The Molecular Structure of Thiane from Electron Diffraction

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The molecular structure of thiane has been determined by gas-phase electron diffraction at 294 K nozzle temperature. The electron diffraction data are consistent with the chair conformation of the molecule, with C_s symmetry and a considerably more puckered ring than that of cyclohexane. Assuming a C_{2v} local symmetry for bond configuration around the carbon atoms, the following bond lengths (r_g), bond angles and torsional angles were obtained: $(C-H)_{mean}$ 1.114 ± 0.002 Å, $(C-C)_{mean}$ 1.528 ± 0.003 Å, S-C 1.811 ± 0.004 Å, C-S-C 97.6 ±0.8°, S-C-C 112.7 ± 0.2°, (S)C-C-C 112.3 ± 0.4°, (C)C-C-C 113.6 ± 0.8°, H-C-H 105.7 ± 0.9°, S-C-C-C 60.8 ± 0.3°, C-C-C-C −58.6 ± 1.1° and C-S-C-C −55.4 ± 1.2°.

Dedicated to Professor Otto Bastiansen on his 70th birthday

Knowledge of the geometry and conformation of cyclohexane and its derivatives is of fundamental importance in organic chemistry. The pioneering work of the Norwegian electron diffraction school is well known in this area. Somewhat surprisingly, no detailed information has been available on the structure of the thiane molecule, although three-, four- and five-membered rings with one sulfur atom, as well as six-membered rings with two and three sulfur atoms, have been investigated rather thoroughly.[1]

An earlier microwave spectroscopic investigation[2] of thiane provided a limited amount of structural information. A chair conformation was deduced, but the rotational constants proved insufficient to uniquely specify the molecular conformation. The structural parameters communicated in the microwave report were based on a single set of rotational constants. Although these parameters are reasonable, they cannot be regarded as well-determined. The present study was initiated in order to obtain further information on this important compound.

Experimental

The sample of thiane was distilled twice before our experiment (b.p. 140–142 °C). Electron diffraction photographs were taken with a modified EG-100A apparatus,[3] using a membrane nozzle system.[4] The nozzle temperature was 294 K. The nominal accelerating voltage of the electron beam was 60 kV, and the electron wavelength was 0.04905 Å. Nozzle-to-plate distances of about 50 and 19 cm were used. Six plates were selected from each camera range for analysis. The tracing of the plates and the data reduction were carried out as in Ref. 5. The ranges of the intensity data used in the analysis were $2.0 \leq s \leq 14.0$ Å^{-1} and $9.5 \leq s \leq 36.0$ Å^{-1}, with data intervals of 0.125 and 0.25 Å^{-1}, respectively [$s = 4\pi\lambda^{-1}\sin(\theta/2)$, where λ is the wavelength and θ is the scattering angle].

The experimental and theoretical intensities corresponding to the last empirical background and refinement A (see later) are shown in Fig. 1. The corresponding radial distributions are shown in Fig. 2. The numbering of atoms is also shown in Fig. 2.

Structure analysis

The structure analysis was carried out with the least-squares method applied to the molecular intensities[6] and, in some calculations, also to the experimental principal moments of inertia[3] with
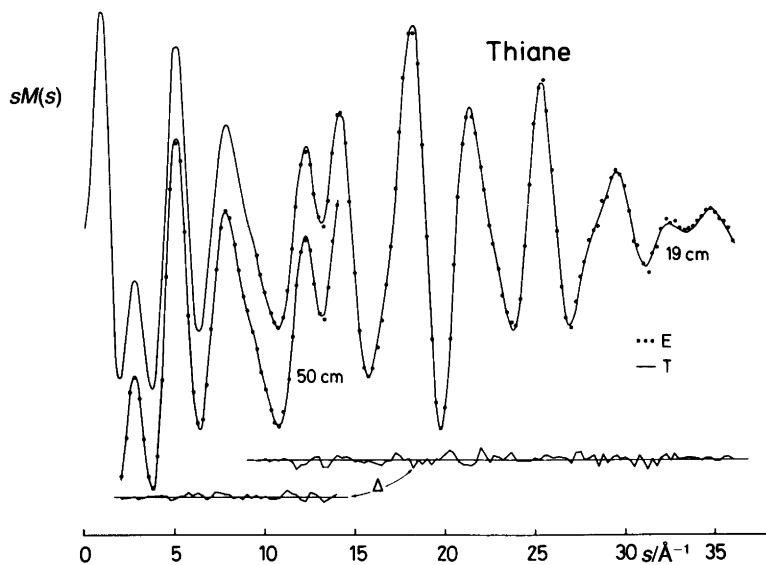
Fig. 1. Experimental (E) and theoretical (T) intensities corresponding to the last empirical background and refinement A.
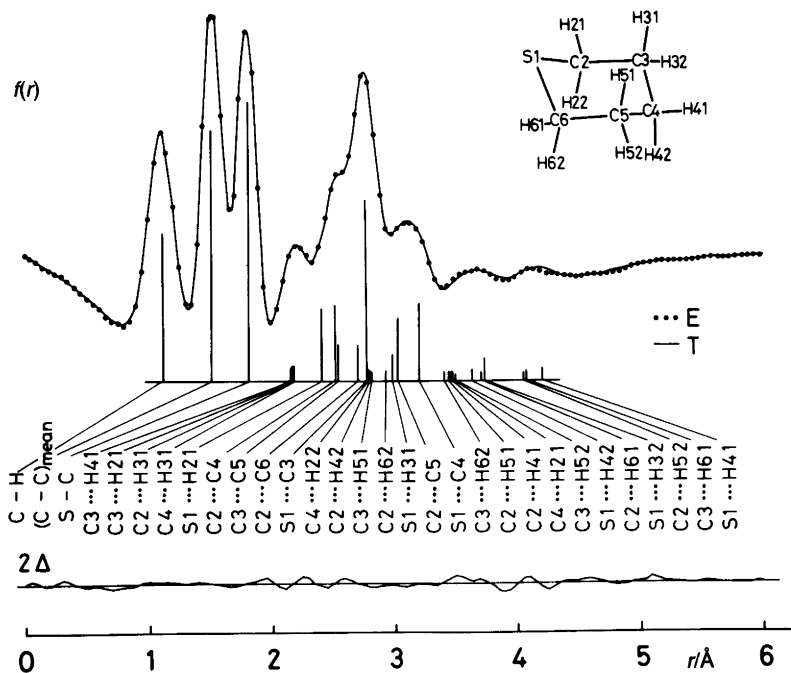

Fig. 2. Experimental (E) and theoretical (T) radial distributions corresponding to the last empirical background and refinement A.

Table 1. Results of least-squares refinements based on electron diffraction alone (A, B) and incorporating microwave data (C). Distances and amplitudes in Å, angles in degrees and principal moments of inertia in Amu Å^2. Standard deviations and mean amplitudes of vibration are given for refinement A.

Parameters	Refinement A		Refinement B	Refinement C
	$r, \angle$	l and coupling	$r, \angle$	$r, \angle$
Independent				
S^1-C^2	1.8097(4)	0.0507(7) i	1.8099	1.8098
<C-C>	1.5267(3)	0.0493(6) ii	1.5264	1.5267
<C-H>	1.1088(7)	0.0732(9) iii	1.1090	1.1091
<H-C-H>	105.5(6)		105.9	106.6
C^6-S^1-C^2	97.6(5)		97.8	97.9
C^3-C^4-C^5	113.6(5)		113.6	113.4
τ_1	49.6(6)		49.5	49.4
τ_2	−52.3(5)		−52.4	−51.7
S-C-H			107.8	108.0
C^2-C^3-H			102.0	109.4
Dependent				
$S^1 \cdots C^3$	2.781(2)	0.065(2) iv		
$S^1 \cdots C^4$	3.217(2)	0.076(2) v		
$C^2 \cdots C^6$	2.723(11)	0.065 iv		
$C^2 \cdots C^4$	2.537(4)	0.074(1) vi		
$C^3 \cdots C^5$	2.556(8)	0.073 vi		
$C^2 \cdots C^5$	3.048(2)	0.075 v		
$S^1 \cdots H^{21}$	2.418(2)	0.123 vi		
$S^1 \cdots H^{31}$	2.991(6)	0.122(9) vii		
$S^1 \cdots H^{32}$	3.756(2)	0.145(9) viii		
$S^1 \cdots H^{41}$	4.215(5)	0.11(2) ix		
$S^1 \cdots H^{42}$	3.648(13)	0.145 viii		
$C^2 \cdots H^{31}$	2.167(2)	0.108(2) x		
$C^3 \cdots H^{41}$	2.163(2)	0.108 x		
$C^3 \cdots H^{21}$	2.166	0.108 x		
$C^4 \cdots H^{31}$	2.167(2)	0.108 x		
S^1-C^2-C^3	112.7(1)			
C^2-C^3-C^4	112.3(3)			
S^1-C^2-C^3-C^4	60.8(2)			
C^2-C^3-C^4-C^5	−58.6(8)			
C^6-S^1-C^2-C^3	−55.4(9)			
R-factor/%	4.73		4.14	4.53
Weight-factor for				
MW data[a]	0.0		0.0	1000.0
ΔI_a[b]	−0.249		−1.024	−0.021
ΔI_b[b]	0.292		1.929	0.159
ΔI_c[b]	0.134		0.800	0.095

[a]In all refinements unit weights were used for electron diffraction intensity data. [b]The difference between experimental (I_a 126.575, I_b 168.333 and I_c 263.948) and calculated moments of inertia.

variable weighting factors. The results proved to be invariant to the inclusion of the microwave data for a broad range of weighting schemes.

The following independent parameters were used to describe the geometry of the molecule: bond lengths <C-C>, C-S, <C-H>, bond angles

C-S-C, C-C^4-C, <H-C-H>, and flap angles C^{6}S^{1}C^2/C^{3}C^{5}C^6 (τ_1), C^{3}C^{4}C^5/C^{3}C^{5}C^6 (τ_2). Local C_{2v} symmetry was assumed for the carbon bond configurations.

Most refinements were carried out for a chair conformation. Employing a boat or a twisted conformation led to a considerable increase in the R-factor. Our molecular mechanics calculations using Allinger's MM2 program[7] also indicated the chair form to be the most stable, viz. by 3.8 kcal mol^{-1} relative to the twisted model and 5.2 kcal mol^{-1} relative to the boat form.

The results of the least-squares refinements are presented in Table 1 (refinement A). Differences between calculated and experimental principal moments of inertia are given, although the microwave data were ignored in the refinements themselves. In addition to the geometrical parameters, ten independent amplitudes of vibration were also refined, many of them representing groups of amplitudes with fixed differences within the group; the coupling scheme is indicated in Table 1. The elements of the correlation matrix exceeding 0.5 in absolute value are given in Table 2.

Attempts to refine the difference between C^2-C^3 and C^3-C^4 bond distances resulted in unreasonable values. Fixing the difference between −0.02 and +0.02 Å indicated that the R-factor is insensitive to this choice. Thus, we concluded that only the mean value of the C-C bond lengths can be determined accurately.

The possibility of departure of bond configuration from C_{2v} symmetry around carbon atoms C^i (i = 2,3,5,6) was also investigated by introduction of two additional bond angles S^1-C^2-H and C^2-C^3-H. Even in this case, it was assumed that the H-C^i-H angle is bisected by the X^{i-1}-C^i-Y^{i+1} plane of the ring, where X,Y = S or C. The least-squares refinements for this more general model were repeated excluding the microwave data (refinement B) and including them (refinement C). The results of refinements B and C for independent geometrical parameters are presented in Table 1. We note that the geometry of the ring is identical in refinements A, B and C. The only noticeable difference is the decrease of the C^2-C^3-H bond angle in refinement B. This decrease may or may not be a real effect. In any case, the incorporation of the microwave data makes a considerable difference to the bond angle C-C-H and shows that the value obtained

Table 2. Elements of the correlation matrix (ϱ_{ij}) exceeding 0.5 in absolute value corresponding to refinement A.

i	j	ϱ_{ij}
∠C-S-C	τ_1	−0.99
	τ_2	−0.79
τ_1		0.78
∠C-C^4-C	∠C-S-C	−0.95
	τ_1	0.95
	τ_2	0.85
l(C-C)	l(S-C)	0.75
l(C-H)		0.53
	l(C-C)	0.50
l(S···C^3)	∠C-S-C	0.89
	τ_1	−0.89
	τ_2	−0.78
	∠C-C^4-C	−0.88
SC1[a]	l(S-C)	0.84
	l(C-C)	0.85
	l(C-H)	0.61

[a]SC1 scale factor for 19 cm camera range.

from the electron diffraction data alone is not very precise.

The bond lengths (r_g), bond angles and torsional angles with estimated total errors corresponding to refinement A are given in the Abstract. The total errors were estimated as in Ref. 8. The following discussion is based on refinement A.

The experimental and theoretical radial distributions display a noticeable discrepancy at about 4.2 Å. This is the region for the contribution of the S^1···H^{41} non-bonded interaction. Removal of the geometrical constraint for this distance reduced the discrepancy, while the changes in the other parameters were negligible. This unconstrained refinement yielded an 0.04 Å "shrinkage" for the S^1···H^{41} distance.

Discussion

The bond lengths of the ring in thiane can appropriately be compared with the corresponding bond lengths in 1,3-dithiane[9] and 4-thiacyclohexanone.[10] The C-C, C-S and C-H bond lengths in the three molecules are the same within experimental error. In thiane and 1,3-dithiane the H-C-H bond angles are also the same within experi-

Table 3. The bond angles and torsional angles of the six-membered ring in cyclohexane and its heterocyclic analogues with one heteroatom, as determined by gas-phase studies. X^1 is the heteroatom in the ring. The angles are given in degrees.

Molecule	Cyclohexane	Thiane	Piperidine	Tetrahydropyran	Silacyclohexane
Angle					
C^6-X^1-C^2		97.6	109.8	111.5	104.2
X^1-C^2-C^3		112.7	110.5	111.8	110.6
C^2-C^3-C^4		112.3	109.3	110.9	113.7
C^3-C^4-C^5		113.6	112.8	108.3	111.4
θ_{mean}	111.5	110.2	110.3	110.9	110.7
C^6-X^1-C^2-C^3		55.4	63.6	59.9	44.0
X^1-C^2-C^3-C^4		60.8	56.9	56.9	57.3
C^2-C^3-C^4-C^5		58.6	51.9	52.5	67.5
Φ_{mean}	54.6	58.2	57.4	56.4	56.3
Ref.	10	This work	13	14	15

mental error. The r_g<C-C> bond length in thiane is somewhat smaller than, though very close to, that in cyclohexane [r_g (C-C) = 1.536 ± 0.002 Å].[11]

The C-S bond length in thiane supports the observation[12] that the longest bonds occur in the four-membered ring in the series of saturated 3-, 4-, 5- and 6-membered rings containing one heteroatom.

The C-S-C angle in thiane is close to the bond angle in the acyclic dimethylsulfide, viz. 99.0 (1)°.[13] The remaining bond angles of the ring are similar, and they are somewhat larger than the C-C-C angle in cyclohexane, viz. 111.4 ± 0.2°.[11] The overall decrease of the average ring angle as compared with cyclohexane gives rise to an increase in the average torsional angle and thus corresponds to enhanced puckering. Table 3 presents the bond angles and torsional angles of cyclohexane and its analogues with one heteroatom in the gas phase. In each hetero-ring the mean torsial angle (Φ_{mean}) is larger than in cyclohexane; the mean values fall in a narrow range: 55–58°. The individual torsional angles are scattered over a wider range. For S and Si the smallest torsional angle is C^6-X^1-C^2-C^3, and for O and N the C^2-C^3-C^4-C^5 torsional angle is the smallest one. A more puckered ring for thiane than for cyclohexane has been predicted on the basis of NMR.[17]

The mean torsional angle is even higher in 1,3-dithiane $(61.2°)$[9] than in thiane. The introduction of the third sulfur atom into the ring further decreases the mean bond angle and consequently further increases the mean torsional angle in 1,3,5-trithiane.[18]

References

1. Bastiansen, O., Seip, H. M. and Boggs, J. E., In: Dunitz, J. O. and Ibers, J. A., Eds., *Perspectives in Structural Chemistry*, Wiley, New York 1971, Vol. 4, Chap. 2.
2. Kitchin, R. W., Malloy, T. M. and Cook, R. L. *J. Mol. Spectrosc. 57* (1975) 79.
3. Hargittai, I., Tremmel, J. and Kolonits, M. *Hung. Sci. Instrum. 50* (1980) 31.
4. Hargittai, I., Hernádi, J., Kolonits, M. and Schultz, Gy. *Rev. Sci. Instrum. 42* (1971) 546.
5. Domenicano, A., Schultz, Gy., Kolonits, M. and Hargittai, I. *J. Mol. Struct. 53* (1973) 197.
6. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand. 23* (1969) 3224.
7. Allinger, N. L. *J. Am. Chem. Soc. 99* (1977) 8127.

8. Hargittai, M. and Hargittai, I. *J. Chem. Phys. 59* (1973) 2513.

9. Adams, W. J. and Bartell, L. S. *J. Mol. Struct. 39* (1977) 261.

10. Seip, R., Seip, H. M. and Smith, Z. *J. Mol. Struct. 32* (1976) 279.

11. Bastiansen, O., Fernholt, L., Seip, H. M., Kambara, H. and Kuchitsu, K. *J. Mol. Struct. 18* (1973) 163.

12. Hargittai, I. *The Structure of Volatile Sulphur Compounds,* Reidel, Dordrecht-Boston-London 1985.

13. Iijima, T., Tsuchiya, S. and Kimura, M. *Bull. Chem. Soc. Jpn. 50* (1977) 2564.

14. Gundersen, G. and Rankin, D. W. H. *Acta Chem. Scand., Ser. A 37* (1983) 865.

15. Breed, H. E., Gundersen, G. and Seip, R. *Acta Chem. Scand., Ser. A 33* (1979) 225.

16. Shen, Q., Hilderbrandt, R. L. and Mastryukov, V. S. *J. Mol. Struct. 54* (1979) 121.

17. Lambert, J. B., Keske, R. G. and Weary, D. K. *J. Am. Chem. Soc. 89* (1967) 5921.

18. Cervellati, R., Corbelli, G., Lister, D. G. and Alonso, J. L. *J. Mol. Struct. 117* (1984) 247.

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