

Synthesis and Properties of Dicyanotrideca-, -pentadeca-, and -heptadecafulvene Derivatives

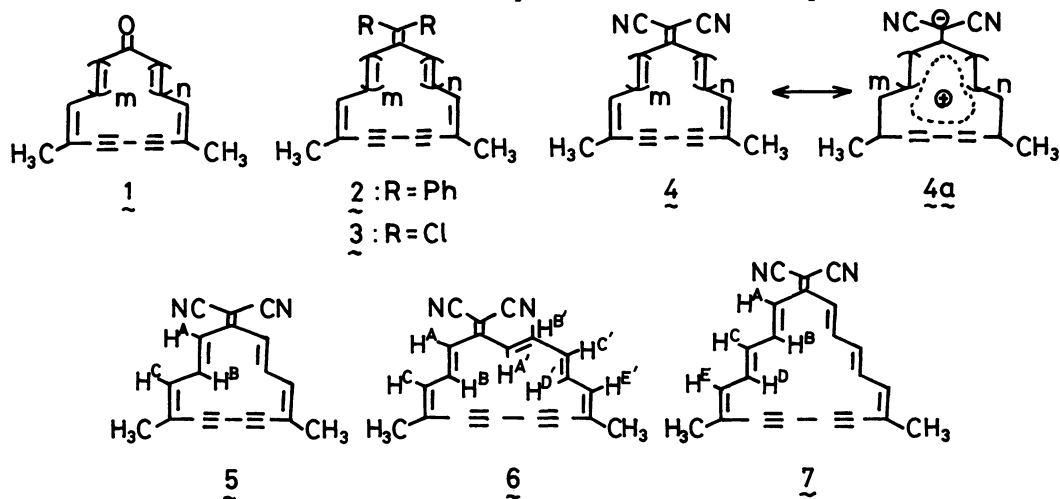
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Title fulvenes were synthesized through the reaction of the large-membered annulenones with malononitrile, and their ¹H NMR spectra were examined proving that the dicyanotrideca- and -heptadecafulvenes are paratropic while the dicyanopentadecafulvene is diatropic.

Recently, we have investigated the cyclic cross-conjugated systems, fulvalenes¹⁾ and fulvenes, derived from the annulenones of type 1.²⁾ Thus, the diphenyl- 2³⁾ and the dichlorofulvene derivatives 3⁴⁾ were prepared by the condensation of annulenones 1 with diphenylketene and dichloroketene, respectively. However, both 2 and 3 were atropic, reflecting an absence of any contribution of a dipolar structure in the ground state of the fulvenes. It prompted us to study the dicyanofulvene derivative 4 in which the cyano-groups are expected to polarize the fulvene system more greatly than the phenyl- and the chloro-groups in 2 and 3, respectively. If the exocyclic bond polarizes as shown in 4a, the fulvenes 5 and 7 would be potentially paratropic, and the fulvene 6 potentially diatropic since the rings of the former contain (4n)π-electrons and that of the latter (4n+2)π-electrons. We have now verified this expectation to be in practice.



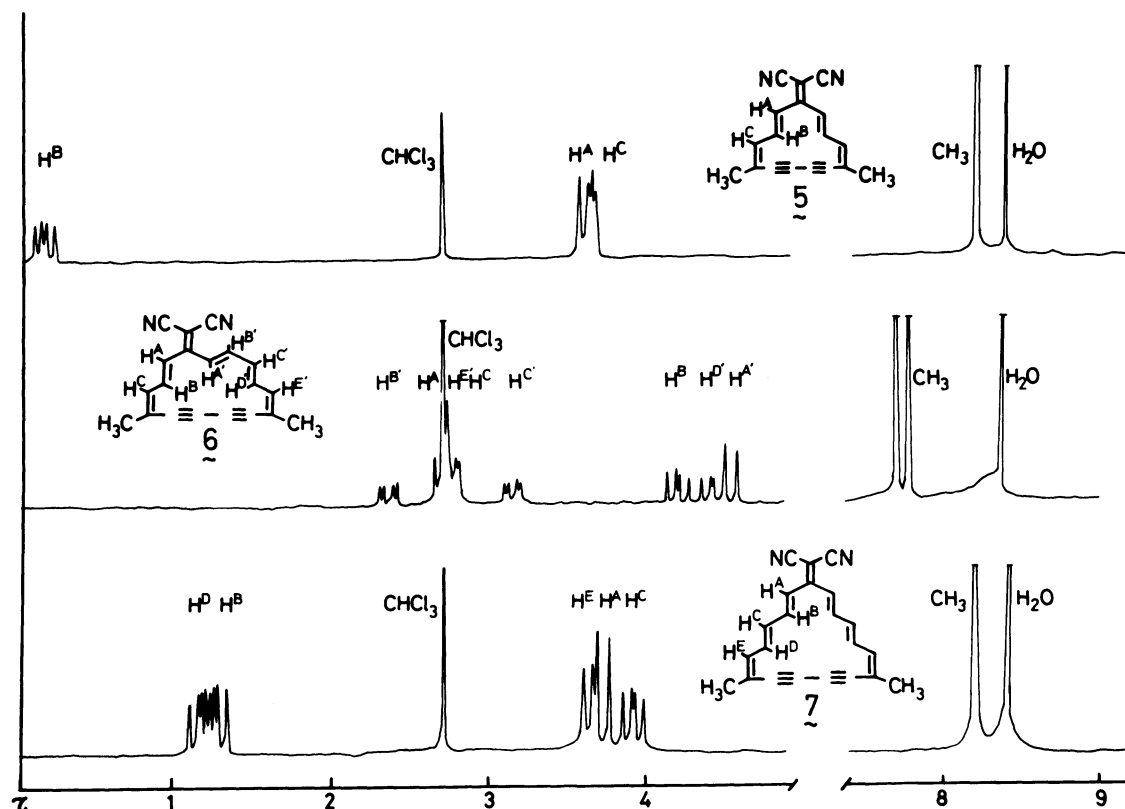
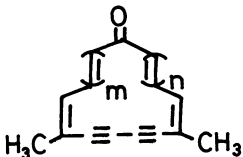
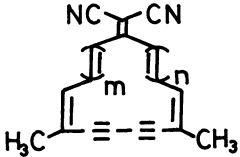
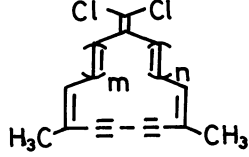


Fig. 1. The 200 MHz ^1H NMR spectra of $\mathbf{5}$ – $\mathbf{7}$ in CDCl_3 .

In this paper, we report the synthesis and properties of the title compounds $\mathbf{5}$ – $\mathbf{7}$ which are the first examples of monocyclic fulvenes containing large-rings to show the ring current effect.⁵⁾

Attempted condensation of $\mathbf{1}$ to obtain $\mathbf{4}$ with malononitrile in the presence of β -alanine⁶⁾ or acetic anhydride,⁷⁾ or with dicyanoketene,⁸⁾ was unsuccessful. However, employing the Ong and Keoshkerian procedure,⁹⁾ with an excess of malononitrile in the presence of titanium tetrachloride and pyridine in dichloromethane at -10 – 0°C , 5,10-dimethyl-6,8-bisdehydro[13]annulenone,^{2a)} 5,10-dimethyl-6,8-bisdehydro[15]annulenone,^{2b)} and 7,12-dimethyl-8,10-bisdehydro[17]annulenone^{2b)} were converted to the dicyanotrideca- $\mathbf{5}$ ¹⁰⁾ [dark red needles, mp 118 – 119°C (dec), 17% yield, ^1H NMR (200 MHz in CDCl_3) $\tau=0.21$ (dd, $J=16, 9$ Hz, H^{B}), 3.65 (d, $J=16$ Hz, H^{A}), 3.69 (d, $J=9$ Hz, H^{C}), 8.23 (s, CH_3)], the dicyanopentadeca- $\mathbf{6}$ [dark red cubes, mp 146 – 147°C (dec), 2.3% yield, ^1H NMR (270 MHz) $\tau=2.39$ (dd, $J=15.5, 5.5$ Hz, $\text{H}^{\text{B}'}$), 2.73 (d, $J=15.5$ Hz, H^{A}), 2.79 (d, $J=11.5$ Hz, $\text{H}^{\text{E}'}$), 2.81 (d, $J=11$ Hz, H^{C}), 3.18 (dd, $J=15.5, 5.5$ Hz, $\text{H}^{\text{C}'}$), 4.23 (dd, $J=15.5, 11$ Hz, H^{B}), 4.45 (dd, $J=15.5, 11.5$ Hz, $\text{H}^{\text{D}'}$), 4.57 (d, $J=15.5$ Hz, $\text{H}^{\text{A}'}$), 7.75 (s, CH_3), 7.83 (s, CH_3)], and the dicyanoheptadeca-fulvene $\mathbf{7}$ [purple needles, mp 152 – 153°C (dec), 4.3% yield, ^1H NMR (200 MHz) $\tau=1.19$ (dd, $J=15, 11$ Hz, H^{D}), 1.30 (dd, $J=15.5, 11$ Hz, H^{B}), 3.66 (d, $J=11$ Hz, H^{E}), 3.75 (d, $J=15.5$ Hz, H^{A}), 3.94 (dd, $J=15, 11$ Hz, H^{C}), 8.21 (s, CH_3)], respectively. These

Table 1. The ^1H NMR Chemical Shifts of Methyl Protons of Annulenones $\mathbf{1}$ (90 MHz), Dichlorofulvenes $\mathbf{3}$ (200 MHz), and Dicyanofulvenes $\mathbf{4}$ ($\mathbf{5}$ - $\mathbf{7}$) (200 or 270 MHz) (CDCl_3 , τ -Values, room temperature)

Large-membered ring			
[13]-	8.26	8.23	8.13
[15]-	7.76, 7.82	7.75, 7.83	8.08
[17]-	8.23	8.21	8.06

dicyanofulvenes were rather unstable to decompose gradually on exposure to diffused light and air.

The ^1H NMR spectra of the fulvenes $\mathbf{5}$ - $\mathbf{7}$ are reproduced in Fig. 1. We can see that the olefinic protons of the trideca- $\mathbf{5}$ and the heptadecafulvene $\mathbf{7}$ resonate at high field, while the inner protons at low field. Thus, the 12π - and 16π -fulvenes $\mathbf{5}$ and $\mathbf{7}$ are paratropic, owing to polarization of an exocyclic bond. On the other hand, it is seen that the outer protons in $\mathbf{6}$ resonate at low field, while the inner protons at high field. Thus, the 14π -fulvene $\mathbf{6}$ is diatropic.

Another proof of the ring current in the macrocyclic system of type $\mathbf{4}$ is provided by methyl ^1H NMR resonances, since the methyl groups must always be in external. The chemical shifts of the methyl resonances of the dicyanofulvenes $\mathbf{5}$ - $\mathbf{7}$ are listed in Table 1, together with those of the corresponding annulenones $\mathbf{1}$ and the dichlorofulvenes $\mathbf{3}$. The alternation of the methyl resonances between the $[4n+1]$ -annulenones ([13]-, [17]annulenone) (relatively high field) and the $[4n+3]$ -annulenone ([15]annulenone) (relatively low field) confirms the paratropicity of the former and the diatropicity of the latter, as has been discussed previously.^{2b)} An alternation of the methyl resonances among dicyanotrideca- $\mathbf{5}$, -pentadeca- $\mathbf{6}$, and -heptadecafulvene $\mathbf{7}$ is seen in the same trend and to the almost same degree as that of the annulenones $\mathbf{1}$, in contrast to the case of the atropic dichlorofulvene series $\mathbf{3}$.

From these results and from 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 the π -electron transfer from the large-ring to the exocyclic moiety, as depicted in $\mathbf{4a}$, occurs in these dicyanofulvenes $\mathbf{5}$ - $\mathbf{7}$.

In electronic spectra, taken in tetrahydrofuran, of the dicyanofulvenes, the

main absorption maxima exhibit a bathochromic shift as the ring size increases, and the shift between the trideca- ξ (λ_{\max} : 302 nm) and the pentadecafulvene ξ (336 nm) is larger than that between the pentadeca- ξ and the heptadecafulvene ζ (345 nm). This might be due to the occurrence of the same sort of alternation as monocyclic annulenes, dehydroannulenes,¹²⁾ and dehydroannulenones,^{2b)} in which the $[4n+2]\pi$ system shows absorption at longer wavelength region than the corresponding $[4n]\pi$ system does.

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References

- 1) T. Asao, N. Morita, J. Ojima, and M. Fujiyoshi, *Tetrahedron Lett.*, **1978**, 2795; N. Morita, T. Asao, J. Ojima, and K. Wada, *Chem. Lett.*, **1981**, 57; J. Ojima, K. Itagawa, and T. Nakada, *Tetrahedron Lett.*, **24**, 5273 (1983); T. Asao, N. Morita, J. Ojima, M. Fujiyoshi, K. Wada, and S. Hamai, *Bull. Chem. Soc. Jpn.*, **59**, 1713 (1986); J. Ojima, K. Itagawa, and T. Nakada, *Bull. Chem. Soc. Jpn.*, **59**, 1723 (1986).
- 2) a) T. M. Cresp, J. Ojima, and F. Sondheimer, *J. Org. Chem.*, **42**, 2130 (1977); b) J. Ojima, Y. Shiroishi, K. Wada, and F. Sondheimer, *ibid.*, **45**, 3564 (1980).
- 3) S. Kuroda, K. Kitatani, and J. Ojima, *Tetrahedron Lett.*, **23**, 2657 (1982); S. Kuroda, J. Ojima, K. Kitatani, M. Kirita, and T. Nakada, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 2987.
- 4) J. Ojima, K. Itagawa, S. Hamai, T. Nakada, and S. Kuroda, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 2997.
- 5) For reviews, see E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968) and F. Pietra, *ibid.*, **73**, 293 (1973).
- 6) F. S. Prout, *J. Org. Chem.*, **18**, 928 (1953).
- 7) M. Oda, M. Funamizu, and Y. Kitahara, *Bull. Chem. Soc. Jpn.*, **42**, 2386 (1969).
- 8) R. Neidlein, personal communication.
- 9) B. S. Ong and B. Keoshkerian, *J. Org. Chem.*, **49**, 5002 (1984).
- 10) All fulvene compounds described in this paper gave IR and mass spectral data consistent with the assigned structures. The elemental analyses were satisfactorily obtained except for the dicyanopentadecafulvene ξ .
- 11) The details will be reported elsewhere.
- 12) P. J. Garratt and K. Grohmann, "Methoden der Organischen Chemie (Houben-Weyl)," Geog Thieme Verlag, Stuttgart (1972), Vol. V, Part Id, p. 533.

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