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Structure of *cyclo*-Tetrakis(*p*-phenylenesulfide)

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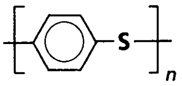
Abstract. 2,7,12,17-Tetrathiapentacyclo[16.2.2.$0^{3,6}$.$0^{8,11}$.$0^{13,16}$]octadecane, $C_{24}H_{16}S_4$, $M_r = 432{\cdot}6$, monoclinic, $P2_1/c$, $a = 11{\cdot}326\,(1)$, $b = 19{\cdot}011\,(2)$, $c = 10{\cdot}507\,(1)$ Å, $\beta = 115{\cdot}076\,(4)°$, $V = 2049{\cdot}3\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}40$, $D_m = 1{\cdot}39$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}46$ mm^{-1}, $F(000) = 896$, $T = 293$ K, $R = 0{\cdot}035$ for 2870 reflections. Four S atoms form a very flattened tetrahedron; the dihedral angle between two SSS triangles is 16·0 (2)°. The S—C bond lengths are 1·776–1·792 (3) Å, C—S—C bond angles 98·4–99·0 (1)°. There is one intermolecular S···S contact of 3·497 (2) Å.

Introduction. As part of structural investigations of organic and organoelement polymer precursors we carried out an X-ray study of the macrocyclic poly(*p*-phenylenesulfides) (I), (III) and (IV). The structure of the pentamer (II) was studied earlier (Kaplan, Reents, Hill & Day, 1982).



$n = 4$ (I)
$n = 5$ (II)
$n = 6$ (III)
$n = 8$ (IV)

Our purpose is to investigate (*a*) the influence of cyclization and ring enlargement on the geometry of diphenylenesulfide moieties; (*b*) the conformational flexibility of *cyclo*-poly(*p*-phenylenesulfides); (*c*) the topology of channels formed in crystals of macrocyclic *p*-phenylenesulfides, *e.g.* (III) and (IV). Macrocyclic *cyclo*-poly(*p*-phenylenesulfides) are interesting also because of their potential ability to form metal complexes of different types, *e.g.* the donor–acceptor complexes with participation of the S atoms of the η-arene complexes *via* the benzene π systems. In this work the data of an X-ray study of (I) are reported.

Experimental. Colourless irregular-shaped crystal. Unit-cell parameters from 24 reflections ($28 \leq 2\theta \leq 32°$). 3984 reflections measured ($-15 \leq h \leq 15$, $0 \leq k \leq 24$, $0 \leq l \leq 15$). Hilger & Watts diffractometer (graphite monochromator, $\theta/2\theta$ scan, $2\theta_{\max} = 60°$). No significant variation in intensities of two standard reflections (002 and 400) measured after every 100 reflections. No absorption or secondary-extinction corrections. Structure solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971) revealing all non-hydrogen atoms and refined by block-diagonal least squares with anisotropic thermal parameters for non-hydrogen atoms using 2870 reflections with $I > 2\sigma$ and minimizing $\sum w(|F_o| - |F_c|)^2$; $w = [\sigma^2(F_o) + kF_o^2]^{-1}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Positions of H atoms are calculated and refined isotropically. Final $R = 0{\cdot}035$, $wR = 0{\cdot}028$, $S = 2{\cdot}1$, max. $(\Delta/\sigma) = 0{\cdot}5$, final electron density fluctuations $\pm 0{\cdot}4$ e Å^{-3}. All calculations carried out with an Eclipse S/200 computer using the *INEXTL* programs (Gerr, Yanovsky & Struchkov, 1983).

Discussion. Positional and thermal atomic parameters are given in Table 1,† and the atom numbering in Fig. 1, wherein the structure of a molecule of (I) is shown. Bond lengths and bond angles are listed in Table 2.

The S(1), S(2), S(3) and S(4) atoms form a very flattened tetrahedron: the deviations from their mean plane *A* are −0·279, 0·330, −0·305 and 0·340 (1) Å respectively. The dihedral angle between the S(1)-

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† Tables of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond lengths and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51272 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* (× 10⁴) *and equivalent isotropic temperature factors* (Å²)

$$B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij}(\mathbf{a}_i\mathbf{a}_j)a_i^*a_j^*.$$

	x	y	z	B_{eq}
S(1)	4725 (8)	1052 (4)	−34 (8)	4·63 (3)
S(2)	−1395 (8)	588 (5)	−2400 (8)	5·43 (3)
S(3)	−2060 (8)	1649 (4)	−8328 (7)	5·24 (3)
S(4)	4077 (8)	1471 (5)	−6230 (8)	5·37 (3)
C(1)	3010 (3)	927 (1)	−675 (2)	3·57 (9)
C(2)	2510 (3)	352 (1)	−281 (3)	3·78 (9)
C(3)	1167 (3)	253 (1)	−808 (3)	3·9 (1)
C(4)	318 (3)	735 (1)	−1744 (2)	3·38 (9)
C(5)	827 (3)	1327 (1)	−2096 (3)	4·4 (1)
C(6)	2158 (3)	1423 (1)	−1583 (3)	4·3 (1)
C(7)	−1851 (3)	848 (1)	−4184 (3)	3·93 (9)
C(8)	−1585 (3)	398 (1)	−5065 (3)	4·4 (1)
C(9)	−1752 (3)	625 (1)	−6375 (3)	4·4 (1)
C(10)	−2147 (3)	1311 (1)	−6788 (2)	3·91 (9)
C(11)	−2487 (3)	1743 (1)	−5952 (3)	4·8 (1)
C(12)	−2344 (3)	1510 (2)	−4641 (3)	4·9 (1)
C(13)	−335 (3)	1683 (1)	−7710 (3)	4·0 (1)
C(14)	219 (3)	1635 (1)	−8642 (3)	4·4 (1)
C(15)	1551 (3)	1598 (1)	−8186 (3)	4·6 (1)
C(16)	2381 (3)	1596 (1)	−6751 (3)	4·0 (1)
C(17)	1817 (3)	1688 (2)	−5829 (3)	4·7 (1)
C(18)	485 (3)	1732 (2)	−6279 (3)	4·5 (1)
C(19)	4567 (3)	1323 (1)	−4392 (3)	4·2 (1)
C(20)	4406 (3)	660 (1)	−3939 (3)	4·5 (1)
C(21)	4525 (3)	567 (1)	−2586 (3)	4·4 (1)
C(22)	4816 (3)	1137 (1)	−1686 (3)	3·9 (9)
C(23)	5082 (3)	1783 (1)	−2106 (3)	4·5 (1)
C(24)	4964 (3)	1881 (1)	−3451 (3)	4·6 (1)

Table 2. *Bond distances* (Å) *and angles* (°)

S(1)—C(1)	1·781 (3)	C(9)—C(10)	1·387 (4)
S(1)—C(22)	1·789 (3)	C(10)—C(11)	1·371 (4)
S(2)—C(4)	1·784 (3)	C(11)—C(12)	1·390 (4)
S(2)—C(7)	1·789 (3)	C(12)—C(7)	1·377 (4)
S(3)—C(10)	1·782 (3)	C(13)—C(14)	1·371 (4)
S(3)—C(13)	1·780 (3)	C(14)—C(15)	1·377 (5)
S(4)—C(16)	1·776 (3)	C(15)—C(16)	1·399 (4)
S(4)—C(19)	1·792 (3)	C(16)—C(17)	1·379 (4)
C(1)—C(2)	1·373 (4)	C(17)—C(18)	1·379 (5)
C(2)—C(3)	1·394 (4)	C(18)—C(13)	1·396 (4)
C(3)—C(4)	1·389 (4)	C(19)—C(20)	1·388 (4)
C(4)—C(5)	1·385 (4)	C(20)—C(21)	1·381 (4)
C(5)—C(6)	1·381 (5)	C(21)—C(22)	1·382 (4)
C(6)—C(1)	1·396 (4)	C(22)—C(23)	1·380 (4)
C(7)—C(8)	1·384 (4)	C(23)—C(24)	1·375 (4)
C(8)—C(9)	1·377 (4)	C(24)—C(19)	1·388 (4)
C(1)S(1)C(22)	98·5 (1)	C(10)C(11)C(12)	119·8 (3)
C(4)S(2)C(7)	98·4 (1)	C(11)C(12)C(7)	119·8 (3)
C(10)S(3)C(13)	99·0 (1)	S(3)C(13)C(14)	120·1 (2)
C(16)S(4)C(19)	98·9 (1)	S(3)C(13)C(18)	121·4 (2)
S(1)C(1)C(2)	121·0 (2)	C(14)C(13)C(18)	118·5 (3)
S(1)C(1)C(6)	119·7 (2)	C(13)C(14)C(15)	121·4 (3)
C(2)C(1)C(6)	119·7 (2)	C(14)C(15)C(16)	120·7 (3)
C(1)C(2)C(3)	120·5 (3)	C(15)C(16)C(17)	117·2 (3)
C(2)C(3)C(4)	120·3 (3)	S(4)C(16)C(15)	118·5 (2)
S(2)C(4)C(3)	118·9 (2)	S(4)C(16)C(17)	124·3 (2)
S(2)C(4)C(5)	122·1 (2)	C(16)C(17)C(18)	122·2 (3)
C(3)C(4)C(5)	119·0 (3)	C(17)C(18)C(13)	119·7 (3)
C(4)C(5)C(6)	120·7 (3)	S(4)C(19)C(20)	119·1 (2)
C(1)C(6)C(5)	120·2 (3)	S(4)C(19)C(24)	120·5 (2)
S(2)C(7)C(8)	118·8 (2)	C(20)C(19)C(24)	120·0 (3)
S(2)C(7)C(12)	120·8 (2)	C(19)C(20)C(21)	119·9 (3)
C(8)C(7)C(12)	120·1 (3)	C(20)C(21)C(22)	119·7 (3)
C(7)C(8)C(9)	119·9 (3)	S(1)C(22)C(21)	119·8 (2)
C(8)C(9)C(10)	119·8 (3)	S(1)C(22)C(23)	120·1 (2)
C(9)C(10)C(11)	120·3 (3)	C(21)C(22)C(23)	119·9 (3)
S(3)C(10)C(9)	119·2 (2)	C(22)C(23)C(24)	120·7 (3)
S(3)C(10)C(11)	120·3 (2)	C(23)C(24)C(19)	119·3 (3)

S(2)S(4) and S(2)S(3)S(4) triangles is 16·0 (2)°. The mutual orientations of the Ph rings are determined by the short non-bonded C···C contacts quoted in Fig. 1; the dihedral angles they form are: *B*/*C* 80·7 (1), *C*/*D* 67·5 (1), *D*/*E* 80·3 (1) and *E*/*B* 76·8 (1)°. The dihedral angles between the *C* and *E* rings and the *A* plane of 72·1 (1) and 74·4 (1)°, respectively, greatly exceed the angles between this plane and the *B* and *D* rings of 46·5 (1) and 17·6 (1)° respectively. The short non-bonded C···C contacts mentioned also distort the planarity (towards a boat conformation) of the *C*, *E* and (to a lesser degree) *D* rings. The *ipso* atoms of these rings are significantly displaced from their mean planes towards the centre of the macrocycle, which in turn

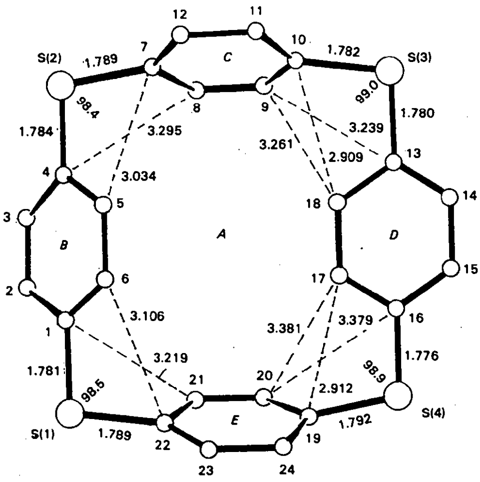

Fig. 1. Structure of a molecule of (I). The main geometrical parameters are given including short C···C contacts. E.s.d.'s of S—C bond lengths 0·003 Å, C—S—C bond angles 0·1°, non-bonded C···C distances 0·004 Å.

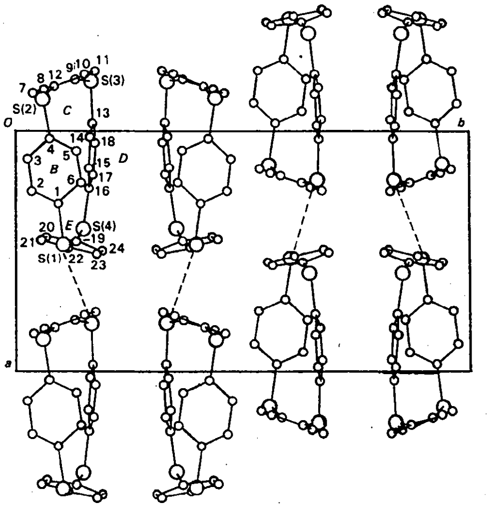

Fig. 2. The *ab* projection of the crystal structure of (I). The short intermolecular S···S contacts are shown by dotted lines.

results in significant deviations of the S atoms from the mean planes of the adjacent Ph rings. These deviations are clearly seen in Fig. 2.

The S—C bond lengths of 1·776–1·792 (3) Å (ave. 1·784 Å) agree well with the values observed in the molecules of (II) [1·771–1·784 (4), ave. 1·778 Å], (III) [1·771–1·788 (4), ave. 1·779 Å] and (IV) [1·773–1·791 (8), ave. 1·781 Å]. Owing to the ring closure the C—S—C bond angles of 98·4–99·0 (1) (ave. 98·7°) in the smallest of the *p*-phenylenesulfide rings in (I) are naturally somewhat smaller than in (II)–(IV), where these values are 101·9–103·0 (3), 100·1–104·0 (2) and 101·7–105·6 (4)° with average values of 102·5, 102·5 and 103·6° respectively. The S—C bond lengths in (I)–(IV) are almost the same as in acyclic diphenylenesulfide (1·771 Å; Rozsondai, Moore, Gregory & Hargittai, 1977) and 1,4-bis(phenylthiobenzene) (ave. 1·780 Å; Andreetti, Garbarczyk & Krolikowska, 1981). The C—S—C bond angles in these acyclic analogues are nearly the same [103·7 and 105·4 (2)°] as in the macrocycles (I)–(IV).

The molecular packing in the crystal (I) is shown in Fig. 2. There is only one intermolecular contact S(1)···S(3) (1+*x*, *y*, 1+*z*) of 3·497 (11) Å shorter than twice the van der Waals radius of S (3·60 Å; Bondi, 1964). These contacts form infinite molecular chains along [101].

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Structure of 1,4-Dihydroxy-2-(1-hydroxy-2,3:4,5-di-*O*-isopropylidene-D-arabinityl)-9,10-anthraquinone

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Abstract. $C_{25}H_{26}O_9$, $M_r = 470$, monoclinic, $P2_1$, $a = 18{\cdot}739\ (8)$, $b = 8{\cdot}263\ (5)$, $c = 7{\cdot}264\ (3)$ Å, $\beta = 95{\cdot}44\ (3)^\circ$, $U = 1120\ (2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}39\ (1)$ (carbon tetrachloride/*n*-pentane), $D_x = 1{\cdot}39$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0{\cdot}797$ mm^{-1}, $F(000) = 496$, $T = 298$ K, final $R = 0{\cdot}027$ for 1604 observed diffractometer data. The hydroxyls at O(1) and O(4) of the planar quinizarin moiety in this hydroxyglycitylquinizarin have close intermolecular approaches to oxygens O(4) and O(9) of neighbouring molecules and are also engaged in intramolecular hydrogen bonds O(1)···O(9) = 2·55 (1) and O(4)···O(10) = 2·59 (1) Å; at the bridge, hydroxyl O(15) has a 2·95 (1) Å intermolecular approach to O(19) of the open-chain arabinose. At the new C(1′)-type benzylic chiral carbon labelled C(15), C(15)—OH makes a torsion angle C(3)—C(2)—C(15)—O(15) = 11·5 (1)° with the quinizarin C(3)—(2) bond.

Introduction. 1,4-Dihydroxy-2-(1-hydroxy-2,3:4,5-di-*O*-isopropylidene-D-arabinityl)-9,10-anthraquinone or 1,4-dihydroxy-2-(1-hydroxy-2,3:4,5-di-*O*-isopropylidene-D-arabinityl)quinizarin (DIHAQ) is a precursor in the preparation (Mincher, Shaw & Declercq, 1983) of tetrasubstituted anthracyclinones, a class of promising antibiotics for cancer treatment (Arcamone,

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