The Crystal and Molecular Structure of *anti*-5,7,9,14,16,18-Hexamethyl-1,3,10,12-tetrathia[3.3]metacyclophane

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The crystal and molecular structure of the title compound, $C_{20}H_{24}S_4$, has been determined by single-crystal *X*-ray analysis and refined to an *R*-value of 0.036. The crystal is monoclinic, space group $P2_1/c$, with a = 8.585(2), b = 15.189(3), c = 7.967(2) Å, β = 115.75(2)°, and Z = 2. The molecule has a crystallographic centre of symmetry and thus adopts the *anti*-conformation. The aromatic rings are nearly planar, while C(7), C(9), and S(1) phenyl substituents are remarkably displaced from coplanarity [0.224(3), 0.130(3), and −0.223(1) Å, respectively] to avoid too close mutual contacts with the bridging C(10) methylenes.

Recently, we have shown that hexathia[3.3]metacyclophanes (1) exist as the *syn*-conformers both in the solid state [1] and in solution.[2] Attempts to synthesize an *anti*-conformer of (1), by coupling mesitylene-2,4-dithiol with sulphur chlorides, led invariably to the formation of the structural isomer *anti*-hexathia[4.2]metacyclophane (2) as the major product, along with minor amounts of its higher homologue heptathia[4.3]-metacyclophane (3). However, the reaction of the above dithiol with dibromomethane afforded the desired *anti*-5,7,9,-14,16,18-hexamethyl-1,3,10,12-tetrathia[3.3]metacyclophane (4).[2]

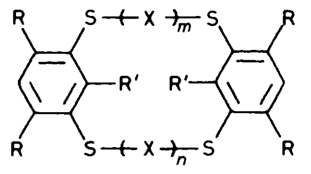
As the structure and geometry of the latter compound (4) are closely related to those of a hypothetical *anti*-conformer of (1), the only difference being in the replacement in the bridging chains of the central S atoms by methylenes, we undertook a single-crystal *X*-ray structure investigation of (4), with the aim of providing further support to the assumption that the specific geometry imposed by the trisulphide bridges, *i.e.*, torsion angles around S–S bonds close to ±90°,[3] might play a major role in preventing the formation of *anti*-hexathia-[3.3]metacyclophanes.

Although several crystallographic studies have been carried out recently dealing with *syn*-[3.3]metacyclophanes [1,4] and *syn*-[3.3](2,6)pyridinophanes,[5] this is the first report, to the best of our knowledge, of an *anti*-[3.3]metacyclophane *X*-ray investigation.

Experimental

Crystal Data.—$C_{20}H_{24}S_4$, *M* 392.7, monoclinic, space group $P2_1/c$, a = 8.585(2), b = 15.189(3), c = 7.967(2) Å, β = 115.75(2)°, Z = 2, D_c = 1.394 g cm^{-3}, μ(Mo-K_α) = 4.87 cm^{-1}.

Crystallographic Measurements.—Intensity data were obtained from a crystal of dimensions 0.10 × 0.38 × 0.40 mm on an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation (λ = 0.710 73 Å). One quadrant of data having 1° ⩽ θ ⩽ 25° was measured by ω–2θ scans of variable rate, designed to yield $I > 50\sigma(I)$ for all significant reflections. Background, Lorentz, and polarization corrections were applied to the data. Absorption corrections were based upon ψ scans of reflections near χ = 90°, and the minimum relative transmission factor was 0.874. Averaging redundant data led to 1 647 unique reflections, of which 1 132 had $F_o > 3\sigma(F_o)$, and were used in the refinement.



	X	R	R′	*m*	*n*
(1)	S	H, Me, OMe, Cl	H	1	1
(2)	S	Me	Me	2	0
(3)	S	Me	Me	2	1
(4)	CH_2	Me	Me	1	1

Structure Analysis.—The structure was solved by direct methods (MULTAN 78) [6] and refined by full-matrix least-squares based upon *F* with weights $w = \sigma^{-2}(F_o)$. Non-hydrogen atoms were treated anisotropically. Hydrogen atoms were located by difference maps and included as fixed contributions to the structure factors after their refinement failed. Convergence was achieved with R = 0.036, R_w = 0.047, GOF = 1.559, and maximum residual 0.25 e Å^{-3}. For structure factor tables see Supplementary Publication No. SUP 23754 (9 pp.).†

Results and Discussion

The molecular structure of (4) consists of discrete molecules; Figures 1 and 2 show perspective and side views of the molecule, respectively, with the atomic labelling scheme. Refined co-ordinates are given in Table 1. The assigned co-ordinates for hydrogen atoms are reported in Table 2, while the interatomic bond lengths and angles are listed in Table 3, with their estimated standard deviations.

The molecule has a crystallographic centre of symmetry, and in agreement with previous ^{1}H n.m.r. observations [2] is found in the *anti*-form. The two benzene rings are displaced stepwise with only small deviation from ring planarity [average deviation: 0.025(3) Å; maximum: 0.047(3) Å]. The averaged bond-length values of C_{Ar}–S (1.781 Å), C(10)–S (1.810 Å), and exocyclic C–C (1.511 Å) are normal. The dimensions in the benzene ring vary significantly. Bond distances in the most crowded parts of the molecule are the longest, ranging from 1.402(3) [C(2)–C(3)] to 1.412(3) Å [C(1)–C(6)]; those in the least crowded parts, namely C(4)–

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† For details of the Supplementary Publications Scheme see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

Table 1. Positional and thermal parameters and their estimated standard deviations[a]

The form of the anisotropic thermal parameter is: $\exp\{-[B(1,1)^*h^2 + B(2,2)^*k^2 + B(3,3)^*l^2 + B(1,2)^*hk + B(1,3)^*hl + \mathrm{B}(2,3)^*kl]\}$.

Atom	x	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
S(1)	0.927 64(8)	0.136 28(5)	0.228 30(9)	0.013 34(10)	0.003 06(3)	0.011 8(1)	0.002 00(10)	0.008 7(2)	0.001 7(1)
S(2)	1.319 19(8)	−0.155 87(5)	0.580 82(10)	0.012 19(9)	0.002 38(3)	0.022 5(1)	0.002 09(9)	0.015 8(2)	0.000 9(1)
C(1)	1.124 9(3)	0.088 8(2)	0.392 8(3)	0.009 9(3)	0.002 7(1)	0.011 9(4)	−0.000 3(3)	0.011 5(5)	0.000 5(4)
C(2)	1.141 6(3)	−0.003 3(2)	0.403 8(3)	0.009 7(3)	0.002 4(1)	0.012 3(4)	−0.000 4(3)	0.011 6(5)	−0.000 6(3)
C(3)	1.287 5(3)	−0.040 1(2)	0.549 6(3)	0.010 7(3)	0.002 5(1)	0.013 8(4)	0.000 2(3)	0.013 4(5)	0.000 0(4)
C(4)	1.420 8(3)	0.013 6(2)	0.673 9(3)	0.010 0(3)	0.003 2(1)	0.012 9(4)	0.000 4(4)	0.010 1(5)	−0.000 0(4)
C(5)	1.406 1(3)	0.103 5(2)	0.646 7(4)	0.009 8(4)	0.003 2(1)	0.015 9(4)	−0.002 7(4)	0.010 2(6)	−0.002 9(4)
C(6)	1.262 4(3)	0.143 7(2)	0.508 6(3)	0.011 6(3)	0.002 3(1)	0.015 2(4)	−0.000 7(3)	0.014 3(5)	−0.000 2(4)
C(7)	1.006 7(4)	−0.059 8(2)	0.255 7(4)	0.014 6(4)	0.002 6(1)	0.013 3(4)	−0.001 5(4)	0.009 5(6)	−0.002 5(4)
C(8)	1.581 2(4)	−0.023 7(2)	0.831 2(4)	0.011 3(4)	0.004 3(1)	0.016 3(5)	0.001 5(4)	0.007 2(7)	−0.000 2(5)
C(9)	1.263 4(4)	0.242 3(2)	0.486 1(4)	0.016 6(5)	0.002 6(1)	0.021 4(5)	−0.003 3(4)	0.014 5(8)	−0.000 1(5)
C(10)	0.861 3(3)	0.196 9(2)	0.382 1(4)	0.015 2(4)	0.002 0(1)	0.019 0(5)	0.000 2(4)	0.014 2(7)	0.000 3(4)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table 2. Assigned co-ordinates for hydrogen atoms

Atom	x	y	z	B,A2
H(5)	1.499	0.140	0.727	3.0
H(71)	0.988	−0.038	0.111	6.0
H(72)	0.899	−0.054	0.263	6.0
H(73)	1.041	−0.120	0.275	6.0
H(81)	1.651	−0.050	0.779	6.0
H(82)	1.549	−0.069	0.894	6.0
H(83)	1.644	0.020	0.916	6.0
H(91)	1.201	0.269	0.572	6.0
H(92)	1.199	0.259	0.359	6.0
H(93)	1.378	0.264	0.530	6.0
H(101)	0.825	0.247	0.328	3.0
H(102)	0.960	0.202	0.489	3.0

Table 3. Interatomic distances and angles for (4) including selected non-bonded intramolecular contacts[a]

Bond lengths (Å)

Bond	Å	Bond	Å
S(1)-C(1)	1.782(2)	C(1)-C(2)	1.405(3)
S(1)-C(10)	1.811(2)	C(2)-C(3)	1.402(3)
S(2)-C(3)	1.780(2)	C(3)-C(4)	1.404(3)
S(2)-C(10)	1.810(2)	C(4)-C(5)	1.380(3)
C(2)-C(7)	1.511(3)	C(5)-C(6)	1.388(3)
C(4)-C(8)	1.512(3)	C(6)-C(1)	1.412(3)
C(6)-C(9)	1.509(3)		

Bond angles (°)

Angle	°	Angle	°
C(1)-S(1)-C(10)	100.7(1)	C(2)-C(3)-C(4)	121.0(2)
S(1)-C(10)-S(2)	118.6(1)	C(3)-C(4)-C(8)	122.5(2)
C(10)-S(2)-C(3)	105.9(1)	C(3)-C(4)-C(5)	118.2(2)
S(1)-C(1)-C(2)	119.2(2)	C(8)-C(4)-C(5)	119.3(2)
S(1)-C(1)-C(6)	119.9(2)	C(4)-C(5)-C(6)	123.3(2)
S(2)-C(3)-C(2)	122.4(2)	C(5)-C(6)-C(9)	118.8(2)
S(2)-C(3)-C(4)	116.5(2)	C(5)-C(6)-C(1)	117.4(2)
C(1)-C(2)-C(7)	119.6(2)	C(9)-C(6)-C(1)	123.7(2)
C(7)-C(2)-C(3)	121.8(2)	C(6)-C(1)-C(2)	120.9(2)
C(1)-C(2)-C(3)	118.6(2)		

Non-bonded contacts (Å)

Contact	Å	Contact	Å
C(7) · · · C(10)	3.332(3)	S(1) · · · C(9)	3.159(2)
C(9) · · · C(10)	3.254(3)	S(2) · · · C(8)	3.028(2)

[a] Estimated standard deviations in parentheses

C(5) and C(5)-C(6), are the shortest, 1.380(3) and 1.388(3) Å, respectively. The endocyclic C-C-C angles average 119.9°, but again significantly smaller angles [from 117.4(2) to 118.6(2)°] are found at carbon atoms bearing the methyl

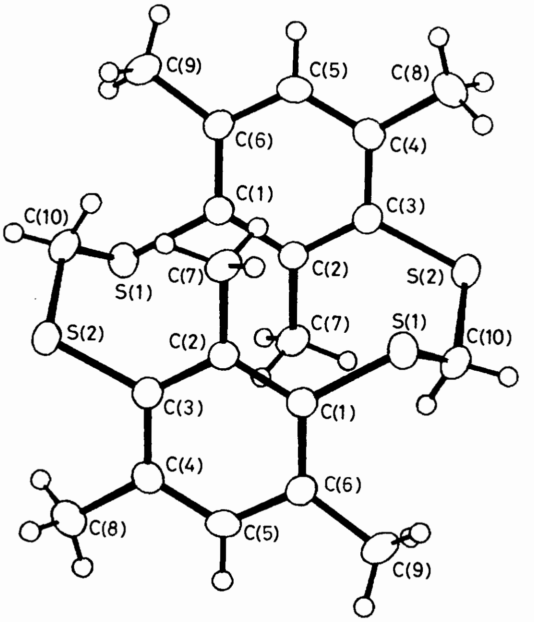

Figure 1. The molecular structure and atomic numbering scheme of compound (4)

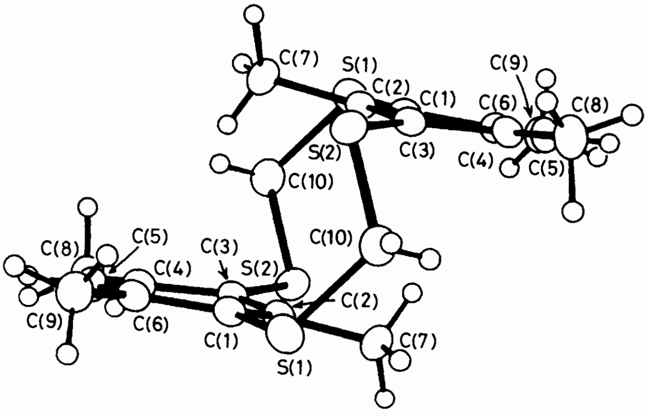

Figure 2. A side view of (4) showing the out-of-plane deformation of substituents

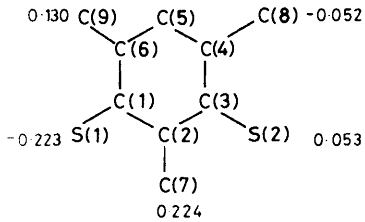

Figure 3. Displacement (Å) of atoms from the best plane of phenyl ring. E.s.d.s of displacements are 0.002—0.003 Å for C and 0.001 Å for S

substituents. The bond angle at C(5) is the largest one [123.3(2)°].

The C(1)-S(1)-C(10) and C(10)-S(2)-C(3) bond angles are 100.7(1) and 105.9(1)°, respectively. In *syn*-1,3,10,12-tetrathia-[3.3](2,6)pyridinophane the corresponding C-S-C angles averaged 100.6(2)°.[5] The S(1)-C(10)-S(2) bond angle [118.6(1)°] is greater than the accepted tetrahedral angle of 109.5°. This angle might be described as having been enlarged to relieve the steric interactions associated with the close proximity of C(7) and C(9) methyl substituents to the bridging C(10) methylenes, as well as to avoid sulphur lone pair–lone pair interactions.

Deviations of substituent atoms from the least-squares plane of the aromatic ring are shown in Figure 3. Remarkably, C(7) and C(9) methyl groups lie out of the plane of the phenyl carbon atoms, and deviate from the main plane toward the outer part of the molecule. Conversely, S(1) atoms bend out of plane on the opposite side from the methyl groups, as a compromise of the steric interactions between the bridged methylenes and C(7) and C(9) methyl substituents. Selected non-bonded intramolecular contacts are shown in Table 3.

The C(10)-S(1)-C(1)-C(2) (119.9°) and C(2)-C(3)-S(2)-C(10) (−60.9°) torsion angles are greater than those observed for *syn*-1,3,10,12-tetrathia[3.3](2,6) pyridinophane (NCSC torsion angles *ca.* 48°).[5] Furthermore, quite different torsion angles around C(10)-S(2) and C(10)-S(1) bonds are observed (see Table 4 for selected torsion angles). In particular, the unusually small torsion angles around C(10)-S(1) bonds (−43.5°) provide further support to the unlikelihood of the structurally related *anti*-hexathia[3.3]metacyclophanes, predicted on the basis of simple considerations on the nature and geometry of the trisulphide bridging chains.[1-3]

Table 4. Selected torsion angles in (4)

Atoms with primes are related to those in the co-ordinate table by inversion through 1, 0, $\frac{1}{2}$ $(2 - x, -y, 1 - z)$.

Atom 1	Atom 2	Atom 3	Atom 4	Angle (°)
C(10)	S(1)	C(1)	C(2)	119.9
S(1)	C(1)	C(2)	C(3)	−171.6
C(1)	C(2)	C(3)	S(2)	178.3
C(2)	C(3)	S(2)	C(10′)	−60.9
C(3)	S(2)	C(10′)	S(1′)	−43.5
S(2)	C(10′)	S(1′)	C(1′)	107.5

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