The Crystal Structure of 7,15,17,19-Tetraethoxy-2,3,4,5,10,11,12,13-octathiatricyclo-[12,2,2,$2^{6,9}$]eicosa-6,8,14,16,17,19-hexaene, a Sulphur Analogue of the Paracyclophanes

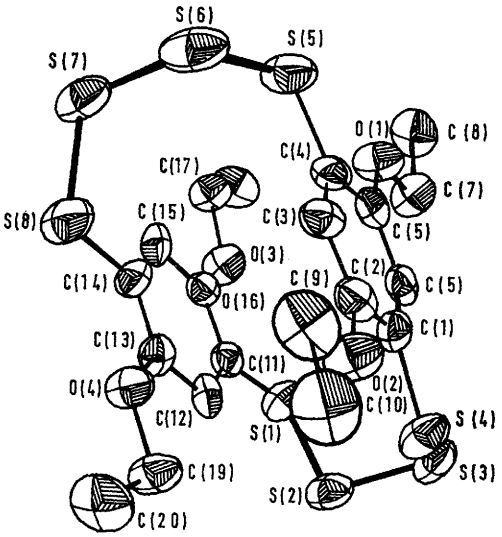
By JOHN S. RICCI, JUN., and IVAN BERNAL*
(*Department of Chemistry, Brookhaven National Laboratory, Upton, Long Island, New York* 11973)

Summary The crystal and molecular structure of the title compound has been determined from three-dimensional single-crystal X-ray data.

ARIYAN and MARTIN[1] reported that under catalytic conditions, dialkoxybenzenes react with sulphur monochloride to give an unexpected set of products, and described physical measurements and chemical degradation reactions which led them to postulate macrocyclic polysulphur compounds as the products of the reaction. Dr. Ariyan kindly supplied us with samples of the tetraethoxy-derivative (I), and we confirm many of the suggestions made by him and Martin on the basis of their spectral and degradative work.

Crystal data. The crystals supplied were massive yellow fragments which were ground to spheres approximately 0·20 mm. in diameter. The cell constants, determined by least-squares fit of 20 well-centred reflections, are a = 10·198(5), b = 9·454(5), c = 29·845(16) Å, β = 115·17(8)°. V = 2604·3 Å^3; D_m = 1·48, D_c = 1·49 g.cm.$^{-3}$, for $Z = 4$, space group $P2_1/c$. Two forms of the asymmetric set were collected using Mo-K_α radiation in the range $0 \leqslant 2\theta \leqslant 50°$. After averaging symmetry equivalent reflections and eliminating all those for which $|F^2| \leqslant 3\sigma$, a unique set of 2850 reflections was retained. The data were collected with a Datex automated G.E. X-RD6 diffractometer.

The structure was solved by means of the Sayre equation, using a program written by Long.[2] The first E-map produced the eight sulphur atoms, the two benzene rings, and one of the oxygens; refinement of the scale factor followed by a Fourier synthesis gave most of the missing atoms. The remaining alkyl carbons were found in a subsequent difference map. The molecule is shown in the Figure, the current values of the discrepancy indices are $R(F) = 6{\cdot}3\%$ and $wR(F) = 7{\cdot}2\%$.



FIGURE

Relevant values of the bond lengths and angles are given in the Table. The benzene rings are planar with normal bond lengths and angles, in contrast to the results obtained by Brown[3] and Lonsdale[4] for di-*p*-xylylene, where steric hindrance causes the benzene rings to buckle. Again, the ring–ring distance in the octasulphide is normal (closest contacts are 3·41 Å) as opposed to the result obtained for di-*p*-xylylene (3·09 Å). Finally, in the octasulphide, the rings are almost parallel.

The sulphur and oxygen substituents of the rings are quite close (average distance, 2·78 Å), which is approximately 0·5 Å shorter than the sum of van der Waals radii for sulphur and oxygen. It is these contacts which account, apparently, for the shift observed in the optical spectra of these compounds.[1] The carbon–sulphur bond lengths average 1·784 Å, which implies some degree (about 15%) of double-bond character, while the C–O bonds are typical of oxygen-aromatic carbon distances. Finally, the bond lengths and valency angles of the sulphurs in the tetrasulphide chains are very similar to those found in orthorhombic sulphur[5] and in di-π-cyclopentadienyltitanium pentasulphide.[6] In (I) the S–S bonds show a slight but distinct alternation† in bond lengths (terminal S–S bonds average 2·027 Å; central S–S bonds average 2·068 Å). Alternation in S–S bond lengths has been observed previously in polysulphide[7] and polythionate chains[8] but not in aromatic systems. The implication is that conjugation of the two rings across an S_4 fragment has been achieved, which obviously requires the formation of C–S and S–S π-bonds.

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TABLE

Estimated standard deviations in bond lengths at this stage of the refinement: S–S *bonds* 0·005 Å; C–S *bonds* 0·008 Å; *other bonds* 0·010 Å

Bond lengths (Å)

S(1)–S(2)	= 2·028	C(2)–O(2)	= 1·370
S(2)–S(3)	= 2·068	C(16)–O(3)	= 1·368
S(3)–S(4)	= 2·027	C(13)–O(4)	= 1·354
S(5)–S(6)	= 2·034	S(1) · · · O(3)	= 2·775[a]
S(6)–S(7)	= 2·067	S(4) · · · O(2)	= 2·744[a]
S(7)–S(8)	= 2·024	S(5) · · · O(1)	= 2·794[a]
C(11)-S(1)	= 1·763	S(8) · · · O(4)	= 2·788[a]
C(1)–S(4)	= 1·767	C–C	= 1·390[b]
C(4)–S(5)	= 1·767	O–C	= 1·444[c]
C(14)–S(8)	= 1·760	C–C	= 1·540[d]
C(5)–O(1)	= 1·367		

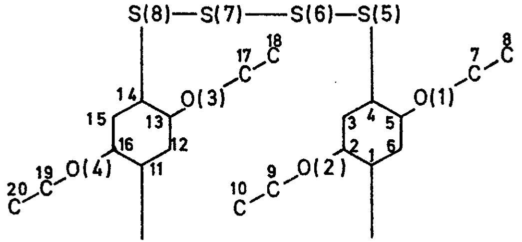
[a] Nonbonded interaction distances.
[b] Average C–C distance in the phenyl rings.
[c] Average value for the $O–CH_2$ distances.
[d] Average value for $H_2C–CH_3$ bonds.

Bond angles (degrees)

C(11)–S(1)–S(2)	= 105·0	C(5)–O(1)–C(7)	= 115·8
S(1)–S(2)–S(3)	= 106·6	C(2)–O(2)–C(9)	= 115·6
S(2)–S(3)–S(4)	= 108·4	C(16)–O(3)–C(17)	= 118·2
S(3)–S(4)–C(1)	= 105·3	C(13)–O(4)–C(19)	= 118·5
C(4)–S(5)–S(6)	= 106·9	O(1)–C(7)–C(8)	= 104·9
S(5)–S(6)–S(7)	= 107·8	O(2)–C(9)–C(10)	= 103·6
S(6)–S(7)–S(8)	= 107·8	O(3)–C(17)–C(18)	= 106·5
S(7)–S(8)–C(14)	= 105·1	O(4)–C(19)–C(20)	= 106·2

Ring–ring contacts (Å)

C(1)–C(12)	= 3·419	C(4)–C(15)	= 3·501
C(1)–C(11)	= 3·594	C(4)–C(14)	= 3·604
C(2)–C(13)	= 3·491	C(5)–C(16)	= 3·517
C(2)–C(12)	= 3·593	C(5)–C(15)	= 3·737
C(3)–C(14)	= 3·506	C(6)–C(11)	= 3·422
C(3)–C(13)	= 3·612	C(6)–C(16)	= 3·687



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† Since at this stage of the refinement σ (S–S, terminal) = σ (S–S, central) = 0·005 Å, $n(\sigma_1^2 + \sigma_2^2)^{1/2} = \Delta = 0{\cdot}041$ Å $= 7n$, or $n \simeq 6$. Therefore, the difference in terminal and central sulphur–sulphur bonds is significant.

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