June, 1986] © 1986 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 59, 1713—1721 (1986) 1713

Syntheses and Properties of Hepta- and Dibenzopentafulvalene Derivatives Containing 13-, 15-, 17-, and 19-Membered Rings[1)]

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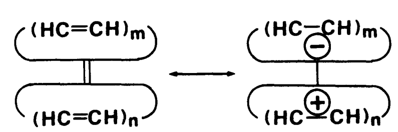
(Received, November 22, 1985)

5,10-Dimethyl-6,8-bisdehydroheptatridecafulvalene **10**, 10-methyl-6,8-bisdehydro-4,5-benzoheptatridecafulvalene **11**, 6,8-bisdehydro-4,5 : 10,11-dibenzoheptatridecafulvalene **12**, 5,10-dimethyl-6,8-bisdehydroheptapentadecafulvalene **13**, 5,10,15-trimethylheptapentadecafulvalene **14**, 7,12-dimethylheptaheptadecafulvalene **15**, and 7,12-dimethylheptanonadecafulvalene **16** were synthesized by a reaction of 8-oxoheptafulvene **8** with the corresponding bisdehydroannulenones **1**—**7**. Dibenzo derivatives of 5,10-dimethyl-6,8-bisdehydropentatridecafulvalene **23**, 10-methyl-6,8-bisdehydro-4,5-benzopentatridecafulvalene **24**, 6,8-bisdehydro-4,5 : 10,11-dibenzopentatridecafulvalene **25**, 5,10-dimethylpentapentadecafulvalene **26**, 5,10,15-trimethylpentapentadecafulvalene **27**, 7,12-dimethylpentaheptadecafulvalene **28**, and 7,12-dimethylpentanonadecafulvalene **29** were also synthesized by the reaction of 9-fluorenylidenemethanone **21** with the corresponding annulenones **1**—**7**. Furthermore, a benzo-annelated series of heptapentadecafulvalenes **30**—**35** was also synthesized. The ^{1}H NMR spectra of these hepta- and dibenzopentafulvalenes are discussed in connection with their tropicity. It can be concluded that a slight polarization of π-electrons through pinch bonds from the seven-membered rings to the many-membered rings in the heptafulvalene system and from the many-membered rings to the five-membered rings in the pentafulvalene system exist regardless of the size of the many-membered rings.

Recently, theoretical and experimental studies on the bicyclic polyene containing a cyclic cross conjugated π-electron system, fulvalene, have been extensively performed.[2)]

One group (A) of these compounds, in which one ring is $(4n+1)$-membered and the other is $(4n+3)$-membered, such as sesquifulvalene (pentaheptafulvalene) or triapentafulvalene (calicene), is potentially aromatic since the polarization of a π-electron through the central double bond (pinch bond) from $(4n+3)$ to $(4n+1)$-membered ring will make both rings a $(4n+2)$ π-electron system. The other group (B) in which both rings are $(4n+1)$- and/or $(4n+3)$-membered, such as pentafulvalene or heptafulvalene, is not potentially aromatic since the polarization of a π-electron through a pinch bond will make one ring a $(4n+2)$ system, and the other ring a $(4n)$ system.



We have investigated the syntheses of fulvalene containing a cycloheptatrienylidene moiety by a reaction of 8-oxoheptafulvene with various annulenones.[3)]

The reaction of 8-oxoheptafulvene with various many-membered annulenones such as trideca-, pentadeca-, heptadeca-, and nonadeca-annulenones may give, by [2+2] cycloaddition followed by an extrusion of carbon dioxide, fulvalenes containing a seven-membered ring in one ring and a many-membered ring in the other ring belonging to the group (A) or (B), depending on the size of the many-membered rings. Furthermore, a similar reaction using 9-fluorenylidenemethanone instead of 8-oxoheptafulvene might give dibenzo derivatives of the pentafulvalenes containing many-membered ring belonging to either group (A) or (B).

Although derivatives of pentaundecafulvalene[4)] belonging to the group (A) and pentatridecafulvalene,[5)] pentaphenafulvalene,[6)] and undecafulvalene[7)] belonging to group (B) are known as macrocyclic compounds of these types, systematic investigations of the syntheses and properties of fulvalenes containing many-membered rings have not been undertaken. Recently, the syntheses of pentafulvalenes containing 13-, 15-, 17-, and 19-membered macrocyclic rings have been reported.[8)]

In this paper, two series of fulvalenes, heptafulvalenes containing 13-, 15-, 17-, and 19-membered macrocyclic rings and dibenzopentafulvalenes containing the similar macrocyclic rings have been synthesized, and their tropicities are discussed in terms of an inspection of their ^{1}H NMR spectra.

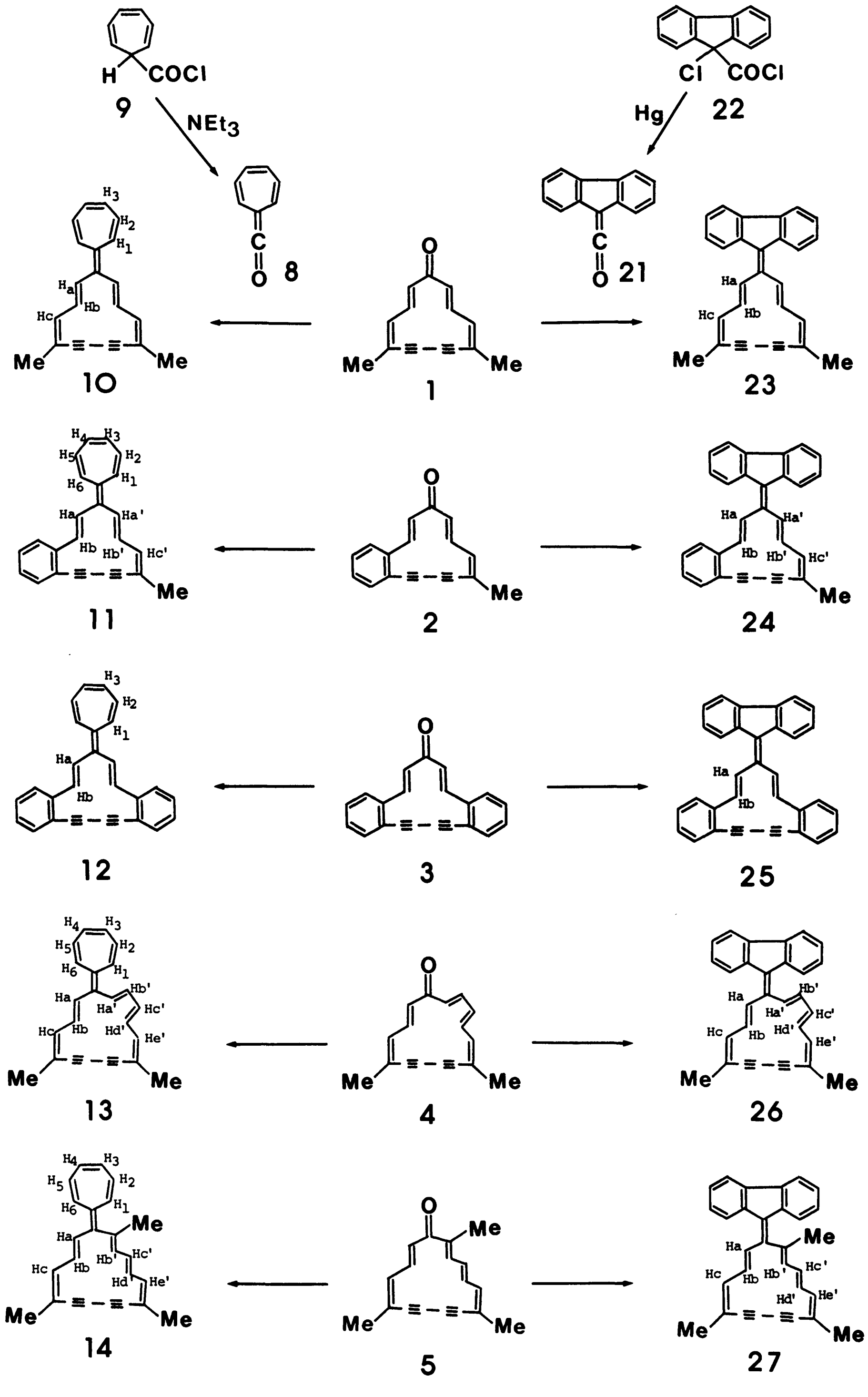
Results and Discussion

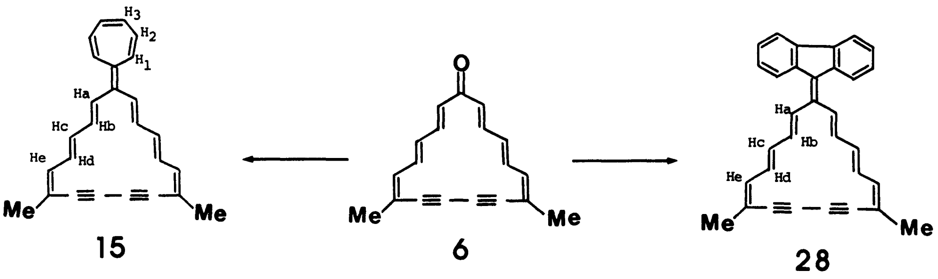
Syntheses. We have reported that a reaction of 8-oxoheptafulvene with tropone and its derivatives afforded heptafulvalenes and [2+8] cycloadducts in a variety of ratios depend on the substituents.[3)] We applied the reaction to derivatives of bisdehydro [13]-, [15]-, [17]-, and [19]annulenones and objective heptafulvalenes were synthesized. The reactions of 5,10-dimethyl-6,8-bisdehydro[13]annulenone **1**,[9)] 10-methyl-6,8-bisdehydro-4,5-benz[13]annulenone **2**,[10)] 6,8-bisdehydro-4,5:10,11-dibenz[13]annulenone **3**,[10)] 5,10-dimethyl-6,8-bisdehydro[15]annulenone **4**,[11)] 5,10,15-trimethyl-6,8-bisdehydro[15]annulenone **5**,[12)] 7,12-dimethyl-8,10-bisdehydro[17]annulenone **6**,[11)] and 7,12-dimethyl-8,10-bisdehydro[19]annulenone **7**[11)] with an excess of 8-oxoheptafulvene **8**[3,13)] formed in situ by a reaction of tropylcarbonyl chloride **9** and triethylamine in dry benzene at refluxing or room temperature afforded 5,10-dimethyl-6,8-bisdehydroheptatridecafulvalene **10**, 10-methyl-6,8-bisdehydro-4,5-benzoheptatridecafulvalene **11**, 6,8-bisdehydro-4,5:10,11-dibenzoheptatridecafulvalene **12**, 5,10-dimethyl-6,8-bisdehydroheptapentadecafulvalene **13**, 5,10,15-trimethyl-6,8-bisdehydroheptapentadecafulvalene **14**, 7,12-dimethyl-8,10-bisdehydroheptaheptadecafulvalene **15**, and 7,12-dimethyl-8,10-bisdehydroheptanonadecafulvalene **16** in 3.9, 67.3, 23.8, 36, 86, 52, and 74% yields, respectively.

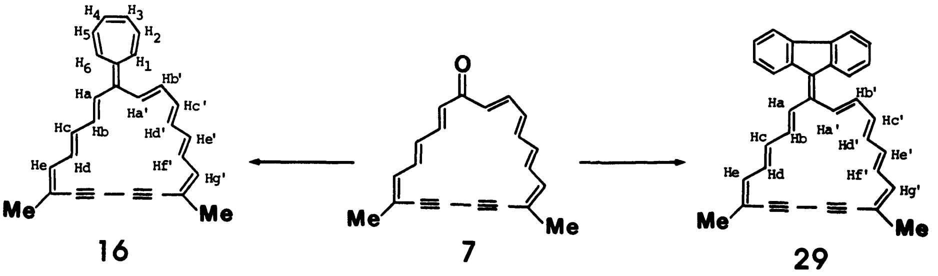
In the case of **1** and **3**, [2+8] cycloadducts **17** and **18** were obtained in yields of 41 and 14%, respectively, both as pale-yellow crystals. 2,13-Dideuterio derivative of **3**[14] afforded the corresponding fulvalene **19** and [2+8] adduct **20** which were very useful compounds for NMR assignment of compounds **12** and **18**,[15] respectively.

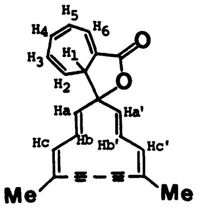
The fulvalenes **10**—**16** were recrystallized from benzene or hexane–benzene to give deep-colored (dark-reddish or dark-brownish) moderately stable crystals. These gradually decomposed upon standing at room temperature or upon exposure to air and diffused light.

On the other hand, reactions of the annulenones **1**—**7** with 9-fluorenylidenemethanone **21** formed in situ by a reaction of 9-chlorofluorene-9-carbonyl chloride









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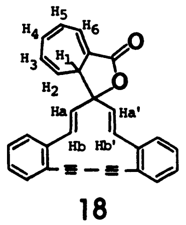

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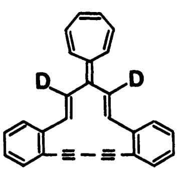

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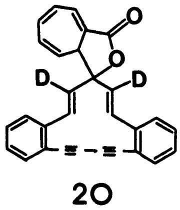

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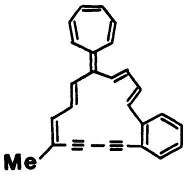

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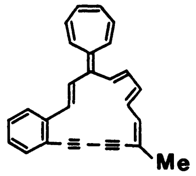

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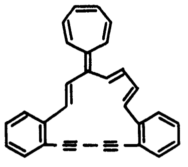

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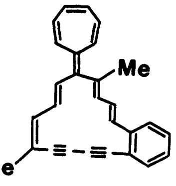

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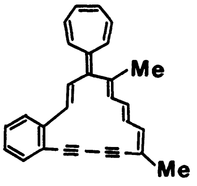

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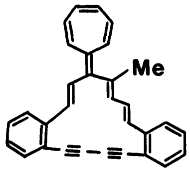

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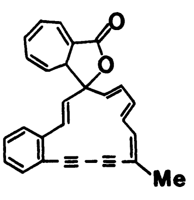

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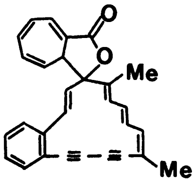

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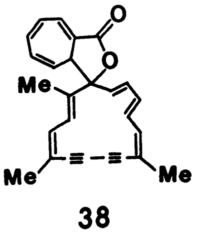

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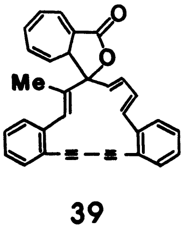

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22 with mercury afforded the corresponding dibenzo derivatives of the pentafulvalenes **23**—**29** containing 13-, 15-, 17-, and 19-membered rings in 28, 27, 4.4, 47, 8.3, 38, and 36% yields, respectively. These fulvalenes were also deep-colored and moderately stable compounds at low temperature and under nitrogen atmosphere.

Furthermore, we studied the synthesis of the series of benzoannelated heptapentadecafulvalenes. The reactions of 10-methyl-4,5-benzo-,[16,17] 5-methyl-10,11-benzo-,[16,17] 4,5:10,11-dibenzo-,[18] 10,15-dimethyl-4,5-benzo-,[16] 5,15-dimethyl-10,11-benzo-,[16] and 15-methyl-4,5:10,11-dibenzo-6,8-bisdehydropentadecaannulenones[16] with 8-oxoheptafulvene **8** afforded the corresponding benzoannelated heptapentadecafulvalenes **30** [81%, mp 119—123 °C (decomp)], **31** [29.4%, mp 108—110 °C (decomp)], **32** [23.6%, mp 150 °C (decomp)], **33** [87%, mp 89 °C (decomp)], **34** (23%, mp not clear), and **35** (77%, mp not clear), and [2+8] cycloadducts **36** [mp 215—225 °C (decomp)] and **37** [mp 189—191 °C (decomp)] in some cases. However, the reactions of 2,5,10-trimethyl-6,8-bisdehydropentadecaannulenone[12] and 2-methyl-4,5:10,11-dibenzo-6,8-bisdehydropentadecaannulenone[12] with **8** were very slow and yielded only

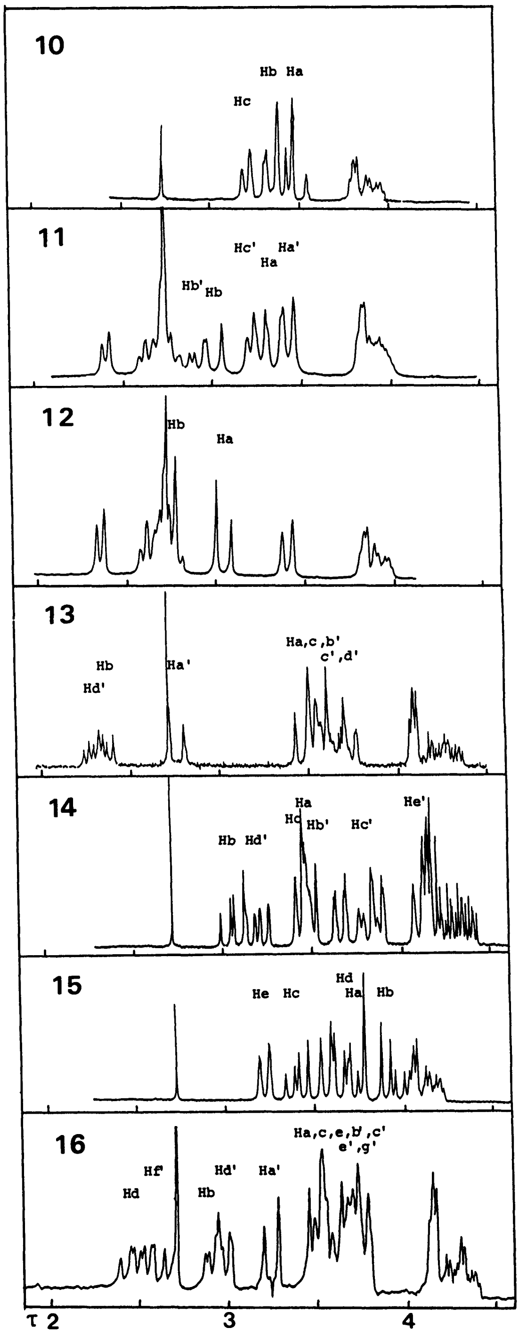


Fig. 1. ¹H NMR (200 MHz) Spectra (partial) of Heptafulvalenes **10**—**16** in CDCl$_3$ (τ values, internal standard, TMS).

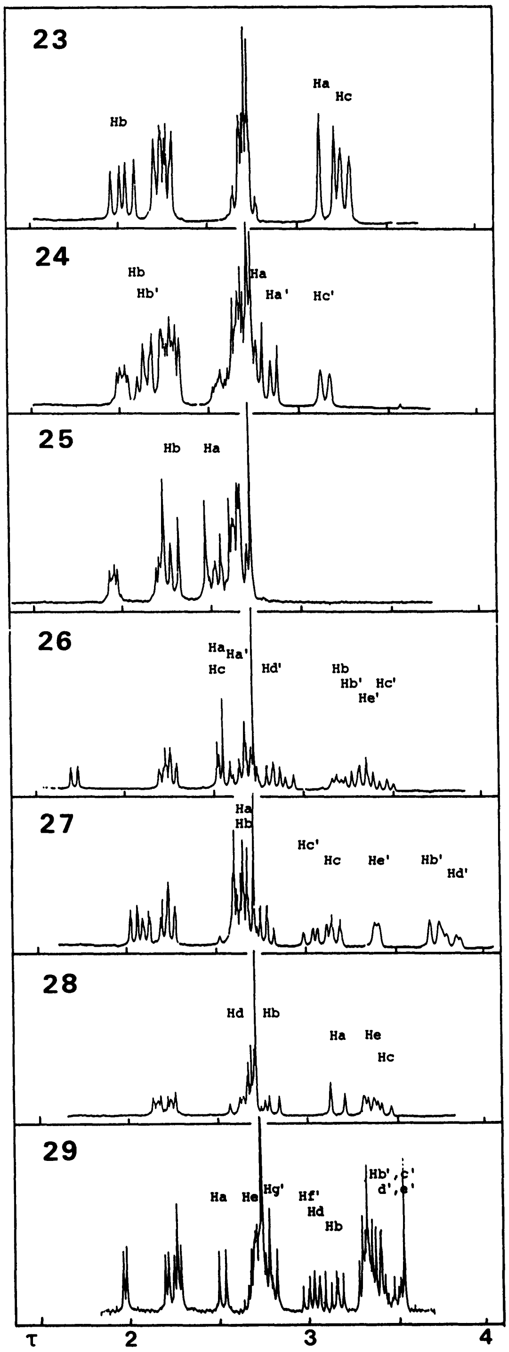


Fig. 2. ¹H NMR (200 MHz) Spectra (partial) of Pentafulvalenes **23**—**28** and ¹H NMR (400 MHz) Spectra of **29** in CDCl$_3$ (τ values, internal standard, TMS).

[2+8] cycloadducts **38** [mp 176 °C (decomp)] and **39** [mp 193—194 °C (decomp)], respectively.

^{1}H NMR. The ^{1}H NMR spectra at 200 MHz of the heptafulvalenes **10**—**16** and the pentafulvalenes **23**—**29** are illustrated in Figs. 1 and 2, respectively. The individual assignments were made on the basis of the multiplicities and coupling constants, which were determined by extensive decoupling experiments.

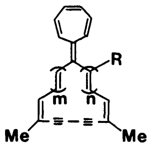
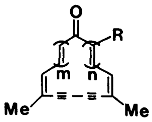
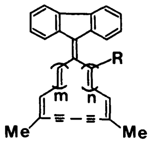
Differences of the outer and inner protons of the many-membered rings of all spectra were considerably smaller than those of starting annulenones; therefore, these fulvalenes have a more polyolefinic character than the starting annulenones.

Figure 1 shows that the seven-membered ring protons of **10**, **11**, **12**, and **15** resonate in a slightly higher magnetic field than those of **13**, **14**, and **16**; the former are almost the same as those of heptafulvalene itself[19] and the latter are almost the same as those of sesquifulvalene (pentaheptafulvalene).[20] On the other hand, the outer and inner protons of the many-membered rings of **10**, **11**, and **12** resonate with each other at lower and higher magnetic fields. The outer and inner protons of the many-membered rings of **13**, **14**, and **16** resonate with each other at higher and lower magnetic fields. These are in accord with that the compounds **10**, **11**, **12**, and **15**, belonging to the group (A), are potentially aromatic by polarization of the π-electrons which makes the seven-membered rings to 6π and the many-membered rings to 14π or 18π systems. Furthermore, it can be considered that the polarization of π-electrons from the seven-membered ring to the many-membered rings occurred even in compounds **13**, **14**, and **16**, belonging to the group (B). These make seven-membered rings to 6π and many-membered rings to paratropic having a 16π or a 20π system.

Figure 2 shows a reverse trend in the pentafulvalene compared to the heptafulvalene system. The outer and inner protons of the many-membered rings of **23**, **24**, **25**, and **28** resonate with each other at higher and lower fields. Those of **26**, **27**, and **29** resonate with each other at lower and higher fields. This shows that polarization of the π-electrons through a pinch bond from the many-membered rings to the five-membered rings occurred in all cases which make many-membered rings of **23**, **24**, **25**, and **28** to paratropic having 12π or 16π system and those of **26**, **27**, and **29** to diatropic having 14π or 18π system. In particular, relative chemical shifts of the corresponding inner protons of the many-membered rings of the hepta- and pentafulvalenes clearly show an inverse direction to each other. This indicates that the polarization of the π-electron from the seven-membered rings to the many-membered rings in the heptafulvalene series and from the many-membered rings to the five-membered rings in the pentafulvalene series occurred regardless of the size of the many-membered rings.

The ^{1}H NMR spectra of benzoannelated heptapentadecafulvalenes **30**—**35** were taken at 90 MHz, and the spectral patterns were similar to those of heptapentadecafulvalenes **11** and **12**; however, the signals were not separated. Therefore, we could not discuss the assignments and the tropicities.

Table 1. Chemical Shifts of Methyl Protons of Annulenones, and Hepta- and Pentafulvalenes

							
[13]-	R=H	**10**	8.08	**1**	8.26	**23**	8.12
[15]-	R=H	**13**	8.18	**4**	7.82, 7.76	**26**	8.06, 8.02
	R=Me	**14**	8.15, 8.13, 8.06	**5**	7.95, 7.90, 7.79	**27**	8.05, 8.04, 7.77
[17]-	R=H	**15**	8.00	**6**	8.23	**28**	8.06
[19]-	R=H	**16**	8.14	**7**	7.87, 7.79	**29**	8.04, 8.00

Furthermore, since the methyl groups of all fulvalenes were always outside of the rings and could be readily recognized in the NMR spectra, we inspected the methyl resonaces of these fulvalenes in the expectation of obtaining information concerning the tropicities.

The chemical shifts of the methyl resonances of the heptafulvalene **10**, **13**, **14**, **15**, and **16** and pentafulvalenes **23**, **26**, **27**, **28**, and **29** are listed in Table 1, together with those of the corresponding annulenones **1**, **4**, **5**, **6**, and **7**. We can see a remarkable alternation of the methyl resonace between $(4n+1)$ annulenones, [13]- and [17]annulenones which show a relatively high field, and $(4n+3)$ annulenones, [15]- and [19]annulenones which show relatively low field. These phenomena indicate paratropicity and diatropicity, respectively, owing to the polarization of the carbonyl group. The same alternation trend can be observed for the pentafulvalene series and a reverse alternation trend was observed for the heptafulvalene series, although the degree of the alternation for both series were much less than that for the annulenones.

Electronic Spectra. The electronic spectra of the heptafulvalenes **10**, **11**, and **12** and the pentafulvalenes **23**, **24**, and **25** are shown in Figs. 3 and 4, respectively. The electronic spectra of the heptafulvalenes **10**, **13**, **15**, and **16** and the pentafulvalenes **23**, **26**, **27**, **28**, and **29** are also shown in Figs. 5 and 6, respectively.

It can be seen from Figs. 3 and 4 that the longest wavelength bands exhibited absorption toward the longer wavelength in the order **10**>**11**>**12**, and **23**>**24**>**25**, respectively, as has been observed for the corresponding annulenones. This indicates that fused benzene rings inhibit the degree of conjugation of a π-electron systems in these fulvalene systems.

From Figs. 5 and 6, we can not see regularity depend on the ring size; the longest bands of nonadecafulvalenes **16** and **29** are shifted to shorter wavelength, which may due to the bending of the many-membered rings.

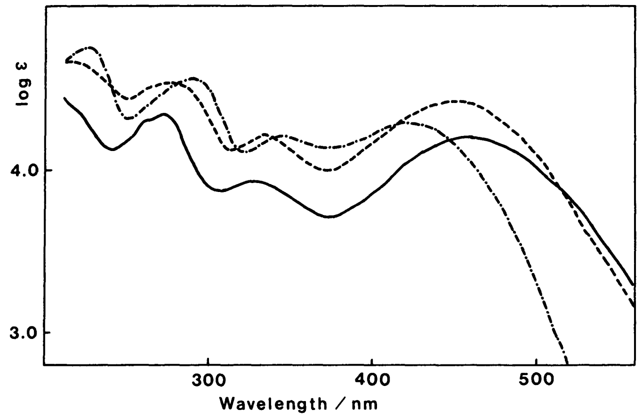


Fig. 3. Electronic Absorption Spectra of **10** (——), **11** (----), and **12** (-·-·-) in EtOH.

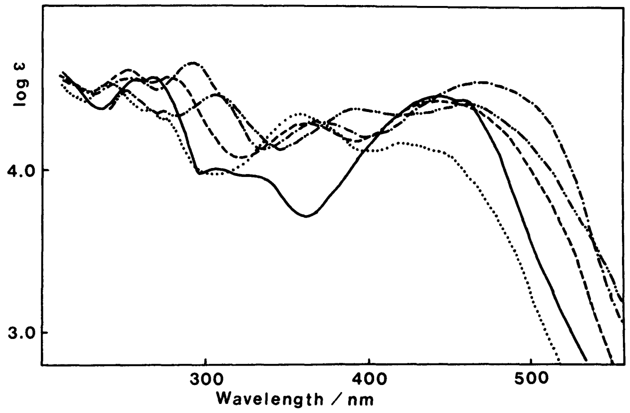


Fig. 6. Electronic Absorption Spectra of **23** (——), **26** (----), **27** (······), **28** (-·-·-), and **29** (-··-··-), in EtOH.

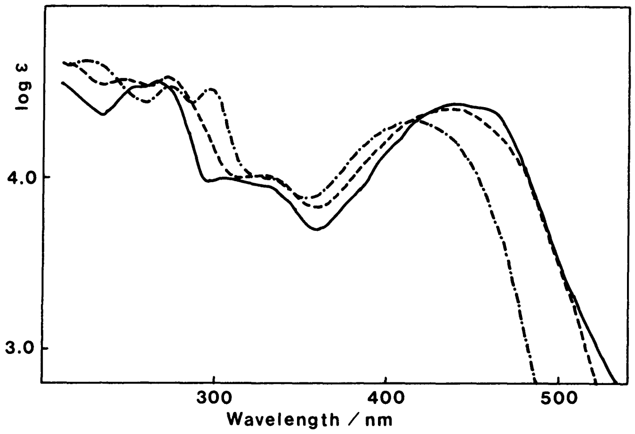


Fig. 4. Electronic Absorption Spectra of **23** (——), **24** (----), and **25** (-·-·-) in EtOH.

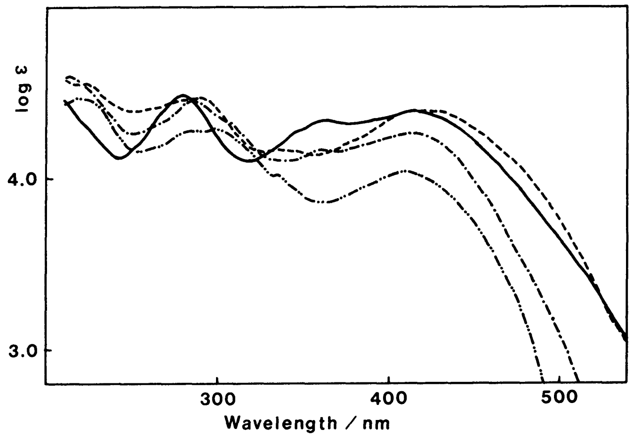


Fig. 7. Electronic Absorption Spectra of **13** (——), **30** (----), **31** (-·-·-), and **32** (-··-··-) in EtOH.

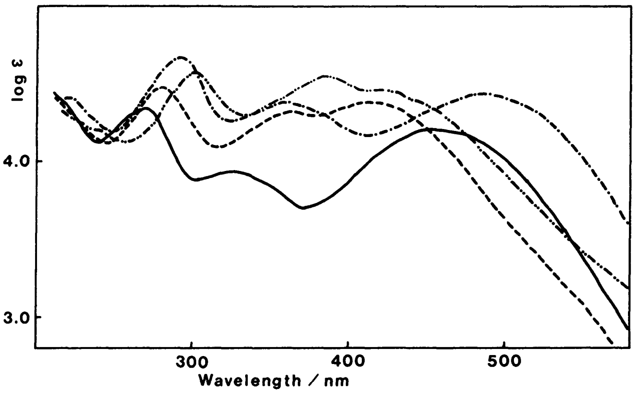


Fig. 5. Electronic Absorption Spectra of **10** (——), **13** (----), **15** (-·-·-), and **16** (-··-··-) in EtOH.

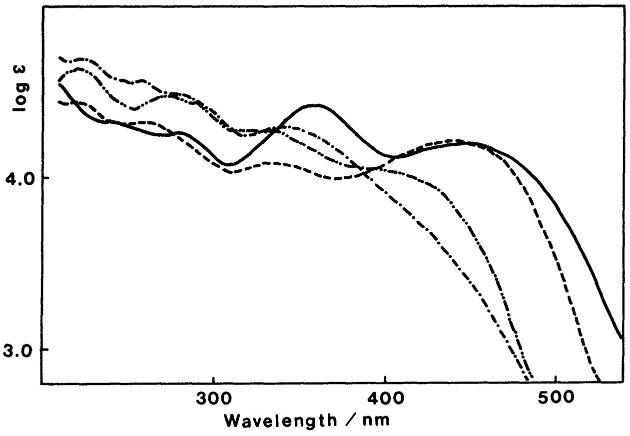


Fig. 8. Electronic Absorption Spectra of **14** (——), **33** (----), **34** (-·-·-), and **35** (-··-··-) in EtOH.

The spectral curves of the benzoannelated series of heptapentadecafulvelnes **30**—**32** and **33**—**35** are illustrated in Figs. 7 and 8 with those of **13** and **14**, respectively. The longest bands of the benzoannelated fulvalenes appeared at shorter wavelengths compared to those of **13** and **14**, as has been observed in Figs. 3 and 4.

Experimental

General. Melting points were determined on a hot-stage apparatus and were uncorrected. The IR spectra were obtained with a Hitachi 215 grating spectrophotometer. The electronic spectra were measured with a Hitachi 340 spectrophotometer. ^{1}H NMR spectra were recorded with a Varian XL-200 (200 MHz), JEOL JX-400 (400 MHz), or Hitachi R-22 (90 MHz) spectrometer in $CDCl_3$ solutions, tetramethylsilane being used as an internal standard; chemical shifts are reported in τ and coupling constants (J) show in Hz. Mass spectra were measured with a JMS D-200 spectrometer at 75 eV.

Reaction of [13]Annulenone 1 and 8-Oxoheptafulvene 8. A solution of tropylcarbonyl chloride **9** (154.6 mg, 1.0 mmol) in dry benzene (10 ml) was added dropwise to a solution of [13]annulenone **1** (104 mg, 0.5 mmol) and triethylamine (214 mg) in dry benzene (15 ml) during a period of 15 min at refluxing temperature under argon atmosphere, and the mixture was refluxed for further 15 min. The solution was submitted to column chromatography on silica gel, and eluted with a mixture of hexane and benzene. From reddish fraction heptatridecafulvalene **10** (5.5 mg, 3.9%) was obtained as dark reddish needles (from a mixture of hexane and benzene), color changed from around 110 °C and decomposed without melting.

From the yellow fraction, [2+8] cycloadduct **17** (67.0 mg, 41%) was obtained as pale-yellow prisms, mp 159—160 °C (decomp) (from benzene). **10**; IR (KBr) 2140 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=3.21 (d, J=9, Hc), 3.36 (d, J=12.5, H-1), 3.37 (d,d, J=15.5, 9, Hb), 3.51 (d, J=15.5, Ha), 3.79—3.98 (m, H-2,3), 8.08 (s, Me).

Found: C, 93.49; H, 6.16%. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43%. **17**; IR (KBr) 2170 cm^{-1} (C≡C), 1745 (C=O); ES λ_{max} (EtOH) 258 nm (log ε 4.38), 316 (3.90); ^{1}H NMR (200 MHz) τ=2.86 (m, H-6), 3.25 (m, H-4, 5), 3.37 (d,d,q, J=5, 1, 1, Hc or Hc′), 3.49 (d,d,q, J=5, 1, 1, Hc′ or Hc), 3.61 (d,d,q, J=15.5, 5, 1, Hb or Hb′), 3.75—3.95 (m, H-3), 3.95 (d,d,q, J=15.5, 5, 1, Hb′ or Hb), 4.59 (d,d, J=9.6, 4, H-2), 4.79 (d,d, J=15.5, 1, Ha′), 4.83 (d,d, J=15.5, 1, Ha), 6.86 (m, H-1), 8.04 (d,d, J=1, 1, Me), 8.07 (d,d, J=1, 1, Me).

Found: C, 84.63; H, 5.53%. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56%.

Heptatridecafulvalene 11. A reaction of [13]annulenone **2** (34 mg, 0.14 mmol), chloride **9** (30 mg, 0.2 mmol), triethylamine (50 mg) in dry benzene (20 ml) was carried out in almost the same manner, conditions and purification procedure as in the case of **1**. Heptatridecafulvalene **11** (29.8 mg, 67.3%) was obtained as dark-reddish crystals, mp 150 °C (decomp). IR (KBr) 2160 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=2.41 (d, J=7.5, 1H, Ar-H), 2.59—2.80 (m, 3H, Ar-H), 2.89 (d,d, J=16, 10.5, Hb′), 3.01 (d, J=16.5, Hb), 3.21 (d, J=10.5, Hc′), 3.26 (d, J=16.5, Ha), 3.43 (d, J=11.5, H-1,6), 3.45 (d, J=16, Ha′), 3.8—4.0 (m, H-2,3,4,5), 8.12 (s, Me).

Found: C, 94.01; H, 5.61%. Calcd for $C_{25}H_{18}$: C, 94.30; H, 5.70%.

Heptatridecafulvalene 12. A solution of chloride **9** (154 mg, 1.0 mmol) in dry benzene (10 ml) was added dropwise to a solution of [13]annulenone **3** (140 mg, 0.5 mmol) and triethylamine (40 ml) at 80 °C under an argon atmosphere for 15 min. The reaction mixture was heated for an additional 30 min, submitted to column chromatography on alumina and eluted with benzene. From the reddish fraction heptatridecafulvalene **12** (42.2 mg, 23.8%) was obtained as dark-reddish crystals, mp decomposed from around 150 °C.

From pale yellow fraction, [2+8] cycloadduct **18** (29.1 mg, 14.5%) was obtained as pale-yellow crystals, mp 191—194 °C. **12**; IR (KBr) 2175 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=2.36 (d, J=8, 2H, Ar-H), 2.57—2.81 (m, 6H, Ar-H), 2.73 (d, J=16.5, Hb), 3.04 (d, J=16.5, Ha), 3.39 (d, J=11.5, H-1), 3.78—3.97 (m, H-2, 3).

Found: C, 94.62; H, 5.08%. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12%. **18**; IR (KBr) 2190 cm^{-1} (C≡C), 1745 (C=O); ES λ_{max} (EtOH) 223 nm (log ε 4.81), 259 (4.52), 273 (4.50), 321 (4.18), 341 (4.16); ^{1}H NMR (200 MHz) τ=2.78 (m, 9H, H-6, Ar-H), 3.09 (d, J=16, Hb or Hb′), 3.22 (m, H-4, 5), 3.35 (d, J=16, Hb′ or Hb), 3.54 (d, J=16, Ha′), 3.61 (d, J=16, Ha), 3.78 (d,m, J=10, H-3), 4.56 (d,d, J=10, 4, H-2), 6,99 (m, H-1).

Found: C, 87.37; H, 4.78%. Calcd for $C_{29}H_{18}O_2$: C, 87.41; H, 4.55%.

Heptapentadecafulvalene 13. A reaction of [15]annulenone **4** (78 mg, 0.33 mmol), chloride **9** (100 mg, 0.65 mmol), triethylamine (100 mg) in dry benzene (20 ml) was carried out in the almost same manner as in the case of **1**. The usual work-up afforded the heptafulvalene **13** (36.9 mg, 36%) as dark-reddish crystals, mp 100—101.5 °C (decomp). IR (KBr) 2160 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=2.31 (d,d, J=14.5, 11, Hd′), 2.34 (d,d, J=15, 11.5, Hb), 2.76 (d, J=15.5, Ha′), 3.43—3.70 (m, Ha,c,b′,c′,e′), 3.56 (d, J=11.5, H-6), 3.73 (d, J=12, H-1), 4.08 (d,d, J=5, 3.5, H-3, 4), 4.25 (d,d,d, J=11.5, 5, 3.5, H-5), 4.27 (d,d,d, J=12, 5.5, 3.5, H-2), 8.18 (s, 2Me).

HRMS; Found: 308.1490. Calcd for $C_{24}H_{20}$: 308.1566.

Heptapentadecafulvalene 14. A reaction of a solution of [15]annulenone **5** (50 mg, 0.20 mmol) in dry benzene (10 ml) and a solution of chloride **9** (100 mg) in dry benzene (10 ml) was carried out in the similar manner in the case of **1**. The usual work-up afforded heptapentadecafulvalene **14** (45 mg, 86%) as dark-reddish crystals, mp 99—100 °C (decomp). IR (CCl_4) 2170 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=3.05 (d,d, J=15, 11.5, Hb), 3.19 (d,d,d, J=15.5, 10, 1, Hd′), 3.44 (d,d, J=11.5, 1.5, Hc), 3.49 (d, J=15, Ha), 3.51 (d, J=5, Hb′), 3.66 (d, J=11.5, H-6), 3.81 (d,d, J=15.5, 5, Hc′), 3.86 (d, J=12, H-1), 4.10 (d, J=10, He′), 4.15 (m, H-3, 4), 4.25 (d,d,d, J=11.7, 5.2, 3.7, H-5), 4.37 (d,d,d, J=12, 5, 4.5, H-2), 8.06 (d, J=1.5, Me), 8.13 (d,d, J=1.5, 1.5, Me), 8.15 (s, Me).

HRMS; Found: 322.1744. Calcd for $C_{25}C_{22}$: 322.1722.

Heptaheptadecafulvalene 15. A solution of [17]annulenone **6** (65 mg, 0.25 mmol), triethylamine (199 mg) in dry benzene (20 ml) and a solution of chloride **9** (100 mg, 0.6 mmol) in dry benzene (10 ml) was reacted, and the usual work-up afforded heptaheptadecafulvalene **15** (44.1 mg, 52%) as dark-brownish needles, mp 180—181 °C (decomp). IR (KBr) 2165 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=3.22 (br d, J=11, He), 3.39 (d,d, J=15, 10, Hc), 3.56 (d, J=11.5, H-1), 3.67 (d,d, J=15, 11, Hd), 3.73 (d, J=15.5, Ha), 3.93 (d,d, J=15.5, 10, Hb), 4.04 (d,d, J=4.5, 4, H-3), 4.15 (d,d,d, J=11.5, 4.5, 4, H-2), 8.00 (s, Me).

HRMS; Found: 334.1732. Calcd for $C_{26}H_{22}$: 334.1722.

Heptanonadecafulvalene 16. A solution of [19]annulenone **7** (50 mg, 0.17 mmol) and triethylamine (132 mg) in dry benzene (10 ml), and a solution of chloride **9** (100 mg) in dry benzene (10 ml) was reacted at room temperature for 20 min under argon atmosphere. The solution was passed through an alumina (deactivated by treating with ethyl acetate and water) column. The colored fraction was collected and purified by further column chromatography using the alumina to obtain heptafulvalene **16** (46.5 mg, 74%) as unstable dark-reddish crystals, mp 144—145 °C (decomp). IR (KBr) 2190 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=2.46 (d,d, J=15, 11, Hd), 2.57 (d,d, J=15, 11, Hf′), 2.93 (d,d, J=15, 11, Hb), 2.95 (d,d, J=15, 11, Hd′), 3.24 (d, J=16, Ha′), 3.45—4.00 (m, H-1, 6, a,c,e,b′,c′,e′,g′), 4.14 (d,d, J=5, 3.5, H-3, 4), 4.19—4.39 (m, H-

2, 5), 8.14 (s, 2Me).

HRMS; Found: 360.1799. Calcd for $C_{28}H_{24}$: 360.1879.

Pentatridecafulvalene 23. A solution of [13]annulenone **1** (50 mg, 0.24 mmol), 9-chlorofluorene-9-carbonyl chloride **22** (150 mg, 0.57 mmol), in dry benzene (20 ml) in the presence of one drop of mercury was stirred at room temperature under an argon atmosphere for 3 d. The reaction mixture was directly submitted to column chromatography using silica gel, and the colored fraction was further purified by chromatography on silica gel. Pentatridecafulvalene **23** (24 mg, 28%) was obtained as dark-reddish crystals, mp 174—175 °C (decomp). IR (KBr) 2150 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=2.03 (d,d, J=16, 10, Hb), 2.20—2.30 (m, 4H, Ar–H), 2.64—2.77 (m, 4H, Ar–H), 3.07 (d, J=16, Ha), 3.27 (d, J=10, Hc), 8.12 (s, Me).

Found: C, 94.11; H, 5.44%. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66%.

Pentatridecafulvalene 24. A solution of [13]annulenone **2** (50 mg, 0.2 mmol), chloride **22** (150 mg) in dry benzene (10 ml) in the presence of one drop of mercury was stirred at room temperature for 30 h under an argon atmosphere. The reaction mixture was submitted to column chromatography using alumina and eluted with benzene. The pentatridecafulvalene **24** (22 mg, 27%) was obtained as dark-reddish crystals, mp 190—192 °C (decomp). IR (KBr) 2165 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=1.97—2.31 (m, 5H, Hb, Ar–H), 2.10 (d,d, J=16.5, 10.5, Hb′), 2.49—2.72 (m, 8H, Ar–H), 2.78 (d, J=16.5, Ha), 2.82 (d, J=16.5, Ha′), 3.13 (d, J=10.5, Hc′), 8.00 (s, Me).

Found: C, 94.72; H, 4.84%. Calcd for $C_{31}H_{20}$: C, 94.86; H, 5.14%.

Pentatridecafulvalene 25. A solution of [13]annulenone **3** (50 mg, 0.18 mmol), chloride **22** (100 mg) and one drop of mercury in dry benzene (10 ml) was stirred at room temperature for 3 d. The usual work-up afforded pentatridecafulvalene **25** (3.4 mg, 4.4%) as dark-reddish crystals, mp 221—223 °C (decomp), and annulenone **3** (20 mg) was recovered. IR (KBr) 2190 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=1.97 (m, 2H, Ar–H), 2.20—2.32 (m, 2H, Ar–H), 2.26 (d, J=16.5, Hb), 2.46—2.71 (m, 12H, Ar–H), 2.49 (d, J=16.5, Ha).

HRMS; Found: 428.1488. Calcd for $C_{34}H_{20}$: 428.1566.

Pentapentadecafulvalene 26. A solution of [15]annulenone **4** (70 mg, 0.30 mmol), chloride **22** (150 mg) in dry benzene in the presence of one drop of mercury was stirred for 1 d at room temperature under an argon atmosphere. The usual work-up afforded pentapentadecafulvalene **26** (55 mg, 47%) as dark-reddish crystals, mp 153.5—155 °C (decomp). IR (KBr) 2160 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=1.70 (d, J=8, 1H, Ar–H), 2.30 (m, 3H, Ar–H), 2.58—2.86 (m, 4H, Ar–H), 2.52 (d, J=5, Ha), 2.53 (d, J=7, Hc), 2.60 (d, J=15.5, Ha′), 2.87 (d,d, J=15, 11, Hd′), 3.17 (d,d, J=7, 5, Hb), 3.28 (d,d, J=15.5, 7, Hb′), 3.32 (d, J=11, He′), 3.43 (d,d, J=15, 7, Hc′), 8.02 (s, Me), 8.06 (s, Me).

HRMS; Found: 382.1690. Calcd for $C_{30}H_{22}$: 382.1722.

Pentapentadecafulvalene 27. A solution of [15]annulenone **5** (50 mg, 0.20 mmol), chloride **22** (100 mg) and one drop of mercury in dry benzene (10 ml) was stirred at room temperature for 1 d under an argon atmosphere. The usual work-up afforded pentapentadecafulvalene **27** (6.6 mg, 8.3%) as dark-reddish crystals, mp 175—177 °C (decomp). IR (KBr) 2160 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=2.05 (d, J=7.5, 1H, Ar–H), 2.11 (br d, J=6.5, 1H, Ar–H), 2.21 (br d, J=6, 1H, Ar–H), 2.26 (br d, J=7.5, 1H, Ar–H), 2.52—2.82 (m, 6H, Ha,b, Ar–H), 3.05 (d,d,d, J=15, 11, 1.5, Hc′), 3.16 (d,m, J=9.5, Hc), 3.39 (br d, J=4.5, He′), 3.71 (d, J=11, Hb′), 3.81 (d,d, J=15, 4.5, Hd′), 7.77 (d, J=1.5, a′-Me), 8.04 (d, J=1.5, d-Me), 8.06 (d, J=1.5, f′-Me).

HRMS; Found: 396.1949. Calcd for $C_{31}H_{24}$: 396.1879.

Pentaheptadecafulvalene 28. A solution of [17]annulenone **6** (50 mg, 0.19 mmol), chloride **22** (150 mg, 0.57 mmol) and one drop of mercury in dry benzene (20 ml) was stirred at room temperature for 1 d under an argon atmosphere. The usual work-up afforded pentaheptadecafulvalene **28** (26.3 mg, 38%) as dark-reddish crystals, mp 273—274 °C (decomp). IR (KBr) 2155 cm^{-1} (C≡C); ^{1}H NMR (200 MHz) τ=2.15 (m, 2H, Ar–H), 2.24 (m, 2H, Ar–H), 2.65 (m, 4H, Ar–H), 2.63 (d,d, J=15.5, 11.5, Hd), 2.77 (d,d, J=15.5, 11, Hb), 3.17 (d, J=15.5, Ha), 3.34 (d, J=11.5, He), 3.40 (d,d, J=15.5, 11, Hc), 8.06 (s, Me).

HRMS; Found: 408.1868. Calcd for $C_{32}H_{24}$: 408.1879.

Pentanonadecafulvalene 29. A solution of [19]annulenone **7** (40 mg, 0.14 mmol), chloride **22** (150 mg) and one drop of mercury in dry benzene (10 ml) was stirred at room temperature for 1 d under an argon atmosphere. The usual work-up afforded pentanonadecafulvalene **29** (22 mg, 36%) as unstable dark-reddish-brown crystals, mp 123—124 °C (decomp). IR (KBr) 2160 cm^{-1} (C≡C); ^{1}H NMR (400 MHz) τ=1.97 (d, J=7, 1H, Ar–H), 2.21 (d, J=7, 1H, Ar–H), 2.26 (d, J=7, 1H, Ar–H), 2.28 (d, J=7, 1H, Ar–H), 2.56 (d, J=15, Ha), 2.65—2.8 (m, 4H, Ar–H), 2.7 (m, He), 2.7—2.8 (m, Ha′), 2.8 (m, Hg′), 3.0 (d,d, J=15, 11, Hf′), 3.06 (d,d, J=15, 11, Hd), 3.16 (d,d, J=15, 11, Hb), 3.3 (m, Hc), 3.35—3.65 (m, Hb′,c′,d′,e′), 7.99 (s, Me), 8.04 (s, Me).

HRMS; Found: 434.2064. Calcd for $C_{34}H_{26}$: 434.2036.

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