53. The Crystal and Molecular Structure of 1-Methyl-1-Thionia-Cyclohexane Iodide

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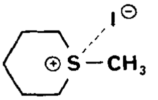
(5. I. 74)

Summary. Crystals of 1-methyl-1-thionia-cyclohexane iodide are orthorhombic with space group $Pna2_1$, a = 18.036, b = 6.611, c = 7.420 Å, Z = 4. The crystal structure was solved by the heavy-atom method. Very strong parameter interactions prevented least-squares refinement of atoms other than S and I. The molecule adopts the chair conformation with the methyl group in equatorial position.

Saturated ring systems containing one or several sulfur atoms have been less studied than those containing elements of the second period, though theoretically interesting conformational features might be associated with the different oxidation states of sulfur. Several cases are known where a bulky exocyclic group attached to an heterosulfur atom prefers to adopt an axial position [1]. The question might arise as to the orientation of a group attached to formally positive sulfur, as in cyclic sulfoniums. We now report the structure of 1-methyl-thionia-cyclohexane iodide (**1**) as determined by X-ray analysis.



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Experimental part. – Prismatic crystals were obtained by very slow evaporation of a solution of **1** in anhydrous ethanol. The unit cell is orthorhombic and its dimensions were measured on calibrated Weissenberg and precession photographs: $a = 18.036 \pm 0.008$ Å, $b = 6.611 \pm 0.005$ Å, $c = 7.420 \pm 0.005$ Å, $U = 884.7$ Å^3. There are 4 molecules in the unit cell. The non-unique set of systematic extinctions is consistent with the space groups $Pna2_1$ and *Pnam* (*Pnma*, with the appropriate axis setting). At a later stage of the investigation, $Pna2_1$ proved to be correct. The crystalline compound **1** is very prone to decomposition under X-ray irradiation, and four crystals were necessary to collect the 1280 reflections used in this determination. Intensity data were measured on a *Hilger & Watts* Y190 linear diffractometer by the moving crystal-stationary counter method, with balanced filter and Mo radiation, at an ω-scan standard time of 140 sec. The main set of 1060 reflections was collected by rotating the crystal about the *c* axis; the correlation factors to bring reflections of various layers to a common intensity scale were calculated by a least-squares procedure including reflections collected from a crystal rotated about the *b* axis. No corrections were made for absorption.

Structure Analysis and Refinement. – The heavy-atom method was used for the determination of the atomic positions of the iodine and sulfur atoms from a three-dimensional *Patterson* synthesis. The number of molecules in the unit cell suggests space group $Pna2_1$ rather than *Pnma*, unless *m* is also a mirror plane for the ion-pair $C_6H_{13}S^+I^-$; the latter possibility entails relationships among the variables of the *Harker* lines. The relationships were absent in the *Patterson* synthesis, which, on the $Pna2_1$ assumption, allowed straightforward determination of the coordinates of the I and S atoms (z_I was arbitrarily fixed at zero). Two- and then three-dimensional *Fourier* syntheses permitted the stepwise determination of all the remaining positional parameters for the non-hydrogen atoms. Atomic scattering curves for the neutral S and I atoms were used. At this stage of the analysis the residual factor was 0.12 with a single isotropic temperature factor for all atoms.

Refinement by the least-squares (LS) method was found unsatisfactory because of the following reasons: The z-coordinates of the I and S atoms differ by approximately 0.5, so that, although the space group is non-centrosymmetric, the heavy atoms themselves form a nearly centrosymmetric arrangement, which imposes special values on the phases[1]. It is actually observed that many phases are close to 0 or π. Moreover, when atoms overlap in projection, strong interdependence prevails between their parameters [2]. This is the case here for the pairs of atoms C(1), C(5) and C(2), C(4), which show correlation coefficients higher than $|0.9|$ between their positional parameters in the LS-correlation matrix. An ill-conditioned LS-matrix results from this strong parameters interdependence [3], and the entire structure is then unrefinable from the available data.

In the present case, the LS-method was used only to refine the positional and anisotropic thermal parameters of the heavy atoms, maintaining 'constant' values for the other parameters. The shifts of the carbon atoms were determined, between the LS runs, by *Fourier* and difference-*Fourier* techniques. Therefore only isotropic temperature factors are given for these atoms. This somewhat lengthy procedure yielded a final R value of 0.057 based on 884 reflections included in the LS-routine (the ring hydrogen atoms were included at calculated positions in the later stages). Standard deviations in the carbon positional parameters, estimated on the basis of the average shifts in the last two *Fourier* syntheses, are in the range 0.010 to 0.016 Å. For the heavy atoms the range is 0.003 to 0.010 Å, the largest values being associated with the z-coordinates.

Discussion of the results. – A perspective view of the conformation of **1** is shown in Figure 1, together with the atom-numbering. Atomic positions are listed in Table 1, anisotropic thermal parameters in Table 2, and molecular geometry parameters in Table 3. The average standard deviation is about 1% in bond distances and

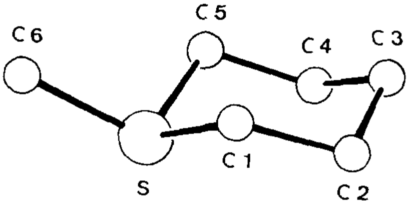

Fig. 1. *Perspective view of the molecular conformation*

Table 1. *Final positional and isotropic thermal parameters*

Atom	x	y	z	B
C(1)	.1305	.6282	.6850	2.70
C(2)	.1976	.7680	.6673	3.40
C(3)	.1940	.8971	.4993	3.70
C(4)	.1965	.7690	.3303	3.40
C(5)	.1300	.6300	.3120	2.70
C(6)	.0419	.3360	.5044	3.75
S	.13182	.4538	.4982	[a]
I	.08495	.14397	−.00734	[a]

[a] See anisotropic thermal parameters in Table 2.

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[1] With $z_I = 0.0$ the 'centres of symmetry' appear at $(0, 0, {}^1/_4)$, $(0, 0, 3/4)$, etc. The actual location of these centres is, however, irrelevant in the following discussion.

Table 2. *Final anisotropic thermal parameters of the heavy atoms* ($\times 10^4$)
The anisotropic temperature factors are of the form
$\exp\text{-}\{b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl\}$

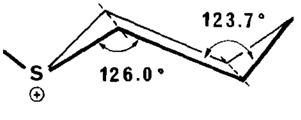
Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S	19	147	137	5	23	64
I	26	224	158	4	5	49

Table 3. *Molecular parameters derived from coordinates of Table 1.* (For atom-numbering system, see Fig. 1)

Bond distances	(Å)	Bond angles	(°)	Torsion angles	(°)
S—C(1)	1.80_4	C(1)—S—C(5)	100.1	S—C(1)—C(2)—C(3)	63.7
S—C(5)	1.80_7	C(1)—S—C(6)	104.8	C(1)—C(2)—C(3)—C(4)	−63.6
S—C(6)	1.79_9	C(5)—S—C(6)	106.4	C(2)—C(3)—C(4)—C(5)	63.9
C(1)—C(2)	1.53	S—C(1)—C(2)	108.1	C(3)—C(4)—C(5)—S	−63.5
C(2)—C(3)	1.51	C(1)—C(2)—C(3)	112.2	C(4)—C(5)—S—C(1)	57.8
C(3)—C(4)	1.52	C(2)—C(3)—C(4)	111.4	C(5)—S—C(1)—C(2)	−58.1
C(4)—C(5)	1.51	C(3)—C(4)—C(5)	113.0	C(6)—S—C(1)—C(2)	−168.0
		C(4)—C(5)—S	107.9	C(4)—C(5)—S—C(6)	166.0

angles. Hydrogen atom positions (not reported here) were calculated from the final distribution of carbon atoms, assuming C–H distance 1.09 Å and local C_{2v}-symmetry of the methylene groups.

As expected, the six-membered ring prefers the 'chair' conformation; however, unlike the more bulky I_2-grouping in the 1,4-dithiane-iodine complex [1b], the methyl substituent of **1** is equatorial. The observed molecular conformation possesses C_s symmetry within limits of error. The S–C and C–C bond distances are close to those found for sulphoxides and sulphones[2]. A measure of comparison of the shape of **1** with the 'chair' conformation of cyclohexane is provided by the dihedral angles θ'_D and θ''_D defined as the angles between the best planes through atoms C(1)–C(2)–C(4)–C(5) and, respectively, S–C(1)–C(5) and C(2)–C(3)–C(4). The values are $\theta'_D = 126.0°$ and $\theta''_D = 123.7°$ (see **2** below); one can therefore say that, perpendicularly to the mirror plane, the heterocycle is more folded than cyclohexane with $\theta_D = 132.1°$[3]. Because of the long S–C bonds, and in spite of the angle C(1)–S–C(5) being smaller than 112°, atoms C(1) and C(5) are farther apart than C(2) and C(4). As a result, C(3) is forced towards the sulfur atom, thus decreasing θ''_D since the



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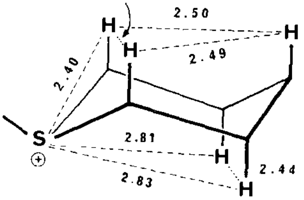

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[2] Structural comparisons are made mainly with experimental values taken from [4].

[3] Calculated for a C—C—C angle of 112°.

angles at C(2), C(3) and C(4) keep their value close to 112°. The increased folding of the 'chair' still does not involve strong interactions between the axial hydrogens, as shown by **3**. It must be stressed that the distances (in Å) given by **3** correspond to *calculated* hydrogen positions. Stronger non-bonded interactions prevail between the sulfur atom and some axial hydrogens, which come closer than the S...H *van der Waals* distance of 3.05 Å. In particular, the short distance of 2.40 Å between S and the vicinal H atoms raises the question of the significance of the *van der Waals* radius in a direction close to that of a chemical bond. It has been suggested [5] to assign to the H atoms an 'interference radius' of 0.6 Å in such cases.

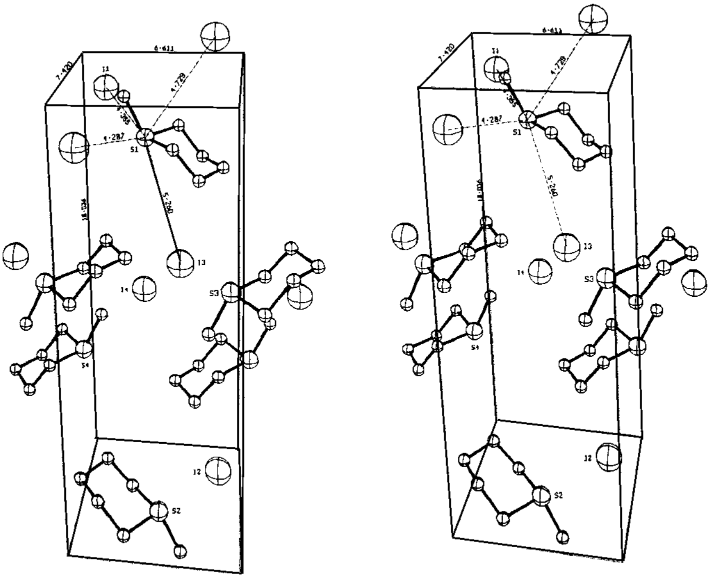

Fig. 2. *Stereoscopic view of the unit cell with some aspects of the molecular packing.*
The origin is in the upper-left, rear corner. The labels specify the four assymetric units. The atom-numbering (not indicated) of the basic molecule *1* (x, y, z) is the same as in **Fig. 1.** Molecule *2* is related to *1* by the screw axis passing through the origin; for convenience, molecule *2* has been translated one unit along *a* and one unit along *b*. Molecules *3* and *4* are generated, respectively, by the glide planes *n* and *a*. Additional atoms and molecules (unlabelled) illustrate some aspects of the packing. The shortest S...I distances are given in Å along the dotted lines bonded to S1. The size of the atoms is proportional to their atomic radii.

The attractive forces in the crystal are mainly ionic in nature, as evident in Figure 2, where it can be seen that the heavy atoms form a three-dimensional network. Zig-zag chains displaying the sequence I...S...I'unfold along the *c*-direction. In the (001) planes, stacked at intervals of $^1/_2$, the separations between the heavy atoms are larger than in a direction perpendicular to them: this is reflected in the easy cleavage of the crystal parallel to (100). The coulombic interactions are partially screened by the hydrocarbon residues; for instance, the iodine ions separated by the [001] translation are in tight contact with the intervening methyl groups. There are relatively few *van der Waals* contacts between the organic components. The main interactions are: a) between S and the axial H attached to C(3) of the molecule at one repeat distance along [010]; b) between the H atoms on C(2) (or C(4)) of one molecule and the H atoms on C(4) (or C(2)) of the symmetric equivalent molecules related by *a* and by *n*.

We express our thanks to Prof. *J. D. Dunitz* (ETH Zürich) for use of the linear diffractometer.

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54. Stereoelectronic Properties of Tetrahedral Species derived from Carbonyl Groups.

Ab initio Study of the Hydroxymethanes

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(10. I. 74)

Summary. Analysis of the electronic structure of the hydroxymethanes provides a consistent picture of stereoelectronic effects in such molecules: The average C—O bond length decreases in the series methanol, methanediol, methanetriol. An oxygen (O′) lone pair, which is *trans*-antiperiplanar (*app*) to another oxygen (O″), shortens and strengthens the C—O′ bond and simultaneously lengthens and weakens the C—O″ bond. This is consistent with solid state structural evidence and with the reactivity patterns of tetrahedral species resulting from nucleophilic addition to a carbonyl group.

Tetrahedral species resulting from nucleophilic addition to carbonyl groups play a central role in the mechanisms and kinetics of many chemical and biochemical reactions. Recent experimental studies have stressed the importance of conformation, in particular the orientation of electronic lone pairs, in controlling the decomposition of such tetrahedral intermediates [1] [2]. The interaction of an antiperiplanar (*app*) lone pair with a σ-bond has been discussed by *Lucken* [3] and has been invoked in the interpretation of the anomeric effect [4] [5].

Following our work on the addition of hydride ion to formaldehyde [6], we have performed non-empirical calculations[2]) on the hydroxymethanes, methanediol (**D**),

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[1]) Part of this work was performed during a stay of *H.-B. Bürgi* in Strasbourg.

[2]) Basis set of gaussian functions: seven s, three p functions on C and O and four s functions on H contracted into three s, two p and two s respectively [6] [7].