Tetrakis(methylthio)ethylene*

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Abstract. $(CH_3S)_2C=C(SCH_3)_2$, $(C_6H_{12}S_4)$, $M_r = 212.4$, triclinic, $P\bar{1}$, $a = 6.451$ (1), $b = 7.883$ (1), $c = 5.216$ (1) Å, $\alpha = 92.44$ (2), $\beta = 90.45$ (2), $\gamma = 111.78$ (1)°, $V = 246.0$ Å^3, $Z = 1$, $D_x = 1.43$ (−35°C), $D_m = 1.42$ (23°C) g cm^{-3}. Full-matrix least-squares refinement of 1356 reflections collected at −35°C on a Syntex $P2_1$ diffractometer yielded a final R of 0.023. At each end of the molecule, methyl groups lie above and below the ethylene plane. The C=C−S—Me torsion angles are 134.3 and 135.0°. The conformation at each end of the molecule is thus *gauche–gauche*.

Introduction. Single crystals of the title compound, TMTE, were obtained by slow evaporation of a pentane solution. Intensity-data collection details are given in Table 1. Standard deviations were assigned to the intensities, and data reduction was effected as described earlier (Riley & Davis, 1976). Acceptance of 1356 reflections for structural analysis was based on the following criteria: $I/\sigma(I) \geq$ XSR and $I_{pk}/I_{end} \geq$ XPR where I_{pk} is the maximum of the peak profile, I_{end} is the average of the ends of the profile and XSR = XPR = 2.0.

* Perheterosubstituted Ethanes and Ethylenes. I.

Table 1. *Experimental summary*

Syntex $P2_1$ autodiffractometer equipped with graphite
  monochromator and Syntex LT-1 low-temperature flow system
Radiation: Mo $K\alpha$, $\lambda = 0.71069$ Å
Mode: ω-scan technique, recentered automatically after every 700
  reflections
Scan range: symmetrically over 0.79° about the $K\alpha_{1,2}$ maximum
Scan rate: variable, 1.5 to 5.0° min^{-1}
Background: offset 1.0° and −1.0° in ω from $K\alpha_{1,2}$ maximum
Check reflections: four remeasured after every 96 reflections;
  analysis† of 20 sets of check reflections indicated that a decay
  correction was not required
1774 reflections measured, $4° \leq 2\theta \leq 65°$
Data-crystal dimensions: 0.24 × 0.21 × 0.50 mm parallel to
  directions **a***, **b***, **c***
Data-crystal faces: seven faces of {100}, {010}, {001} and {101}
Data-crystal volume: 0.0169 mm^3
Mosiac character: peak widths at half height, ~0.4° in ω
Absorption coefficient: μ(Mo $K\alpha$) = 8.58 cm^{-1}
Transmission-factor range: 0.82 to 0.84

† Henslee & Davis (1975).

Positions of the non-hydrogen atoms were determined from a sharpened Patterson map. Full-matrix least-squares refinement (*NUCLS*: J. A. Ibers's version of *ORFLS*) of positional and anisotropic thermal parameters of these atoms resulted in $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.039$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.075$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weights, w, are $1/\sigma(|F|)^2$. The H atoms were then located in a difference map. Addition of H positional parameters and an extinction parameter to the refinement yielded a final R of 0.023 and R_w of 0.031.† The isotropic thermal factor for each H atom was fixed at 1.0 Å^2 greater than that for the C to which it is bonded. No correlation coefficients greater than 0.5 were noted during the course of the refinement. Maximum residual difference density was less than 0.24 e Å^{-3}. Atomic scattering factors for S and C were taken from *International Tables for X-ray Crystallography* (1974); those of Stewart, Davidson & Simpson (1965) were used for the H atoms. Real and imaginary anomalous dispersion terms were included for S. The extinction parameter refined to 1.02 (3) × 10^{-4}. Atomic parameters are given in Table 2.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32884 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic parameters, with e.s.d.'s in parentheses*

Atomic fractional coordinates for non-hydrogens appear ×10^4; those for hydrogen appear ×10^3.

	x	y	z	B (Å^2)
S(1)	1961 (1)	−505 (1)	−3142 (1)	
S(2)	−1425 (1)	−2961 (0)	413 (1)	
C(1)	3406 (3)	−1984 (2)	−2329 (4)	
C(2)	−2414 (3)	−4258 (2)	−2580 (3)	
C(3)	119 (2)	−743 (2)	−583 (2)	
H(1)	453 (3)	−178 (3)	−349 (4)	3.98
H(2)	401 (3)	−163 (3)	−76 (4)	3.98
H(3)	249 (4)	−314 (3)	−235 (4)	3.98
H(4)	−371 (3)	−525 (3)	−222 (4)	3.72
H(5)	−285 (3)	−358 (3)	−370 (4)	3.72
H(6)	−140 (3)	−452 (3)	−335 (4)	3.72

Discussion. The chemical properties and spectra (ESR, photoelectron) of a wide variety of ethane hexathio-ethers, ethylene tetrathioethers and related perhetero-substituted compounds have been studied by Seebach and his collaborators (see, for example, Stegmann, Scheffler & Seebach, 1975; Bock, Wagner, Wittel, Sauer & Seebach, 1974; and references therein). The structure of one of these compounds has been reported (Roelofsen, Kanters & Seebach, 1974). This is the first in a series of reports of our structural studies of these compounds. A summary paper discussing and comparing structural and conformational details in terms of the chemical and spectroscopic properties of these compounds will appear later (Seebach, Collins & Davis, 1978).

A stereoview of the molecule illustrating the atom-numbering scheme is given in Fig. 1 and metrical details are listed in Table 3. Nonbonded-contact distances were computed with H atom positions which were shifted along their respective C—H bond axes to give C—H bond distances of 1·09 Å.

TMTE occupies a crystallographic inversion center, and displays local $2/m$ symmetry to within 0·02 Å for the C atom positions and to within 0·25 Å for the H atom positions. Deviations from this symmetry are

expressed principally in a 0·7° difference in the C=C—S—Me torsion angles and in 12–17° differences in the C—S—C—H torsion angles (see Table 4). The orientation of the H(4–6) atoms about the C(2)—S(2) bond axis generates approximately equal S(1)···H(5) and S(1)···H(6) intramolecular contacts, 3·16 and 3·10 Å respectively. A different orientation is found for the H(1–3) atoms. The H(1) atom is *trans* to the C(3)—S(1) bond (∠C—S—C—H, −172°). The S(2)···H(2) contact, 3·38 Å, and the S(2)···H(3) contact, 2·92 Å, are not equal. No H···H contacts shorter than the 2·0 Å distance suggested by Baur (1972) are observed, the shortest being H(3)···H(6), 2·12 Å. Inspection of the different crystal-packing environments (Fig. 2) for the two methyl groups has not provided an explanation for the different methyl group orientations.

The S—C(sp^2) distance, 1·764 (1) Å, in TMTE is in excellent agreement with those found for tetrakis-(phenylthio)ethylene (Collins & Davis, 1978), 1·765 (2) to 1·770 (3) Å. The S—C(sp^3) distance in TMTE is 1·804 (2) Å. The S—C(sp^2) and S—C(sp^3) distances found in electron diffraction studies are for methylthioethylene (Samdal & Seip, 1975), 1·748 (5) and 1·806 (6) Å respectively, and for 1,1-bis(methyl-
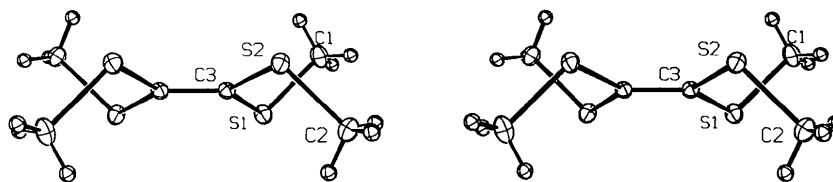

Fig. 1. A stereoview of (MeS)$_2$C=C(SMe)$_2$ illustrating the atom-numbering scheme. Atoms are shown with 20% equiprobability ellipsoids. Hydrogen atoms are shown as 0·15 Å radius spheres.

Table 3. *Metrical details*

Distances (Å) and angles (°) for non-hydrogen atoms

S(1)—S(2)	3·032 (0)	S(2)—C(2)	1·804 (2)	C(3)—S(1)—C(1)	102·5 (1)
S(1)—S(2')	3·161 (0)	S(2)—C(3)	1·765 (1)	C(3)—S(2)—C(2)	103·0 (1)
S(1)—C(1)	1·804 (2)	C(3)—C(3')	1·357 (2)	S(2)—C(3)—S(1)	118·5 (1)
S(1)—C(3)	1·764 (1)			C(3')—C(3)—S(1)	120·8 (1)
				C(3')—C(3)—S(2)	120·7 (1)

Distances (Å) and angles (°) involving hydrogen atoms.

E.s.d.'s in C—H distances are 0·02 Å, in S—C—H angles, 1°, and in H—C—H angles, 2°.

C(1)—H(1)	0·92	S(1)—C(1)—H(1)	106	H(1)—C(1)—H(2)	109
C(1)—H(2)	0·89	S(1)—C(1)—H(2)	108	H(1)—C(1)—H(3)	113
C(1)—H(3)	0·88	S(1)—C(1)—H(3)	112	H(2)—C(1)—H(3)	110
C(2)—H(4)	0·93	S(2)—C(2)—H(4)	107	H(4)—C(2)—H(5)	106
C(2)—H(5)	0·92	S(2)—C(2)—H(5)	110	H(4)—C(2)—H(6)	116
C(2)—H(6)	0·86	S(2)—C(2)—H(6)	113	H(5)—C(2)—H(6)	105

Torsion angles (°)

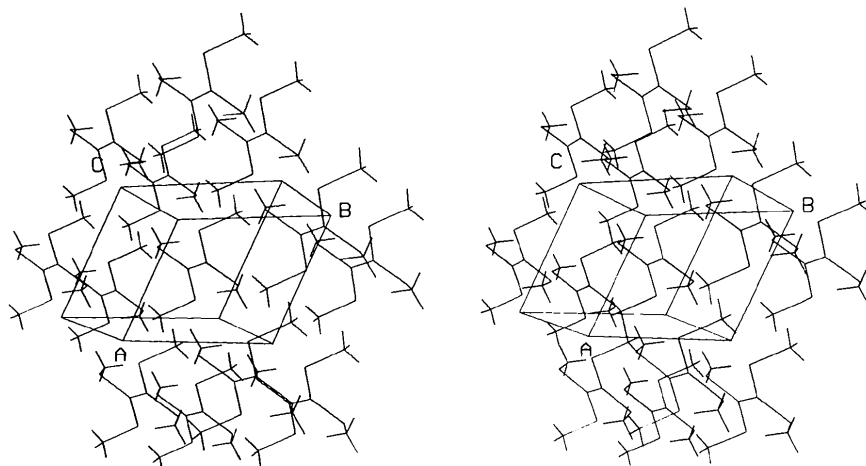| C(3')—C(3)—S(1)—C(1)	134·3	C(3')—C(3)—S(2)—C(2)	135·0
C(3)—S(1)—C(1)—H(1)	−172	C(3)—S(2)—C(2)—H(4)	−155
C(3)—S(1)—C(1)—H(2)	−56	C(3)—S(2)—C(2)—H(5)	−41
C(3)—S(1)—C(1)—H(3)	65	C(3)—S(2)—C(2)—H(6)	77

Fig. 2. Packing diagram for (MeS)$_2$C=C(SMe)$_2$. The unit-cell outline extends from $-\frac{1}{2}$ to $+\frac{1}{2}$ in each direction.

thio)ethylene (Jandal, Seip & Torgrimsen, 1976), 1·762 (5) and 1·817 (5) Å respectively.

References

Baur, W. H. (1972). Acta Cryst. B28, 1456–1465.

Bock, H., Wagner, G., Wittel, K., Sauer, J. & Seebach, D. (1974). Chem. Ber. 107, 1869–1881.

Collins. R. C. & Davis, R. E. (1978). Acta Cryst. B34, 285–287.

Henslee, W. H. & Davis, R. E. (1975). Acta Cryst. B31, 1511–1519.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Jandal, P., Seip, H. M. & Torgrimsen, T. (1976). J. Mol. Struct. 32, 369–377.

Riley, P. E. & Davis, R. E. (1976). Acta Cryst. B32, 381–386.

Roelofsen, G., Kanters, J. A. & Seebach, D. (1974). Chem. Ber. 107, 253–262.

Samdal, S. & Seip, H. M. (1975). J. Mol. Struct. 28, 193–203.

Seebach, D., Collins, R. L. & Davis, R. E. (1978). To be published.

Stegmann, H. B., Scheffler, K. & Seebach, D. (1975). Chem. Ber. 105, 64–70.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

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Abstract. (C$_6$H$_5$S)$_2$C=C(SC$_6$H$_5$)$_2$, (C$_{14}$H$_{10}$S$_4$), M_r = 470·7, orthorhombic, Pbca, a = 9·537 (2), b = 19·418 (4), c = 12·462 (3) Å, V = 2307·7 Å^3, Z = 4, D_x = 1·33 (−35°C), D_m = 1·30 (23°C) g cm^{-3}. Full-matrix least-squares refinement with 1610 reflections collected at −35°C on a Syntex $P2_1$ diffractometer yielded a final R of 0·040. The C=C—S—Ph torsion angles are 135·3 and 142·9°. The conformation at

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