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Syntheses and Properties of Pentatrideca-, Pentapentadeca-, Pentaheptadeca-, and Pentanonadecafulvalene Derivatives

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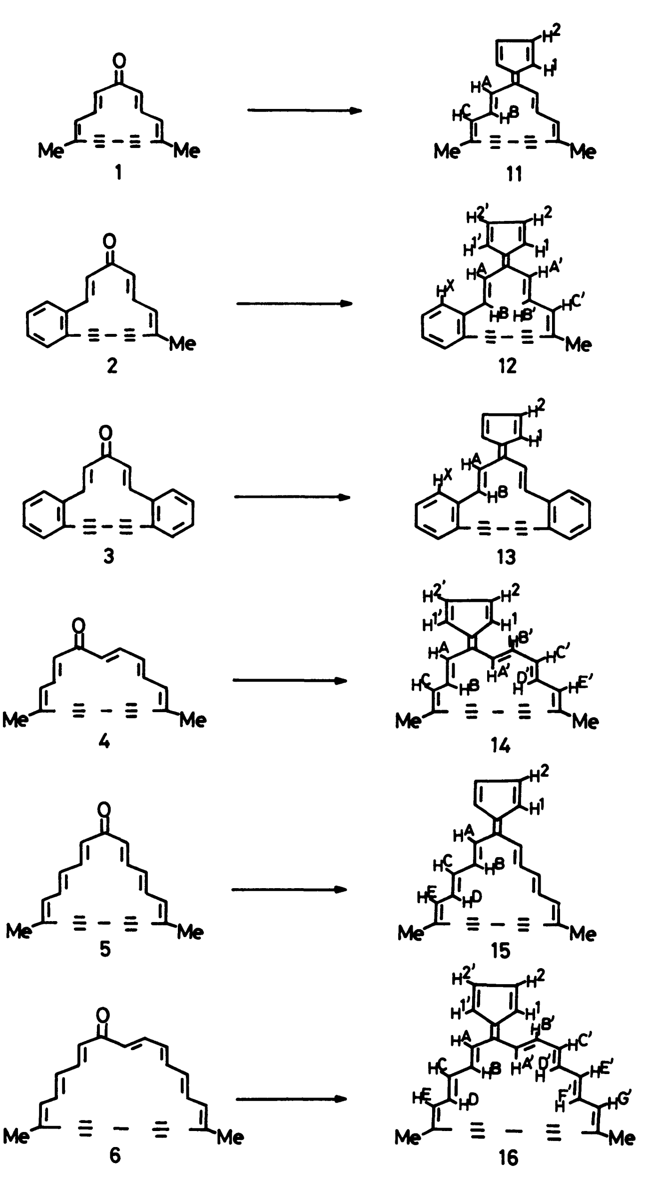
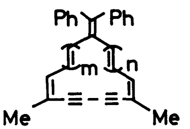
5,10-Dimethyl-6,8-bisdehydropentatridecafulvalene **11**, 10-methyl-6,8-bisdehydro-4,5-benzopentatridecafulvalene **12**, 6,8-bisdehydro-4,5:10,11-dibenzopentatridecafulvalene **13**, 5,10-dimethyl-6,8-bisdehydropentapentadecafulvalene **14**, 7,12-dimethyl-8,10-bisdehydropentaheptadecafulvalene **15**, and 7,12-dimethyl-8,10-bisdehydropentanonadecafulvalene **16** were synthesized through the reaction of the corresponding bisdehydroannulenones **1**—**6** with cyclopentadienide. The tropic nature of these pentafulvalenes is discussed on the basis of ^{1}H NMR and electronic spectra as well as those of the corresponding heptafulvalene derivatives.

Syntheses of a series of paratropic dimethylbisdehydro[13]-**1**[1] and dimethylbisdehydro[17]annulenone **5**[2] and the diatropic dimethylbisdehydro[15]-**4**[2] and dimethylbisdehydro[19]annulenone **6**[2] as well as their α-methyl,[3] α-ethyl-substituted,[4] and benzo-annelated derivatives,[3] (e.g. **2** and **3**) have been described previously. Higher analogs 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**—**6** they appeared to be the desirable starting materials for the synthesis of the cross-conjugated π-electron systems. In fact, the syntheses of the diphenylfulvene **7**[7] and the dichlorofulvene derivatives **8**[8] containing macrocyclic system by the reaction of these annulenones with diphenylketene and dichloroketene, respectively, have been achieved. Also, in the preceding paper,[9] of an another cross-conjugated system, fulvalene, which might be derived from the annulenones **1**—**6**, we reported the syntheses of heptafulvalenes **9** and dibenzo derivatives **10** of pentafulvalene using an addition reaction of ketene (8-oxoheptafulvene and 9-fluorenylidenemethanone) as similarly to preparation of **7** and **8**, and it was suggested that only a little π-electron polarization of the central double bond occurs in both the heptafulvalenes **9** and the dibenzopentafulvalenes **10** to form polar structures **9a** and **10a**. It can be seen from the polar structures that the heptafulvalene derivatives **9** polarize in such a way that the positive end of the dipole is localized in the 7-membered ring and the negative pole in the large ring, whereas the dibenzopentafulvalene derivatives **10** do in the reverse direction to **9**. Thus, the pentafulvalenes **10** are expected to exhibit the opposite polarization to those of the heptafulvalene derivatives **9**, but this potentiality would be diminished by benzo-annelation upon the 5-membered ring. Therefore, non-benzo-annelated pentafulvalene derivatives are more desirable to enhance the polarization of the central double bond and are expected to possess a greater extended π-electron system, compared with dibenzo-annelated fulvalenes **10**, and to show the reverse tropicity to the heptafulvalenes containing the same-membered large rings. Thus, starting from the annulenones, we were interested in syntheses of a series of the pentafulvalenes, in which the number of the double bond could be increased systematically and a study of their spectral properties and comparison with those of the heptafulvalene derivatives **9** appeared to be particularly informative.

This paper is concerned with the syntheses and





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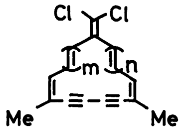

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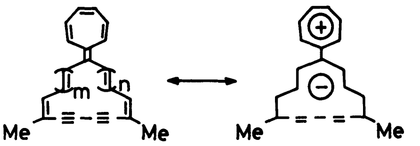

9 9a

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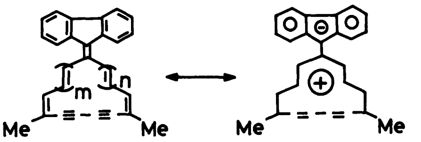


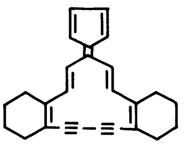
10 10a

m : 1 ~ 2
n : 1 ~ 3

properties of fulvalene derivatives containing cyclopentadienylidene moiety, **11**, **14**—**16**, and the benzo-annelated derivatives **12**, **13** of the pentatridecafulvalene derivative **11**.[11] The ^{1}H NMR and electronic absorption spectra of these pentafulvalenes as well as comparison with those of the heptafulvalene derivatives are described in connection with tropicity.

Results and Discussion

Synthesis. In 1977, Howes and Sondheimer reported a synthesis of bis(cyclohexene)-annelated pentatridecafulvalene **17** through the reaction of the corresponding bisdehydroannulenone with a large excess of cyclopentadienide, but did a conjugative addition product when they used a little excess of cyclopentadienide. Thus, although only the pentatridecafulvalene **17** had been obtained, no systematic discussion of the tropicity has been done. We advantageously applied this procedure to the synthesis of pentafulvalenes derived from the annulenones **1**—**6**.



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We first attempted the reaction of the acyclic ketones (precursors of annulenones), with a large excess of sodium cyclopentadienide, since the corresponding acyclic compounds for the desired fulvalenes would be the most appropriate compounds to examine the tropicity of fulvalenes, as has been made for the fulvene derivatives **7** and **8**.[7,8] However, all attempts to prepare the acyclic model compounds for the desired pentafulvalenes were unsuccessful. The objective pentafulvalene derivatives were synthesized by treatment of the annulenones **1**—**6** with cyclopentadienide according to the procedure of Howes and Sondheimer.[12] Reaction of 5,10-dimethyl-6,8-bisdehydro[13]annulenone **1**,[1] 10-methyl-6,8-bisdehydro-4,5-benz[13]annulenone **2**,[3a] 6,8-bisdehydro-4,5:10,11-dibenz[13]annulenone **3**,[3a] 5,10-dimethyl-6,8-bisdehydro[15]annulenone **4**,[2] 7,12-dimethyl-8,10-bisdehydro[17]annulenone **5**,[2] and 7,12-dimethyl-8,10-bisdehydro[19]annulenone **6**,[2] with a large excess of sodium cyclopentadienide in tetrahydrofuran at −10—0 °C gave 5,10-dimethyl-6,8-bisdehydropentatridecafulvalene **11** (11%), 10-methyl-6,8-bisdehydro-4,5-benzopentatridecafulvalene **12** (7.8%), 6,8-bisdehydro-4,5:10,11-dibenzopentatridecafulvalene **13** (3.9%), 5,10-dimethyl-6,8-bisdehydropentapentadecafulvalene **14** (4.9%), 7,12-dimethyl-8,10-bisdehydropentaheptadecafulvalene **15** (4.6%), and 7,12-dimethyl-8,10-bisdehydropentanonadecafulvalene **16** (6.8%), respectively. These fulvalene derivatives **11**—**16** thus obtained decomposed on attempted melting-point determination, and proved to be rather unstable. These substances decomposed gradually on exposure to diffused light and air.

^{1}H NMR Spectra. The ^{1}H NMR spectra of the fulvalenes **11**, **14**—**16** and the corresponding heptafulvalene derivatives **9** at 200 MHz are illustrated in Figs. 1 and 2, respectively. The individual assignments were made on the basis of the multiplicities and coupling constants, given in the Experimental section. In contrast to the cases of the heptafulvalenes **9** and in accord with the cases of the dibenzopentafulvalenes **10**, containing the same-membered ring, it is predicted that the compounds of **11** and **15** are not aromatic, since polarization of the central double bond would make one ring a $(4n+2)\pi$-system, but the other a $(4n)\pi$-system. On the other hand, the compounds **14** and **16** are aromatic since polarization of the central bond would make both rings $(4n+2)\pi$-systems.

From the Figs. 1 and 2, it is seen that the outer protons of the large rings of the pentatrideca- **11** and the pentaheptadecafulvalene **15** resonate in a higher field than the inner protons, while the reverse is seen in the spectra of the corresponding heptatridecafulvalene and heptaheptadecafulvalene. Thus, the large rings of **11** and **15** are suggested to be paratropic, as expected of 12π- and 16π-electron systems, respectively, owing to polarization of the central double bond. On the other hand, in the spectra of the pentapentadeca- **14** and the pentanonadecafulvalene **16**, the olefinic protons of the large rings resonate in a very narrow region, whereas the outer protons of the heptapentadecafulvalene and the heptanonadecafulvalene resonate in a higher field

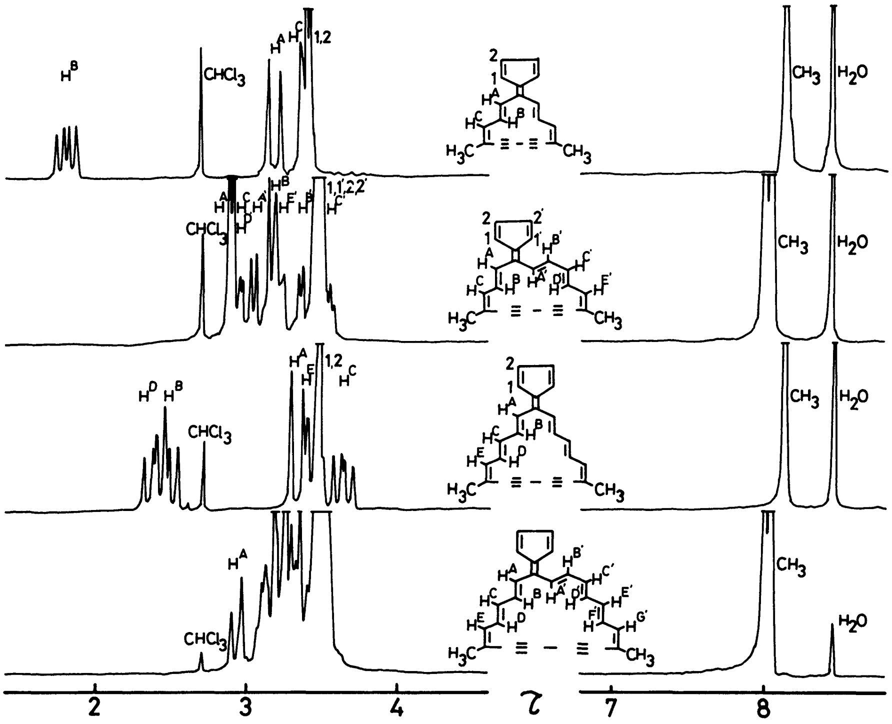


Fig. 1. ^{1}H NMR spectra of Pentatrideca- **11**, Pentapentadeca- **14**, Pentaheptadeca- **15**, and Pentanonadecafulvalene **16** in $CDCl_3$ at 21 °C (200 MHz, τ values, internal standard, TMS).

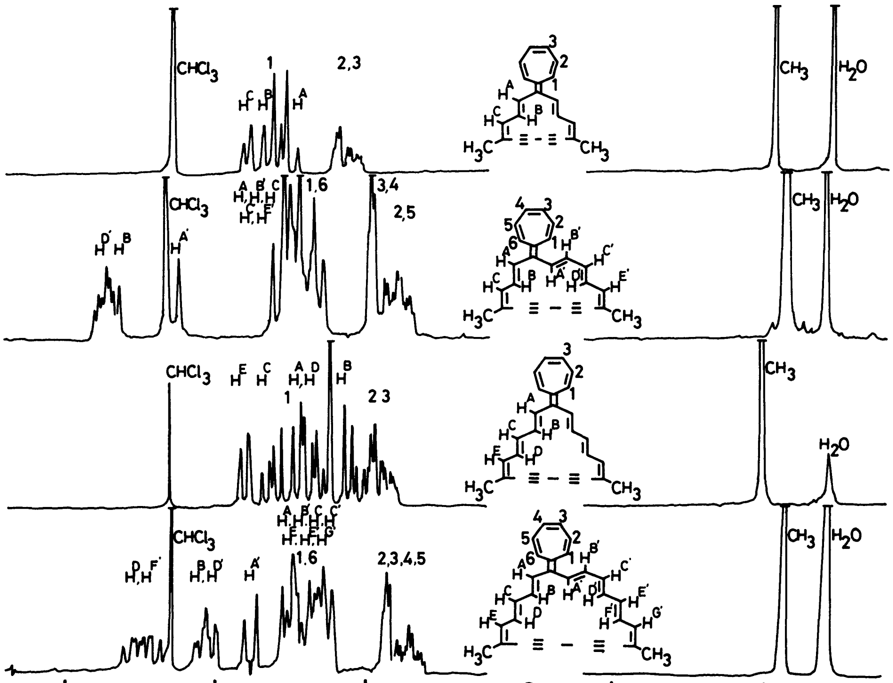


Fig. 2. ^{1}H NMR spectra of Heptatrideca-, Heptapentadeca-, Heptaheptadeca-, and Heptanonadecafulvalene in $CDCl_3$ at 21 °C (200 MHz, τ values, internal standard, TMS).

than the inner protons, as expected of 16π- and 20π-electron systems as before. Thus, although the large membered rings of **14** and **16** are suggested to be atropic, we considered that a systematic examination of the methyl resonances of these fulvalenes would provide a diagnostic tool to test the tropicity since the methyl groups must always be outside the ring and can readily be recognized.[2,6]

Table 1. The ^{1}H NMR Chemical Shifts of Methyl Protons of Compounds **1**, **4**—**6** (90 MHz), **9** (200 MHz), and **11**, **14**—**16** (200 MHz) ($CDCl_3$, τ Value, at 21 °C

Large-membered ring	Annulenones **1**, **4**—**6**	Heptafulvalenes **9**	Pentafulvalenes **11**, **14**—**16**
[13]	8.26	8.08	8.13
[15]	7.76, 7.82	8.18	8.00, 8.05
[17]	8.23	8.00	8.12
[19]	7.79, 7.83	8.14	8.00, 8.04

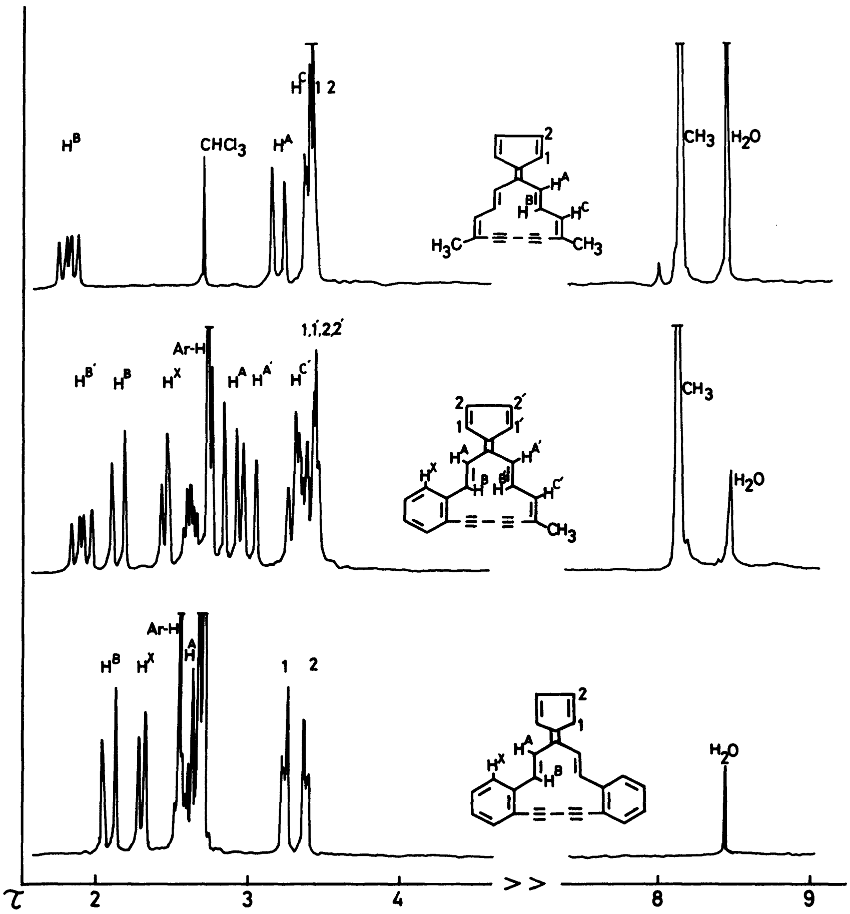


Fig. 3. ^{1}H NMR spectra of pentatrideca- **11**, Benzpentatrideca- **12**, and Dibenzpentatridecafulvalene **13** in $CDCl_3$ at 21 °C (200 MHz, τ values, internal standard, TMS).

The chemical shifts of the methyl resonances of the pentafulvalenes **11**, **14**—**16** are listed in Table 1, altogether with those of the corresponding annulenones **1**, **4**—**6** and the heptafulvalenes **9**. As can be seen from the Table 1, the alternation of the methyl resonances between the [4n+1]annulenones ([13]- **1**, [17]annulenone **5**) (relatively high field) and [4n+3]annulenones ([15]- **4**, [19]annulenone **6**) (relatively low field) confirm the paratropicity of the former and the diatropicity of the latter,[2,6] owing to polarization of a carbonyl group. As expected from polarization of the central double bond of the pentafulvalenes, the alternation of the methyl resonances of the large-membered rings between the trideca- **11**, the heptadeca- **15** and pentadeca- **14**, the nonadecafulvalene **16** is seen in the same trend as that in the cases of annulenones **1**, **4**—**6**, albeit the degree of the alternation being much less than that of annulenones. On the other hand, the alternation of the methyl resonances between 13-, 17- and 15, 19-membered rings of the heptafulvalenes is seen in the reverse trend, as compared with that of annulenones and the pentafulvalenes, in agreement with that the heptafulvalenes **9** polarize from 7-membered ring to large ring. Thus, it can be suggested that a very little π-electron polarization from the large rings to 5-membered ring occurs in these pentafulvalenes **11**, **14**—**16**.

The ^{1}H NMR spectra of the pentatridecafulvalene **11** and its benzo-annelated derivatives **12**, **13** are shown in Fig. 3. As is seen from the Fig. 3, the differences of the chemical shifts between the inner

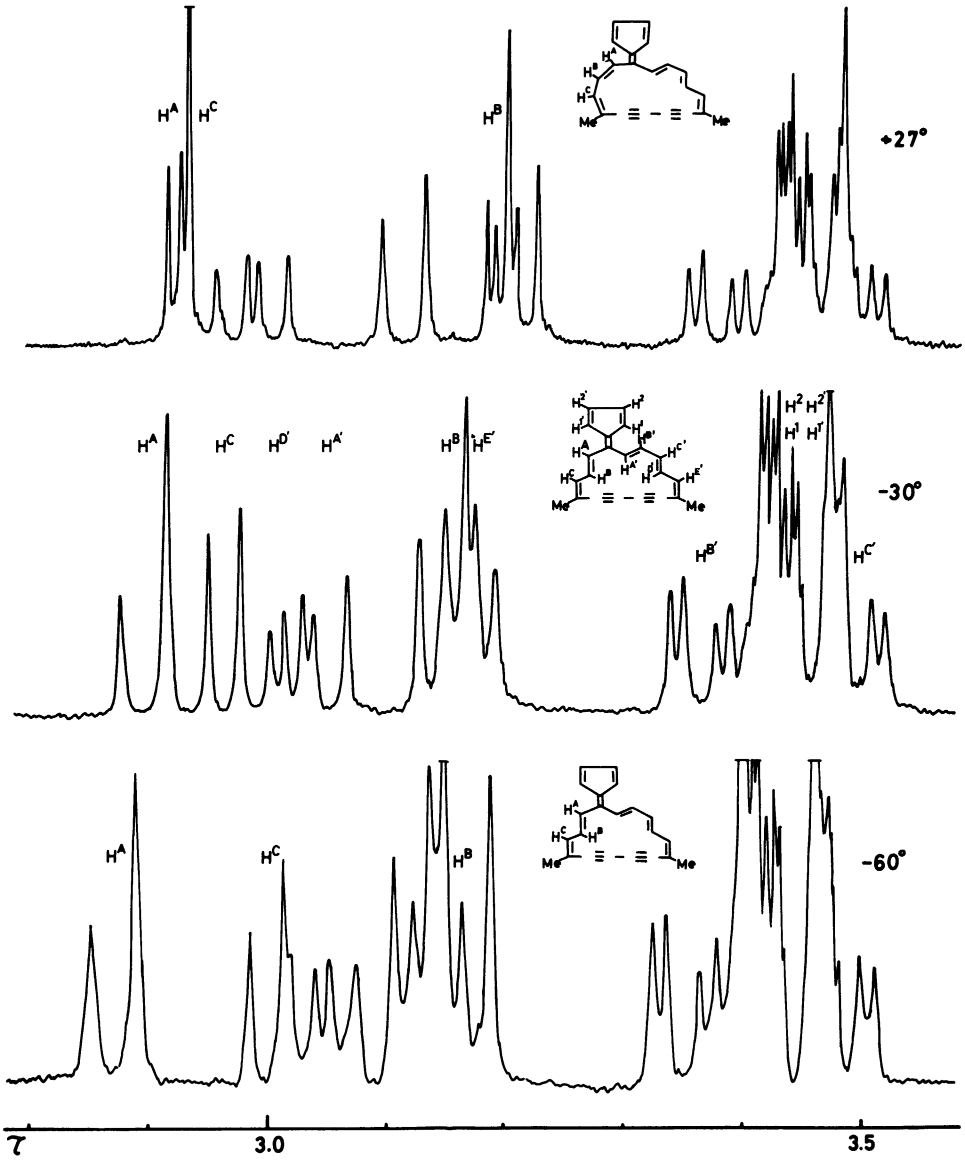
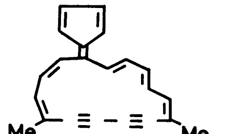


Fig. 4. ^{1}H NMR spectra of Pentapentadecafulvalene **14** at 27 °C, −30 °C, and −60 °C in $CDCl_3$ (400 MHz, τ values, internal standard, TMS).

protons and the outer protons of the large rings, which can be regarded as an approximate measure of the tropicity, become small in the sequence of **11**>**12**>**13**, with increasing number of fused benzene rings on the large rings. This fact suggests that the benzo-annelated fulvalenes **12**, **13** have less delocalized π-electron systems than that of non-benzo-annelated one **11**, as evidenced from the electronic absorption spectra of these compounds (vide infra) and has been demonstrated for the annulene,[10] dehydroannulene,[10] and dehydroannulenone[3] system.

Variable-temperature ^{1}H NMR spectra of these fulvalenes were run at 200 MHz over the range of −60 to 60 °C, and the results show the spectra of the fulvalenes **11**—**13**, **15**, **16** to be essentially temperature-independent, excluding any change of the indicated conformations between these temperatures. On the other hand, the spectra of the pentapentadecafulvalene **14** are temperature-dependent, as illustrated in Fig. 4 which shows the spectra taken at 400 MHz and the resonances of only the olefinic protons.

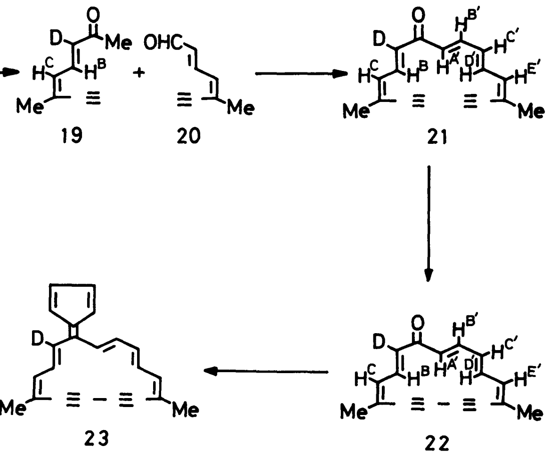


14a

In rather surprisingly contrast to the cases of **11**, **15**, and **16**, the pentadecafulvalene does not exist in the conformation **14**, but in the more unlike conformation **14a** at room temperature. This follows from the fact that the value of $J_{B,C}$ value is 4.5 Hz, indicating an s-cis relationship of the CH^B-CH^C bond, and both the H^A and H^C protons resonate in almost same field. On

Table 2. Electronic Absorption Spectra of the Fulvalenes **11**—**16** (a in THF, b in Acetonitrile); Maxima or Shoulders (sh) in nm (a, ε Values; b, Relative Extinction Coefficients, in Parentheses)

11	a	248 sh (15500),	261 (23200),	274 (21000),	310 (18900),	376 sh (25000),	397 (33600),	417 sh (28200)
	b	247 sh (0.58),	259 (0.79),	272 (0.69),	308 (0.60),	373 sh (0.76),	392 (1.00),	413 sh (0.84)
12	a		274 (25800),	285 (27000),	318 (19900),		392 (24300),	413 sh (19100)
	b		269 sh (0.98),	283 (1.00),	316 (0.73),		387 (0.75),	411 sh (0.59)
13	a		280 sh (32000),	294 (41800),	322 (28400),		379 (28900),	401 sh (20600)
	b		277 sh (0.75),	291 (1.00),	320 (0.71),		376 (0.70),	397 sh (0.51)
14	a	268 sh (19700),	279 (23700),		343 (29000),			432 (18200)
	b	260 sh (0.66),	277 (0.88),		338 (1.00),			427 (0.60)
15	a	276 sh (23000),	288 (34600),	304 (28800),	355 (25700),		428 (26500),	469 sh (15000)
	b	275 sh (0.74),	286 (1.00),	302 (0.82),	354 (0.74),		419 (0.75),	468 sh (0.51)
16	a		303 (35000),		371 (47900),		460 sh (20800)	
	b		302 (0.73),		369 (1.00),		458 sh (0.41)	



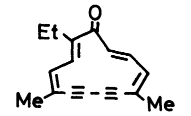
Scheme 1.

cooling, the H^A proton resonance moves to a slightly lower field and the H^C proton resonance to a slightly higher field, and the $J_{B,C}$ value varies to 10.5 Hz, indicating an s-trans relationship of the CH^B-CH^C bond at −30 °C. Further cooling results in an increasing separation of the H^A and H^C resonances. Thus, **14** exists in the similar conformation to those of **11**, **15**, and **16** at low temperature.

The observed temperature-dependency of the spectrum of **14** suggests that the molecular skeleton of **14** is mobile, particularly around CH^A-CH^B-CH^C moiety at room temperature, presumably due to a steric hindrance between H^1 and $H^{B'}$ protons. It is predicted that the pentanonadecafulvalene **16** would experience the similar hindrance, but the skeleton of **16** might presumably relieve the hindrance since a larger 19-membered ring would be more flexible than a 15-membered ring.[6)]

We undertook a synthesis of 2-deuterio-labeled isomer **23** according to the reaction sequence in the Scheme 1 in order to understand the temperature-dependency of the ^{1}H NMR spectrum of **14** more exactly as well as to make the spectrum simple for assignment. However, the content of the deuterium of the isomer **23** obtained is quite small, and we could not get a significant result from comparison of the spectra between **14** and **23**.

We also attempted to obtain α-ethyl substituted pentafulvalenes as similarly as described for preparation of **11** and **14**, but we could not isolate any isomer from both 2-ethyl-5,10-dimethyl-6,8-bisdehydro[13]annulenone (**24**)[4a)] and 15-ethyl-5,10-dimethyl-6,8-bisdehydro[15]annulenone (**25**).[4b)] From 2-ethyl-5,10-dimethyl-6,8-bisdehydro[15]annulenone (**26**),[4b)] we isolated only the compound **27** which formed by conjugative addition between cyclopentadienide and **26**.



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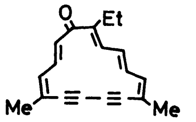

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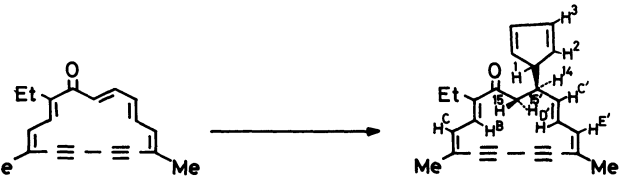

Electronic Spectra. The electronic absorption maxima of the pentafulvalenes **11**—**16**, determined in both tetrahydrofuran and acetonitrile, are listed in Table 2. As is seen from the Table 2, it is evident that all the bands of the fulvalenes **11**—**16** shows small bathochromic shift by changing the solvent from nonpolar (tetrahydrofuran) to polar solvent (acetonitrile). This solvent effect strongly supports the interpretation that a little π-electron polarization occurrs at the central double bond in the ground state of the pentafulvalene system, in agreement with the above-mentioned result from the examination of ^{1}H NMR spectra.

It is recognized that $(4n+2)\pi$-electron systems show the main maxima at higher wavelengths than $(4n)\pi$-systems in monocyclic annulenes,[13] dehydroannulenes,[13] dehydroannulenones,[2] and the fulvenes **7**, **8**.[7,8] Although the electronic spectra of these fulvalenes are not illustrated, the absorption curves are complex, but the spectra of the trideca- **11** and the pentadecafulvalene **14** are rather similar to those of the heptadeca- **15** and the nonadecafulvalene **16**, respectively. In the spectra of **11**, **14**—**16**, the main absorption bands exhibit a bathochromic shift as the ring size increases (Table 2), but it is not clear that the same sort of alternation of the main maxima occurrs between **11**, **15**, and **14**, **16**, as recognized in monocyclic $(4n+2)\pi$- and $(4n)\pi$-systems.[13]

The spectra of **11**—**13** are similar to one another as expected (Table 2),[11] and the medium bands shift to shorter wavelengths in the order of **13**>**12**>**11**, revealing that the fusion of benzene rings results in an appreciable bathochromic shift, as has been observed in benzo-annelated annulenes.[14] In contrast, the longest wavelength bands exhibit absorption toward longer wavelengths in the sequence of **11**>**12**>**13**, demonstrating that the fused benzene rings inhibit the degree of conjugation of π-electrons in these fulvalene system.[10]

Experimental

Melting points were determined on a hot-stage apparatus and are uncorrected. IR spectra were measured on Hitachi 260-50 spectrophotometer as KBr disk unless otherwise stated; only significant maxima are reported. Electronic spectra were determined on Hitachi 220A spectrophotometer (sh= shoulder). ^{1}H NMR spectra were measured on Varian XL-200 (200 MHz), JEOL FX-200 (200 MHz), or JEOL JX-400 (400 MHz) spectrometer and refer to solutions in $CDCl_3$, in τ-values with TMS as an internal standard. The coupling constants (J) are given in Hz. Assignments were assisted by decoupling experiments where necessary. Mass spectra were determined with JMS D-200 spectrometer at 75 eV using a direct inlet system. Alumina for column chromatography refers to Merck activity II-III. Reactions were followed by TLC aluminum sheets precoated with Merck Silica gel F_{254}. Freshly deoxygenated ether was used to minimize oxidation of the compounds employed for aldol condensation and was prepared by passing through a short column of Woelm basic alumina (activity I), followed by flushing with nitrogen, immediately before use. Organic extracts were dried over sodium sulfate prior to solvent removal.

5,10-Dimethyl-6,8-bisdehydropentatridecafulvalene (11). Freshly distilled cyclopentadiene (100 ml) was added to a stirred solution of sodium methoxide [from sodium (2.0 g) and dry methanol (350 ml)] during 15 min at −8 °C under nitrogen, and the solution was stirred for a further 10 min. A solution of [13]annulenone **1**[1] (453 mg, 2.17 mmol) in dry THF (100 ml) was then added at −8 °C during 25 min, and the solution was stirred for a further 1 h at the same temperature. After addition of ethyl acetate (50 ml), the mixture was poured into water. The separated aqueous layer was extracted with benzene and the combined organic extracts were washed with water. The residue after solvent removal was passed through a short column of alumina (3.7×3.0 cm) with 30% ether in hexane. The residual liquid obtained by concentrating the eluents was chromatographed on alumina (3.7×9.0 cm). The initial fractions, eluted with hexane, afforded fulvalene **11** (59.8 mg, 10.7%). It formed dark red needles, mp 103 °C, from hexane–benzene: MS m/z 256 (M^+, 39%) and 239 (100); mol wt 256.3; UV, see Table 2; IR 2150 (C≡C) and 970 cm^{-1} (*trans* HC=CH); ^{1}H NMR (200 MHz) τ=1.81 (dd, J=16, 10 Hz, 2H, H^B), 3.19 (d, J=16 Hz, 2H, H^A), 3.38 (d, J=10 Hz, 2H, H^C), 3.38—3.42 (m, 4H, H^1, H^2), 8.13 (s, 6H, Me), and see Fig. 1.

Found: C, 93.33; H, 6.43%. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.43%.

10-Methyl-6,8-bisdehydro-4,5-benzopentatridecafulvalene (12). To a cyclopentadienide solution, prepared from cyclopentadiene (100 ml), sodium (2.0 g), dry methanol (350 ml) as described for the preparation of **11**, was added dropwise a solution of benz[13]annulenone **2**[3a] (501 mg, 1.72 mmol) in dry THF (100 ml) during 25 min at −9 °C under nitrogen and the solution was stirred for a further 1 h at the same temperature. After work up as described for the isolation of **11**, the product was passed through a short column of alumina (3.0×4.0 cm) with hexane–ether (2:3). The residual red liquid after solvent removal was chromatographed on alumina (3.0×8.0 cm). The fractions eluted with 3% ether in hexane afforded fulvalene **12** (46.8 mg, 7.8%). It formed brown needles, mp 108 °C (decomp), from hexane–benzene: MS m/z 292 (M^+, 83%) and 276 (100); mol wt 292.3; UV, see Table 2; IR 2175 (C≡C) and 960 cm^{-1} (*trans* HC=CH); ^{1}H NMR (200 MHz) τ=1.91 (dd, J=16, 10.5 Hz, 1H, $H^{B'}$), 2.15 (d, J=16.5 Hz, 1H, H^B), 2.45 (d, J=7.5 Hz, 1H, H^X), 2.58—2.77 (m, 3H, Ar–H), 2.89 (d, J=16.5 Hz, 1H, H^A), 3.02 (d, J=16 Hz, 1H, $H^{A'}$), 3.29 (d, J=10.5 Hz, 1H, $H^{C'}$), 3.30—3.48 (m, 4H, H^1, $H^{1'}$, H^2, $H^{2'}$), 8.12 (s, 3H, Me), and see Fig. 3.

Found: C, 94.58; H, 5.32%. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52%.

6,8-Bisdehydro-4,5:10,11-dibenzopentatridecafulvalene (13). To a cyclopentadienide solution, prepared from cyclopentadiene (100 ml), sodium (2.0 g), dry methanol (350 ml) as described above, was added dropwise a solution of dibenz[13]annulenone **3**[3a] (732 mg, 2.61 mmol) in dry THF (100 ml) during 30 min at −7 °C under nitrogen and the solution was stirred for a further 1.5 h at the same temperature. After work up as for the isolation of **11**, the product was passed through a short column of alumina (3.0×4.0 cm) with ether–hexane (1:1). The residue after solvent removal was chromatographed on alumina (3.7×7.5 cm). The fractions eluted with 3—5% ether in hexane afforded fulvalene **13** (33.0 mg, 3.85%). It formed brown needles, mp 173 °C (decomp), from hexane–benzene: MS m/z 328 (M^+, 96%)

and 326 (100); mol wt 328.3; UV, see Table 2; IR 2190 (C≡C) and 965 cm^{-1} (*trans* HC=CH); ^{1}H NMR (200 MHz) τ=2.09 (d, J=16.5 Hz, 2H, H^{B}), 2.30 (d, J=7.5 Hz, 2H, H^{X}), 2.59 (d, J=16.5 Hz, H^{A}), 2.52—2.74 (m, 6H, Ar-H), 3.22—3.26 (m, 2H, H^{1}), 3.36—3.40 (m, 2H, H^{2}), and see Fig. 3.

Found: C, 95.06; H, 4.75%. Calcd for C$_{26}$H$_{16}$: C, 95.05; H, 4.91%.

5,10-Dimethyl-6,8-bisdehydropentapentadecafulvalene (14). To a cyclopentadienide solution, prepared from cyclopentadiene (100 ml), sodium (2.0 g), dry methanol (300 ml) as described above, was added dropwise a solution of [15]annulenone **4**[2] (624 mg, 2.21 mmol) in dry THF (80 ml) during 20 min at −4 °C under nitrogen, and the solution was stirred for a further 40 min at the same temperature. After work up as for the isolation of **11**, the product was passed through a short column of alumina (3.7×3.5 cm) with ether. The residual red liquid after solvent removal was chromatographed on alumina (3.7×8.0 cm). The fractions eluted with 2% ether in hexane afforded fulvalene **14** (31.7 mg, 4.9%). It formed brown needles, mp 164 °C (decomp), from hexane–benzene: MS *m/z* 282 (M^{+}, 68%) and 265 (100); mol wt 282.3; UV, see Table 2; IR 2160 (C≡C), 980, and 960 cm^{-1} (*trans* HC=CH); ^{1}H NMR (400 MHz, 27 °C) τ=2.92 (d, J=7 Hz, 1H, H^{A}), 2.93 (d, J=4.5 Hz, 1H, H^{C}), 2.98 (dd, J=15, 11 Hz, 1H, H$^{D\prime}$), 3.13 (d, J=16 Hz, 1H, H$^{A\prime}$), 3.21 (dd, J=7, 4.5 Hz, 1H, H^{B}), 3.24 (d, J=11 Hz, 1H, H$^{E\prime}$), 3.41 (dd, J=16, 5 Hz, 1H, H$^{B\prime}$), 3.45—3.54 (m, 4H, H^{1}, H$^{1\prime}$, H^{2}, H$^{2\prime}$), 3.54 (dd, J=16, 5 Hz, 1H, H$^{C\prime}$), 8.00 (s, 3H, Me), 8.05 (s, 3H, Me), and see Figs. 1 and 4; (400 MHz, −60 °C) τ=2.87 (d, J=15 Hz, 1H, H^{A}), 3.00 (d, J=10.5 Hz, 1H, H^{C}), 3.04 (dd, J=15, 11 Hz, 1H, H$^{D\prime}$), 3.12 (dd, J=11 Hz, 1H, H$^{E\prime}$), 3.17 (d, J=15 Hz, 1H, H$^{A\prime}$), 3.18 (dd, J=15, 11 Hz, 1H, H^{B}), 3.35 (dd, J=16, 5 Hz, 1H, H$^{B\prime}$), 3.38—3.48 (m, 4H, H^{1} and H^{2}), 3.49 (dd, J=16, 5 Hz, 1H, H$^{C\prime}$), 8.03 (s, 3H, Me), 8.07 (s, 3H, Me), and see Fig. 4.

Found: C, 93.52; H, 6.30%. Calcd for C$_{22}$H$_{18}$: C, 93.57; H, 6.43%.

7,12-Dimethyl-8,10-bisdehydropentaheptadecafulvalene (15). To a solution of cyclopentadienide, prepared from cyclopentadiene (100 ml), sodium (2.0 g), dry methanol (350 ml), was added dropwise a solution of [17]annulenone **5**[2] (808 mg, 3.10 mmol) in dry THF (100 ml) during 30 min at −5 °C under nitrogen, and the solution was stirred for a further 40 min at the same temperature. After work up as for the isolation of **11**, the product was passed through a short column of alumina (3.7×3.0 cm) with ether. The residual red liquid after solvent removal was chromatographed on alumina (3.7×8.0 cm). The fractions eluted with 2% ether in hexane afforded fulvalene **15** (44.1 mg, 4.61%). It formed dark brown needles, mp 177 °C (decomp), from hexane–benzene: MS *m/z* 308 (M^{+}, 53%) and 277 (100); mol wt 308.4; UV, see Table 2; IR 2170 (C≡C) and 985 cm^{-1} (*trans* HC=CH); ^{1}H NMR (200 MHz) τ=2.39 (dd, J=16, 11 Hz, 2H, H^{D}), 2.48 (dd, J=16, 11 Hz, 2H, H^{B}), 3.34 (d, J=16 Hz, 2H, H^{A}), 3.44 (d, J=11 Hz, 2H, H^{E}), 3.46—3.50 (m, 4H, H^{1}, H^{2}), 3.65 (dd, J=16, 11 Hz, 2H, H^{C}), 8.12 (s, 6H, Me), and see Fig. 1.

Found: C, 93.39; H, 6.53%. Calcd for C$_{24}$H$_{20}$: C, 93.46; H, 6.54%.

7,12-Dimethyl-8,10-bisdehydropentanonadecafulvalene (16). To a solution of cyclopentadienide, prepared from cyclopentadiene (100 ml), sodium (2.0 g), dry methanol (350 ml), was added dropwise a solution of [19]annulenone **6**[2] (704 mg, 2.46 mmol) in dry THF (100 ml) during 25 min at −6 °C under nitrogen and the solution was stirred for a further 50 min at the same temperature. After work up as for the isolation of **11**, the product was passed through a short column of alumina (3.7×3.5 cm) with hexane–ether (1:1). The residual red liquid after solvent removal was chromatographed on alumina (3.7×8.0 cm). The fractions eluted with 5% ether in hexane afforded fulvalene **16** (56.0 mg, 6.81%). It formed dark purple cubes, mp 158 °C (decomp), from hexane–benzene: MS *m/z* 334 (M^{+}, 78%) and 303 (100); mol wt 334.4; UV, see Table 2; IR 2170 (C≡C) and 985 cm^{-1} (*trans* HC=CH); ^{1}H NMR (400 MHz) τ=2.97 (d, J=15 Hz, 1H, H^{A}), 3.17 (dd, J=15, 11 Hz, 1H, H^{D}), 3.18 (dd, J=15, 11 Hz, 1H, H$^{F\prime}$), 3.18 (d, J=15 Hz, 1H, H$^{A\prime}$), 3.30 (d, J=11 Hz, 1H, H$^{G\prime}$), 3.32 (dd, J=15, 11 Hz, 1H, H^{B}), 3.32 (d, J=11 Hz, 1H, H^{E}), 3.41 (dd, J=15, 11 Hz, 1H, H$^{D\prime}$), 3.49—3.58 (m, 8H, H$^{B\prime}$, H^{C}, H$^{C\prime}$, H$^{E\prime}$, H^{1}, H$^{1\prime}$, H^{2}, H$^{2\prime}$), 8.00 (s, 3H, Me), 8.04 (s, 3H, Me), and see Fig. 1.

Found: C, 93.54; H, 6.70%. Calcd for C$_{26}$H$_{22}$: C, 93.37; H, 6.63%.

3-Deuterio-6-methyl-3,5-octadien-7-yn-2-one (19). An ice-cooled solution of sodium hydroxide (0.65 M (1 mol dm^{-3}), 5.0 ml) in heavy water (D$_2$O) and ethanol-d_4 (5.0 ml) was added in one portion to an ice-cooled solution of (*Z*)-3-methyl-2-penten-4-ynal **18**[15] (1.70 g, 18.1 mmol) in acetone-d_6 (10.0 ml). The solution was stirred for a further 1 h at 0 °C and dilute sulfuric acid (2 M, 10 ml) was then added. The solution was poured into water and extracted with benzene. The combined extracts were washed successively with aqueous sodium hydrogencarbonate and brine. The residue after solvent removal was chromatographed on alumina (3.7×10.0 cm). The fractions eluted with 5% ether in hexane afforded the ketone **19** (1.01 g, 40%) as a yellow liquid: MS *m/z* 135 (M^{+}, 41%) and 120 (100); mol wt 135.2; IR (neat) 3300, 3250 (C≡CH), 2100 (C≡C), 1660 (C=O), 1610 (C=C), and 990 cm^{-1} (*trans* HC=CH); UV (EtOH) $\lambda_{\max}$ 299 nm (ε 17800); ^{1}H NMR (90 MHz) τ=2.49 (d, J=11 Hz, 1H, H^{B}), 3.59 (d, J=11 Hz, 1H, H^{C}), 6.51 (s, 1H, C≡CH), 7.69 (s, 3H, Me), 7.96 (s, 3H, Me).

6-Deuterio-3,13-dimethyl-3,5,8,10,12-pentadecapentaene-1,14-diyn-7-one (21). An ethanolic sodium ethoxide (3.0 ml) from sodium (380 mg) and dry ethanol (50 ml) was added in one portion to a solution of ketone **19** (1.01 g, 7.29 mmol) and (2*E*,4*Z*)-5-methyl-2,4-heptadien-6-ynal **20**[16] (1.0 g, 8.3 mmol) in deoxygenated ether (50 ml). After being stirred for a further 6 h at 3—5 °C, the reaction was quenched by addition of 2 M sulfuric acid (10 ml). After work up as for the isolation of **19**, the residue after solvent removal was chromatographed on alumina (4.0×9.0 cm). The fractions eluted with 30% ether in hexane afforded ketone **21** (606 mg, 35%). It formed yellow needles, mp 105—106 °C, from hexane–benzene: MS *m/z* 237.1237, calcd for 237.1263; UV (Et$_2$O) $\lambda_{\max}$ 230 (sh, ε 8000), 246 (sh, 12100), and 360 nm (32300); IR 3280 (C≡CH), 2100 (C≡C), 1655 (C=O), 1605, 1595 (C=C), and 1005 cm^{-1} (*trans* HC=CH); ^{1}H NMR (90 MHz) τ=2.32 (d, J=11 Hz, 1H, H^{B}), 2.61 (dd, J=16, 11 Hz, 1H, H$^{B\prime}$), 2.92 (dd, J=16, 11 Hz, 1H, H$^{D\prime}$), 3.45—3.66 (m, 4H, H$^{A\prime}$, H^{C}, H$^{C\prime}$, H$^{E\prime}$), 6.51 (s, 1H, C≡CH), 6.57 (s, 1H, C≡CH), 7.96 (s, 3H, Me), 8.00 (s, 3H, Me).

2-Deuterio-5,10-dimethyl-6,8-bisdehydro[15]annulenone (22). A solution of ketone **21** (1.25 g, 5.26 mmol) in pyridine and dry ether (3:1, 120 ml) was added dropwise during 4 h to a stirred solution of anhydrous copper(II) acetate (6.8 g) in pyridine and dry ether (3:1, 400 ml) at 50—52 °C. The solution was stirred for a further 30 min at the same temperature and was then cooled. The reaction mixture was poured into water and extracted with benzene. The combined extracts were washed with 5% hydrochloric acid until it turned acidic, then with aqueous sodium hydrogencarbonate solution, successively. The dark red liquid after solvent removal was chromatographed on alumina (3.7×8.0 cm). The fractions eluted with 30% ether in hexane afforded annulenone **22** (427 mg, 25%). It formed yellow needles, mp 159 °C (decomp), from hexane–benzene: MS *m/z* 235.1107, Calcd for 235.1107; UV (Et_2O) λ_{max} 245 (ε 11600), 257 (13100), 302 (35800), and 382 nm (5900); IR 2180 (C≡C), 1635 (C=O), 1605 (C=C), and 980 cm^{-1} (*trans* HC=CH); ^1H NMR (90 MHz) τ=2.46 (dd, *J*=16, 5 Hz, 1H, $H^{B'}$), 2.80 (d, *J*=11 Hz, 2H, H^C, $H^{E'}$), 3.20 (dd, *J*=16, 5 Hz, 1H, $H^{C'}$), 4.22 (d, *J*=11 Hz, 1H, H^B), 4.39 (d, *J*=16 Hz, 1H, $H^{A'}$), 4.57 (dd, *J*=16, 11 Hz, 1H, $H^{D'}$), 7.76 (s, 3H, Me), and 7.82 (s, 3H, Me).

2-Deuterio-5,10-dimethyl-6,8-bisdehydropentapentadecafulvalene (23). To a solution of cyclopentadienide, prepared from cyclopentadiene (100 ml), sodium (2.0 g), dry methanol (300 ml), was added dropwise a solution of annulenone **22** (363 mg, 1.54 mmol) in dry THF (50 ml) during 20 min at −6 °C and the solution was stirred for a further 1 h at the same temperature. After work up as for the isolation of **11**, the product was passed through a short column of alumina (3.7×4.0 cm) with hexane-ether (3:2). The residual red liquid after solvent removal was chromatographed on alumina (3.7×8.0 cm). The fractions eluted with hexane afforded fulvalene **23** (10.6 mg, 2.3%). It formed brown needles, mp 158 °C (decomp), from hexane–benzene: MS *m/z* 283.1543, Calcd for 283.1472; The IR, UV, and ^1H NMR were almost the same as those of **14**.

Attempts to obtain α-ethyl-substituted fulvalenes from the α-ethyl-substituted [13]annulenone **24**[4a)] and [15]annulenone **25**[4b)] were carried out as the exactly same conditions as for the isolation of **11**. However, none of fulvalene was isolated.

14-(2,4-Cyclopentadienyl)-2-ethyl-5,10-dimethyl-2,4,10,12-cyclopentadecatetraene-6,8-diyn-1-one (27). Conjugative Adduct of Cyclopentadiene and 26. To a solution of cyclopentadienide, prepared from cyclopentadiene (100 ml), sodium (2.0 g), dry methanol (250 ml), was added dropwise a solution of [15]annulenone **26**[4b)] (770 mg, 2.94 mmol) in dry THF (100 ml) during 30 min at −8 °C under nitrogen and the solution was stirred for a further 1 h at the same temperature. After work up as for the isolation of **11**, the product was passed through a short column of alumina (4.0×3.0 cm) with 30% ether in hexane. The residual red liquid after solvent removal was chromatographed on alumina (3.7×7.5 cm). The fractions eluted with 10% ether in hexane afforded the adduct **27** (513 mg, 56.3%). It formed yellow needles, mp 139—140 °C, from hexane–benzene: MS *m/z* 328 (M^+, 100%); mol wt 328.4; UV (THF) λ_{max} 239 (sh, ε 11700), 250 (sh, 14400), 276 (sh, 35500), 287 (43700), 381 (6350), and 423 nm (sh, 4260); IR 2170 (C≡C), 1665 (C=O), 1630, 1600 (C=C), and 970 cm^{-1} (*trans* HC=CH); ^1H NMR (90 MHz) τ=2.10 (d, *J*=11 Hz, 1H, H^C), 2.88—3.06 (m, 8H, H^B, $H^{C'}$, $H^{D'}$, $H^{E'}$, H^2, H^2, H^3, H^3), 5.96—6.22 (m, 1H, H^{14}), 6.39 (dd, *J*=16.5, 3 Hz, 1H, $H^{15'}$), 6.92 (dd, *J*=16.5, 11 Hz, 1H, H^{15}), 7.05 (s, 1H, H^1), 7.63 (q, *J*=7 Hz, 2H, $-C\underline{H}_2CH_3$), 7.99 (s, 3H, Me), 8.13 (s, 3H, Me), and 9.06 (t, *J*=7 Hz, 3H, $-CH_2C\underline{H}_3$).

Found: C, 87.46; H, 7.36%. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.36%.

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