The Molecular Structure of 1,3,5-Trithiane from Electron Diffraction

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The molecular structure of 1,3,5-trithiane has been determined by gas-phase electron diffraction at 466 K nozzle temperature. The experimental data are consistent with the chair conformation of the molecule with C_{3v} symmetry. The ring is considerably more puckered than that of cyclohexane. The following bond lengths (r_g), bond angles and torsional angle were obtained: S-C 1.812 ± 0.004, C-H 1.114 ± 0.004 Å, C-S-C 99.1 ± 0.4, S-C-S 115.8±0.1, H-C-H 109.7 ± 1.2, S-C-S-C 65.2 ± 0.5°.

The present study is a sequel to our recent report on the thiane molecular structure.[1] An early electron diffraction investigation of 1,3,5-trithiane by Hassel and Viervoll[2] as well as X-ray crystallography[3] and microwave spectroscopy[4] showed the presence of the chair conformation, but the geometrical parameters have not been known accurately. With detailed structural information now available for thiane[1] and 1,3-dithiane[5] from electron diffraction, our results on 1,3,5-trithiane make meaningful structural comparisons possible for this interesting series.

Experimental

The sample of 1,3,5-trithiane was prepared by the reaction of aqueous formaldehyde solution with hydrogen sulfide gas in the presence of hydrochloric acid. The white precipitate produced was then recrystallized from toluene. The purity of the sample was checked by gas chromatography. The electron diffraction photographs were taken by a modified EG-100A apparatus[6] using a membrane nozzle system[7] for volatile species. The nozzle temperature was about 466 K. The accelerating voltage of the electron beam was 60 kV. The electron wavelength was calibrated with a TlCl powder pattern,[8] and found to be 0.04919 Å. Nozzle-to-plate distances of about 50 and 19 cm were used. For each camera range six plates were selected for analysis. The treatment of experimental data was the same as described elsewhere.[9] The ranges of the intensity data used in the analysis were $2.0 \leq s \leq 14.0$ and $10.0 \leq s \leq 35.75$ Å^{-1}, with data intervals $\Delta s = 0.125$ and 0.25 Å^{-1}, respectively [$s = 4\pi\lambda^{-1} \sin(\theta/2)$, where θ is the scattering angle]. The

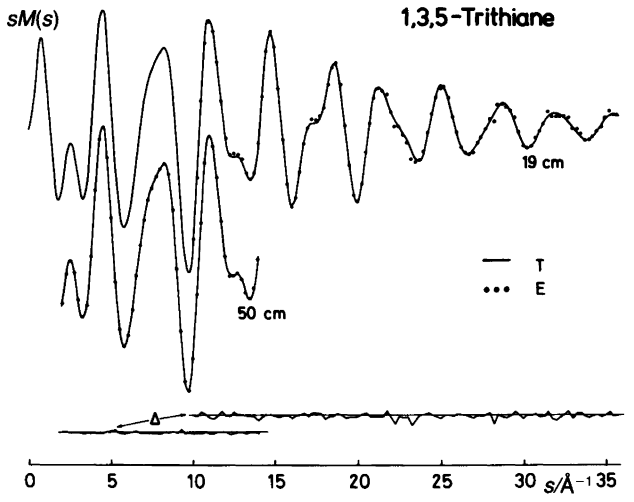

Fig. 1. Molecular intensity curves for the two camera ranges (E, experimental; T, theoretical). Also shown are the difference curves (experimental – theoretical).

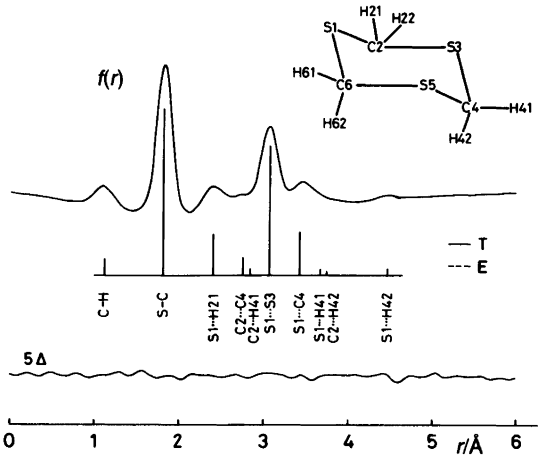

Fig. 2. Radial distribution curves (E, experimental; T, theoretical). The positions of the distances (except H···H) are marked with vertical bars whose height is proportional to the relative contribution of the distance. The difference curve (experimental – theoretical) and the numbering of atoms are also shown.

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total experimental intensities are available from the authors (G.S.). The experimental molecular intensities and their theoretical counterparts are presented in Fig. 1. Experimental and calculated radial distributions are shown in Fig. 2; they were calculated using the artificial damping factor $\exp(-as^2)$, where $a=0.002$ Å^2. The numbering of atoms in the molecule is also shown in Fig. 2.

Structural analysis

The least-squares method was applied to the molecular intensities using a modified version of the program by Seip and co-workers.[10] The geometry of the molecule was characterized by five independent parameters: two bond lengths, C-S and C-H, and three bond angles, C-S-C, S-C-S and H-C-H. C_{2v} symmetry was assumed for the bond configuration around the carbon atoms. All the C-H and C-S bond lengths as well as the bond angles S-C-S, C-S-C and H-C-H were taken to be equal.

There are three possible conformations of the molecule, consistent with the geometrical assumptions of a chair, boat or twist boat. The best fit to the experimental diffraction data was obtained by assuming the chair conformation having C_{3v} symmetry ($R=3.69\,\%$). The assumption of a boat or twist boat conformation yielded an inferior agreement with the experimental data. ($R=7.52$ and 16.3 % for the boat and twist boat, respectively.)

In addition to the five geometrical parameters, nine mean amplitudes of vibration were refined as independent parameters. One of these amplitudes, *l*(S1···H41), was coupled with another, *l*(C2···H42) by an assumed difference. The choice of this difference did not appreciably influence the results of the refinements.

The results of the least-squares refinements are given in Table 1. The elements of the correlation matrix exceeding 0.4 in absolute value are given in Table 2. The bond lengths (r_g) and bond angles with estimated total errors[11] are given in Table 3.

The outer part of the experimental and theoretical radial distribution curves for the chair, boat and twist boat conformations are compared in Fig. 3.

The least-squares refinement carried out under the assumption of the simultaneous presence of two conformers,

Table 1. Molecular parameters of 1,3,5-trithiane from the electron diffraction least-squares refinement. Distances and vibrational amplitudes in Å, angles in degrees. Least-squares standard deviations are given in parentheses as units in the last digit.[a]

Parameters	Multiplicity	r_a, ∠	*l*
Independent			
S-C	6	1.8106(3)	0.0570(5)
C-H	6	1.110(2)	0.067(2)
S-C-S		115.77(7)	
C-S-C		99.1(3)	
H-C-H		109.7(8)	
Dependent			
S1···S3	3	3.067(1)	0.0810(7)
S1···C4	3	3.425(3)	0.115(3)
C2···C4	3	2.756(6)	0.100(7)
S1···H21	12	2.396(2)	0.110(2)
S1···H42	3	4.468(3)	0.117(13)
S1···H41	3	3.661(11)	0.164(12)
C2···H42	6	3.743(6)	0.164
C2···H41	6	2.850(13)	0.16(5)
S-C-S-C		65.2(3)	
R		3.69 %	

[a]The H···H interactions are not shown; they have all been given a fixed amplitude.

Table 2. Elements of the correlation matrix exceeding 0.4 in absolute value.

i	*j*	ϱij $(i \neq j)$
C-H	H-C-H	0.523
C-S-C	*l*(S1···S3)	0.527
C-S-C	*l*(S1···H21)	0.401
l(S1···C4)	*l*(S1···H41)	0.572
l(C2···C4)	C-S-C	−0.747
l(C2···C4)	S-C-S	0.600
l(C2···C4)	*l*(S1···S3)	−0.442
l(C2···H41)	C-S-C	0.847
l(C2···H41)	S-C-S	−0.642
l(C2···H41)	*l*(S1···S3)	0.600
l(C2···H41)	*l*(C2···C4)	−0.866
Sc1[a]	*l*(S-C)	0.770
Sc1[a]	*l*(S1···S3)	0.408
Sc2[b]	*l*(S-C)	0.471

[a]Scale factor for short-distance camera range. [b]Scale factor for long-distance camera range.

Table 3. Geometrical parameters of thiane,[1] 1,3-dithiane,[5] and 1,3,5-trithiane (present study) as determined by electron diffraction. Bond lengths (r_g) in Å, angles in degrees.

Molecule	Thiane[a]	1,3-Dithiane[b]	1,3,5-Trithiane[a]
S-C	1.811±0.004	1.812(3)	1.812±0.004
C-H	1.114±0.002	1.116(10)	1.114±0.004
S-C-S		115.0(3)	115.8±0.1
C-S-C	97.6±0.8	98.1(7)	99.1±0.4
C-C-S	112.7±0.2	114.9(4)	
(S)C-C-C	112.3±0.4	113.6(33)	
(C)C-C-C	113.6±0.8		
H-C-H	105.7±0.9	104.1(45)	109.7±1.2
Θ[c]	110.2	109.1	107.4
Φ[d]	58.2	61.3	65.2
Nozzle temperature/K	294	373	466

[a]Total errors are given as error limits. [b]Parenthesized quantities correspond to 3σ, where σ is the estimated standard deviation. [c]The mean bond angle in the ring. [d]The mean torsional angle in the ring.

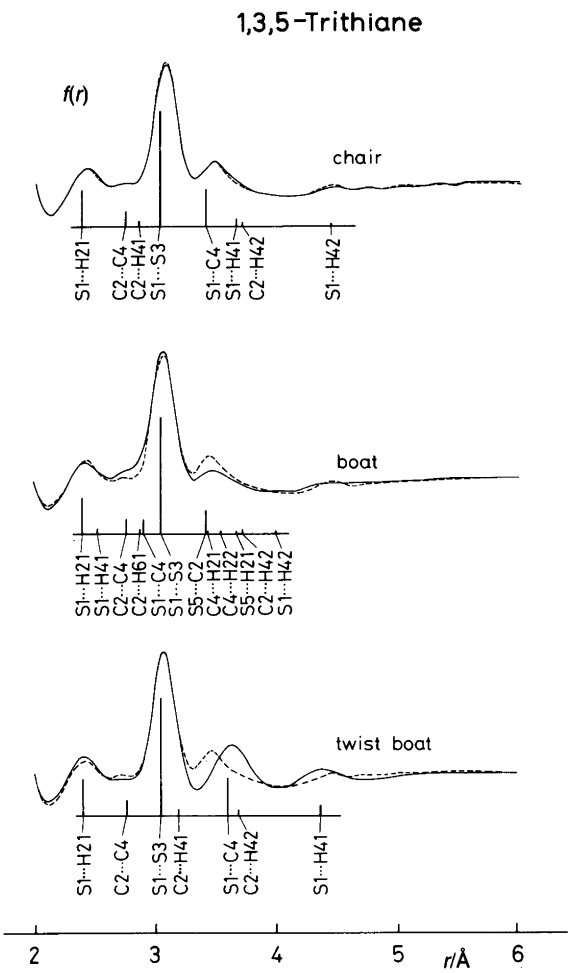

Fig. 3. Comparison of the outer parts of experimental (broken curve) and theoretical (solid curve) radial distribution curves for chair, boat, and twist boat conformations of 1,3,5-trithiane. The positions of distances (except H···H) are marked with bars whose height is proportional to the relative contribution of the distances. The numbering of the atoms is given in Fig. 2.

chair and boat or chair and twist boat, resulted in no decrease of the *R*-factor. The obtained concentrations of the boat and twist boat conformers in the assumed binary mixtures were 7(5) and 3(3) %, respectively. From these results it may be concluded that the concentration of boat or twist boat conformers is below the limit of reliable detection, if these forms are present at all.

Discussion

A microwave study of 1,3,5-trithiane[4] provided the rotational constant B_0 and low-resolution rotational constants $A+B$. The corresponding rotational constants calculated from the r_a parameters of the present study reproduce these quantities well. The rotational constants $2B_0$ for $(^{12}CH_2{}^{32}S)_3$ and $(A+B)$ for $(^{12}CH_2{}^{32}S)_2{}^{12}CH_2{}^{34}S$ and $(^{12}CH_2{}^{32}S)_2{}^{13}CH_2{}^{32}S$ calculated from r_a are 4421, 4361 and 4393 MHz, respectively; the deviation from the values obtained by MW spectroscopy is 0.3 % or less.

Table 4. Mean amplitudes of vibration (Å) involving ring atoms and C-H bonds in thiane, 1,3-dithiane and 1,3,5-trithiane.

Molecule	Thiane	1,3-Dithiane	1,3,5-Trithiane
l(S-C)	0.0507(7)	0.052(4)	0.0530(5)
l(S1···C4)	0.076(2)	0.077(7)	0.115(3)
l(S1···S3)		0.070(6)	0.0810(7)
l(C2···C4)	0.074(1)	0.070(6)	0.100(7)
Reference	1	5	Present study

In Table 3 the relevant geometrical parameters of 1,3,5-trithiane obtained by electron diffraction in the present study are compared with those obtained previously for thiane[1] and 1,3-dithiane.[5] The S-C and C-H bond lengths are identical in the three molecules, and the bond angles in the rings with central S or C atoms exhibit limited variations. These angles are close to the values obtained in open-chain molecules: C-C-C is 112.4(2)° in propane[12] and C-S-C is 98.8(1)° in dimethyl sulfide.[13]

It has been observed[5,14] that introduction of a sulfur heteroatom into a six-membered carbon ring increases the ring puckering in comparison with the conformation of cyclohexane.[15] The data in Table 3 show a gradually increasing puckering with an increasing number of sulfur atoms in the ring. The ring puckering is characterized by the mean torsional angle, Φ, which can be calculated from the mean endocyclic bond angle, Θ, according to eqn. (1)

$$\cos\Phi = -\cos\Theta/(1+\cos\Theta) \qquad (1)$$

which holds exactly for the chair conformation of cyclohexane[16] and approximately for the chair conformations of other six-membered rings with lower symmetry.[17]

The mean amplitudes of vibration of corresponding intra-ring distances in thiane, 1,3-dithiane and 1,3,5-trithiane are presented in Table 4. The amplitudes of C-S bonds are equal in these molecules. The amplitudes characterizing nonbonded interactions in the ring of 1,3,5-trithiane are higher than the corresponding values in thiane and 1,3-dithiane. This may partly originate from the higher-temperature experimental conditions, and may also indicate greater flexibility of the ring in 1,3,5-trithiane than in the other two molecules.

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