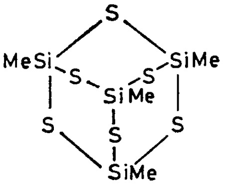
Crystal and Molecular Structure of Tetra(methylsilicon) Hexasulphide (1,3,5,7-Tetramethyl-2,4,6,8,9,10-hexathia-1,3,5,7-tetrasila-adamantane)

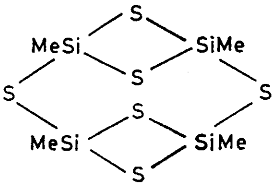
By **Jan C. J. Bart** * and **John J. Daly**, Monsanto Research S.A., Eggbühlstr. 36, CH-8050 Zürich, Switzerland

The crystal structure of the title compound has been determined by single-crystal *X*-ray diffraction methods. Crystals are monoclinic, space group *C*2/*c*, with $a = 9.382(10)$, $b = 16.513(20)$, $c = 10.584(11)$ Å, $\beta = 107°\ 10(10)'$, and $Z = 4$. The structure was solved by direct methods and refined by block-diagonal least-squares techniques to *R* 4.4% for 1 284 independent reflections measured by diffractometer. The molecule exhibits the crystallographically required C_2 symmetry and approximates closely to T_d ($\bar{4}3m$) symmetry like the corresponding Ge and Sn compounds. Mean molecular parameters in the adamantane-type structure are: Si–S 2.129, Si–C 1.836 Å; Si–S–Si 104.6, S–Si–S 111.8, and S–Si–C 107.0°. The Si valence angles show a smaller distortion from the tetrahedral value than do those at S. The molecular conformation and crystal packing are compared with that in other hexathia-adamantanes.

THE molecular structures of tetra(alkylsilicon) hexasulphides,[1] the corresponding selenides,[2] and tetra(methylgermanium) hexasulphide[3] have been the subjects of discussion. From consideration of tetraethenyl hexasulphide,[4-6] a strain-free adamantanoid structure (I) was reasonably expected[2,3] to be more likely than the Candiani four-membered ring structure (II) consisting of Si(Ge) and S(Se) atoms linked by S(Se) bridges.[5,7]



(I)



(II)

An *X*-ray analysis of $(MeSi)_4S_6$ has now been undertaken to produce conclusive evidence for its structure. The symmetry (2 or $\bar{1}$), imposed upon the molecule by the space group, was not sufficient to distinguish unambiguously between the two possible structures.

A brief report has appeared,[8] and we now present details of the structure.

EXPERIMENTAL

The compound was synthesized according to reaction (1).

$$4\ MeSiBr_3 + 6\ H_2S + 12\ NEt_3 \longrightarrow (MeSiS_{1.5})_4 + 12\ Et_3N{\cdot}HBr \quad (1)$$

Crystals (m.p. 272—275 °C) suitable for diffraction experiments were obtained from benzene.

Cell parameters were determined from zero-layer 30° precession photographs recorded with Mo-K_α radiation.

Crystal Data.—$C_4H_{12}Si_4S_6$, $M = 365$, $a = 9.382(10)$, $b = 16.513(20)$, $c = 10.584(11)$ Å, $\beta = 107°\ 10'(10)$, $U = 1560.9$ Å^3; $D_o = 1.57$ g cm^3, $Z = 4$, $D_c = 1.552$ g cm^{-3}, $F(000) = 752$. Space group *Cc* or *C*2/*c* from systematic absences: *hkl* for $h + k = 2n + 1$, and *h*0*l* for $l = 2n + 1$; shown to be the latter by the subsequent successful refinement. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 11.0 cm^{-1}.

Intensity data were collected with Mo-K_α radiation from a needle-shaped crystal on a Hilger–Watts diffractometer[9] by use of the balanced-filter technique ($SrCO_3/ZrO_2$) and a scintillation counter with pulse-height discrimination. Four standard reflections were regularly monitored. The crystal was parallel to [*c*] and showed {110} and {010} with approximate cross-section 0.45 × 0.25 mm^2. A 1 min oscillation motor was employed throughout. Each independent reflection was recorded twice up to $\theta_{max.}$ 22.5° with mean estimated ΔF_o *ca.* 2%. The intensities of the 1 284 strongest reflections were used in the analysis. No absorption correction was applied. Lorentz and polarization corrections were applied as usual.

Structure Determination and Refinement.—The phase problem was solved by direct methods.[10,11] The *E* map showed all heavy-atom positions and structure factors in the low sin θ/λ range immediately gave *R* 0.43. Refinement was carried out by 3 × 3 and 6 × 6 block-diagonal least-squares. Hydrogen atoms were located in a ΔF map when *R* was 0.055, and were refined isotropically together with the anisotropic thermal parameters of the heavy atoms. Refinement was terminated when all shifts were $<\sigma$ and random. The final *R* was 0.044 and R' $[= \Sigma w|\Delta^2|/wF_o^2]$ 0.005, excluding rejected planes. Throughout the calculations planes with $3|F_o| \leqslant |F_o|$ were omitted from the least-squares totals (52 planes in the last cycle). A modified Cruickshank[12] weighting scheme $w_1 = 1/(5.5 + |F_o| + 0.1|F_o|^2)$ if $|F_o| > 5.5$ and $w_2 = w_1\,(|F_o|/5.5)^2$ if $|F_o| \leqslant 5.5$ was applied and seemed to be satisfactory as the analyses of $\Sigma w\Delta^2/n$ in terms of $|F_o|$ and $\sin^2\theta/\lambda^2$ showed. Atomic scattering factors were taken from ref. 13. Final observed and calculated structure

---

* *Present address:* Montedison Research Laboratories, G. Donegani, Novara, Italy.

[1] Y. P. Etienne, *Bull. Soc. chim. France*, 1953, 791; *Angew. Chem.*, 1955, **67**, 753.

[2] J. P. Forstner and E. L. Muetterties, *Inorg. Chem.*, 1966, **5**, 552.

[3] K. Moedritzer, *Inorg. Chem.*, 1967, **6**, 1248.

[4] J. Bongartz, *Ber.*, 1886, **19**, 2182.

[5] P. Candiani, *Gazzetta*, 1895, **25**, 81.

[6] A. Fredga, *Arkiv. Kemi, Min. Geol.*, 1947, **25B**, No. 8.

[7] V. D. Reikhsfel'd and E. P. Lebedev, *Zhur. obshchei Khim.*, 1967, **37**, 1412.

[8] J. C. J. Bart and J. J. Daly, *Chem. Comm.*, 1968, 1207.

[9] U. W. Arndt and D. C. Phillips, *Acta Cryst.*, 1961, **14**, 807.

[10] D. Sayre, *Acta Cryst.*, 1962, **5**, 60.

[11] H. Hauptman and J. Karle, ' Solution of the Phase Problem. I. The Centrosymmetric Crystals,' A.C.A. Monograph No. 3, Polycrystal Book Service, Brooklyn, 1953.

[12] D. W. J. Cruickshank, in ' Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon Press, Oxford, 1961, p. 32.

[13] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.

factors are listed in Supplementary Publication No. SUP 21339 (9 pp, 1 microfiche).* All computations were carried out on an Elliott 803*B* computer with programs of ref. 14.

RESULTS

Final atomic co-ordinates and thermal parameters are given in Tables 1 and 2. The labelling of the atoms is indicated in Figure 1. Table 3 lists intramolecular distances and angles together with standard deviations estimated by use of the normal least-squares equations for the individual measurements. As estimated standard deviations do not allow for errors in cell dimensions or for rotational corrections, they are likely to be underestimated. Root-mean-square values are quoted for each mean in Tables 3, 7, and 8.

TABLE 1

Final atomic co-ordinates (Å), referred to the monoclinic axes, with standard deviations in parentheses

Atom	*X*	*Y*	*Z*
S(1)	0 *	12.2343(9)	2.6462 *
S(2)	0 *	17.2217(9)	2.6462 *
S(3)	1.8154(8)	14.7406(7)	4.9745(8)
S(4)	1.8835(8)	14.7152(7)	1.4789(8)
Si(1)	−0.0247(8)	13.5387(7)	4.3265(8)
Si(2)	1.7559(7)	15.9246(7)	3.1868(7)
C(1)	−0.0496(40)	12.4926(33)	5.8271(38)
C(2)	3.3082(31)	17.0066(35)	3.6428(35)
H(1)	−0.857(45)	12.055(38)	5.565(42)
H(2)	0.640(51)	12.058(39)	6.163(46)
H(3)	−0.156(42)	12.945(42)	6.494(44)
H(4)	4.124(38)	16.460(41)	3.886(38)
H(5)	3.293(40)	17.513(38)	2.899(43)
H(6)	3.254(39)	17.441(40)	4.451(39)

* Parameters fixed by symmetry.

TABLE 2

Thermal parameters (Å^2 × 10^4) in the form exp $-2\pi^2$-$(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})$, with standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
S(1)	861(11)	334(7)	532(10)	0 †	0 †	656(17)
S(2)	460(7)	361(7)	464(8)	0 †	0 †	266(12)
S(3)	517(6)	522(6)	371(6)	58(9)	99(9)	203(9)
S(4)	513(6)	513(6)	480(7)	32(9)	−50(9)	505(10)
Si(1)	588(7)	375(6)	413(7)	25(9)	89(9)	457(11)
Si(2)	381(5)	426(6)	386(6)	−31(8)	16(9)	238(9)
C(1)	954(36)	576(28)	590(30)	207(49)	519(47)	823(51)
C(2)	504(24)	714(30)	595(29)	−401(44)	−80(49)	239(42)

All hydrogen atoms are assigned an isotropic thermal parameter *U* of 0.065 Å^2.

† Parameters fixed by symmetry.

TABLE 3

Bond lengths (Å) and angles (°). Least-squares standard deviations are given in parentheses as units in the last place; an estimate of that of the mean values is given as $s/n^{1/2}$

S(1)–Si(1)	2.133(1)	S(1)–Si(1)–C(1)	107.55(12)
S(2)–Si(2)	2.121(1)	S(2)–Si(2)–C(2)	106.18(11)
S(3)–Si(1)	2.132(1)	S(3)–Si(1)–C(1)	106.95(12)
S(3)–Si(2)	2.130(1)	S(3)–Si(2)–C(2)	107.88(11)
S(4)–Si(2)	2.127(1)	S(4)–Si(2)–C(2)	106.73(11)
S(4)–Si(1′)	2.131(1)	S(4)–Si(1′)–C(1′)	106.86(12)
Mean S–Si	2.129(2)	Mean S–Si–C	107.00(24)
Si(1)–C(1)	1.835(4)	Si(1)–S(3)–Si(2)	104.50(4)
Si(2)–C(2)	1.836(4)	Si(1)–S(1)–Si(1′)	104.60(4)
Mean Si–C	1.836(1)	Si(2)–S(2)–Si(2′)	104.58(4)
		Si(2)–S(4)–Si(1′)	104.62(4)
		Mean Si–S–Si	104.57(3)
C(1)–H(1)	0.89(4)	Si(1)–C(1)–H(1)	105.7(28)
C(1)–H(2)	0.80(5)	Si(1)–C(1)–H(2)	115.8(33)
C(1)–H(3)	0.84(4)	Si(1)–C(1)–H(3)	112.2(29)
C(2)–H(4)	0.95(4)	Si(2)–C(2)–H(4)	108.9(24)
C(2)–H(5)	0.90(4)	Si(2)–C(2)–H(5)	108.8(26)
C(2)–H(6)	0.93(4)	Si(2)–C(2)–H(6)	103.3(25)
Mean C–H	0.89(2)	Mean Si–C–H	109.1(19)
S(1)–Si(1)–S(3)	111.99(4)	H(1)–C(1)–H(2)	117.0(43)
S(1)–Si(1)–S(4′)	111.11(4)	H(1)–C(1)–H(3)	100.5(40)
S(2)–Si(2)–S(3)	111.70(4)	H(2)–C(1)–H(3)	104.8(44)
S(2)–Si(2)–S(4)	112.61(4)	H(4)–C(2)–H(5)	109.9(36)
S(3)–Si(2)–S(4)	111.37(4)	H(4)–C(2)–H(6)	108.0(34)
S(3)–Si(1)–S(4′)	112.04(4)	H(5)–C(2)–H(6)	117.6(36)
Mean S–Si–S	111.80(21	Mean H–C–H	109.6(28)

TABLE 4

Interplanar spacings of (I)

d_o (Å)	d_c (Å)	*h*	*k*	*l*	I/I_0
7.844	7.856	1	1	0	100
7.157	7.208	−1	1	1	20
6.375	6.386	0	2	1	13
5.549	5.516	1	1	1	7
4.864	4.880	−1	1	2	2
4.683	4.686	1	3	0	4
4.314	4.300	0	2	2	4
4.028	4.028	−2	2	1	4
		1	3	1	
3.933	3.928	2	2	0	60
3.739	3.744	−1	3	2	10
3.444	3.441	−1	1	3	2
3.386	3.365	2	2	1	9
3.198	3.193	0	4	2	6
3.125	3.111	0	2	3	5
3.081	3.085	−2	4	1	2
3.035	3.031	2	4	0	14
2.965	2.965	−1	3	3	6
2.939	2.939	−3	1	2	6
		3	1	0	
2.762	2.758	2	2	2	5
2.718	2.719	−3	3	1	12
2.656	2.655	0	6	1	1
2.622	2.619	3	3	0	1
2.529	2.527	−2	4	3	1
2.429	2.440	−2	2	4	1
2.396	2.403	−3	3	3	5
2.346	2.343	2	6	0	1
2.270	2.270	−3	5	1	1
		2	2	3	
		−2	6	2	
2.241	2.235	−4	2	2	5
2.214	2.211	3	5	0	7
2.170	2.170	−2	4	4	1
2.164	2.165	1	5	3	3
2.071	2.065	−1	5	4	1
2.035	2.033	−4	4	1	1
1.884	1.883	−3	7	1	1
1.871	1.872	−2	6	4	1
1.851	1.853	−3	7	2	2
1.828	1.835	−2	8	2	2
1.802	1.802	−4	4	4	1
1.782	1.781	−4	6	1	5
1.764	1.765	2	4	4	3
1.760	1.761	−1	7	4	4
1.746	1.751	1	9	1	1
1.712	1.716	−4	6	3	1

An indexed *X*-ray powder diagram, recorded with a conventional Philips diffractometer set-up by use of Cu-K_α radiation and a scanning rate of 1/4° min^{-1}, after calibration with a silicon standard, is given in Table 4.

---

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full size copies).

[14] J. J. Daly, F. S. Stephens, and P. J. Wheatley, unpublished work.

DISCUSSION

Molecular Conformation.—The structure determination shows that the configuration with cubic molecular symmetry (I) is correct.

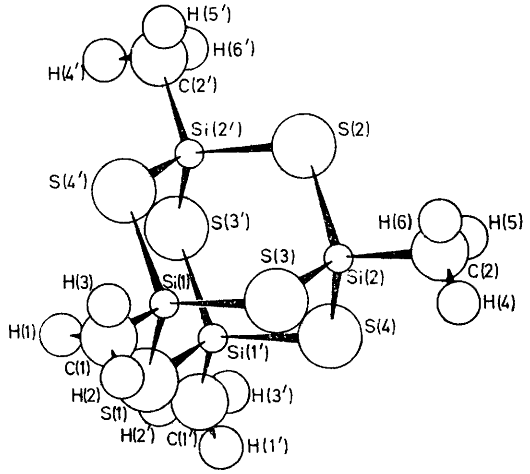


FIGURE 1 Molecular conformation and labelling of the atoms in (I)

The molecule thus belongs to the class of adamantane-type structures, having methyl substituents in the equatorial positions of the component six-membered rings. According to the nomenclature of Stetter,[15,16] the compound is thus 1,3,5,7-tetramethyl-2,4,6,8,9,10-hexathiasilamantane. The adamantane structure has also been ascertained for $(MeGe)_4S_6$ (ref. 17) and $(MeSn)_4S_6$ (refs. 18 and 19) and is generally assigned to organosilyl-selenides [2] and -phosphines and organogermylphosphines [20] on the basis of spectroscopic data.

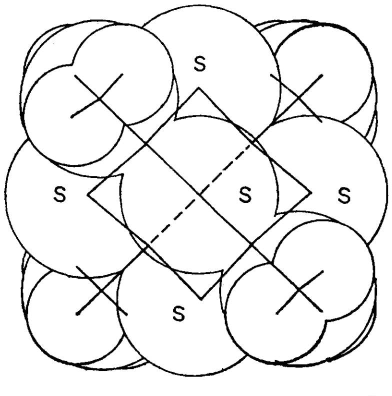


FIGURE 2 (I) seen along the molecular $\bar{4}$ axis

The configuration of (I) is shown in Figures 1 and 2. The molecular geometry can be described in terms of three cubes with a common centre, namely an innermost and a central cube of sides 2.38 and 4.50 Å with Si and C atoms respectively at four of their corners, and an outermost cube (side 4.99 Å) with the bridging S atoms at the centres of its six faces. Alternatively, it may be considered as having four silicon and four carbon atoms at the corners of slightly irregular tetrahedra with edges of 3.368 and 6.364 Å respectively and the six sulphur atoms at the corners of an octahedron with the same centre of gravity; two sulphur atoms on a molecular four-fold inversion axis occupy positions on the crystallographic two-fold axis. The mean S • • • S distance along edges of the S_6 octahedron, corresponding to S–Si–S links, is 3.526(10) Å (3.02 Å in hexathia-adamantane [21]). The dihedral angles in the Si-tetrahedron are 70.23, 70.56, 70.57, and 70.62°, in the C-tetrahedron 70.00, 70.20, 70.30, and 70.98°, and 110.00, 109.93, 109.83, and 109.10° in the S-octahedron.

Ideally, the fused ring system of (I) can be described by two parameters only, say the Si • • • Si distance and Si–S–Si valence angle. Similarly, the values of only three parameters define the geometry of the Si, S, C framework and from them all interatomic distances can be calculated. The distortion from T_d ($\bar{4}3m$) molecular symmetry is given in Table 5, where the molecular dimensions are expressed, with mean and maximum deviations, in terms of the following co-ordinates: Si (a, a, a), ($a, \bar{a}, \bar{a}$), ($\bar{a}, \bar{a}, a$), and ($\bar{a}, a, \bar{a}$); S ($\pm b$, 0, 0), (0, $\pm b$, 0), and (0, 0, $\pm b$); and C (c, c, c), ($c, \bar{c}, \bar{c}$), ($\bar{c}, \bar{c}, c$), and ($\bar{c}, c, \bar{c}$). As is apparent from Tables 3 and 5, departures from the higher cubic symmetry T_d are very small, implying that the molecules with the crystallographically required symmetry C_2 (2) effectively conform to the T_d point group.

TABLE 5

Deviations from T_d molecular symmetry

Atom	Parameter(Å)	Devn.(Å)	
		Max.	Mean
Si	a 1.191	0.009	0.005
S	b 2.493	0.010	0.006
C	c 2.251	0.037	0.015

The almost equal Si–S bond lengths (2.121 and 2.133 Å) are slightly shorter than the sum of the covalent radii of the relevant atoms (2.22 Å) and close to both the corrected sum (2.15 Å) [22] and values found for *e.g.* $SiCl_3{\cdot}SH$, $(Me_2SiS)_n$ ($n = 2$ or 3) (2.14 Å),[23] and in tetrahedral $[SiS_4]^{2-}$ arrangements such as in Mn_2SiS_4.[24] The Si(sp^3)–C(sp^3) distance (1.836 Å) is slightly shorter than the corrected Schomaker–Stevenson distance (1.88 Å) and those determined experimentally for alkylsilanes (1.870 ± 0.005 Å) and cyclic organosilicon compounds

---

[15] H. Stetter and K. H. Steinacker, *Chem. Ber.*, 1952, **85**, 451.

[16] H. Stetter, *Angew. Chem.*, 1954, **66**, 217.

[17] R. H. Benno and C. J. Fritchie, *J.C.S. Dalton*, 1973, 543.

[18] C. Dörfelt, A. Janeck, D. Kobelt, E. F. Paulus, and H. Scherer, *J. Organometallic Chem.*, 1968, **14**, P22.

[19] D. Kobelt, E. F. Paulus, and H. Scherer, *Acta Cryst.*, 1972, **B28**, 2323.

[20] H. Schumann and H. Benda, *Angew. Chem. Internat. Edn.*, 1969, **8**, 989.

[21] E. K. Andersen and I. Lindqvist, *Arkiv. Kemi*, 1956, **9**, 169.

[22] V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

[23] Ref. 13, p. 264.

[24] A. Hardy, G. Perez, and J. Serment, *Bull. Soc. chim. France*, 1965, 2638.

(*ca.* 1.88 Å), as indicated in Table 6.[25-33] The shortness of this bond may be due, at least in part, to the large thermal motion of the carbon atoms (*cf.* discussion on Si–C bond lengths in ref. 33). Before introduction of hydrogen atoms the mean Si–C distance was 1.854(5) Å.[8]

TABLE 6

Si–C(sp^3) Bond lengths in cyclic organosilicon compounds

Molecule	Si–C(Å)
$Me_8Si_8O_8$ [a]	1.88(4) [b]
$Me_8Si_5O_6$ [c]	1.88(3)
$(Me_2SiO)_3$ [d]	1.929
$(Me_2SiO)_4$ [e]	1.92(5)
$(MeSiO_{1.5})_8$ [f]	1.90(4)
$(Me_4Si_2O)_2$ [g]	1.88(4) [b]
$(Me_3NSiMe_2)_2$ [h]	1.886(4)
$(Me_2SiNH)_4$ [i]	1.878(10)
$C_6H_4[(SiMe_2)_2O]_2$ [j]	1.848(6)
$(MeSi)_4S_6$ [k]	1.836(1)

Reported deviations refer to mean values. [a] Ref. 25. [b] Estimated standard deviation. [c] Ref. 26. [d] Ref. 27. [e] Ref. 28. [f] Ref. 29. [g] Ref. 30. [h] Ref. 31. [i] Ref. 32. [j] Ref. 33. [k] Present work.

Mean values of the most significant non-bonded distances are given in Table 7. The four crystallographically non-identical nearest-neighbour Si ••• Si distances are: Si(1) ••• Si(1') 3.376, Si(1) ••• Si(2) 3.370 and 3.370, and Si(2) ••• Si(2') 3.356 Å. The six crystallographically non-identical S ••• S distances along the edges of the octahedron are: S(1) ••• S(3) 3.536, S(1) ••• S(4) 3.516, S(2) ••• S(3) 3.518, S(2) ••• S(4) 3.534, and S(3) ••• S(4) 3.516 and 3.535 Å; the four crystallographically non-identical C ••• C distances are: C(1) ••• C(1') 6.392, C(1) ••• C(2) 6.384 and 6.357, and C(2) ••• C(2') 6.322 Å. The fourth-neighbour S ••• S distances across the molecule (4.987, 4.989, and 4.983 Å) are slightly higher than the theoretical value [$4\overline{\mathrm{SiS}}\cos(109° 28'/2)$, 4.91 Å] in an ideal adamantane structure, as a consequence of angle distortions.

TABLE 7

Mean non-bonded distances (Å)

Neighbours		
2nd	Si ••• Si	3.368(5)
	S ••• S	3.526(5)
	C ••• S	3.192(9)
3rd	Si ••• S	4.051(5)
	Si ••• C	4.981(8)
4th	S ••• S	4.986(3)
	C ••• S	5.711(10)
	C ••• C	6.364(16)

The S–Si–S angles do not deviate appreciably from the mean (111.80°), but differ significantly from the tetrahedral value (109° 28'). The same concepts are also clearly expressed by Table 5: only in the case of $b = 2a$ are cage angles exactly tetrahedral. The flattening of the bridgehead angles leads to a distortion of the Si–S–Si angles, since in the closed framework of the (I) skeleton the angles cannot be varied independently. Namely, with T_d ($\bar{4}3m$) molecular symmetry, if the S–Si–S bond angle is $109° 28' + \Delta$, then the angle at S is $109° 28' - 2\Delta$; accordingly, with S–Si–S 111.8° the calculated value of Si–S–Si is 104.8° (found 104.6°). This interrelation of bond angles in the cage-like structure accounts for the fact that in adamantane[34-36] all bond angles are equal to the exact tetrahedral value, differing from those in cyclohexane. While electron-diffraction experiments have provided information about Si–Se–Si bond angles,[37] there have been no comparable determinations of Si–S–Si bond angles; comparison with angles for the Ge and Sn analogues of (I) (Table 8) indicates a considerably higher flexibility of the bond angles around sulphur than those around Si (Ge or Sn). The S–Si–S angles (111.8°) are very close to the C–C–C angles both observed (111.5°)[38] and calculated for cyclohexane on the basis of force-field models (111.3°).[36] Similarly, there is greater flexibility reflected by Si–O–Si angles in siloxanes[25-30] than by the more rigid Si–C–Si; this probably derives from hybridization valence requirements of the S(O) atoms and geometrical constraints which serve to keep at a minimum angle (Baeyer) and conformational (Pitzer) strain in the molecule. The hybridization of the heteroatoms composing the molecular skeleton in hexathia-adamantanes and internal angular strain conditions lead to a well defined conformation, as indicated in Table 8, for a number of structural analogues. Starting from the idealized adamantanoid conformation, the small angle distortions required for achieving a ' comfortable ' configuration in the heterocyclic molecule should not be energetically expensive.

Assuming C_{3v} symmetry, the S–Si–S (ϕ) and S–Si–C angles (θ) are related by the function $3\cos^2\theta = 2\cos\phi + 1$. With $\phi = 111.8°$ the calculated value of S–Si–C is 107.0°, as observed, with no significant deviations from the mean. Similar observations hold for other hexathia-adamantanes (Table 8). The mean bond angles around the carbon atoms are not significantly different from 109° 28'. The mean S–Si–S–Si torsional angle is 63.2°, maximum deviation 1.2°. Mean and maximum deviations of the C–Si–S–Si torsion angles from 180° are 0.75 and 2.85°.

In accordance with the findings for the Ge analogue, the hydrogen atoms in (I) take up very nearly staggered positions, with deviations of *ca.* 6 and 3° from ideal positions for the methyl substituents at Si(1) and Si(2). Intermolecular forces thus have little effect on the orientation of the methyl groups.

Crystal Structure.—The packing of the molecules in the unit cell is shown in Figure 3. The orientation of the

---

[25] T. Higuchi and A. Shimada, *Bull. Chem. Soc. Japan*, 1966. **39**, 1316.

[26] W. L. Roth and D. Harker, *Acta Cryst.*, 1948, **1**, 34.

[27] G. Peyronel, *Rend. Accad. Sci. fis. mat.*, 1953, **8**, 15, 402; 1954 **16**, 231.

[28] H. Steinfink, B. Post, and I. Fankuchen, *Acta Cryst.*, 1955, **8**, 420.

[29] K. Larsson, *Arkiv. Kemi*, 1960, **16**, 203.

[30] T. Takano, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Japan*, 1963, **36**, 585.

[31] P. J. Wheatley, *J. Chem. Soc.*, 1962, 1721.

[32] G. S. Smith and L. E. Alexander, *Acta Cryst.*, 1963, **16**, 1015.

[33] J. J. Daly and F. Sanz, *J.C.S. Dalton*, 1973, 2474.

[34] J. Donohue and S. H. Goodman, *Acta Cryst.*, 1967, **22**, 352.

[35] I. Hargittai and K. Hedberg, *Chem. Comm.*, 1971, 1499.

[36] E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 8005.

[37] A. Almenningen, L. Fernholt, and H. M. Seip, *Acta Chem. Scand.*, 1968, **22**, 51.

[38] M. Davis and O. Hassel, *Acta Chem. Scand.*, 1963, **17**, 1181.

molecules is such that rotation around the S(1) ··· S(2) direction (*i.e.* the *b* axis) leads to a C(1)–Si(1)–S(1)–Si(1′)–C(1′) plane very approximately parallel to (100). By analogy with P_4O_{10},[39] each molecule can be described as having four spikes [C(1), C(2), C(1′), and C(2′)] and four recesses, which are formed at the centres of sets of three sulphur atoms [S(1), S(3), and S(4), and S(2), S(3), and S(4), *etc.*]. The spikes of the molecules along the *c* axis (A_{000} and $\bar{B}_{020}$, Figure 3) protrude into recesses of the nearest molecules located at $a = 1/2$ ($D_{0\bar{1}0}$ and $\bar{C}_{011}$) and *vice versa*.

TABLE 8

Bond lengths (Å) and angles (°) in some hexathia-adamantanes

Compound	S–X–S	X–S–X	S–X–C	X–C	X–S	X
$(CH)_4S_6$ [a,b]	110.4	107.2			1.84	C
$(MeSi)_4S_6$ [c]	111.8(2) [d]	104.5(3)	107.0(3)	1.836(1)	2.129(2)	Si
$(MeGe)_4S_6$ [e]	111.8(3)	104.6(2)	107.0(3)	1.922(10)	2.218(3)	Ge
$(MeSn)_4S_6$ [f]	111.3(6)	105.7(2)	107.5(6)	2.147(10)	2.392(3)	Sn

[a] Partially refined crystal structure only. [b] Ref. 21. [c] This work. [d] Estimate of standard deviation is based on $s/n^{\frac{1}{2}}$. [e] Ref. 17. [f] Ref. 19.

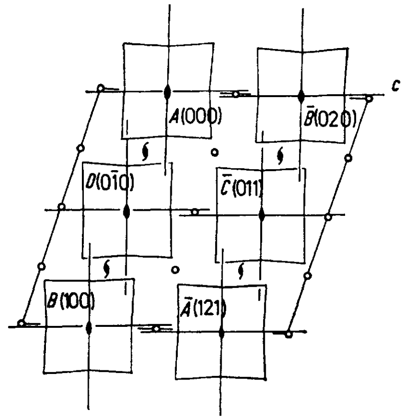


FIGURE 3 Packing mode of (I) parallel to (010). For key to molecular designations see Table 9

As is evident from Table 9, which lists the non-equivalent intermolecular approaches up to the sum of the van der Waals radii plus 0.4 Å, most contacts between molecules related by the centres of symmetry along *c* also involve spikes and recesses, together with weak S ··· S contacts of *ca.* 4.0 Å. As however the latter distances are well beyond the van der Waals separation (3.7 Å) there is no reason here for assuming any special bonding forces between the sulphur atoms. This differs from the situation in hexathia-adamantane,[21] in which the intermolecular S ··· S distances are remarkably small, only 3.5 Å. Molecules separated by the full cell-edge *a* or *c* (B_{100}, $\bar{A}_{121}$, and B_{001}) are mainly in close C ··· H and H ··· H contact.

TABLE 9

Intermolecular contacts (arbitrarily bounded at the sums of van der Waals radii plus 0.4 Å*)

	d/Å
$A(000) \cdots C(\bar{1}\bar{1}0)$	
S(1) ··· C(2)	3.98
S(1) ··· H(5)	3.33
$A(000) \cdots D(0\bar{1}0)$	
S(1) ··· C(2)	3.98
S(1) ··· H(5)	3.33
$A(000) \cdots D(01\bar{1})$	
S(4) ··· C(1)	4.00
S(4) ··· H(1)	3.26
$A(000) \cdots \bar{C}(011)$	
S(3) ··· C(1)	3.88
S(3) ··· H(2)	3.19
$A(000) \cdots \bar{B}(02\bar{1})$	
S(2) ··· S(3)	4.05
S(2) ··· C(1)	3.92
S(2) ··· H(3)	3.19
S(4) ··· C(2)	4.02
S(4) ··· H(6)	3.15
$A(000) \cdots \bar{B}(020)$	
S(3) ··· S(4)	3.99
S(3) ··· C(2)	4.01
S(3) ··· H(5)	3.21
$A(000) \cdots \bar{A}(021)$	
S(2) ··· S(3)	4.05
S(2) ··· C(1)	3.92
S(2) ··· H(3)	3.19
$A(000) \cdots B(100)$	
C(2) ··· C(2)	3.86
$A(000) \cdots \bar{A}(121)$	
C(2) ··· C(2)	3.76
C(2) ··· H(4)	3.13
H(4) ··· H(4)	2.71
H(4) ··· H(6)	2.68

Atoms in various asymmetric units are indicated by the symbols A for co-ordinates (x, y, z), $\bar{A}$ $(\bar{x}, \bar{y}, \bar{z})$, B $(\bar{x}, y, \frac{1}{2} - z)$, $\bar{B}$ $(x, \bar{y}, \frac{1}{2} + z)$, C $(\frac{1}{2} + x, \frac{1}{2} + y, z)$, $\bar{C}$ $(\frac{1}{2} - x, \frac{1}{2} - y, \bar{z})$, D $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $\bar{D}$ $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$. In this notation $B(\alpha\beta\gamma)$ stands for fractional co-ordinates $(\alpha - x, \beta + y, \gamma + \frac{1}{2} - z)$; the reference molecule with co-ordinates (x, y, z) is $A(000)$.

* L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.

Whereas structurally related molecules with T_d symmetry, such as adamantane,[40] and hexamethylenetetramine,[41] both crystallize in cubic space groups due to their spherical shape, hexathia-adamantane [21] is tetragonal and the less symmetric (I) has still lower crystal symmetry. This is undoubtedly the result of the greater space requirements of the MeSi groups as compared with the sulphur atoms. In spite of the lowering of crystal symmetry for packing requirements, (I) is less densely packed than hexathia-adamantane, as is obvious from their densities (1.56 and 2.07 g cm^{-3}). By assuming a monoclinic space group, offset of adjoining molecules of (I) by *ca.* 1.4 Å, due to the β-angle and a slight twisting about the [010] axis, considerably improves the packing arrangement, allowing the molecular centres to come closer together for the same minimum interatomic distances. Indeed, the smallest distance between centres of molecules ($\bar{B}_{021} \cdots A_{000} \cdots \bar{B}_{020}$, *etc.*) is of the order of 6.4 Å, which compares very favourably with the disordered adamantane structure (6.7 Å) and that of hexamethylenetetramine (6.1 Å). In the latter structure, forces other than purely van der Waals were postulated,[41] and, similarly, electronic forces might also be of importance in (I). In accordance with Cruickshank's [42] thermodynamic

---

[39] D. W. J. Cruickshank, *Acta Cryst.*, 1964, **17**, 677.

[40] C. E. Nordman and D. L. Schmitkons, *Acta Cryst.*, 1965, **18**, 764.

[41] P. A. Shaffer, *J. Amer. Chem. Soc.*, 1947, **69**, 1557.

[42] L. N. Becka and D. W. J. Cruickshank, *Proc. Roy. Soc.*, 1963, **273A**, 435.

arguments, the high molecular symmetry is thought to be mainly responsible for a melting point which is higher than usual for most substances of similar molecular weight. Nevertheless, the lowering in melting point from adamantane (269 °C)[43] to 1,3,5,7-tetramethyladamantane (67 °C)[44] is much less pronounced in hexathia-adamantanes [2,4,6,8,9,10-hexathia-adamantane, 330 (decomp.);[45] 1,3,5,7-tetramethyl-2,4,6,8,9,10-hexathia-adamantane, 225;[46] 1,3,5,7-tetramethyl-2,4,6,-8,9,10-hexathia-silamantane, 275 °C [2]], suggesting some influence of intermolecular forces involving sulphur atoms. While in (I) all intermolecular distances are compatible with accepted van der Waals radii, a number of S • • • H distances were found to be close to the expected sum.

Table 10

Crystallographic data for isostructural tetramethylhexathia-adamantanes

Compound	Unit-cell parameters					D_m/ g cm^{-3}	M.p. (t/ °C)
	a/Å	b/Å	c/Å	β/°	U/Å^3		
$(MeSi)_4S_6$	9.382	16.513	10.584	107.16	1 560.9	1.560	272—275
$(MeGe)_4S_6$	9.422	16.779	10.708	107.94	1 611.0	2.239	345—346
$(MeSn)_4S_6$	9.772	17.351	10.958	109.0	1 757.0	2.750	

As is obvious from Figure 2 the molecular shape of tetramethylhexathia-adamantanes is not greatly influenced by the variations in the atomic radii of the Si, Ge, and Sn atoms but the intramolecular dimensions do vary because bond lengths increase while the valence angles are constant (Table 8). Consequently, cell dimensions vary: Δb in the first approximation corresponds to twice the increase in the fourth neighbour S • • • S distance (*ca.* 8.7, 8.9, and 9.3 Å for the Si, Ge, and Sn analogues, including van der Waals radii), while Δa and Δc are more closely related to the variation in the C • • • C distance across the molecule. Crystallographic data for some isostructural tetramethylhexathia-adamantanes are collected in Table 10; 1,3,5,7-tetramethyl-2,4,6,8,9,10-hexathia-adamantane is not isostructural with the Si, Ge, and Sn analogues, crystallizing in space group $P2_1/c$, with $a = 13.06$, $b = 12.22$, $c = 8.41$ Å, $\beta = 93.29°$, and with the molecules in general positions.[6]

We thank Dr. K. Moedritzer, Monsanto Corporate Research Department, St. Louis, for preparing the sample of (I).

[4/2003 *Received, 30th September,* 1974]

---

[43] S. Landa and V. Macháček, *Coll. Czech. Chem. Comm.*, 1933, **5**, 1.

[44] S. Landa and Z. Kamýček, *Coll. Czech. Chem. Comm.*, 1959, **14**, 4004.

[45] A. Fredga and K. Olsson, *Arkiv. Kemi.* 1956, **9**, 163.

[46] K. Olsson, *Acta Chem. Scand.*, 1958, **12**, 366; *Arkiv. Kemi,* 1959, **14**, 371.