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Structure of 2,5,7,9-Tetrathiabicyclo[4.3.0]non-1(6)-en-8-one (TTBEO)

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Abstract. $C_5H_4OS_4$, $M_r = 208{\cdot}32$, monoclinic, $P2_1/n$, $a = 6{\cdot}650$ (7), $b = 16{\cdot}534$ (5), $c = 7{\cdot}272$ (8) Å, $\beta = 97{\cdot}87$ (7)°, $V = 792{\cdot}2$ (8) Å^3, $Z = 4$, D_m (295 K) = 1·69, $D_x = 1{\cdot}75$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 10{\cdot}8$ cm^{-1}, $F(000) = 424$, $T = 295$ K, $R = 0{\cdot}0497$, $wR = 0{\cdot}0645$, 743 observed reflections with $I > 3\sigma(I)$. The structure found here around the tetrathioethylene unit is essentially the same as that reported for the 5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT) anion. This molecule is the precursor to a number of new thiolenes. Bond lengths: C=C = 1·337 (8) Å; mean C–S = 1·756 (6) Å; C=O = 1·226 (7) Å; mean C–S–C bond angle 98·8 (3)°.

Experimental. Title compound prepared by previously described methods (Hartke, Kissel, Quante & Matusch, 1980). D_m by flotation in potassium iodide solution of increasing concentration. Transparent yellow crystals suitable for X-ray analysis obtained by recrystallization from deuterated chloroform. Crystal size 0·20 × 0·30 × 0·40 mm; Nicolet *R3m* diffractometer, graphite monochromator; accurate unit-cell parameters (Campana, 1986) from least-squares refinement of 14 reflections (θ range 10–20°); 1 standard reflection (110) measured every 50 reflections, 4% variation from start to finish. Range of *hkl*: $-7 \le h \le 7$, $0 \le k \le 17$, $0 \le l \le 8$. Data taken as $\theta/2\theta$ scans at room temperature, 999 data measured ($3 \le 2\theta \le 42°$) with 743 observed [$I \ge 3\sigma(I)$]; corrections for Lorentz and polarization effects (decay correction ignored). Empirical absorption correction applied. Max. and min. transmission coefficients 0·651 and 0·561, respectively. Trial structure from direct methods, refined by block-diagonal least-squares procedures, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/|\sigma^2(F) + G(F)^2|$, $G = 0{\cdot}016$; non-H atoms anisotropic, H atoms idealized coordinates calculated, not refined, isotropic thermal parameters assigned as 0·098 Å^2; $R = 0{\cdot}0497$, $wR = 0{\cdot}0645$, $S = 0{\cdot}716$. Scattering factors for S, O, C and H from *International Tables for X-ray Crystallography* (1962). Anomalous-dispersion corrections for S applied towards end of refinement (Cromer, 1965). In final cycle, largest shift in any parameter was 0·007σ. Final difference map showed no peaks larger than 0·38 e Å^{-3} at 1·15 Å from C(1). Calculations carried out with Nicolet *XTL* and *SHELXTL* 5·1 structure-solving package on a Nicolet *R3m/u* crystallographic system (Sheldrick, 1980).

The atomic fractional coordinates with their standard deviations and U_{eq} values (Hamilton, 1959) are given in Table 1.* The structure and numbering scheme are shown in Fig. 1. Table 2 contains a listing of interatomic bond distances and angles with their e.s.d.'s.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43369 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

	x	*y*	*z*	U_{eq}*
C(1)	−1255 (9)	9482 (3)	2204 (7)	45 (2)
S(2)	−3371 (2)	8849 (1)	1810 (3)	70 (1)
C(3)	−2294 (12)	7902 (4)	2695 (10)	78 (3)
C(4)	−399 (9)	7686 (4)	2006 (9)	77 (3)
S(5)	1759 (2)	8302 (1)	2742 (2)	61 (1)
C(6)	709 (8)	9286 (3)	2579 (7)	43 (2)
S(7)	−1819 (2)	10514 (1)	2136 (2)	53 (1)
C(8)	695 (9)	10844 (3)	2624 (7)	49 (2)
S(9)	2449 (2)	10058 (1)	2944 (2)	52 (1)
O	1147 (7)	11564 (3)	2690 (5)	65 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

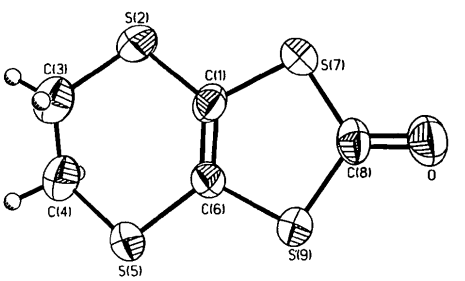

Fig. 1. The structure and numbering scheme for TTBEO. All non-H atoms are represented as thermal ellipsoids scaled to enclose 50% probability. H atoms are represented as spheres with 0·15 Å radius in this illustration.

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

C(1)–S(2)	1·746 (6)	C(1)–C(6)	1·337 (8)
C(1)–S(7)	1·747 (6)	S(2)–C(3)	1·804 (7)
C(3)–H(3*A*)	0·960 (1)	C(3)–H(3*B*)	0·960 (1)
C(3)–C(4)	1·462 (10)	C(4)–H(4*A*)	0·960 (1)
C(4)–H(4*B*)	0·960 (1)	C(4)–S(5)	1·781 (6)
S(5)–C(6)	1·767 (5)	C(6)–S(9)	1·720 (5)
S(7)–C(8)	1·748 (6)	C(8)–S(9)	1·741 (6)
C(8)–O	1·226 (7)		

S(2)–C(1)–C(6)	129·1 (4)	S(2)–C(1)–S(7)	114·6 (3)
C(6)–C(1)–S(7)	116·3 (4)	C(1)–S(2)–C(3)	100·9 (3)
S(2)–C(3)–H(3*A*)	108·3 (2)	S(2)–C(3)–H(3*B*)	108·3 (2)
H(3*A*)–C(3)–H(3*B*)	109·5 (1)	S(2)–C(3)–C(4)	114·1 (5)
H(3*A*)–C(3)–C(4)	108·3 (4)	H(3*B*)–C(3)–C(4)	108·3 (4)
C(3)–C(4)–H(4*A*)	107·5 (4)	C(3)–C(4)–H(4*B*)	107·6 (4)
H(4*A*)–C(4)–H(4*B*)	109·5 (1)	C(3)–C(4)–S(5)	117·0 (5)
H(4*A*)–C(4)–S(5)	107·5 (2)	H(4*B*)–C(4)–S(5)	107·6 (2)
C(4)–S(5)–C(6)	102·2 (3)	C(1)–C(6)–S(5)	127·1 (4)
C(1)–C(6)–S(9)	118·0 (4)	S(5)–C(6)–S(9)	115·0 (3)
C(1)–S(7)–C(8)	95·9 (3)	S(7)–C(8)–S(9)	113·5 (3)
S(7)–C(8)–O	122·2 (5)	S(9)–C(8)–O	124·3 (5)
C(6)–S(9)–C(8)	96·3 (3)		

Related literature. We have published the synthesis of 5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT) and the crystal structure of $[N(C_2H_5)_4]^+.[Ni(DDDT)_2]^-$ (Vance, Bereman, Bordner, Hatfield & Helms, 1985).

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Structure of 7-Phenylthio-1,4-dioxaspiro[4.5]decan-8-one

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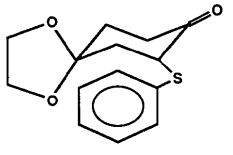
Abstract. $C_{14}H_{16}O_3S$, $M_r = 264·34$, monoclinic, $P2_1/c$, $a = 14·291$ (7), $b = 5·665$ (2), $c = 15·872$ (5) Å, $\beta = 94·63$ (3)°, $V = 1280·8$ (9) Å^3, $Z = 4$, $D_x = 1·37$ (163 K), $D_m = 1·32$ g cm^{-3} (295 K), λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2·38$ cm^{-1}, $F(000) = 560$, $T = 163$ K, $R = 0·0450$ for 2005 unique observed reflections. The cyclohexanone ring is in the chair conformation. The phenylthio group is forced to be in the equatorial position by the presence of the dioxolane moiety. There is a close, non-bonded intramolecular S···O contact [2·802 (2) Å] involving the carbonyl O atom.

Experimental. Title compound synthesized by extension of the methods described by Trost, Salzmann & Hiroi (1976) to monoketalized 1,4-cyclohexanedione prepared according to Haslanger & Lawton (1974).



Colorless plate, cut from a larger crystal, 0·06 × 0·31 × 0·50 mm from hexane. Crystal density by flotation method in aqueous $ZnCl_2$. Syntex $P2_1$ diffractometer, graphite monochromator, Syntex LT-1 low-temperature delivery system (163 K). Lattice parameters from least-squares refinement of 45 reflections with $18·0 < 2\theta < 25·2°$. ω-scan technique (5079 reflections, 2578 unique, $R_{int} = 0·038$), 2θ range 4·0–52·5°, 1° ω scan at 2·5–5·0° min^{-1} ($h = -4 \rightarrow 17$, $k = -7 \rightarrow 6$, $l = -19 \rightarrow 19$). The space group was determined from systematic absences. Four reflections ($\bar{3}00$, $\bar{1}\bar{1}2$, 211, $1\bar{1}\bar{1}$) remeasured every 96 reflections to monitor instrument and crystal stability. Analysis of these data indicated that no such corrections were necessary. Data corrected for Lp effects and absorption (based on crystal shape; transmission factors 0·932–0·987). Data reduction described in Riley & Davis (1976). Reflections having $F_o < 4\sigma(F_o)$ considered unobserved (573 reflections). Structure solved by the heavy-atom method and refined by full-matrix least-squares procedures (Sheldrick, 1976) with anisotropic thermal parameters for the non-H atoms. H atoms from a ΔF map and refined with isotropic thermal parameters; 227 parameters refined. $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = [0·5kI^{-1/2}\{[\sigma(I)]^2 + (0·04I)^2\}^{1/2}]$. Intensity, I, given by $(I_{peak} - I_{background}) \times$ (scan rate); 0·04 is a factor to downweight intense reflections and to account for instrument instability and k is the correction due to Lp

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