

Studies on Molecules with Five-membered Rings

IV. Calculation of Conformational Energies and Electron Diffraction Investigation of Gaseous Tetrahydrothiophene

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Gaseous tetrahydrothiophene has been studied by electron diffraction, and its conformational energies have been calculated by the Westheimer-Hendrickson method. The conformation with C_2 symmetry was found to be between 1.96 and 3.03 kcal/mole more stable than the C_s conformation. The results of the electron-diffraction investigation are in accordance with these calculations. While it was impossible to obtain a good fit between experimental and theoretical electron diffraction data by assuming C_s symmetry, satisfactory agreement was achieved with a C_2 model. The following values were found for the bond lengths, bond angles, and torsional angles: $r(\text{C}-\text{S})=1.839$ (0.002) Å, $r(\text{C}-\text{C})=1.536$ (0.002) Å, $r(\text{C}-\text{H})=1.120$ (0.005) Å, $\angle \text{CSC}=93.4$ (0.5)°, $\angle \text{SCC}=106.1$ (0.4)°, $\angle \text{CCC}=105.0$ (0.5)°, $\angle \text{HCH}=107.5$ (2.6)°; $\phi(\text{S}_1-\text{C}_2)=14.8$ (0.5)°, $\phi(\text{C}_2-\text{C}_3)=-40.5$ (1.2)°, $\phi(\text{C}_3-\text{C}_4)=52.5$ (1.6)°. The values in parentheses are standard deviations.

The observed angles are in satisfactory agreement with the angles calculated by the Westheimer-Hendrickson method.

Calculations described in the first paper of this series¹ indicated that tetrahydrofuran has nearly the same energy in the C_2 and C_s conformations as well as in intermediate conformations. Investigations of the compound in the gaseous phase by electron diffraction supported this conclusion as a mixture of conformations gave very good agreement between experimental and theoretical radial distribution (RD) curves.² On the other hand the compound 1,2,4-trioxacyclopentane may well exist effectively in the C_2 conformation.^{1,3} In the present paper we report the results of a similar investigation of tetrahydrothiophene (THT).

Some evidence exists that the pseudo-rotation of the ring puckering in THT is restricted and that the conformation possessing C_2 symmetry is preferred. Pitzer and Donath⁴ estimated this conformation to be about

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Table 1. Conformational energies E (in kcal/mole) and the corresponding angle parameters (in degrees) in THT.

Conformation angles		a	b	c	d	e
I (approx.) C_2 sym.)	\angle CSC	93.9	93.8	93.8	94.2	93.9
	\angle SCC	106.4	106.3	106.3	106.4	105.6
	$\phi(S_1-C_2)$	13.7	13.9	13.9	13.4	14.7
	$\phi(S_1-C_5)$	13.8	14.0	14.0	13.5	14.9
	E	4.92	6.51	6.20	6.64	4.78
II	\angle CSC	93.6	93.5	93.5	93.9	93.5
	\angle SCC	104.8	104.7	104.7	104.8	103.7
	$\phi(S_1-C_2)$	25.6	26.0	25.9	25.0	27.6
	$\phi(S_1-C_5)$	0.0 *	0.0 *	0.0 *	0.0 *	0.0 *
	E	5.35	6.81	6.53	6.98	5.15
III	\angle CSC	92.6	92.5	92.5	93.0	92.4
	\angle SCC	103.4	103.2	103.2	103.5	102.0
	$\phi(S_1-C_2)$	34.4	34.8	34.8	33.4	37.1
	$\phi(S_1-C_5)$	-13.0 *	-13.0 *	-13.0 *	-12.5 *	-14.0 *
	E	6.29	7.45	7.22	7.70	5.94
IV	\angle CSC	91.1	91.0	91.0	91.5	90.7
	\angle SCC	102.9	102.7	102.7	103.1	101.4
	$\phi(S_1-C_2)$	40.0	40.6	40.5	39.1	43.2
	$\phi(S_1-C_5)$	-25.0 *	-25.0 *	-25.0 *	-24.5 *	-26.5 *
	E	7.25	8.05	7.89	8.46	6.66
V	\angle CSC	89.8	89.5	89.6	90.4	88.9
	\angle SCC	103.7	103.5	103.5	103.8	102.3
	$\phi(S_1-C_2)$	41.6	42.7	42.5	40.5	45.5
	$\phi(S_1-C_5)$	-33.5 *	-34.5 *	-34.0 *	-32.5 *	-37.0 *
	E	7.80	8.38	8.26	8.87	7.08
VI **	\angle CSC	90.0	89.2	89.3	90.4	88.5
	\angle SCC	106.2	105.5	105.6	105.9	104.6
	$\phi(S_1-C_2)$	36.8	39.7	39.2	36.6	42.4
	$\phi(S_1-C_5)$	-36.8	-39.7	-39.2	-36.6	-42.4
	E	7.95	8.47	8.38	9.00	7.19
$E(C_s) - E(C_2)$		3.03	1.96	2.18	2.36	2.41

* Not varied.

** Energyminimum with the restriction of C_s symmetry.Below k is given in kcal/mole-degree² and V^0 in kcal/mole.Bond distances: $r(C-S) = 1.839 \text{ \AA}$, $r(C-C) = 1.536 \text{ \AA}$, $r(C-H) = 1.120 \text{ \AA}$, $\angle HCH = 107.5^\circ$ a: $\theta_{CSC}^0 = 99^\circ$, $\theta_{SCC}^0 = \theta_{CCC}^0 = 112^\circ$ $k_{CSC} = 0.035$, $k_{SCC} = k_{CCC} = 0.030$; $V_{CS}^0 = 1.27$, $V_{CC}^0 = 2.9$ b: $\theta_{CSC}^0 = 99^\circ$, $\theta_{SCC}^0 = \theta_{CCC}^0 = 112^\circ$ $k_{CSC} = 0.035$, $k_{SCC} = k_{CCC} = 0.030$; $V_{CS}^0 = 2.18$, $V_{CC}^0 = 2.9$ c: $\theta_{CSC}^0 = 99^\circ$, $\theta_{SCC}^0 = \theta_{CCC}^0 = 112^\circ$ $k_{CSC} = 0.035$, $k_{SCC} = k_{CCC} = 0.030$; $V_{CS}^0 = 2.0$, $V_{CC}^0 = 2.9$ d: $\theta_{CSC}^0 = 99^\circ$, $\theta_{SCC}^0 = \theta_{CCC}^0 = 112^\circ$ $k_{CSC} = 0.045$, $k_{SCC} = k_{CCC} = 0.035$; $V_{CS}^0 = 2.0$, $V_{CC}^0 = 2.9$ e: $\theta_{CSC}^0 = 98^\circ$, $\theta_{SCC}^0 = \theta_{CCC}^0 = 110^\circ$ $k_{CSC} = 0.035$, $k_{SCC} = k_{CCC} = 0.030$; $V_{CS}^0 = 2.0$, $V_{CC}^0 = 2.9$

3 kcal/mole more stable than the conformation with C_s symmetry. Hubbard *et al.*⁵ determined the energy difference to ± 2.8 kcal/mole, and later Crowder and Scott⁶ found further evidence of hindered pseudo-rotation from the far infrared spectrum.

So far no attempts to establish the geometry of the free molecule by gas electron diffraction or microwave spectroscopy have been reported.

CALCULATION OF CONFORMATION ENERGIES

BY THE WESTHEIMER-HENDRICKSON METHOD

The energies of six conformations of THT ranging from C_2 symmetry (model I) to C_s symmetry (model VI) were calculated as described previously.¹ As there are great differences in the values of some of the constants required in these calculations, depending on the literature source consulted, several computations were carried out (see Table 1).

The bond distances applied in these calculations were taken from the electron diffraction investigation described below (Table 2). The "normal" angles θ° (Ref. 1) adopted from the literature are given in Table 1. The angle

Table 2. Values for interatomic distances (r_a^{17}), the corresponding mean amplitudes of vibration (u), bond angles and torsional angles. The standard deviations given in parentheses are twice the values obtained in the least-squares refinement. Calculated values for the angles (*cf.* Table 1 column e) are given for comparison.

	r (Å)	u (Å)
S—C	1.839 (0.002)	0.058 (0.002)
C—C	1.536 (0.002)	0.053 (0.002)
C—H	1.120 (0.005)	0.079 (0.004)
S ₁ ⋯C ₃	2.703 (0.007)	0.066 (0.007)
C ₂ ⋯C ₃	2.676 (0.010)	0.064 (0.035)
C ₂ ⋯C ₄	2.437 (0.008)	0.070 (0.008)

	Angles (degrees)	
	Experimental	Calculated
\angle CSC	93.4 (0.5)	93.9
\angle SCC	106.1 (0.4)	105.6
\angle CCC	105.0 (0.5)	105.2
\angle HCH	107.5 (2.6)	
ϕ (S—C)	14.8 (0.5)	14.8
ϕ (C ₂ —C ₃)	-40.4 (1.2)	-40.5
ϕ (C ₃ —C ₄)	52.5 (1.6)	53.0

CCC in normal paraffins is usually between 112° and 113° (Ref. 1). In methyl sulfide⁷ the angle CSC was determined by microwave spectroscopy to be 98.87° .

The bending force constant k_{CCC} is usually found to be about 0.035 kcal/mole·degree² (Ref. 8). The value for k_{CCS} is probably not too different from this value. Siebert⁷ determined the constant $k_{\text{CSC}}=0.044$ kcal/mole·degree² for methyl sulfide.

The rotational barrier V_{CC^0} was taken from ethane^{8,10} (2.9 kcal/mole). The barriers to rotation about the bond C—S are considerably different in methylsulfide^{7,12} (2.176 kcal/mole) and in methyl mercaptan^{11,12} (1.270 kcal/mole) as is the case for methylether and methanol.¹ Consequently various values of V_{CS^0} were used.

The van der Waals energy was calculated according to Eliel *et al.*⁸ using their constants. As for the other molecules we have studied¹ this energy differs only slightly from one model to another, and the contribution could have been omitted without changing the conclusions significantly.

The calculated bond and torsional angles, and the conformational energies for the six models are presented in Table 1; corresponding values for the constants assumed in these calculations are also given. The resulting angles are influenced only slightly by the choice of constants. In all cases considered the energy minimum was found to correspond closely to a conformation of C_2 symmetry. The energy difference between the conformation VI (C_s) and I (approx. C_2) varies between 1.96 and 3.03 kcal/mole. These results contrast with our previous calculations for tetrahydrofuran¹ where the corresponding difference lying between -0.73 and $+1.25$ kcal/mole, indicates that essentially free pseudorotation takes place.

ELECTRON DIFFRACTION INVESTIGATION

Experiment and data processing. Commercially supplied THT was fractionally distilled using a rectification column, and the purity established by IR spectroscopy and gas-liquid chromatography; b.p. = 121°C/760 mm Hg (lit.¹³ 121.25°C/760 mm Hg), $n_D^{25} = 1.5027$ (lit.¹³ $n_D^{25} = 1.5023$).

The diffraction photographs were obtained in the usual way with the Oslo apparatus.¹⁴ The nozzle temperature was approximately 52°C; the electron wave length was determined from a gold foil diffraction pattern and corrected by an experiment with CO₂. The value 0.064890 Å corresponds to an accelerating potential of about 36 kV. Four photographic plates obtained at a nozzle-to-plate distance of about 20 cm and another four at about 48 cm were applied.

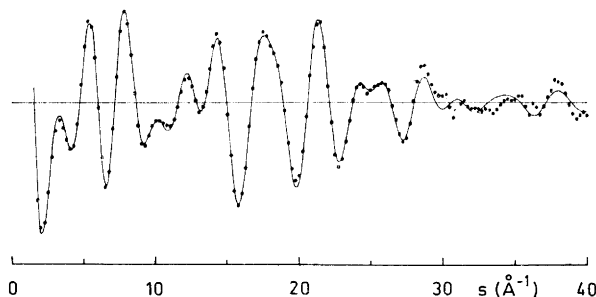


Fig. 1. The experimental (dotted) and theoretical intensity curves for the model with C_2 symmetry.

The plates were photometered, and the data processed in the usual way¹⁵ by a CDC 3300 computer. Four experimental intensity curves were obtained, each being formed by connecting the data from one of the 20 cm plates to the data from one of the 48 cm plates. The curves obtained covered the s range 1.75–40.00 Å⁻¹ and as they showed satisfactory mutual agreement, the average curve (Fig. 1) was used in the structure analysis. The experimental radial distribution (RD) function¹⁵ calculated is presented in Fig. 2.

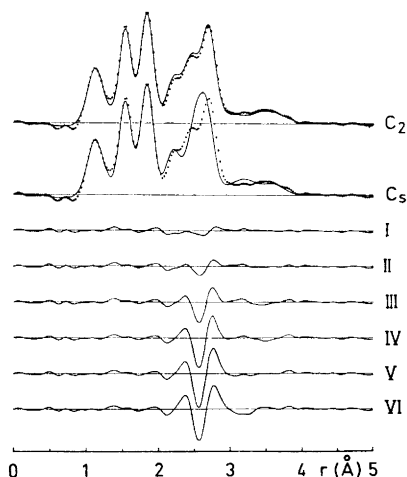


Fig. 2. The experimental (dotted) and theoretical RD curves for the models with C_2 and C_s symmetries. An artificial damping constant $k=0.002$ Å² has been applied. The curves I–VI show the differences between the experimental RD curve and the corresponding theoretical curves for the conformations I–VI of Table 1.

Least-squares refinement. Approximate values for the bond lengths were obtained from the RD curve (Fig. 2). The inner peak (around 1.12 Å) corresponds to the C–H bond distances, the second (1.54 Å) to the C–C, and the third to the C–S bond distances. The non-bonded C···S and C···C distances contribute to the complex peak between 2.0 Å and 3.1 Å; the C···S distances being probably about 2.70 Å. The C···H and S···H distances contribute also to this peak as well as to the outer part of the curve.

Least-squares refinements were carried out for models with C_2 and C_s symmetries. These models are shown in Fig. 1 of Ref. 2. The C–C bond distances were assumed equal, as were all the HCH angles. The planes through the atoms HCH were assumed perpendicular to the planes through XCC (X=S or C) bisecting the XCC angle.²

A good agreement between experimental and theoretical intensity and RD curves was obtained for the C_2 model as can be seen from Figs. 1 and 2. The refined structural parameters are given in Table 2.

The refinement of a model with C_s symmetry resulted in some very unreasonable parameters, *i.e.* $\angle CSC=83.8^\circ$ and $u(C_2\cdots C_4)=0.22$ Å.* Even then the agreement was far from satisfactory and this model can certainly be rejected.

The standard deviations given in Table 2 require some comments. A diagonal weight matrix was applied in the least-squares calculations carried out on the total intensity curve (covering the s range 1.75–40.0 Å⁻¹). However, least-squares calculations using both a diagonal weight matrix and a weight matrix with off-diagonal elements different from zero,¹⁶ were carried out on the average intensity curve corresponding to the short nozzle-to-plate distance (s range 6.5–40.0 Å⁻¹). The inclusion of the correlation between the intensity values increases usually the standard deviations by a factor of about 2.0. The standard deviations in Table 2 have been estimated taking this factor and the uncertainty in the wave length into account.

* The usual IUPAC numbering of the ring applied.

DISCUSSION

The results of energy calculation and electron diffraction investigation indicate strongly that THT exists effectively in the C_2 conformation. The refined angles are in a surprisingly good agreement with the values found to correspond to the energy minimum by the Westheimer-Hendrickson method (see Table 2).

We also examined the agreement between experimental and theoretical RD curves for the intermediate models II–V (from Table 1). In the calculations of theoretical curves for these conformations the final values of bond distances and u values from Table 2 were used as well as the torsional and bond angles from Table 1, column e . Fig. 2 shows the curves which represent the differences between the experimental and the respective theoretical RD curves for models I–VI. It is obvious that the discrepancy increases as the model adopted approaches C_s symmetry. This conclusion remained unaltered if the angles in the other columns of Table 1 were applied. Also the choice of $\angle \text{HCH} = 110^\circ$ altered the difference curves in Fig. 2 only slightly.

A theoretical RD curve with contributions from six conformations according to the energies given in Table 1 column e was also compared to the experimental curve. The correspondence was not quite as good as for the C_2 model alone. However, the difference in agreement seems too small to conclude that the increase in energy with deviation from C_2 symmetry is greater than the values in Table 1 indicate.

The ring angles given in Table 2 are several degrees smaller than the corresponding bond angles in unstrained molecules. A similar angle deformation was observed in the case of tetrahydrofuran.² The angle $\text{CSC} = 93.4^\circ$ in THT is smaller than the corresponding angle COC in tetrahydrofuran² which was found to vary between 106.4° and 109.7° . A similar difference exists between $\angle \text{CSC}$ in methyl sulfide⁷ (99°) and $\angle \text{COC}$ in methyl ether¹ (111.5°).

The C–S bond distance (Table 2) in THT is somewhat longer than the distance of 1.802 Å reported in methyl sulfide.⁷ This difference seems consistent with the smaller values for the CSC angle and the torsional angles around the C–S bonds in THT. The C–C and C–H distances given in Table 2 are close to the usual values for these bonds.

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