and 8.10 (6 H, s, Me) (Found: C, 93.9; H, 6.3. $C_{28}H_{22}$ requires C, 93.8; H, 6.2%).

4,9-*Dimethyl*-15-*diphenylmethylene*-5,6,7,8-*tetradehydrocyclopentadecene* (8) *from Annulenone* (2).—A solution of diphenylacetyl chloride (prepared from 1.2 g of diphenylacetic acid and 10 ml of thionyl chloride as described above) in dry ether (10 ml) was added during 20 min to a solution of triethylamine (1.5 ml) in dry ether (20 ml) with stirring at room temperature under nitrogen. After stirring for a further 20 min, a solution of the [15]annulenone (2) [2] (150 mg, 0.43 mmol) in dry ether–dry benzene (1 : 1, 40 ml) was added during 30 min and was stirred overnight at the same temperture. The product was passed through a short column of alumina (2 × 3 cm) and eluted with benzene. The residual red liquid obtained from the eluates after removal of the solvent was chromatographed on alumina (3 × 19 cm). Fractions, eluted with hexane, gave the pentadecafulvene (8) (85 mg, 51%) as a partly crystallized liquid. Crystallization from hexane afforded red *plates*, m.p. 160—161 °C; *m/z* 384 (M^+, 100%); *M*, 384.4; $\nu_{max.}$ 2 170 (C≡C), 1 600 (C=C), 970 (*trans*-C=C), and 700 cm^{-1} (*cis*-C=C); for u.v. data see Table 2 and ref. 11; τ 2.24 (1 H, dd, *J* 16 and 11.5 Hz, H^B), 2.40 (1 H, dd, *J* 15.5 and 10.5 Hz, $H^{D'}$), 2.64 (1 H, d, *J* 16 Hz, $H^{A'}$), *ca.* 2.7—2.9 (10 H, m, ArH), 3.57 (1 H, d, *J* 10.5 Hz, $H^{E'}$), 3.60 (1 H, d, *J* 11.5 Hz, H^C), 3.61 (1 H, d, *J* 16 Hz, H^A), 3.93 (1 H, dd, *J* 15.5 and 5.5 Hz, $H^{C'}$), 4.15 (1 H, dd, *J* 16 and 5.5 Hz, $H^{B'}$), and 8.20 (6 H, s, Me) (see also ref. 13) (Found: C, C, 94.0; H, 6.3. $C_{30}H_{24}$ requires C, 93.7; H, 6.3%).

6,11-*Dimethyl*-17-*diphenylmethylene*-7,8,9,10-*tetradehydrocycloheptadecene* (9) *from Annulenone* (3).—A solution of diphenylacetyl chloride (prepared from 1.0 g of diphenylacetic acid and 10 ml of thionyl chloride) in dry ether (10 ml) was added dropwise during 15 min to a stirred solution of triethylamine (1.5 ml) in dry ether (15 ml) at room temperature under nitrogen. After stirring for a further 10 min, a solution of the [17]annulenone (3) [2] (150 mg, 0.58 mmol) in dry ether–dry benzene (1 : 1, 40 ml) was then added dropwise during 30 min and the mixture was stirred for a further 3 h at the same temperature, then passed through a short column of alumina (2 × 3 cm) and eluted with benzene. The red liquid obtained from the eluates after removal of the solvent was chromatographed on alumina (3 × 9 cm). The initial fractions, eluted with hexane, gave the heptadecafulvene (9) (76 mg, 58%) as a solid. Recrystallization from hexane afforded red *needles*, m.p. 209—210 °C; *m/z* 410 (M^+, 100%); *M*, 410.5; $\nu_{max.}$ 2 170 (C≡C), 1 595 (C=C), and 990 cm^{-1} (*trans*-C=C); for u.v. data see Table 2 and ref. 11; τ 2.65—2.70 (6 H, m, ArH), 2.74—2.81 (4 H, m, ArH), 3.29 (2 H, d, *J* 10 Hz, H^E), 3.37—3.60 (6 H, m, H^B, H^C, and H^D), 3.89 (2 H, d, *J* 15.5 Hz, H^A), and 8.06 (6 H, s, Me) (Found: C, 93.8; H, 6.6. $C_{32}H_{26}$ requires C, 93.6; H, 6.4%).

6,11-*Dimethyl*-19-*diphenylmethylene*-7,8,9,10-*tetradehydrocyclononadecene* (10) *from Annulenone* (4).—A solution of diphenylacetyl chloride (prepared from 1.0 g of diphenylacetic acid and 4.0 ml of thionyl chloride) in dry benzene (17 ml) was added dropwise during 15 min to a stirred solution of triethylamine (2.0 ml) in dry benzene (5 ml) at room temperature under nitrogen. After stirring for a further 20 min, a solution of the [19]annulenone (4) [2] (116 mg, 0.41 mmol) in dry ether–dry benzene (1 : 2, 30 ml) was then added dropwise during 30 min at the same temperature and the mixture was heated under reflux for 4 h. The product was passed through a short column of alumina (2 × 3 cm) and eluted with ether–benzene (1 : 1). The orange liquid obtained by concentrating the eluates was chromatographed on alumina (3 × 15 cm). Fractions eluted with 5% ether in hexane gave the nonadecafulvene (10) (63 mg, 35%) as a solid. Recrystallization from hexane afforded red *needles*, m.p. 212—213 °C; *m/z* 436 (M^+, 100%); *M*, 436.5; $\nu_{max.}$ 2 170 (C≡C), 1 600 (C=C), 995, 985 (*trans*-C=C), and 700 cm^{-1} (*cis*-C=C); for u.v. data see Table 2 and ref. 11; τ 2.62 (1 H, dd, *J* 15 and 11 Hz, H^D), 2.60—2.86 (11 H, m, $H^{F'}$ and ArH), 2.89 (1 H, dd, *J* 15.5 and 11 Hz, H^B), 3.12 (1 H, dd, *J* 15.5 and 10.5 Hz, $H^{D'}$), 3.30 (1 H, d, *J* 16 Hz, $H^{A'}$), 3.44—3.88 (7 H, m, H^A, $H^{B'}$, H^C, $H^{C'}$, H^E, H^E, and $H^{G'}$), 8.13 (3 H, s, Me), and 8.15 (3 H, s, Me) (Found: C, 93.6; H, 6.8. $C_{34}H_{28}$ requires C, 93.5; H, 6.5%).

3,11-*Dimethyl*-7-*diphenylmethylenetrideca*-3,5,8,10-*tetraene*-1,12-*diyne* (11).—A solution of diphenylacetyl chloride (prepared from 1.5 g of diphenylacetic acid and 10 ml of thionyl chloride) in dry ether (15 ml) was added dropwise during 30 min to a stirred solution of triethylamine (3.0 ml) in dry ether (15 ml) at room temperature under nitrogen and the mixture was stirred for a further 15 min at the same temperature. Then a solution of the acyclic ketone (15) [1] (300 mg, 1.43 mmol) in dry ether (10 ml) was added dropwise during 10 min and stirring was continued overnight at room temperature. The reaction mixture was passed through a short column of silica gel (2 × 3 cm) and eluted with benzene. The residual liquid obtained by concentrating the eluates was chromatographed on silica gel (5 × 20 cm). The initial fractions, eluted with 40% benzene in hexane, gave the desired product (11) (183 mg, 36%) as a solid. Recrystallization from hexane afforded yellow *needles*, m.p. 141—143 °C; *m/z* 360 (M^+, 85%) and 165 (100); *M*, 360.4; $\nu_{max.}$ 3 275 (C≡CH), 2 090 (C≡C), 1 600 (C=C), and 975 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 259 (ε 42 900), 272sh (34 600), 333 (39 200), and 365 nm (45 400); τ 2.65—2.86 (10 H, m, ArH), 2.92 (2 H, dd, *J* 16 and 11 Hz, H^B), 3.62 (2 H, d, *J* 16 Hz, H^A), 3.68 (2 H, d, *J* 11 Hz, H^C), 6.73 (2 H, s, C≡H), and 8.07 (6 H, s, Me) (Found: C, 93.1; H, 6.45. $C_{28}H_{24}$ requires C, 93.3; H, 6.7%).

3,13-*Dimethyl*-7-*diphenylmethylenepentadeca*-3,5,8,10,12-*pentaene*-1,14-*diyne* (12).—A solution of diphenylacetyl chloride (prepared from 1.5 g of diphenylacetic acid and 10 ml of thionyl chloride) in dry ether (15 ml) was added dropwise to a stirred solution of triethylamine (3.0 ml) in dry ether (15 ml) during 20 min at room temperature under nitrogen and the mixture was stirred for a further 15 min. A solution of the acyclic ketone (16) [2] (190 mg, 0.81 mmol) in dry ether (10 ml) was then added dropwise during 10 min and the mixture was stirred overnight at the same temperature. The product was passed through a short column of silica gel (5 × 8 cm) and eluted with benzene. The liquid obtained by concentrating the eluates was chromatographed on silica gel (5 × 20 cm). The initial fractions, eluted with hexane–benzene (1 : 1), gave the desired product (12) (110 mg, 35%) as a solid. Recrystallization from hexane–benzene afforded orange *needles*, m.p. 109—110 °C; *m/z* 386 (M^+, 100%); *M*, 386.5; $\nu_{max.}$ 3 280, 3 270 (C≡CH), 2 080 (C≡C), 1 600 (C=C), and 985 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 271 (ε 36 500), 289sh (25 500), 334sh (36 600), 350 (44 600), and 380 nm (49 500); τ 2.69—2.88 (10 H, m, ArH), 3.03 (1 H, dd, *J* 15.5 and 11.5 Hz, H^B or $H^{B'}$ or $H^{D'}$), 3.31 (1 H, dd, *J* 15.5 and 11.5 Hz, $H^{B'}$ or H^B or $H^{D'}$), 3.33 (1 H, dd, *J* 15.5 and 11.5 Hz, $H^{D'}$ or H^B or $H^{B'}$), 3.63 (1 H, d, *J* 15.5 Hz, $H^{A'}$), 3.65 (1 H, d, *J* 15.5 Hz, H^A), 3.67 (2 H, d, *J* 11.5 Hz, H^C and $H^{E'}$), 3.68 (1 H, dd, *J* 15.5 and 11.5 Hz, $H^{C'}$), 6.68 (1 H, s, C≡CH), 6.72 (1 H, s, C≡CH), and 8.07 (6 H, s, Me) (Found: C, 93.4; H, 6.6. $C_{30}H_{26}$ requires C, 93.2; H, 6.8%).

3,15-*Dimethyl*-9-*diphenylmethyleneheptadeca*-3,5,7,10,12,14-*hexaene*-1,16-*diyne* (13).—A solution of diphenylacetyl chloride (prepared from 1.5 g of diphenylacetic acid and 5.0 ml of thionyl chloride) in dry benzene (25 ml) was added dropwise during 15 min to a stirred solution of triethylamine (3.0 ml) in dry benzene (8 ml) at room temperature under nitrogen and the mixture was stirred for a further 20 min. Then a solution of the acyclic ketone (17) [2] (500 mg, 1.91 mmol) in dry benzene (10 ml) was added dropwise during 15 min at the same temperature and the mixture was heated under reflux for 45 min, then chilled, and poured onto water. The organic layer, combined with the benzene extracts from the aqueous layer, was washed successively with dilute hydrochloric acid, water, aqueous sodium hydrogen carbonate, and brine. Drying followed by solvent removal gave a brown liquid which was chromatographed on alumina (3 × 20 cm). Fractions, eluted with hexane–ether (1 : 1), were collected. The residual liquid obtained after solvent removal was again chromatographed on alumina (4 × 13 cm). The initial fractions, eluted with 3% ether–hexane, gave the desired product (13) (174 mg, 22%) as a solid. Recrystallization from hexane–benzene afforded yellow *cubes*, m.p. 151—152 °C (decomp.); *m/z* 412 (M^+, 15%) and 182 (100); *M*, 412.5; $\nu_{max.}$ 3 290 (C≡CH), 2 090 (C≡C), 1 605 (C≡C), and 995 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 278sh (ε 38 300), 290 (43 600), 301 (40 600), 347sh (56 200), 366 (68 000), and 396sh nm (60 200); τ 2.59—2.85 (10 H, m, ArH), 3.26 (2 H, dd, *J* 15.5 and 10.5 Hz, H^B), 3.36 (2 H, dd, *J* 15.5 and 11.5 Hz, H^D), 3.62 (2 H, d, *J* 15.5 Hz, H^A), 3.63 (2 H, d, *J* 11.5 Hz, H^E), 3.65 (2 H, dd, *J* 15.5 and 10.5 Hz, H^C), 6.62 (2 H, s, C≡CH), and 8.03 (6 H, s, Me) (Found: C, 92.9; H, 7.1. $C_{32}H_{28}$ requires C, 93.2; H, 6.8%).

3,17-*Dimethyl*-9-*diphenylmethylenenonadeca*-3,5,7,10,12,14,-16-*heptaene*-1,18-*diyne* (14).—A solution of diphenylacetyl chloride (prepared from 1.5 g of diphenylacetic acid and 10 ml of thionyl chloride) in dry benzene (20 ml) was added dropwise during 15 min to a stirred solution of triethylamine (3.0 ml) in dry benzene (25 ml) at room temperature under nitrogen and the mixture was stirred for a further 20 min. Then a solution of the acyclic ketone (18) [2] (328 mg, 1.14 mmol) in dry benzene (20 ml) was added dropwise during 15 min at the same temperature and the mixture was heated under reflux for 1 h. After work-up as for the isolation of (13), the product was chromatographed on alumina (4 × 11 cm). Fractions, eluted with 2% ether–hexane, gave the desired product (14) (92 mg, 18%) as a yellow liquid. Although the liquid solidified on standing in a dry ice–acetone bath, attempts to crystallize it from a variety of solvents, after repeated preparative t.l.c., were unsuccessful; *m/z* (field desorption method) 438 (M^+, 100%); *M*, 438.5; $\nu_{max.}$ (CCl_4) 3 300 (C≡CH), 2 090 (C≡C), 1 600 (C=C), and 990 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 279sh (ε 17 500), 292sh (22 700), 304 (26 000), 317 (23 200), 363sh (42 300), 381 (48 500), and 406sh nm (41 800); τ 2.60—2.86 (10 H, m, ArH), 3.20—3.75 (12 H, m, olefinic H), 6.66 (2 H, s, C≡CH), and 8.06 (6 H, s, Me).

The Tridecafulvene (7) *from the Tetraene-diyne* (11).—A solution of the acyclic compound (11) (151 mg, 0.42) in pyridine–dry ether (3 : 1, 16 ml) was added dropwise during 2 h to a stirred solution of anhydrous copper(II) acetate (0.94 g) in pyridine–dry ether (3 : 1; 48 ml) at 51—52 °C. After being stirred for a further 1 h at the same temperature, the solution was cooled and filtered through Hyflo Super-Cel. The precipitates formed were washed with benzene (100 ml × 2), and the filtrate was poured onto water. The organic layer, combined with the benzene extracts from the aqueous layer, was washed successively with 3M-hydrochloric acid until it turned acidic, then with water, aqueous sodium hydrogen carbonate, and brine. Drying followed by removal of solvent gave a dark red liquid which was chromatographed on alumina (4 × 8 cm). Fractions, eluted with hexane, gave the tridecafulvene (7) (93 mg, 62%) which was identical with that obtained from (1).

The Pentadecafulvene (8) *from the Pentaene-diyne* (12).—A solution of the acyclic compound (12) (568 mg, 1.47 mmol) in pyridine–dry ether (3 : 1; 57 ml) was added dropwise during 2.5 h to a stirred solution of anhydrous copper(II) acetate 3.3 g) in pyridine–dry ether (3 : 1, 169 ml) at 50—51 °C, and the solution was stirred for a further 45 min at the same temperature. After work-up as for the isolation of (7), the product was chromatographed on alumina (4 × 9 cm). Fractions, eluted with hexane, gave the pentadecafulvene (8) (198 mg, 35%) which was identical with that obtained from (2).

The Heptadecafulvene (9) *from the Hexaene-diyne* (13).—A solution of the acyclic compound (13) (226 mg, 0.55 mmol) in pyridine–dry ether (3 : 1; 12 ml) was added dropwise during 45 min to a stirred solution of anhydrous copper(II) acetate (0.71 g) in pyridine–dry ether (3 : 1; 36 ml) at 50—52 °C and the solution was stirred for a further 45 min at the same temperature. After work-up as for the isolation of (7), the product was chromatographed on alumina (4 × 9 cm). Fractions, eluted with 3% ether–hexane, gave the heptadecafulvene (9) (161 mg, 72%) which was identical with that obtained from (3).

The Nonadecafulvene (10) *from the Heptaene-diyne* (14).—A solution of the acyclic compound (14) (383 mg, 0.87 mmol) in pyridine–dry ether (3 : 1; 18 ml) was added dropwise during 1.5 h to a stirred solution of anhydrous copper(II) acetate (1.1 g) in pyridine–dry ether (3 : 1; 40 ml) at 49—52 °C, and the solution was stirred for a further 1 h at the same temperature. After work-up as for the isolation of (7), the product was chromatographed on alumina (4 × 6 cm). Fractions, eluted with 3% ether–hexane, gave the nonadecafulvene (10) (381 mg, 30%) which was identical with that obtained from (4).

11-(o-*Ethynylphenyl*)-3-*methyl*-9-*diphenylmethyleneundeca*-3,5,7,10-*tetraen*-1-*yne* (22).—A solution of diphenylacetyl chloride (prepared from 12.9 g of diphenylacetic acid and 87 ml of thionyl chloride) in dry benzene (33 ml) was added dropwise during 15 min to a stirred solution of triethylamine (27 ml) in dry benzene (36 ml) at room temperature under nitrogen. After stirring for a further 20 min, a solution of the acyclic ketone (19) [18] (1.66 g, 6.11 mmol) in dry benzene (13 ml) was added dropwise during 15 min and the mixture was stirred for a further 20 h at the same temperature, then 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 removal of solvent gave a red liquid which was chromatographed on alumina (4 × 9 cm). Initial fractions, eluted with 5% ether–hexane, gave the desired acyclic compound (22) (684 mg, 38%) as a solid. It formed yellow *needles* from hexane–benzene, m.p. 134—135 °C; *m/z* 422 (M^+, 100%); *M*, 422.5; $\nu_{max.}$ 3 290 (C≡CH), 2 105, 2 090 (C≡C), 1 600 (C=C), 1 005, and 990 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 241 (ε 21 800), 268 (25 600), and 375 nm (38 600); τ 2.57 (1 H, d, *J* 16.5 Hz, H^B), 2.47—2.84 (14 H, m, ArH), 3.10 (1 H, dd, *J* 16 and 11.5 Hz, $H^{B'}$), 3.13 (1 H, d, *J* 16.5 Hz, H^A), 3.26 (1 H, dd, *J* 16 and 11.5 Hz, $H^{D'}$), 3.54 (1 H, d, *J* 16 Hz, $H^{A'}$), 3.64 (1 H, d, *J* 11.5 Hz, $H^{E'}$), 3.64 (1 H, dd, *J* 16 and 11.5 Hz, $H^{C'}$), 6.66 (2 H, s, C≡H), and 8.06 (3 H, s, Me) (Found: C, 93.65; H, 6.3. $C_{33}H_{26}$ requires C, 93.8; H, 6.2%).

13-*Methyl*-7-*diphenylmethylene*-14,15,16,17-*tetradehydrobenzocyclopentadecene* (25).—A solution of the acyclic compound (22) (1.33 g, 3.15 mmol) in pyridine–dry ether (3 : 1; 75 ml) was added dropwise during 2 h to a stirred solution of anhydrous copper(II) acetate (3.8 g) in pyridine–dry ether (3 : 1; 151 ml) at 55—60 °C. After being stirred for a further 1 h at the same temperature, the solution was cooled. After addition of benzene (50 ml), the mixture was filtered through Hyflo Super-Cel. The precipitates formed were washed with benzene (50 ml × 2), then the filtrate was poured onto water. The organic layer, combined with the benzene extracts from the aqueous layer, was washed with 7% hydrochloric acid until it turned acidic, then with water, aqueous sodium hydrogen carbonate, and brine. Drying followed by removal of solvent gave a dark red liquid which was chromatographed on alumina (4 × 11 cm). Fractions, eluted with 5% ether–hexane, gave the monobenzannelated fulvene (25) (861 mg, 65%) as a solid. It formed orange *plates* from hexane–benzene, m.p. 174—175 °C; *m/z* 420 (M^+, 100%); *M*, 420.5; $\nu_{max.}$ 2 100 (C≡C), 1 605 (C=C), 980, and 970 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 229 (ε 27 400), 270sh (30 000), 288 (33 200), 301sh (31 100), 337 (25 300), and 374 nm (17 900); τ 2.25 (1 H, d, *J* 16.5 Hz, H^B), 2.60—2.90 (16 H, m, $H^{A'}$, $H^{D'}$, and ArH), 3.00 (1 H, d, *J* 16.5 Hz, H^A), 3.52 (1 H, d, *J* 10 Hz, $H^{E'}$), 3.69 (1 H, dd, *J* 16 and 7 Hz, $H^{C'}$), 4.11 (1 H, dd, *J* 16 and 7 Hz, $H^{B'}$), and 8.16 (3 H, s, Me) (see also ref. 13) (Found: C, 94.45; H, 5.7. $C_{33}H_{24}$ requires C, 94.25; H, 5.75%).

11-(o-*Ethynylphenyl*)-3-*methyl*-7-*diphenylmethyleneundeca*-3,5,8,10-*tetraen*-1-*yne* (23).—A solution of diphenylacetyl chloride (prepared from 4.9 g of diphenylacetic acid and 33 ml of thionyl chloride) in dry benzene (12 ml) was added dropwise during 15 min to a stirred solution of triethylamine (10 ml) in dry benzene (24 ml) at room temperature under nitrogen. After stirring for a further 20 min, a solution of the acyclic ketone (20) [18] (622 mg, 2.29 mmol) in dry benzene (5 ml) was then added dropwise during 15 min and the mixture was stirred for a further 20 h at the same temperature. After work-up as for the isolation of (22), the product was chromatographed on alumina (4 × 10 cm). Initial fractions, eluted with 5% ether–hexane, gave the acyclic compound (23) (326 mg, 34%) as a solid. It formed yellow *needles* from hexane–benzene, m.p. 143—144 °C; *m/z* (M^+, 97%) and 230 (100); *M*, 422.5; $\nu_{max.}$ 3 300 (C≡CH), 2100, 2 110 (C≡C), 1 600 (C=C), 1 005, and 995 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 239 (ε 35 800), 267 (47 300), 347 (54 100), and 373 nm (57 200); τ 2.37—2.82 (14 H, m, ArH), 2.89 (1 H, d, *J* 16 Hz, $H^{D'}$), 2.95 (1 H, dd, *J* 16 and 11 Hz, H^B), 3.02—3.24 (2 H, m, H^B, and $H^{C'}$), 3.52 (1 H, d, *J* 16 Hz, H^A), 3.61 (1H, d, *J* 16 Hz, $H^{A'}$), 3.63 (1 H, d, *J* 11 Hz, H^C), 6.65 (1 H, s, C≡CH), 6.70 (1 H, s, C≡CH), and 8.05 (3 H, s, Me) (Found: C, 93.5; H, 6.2. $C_{33}H_{26}$ requires C, 93.8; H, 6.2%).

13-*Methyl*-9-*diphenylmethylene*-14,15,16,17-*tetradehydrobenzocyclopentadecene* (26).—A solution of the acyclic com-

pound (23) (164 mg, 0.39 mmol) in pyridine–dry ether (3 : 1; 10 ml) was added dropwise to a stirred solution of anhydrous copper(II) acetate (0.47 g) in pyridine–dry ether (3 : 1; 19 ml) during 45 min at 49—54 °C. After being stirred for a further 1 h at the same temperature, the solution was cooled. After work-up as for the isolation of (25), the product was chromatographed on alumina (4 × 6 cm). Fractions, eluted with 3% ether–hexane, gave the monobenzannelated fulvene (26) (75 mg, 46%) as a solid. It formed yellow *needles* from hexane–benzene, m.p. 177—178 °C; *m/z* 420 (M^+, 100%); *M*, 420.5; $\nu_{max.}$ 2180, 2170(C≡C), 1600(C=C), and 985 cm^{-1} (*trans*-C=C); $\nu_{max.}$ 231 (ε 23 300), 247sh (20 300), 277 (23 700), 291sh (22 900), 329 (19 800), and 383 nm (16 800); τ (27 °C) 2.47 (1 H, dd, *J* 16 and 11 Hz, H^B), 2.61—2.86 (15 H, m, $H^{D'}$ and ArH), 3.36—3.56 (5 H, m, H^A, $H^{A'}$, $H^{B'}$, H^C, and $H^{C'}$), and 8.15 (3 H, s, Me) (see also ref. 13); τ (−60 °C) 2.47 (1 H, dd, *J* 16 and 11 Hz, H^B), 2.56—2.86 (15 H, m, $H^{D'}$ and ArH), 3.16 (1 H, dd, *J* 16 and 11 Hz, $H^{B'}$), 3.43 (1 H, d, *J* 11 Hz, H^C), 3.44 (1 H, d, *J* 16 Hz, $H^{A'}$), 3.46 (1 H, dd, *J* 16 and 11 Hz, $H^{C'}$), 3.50 (1 H, d, *J* 16 Hz, H^A), and 8.10 (3 H, s, Me) (Found: C, 94.0; H, 5.8. $C_{33}H_{24}$ requires C, 94.25; H, 5.75%).

1,7-*Bis*(o-*ethynylphenyl*)-3-*diphenylmethylenehepta*-1,4,6-*triene* (24).—A solution of diphenylacetyl chloride (prepared from 6.0 g of diphenylacetic acid and 40 ml of thionyl chloride) in dry benzene (15 ml) was added dropwise during 15 min to a stirred solution of triethylamine (12 ml) in dry benzene (30 ml) at room temperature under nitrogen. After stirring for a further 20 min, a solution of the acyclic ketone (21) [3c] (865 mg, 2.81 mmol) in dry benzene (6 ml) was added dropwise during 15 min and the mixture was stirred for a further 20 h at the same temperature. After work-up as for the isolation of (22), the product was chromatographed on alumina (4 × 8 cm). Fractions, eluted with 10% ether–hexane, gave the acyclic compound (24) (699 mg, 54%) as a solid. It formed pale yellow *needles* from hexane–benzene, m.p. 170—171 °C; *m/z* 458 (M^+, 100%); *M*, 458.5; $\nu_{max.}$ 3300 (C≡CH), 2100 (C≡C), 1595 (C=C), 1005, and 985 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 240 (ε 46 100), 263 (45 700), 350sh (48 900), and 372 nm (54 800); τ 2.51 (1 H, d, *J* 16.5 Hz, H^B), 2.36—2.84 (15 H, m, $H^{D'}$ and ArH), 2.86—3.22 (2 H, m, $H^{B'}$ and $H^{C'}$), 3.11 (1 H, d, *J* 16.5 Hz, H^A), 3.44 (1 H, d, *J* 15.5 Hz, $H^{A'}$), 6.62 (1 H, s, C≡CH), and 6.68 (1 H, s, C≡CH) (Found: C, 94.4; H, 5.7. $C_{36}H_{26}$ requires C, 94.3; H, 5.7%).

7-*Diphenylmethylene*-16,17,18,19-*tetradehydrodibenzo*[a,g]-*cyclopentadecene* (27).—A solution of the acyclic compound (24) (332 mg, 0.72 mmol) in pyridine–dry ether (3 : 1; 28 ml) was added dropwise during 1 h to a stirred solution of anhydrous copper(II) acetate (1.64 g) in pyridine–dry ether (3 : 1; 83 ml) at 50—55 °C. After being stirred for a further 1.5 h at the same temperature, the solution was cooled. After work-up as for the isolation of (25), the product was chromatographed on alumina (4 × 11 cm). Fractions, eluted with 5% ether–hexane, gave the dibenzannelated fulvene (27) (226 mg, 68%) as a solid. It formed pale yellow *needles* from hexane–benzene, m.p. 175—176 °C; *m/z* 456 (M^+, 55%) and 78 (100) *M*, 456.5; $\nu_{max.}$ 2200 (C≡C), 1620 (C=C), 1000, 990, and 980 cm^{-1} (*trans*-C=C); $\lambda_{max.}$ 230 (ε 31 900), 286sh (28 500), 300 (32 400), 335sh (23 800), and 368 nm (18 500); τ 2.38 (1 H, d, *J* 16.5 Hz, H^B), 2.60—2.91 (18 H, m, ArH), 3.00 (1 H, d, *J* 16.5 Hz, H^A), 3.09 (1 H, d, *J* 15.5 Hz, $H^{D'}$), 3.32 (1 H, d, *J* 15.5 Hz, $H^{A'}$), 3.33 (1 H, dd, *J* 15.5 and 10 Hz, $H^{C'}$), and 3.59 (1 H, dd, *J* 15.5 and 10 Hz, $H^{B'}$) (see also ref. 13) (Found: C, 94.8; H, 5.4. $C_{36}H_{24}$ requires C, 94.7; H, 5.3%).

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