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THE SYNTHESIS OF DIBENZO DERIVATIVES OF PENTATRIDECA-, PENTAPENTADECA-, PENTAHEPTADECA-, AND PENTANONADECAFULVALENES

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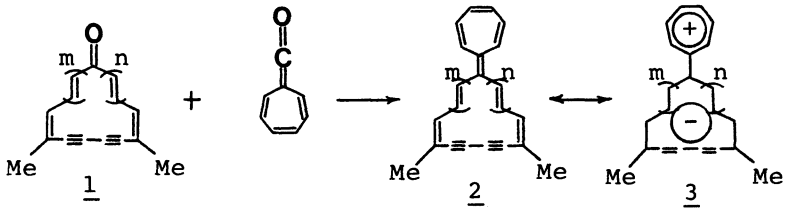
The title fulvalenes were synthesized by the reaction of the corresponding large membered annulenones with diphenyleneketene and the ^{1}H-NMR spectra were discussed in connection with their tropicity.

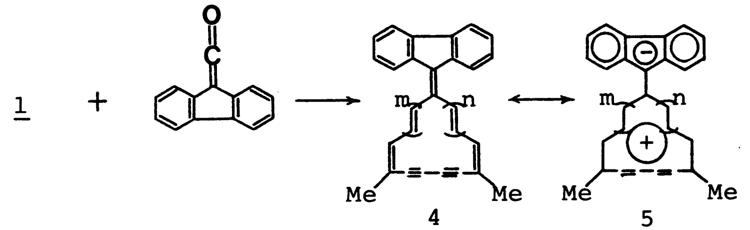
We have reported the synthesis of heptatrideca-, heptapentadeca-, heptaheptadeca-, and heptanonadecafulvalene derivatives (2) by the reaction of the corresponding large membered annulenones (1) with 8-oxoheptafulvene, and have discussed the ^{1}H-NMR spectra in connection with their tropicity. We have concluded that these fulvalenes are rather polyolefinic but there are a little π-electron polarization from seven membered ring to the large membered ring to form a polar structure (3).$^{1)}$



In this paper, we will report the synthesis and properties of fulvalenes (4) containing dibenzocyclopentadienylidene (fluorenylidene) and large membered unsaturated cyclic moieties, namely dibenzo derivatives of pentatrideca-, pentapentadeca-, pentaheptadeca-, and pentanonadecafulvalenes, which will be expected to exhibit opposite π-electron polarization to the heptafulvalenes (2) to form a polar structure (5). Although pentatridecafulvalene (A) has been synthesized, no systematic discussion of its tropicity has been done.$^{2)}$

The synthesis was accomplished by the reaction of large membered annulenones with diphenyleneketene. Thus the reaction of 5,10-dimethyl-6,8-bisdehydro[13]-annulenone,$^{3)}$ and its benzo[d] and dibenzo[d,j] derivatives,$^{4)}$ 5,10-dimethyl-6,8-bisdehydro[15]annulenone,$^{5)}$ 5,10,15-trimethyl-6,8-bisdehydro[15]annulenone,$^{6)}$

7,12-dimethyl-8,10-bisdehydro[17]annulenone,[5] and 7,12-dimethyl-8,10-bisdehydro-[19]annulenone[5] with diphenyleneketene in anhydrous benzene at room temperature afforded the corresponding pentatrideca- [6, mp 174-175 °C (d), yield 28%; 7, mp 190-192 °C (d), 27%; 8, mp 221-223 °C (d), 4.4%], pentapentadeca- [9, mp 153.5-155 °C (d), 47%; 10, mp 175-177 °C (d), 8.3%], pentaheptadeca- [11, mp 273-274 °C (d), 38%], and pentanonadecafulvalene [12, mp 123-124 °C (d), 36%], respectively. The structures of these fulvalenes were determined by their spectroscopic data as well as elemental analyses and/or mass spectral data.



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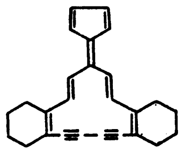

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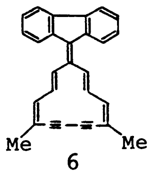

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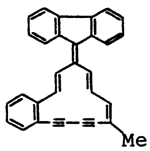

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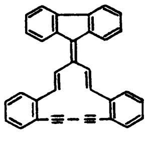

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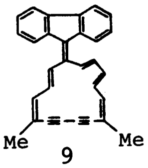

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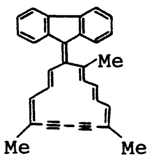

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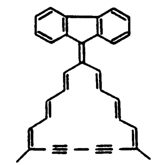

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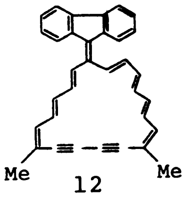

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^{1}H-NMR spectra of the pentafulvalenes (6, 7, 9-12) and the corresponding heptafulvalenes are shown in Fig. 1 and Fig. 2, respectively.[7] The down or high field shifts due to the outer or inner protons of large rings in these fulvalenes are not seen clearly as has been observed in annulenones.[3,5] However, it can be seen from the figures that the outer protons of pentatridecafulvalenes (6 and 7) and pentaheptadecafulvalene (11) resonate at higher field than the inner protons, and the outer and the inner protons resonate at higher and lower field, respectively, than the corresponding protons of heptatrideca- and heptaheptadecafulvalenes. This suggests that the large membered rings of 6, 7, and 11 are slightly paratropic with 12π or 16π electron systems owing to polarization of π-electron through the pinch bond from the large membered ring to the five membered ring. In contrast, the outer and the inner protons of pentapentadecafulvalenes (9 and 10) and pentanonadecafulvalene (12) resonate at lower and higher field, respectively, than the corresponding heptapentadeca- and heptanonadecafulvalenes. This also suggests that the large membered rings of 9, 10, and 12 are slightly diatropic with 14π or 18π electron by polarization of π-electron from the large membered ring to the five membered ring. These suggestions were supported by a systematic examination of the chemical shifts of the methyl groups of the large membered rings, which must always be external.

The chemical shifts of methyl protons of the pentafulvalenes together with those of the corresponding annulenones (1) and heptafulvalenes (2) are shown in Table 1. We can see a remarkable alternation of the methyl resonance between [4n + 1]annulenones ([13]-, [17]annulenones; relatively high field) and [4n + 3]

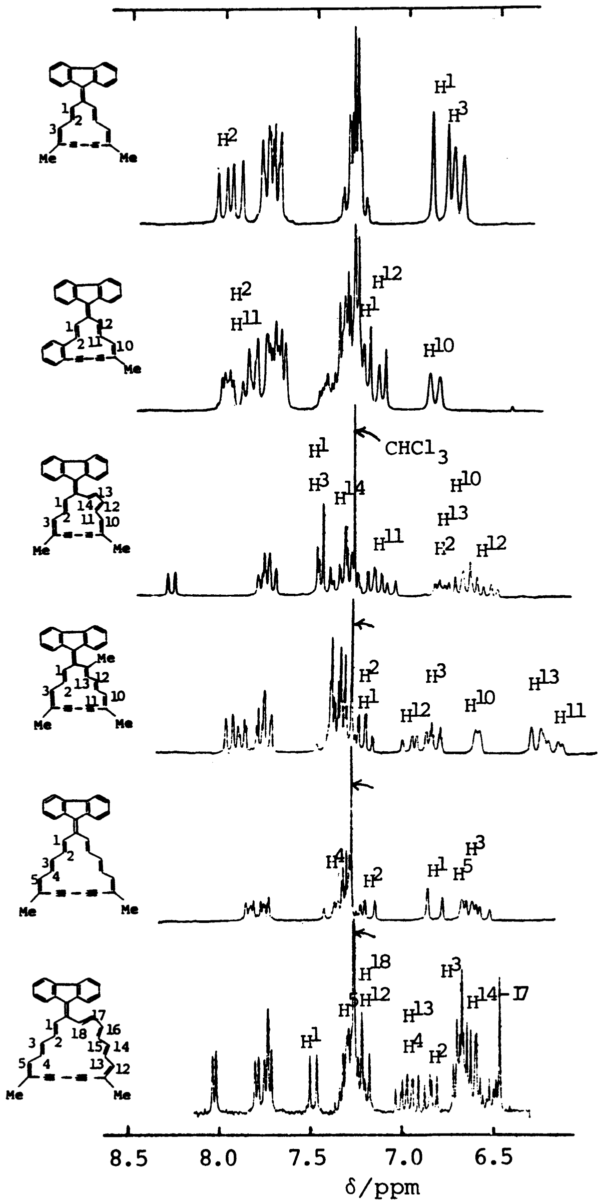


Fig. 1. ^{1}H-NMR spectra of pentafulvalenes in CDCl$_3$.

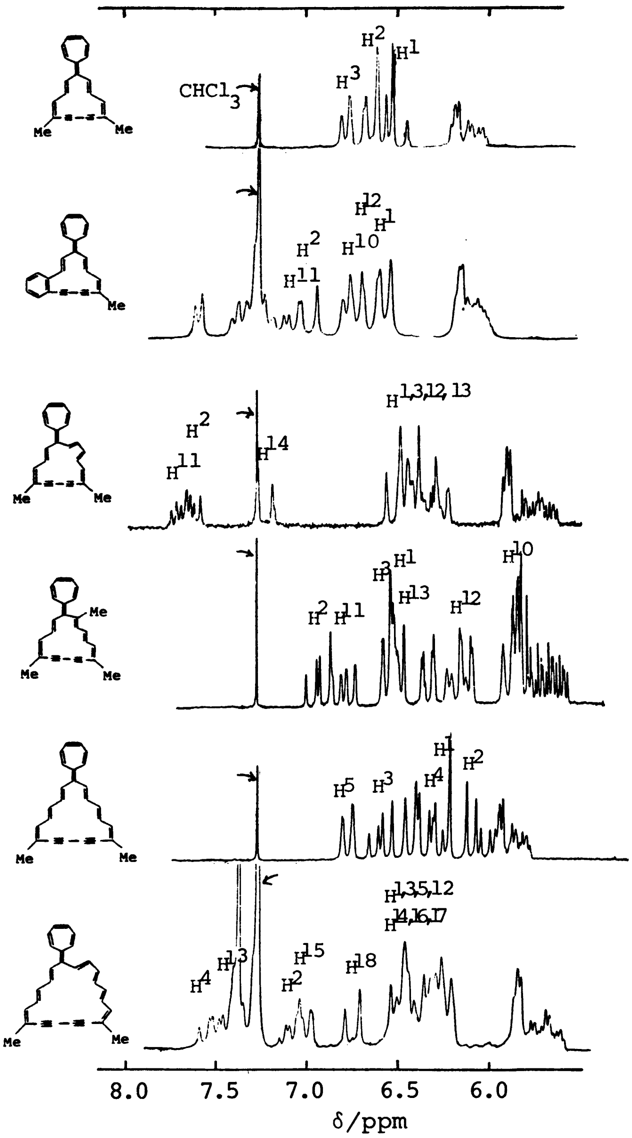
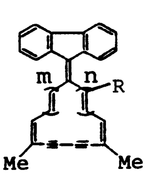
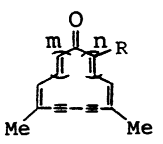
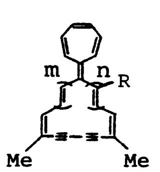


Fig. 2. ^{1}H-NMR spectra of heptafulvalenes in CDCl$_3$.

Table 1. Chemical shifts of methyl protons of 1, 2, 6, 9-12 (CDCl$_3$, r.t.).

				
[13]-	R=H	(6) 1.88	1.74	1.92
[15]-	R=H	(9) 1.94, 1.98	2.18, 2.24	1.82
	R=Me	(10) 1.94, 1.96, 2.23	2.05, 2.10, 2.21	1.85, 1.87, 1.94
[17]-	R=H	(11) 1.94	1.77	2.00
[19]-	R=H	(12) 1.96, 2.00	2.17, 2.21	1.86

annulenones ([15]-, [19]annulenones; relatively low field), which indicate the paratropicity and the diatropicity, respectively. The similar trend of alternation is observed for pentafulvalenes and the reverse trend for heptafulvalenes although the degree of the alternation being much less than that of annulenones.

The electronic spectra of 6, 7, and 8 are shown in Fig. 3 and those of 6, 9, 11, and 12 are also illustrated in Fig. 4. It is found from Fig. 3 that the longest wavelength bands exhibit absorption toward longer wavelength in the order 6 > 7 > 8, as has been observed for the corresponding heptafulvalenes and annulenones which indicate the fused benzene rings inhibit the degree of conjugation of π-electron in these fulvalene sytem. The longest wavelength bands shown in Fig. 4 shift to longer wavelength in the order 11 > 12 > 9 ≥ 6, which may indicate that the large ring of 12 is less planar than others due to unsymmetrical structure of the molecule.

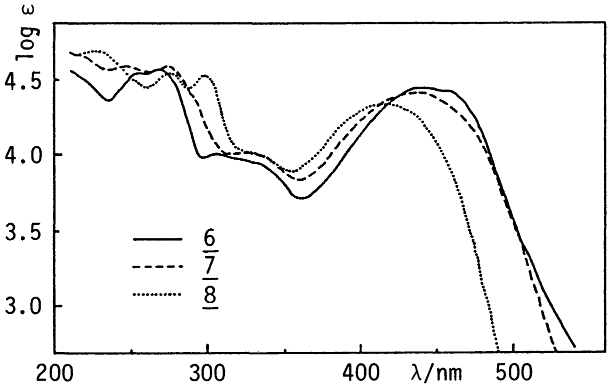


Fig. 3. Electronic spectra of 6, 7, and 8 in EtOH.

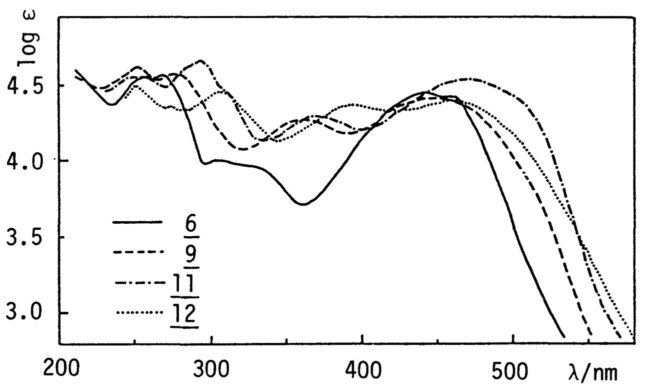


Fig. 4. Electronic spectra of 6, 9, 11, and 12 in EtOH.

It has been reported for [5.6.7]quinarene system that the steric crowding caused a twisting of the molecule around pinch bond resulting in a further increase of charge separation.[8)] It is assumed that a considerable steric crowding between fluorenylidene and large membered rings in the fulvalene system reported in this paper exists, but we can not conclude at present that the steric crowding causes a twisting of the molecule around pinch bond or a conformational changing of the large membered ring.

References

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7) All the NMR except 12 were taken at 200 MHz and assignments were assisted by extensive decoupling techniques, and NMR of 12 was taken at 400 MHz, but the assignment could not be fully made, and a tentative one was shown in Fig. 1.
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