

## The Crystal and Molecular Structure of Tetrakis(chloromethyl)hexathiaadamantane

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The crystal structure has been determined from 672 reflexions. The crystals are tetragonal with space group  $I4_1/a$  with 4 molecules per unit cell. The cell dimensions are  $a=b=8.681$ ,  $c=20.46$  Å. The structure was solved by the heavy-atom technique and refined by block-diagonal least-squares calculations to  $R=0.060$ . The molecule has a  $\bar{4}$  axis through two of the S atoms, the other four lying in a plane perpendicular to the axis. Four C atoms lie outside the faces of the S octahedron and with the attached C-Cl groups form planes roughly parallel to the  $\bar{4}$  axes. The bond lengths and angles are all normal. The molecules pack in the form of a nested, interlocking structure with no especially short contacts.

### Introduction

Sulphur compounds with adamantane structures have been studied for many years; for reviews see Fredga (1973) and Olsson (1967). The crystal structure of hexathiaadamantane,  $(\text{CH})_4\text{S}_6$ , was described by Krogh Andersen & Lindqvist (1956). Infrared and Raman spectra of tetramethylhexathiaadamantane have been reported by Barnes, Dalziel & Ross (1971). During continued work on its alkyl derivatives, Olsson, Baekström & Engwall (1966) found some unexpected properties of tetrakis(chloromethyl)hexathiaadamantane. This substance forms colourless crystals with very low solubility in most solvents. Sublimation occurs only above  $250^\circ$  and the crystals decompose without melting at approximately  $290^\circ$ . A comparable substance such as tetraethylhexathiaadamantane melts at  $123^\circ$  and is readily soluble (Fredga & Bauer, 1950). Some kind of intermolecular interaction involving the chlorine atoms was supposed to exist. A single-crystal analysis was undertaken to study the situation.

### Experimental

The crystals were somewhat distorted octahedrons crystallized from *p*-dioxane. Preliminary cell dimensions were obtained from rotation and Weissenberg photographs which also showed the space group to be  $I4_1/a$ . A crystal with the dimensions  $0.18 \times 0.25$  mm (the rectangular cross section) and  $0.44$  mm (the length of the octahedron) was mounted along the  $0.25$  mm edge which was found to be the  $a$  axis. The data were collected on a Picker FACS-1 automatic four-circle diffractometer using graphite-monochromatized Cu  $K\alpha$  radiation ( $\lambda=1.54051$  Å, take-off angle  $3.5^\circ$ ).

The cell dimensions were determined from 12 reflexions with  $2\theta$  between  $50$  and  $106^\circ$  by a least-squares fit. The following values (with standard deviations) were obtained:  $a=b=8.681$  (1) Å,  $c=20.46$  (2) Å. The data collection was performed by  $\theta/2\theta$  scan with a constant scanning speed of  $1^\circ$  ( $2\theta$ )  $\text{min}^{-1}$ . The scan width

was  $2.5^\circ$  plus a dispersion correction. The background was measured for 10 s at each end of the scan range. Attenuators were inserted when the count rate exceeded 10 000 c.p.s. Three standard reflexions were measured after every 50 reflexions. The sum of these reflexions was used to scale the observed intensities by interpolation between the groups of standards. The maximum correction (in the structure factors) was 1.0%.

Three separate sets of reflexions were measured. The average value of the standard reflexions over the whole sets decreased by about 2% between the sets. A comparison of some reflexions in the three sets indicated (after correction for the 2% fall off) a reproducibility of better than 2%.

The background count was subtracted and those reflexions having an intensity exceeding 2 standard deviations [calculated as  $=(c_p + c_b)^{1/2}$ , where  $c_p$  is the number of counts during the peak scan and  $c_b$  is the background count during the same time estimated by linear interpolation between measurements at the ends of the scan) were treated as observed. Thus 681 of the 727 measured reflexions with  $2\theta < 125^\circ$  were retained and  $L_p$ -corrected. Some weak reflexions forbidden by the space group were removed so that the final set of observed data comprised 672 reflexions.

### Structure determination

The following systematic absences were observed in the photographic data and confirmed by a separate data collection on the diffractometer without any reject routine:  $hkl$  for  $h+k+l=2n+1$ ;  $hk0$  for  $h=2n$ ,  $k=2n$ ;  $00l$  for  $l=4n$ .

Some reflexions (especially  $00l$ ,  $l \neq 4n$ ) were also tested by separate measurements on the calculated peak positions for longer times and compared with the local background to establish the absence safely. The absences correspond to the space group  $I4_1/a$  (No. 88).

The observed density (by flotation) of the crystals is  $1.93$   $\text{g cm}^{-3}$ . With 4 molecules in the unit cell the

calculated value is 1.89. The fourfold positions of the space group require the molecule to have the point symmetry  $\bar{4}$ . The structure proposed by Olsson *et al.* (1966) has three  $\bar{4}$  axes through pairs of S atoms. The origin was therefore chosen to be on the  $\bar{4}$  axis rather than in the centre of symmetry. A Patterson function was calculated and showed the expected S-S peaks from atoms in  $0,0,z_1$ ;  $0,0,-z_1$ ;  $x_2,y_2,0$ ;  $-x_2,-y_2,0$ ;  $-y_2,x_2,0$  and  $y_2,-x_2,0$ . A structure-factor calculation with  $z_1=0.106$ ,  $x_2=0.237$ ,  $y_2=0.041$  gave  $R=0.60$  and the corresponding  $F_{obs}$  synthesis showed the Cl position. With this atom included  $R=0.30$  was obtained and the electron density showed the two carbon atoms. Inclusion of these then gave  $R=0.18$ . Block-diagonal refinement with isotropic temperature factors and H atoms in calculated positions (in accordance with a difference map) gave  $R=0.063$  but the weighting scheme was then rather poor.

At this stage the data were corrected for absorption (by numerical evaluation with a grid of  $6 \times 10 \times 6$  points). The absorption coefficient was  $\mu=141 \text{ cm}^{-1}$  and the transmissions obtained ranged from 0.097 to 0.266. The refinement was then restarted with the non-hydrogen atoms treated anisotropically. Anomalous dispersion was also included in the calculations for S and Cl. Some different weighting schemes were tried and the best agreement between  $|F_c|$  and  $|F_o|$  over the whole range of  $|F_o|$  was obtained with the Hughes scheme with  $w=1/|F_o|^2$  for  $|F_o| > 12$  and  $w=1/(12)^2$  for  $|F_o| \leq 12$ . The refinement converged to  $R=0.062$ . The maximum shift in positional parameters in the last cycle was 0.18 times the corresponding standard deviation (0.31 for H atoms) and in the vibration parameters 0.35. The weight analysis for the final cycle is given in Table 1. Seven weak reflexions with  $|F_o|/|F_c| < 0.5$  or  $|F_o|/|F_c| > 4.0$  were given zero weight.

Table 1. Weight analysis for the final cycle

$ F_o $ interval	$w( F_o  -  F_c )^2$	No. of reflexions
0.0- 3.2	0.984	60
3.2- 5.1	0.904	67
5.1- 7.5	0.845	67
7.5- 10.5	0.578	67
10.5- 13.4	0.994	68
13.4- 16.9	0.986	67
16.9- 22.3	1.033	67
22.3- 29.1	1.095	67
29.1- 44.1	1.047	67
44.1-112.1	1.535	68

Finally an isotropic secondary extinction parameter ( $g$ ) was introduced and refined together with the other parameters for some cycles. The resulting value of  $g$  was  $0.753 \times 10^4$  which corresponds to  $\eta=7.7''$  for type 1 extinction and  $1.16 \mu\text{m}$  for type 2. No significant changes in the positional parameters appeared but some temperature parameters shifted appreciably [especially for S(2) and Cl(1)]. The  $R$  value dropped to 0.060 (weighted  $R=0.085$ ) and the goodness-of-fit {defined as  $[\sum w(F_o - F_c)^2 / (r-p)]^{1/2}$ } then was 6.19.

The calculations were performed with the following programs in the program system of the Institute of Inorganic Chemistry: *DATAP2* (originally written by

Table 2. Final atomic fractional coordinates with estimated standard deviations (in the last digit) in parentheses

	$x$	$y$	$z$
S(1)	0.0	0.0	0.10421 (6)
S(2)	0.24547 (11)	0.04566 (11)	0.0
Cl(1)	0.28419 (15)	0.38970 (14)	-0.05200 (6)
C(1)	0.0944 (4)	0.1353 (4)	-0.0481 (2)
C(2)	0.1712 (5)	0.2517 (5)	-0.0945 (2)
H(1)	0.229 (6)	0.218 (5)	-0.126 (3)
H(2)	0.081 (6)	0.322 (6)	-0.118 (3)

Table 3. Final thermal parameters with estimated standard deviations

The anisotropic temperature factor is  $\exp [(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - 2B_{12}hk - 2B_{13}hl - 2B_{23}kl)10^{-3}]$  and the isotropic factor  $\exp [-B \sin^2 \theta / \lambda^2]$ .

	$B$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
S(1)		841 (23)	863 (23)	136 (4)	-66 (14)	24	24
S(2)		641 (19)	817 (19)	175 (4)	-28 (10)	2 (4)	66 (4)
Cl(1)		1546 (25)	1117 (22)	290 (5)	-468 (14)	-53 (6)	124 (5)
C(1)		691 (54)	677 (53)	155 (10)	-32 (39)	12 (15)	8 (16)
C(2)		976 (61)	850 (58)	165 (10)	-14 (53)	101 (20)	71 (20)
H(1)	3.1 (10)						
H(2)	4.0 (10)						

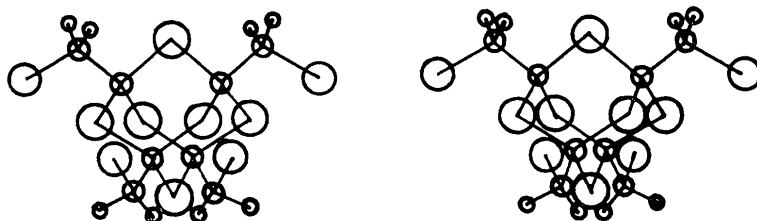


Fig. 1. Stereoscopic view of the molecule.

A. Zalkin), *BLOCK* (written by O. Lindgren at this Institute, *DISTAN* (originally written by A. Zalkin), *LINUS* (the Hamilton version of Busing & Levy's *ORFLS*), *PLANEFIT* (according to a procedure of D. M. Blow) and *ORTEP* (written by C. Johnson). The form factors used were taken from Doyle & Turner (1968) and (for H) from Stewart, Davidson & Simpson (1965). The final parameters are listed in Tables 2 and 3 and the final structure factors in Table 4.\*

\* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30591 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

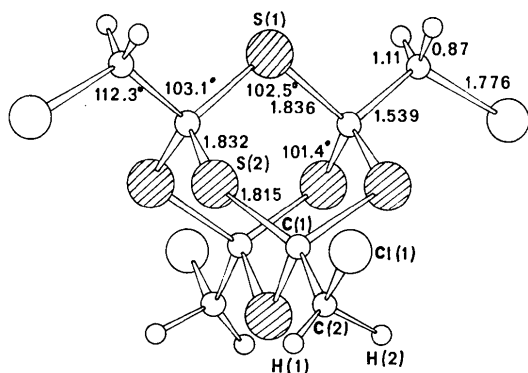


Fig. 2. Schematic view of the molecule with atom numbering and some bond lengths and angles.

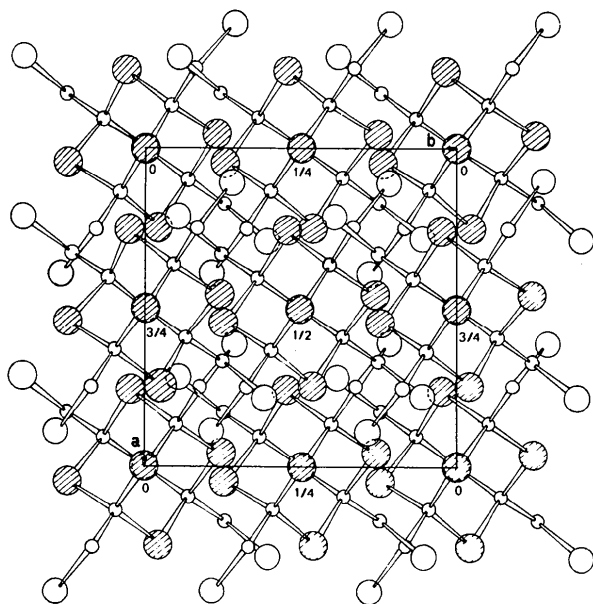


Fig. 3. Schematic view of the structure seen along the *c* axis. Hydrogen atoms are not shown. At the (overlapping) S(1) atoms the *z* coordinate of the center of the molecule is given.

## Results and discussion

### Molecular geometry

A stereoscopic view of the molecule is shown in Fig. 1, and a schematic view (also showing the atom labelling) from roughly the same direction in Fig. 2. The S atoms form an octahedron which is slightly compressed along the *c* axis which is also the  $\bar{4}$  axis of the molecule. The octahedron edges in the *ab* plane [between atoms S(2)] are 3.065 Å and the edges out of this plane [between S(1) and S(2) atoms] are 3.040 Å.

S—C—S distances have been determined by *e.g.* Hassel & Viervoll (1947) (by electron diffraction) who found the value 3.05 Å for S—S in 1,3,5-trithiane and its 2,4,6-trimethyl derivative. The diagonal of the square of S(2) atoms is 4.335 Å while the distance between the two S(1) atoms is 4.264 Å.

The C(1) atoms are situated outside four of the faces of the octahedron, their distance from the plane being 0.49 Å. These carbon atoms form a tetrahedron with edge 2.84 Å with no significant deviations from regularity. The plane of the chain C(1)—C(2)—Cl(1) is slightly inclined to the 'vertical' plane (*i.e.* a plane perpendicular to the *ab* plane) through C(1) and S(1). This can be seen in Fig. 3 which shows the structure as seen along the fourfold axis. C(2) is situated 0.03 Å to one side of the vertical plane and Cl(1) 0.10 Å to the other side. The torsion angle C(1)—S(1)—C(1)—C(2) is 2.4° and S(1)—C(1)—C(2)—Cl(1) 6.9°.

### Bond lengths and angles

Table 5 shows the bond lengths and Table 6 the angles between bonds together with the estimated standard deviations. Some of the numbers are also shown in Fig. 2. They are not corrected for thermal motion.

Table 5. Bond lengths with estimated standard deviations (Å)

S(1)—C(1)	1.836 (4)	} average 1.828
S(2)—C(1)	1.815 (4)	
C(1)—C(2)	1.832 (4)	
C(1)—C(2)	1.539 (6)	} average 0.99
C(2)—Cl(1)	1.776 (4)	
C(2)—H(1)	0.87 (5)	
C(2)—H(2)	1.11 (5)	

Table 6. Bond angles with estimated standard deviations (°)

C(1)—S(1)—C(1)	102.5 (2)	C(1)—C(2)—Cl(1)	112.3 (3)
C(1)—S(2)—C(1)	101.4 (2)	C(1)—C(2)—H(1)	119 (3)
S(1)—C(1)—C(2)	103.1 (3)	C(1)—C(2)—H(2)	109 (3)
S(2)—C(1)—S(2)	114.4 (2)	H(1)—C(2)—H(2)	106 (4)
S(1)—C(1)—S(2)	112.8 (2)	H(1)—C(2)—Cl(1)	106 (3)
	111.9 (2)	H(2)—C(2)—Cl(1)	104 (3)
S(2)—C(1)—C(2)	107.6 (3)		
	106.0 (3)		

The three S–C distances from C(1) are hardly significantly different. The average is 1.828 Å which can be compared with the average literature value 1.817 (5) (Sutton, 1965). C(1) is thus symmetrically situated with respect to the triangle of S atoms but the angles at C(1) indicate that this atom is forced towards the triangle [the distance of C(1) from the plane of the triangle should be 0.61 Å with normal tetrahedral angles but is actually 0.49 Å]. Moreover, the chain C(2)–Cl(1) is forced somewhat away from the plane through the S(2) atoms.

The C–C distance 1.539 Å can be considered normal as well as the average C–H distance 0.99 Å. The C–Cl distance 1.776 Å compares well with the value 1.783 (3) for methyl chloride (Bartell & Brockway, 1955).

#### Molecular packing

In Fig 3, the structure is shown as seen along the fourfold axis. Adjacent molecules have their centres displaced  $c/4$ , *i.e.* 5.1 Å, along the line of view. The projection of the centres forms squares with edge 4.34 Å. This structure is quite different from that of hexathiaadamantane (Krogh Andersen & Lindqvist, 1956) where the molecules have their centres on squares with the edge 7.12 Å with one molecular center 3.9 Å above the center of the square.

The molecules are turned so that the edges of the sulphur octahedra form an angle 10.5° with the *a* and *b* axes. A similar turning exists in hexathiaadamantane with 25°. The structure can be looked upon as spirals of sulphur octahedra around the  $4_1$  axes. Inside the spiral is a tunnel into which the side chains project. Fig. 4 shows (schematically) the structure seen along the *ab* diagonal. This shows layers of molecules with a separation of  $c/4$  between the layers. Within these layers the distance between molecular centres is 8.68 Å.

The shortest intermolecular contact between S atoms is between S(1) and S(2) atoms in different layers. The distance is 3.73 Å which is a normal van der Waals distance.

The shortest Cl–Cl distance, 3.66 Å, is between atoms in the same layer. This is also a normal van der Waals contact. Contacts between S and Cl also exist with a

distance 3.93 Å as minimum. The closest contact between atoms in the 'tunnel' region, 4.29 Å, is between Cl(1) and C(2) in neighbouring layers [the distance Cl(1)–H(1) is 3.80 and Cl(1)–H(2) is 3.78 Å]. Between S(2) and C(2) there is a contact of 4.02 Å.

No exceptionally short distances are thus found between the molecules. The reason for the high melting point and the very low solubility may be that the packing of the molecules is very favourable and results in a high total van der Waals attraction. This is supported by the high density of 1.89 g cm<sup>-3</sup>. It is also probable that the 'nested' structure (which is illus-

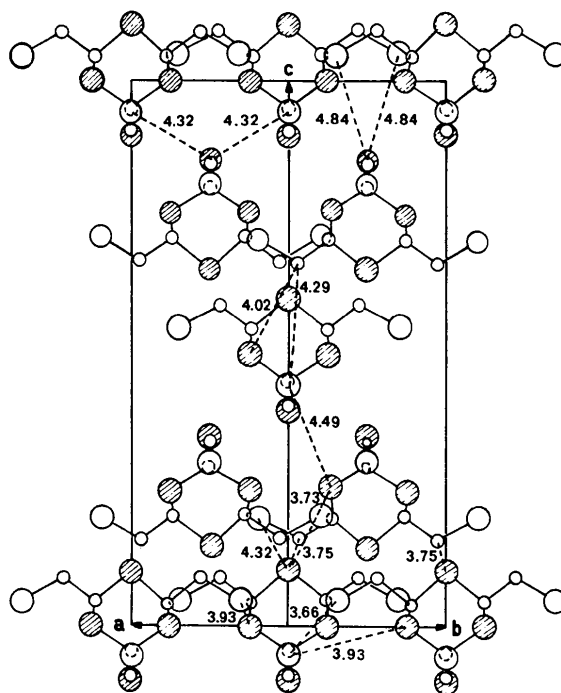


Fig. 4. Schematic view of the structure seen roughly along the *ab* diagonal. The hydrogen atoms and the effect of the 10.5° turning are not shown. Some intermolecular contact distances are given.

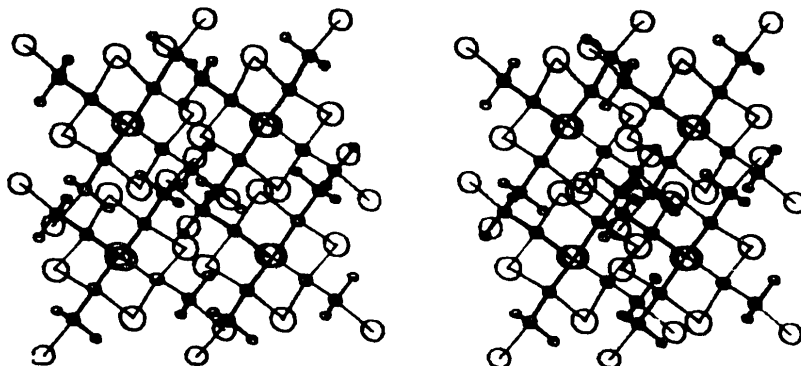


Fig. 5. Stereoscopic view of the molecular packing seen along the *c* axis.

trated in Fig. 3 and stereoscopically in Fig. 5) has an influence on the properties. To remove a molecule from the surface of a crystal seems to require a severe deformation of the side chains which 'anchor' it to the remaining molecules.

#### Thermal motion

Table 7 shows the magnitudes (in Å<sup>2</sup>) and direction cosines (relative to the *a*, *b* and *c* axes) of the principal axes of the vibration ellipsoids. Some anisotropy can be observed. It is rather small for the atoms forming the 'cage' [S(1), S(2) and C(1)] for which  $B_{\max}/B_{\min}$  is around 1.5. For C(2) the corresponding value is 2.0 and for Cl(1) 2.6. These values correlate well with the average *B* (= the geometric mean of the three magnitudes) which is 2.5 for S(1), 2.4 for S(2), 2.2 for C(1), 2.7 for C(2) and 4.0 for Cl(1). As can be expected the side chains are thus more flexible than the cage.

Table 7. Magnitudes and direction cosines (relative to the *a*, *b* and *c* axes) of the principal axes of the vibration ellipsoids

	<i>B</i>	<i>a</i>	<i>b</i>	<i>c</i>
S(1)	2.08	0.473	0.430	-0.769
	2.57	-0.627	-0.450	-0.637
	2.77	0.619	-0.783	-0.057
S(2)	1.91	0.970	0.227	-0.091
	2.19	-0.241	0.818	-0.522
	3.22	0.044	-0.528	-0.848
Cl(1)	2.34	0.479	0.849	-0.225
	4.44	-0.591	0.122	-0.798
	6.11	0.649	-0.515	-0.560
C(1)	1.95	0.637	0.756	-0.150
	2.16	0.757	-0.650	-0.063
	2.61	-0.146	-0.074	-0.987
C(2)	1.87	0.485	0.535	-0.692
	2.73	0.568	-0.794	-0.215
	3.67	-0.665	-0.289	-0.689

The maximum vibration for Cl(1) is roughly perpendicular to the plane of the chain C(1)-C(2)-Cl(1) while that for C(2) lies close to the chain plane. The

minimum vibration is for both atoms roughly in the chain plane. The angle between the two directions of maximum vibration is 84°.

The isotropic *B*'s for the hydrogen atoms (3.1 and 4.0) are not significantly different and are slightly higher than that for the parent atom [2.6 for C(2)].

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