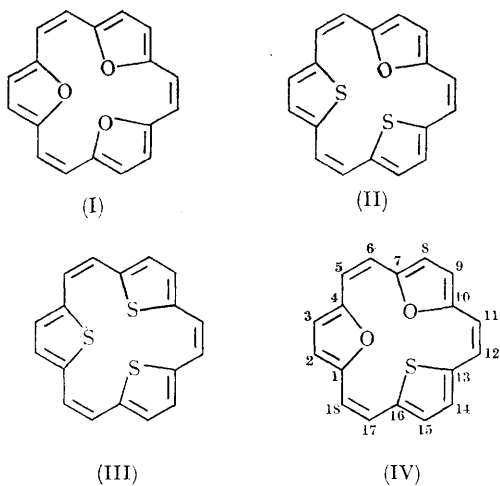


The Synthesis of [18]Annulene Dioxide Sulphide

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THE aromatic nature of [18]annulene trioxide (I)¹ (two peaks of equal area at very low field, τ 1.32, 1.34, in the n.m.r. spectrum) and the non-aromatic nature of [18]annulene oxide disulphide (II)^{1,2} (n.m.r. τ 2.9—3.58) and of [18]annulene trisulphide (III)^{3,4} (n.m.r. τ 3.27, 3.33) prompted us to synthesise the other member of this series, namely [18]-annulene dioxide sulphide (IV). Catalin models of these molecules suggest that [18]annulene trioxide (I) is planar, that [18]annulene dioxide sulphide (IV) may be nearly planar, but that [18]annulene oxide disulphide (II) and [18]annulene trisulphide (III) are non-planar.



Furan-2,5-diacetic acid⁵ and methyl *cis*- α -(5-formyl-2-thienyl)- β -(5'-formyl-2'-furyl)acrylate⁶

m.p. 133—134°, were condensed in acetic anhydride and triethylamine to give methyl 6,11-dicarboxy-1,4-epithio-7(10),13(16)-diepoxy [18]annulene-18-carboxylate, which was esterified to form methyl 1,4-epithio-7(10),13(16)-diepoxy[18]annulene-6,11,18-tricarboxylate, m.p. 210—212°. The related ester, methyl 1,4-epithio-7(10),13(16)-diepoxy[18]annulene-5,11,18-tricarboxylate, m.p. 192—193°, was prepared by condensation of thiophen-2,5-diacetic acid^{3,4} and methyl *cis*- α - β -(5-formyl-2-furyl)acrylate.¹

Hydrolysis of the former triester gave the 6,11,18-tricarboxylic acid, m.p. > 360°, which was decarboxylated by treatment with copper chromite in quinoline at 195—200°; and decarboxylation of the 5,11,18-tricarboxylic acid was achieved in the same way. The required [18]annulene 1(4),7(10)-dioxide-13(16)-sulphide (IV) formed scarlet plates (from cyclohexane) which decomposed without melting at 250—251°. The ultraviolet absorption spectrum (ethanol) showed λ_{\max} 224 (ϵ 14,400), 244 (ϵ 11,700), 320 (ϵ 18,200), 333 (ϵ 43,000), 343 (ϵ 95,000), 376 (ϵ 5100), 391 (ϵ 7100), 413 (ϵ 16,600), 431 $m\mu$ (ϵ 2,100), and was remarkably similar to that given by [18]annulene trioxide¹ and by the aromatic hydrocarbon tridehydro[18]annulene.⁶ The n.m.r. spectrum ($CDCl_3$) showed an AB quartet ($J = 12.5$ c./sec., 4 protons) and a singlet (2 protons) due to protons at the 5-, 6-, 11-, 12-, 17-, and 18-positions, and an AB quartet ($J = 3.4$ c./sec., 4 protons) and a single peak (2 protons) due to protons at the 2-, 3-, 8-, 9-, 14- and 15-positions. All peaks arose in the range τ 1.00—1.72, confirming the aromaticity of [18]annulene dioxide sulphide.

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