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The Synthesis of [18]Annulene Trioxide and of [18]Annulene Oxide Disulphide

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CYCLO-OCTADECANONAENE, or [18]annulene, contains $(4n + 2)$ π-electrons $(n = 4)$ and therefore complies with Huckel's rule for aromaticity. This compound has been synthesised by Sondheimer and his colleagues, and there is no doubt that it must be regarded as an aromatic compound.[1,2,3,4] For example, the n.m.r. spectrum[2] showed two bands, one at very low field (τ 1·1) due to the twelve "outer" protons, and one at very high field (τ 11·8) due to the six "inner" protons. Heterocyclic analogues of [18]annulene are possible in which the six inner hydrogens are replaced by three oxide, sulphide, imine, or related bridges, or by any combination of these. Catalin models of [18]annulene 1,4;7,10;13,16-trisulphide (I) suggest that this system cannot be planar,[5] and a similar model of [18]annulene 1,4-oxide- 7,10;13,16-disulphide (II) is also non-planar: but as oxygen is a much smaller atom than sulphur a planar model of [18]annulene 1,4;7,10;13,16-trioxide (III) can be constructed without difficulty.[5]

The synthesis of [18]annulene trisulphide (I) has already been described.[5,6] It was found to be a stable, pale yellow, crystalline compound and the ultraviolet spectrum was consistent with its formulation as a compound having three thiophen rings linked by three essentially olefinic vinylene groups.[5,7] In agreement with this view the n.m.r. spectrum showed two bands of equal area at τ 3·27 and 3·33.[5] Moreover, resolution of the 5,11,18-tricarboxylic acid was attempted; the brucine salt showed marked mutarotation in solution, and it may be confidently assumed that the parent compound is not planar. We have now prepared [18]annulene 1,4-oxide- 7,10;13,16-disulphide (II) and [18]annulene 1,4;7,10;13,16-trioxide (III). The former has been found to resemble [18]annulene trisulphide (I) and must likewise be regarded as a system in which the three heterocyclic rings are linked by three vinylene groups. On the other hand, the spectral properties of [18]annulene trioxide (III) suggest that it must be regarded as an aromatic compound.

Furan-2,5-diacetic acid[8] and methyl *cis*-$\alpha\beta$-di-(5-formyl-2-furyl)acrylate, m.p. 126—127°, were condensed in acetic anhydride and triethylamine,

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[1] F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 260.

[2] L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Amer. Chem. Soc.*, 1962, **84**, 4307.

[3] F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, 1960, **82**, 5765.

[4] J. Bregman and D. Rabinovich, *Acta Cryst.*, 1960, **13**, 1047.

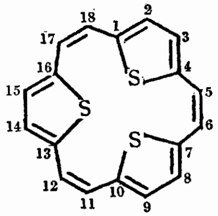
[5] G. M. Badger, J. A. Elix, and G. E. Lewis, *Austral. J. Chem.*, 1965, **18**, 70.

[6] G. M. Badger, J. A. Elix, and G. E. Lewis, *Proc. Chem. Soc.*, 1964, 82.

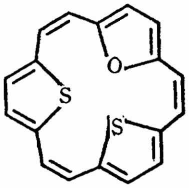
[7] C. A. Coulson and M. D. Poole, *Proc. Chem. Soc.*, 1964, 220.

[8] K. Y. Novitskii, K. Y. Yur'ev, and V. N. Zhingareva, *Zhur. obshchei Khim.*, 1962; **32**, 3303; *J. Gen. Chem. U.S.S.R.*, 1962, **32**, 3245.

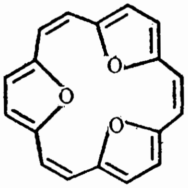
and the product esterified to form methyl 1,4;7,10;13,16-tri-epoxy[18]annulene-5,11,18-tricarboxylate, m.p. 147—149°. Hydrolysis of this ester gave the tricarboxylic acid, m.p. > 360°, which was decarboxylated with copper chromite and quinoline at 200—205°. The trioxide (III) crystallised from aqueous dioxan as red plates which decomposed, without melting, at 215—216°. The ultraviolet spectrum (ethanol) showed λ_{max} 220 (ϵ 7,700), 239 (7,400), 309 (18,300), 323 (64,500), 332 (288,000), 370 (3,200), 391 (5,500), 405 mμ (17,200), and was remarkably similar to that given by the aromatic hydrocarbon, tridehydro[18]annulene.[1] The n.m.r. spectrum (CCl_4) showed two peaks of equal area at very low field (τ 1·32, 1·34), indicating the presence of an appreciable ring current.



(I)



(II)



(III)

[18]Annulene 1,4-oxide- 7,10;13,16-disulphide (II) was obtained by a similar synthetic scheme, and crystallised from aqueous methanol in orange needles, m.p. 103—103·5°. The ultraviolet spectrum (ethanol) showed λ_{max} 229 (ϵ 15,400), 281 (28,900), 292 (29,300), 405 (9,000), and 425 mμ (9,500), and resembled that of [18]annulene trisulphide except that absorption extended to somewhat longer wavelengths. The n.m.r. spectrum ($CDCl_3$) showed six bands at relatively high field (τ 3·39, 3·34, 3·26, 3·21, 3·14, and 2·90), indicating the absence of any significant ring current.

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