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THE SYNTHESIS OF PENTATRIDECA-, PENTAPENTADECA-, PENTAHEPTADECA-, AND PENTANONADECAFULVALENE DERIVATIVES

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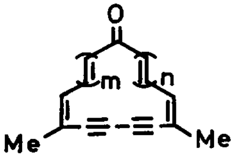
Summary: Title fulvalenes were synthesized through the reaction of the large-membered annulenones with cyclopentadienide, and the ^{1}H-NMR spectra are discussed in connection with tropicity of these fulvalenes.

Recently, we have investigated the cross-conjugated systems, fulvalene and fulvene, derived from the annulenones of type (1).1) Thus, the heptafulvalene (2),2) the dibenzopentafulvalene (3),3) the diphenylfulvene (4),4) and dichlorofulvene (5)5) have been studied so far.



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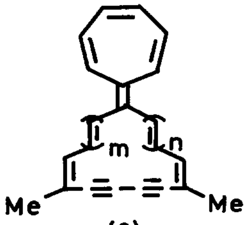

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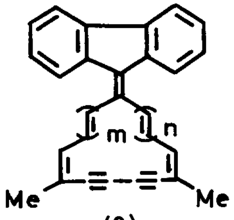

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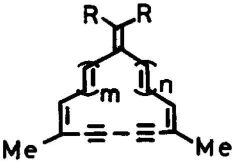
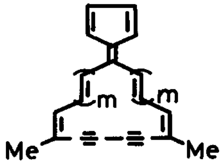
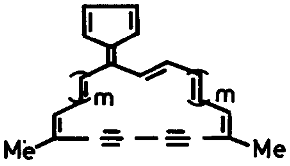


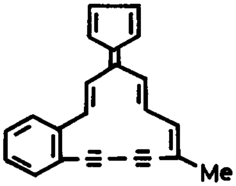
(4): R = Ph
(5): R = Cl



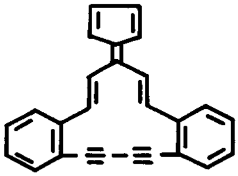
(6): m = 1
(7): m = 2



(8): m = 1
(9): m = 2



(10)



(11)

We wish to report here the synthesis and properties of fulvalene derivatives containing cyclopentadienylidene moiety (6)–(9) and the benzannelated derivatives (10), (11) of the pentatridecafulvalene (6).

Although the bis(cyclohexene)-annelated pentatridecafulvalene has been synthesized, no systematic discussion of its tropicity has been done.6) As has been made for the corresponding heptafulvalene derivatives (2),7) it is predicted that the compounds of (6) and (7) are not aromatic, since polarization of the central bond will make one ring a (4n+2)π-system, but the other a (4n)π-system. On the other hand, the compounds of (**8**) and (**9**) are aromatic since polarization of the central bond will make both rings $(4n+2)\pi$-systems.

The fulvalenes were synthesized by treatment of the annulenones with cyclopentadienide according to the procedure of Howes and Sondheimer.[6)] Reaction of 5,10-dimethyl-6,8-bisdehydro[13]annulenone,[1a)] 10-methylbenzo[d]-6,8-bisdehydro[13]annulenone,[8)] dibenzo[d,j]-6,8-bisdehydro[13]annulenone,[8)] 5,10-dimethyl-6,8-bisdehydro[15]annulenone,[1b)] 7,12-dimethyl-8,10-bisdehydro[17]-annulenone,[1b)] and 7,12-dimethyl-8,10-bisdehydro[19]annulenone,[1b)] with a large excess of sodium cyclopentadienide in ether or tetrahydrofuran at -10–0°C gave dimethylpentatrideca- (**6**) (dark red needles, mp 103–104°C (dec), 11%),[9)] methylpentabenzotrideca- (**10**) (brown needles, mp 108–109°C (dec), 7.8%), pentadibenzotrideca- (**11**) (brown needles, mp 173–174°C (dec), 3.9%), dimethylpentapentadeca- (**8**) (brown needles, mp 164–165°C (dec), 4.9%), dimethylpentaheptadeca- (**7**) (dark brown needles, mp 177–179°C (dec), 4.6%), and dimethylpentanonadecafulvalene (**9**) (dark purple cubes, mp 158–159°C (dec), 6.8%), respectively. These fulvalene derivatives thus obtained proved to be rather unstable, and decomposed gradually on exposure to diffused light and air.

The ^{1}H-NMR spectra of the fulvalenes (**6**)–(**9**) and the corresponding heptafulvalenes (**2**) are reproduced in Figures 1 and 2, respectively.

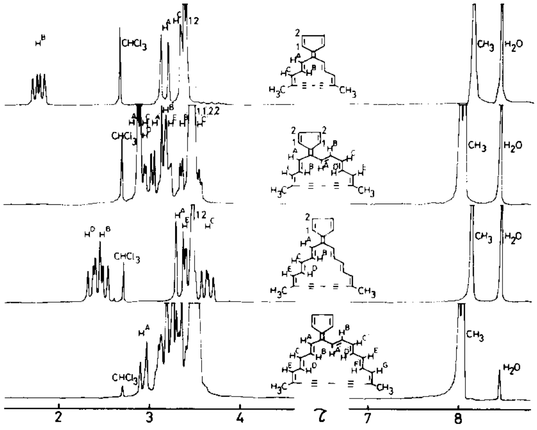


Fig. 1. ^{1}H-NMR spectra of pentafulvalenes (**6**)–(**9**) at 200 MHz in $CDCl_3$

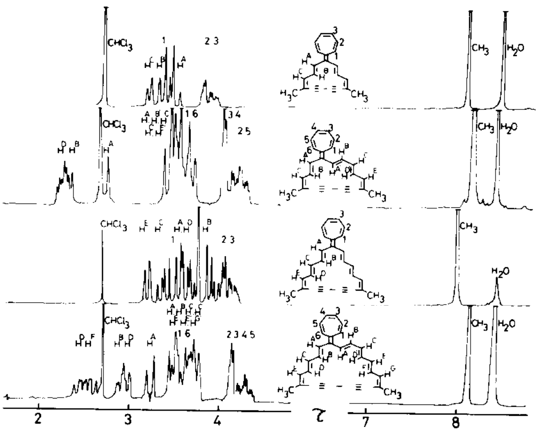
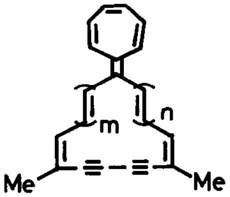
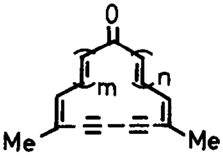
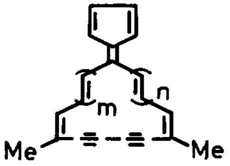


Fig. 2. ^{1}H-NMR spectra of heptafulvalenes (**2**) at 200 MHz in $CDCl_3$

From these Figures, it is seen that the outer protons of the large-membered rings of the pentatrideca- (**6**) and pentaheptadecafulvalene (**7**) resonate in a higher field than the inner protons, while the reverse is seen in the spectra of the heptatrideca- and heptaheptadecafulvalene. Thus, the large-membered rings of (**6**) and (**7**) are suggested to be paratropic, in accord with that they are expected to be 12π- and 16π-electron systems, respectively, owing to polarization of the central bond. On the other hand, in the spectra of the pentapentadeca- (**8**) and pentanonadecafulvalene (**9**), the olefinic protons of the large-membered rings resonate in a very narrow region, whereas the outer protons of the heptapentadeca- and heptanonadecafulvalenes resonate in a higher field than the inner protons in accord with that they are expected to be 16π- and 20π-electron systems as before. Thus, although the large-membered rings of (8) and (9) are suggested to be atropic, we considered that a systematic inspection of the methyl resonances of these fulvalenes would provide a diagnostic tool to test the tropicity since methyl group must always be outside the ring and can readily be recognized.

Table 1. The ^{1}H-NMR Chemical Shifts of Methyl Protons of Compounds (1) (90 MHz), (2) (200 MHz), and (6)–(9) (200 MHz) (CDCl$_3$, τ-Values, room temperature)

large-membered ring			
[13]-	8.08	8.26	8.13
[15]-	8.18	7.76, 7.82	8.00, 8.05
[17]-	8.00	8.23	8.12
[19]-	8.14	7.79, 7.83	8.00, 8.04 10)

The chemical shifts of the methyl resonances of the pentafulvalenes (6)–(9) are listed in Table 1, altogether with those of the corresponding annulenones (1) and heptafulvalenes (2). As can be seen from the Table, the alternation of the methyl resonances between the [4n+1]annulenones ([13]-, [17]annulenone) (relatively high field) and the [4n-1]annulenones ([15]-, [19]annulenone) (relatively low field) confirms the paratropicity of the former and the diatropicity of the latter.1) As expected from polarization of the central bond of the pentafulvalenes, the alternation of the methyl resonances of the large-membered rings between trideca- (6), heptadeca- (7) and pentadeca- (8), nonadecafulvalene (9) is seen in the same trend as that in the cases of annulenones, 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 that of annulenones and pentafulvalenes.

From this result and the observation of the hypsochromic shifts of the absorption bands by changing from nonpolar (tetrahydrofuran) to polar solvent (acetonitrile) in the electronic spectra,11) it can be suggested that a very little π-electron polarization from the large-membered rings to 5-membered ring occurs in these pentafulvalenes (6)–(9).

The electronic spectra of the fulvalenes (6), (10), (11) are illustrated in Figure 3. As expected, the spectra are similar to one another, the shortest and medium bands exhibiting to shorter wavelength along the series (6) > (10) > (11), revealing that the fusion of benzene rings results in an appreciable bathochromic shift, as has been observed for benzannelated annulenes.[12] In contrast, the longest wavelength bands of the fulvalenes exhibit absorption toward longer wavelengths in the order (9) > (10) > (11), demonstrating the sequence for the degree of extended conjugation of π-electron system in these cross-conjugated systems.

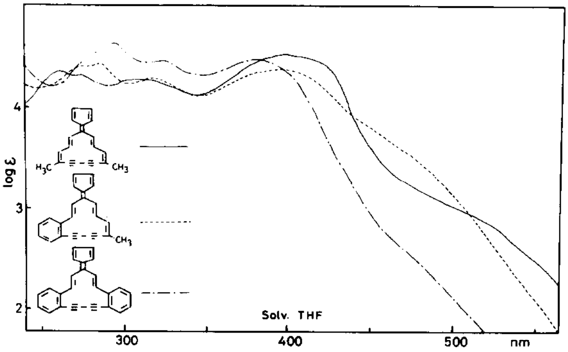


Fig. 3. The UV spectra of (9), (10), and (11)

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References and Notes

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5) J. Ojima, K. Itagawa, S. Hamai, T. Nakada, and S. Kuroda, *J. Chem. Soc., Perkin Trans. I*, in press.
6) P. D. Howes and F. Sondheimer, *J. Org. Chem.*, 43, 2158 (1978).
7) In the heptafulvalene derivatives, it is predicted that the compounds bearing 13- and 17-membered rings are aromatic, while the ones bearing 15- and 19-membered rings are not aromatic.
8) J. Ojima, Y. Yokoyama, and M. Enkaku, *Bull. Chem. Soc. Jpn.*, 43, 1522 (1977).
9) All new compounds described in this paper gave satisfactory spectral and analytical data.
10) T. Asao, N. Morita, J. Ojima, and K. Wada, unpublished data.
11) The details will be reported elsewhere.
12) N. Darby, T. M. Cresp, and F. Sondheimer, *J. Org. Chem.*, 42, 1960 (1977).

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