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Structural Aspects of Metacyclophanes.
Structures of 5,7,14,16-Tetramethoxy-1,2,3,10,11,12-hexathia[3.3]metacyclophane and 6,8,10,14,16,18-Hexamethyl-1,2,3,4,11,12-hexathia[4.2]metacyclophane

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Abstract

The crystal and molecular structures of the title compounds have been determined from three-dimensional X-ray data. The crystals of $C_{16}H_{16}O_4S_6$ (I) are triclinic, space group $P\bar{1}$, with $Z = 2$ and cell parameters $a = 13 \cdot 86$ (1), $b = 10 \cdot 86$ (1), $c = 8 \cdot 155$ (7) Å, $\alpha = 93 \cdot 83$ (8), $\beta = 96 \cdot 12$ (8), $\gamma = 124 \cdot 18$ (8)°, whereas those of $C_{18}H_{20}S_6$ (II) are orthorhombic, space group $Pca2_1$, with $Z = 8$ and cell parameters $a = 14 \cdot 895$ (7), $b = 17 \cdot 154$ (7), $c = 15 \cdot 622$ (7) Å. The structures were refined to R values of $0 \cdot 047$ (I) and $0 \cdot 033$ (II), using 1940 and 3849 independent reflections respectively. Compound (I) is the [3.3] isomer in the *syn* form, whereas compound (II) is the [4.2] isomer in the *anti* form. No significant deviation from planarity of the bridged benzene rings was detected in either compound. The twelve-atom ring assumes a crown-like conformation, both in (I) and (II), suggesting a particular stability of this conformation which provokes the molecules to have either *syn* or *anti* forms depending upon the different lengths of the two polysulphur chains. Simple relationships of torsion angles around the S—S bonds with the chain length and S—S bond lengths are detected.

Introduction

Recently, the stereochemistries of metacyclophane systems have excited interest because of their peculiarities, such as deformations of the bridged rings, interconversion among different conformers, and the nature of the bridging chains. A great deal of work has been reported on systems having phenyl groups bridged by one or more aliphatic CH_2 chains (Vögtle & Newmann, 1972). Few structural data, however, have been reported for heterophanes (Bresciani-Pahor, Calligaris & Randaccio, 1978) or metacyclophanes having different types of bridges, such as polysulphide chains.

Thus, we have determined the structure of the title compounds to establish their geometries in the solid state. These compounds have been synthesized by Bottino, Foti & Pappalardo (1980), who suggested the hexathia[3.3] structure for (I). Preliminary results for compound (II) have already been reported (Bottino, Foti, Pappalardo & Bresciani-Pahor, 1979).

Experimental

Crystal data

(I) $C_{16}H_{16}O_4S_6$, $M_r = 464 \cdot 7$, triclinic, $a = 13 \cdot 86$ (1), $b = 10 \cdot 86$ (1), $c = 8 \cdot 155$ (7) Å, $\alpha = 93 \cdot 83$ (8), $\beta = 96 \cdot 12$ (8), $\gamma = 124 \cdot 18$ (8)°, $U = 997 \cdot 7$ Å^3, $D_m = 1 \cdot 56$

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(by flotation), $Z = 2$, $D_c = 1 \cdot 55$ Mg m^{-3}. Space group $P\bar{1}$ (from structure refinement). Mo $K\alpha$ radiation, $\lambda = 0 \cdot 7107$ Å, μ(Mo $K\alpha$) $= 0 \cdot 70$ mm^{-1}.

(II) $C_{18}H_{20}S_6$, $M_r = 428 \cdot 7$, orthorhombic, $a = 14 \cdot 895$ (7), $b = 17 \cdot 154$ (7), $c = 15 \cdot 622$ (7) Å, $U = 3991 \cdot 6$ Å^3, $D_m = 1 \cdot 44$, $Z = 8$, $D_c = 1 \cdot 43$ Mg m^{-3}. Space group $Pca2_1$ (from Patterson analysis and structure refinement). Mo $K\alpha$ radiation, $\lambda = 0 \cdot 7107$ Å, μ(Mo $K\alpha$) $= 0 \cdot 66$ mm^{-1}.

Cell parameters were determined from Weissenberg and precession photographs and refined with an on-line single-crystal Siemens diffractometer using Mo $K\alpha$ radiation.

Intensity measurements

Three-dimensional intensity data were collected for both complexes on a Siemens diffractometer by the θ–2θ scan procedure using Mo $K\alpha$ radiation to a θ_{max} of $27°$ for (I) and $28°$ for (II). Reflections having $I_o \leq 3\sigma(I_o)$ were rejected, the remainder being corrected for Lorentz–polarization factors. Totals of 1940 (I) and 3849 (II) independent reflections were used in the subsequent calculations. No correction for absorption was applied.

Structure determination and refinement

The structure of (I) was solved by the Patterson method for S atoms. The subsequent Fourier map allowed the location of all other non-hydrogen atoms assuming the space group $P\bar{1}$, which was confirmed by the successful refinement. The structure of (II) was solved by direct methods using the *MULTAN* program of Germain, Main & Woolfson (1971). The E map based on the phases obtained for the 205 reflections with $|E| > 1 \cdot 70$ revealed all non-hydrogen atoms. The choice of space group $Pca2_1$ was suggested by the vector distribution on the Patterson map and confirmed by the final refinement. Both structures were refined by isotropic refinement and, after three cycles of aniso-tropic refinement, a difference Fourier series was calculated to locate the H atoms. The calculated positions [$C(sp^2)$ $0 \cdot 98$ Å and $C(sp^3)$ $1 \cdot 00$ Å] of these all occurred in regions of positive electron density. Final anisotropic block-diagonal least-squares refinement, including the contribution of H atoms held constant at $B = 5$ Å^2, gave R values of $0 \cdot 047$ for (I) and $0 \cdot 033$ for (II). Final weighting schemes were: $w = 1/(A + |F_o| + B|F_o|^2)$, where $A = 7 \cdot 0$, $B = 0 \cdot 007$ for (I) and $A = 6 \cdot 9$, $B = 0 \cdot 004$ for (II), chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and (sin $\theta/\lambda)^2$. Four reflections of (II) having large $|F_o|$ and low θ values (004, 400, 006 and 032) were excluded from the refinement because of the large discrepancies between the calculated and observed values. The latter are systematically smaller, suggesting they are affected

Table 1. *Atomic positional parameters* ($\times 10^4$ *for non-hydrogen atoms*, $\times 10^3$ *for* H) *for* (I), *with their e.s.d.'s in parentheses*

	x	y	z
S(1)	2649 (1)	1920 (2)	2979 (2)
S(2)	851 (1)	899 (1)	2354 (2)
S(3)	357 (1)	1671 (1)	4253 (2)
S(4)	4772 (1)	7987 (2)	3895 (2)
S(5)	3626 (1)	8582 (1)	3311 (2)
S(6)	2379 (1)	7711 (2)	4845 (2)
O(1)	−1394 (3)	1458 (4)	1691 (5)
O(2)	340 (3)	6806 (4)	2244 (5)
O(3)	2793 (3)	2266 (4)	−565 (5)
O(4)	4555 (3)	7607 (4)	214 (5)
C(1)	1259 (4)	4661 (5)	4237 (6)
C(2)	1257 (4)	5864 (5)	3812 (6)
C(3)	305 (4)	5587 (5)	2628 (6)
C(4)	−598 (4)	4111 (5)	1908 (6)
C(5)	−569 (4)	2919 (5)	2344 (6)
C(6)	372 (4)	3181 (5)	3541 (6)
C(7)	−2376 (5)	1121 (6)	461 (8)
C(8)	−709 (4)	6557 (6)	1303 (8)
C(9)	3708 (4)	4954 (6)	3112 (7)
C(10)	3246 (4)	3594 (6)	2099 (6)
C(11)	3250 (4)	3617 (5)	353 (7)
C(12)	3692 (4)	4934 (6)	−290 (6)
C(13)	4136 (4)	6279 (6)	740 (7)
C(14)	4146 (4)	6284 (6)	2494 (7)
C(15)	2743 (5)	2180 (6)	−2369 (7)
C(16)	4556 (6)	7664 (7)	−1561 (8)
H(C1)	193	486	506
H(C4)	−126	392	108
H(C9)	372	497	432
H(C12)	370	492	−151
H1(C7)	−292	1	6
H2(C7)	−208	165	−52
H3(C7)	−283	147	96
H1(C8)	−57	754	111
H2(C8)	−139	602	193
H3(C8)	−93	592	20
H1(C15)	239	112	−290
H2(C15)	357	286	−263
H3(C15)	225	252	−286
H1(C16)	489	871	−179
H2(C16)	373	697	−220
H3(C16)	505	733	−196

by extinction. Atomic scattering factors were calculated according to Moore (1963). Final atomic positional parameters are listed in Tables 1 and 2, together with their estimated standard deviations.* Bond lengths and angles are given in Tables 3 and 4.

Calculations

All calculations were carried out on a CDC 6200 computer with programs described by Albano, Domenicano & Vaciago (1966).

Table 2. *Atomic positional parameters* ($\times 10^4$ *for non-hydrogen atoms,* $\times 10^3$ *for* H) *for* (II), *with their e.s.d.'s in parentheses*

	Molecule A			Molecule B		
	x	y	z	x	y	z
S(1)	1977 (1)	−1617 (1)	284 (1)	2281 (1)	6372 (1)	2637 (1)
S(2)	2978 (1)	−2318 (1)	773 (1)	3216 (1)	7046 (1)	3264 (1)
S(3)	4124 (1)	−2205 (1)	29 (1)	4341 (1)	7157 (1)	2492 (1)
S(4)	5075 (1)	−1576 (1)	692 (1)	5372 (1)	6509 (1)	3012 (1)
S(5)	4005 (1)	1475 (1)	1190 (1)	4695 (1)	3351 (1)	2720 (1)
S(6)	2718 (1)	1515 (1)	669 (1)	3396 (1)	3322 (1)	2227 (1)
C(1)	2297 (3)	−56 (2)	558 (3)	2788 (3)	4828 (2)	2515 (3)
C(2)	1990 (3)	−759 (2)	928 (3)	2429 (3)	5412 (2)	3050 (3)
C(3)	1671 (3)	−791 (3)	1770 (3)	2127 (3)	5242 (3)	3881 (3)
C(4)	1651 (3)	−109 (3)	2247 (3)	2199 (3)	4475 (3)	4171 (3)
C(5)	1942 (3)	607 (3)	1915 (3)	2563 (3)	3890 (2)	3678 (3)
C(6)	2274 (3)	625 (2)	1069 (3)	2863 (3)	4070 (2)	2849 (3)
C(7)	2630 (3)	−52 (3)	−359 (3)	3081 (3)	5026 (3)	1602 (3)
C(8)	1340 (4)	−1532 (3)	2195 (5)	1757 (4)	5869 (3)	4470 (4)
C(9)	1916 (4)	1323 (3)	2471 (4)	2628 (4)	3071 (3)	4050 (4)
C(10)	4586 (3)	−34 (2)	855 (3)	5074 (3)	4929 (3)	2779 (3)
C(11)	4521 (3)	735 (2)	545 (3)	5101 (3)	4245 (2)	2284 (3)
C(12)	4818 (3)	931 (3)	−274 (3)	5408 (3)	4254 (3)	1432 (3)
C(13)	5186 (3)	350 (3)	−783 (3)	5699 (3)	4955 (3)	1086 (3)
C(14)	5261 (3)	−424 (3)	−514 (3)	5696 (3)	5651 (3)	1560 (3)
C(15)	4958 (3)	−600 (2)	312 (3)	5379 (3)	5630 (2)	2394 (3)
C(16)	4290 (4)	−251 (3)	1751 (3)	4745 (3)	4939 (3)	3695 (3)
C(17)	4735 (4)	1753 (3)	−632 (4)	5426 (5)	3535 (3)	874 (4)
C(18)	5682 (4)	−1025 (4)	−1105 (4)	6039 (4)	6386 (3)	1122 (5)
H(C4)	142	−12	284	196	435	475
H(C13)	540	48	−136	592	496	50
H1(C7)	283	48	−53	333	454	131
H2(C7)	214	−23	−75	358	542	161
H3(C7)	316	−42	−41	257	523	126
H1(C8)	114	−143	279	158	563	503
H2(C8)	183	−193	219	122	612	420
H3(C8)	82	−175	185	223	628	457
H1(C9)	166	119	304	237	306	465
H2(C9)	153	173	218	326	289	406
H3(C9)	254	153	254	226	270	368
H1(C16)	406	21	205	455	440	387
H2(C16)	481	−48	207	421	529	375
H3(C16)	380	−66	171	523	512	409
H1(C17)	499	176	−123	567	367	30
H2(C17)	507	213	−27	481	332	81
H3(C17)	409	190	−66	582	313	115
H1(C18)	585	−78	−167	623	626	53
H2(C18)	523	−146	−123	656	660	145
H3(C18)	623	−126	−85	555	679	111

Description of the structures

Structure of (I)

A view of a molecule of (I) with the atom-numbering scheme is given in Fig. 1. Crystals are built up of discrete molecules, showing that of the three possible [1.5], [2.4], and [3.3] isomers, only the last is formed, in agreement with the previous structure assignment. The molecule, which possesses approximate C_{2v} symmetry, exists in the *syn* form in the solid state, the phenyl rings (planar within ±0·005 Å) being bent away from a parallel arrangement, with a dihedral

syn   anti
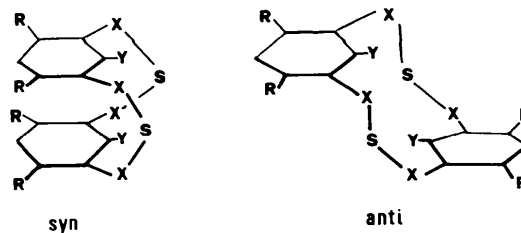
(I)   X = S , Y = H , R = OMe

(III)   X = CH₂, Y = Me , R = H

angle of 125·3° (Fig. 2). So far the *syn* form has only been found in 9,18-dimethyl-2,11-dithia[3.3]meta-cyclophane (III) (Davis & Bernal, 1971). On the other

hand, the different nature of the bridges and substituents in the latter compound determine a nearly parallel arrangement of the benzene rings which make a dihedral angle of 169·7° (see below). The other atoms attached to the benzene rings are slightly displaced from their planes as shown in Fig. 3, where the torsion angles along the bridging chains are also reported. The values of the torsion angles around the S—S bonds, ranging from 86·6 to 95·6°, are not far from those previously reported for bridging polysulphide chains, *e.g.* 86·9° in the four-S bridged paracyclophane 7,15,17,19-tetraethoxy-2,3,4,5,10,11,12,13-octathiatricyclo[12.2.2.2]icosa-6,8,14,16,17,19-hexaene (IV), $C_{12}H_{20}S_6$ (Ricci & Bernal, 1971), and 81° in *trans, trans*-perhydrodibenzo[d,i][1,2,3,6,7,8]hexathiecin (Lemmer, Fehér, Gieren, Hechtfischer & Hoppe, 1973). A slight, though significant, difference is found in the S—S lengths of the two bridges, the mean values being 2·064 and 2·053 Å respectively. They are, how-
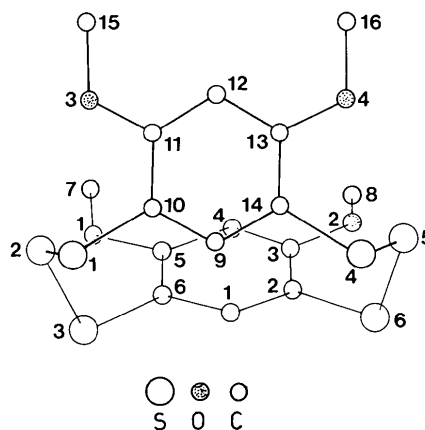
Table 3. *Bond lengths (Å) and angles (°) with their e.s.d.'s in parentheses for compound* (I)

S(1)—S(2)	2·061 (2)	C(6)—C(5)—O(1)	115·0 (5)
S(2)—S(3)	2·066 (2)	C(5)—O(1)—C(7)	117·5 (5)
S(4)—S(5)	2·049 (3)	C(1)—C(6)—C(5)	117·8 (5)
S(5)—S(6)	2·056 (2)	C(6)—C(5)—C(4)	120·5 (4)
S(1)—C(10)	1·765 (6)	C(5)—C(4)—C(3)	120·4 (5)
S(3)—C(6)	1·766 (6)	C(4)—C(3)—C(2)	119·5 (5)
S(4)—C(14)	1·784 (6)	C(3)—C(2)—C(1)	118·9 (4)
S(6)—C(2)	1·772 (4)	C(2)—C(1)—C(6)	122·8 (5)
C(1)—C(2)	1·375 (9)	O(1)—C(5)—C(4)	124·5 (5)
C(2)—C(3)	1·417 (8)	C(2)—C(3)—O(2)	116·9 (3)
C(3)—C(4)	1·394 (5)	C(4)—C(3)—O(2)	123·5 (5)
C(4)—C(5)	1·386 (9)	C(3)—O(2)—C(8)	118·1 (3)
C(5)—C(6)	1·418 (8)	C(3)—C(2)—S(6)	121·0 (4)
C(6)—C(1)	1·388 (5)	C(1)—C(2)—S(6)	119·9 (4)
C(9)—C(10)	1·391 (8)	C(2)—S(6)—S(5)	104·7 (2)
C(10)—C(11)	1·426 (8)	S(6)—S(5)—S(4)	108·85 (10)
C(11)—C(12)	1·371 (8)	S(5)—S(4)—C(14)	103·5 (2)
C(12)—C(13)	1·391 (8)	S(4)—C(14)—C(13)	121·4 (4)
C(13)—C(14)	1·429 (8)	S(4)—C(14)—C(9)	119·7 (4)
C(14)—C(9)	1·373 (9)	C(14)—C(13)—O(4)	115·9 (5)
C(5)—O(1)	1·352 (5)	C(13)—O(4)—C(16)	118·2 (5)
O(1)—C(7)	1·447 (8)	C(12)—C(13)—O(4)	124·9 (5)
C(3)—O(2)	1·356 (8)	C(12)—C(11)—O(3)	124·4 (5)
O(2)—C(8)	1·438 (7)	C(10)—C(11)—O(3)	114·7 (5)
C(11)—O(3)	1·350 (6)	C(11)—O(3)—C(15)	118·4 (4)
O(3)—C(15)	1·460 (7)	C(9)—C(10)—S(1)	120·0 (4)
C(13)—O(4)	1·340 (7)	C(11)—C(10)—S(1)	122·5 (4)
O(4)—C(6)	1·453 (8)	C(9)—C(10)—C(11)	117·4 (5)
		C(10)—C(11)—C(12)	120·8 (5)
C(10)—S(1)—S(2)	102·5 (2)	C(11)—C(12)—C(13)	120·9 (5)
S(1)—S(2)—S(3)	107·10 (8)	C(12)—C(13)—C(14)	119·2 (5)
S(2)—S(3)—C(6)	104·3 (2)	C(13)—C(14)—C(9)	118·9 (5)
S(3)—C(6)—C(1)	120·8 (4)	C(14)—C(9)—C(10)	122·7 (5)
S(3)—C(6)—C(5)	121·2 (3)		

Fig. 1. A view of (I) together with the numbering scheme.

Table 4. *Bond lengths (Å) and angles (°) with their e.s.d.'s in parentheses for* (II)

|	Molecule A	Molecule B		Molecule A	Molecule B		Molecule A	Molecule B
S(1)—C(2)	1·783 (4)	1·782 (4)	C(14)—C(15)	1·400 (7)	1·386 (7)	C(2)—C(1)—C(7)	119·8 (4)	120·2 (4)
S(1)—S(2)	2·062 (2)	2·058 (2)	C(10)—C(16)	1·514 (7)	1·513 (7)	C(2)—C(3)—C(4)	118·6 (4)	118·1 (4)
S(2)—S(3)	2·074 (2)	2·073 (2)	C(12)—C(17)	1·522 (7)	1·511 (7)	C(2)—C(3)—C(8)	123·7 (5)	121·9 (4)
S(3)—S(4)	2·060 (2)	2·062 (2)	C(14)—C(18)	1·519 (8)	1·523 (8)	C(3)—C(4)—C(5)	122·2 (4)	122·4 (4)
S(4)—C(15)	1·785 (4)	1·790 (4)	S(1)—S(2)—S(3)	109·5 (1)	108·8 (1)	C(4)—C(3)—C(8)	117·7 (5)	119·9 (4)
S(5)—C(11)	1·794 (4)	1·784 (4)	S(1)—C(2)—C(1)	118·5 (4)	119·3 (3)	C(4)—C(5)—C(6)	118·3 (4)	118·8 (4)
S(5)—S(6)	2·084 (2)	2·083 (2)	S(1)—C(2)—C(3)	119·6 (3)	119·1 (3)	C(4)—C(5)—C(9)	119·6 (4)	119·0 (4)
S(6)—C(6)	1·777 (4)	1·795 (4)	S(2)—S(1)—C(2)	105·3 (2)	105·3 (2)	C(6)—C(1)—C(7)	122·5 (5)	121·9 (4)
C(1)—C(2)	1·413 (5)	1·410 (6)	S(2)—S(3)—S(4)	109·5 (1)	108·9 (1)	C(6)—C(5)—C(9)	122·1 (4)	122·3 (4)
C(1)—C(6)	1·415 (5)	1·406 (5)	S(3)—S(4)—C(15)	104·9 (2)	104·2 (2)	C(10)—C(11)—C(12)	121·3 (4)	121·4 (4)
C(2)—C(3)	1·400 (7)	1·405 (7)	S(4)—C(15)—C(10)	119·1 (3)	118·9 (4)	C(10)—C(15)—C(14)	122·4 (4)	122·0 (4)
C(3)—C(4)	1·387 (7)	1·396 (7)	S(4)—C(15)—C(14)	118·5 (3)	119·1 (3)	C(11)—C(10)—C(15)	117·9 (4)	117·7 (4)
C(4)—C(5)	1·402 (7)	1·376 (6)	S(5)—S(6)—C(6)	100·2 (2)	101·2 (2)	C(11)—C(10)—C(16)	121·9 (4)	122·6 (4)
C(5)—C(6)	1·411 (7)	1·404 (7)	S(5)—C(11)—C(10)	119·9 (4)	119·9 (4)	C(11)—C(12)—C(13)	118·5 (4)	118·6 (4)
C(1)—C(7)	1·516 (7)	1·530 (7)	S(5)—C(11)—C(12)	118·7 (3)	118·7 (3)	C(11)—C(12)—C(17)	122·3 (4)	122·9 (4)
C(3)—C(8)	1·516 (8)	1·519 (7)	S(6)—S(5)—C(11)	101·4 (2)	101·2 (2)	C(12)—C(13)—C(14)	122·8 (4)	122·0 (4)
C(5)—C(9)	1·505 (7)	1·523 (6)	S(6)—C(6)—C(1)	120·1 (4)	119·7 (4)	C(13)—C(12)—C(17)	119·1 (4)	118·5 (4)
C(10)—C(11)	1·409 (5)	1·406 (6)	S(6)—C(6)—C(5)	118·6 (3)	118·9 (3)	C(13)—C(14)—C(15)	117·2 (4)	118·3 (4)
C(10)—C(15)	1·403 (6)	1·419 (6)	C(1)—C(2)—C(3)	121·9 (4)	121·5 (4)	C(13)—C(14)—C(18)	119·7 (5)	117·8 (5)
C(11)—C(12)	1·395 (7)	1·407 (7)	C(1)—C(6)—C(5)	121·2 (4)	121·4 (4)	C(15)—C(10)—C(16)	120·3 (4)	119·7 (4)
C(12)—C(13)	1·388 (7)	1·388 (7)	C(2)—C(1)—C(6)	117·8 (4)	117·9 (4)	C(15)—C(14)—C(18)	123·2 (5)	123·9 (5)
C(13)—C(14)	1·397 (7)	1·405 (7)						
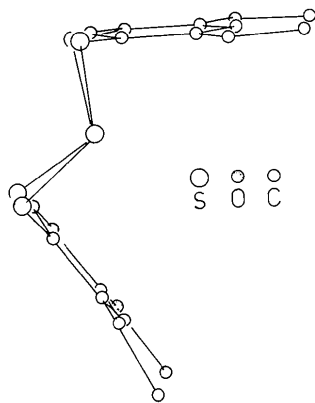
Fig. 2. A side view of (I) along the direction passing through the two middle S atoms of each bridge.
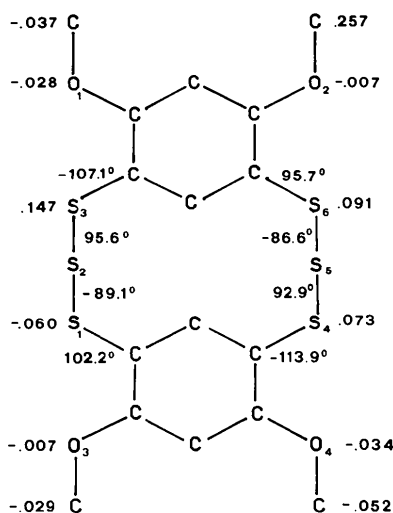

Fig. 3. Displacements (Å) of atoms substituted in the phenyl groups from their mean planes and torsion angles along the chain bonds in (I). A positive value indicates that the atom is displaced above the phenyl ring on the opposite side of the bridging chains. The e.s.d's of displacements are 0·006 Å (S) and 0·008 Å (C,O) and of torsion angles in the range 0·2–0·4°.

ever, in the normal range of values reported, as are the S—S—S bond angles, which average to 108·0°. The values of C—S—S bond angles are significantly lower, averaging 103·8°. The C—S bond lengths range from 1·765 (6) to 1·784 (6) Å (mean 1·772 Å), which could imply the existence of a certain amount of double-bond character. In fact, the mean value is significantly shorter than the 1·859 (4) Å found in $C_{12}H_{20}S_6$ for the S—C(sp^3) distance, even after correction for the different atomic radii of C(sp^3) and C(sp^2). On the other hand, it becomes comparable with the values of 1·802 (2) Å in $(CH_3)_2S_2$ (Beagly & McAloon, 1971) and 1·821 (7) Å for the S—CH_2 distance in 2,11,20-trithia[3.3.3][1,3,5]cyclophane (Hanson & Macaulay, 1972), after allowance for the different hybridizations of the C atoms, so that the actual presence of the π-

bonding contribution in the C—S bonds appears highly questionable.

Finally, the methoxy substituents are nearly co-planar (Fig. 3) with their respective benzene rings, suggesting, together with the values of the angles at the O atoms [mean 118·1 (3)°] and the O—C(phenyl) distances [mean 1·350 (7) Å], a certain amount of double-bond character in the C—OCH_3 bonds. The requirement of coplanarity of the methoxy groups and benzene rings imposes a strong repulsion between the O—CH_3 groups and the H atoms of C(4) and C(12), which is alleviated by an in-plane bending of the C—O bonds towards the S atoms.

Structure of (II)

The structure of (II) consists of discrete molecules. A view of a molecule of (II) is shown in Fig. 4, together with the labelling scheme used. In contrast to compound (I), the [4.2] isomer is obtained, as suggested previously by Bottino et al. (1979). In the crystals there are two crystallographically independent molecules (A and B) which are very similar in shape and almost have C_2 symmetry, the pseudo twofold axis passing through the mid-points of the S(5)—S(6) and S(2)—S(3) bonds (Fig. 4). Both molecules are found in the anti form in the solid state. The asymmetry of the two polysulphide bridges leads the benzene planes to be inclined towards the pseudo C_2 axis, making a dihedral angle of 157° in both molecules A and B. The benzene groups of molecule A are both planar within ±0·005 and ±0·007 Å respectively, the corresponding figures for molecule B being ±0·012 and ±0·006 Å. The other atoms directly bonded to the benzene rings are displaced from their respective phenyl planes as shown in Fig. 5, where the torsion angles around the bonds of the bridging chains are also reported. The torsion angles around S(5)—S(6) bonds are 72·8 and 72·1°, whereas those along the S(1)—S(2)—S(3)—S(4) chains are in the ranges 96·8–107·5° and 97·0–108·5° in A and B respectively. Comparing these figures with the values of the torsion angles in the three-S bridges of (I), we
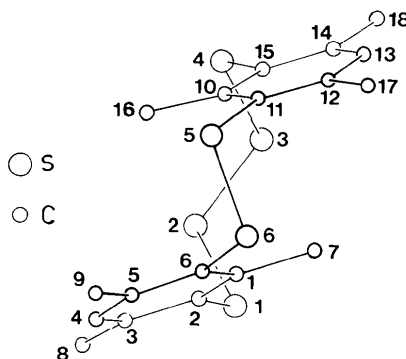

Fig. 4. A view of (II) together with the numbering scheme for molecules A and B.
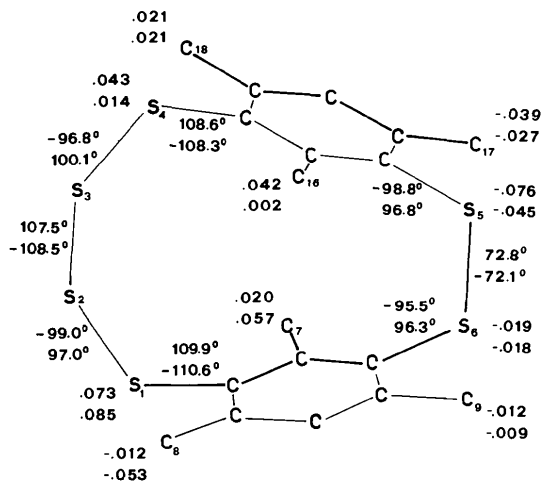
Fig. 5. Displacements (Å) of atoms substituted in the phenyl groups from their mean planes and torsion angles along the bridging chains in (II). The upper numbers refer to the displacement or the torsion angle in molecule *A*, the lower numbers to those in molecule *B*. For + and − see Fig. 3. The e.s.d.'s of displacements are 0·004 Å (S) and 0·007 Å (C) and of torsion angles in the range 0·1–0·4°.

Table 5. *Values of inner and outer* S—S *bond lengths* (Å) *in* S_4 *chains*

	Inner	Outer (mean)	References
S_4Ba	2·063 (4)	2·074 (4)	Abrahams & Bernstein (1969)
S_4Na_2	2·064 (4)	2·074 (1)	Tegman (1973)
$O_3S—S_4—SO_3$	2·056	2·042	Marøy (1973)
$S_4(NH)_2$	2·051 (6)	2·035 (6)	van de Grampel & Vos (1969)
$(PhCHN)_2S_4$	2·083 (4)	2·026 (3)	Barrick, Calvo & Olsen (1973)
(II)	2·074 (2)	2·061 (2)	This work
(IV)*	2·066 (2)	2·028 (2)	Ricci & Bernal (1971)

* 7,15,17,19-Tetraethoxy-2,3,4,5,10,11,12,13-octathiatricyclo-[12.2.2.2]icosa-6,8,14,16,17,19-hexaene.

observe an increase of the mean absolute value of the torsion angles around S—S bonds going from two-S to four-S bridges. In fact these values are 72·5° for two-S, 91·1° for three-S and 101·5° for four-S bridges.

No appreciable difference between the two molecules may be observed at bond-length and -angle level (Table 4). The four-S bridge is characterized by an inner S—S bond length [mean 2·074 (2) Å] which is slightly longer than the outer ones [mean 2·061 (2) Å] in both molecules. A similar effect, although of different magnitude, has been observed in other S_4 bridging chains and the corresponding values are given in Table 5. On the other hand, in the free chains of the tetrasulphide anion, S_4^{2-}, this trend is just the opposite (Table 5).

Discussion

The following points are worth mentioning on the basis of the above results: (i) no deformation is observed in the bridged benzene rings showing that no strain occurs in such S-bridged metacyclophanes, in contrast to the severe strains observed in [2.2] phanes; (ii) compound (I) is the [3.3] isomer, whereas compound (II) is the [2.4] isomer; (iii) the conformation found in the solid state is *syn* for (I) and *anti* for (II). In both cases, however, the twelve-atom ring (Fig. 6) assumes a crown-like conformation; (iv) no clear evidence of electronic interaction between the benzene groups across the bridging chains is revealed from the structural data. On the contrary, a relationship between the length of the polysulphide chain and the geometrical parameters is evident. The latter two points merit further discussion.

The crown-like conformation of (I) is shown in Fig. 6, where the + and − values indicate atoms above and below the mean plane respectively. The same −, +, − sequence on the two groups of C atoms indicates that the two benzene groups are *syn*, whereas in (II) the opposite sign sequence on the C atoms indicates that the benzene groups are *anti*. Furthermore it may be observed that in both (I) and (II) the signs of the two central C_m atoms are opposite to those of the two outer S atoms of the C_m—C—S—S fragments. Such an arrangement minimizes the repulsion among these S atoms and the H atoms attached to the C_m atoms. The particular stability of a crown-like conformation is confirmed by the result found for compound (III), where methyl groups are attached to C_m (Davis & Bernal, 1971). Thus if we assume that the crown-like confor-
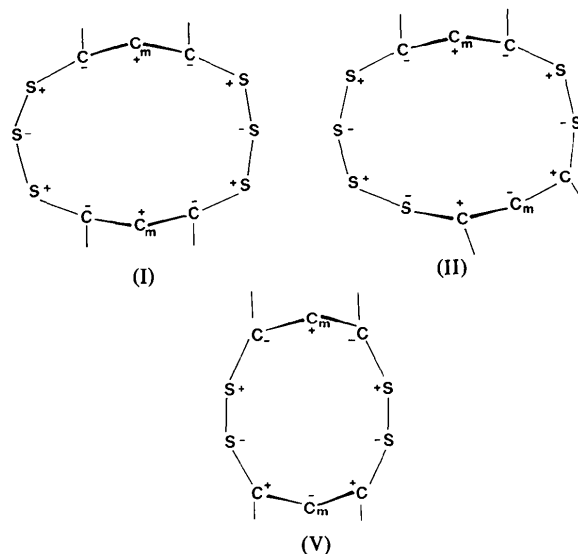

Fig. 6. Crown-like conformation of the twelve-membered rings in the [3.3] and [4.2] isomers and of the ten-membered ring in the [2.2] derivative.

Table 6. *Mean S—S distances (Å) and torsion angles (°) in compounds having bridging polysulphide chains*

Bridge	S—S	R—S—S—R	References
Two-S	2·084 (2)	72·5 (2)	This work
Four-S	2·074 (2)	108·0 (1)	This work
	2·061 (2)	98·2 (2)	
Four-S	2·066 (2)	86·9 (1)	Ricci & Bernal (1971)
Three-S	2·064 (2)	92·4 (2)	This work
	2·053 (2)	89·8 (2)	
Three-S	2·054 (1)	81·0 (1)	Lemmer et al. (1973)
S₄(NH)₂	2·051 (6)	99·7 (2)	van de Grampel & Vos (1969)
PhHCN—S₄—NCHPh	2·083 (4)	106·5 (2)	Barrick et al. (1973)

mation is the most stable, we may predict that the [2.2] derivatives (V) (Fig. 6) will exhibit the *anti* conformation.

As far as point (iv) is concerned, we have already observed that there is an increase in the mean of the torsion angles around the S—S bonds with an increase in the length of the polysulphide chain. Furthermore, the geometrical parameters of different kinds of $R—S—S—R'$ chains seem to be qualitatively in agreement with the relationship found by Hordvik (1966), who observed that the shortest S—S bond length (d) corresponds to a dihedral angle φ of about 90°, while smaller dihedral angles correspond to longer bonds. From Table 6, where d and φ values are reported for ours and other bridging chains, we suggest that, in addition to this statement, it may be assumed that dihedral angles larger than 90° also correspond to longer bonds.

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Prostadienoic Acids PGE₂ and PGF₂β: Crystallographic Studies of Conformational Transmission and Receptor Recognition

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Abstract

The conformations of the prostadienoic acids PGE₂ and PGF₂β have been determined by X-ray diffraction techniques. While both molecules are 'hairpin' shaped, *i.e.* their side chains are ~5 Å apart at their ends and are approximately parallel, subtle yet significant variations in conformation distinguish the two prostaglandins. The variations in conformation have been traced to a short (2·81 Å) C(6)···O(9) contact which precludes PGE₂ from attaining the C(8) ring/

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