

trans*-1,2-Bis(trimethylsilyl)-1,2-bis(methylthio)ethylene

BY R. C. COLLINS AND RAYMOND E. DAVIS

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, USA

(Received 12 May 1977; accepted 19 July 1977)

Abstract. *trans*-[(CH₃)₃Si](CH₃S)C=C(SCH)₃-[Si(CH₃)₃], (C₁₀H₂₄Si₂S₂), *M_r* = 246.6, triclinic, *P*1̄, *a* = 8.909 (1), *b* = 11.002 (2), *c* = 8.850 (1) Å, α = 96.84 (2), β = 110.04 (1), γ = 97.10 (2)°, *V* = 796.4 Å³, *Z* = 2, *D_x* = 1.10 (−35°C), *D_m* = 1.09 (23°C) g cm^{−3}. Full-matrix least-squares refinement with 2243 reflections collected at −35°C with ω scans on a Syntex P2₁ diffractometer yielded a final *R* of 0.030. The two crystallographically independent molecules in the unit cell both reside at inversion centers and adopt very similar conformations.

Introduction. Crystals of the title compound, SIMTE, were obtained by sublimation. ω scans revealed peaks which were single but asymmetric, tailing to one side. After examination of several crystals, one was found for which the scans, although still somewhat asymmetric, were sufficiently narrow and well centered to permit data collection (Table 1). Intensity data were corrected for Lorentz and polarization effects. No absorption correction was applied. Standard deviations were assigned to the intensity data with a *p* factor of 0.06 as described by Riley & Davis (1976).

The structure was solved by the heavy-atom method. Anisotropic refinement (2243 reflections, XPR = XSR = 2.0) (Collins & Davis, 1978) of the non-hydrogen

atoms yielded *R* = 0.052 and *R_w* = 0.096. A difference map then indicated positions for the H atoms, but these positions failed to refine satisfactorily. H atoms were then added to the model at calculated positions which corresponded closely to those suggested by the difference map. X–C–H bond angles of 109.5°, C–H distances of 0.9 Å and Y–X–C–H torsion angles of 180, −60 and 60° were used for the calculated positions where *X* is S or Si and *Y* is the ethylene C bonded to *X*. Subsequent refinement† of the non-hydrogen atoms resulted in a final *R* = 0.030 and *R_w* = 0.046. Maximum residual difference density was 0.3 e Å^{−3}. No correlation coefficients greater than 0.5 were noted during the course of the refinement.

Atomic scattering factors for S, Si, 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 and Si. Atomic parameters are given in Table 2.

† Lists of structure factors, non-hydrogen anisotropic thermal parameters and hydrogen atomic parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32886 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* Perheterosubstituted Ethanes and Ethylenes. III.

Table 1. *Experimental summary*

Syntex P2₁ autodiffractometer equipped with a graphite monochromator and Syntex LT-1 low-temperature flow system
Radiation: Mo *K*α, λ = 0.71069 Å
Mode: ω-scan technique, recentered automatically after every 700 reflections
Scan range: symmetrically over 0.95° about the *K*α_{1,2} maximum
Scan rate: variable, 1.5 to 5.0° min^{−1}
Background: offset 1.0 and −1.0° in ω from *K*α_{1,2} maximum
Check reflections: four remeasured after every 96 reflections; analysis* of 39 sets of check reflections indicated that a decay correction was not required
3664 reflections measured, 4° ≤ 2θ ≤ 55°
Data-crystal dimensions: 0.2 × 0.3 × 0.5 mm
Mosaic character: asymmetric peaks with peak width at half height of 0.4° in ω
Absorption coefficient: μ(Mo *K*α) = 4.39 cm^{−1}

* Henslee & Davis (1975).

Table 2. *Atomic coordinates (×10⁴) for the non-hydrogen atoms with e.s.d.'s in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
(a) For the molecule at inversion center 0,0,0			
S(1)	275 (1)	−1650 (1)	−1434 (1)
Si(1)	2611 (1)	−5 (1)	1931 (1)
C(1)	616 (2)	−315 (2)	102 (2)
C(2)	1619 (4)	−1115 (3)	−2443 (4)
C(3)	2245 (3)	−125 (3)	3859 (3)
C(4)	3849 (3)	1524 (2)	2068 (3)
C(5)	3824 (4)	−1235 (3)	1704 (4)
(b) For the molecule at inversion center 0,½,½			
S(2)	−1776 (1)	3869 (1)	5676 (1)
Si(2)	2062 (1)	4302 (1)	7023 (1)
C(6)	80 (3)	4642 (2)	5589 (3)
C(7)	−1737 (5)	4679 (4)	7599 (4)
C(8)	3281 (5)	3658 (3)	5896 (5)
C(9)	3207 (4)	5741 (3)	8509 (4)
C(10)	1618 (5)	3078 (3)	8174 (5)

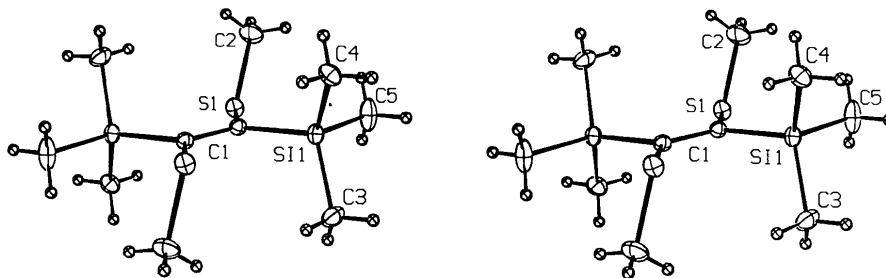


Fig. 1. A stereoview of the molecule at inversion center 0,0,0, illustrating the atom-numbering scheme. The molecule at $0, \frac{1}{2}, \frac{1}{2}$ is numbered S(2), Si(2) and C(6) to C(10), corresponding to S(1), Si(1) and C(1) to C(5) respectively. Non-hydrogen atoms are shown as 20% equiprobability ellipsoids. Hydrogen atoms appear as 0.11 Å radius spheres.

Table 3. *Metrical details*

Molecule at inversion center			
0,0,0		$0, \frac{1}{2}, \frac{1}{2}$	
(a) Interatomic distances			
S(1)—Si(1)	3.165 (1)	S(2)—Si(2)	3.164 (1)
S(1)—Si(1')	3.270 (1)	S(2)—Si(2')	3.269 (1)
S(1)—C(1)	1.798 (2)	S(2)—C(6)	1.795 (2)
Si(1)—C(1)	1.909 (2)	Si(2)—C(6)	1.901 (2)
S(1)—C(2)	1.806 (3)	S(2)—C(7)	1.812 (4)
Si(1)—C(3)	1.861 (3)	Si(2)—C(8)	1.855 (4)
Si(1)—C(4)	1.862 (3)	Si(2)—C(9)	1.861 (3)
Si(1)—C(5)	1.867 (3)	Si(2)—C(10)	1.865 (4)
C(1)—C(1')	1.342 (3)	C(6)—C(6')	1.360 (3)
(b) Interatomic angles			
C(1')—C(1)—S(1)	116.1 (2)	C(6')—C(6)—S(2)	116.0 (2)
C(1')—C(1)—Si(1)	126.4 (2)	C(6')—C(6)—Si(2)	126.1 (2)
S(1)—C(1)—Si(1)	117.3 (1)	S(2)—C(6)—Si(2)	117.8 (1)
C(1)—S(1)—C(2)	101.1 (1)	C(6)—S(2)—C(7)	101.1 (1)
C(1)—Si(1)—C(3)	111.1 (1)	C(6)—Si(2)—C(8)	111.9 (1)
C(1)—Si(1)—C(4)	111.5 (1)	C(6)—Si(2)—C(9)	109.1 (1)
C(1)—Si(1)—C(5)	109.3 (1)	C(6)—Si(2)—C(10)	109.5 (1)
C(3)—Si(1)—C(4)	111.3 (1)	C(8)—Si(2)—C(9)	111.9 (2)
C(3)—Si(1)—C(5)	105.6 (1)	C(8)—Si(2)—C(10)	105.7 (2)
C(4)—Si(1)—C(5)	107.7 (1)	C(9)—Si(2)—C(10)	108.6 (2)
(c) Torsion angles			
C(1')—C(1)—S(1)—C(2)	110.2	C(6')—C(6)—S(2)—C(7)	111.9
C(1')—C(1)—Si(1)—C(3)	58.4	C(6')—C(6)—Si(2)—C(8)	54.1
C(1')—C(1)—Si(1)—C(4)	-66.4	C(6')—C(6)—Si(2)—C(9)	-70.4
C(1')—C(1)—Si(1)—C(5)	174.6	C(6')—C(6)—Si(2)—C(10)	170.9
S(1)—C(1)—Si(1)—C(5)	-0.3	S(2)—C(6)—Si(2)—C(10)	-4.3

Discussion. The two crystallographically independent molecules occupy inversion centers at 0,0,0 and at $0, \frac{1}{2}, \frac{1}{2}$. Metrical details of these molecules are compared in Table 3. Inspection of this information reveals that the two independent molecules are virtually identical. Thus, the molecular structure will be discussed in terms of the molecule at 0,0,0 (Fig. 1).

Departures from the ideal trigonal angles of 120° about the sp^2 carbon atom C(1) decrease the non-bonded interactions of the C(4) and C(5) methyl groups

with the C(2) methyl group [C(4)···C(2) and C(5)···C(2), 4.32 and 3.55 Å respectively] at the expense of interactions of the C(3') methyl group with the C(2) methyl group [C(3')···C(2), 3.73 Å]. The Si(1)—C(1) bond length is 1.909 (2) Å. This Si—C(sp^2) distance is longer than the average Si—C(sp^3) bond distance in this molecule, 1.863 Å, and the Me₃Si—C(sp^2) distance, 1.871 (3) Å, in a cyclobutadiene complex (Rausch, Bernal, Davies, Siegel, Higbie & Westover, 1973). The S(1)—C(1) bond length, 1.798 (2) Å, is longer than the S—C(sp^2) distances in other thiosubstituted ethylenes for which the range 1.748 (6) to 1.767 (3) Å (Collins & Davis, 1978) is observed. These distances also suggest the presence of substantial nonbonded repulsions since increases in the S(1)—C(1) and Si(1)—C(1) bond distances decrease methyl-group interactions.

This work was supported by the Robert A. Welch Foundation (Grant No. F-233). We are also indebted to the National Science Foundation for the purchase of the Syntex P₂ diffractometer (Grant No. GP-37028) and especially to Professor Dieter Seebach at the Justus Liebig-Universität, Giessen, Federal Republic of Germany, for supplying a sample of this compound.

References

- COLLINS, R. C. & DAVIS, R. E. (1978). *Acta Cryst.* B34, 283–285.
 HENSLEE, W. H. & DAVIS, R. E. (1975). *Acta Cryst.* B31, 1511–1519.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 RAUSCH, M. D., BERNAL, I., DAVIES, B. R., SIEGEL, A., HIGBIE, F. A. & WESTOVER, G. F. (1973). *J. Coord. Chem.* 3, 149–159.
 RILEY, P. E. & DAVIS, R. E. (1976). *Acta Cryst.* B32, 381–386.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.