

Structure of O₆[9]aneS₃ (1,4,7-Trithiacyclononane 1,1,4,4,7,7-Hexaoxide)

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(Received 31 October 1990; accepted 29 April 1991)

Abstract. C₆H₁₂O₆S₃, $M_r = 276.31$, monoclinic, $P2_1/n$, $a = 5.9978$ (5), $b = 12.9947$ (16), $c = 13.8201$ (12) Å, $\beta = 101.294$ (8)°, $V = 1056.3$ Å³, $Z = 4$, $D_x = 1.737$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.68$ mm⁻¹, $F(000) = 576$, $T = 298$ K, $R = 0.0246$ for 1672 unique observed reflections. Although O₆[9]aneS₃ lacks the crystallographically imposed C_3 symmetry of the parent [9]aneS₃, it also adopts a symmetrical [333] conformation in the crystal.

Experimental. Compound prepared by oxidation of [9]aneS₃ using H₂O₂/H₂O/glacial acetic acid (Küppers, Wieghardt, Nuber, Weiss, Bill & Trautwein, 1987) at 333 K, crystals obtained by diffusion of MeOH into DMSO solution. Colourless columnar crystal, 0.18 × 0.21 × 0.42 mm; Stoe Stadi-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ X-radiation; cell parameters from 2θ values of 18 reflections measured at $\pm \omega$ ($30 \leq 2\theta \leq 32^\circ$). For data collection, ω - 2θ scans employing the learnt-profile method (Clegg, 1981), $2\theta_{\text{max}} = 50^\circ$, $h - 6 \rightarrow 6$, $k 0 \rightarrow 15$, $l 0 \rightarrow 16$; no significant crystal movement or decay; 1937 unique reflections, giving 1672 with $F > 6\sigma(F)$ for structure solution [by automatic direct methods (Sheldrick, 1986)] and refinement [using full-matrix least squares on F (Sheldrick, 1976)]. Anisotropic thermal parameters for all non-H atoms, H atoms refined freely with a common U_{iso} of 0.0368 (16) Å². At final convergence $R = 0.0246$, $wR = 0.0370$, $S = 1.322$ for 173 parameters; $(\Delta/\sigma)_{\text{max}}$ in final cycle 0.07, maximum and minimum residues in final ΔF synthesis 0.35, -0.28 e Å⁻³ respectively. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000225F^2$ gave satisfactory agreement analyses. Scattering factors were inlaid (Sheldrick, 1976). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, while bond lengths, angles and torsion angles appear in Table 2.† Fig. 1 was generated using an interactive version

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å²) with e.s.d.'s in parentheses
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} |
|-------|---------------|--------------|--------------|-----------------|
| S(1) | 0.22286 (7) | 0.81848 (3) | 0.71777 (3) | 0.0236 (3) |
| O(1A) | 0.14158 (22) | 0.92314 (10) | 0.71563 (10) | 0.0343 (7) |
| O(1B) | 0.44842 (22) | 0.79873 (11) | 0.70156 (10) | 0.0355 (8) |
| C(2) | 0.2063 (3) | 0.76402 (15) | 0.83449 (12) | 0.0266 (9) |
| C(3) | -0.0323 (3) | 0.76380 (14) | 0.85749 (13) | 0.0263 (9) |
| S(4) | -0.09831 (8) | 0.64568 (3) | 0.91200 (3) | 0.0268 (3) |
| O(4A) | -0.32594 (23) | 0.65627 (11) | 0.92914 (10) | 0.0417 (9) |
| O(4B) | 0.08376 (25) | 0.62255 (12) | 0.99258 (9) | 0.0425 (8) |
| C(5) | -0.1009 (4) | 0.54884 (14) | 0.82013 (13) | 0.0288 (10) |
| C(6) | -0.2696 (3) | 0.57101 (15) | 0.72422 (13) | 0.0276 (10) |
| S(7) | -0.16383 (8) | 0.55492 (3) | 0.61309 (3) | 0.0255 (3) |
| O(7A) | -0.33424 (25) | 0.59498 (12) | 0.53507 (10) | 0.0422 (8) |
| O(7B) | -0.09129 (25) | 0.45034 (10) | 0.60703 (9) | 0.0370 (8) |
| C(8) | 0.0818 (3) | 0.63461 (14) | 0.62433 (14) | 0.0285 (10) |
| C(9) | 0.0265 (3) | 0.74957 (14) | 0.62732 (12) | 0.0277 (10) |

Table 2. Bond lengths (Å), angles (°) and torsion angles (°) with e.s.d.'s in parentheses

| | | | |
|----------------------|--------------|----------------------|--------------|
| S(1)—O(1A) | 1.4431 (14) | S(4)—C(5) | 1.7855 (20) |
| S(1)—O(1B) | 1.4370 (14) | C(5)—C(6) | 1.529 (3) |
| S(1)—C(2) | 1.7820 (19) | C(6)—S(7) | 1.7852 (19) |
| S(1)—C(9) | 1.7817 (19) | S(7)—O(7A) | 1.4306 (15) |
| C(2)—C(3) | 1.525 (3) | S(7)—O(7B) | 1.4344 (14) |
| C(3)—S(4) | 1.7881 (19) | S(7)—C(8) | 1.7826 (19) |
| S(4)—O(4A) | 1.4373 (15) | C(8)—C(9) | 1.533 (3) |
| S(4)—O(4B) | 1.4306 (15) | | |
| O(1A)—S(1)—O(1B) | 119.32 (8) | O(4A)—S(4)—C(5) | 107.96 (9) |
| O(1A)—S(1)—C(2) | 108.32 (8) | O(4B)—S(4)—C(5) | 107.73 (9) |
| O(1A)—S(1)—C(9) | 106.56 (8) | S(4)—C(5)—C(6) | 113.31 (13) |
| O(1B)—S(1)—C(2) | 106.93 (8) | C(5)—C(6)—S(7) | 115.92 (13) |
| O(1B)—S(1)—C(9) | 108.30 (8) | C(6)—S(7)—O(7A) | 106.49 (9) |
| C(2)—S(1)—C(9) | 106.81 (8) | C(6)—S(7)—O(7B) | 108.92 (8) |
| S(1)—C(2)—C(3) | 114.22 (13) | C(6)—S(7)—C(8) | 106.50 (9) |
| C(2)—C(3)—S(4) | 112.56 (13) | O(7A)—S(7)—O(7B) | 118.74 (9) |
| C(3)—S(4)—O(4A) | 106.45 (8) | O(7A)—S(7)—C(8) | 108.10 (9) |
| C(3)—S(4)—O(4B) | 108.06 (9) | O(7B)—S(7)—C(8) | 107.49 (8) |
| C(3)—S(4)—C(5) | 106.10 (9) | S(7)—C(8)—C(9) | 112.89 (13) |
| O(4A)—S(4)—O(4B) | 119.79 (9) | S(1)—C(9)—C(8) | 113.08 (13) |
| O(1A)—S(1)—C(2)—C(3) | 58.70 (15) | O(4A)—S(4)—C(5)—C(6) | 56.20 (15) |
| O(1B)—S(1)—C(2)—C(3) | -171.51 (13) | O(4B)—S(4)—C(5)—C(6) | -173.12 (13) |
| C(9)—S(1)—C(2)—C(3) | -55.74 (15) | S(4)—C(5)—C(6)—S(7) | 133.28 (12) |
| O(1A)—S(1)—C(9)—C(8) | -176.74 (13) | C(5)—C(6)—S(7)—O(7A) | -170.91 (14) |
| O(1B)—S(1)—C(9)—C(8) | 53.73 (15) | C(5)—C(6)—S(7)—O(7B) | 59.92 (16) |
| C(2)—S(1)—C(9)—C(8) | -61.12 (15) | C(5)—C(6)—S(7)—C(8) | -55.72 (16) |
| S(1)—C(2)—C(3)—S(4) | 137.52 (11) | C(6)—S(7)—C(8)—C(9) | -65.72 (15) |
| C(2)—C(3)—S(4)—O(4A) | -179.80 (13) | O(7A)—S(7)—C(8)—C(9) | 48.37 (15) |
| C(2)—C(3)—S(4)—O(4B) | 50.33 (15) | O(7B)—S(7)—C(8)—C(9) | 177.67 (13) |
| C(2)—C(3)—S(4)—C(5) | -64.98 (15) | S(7)—C(8)—C(9)—S(1) | 137.22 (11) |
| C(3)—S(4)—C(5)—C(6) | -57.59 (15) | | |

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† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54149 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of ORTEPII (GX; Mallinson & Muir, 1985) and shows (a) a projection onto the least-squares molecular plane with the atom-numbering scheme used and (b) an orthogonal view illustrating the conformation

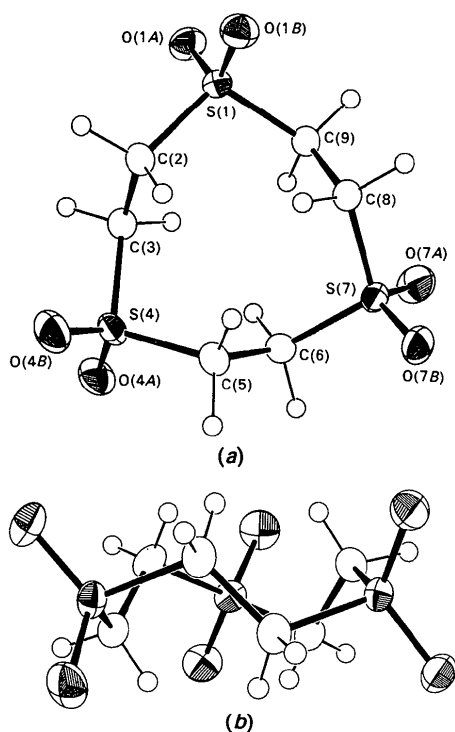


Fig. 1. (a) A general view of the O₆[9]aneS₃ molecule showing the atom-numbering scheme: thermal ellipsoids are drawn at the 30% probability level, except those of H which have artificial radii of 0.1 Å for clarity. (b) An orthogonal view showing the conformation of the nine-membered ring.

of the ring. Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

Related literature. Structure determinations have been reported for [9]aneS₃ (Glass, Wilson & Setzer, 1980) and for other oxidation products such as the sulfoxide in [Fe([9]aneS₃){[9]aneS₂(SO)}]²⁺ (Küppers, Wieghardt, Nuber, Weiss, Bill & Trautwein, 1987) and the bicyclic sulfonium cation 4,7-dithia-1-thioniabicyclo[4.3.0]nonane (Blake, Holder, Hyde, Schröder & Taylor, 1991).

We thank the SERC for support.

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Acta Cryst. (1991). **C47**, 2718–2720

Structure of Tris(5-acetyl-3-thienyl)methane–Benzene (2/1) Inclusion Compound

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(Received 10 December 1990; accepted 25 June 1991)

Abstract. 2C₁₉H₁₆O₃S₃·C₆H₆, *M_r* = 855.2, triclinic, *P* $\bar{1}$, *a* = 14.197 (5), *b* = 13.560 (5), *c* = 11.538 (5) Å, α = 104.45 (5), β = 103.40 (5), γ = 89.68 (5)°, *V* = 2089 (1) Å³, *Z* = 2, *D_x* = 1.36 Mg m⁻³, λ (Mo *K*α) = 0.7107 Å, μ = 0.323 mm⁻¹, *F*(000) = 892, *T* = 298 K, final *wR* = 0.060, *R* = 0.083 for 4196 observed reflections with *F* > 2σ(*F_o*) and 580 variable parameters. The clathrate structure consists of two tris(5-acetyl-3-thienyl)methane host molecules and one benzene guest molecule. The shortest non-hydrogen non-bonded distance between host and guest molecules is 3.437 Å [O(6)⋯C(43)]. The guest molecule interacts with only one acetylthienyl substituent of each host molecule.

Experimental. The host molecule, tris(5-acetyl-3-thienyl)methane (TATM), is formed by the reaction of chloroform and 2-acetylthiophene (Yakubov, Sudarushkin, Belenkii & Gold'Farb, 1973), and crystallization with many solvents yields 2/1 solute/solvent complexes (Bin Din & Meth-Cohn, 1977). Crystallization of TATM with benzene yielded pale-yellow crystals with approximate dimensions 0.3 × 0.3 × 0.3 mm, m.p. 379–383 K. Philips PW 1100 diffractometer, graphite-monochromated radiation, unit cell from 25 reflections ($\theta < 13^\circ$), 7391 reflections for $3 \leq \theta \leq 24^\circ$ in the range $-16 \leq h \leq 16$, $-15 \leq k \leq 15$, $0 \leq l \leq 13$ using $\omega/2\theta$ scans, scan speed 0.048° s⁻¹, scan width 1.20°. Three standard