

Conformational Composition in the Gas Phase and in Solution, Structure and Intramolecular Hydrogen Bonding of Thiiranemethanethiol as Studied by Microwave and NMR Spectroscopy and *Ab Initio* Calculations

K.-M. Marstokk,^a Harald Møllendal,^{†,a} and Yngve Stenstrøm^b

^aDepartment of Chemistry, The University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway and ^bAgricultural University of Norway, Department of Biotechnological Sciences, PO Box 5040, N-1432 Ås, Norway

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The microwave spectrum of thiiranemethanethiol and one deuterated species (mercapto group) has been investigated in the gas phase in the 18.0–39.0 GHz spectral region at -15°C . Four conformers were assigned. Three of these possess a weak intramolecular hydrogen bond, while the fourth rotamer is not stabilized by this interaction. The most stable rotamer is denoted *H bond outer 2*. This conformer has an internal hydrogen bond formed between the mercapto group hydrogen atom and the pseudo- π electrons along the C–C edge of the thiirane ring. The next rotamer, *H bond outer 1*, is $0.9(3)$ kJ mol^{-1} less stable than *H bond outer 2*. The internal H bond is formed between the mercapto group hydrogen atom and the pseudo- π electrons of the C–S bond of the ring in *H bond outer 1*. The third conformer, *H bond inner*, which is $1.4(3)$ kJ mol^{-1} less stable than *H bond outer 2*, has a S–H \cdots S hydrogen bond. The fourth rotamer assigned is denoted *Conformer IV*. It is $3.5(4)$ kJ mol^{-1} less stable than *H bond outer 2* and has no hydrogen bond. *Conformer IV* is similar to *H bond outer 2*, with the exception that the H–S–C–C dihedral angle is approximately 180° , compared to 60° in *H bond outer 2*. The microwave work has been assisted by *ab initio* computations at the 6-31G* and MP2/6-31G* levels of theory. A detailed NMR analysis of the conformational composition of the title compound in dilute CDCl_3 solution has been performed. The ratio of *H bond outer 2*:*H bond outer 1*:*H bond inner* was found to be 43:23:34. This is similar to the composition in the gas phase.

Several recent studies^{1–7} of free molecules have shown that the mercapto group can participate in intramolecular hydrogen (H) bonding as a weak proton donor with a variety of acceptors. Examples include allyl mercaptan, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{SH}$,¹ 3-butene-1-thiol, $\text{HSCH}_2\text{CH}_2\text{CH}=\text{CH}_2$,² 3-mercaptopropionitrile, $\text{HSCH}_2\text{CH}_2\text{C}\equiv\text{N}$,³ cyclopropanemethanethiol,⁴ ethanedithiol, $\text{HSCH}_2\text{CH}_2\text{SH}$,⁵ 2-aminoethanethiol, $\text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$,⁶ and 2-furanmethanethiol.⁷ In these compounds at least one of the stable conformers observed is stabilized with an interaction that could be described as a weak internal H bond, as discussed in more detail in our paper on the last-mentioned compound.⁷

Thiiranemethanethiol was chosen for study because internal H bonds with the mercapto group as donor are possible in three (Figs. 1 and 2) of the many conforma-

tions which are theoretically possible for this molecule. The H bonds in these three conformers are of three different kinds. In the *idealized* models shown in these two figures, the conformation denoted *H bond inner* is characterized by the dihedral angle formed by the atom chains S1–C1–C2–S2 and H1–S1–C1–C2. These angles are 30° from *syn*, and -60° from *syn*, respectively. This allows the formation of a S–H \cdots S intramolecular H bond. This kind of intramolecular H bonding, which is claimed to be present in one of the low-energy conformers of ethanedithiol, is obviously rather weak.⁵

In *H bond outer 1* the same two dihedral angles are -60° and 60° , respectively. The intramolecular H bond in this case is perhaps best described to be formed between the H1 atom of the mercapto group and the pseudo- π electrons⁸ along the C2–S2 edge of the ring. The lone pairs on the sulfur atom may also help in forming this bond. No gas-phase studies have previously

[†] To whom correspondence should be addressed.

been reported where this kind of internal H bonding is present.

In *H bond outer 2* the S1–C1–C2–S2 and H1–S1–C1–C2 dihedral angles are 150 and 60°, respectively. Here, the H bond is formed between the H1 atom of the mercapto group and the pseudo- π electrons on the outside of the C2–C3 edge.⁸ An interaction of this kind has already been observed in the case of cyclopropanemethanethiol,⁴ where the conformer corresponding to *H bond outer 2* is the most stable form of the molecule. It will be shown in this work that internal H bonding, although weak, is essential for the conformational preferences that thiiranemethanethiol makes.

Experimental

Synthesis. Thiiranemethanethiol was prepared by a modification of a previously published procedure.⁹ Care must be taken to avoid severe polymerisation. Potassium hydrogen sulfate was slowly heated to 190°C, cooled and finely crushed in a mortar. A mixture of 10.00 g (73.4 mmol) potassium hydrogen sulfate and 10.02 g (80.5 mmol) 2,3-dimercaptopropanol was placed in a Claisen distillation apparatus. The pressure was set to

10 mmHg before the mixture was lowered into an oil bath preheated to 130°C and slowly increased to 150°C. A clear liquid distilled at 65°C and was collected in an ice-cooled receiver. Redistillation gave 5.52 g (71%) of the product, pure enough for NMR analysis, b.p. 55–56°C/1.36 kPa (10 mmHg) [lit.¹⁰ 66–67°C/2.6 kPa (20 mmHg)].

According to GLC at least four impurities, two more volatile and two less volatile than the title compound, were present (<4% altogether). Since impurities with possible high dipole moments may complicate the analysis of the MW spectrum, they were removed by preparative GLC. The title compound was thermally labile, and the conditions had to be set with great care prior to injection. Best results were achieved with the following parameters: $t(\text{injector})$: 200°C, $t(\text{detector})$: 220°C, $t(\text{column})$: start: 70°C (2 min), 10°C min⁻¹, end: 250°C. But even these conditions gave severe deterioration.

Microwave experiment. The MW spectrum was studied using the Oslo spectrometer, which is described in Ref. 11. The 18.0–39.0 GHz spectral region was investigated with the microwave absorption cell cooled to about -15°C. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 4–6 Pa when the spectra were recorded. The accuracy of the spectral measurements is presumed to be better than ± 0.10 MHz. The deuterated species were produced by conditioning the cell with heavy water and then introducing the parent species. In this manner 20–30% deuteration was achieved.

NMR and GLC experiments. The NMR spectra were recorded at ambient temperature employing a JEOL JNM-

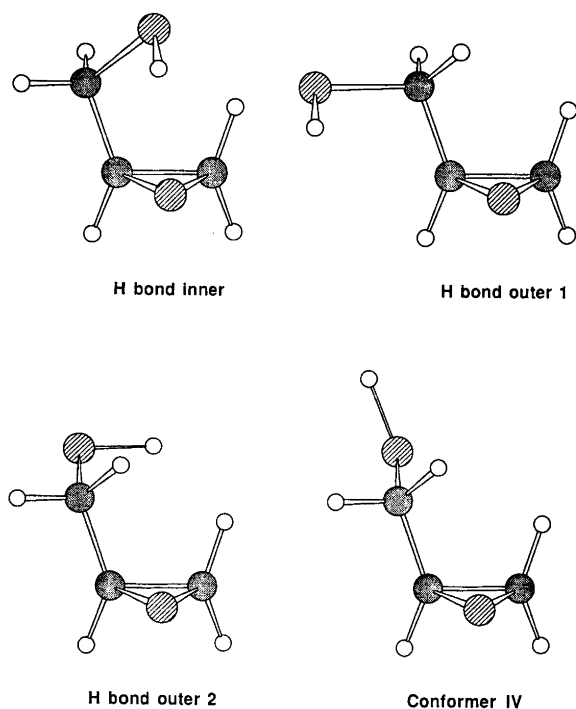


Fig. 1. The four conformers of thiiranemethanethiol assigned in this work. *H bond inner*, *H bond outer 1* and *H bond outer 2* each possess an intramolecular hydrogen bond, while this interaction is absent in *Conformer IV*. *H bond outer 2* is the most stable conformer. It is 0.9(3) kJ mol⁻¹ more stable than *H bond outer 1*; 1.4(3) kJ mol⁻¹ more stable than *H bond inner*; and 3.5(4) kJ mol⁻¹ more stable than *Conformer IV*.

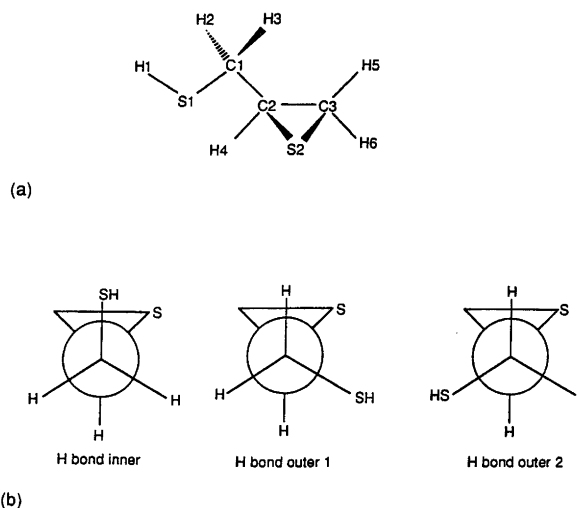


Fig. 2. Atom numbering (a) and Newman projections (b). The Newman projections are viewed along the C1–C2 bond. The conformation of the mercapto group is not indicated. (The Newman projection along this C1–C2 bond of *Conformer IV* is the same as that of *H bond outer 2*).

GX270 instrument. TMS was used as the internal standard and CDCl_3 as solvent in both the ^1H NMR and ^{13}C NMR spectra. The numbering of the ^1H and ^{13}C atoms is given in Fig. 2. The shifts were assigned by using a combination of COSY, standard irradiation techniques and analysis of the coupling pattern. The exact shift values were found. Comparison of the ^1H NMR spectrum with the published one of methylthiirane¹² confirmed the assignments including the coupling constants of the ring protons. ^1H NMR (270 MHz, 3 mM): δ 1.69 (dd, $J_{1,2}$ 7.3 Hz, $J_{2,3}$ 7.9 Hz, SH), 2.28 (dd, $J_{5,6}$ 1.0 Hz, $J_{4,5}$ 5.4 Hz, H5), 2.58 (dd, $J_{5,6}$ 1.0 Hz, $J_{4,6}$ 5.9 Hz, H6), 2.65 (ddd, $J_{1,2}$ 7.3, $J_{2,4}$ 7.9, $J_{2,3}$ 13.5 Hz, H2), 2.94 (ddd, $J_{3,4}$ 5.4, $J_{1,3}$ 7.9, $J_{2,3}$ 13.5 Hz, H3), 3.15 (dddd, $J_{3,4}$ 5.4, $J_{4,5}$ 5.4, $J_{4,6}$ 5.9, $J_{2,4}$ 7.9 Hz, H4). ^{13}C NMR (66.5 MHz, 3 mM): δ 25.93 (C3), 30.82 (C1), 36.98 (C2).

Analytical GLC was performed utilizing an 25 m OV 17 capillary column, while the preparative work was done with a 10% SP 2100 (SE30) column, both on a Varian GC 3300 instrument.

Results

Ab initio calculations. Thiiranemethanethiol has not previously been subject to high-level *ab initio* calculations. It was therefore decided to perform such computations in order to assist the MW work. The calculations were made at the 6-31G* and MP2/6-31G* levels of theory using the Gaussian 90¹³ and 92¹⁴ program packages running on the Cray Y-MP computer in Trondheim.

A full mapping of the potential surface of thiiranemethanethiol using high-level *ab initio* calculations has not been possible for economic reasons. Restrictions have to be made, and computations at this high level of theory were only carried out for the four conformers (Fig. 1) assigned in this work. The three H-bonded conformers of Figs. 1 and 2 were presumed to be more stable than conformers where internal H bonding is not possible, and computations were first made for these three forms. However, in the course of the MW analysis *Conformer IV* was also assigned, and computations were then made for this rotamer as well.

The starting points for the computations were the four idealized conformations depicted in the two figures. The geometries of these four forms were fully optimized in both the 6-31G* and MP2/6-31G* computations. The structures, dipole moments and energy differences between the four forms were rather similar in these two computational procedures. Only selected MP2/6-31G* results are therefore reported in Table 1. The four rotamers were all found to be minima on the energy hypersurface (no imaginary vibrational frequencies¹⁵ were computed for any of them).

A few remarks about the optimized structures of the five rotamers (Table 1) are in order: The structure of the thiirane ring in all four forms is very similar to that found in the MW work on thiirane.¹⁶ The structures of the

$-\text{CH}_2\text{SH}$ part of the different rotamers is also close to that of methanethiol.¹⁷

The S1–C1–C2–S2 and H1–S1–C1–C2 dihedral angles determine the conformation of the molecule. The S1–C1–C2–S2 dihedral angle deviate (Table 1) several degrees from the idealized cases shown in Fig. 1, as was expected, while the H1–S1–C1–C2 dihedral angles are rather 'normal' in the three H-bonded conformations, but deviates about 13° from 180° in *Conformer IV*.

The non-bonded S1···S2 and H1···S2 distances of the *H bond inner* conformer are both slightly shorter (15–20 pm) than the sum of the van der Waals radii of the atoms in question.¹⁸ This is indicative of a weak H bond interaction.

The H1···C2 distance in *H bond outer 1* is rather short, while the H1···S2 distance is slightly longer than the sum of the van der Waals radii of sulfur and hydrogen¹⁸ and indicates that little interaction exists between the H1 and S2 atoms. The H bond in this case is thus perhaps best described as being formed between H1 and the pseudo- π electron along the C2–S2 edge of the ring.

The H1···C2 and H1···C3 non-bonded distances in *H bond outer 2* are rather short, and indicate that interaction with the pseudo- π electrons along the edges of the ring is perhaps the decisive stabilizing interaction in this conformer. *Conformer IV* is characterized by possessing a completely 'relaxed' structure with no close non-bonded interactions. Moreover, the computations correctly indicate (see below) that *H bond outer 2* is a low-energy conformer with small energy differences between this rotamer and the three others listed in Table 1.

MW spectrum and assignment of H bond outer 1. The survey spectra revealed a very rich and complex spectrum with absorption lines occurring every few MHz throughout the entire MW region. The peak absorption intensities of the high-*J* *b*-type *Q*-branch lines in the upper *R*-band of *H bond outer 1*, which were the strongest lines observed, had intensities of roughly $4.0 \times 10^{-7} \text{ cm}^{-1}$ at -15°C .

According to the *ab initio* computations (Table 1), *H bond outer 1* and *H bond outer 2* were predicted to be close in energy, as well as the two most stable forms. The former of these was predicted (Table 1) to possess a rather large μ_b dipole moment component of about $7.6 \times 10^{-30} \text{ C m}$, whereas *H bond outer 2* was predicted to have a μ_b component roughly half this large ($4.3 \times 10^{-30} \text{ C m}$) as its largest principal-axis dipole-moment component. If a small energy difference similar to the computed one (Table 1) exists between these two conformers, the spectrum of *H bond outer 1* was expected to have the strongest spectrum, since the intensities are proportional to the square of the dipole moment components along the principal inertial axes. Searches were therefore first made for the *b*-type *Q*-branch transitions of this rotamer predicted to occur in the 18.0–26.5 GHz spectral region. These lines were indeed the strongest ones in this region, and they were readily assigned.

Table 1. Structure,^a rotational constants, principal-axis coordinates of the H1 atom of the mercapto group, principal-axis dipole moment components and energy differences and four rotamers assigned for thiiranemethanethiol, as calculated by the MP2/6-31G* procedure.

Conformer:	<i>H bond inner</i>	<i>H bond outer 1</i>	<i>H bond outer 2</i>	<i>Conformer IV</i>
Distance/pm				
H1–S1	134.1	134.2	134.2	134.1
C1–S1	181.3	181.6	182.1	182.8
C1–H2	109.3	109.5	109.3	109.2
C1–H3	109.6	109.3	109.3	109.2
C1–C2	151.5	150.4	150.3	150.3
C2–C3	147.7	147.9	147.9	147.9
C2–S2	181.8	181.9	182.1	181.8
C3–S2	182.1	181.9	181.7	181.8
C2–H4	108.9	108.8	108.7	108.8
C3–H5	108.6	108.6	108.8	108.7
C3–H6	108.6	108.7	108.6	108.6
Angle/°				
H1–S1–C1	96.1	95.4	96.1	96.5
S1–C1–H2	109.7	105.6	110.8	110.8
S1–C1–H3	105.0	110.1	105.5	109.8
S1–C1–C2	116.8	113.7	112.1	107.8
C1–C2–C3	122.3	119.1	119.3	119.1
C1–C2–S2	120.6	117.9	117.9	117.9
S2–C2–C3	66.2	66.0	65.9	66.0
C2–S2–C3	47.9	48.0	48.0	48.0
C2–C3–C2	65.9	66.0	66.1	66.0
C1–C2–H4	112.1	114.7	114.7	114.8
C2–C3–H5	117.4	118.5	118.6	117.4
C2–C3–H6	118.2	117.8	117.7	118.4
Dihedral angle ^b /°				
H1–S1–C1–H2	63.9	–178.1	60.6	–73.6
H1–S1–C1–H3	178.9	–61.6	176.7	46.6
H1–S1–C1–C2	–61.4	62.1	–62.8	166.7
S1–C1–C2–C3	–32.9	–156.5	86.6	80.6
S1–C1–C2–S2	46.6	–79.9	163.1	157.2
S1–C1–C2–H4	–177.0	58.0	–58.3	–64.2
C1–C2–C3–H5	5.6	2.7	2.6	2.4
C1–C2–C3–H6	–140.6	–142.8	–142.8	–142.8
Non-bonded distance ^{c,d} /pm				
S1···S2	349.4	373.3	445.8	438.7
H1···S2	291.7	313.9	444.7	522.2
S1···C2	283.9	278.4	276.3	269.8
H1···C2	297.5	290.5	290.1	367.2
H1···C3	335.3	408.4	310.8	454.3
Rotational constant ^c /MHz				
A	6 168.2	7 418.1	10 801.5	10 762.4
B	1 932.6	1 708.4	1 424.0	1 455.7
C	1 801.2	1 471.5	1 324.0	1 349.6
Principal-axis coordinates of the H1 atom ^c /pm				
<i>a</i>	124.4	157.7	202.4	308.6
<i>b</i>	143.4	137.0	124.1	77.8
<i>c</i>	41.7	34.4	49.1	36.3

(Table 1 continued next page)

Table 1. Continued

Conformer:	<i>H bond inner</i>	<i>H bond outer 1</i>	<i>H bond outer 2</i>	Conformer IV
Principal-axis dipole moment component ^e /10 ⁻³⁰ C m				
μ_a	0.78	3.59	1.11	3.78
μ_b	6.95	7.61	4.34	0.89
μ_c	0.36	0.53	0.93	0.69
Energy difference ^{f,g} /kJ mol ⁻¹				
	3.06	0.00	0.30	4.50

^aSee Fig. 2 for atom numbering. ^bMeasured from $\text{syn}=0^\circ$. ^cCalculated from structure above. ^dSum of van der Waals radii: ¹⁸S...S 370 pm; S...C (half-thickness of aromatic molecule) 355 pm; S...H 305 pm; H...C (half-thickness of aromatic molecule) 290 pm. ^eCalculated from the structures given above in this table. ^f1 D=3.335×10⁻³⁰ C m. ^gThe total energy of conformer *H bond outer 1* was calculated to be -2396331.86 kJ mol⁻¹. ^hEnergy difference between each of the three other conformations and *H bond outer 1*.

H bond outer 1 is a rather prolate asymmetric top with the asymmetry parameter $\kappa = -0.91$. In addition, μ_a is expected to be sizable (3.6×10^{-30} C m; Table 1). *a*-Type *R*-branch pile-ups typical for near-prolate asymmetric tops were therefore expected in the *R*-band spectral region. The 10←9 series of *a**R*-pile-up transitions with fast Stark effects were immediately noted around 32.2 GHz when this spectral region was scanned employing a low (ca. 60 V cm⁻¹) Stark voltage. All three rotational constants could now be determined. Refinements of the spectroscopic constants were then made by successively including *b*-type lines involving higher and higher values of *J* and *K*₋₁ up to the 103₂₆←102₂₇ coalescing *K*₋₁ pair of transitions. Inclusion of four sextic centrifugal distortion constants had to be made in order to get a fit with a root mean-square deviation comparable to the experimental uncertainty of about ±0.05 MHz. *c*-Type lines, whose hypothetical frequencies could be very accurately predicted, were searched for, but not found, presumably because μ_c is too small. This is in accord with the theoretical predictions in Table 1 ($\mu_c = 0.5 \times 10^{-30}$ C m). A total of 262 transitions were employed in the least-squares fit.[†] The spectroscopic constants (*A*-reduction *f*-representation)¹⁹ of the ground vibrational state are found in Table 2.

The ground-state spectrum was accompanied by one prominent vibrationally excited state assumed to be the first excited state of the C1–C2 torsional fundamental. 107 transitions within a maximum *J* = 77 were measured for this excited state and used to determine its spectroscopic constants, including two sextic centrifugal distortion constants. The results are shown in Table 3. Relative intensity measurements performed largely as described in Ref. 20 yielded 144(20) cm⁻¹ for this vibration, compared to 101 cm⁻¹ calculated by *ab initio* methods (6-

31G* basis set; not given in Table 1). That the frequency obtained theoretically is too low is hard to explain, but could reflect an inadequate treatment of the anharmonic part of the potential surface. The second lowest fundamental frequency was computed by *ab initio* methods to be 204 cm⁻¹, but no assignment was made for this excited state, owing to the crowded nature of the spectrum and the presumed weakness of the rotational transitions of this vibrationally excited state.

The deuterated species (mercapto group) was studied to locate the position of the H1 atom of the mercapto group. The assignment of this spectrum was straightforward. The spectroscopic constants determined from 41 transitions with a maximum value of *J* = 30 are listed in Table 2. The substitution coordinates²¹ of H1 were calculated as $|a| = 143.957(44)$, $|b| = 136.932(49)$ and

Table 2. Ground-state spectroscopic constants^{a,b} of *H bond outer 1* of thiiranemethanethiol.

Species:	Parent	Deuterated
No. of transitions:	262	41
R.m.s. dev. ^c /MHz:	0.051	0.100
<i>J</i> _{Qmax} ^d	33	30
<i>J</i> _{P,Rmax} ^e	103	12
<i>A</i> ₀ /MHz	7354.8592(23)	7149.189(17)
<i>B</i> ₀ /MHz	1727.44609(54)	1714.5281(89)
<i>C</i> ₀ /MHz	1483.41607(56)	1466.4548(86)
Δ_J /kHz	0.65429(84)	0.813(36)
Δ_{JK} /kHz	-3.0268(90)	-2.901(53)
Δ_K /kHz	13.4508(75)	9.4(13)
δ_J /kHz	0.14011(19)	0.14357(97)
δ_K /kHz	1.889(17)	1.569(72)
Φ_J /Hz	0.00191(39)	^g
Φ_{JK} /Hz	0.0432(87)	
Φ_{KJ} /Hz	-0.0600(41)	
Φ_{Ki} /Hz	0.288(29)	

^a*A*-reduction, *f*-representation.¹⁹ ^bUncertainties represent one standard deviation. ^cRoot-mean-square deviation. ^dMaximum value of *J* of the assigned *Q*-branch transitions. ^eMaximum value of *J* of the assigned *P*- or *R*-branch transitions. ^fFurther sextic constants preset at zero. ^gSextic constants preset at zero.

[†] The complete spectra of the four conformers are available from the authors upon request, or from the Molecular Spectra Data Center, National Institute of Standards and Technology, Molecular Physics Division, Bldg. 221, Rm. B265, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 3. Spectroscopic constants^{a,b} of the first excited state of the C1–C2 torsional vibration of *H bond outer 1* of thiiranemethanethiol.

No. of transitions:	107
R.m.s. dev. ^c /MHz:	0.050
$J_{Q_{\max}}^d$	23
$J_{P,R_{\max}}^e$	77
A_v /MHz	7376.3511(42)
B_v /MHz	1722.48002(97)
C_v /MHz	1480.3244(12)
Δ_J /kHz	0.6351(18)
Δ_{JK} /kHz	-3.155(17)
Δ_K /kHz	14.165(18)
δ_J /kHz	0.13862(70)
δ_K /kHz	1.903(46)
Φ_J /Hz	0.00135(17)
Φ_{JK}^f /Hz	0.0230(38)

^{a-f}Comments as for Table 2.

$|c| = 35.54(19)$ pm. These values are in fair agreement with those predicted for H1 of *H bond outer 1* (Table 1) and represent additional conclusive evidence that *H bond outer 1* has indeed been assigned.

The dipole moment could not be obtained for any of the four conformers assigned in this work because the low- J transitions are too weak to allow quantitative Stark effect measurements to be made.

Assignment of H bond outer 2. This rotamer was predicted (Table 1) to be the second most stable conformer of thiiranemethanethiol, and to have its largest component of the dipole moment along the b -inertial axis, as already mentioned. The strong bQ -lines were first found for this conformer, which has the second strongest spectrum. The low- J bR -transitions were then identified using a trial and error procedure. The assignments were next gradually extended up to 118₂₀←119₁₉ coalescing pair of b -type transitions. Two sextic centrifugal distortion constants were utilized in this case to get a satisfactory least-squares fit. No a - or c -type transitions could be identified with certainty, although their hypothetical frequencies could presumably be predicted very accurately. This is consistent with small values for μ_a and μ_c (Table 1). The spectroscopic constants obtained using 203 transitions are shown in Table 4.

One vibrationally excited state was assigned for this rotamer; its spectroscopic constants are listed in Table 5. Relative intensity measurements yielded 133(20) cm⁻¹ for this fundamental mode, which is assumed to be the C1–C2 torsional vibration, while 108 cm⁻¹ (not given in Table 1) was calculated by *ab initio* methods.

The deuterated species (mercapto group) was assigned in a straightforward manner. The spectroscopic constants obtained from 30 transitions with a maximum value of $J=42$ are found in Table 4. The substitution coordinates²¹ for the H1 atom are calculated to be $|a| = 204.617(42)$, $|b| = 122.125(75)$ and $|c| = 55.30(16)$

Table 4. Ground-state spectroscopic constants^{a,b} of *H bond outer 2* of thiiranemethanethiol.

Species:	Parent	Deuterated
No. of transitions:	203	30
R.m.s. dev. ^c /MHz:	0.052	0.062
$J_{Q_{\max}}^d$	43	42
$J_{P,R_{\max}}^e$	119	15
A_0 /MHz	10701.1655(29)	10315.071(23)
B_0 /MHz	1423.94189(39)	1406.1878(55)
C_0 /MHz	1323.65338(43)	1304.2515(54)
Δ_J /kHz	0.181150(19)	0.165(16)
Δ_{JK} /kHz	0.1011(35)	-0.158(22)
Δ_K /kHz	10.278(14)	10.27 ^g
δ_J /kHz	0.015588(35)	0.016254(75)
δ_K /kHz	0.8919(77)	0.892 ^g
Φ_J /Hz	-0.0001491(66)	^h
Φ_{JK}^f /Hz	-0.00967(18)	

^{a-f}Comments as for Table 2. ^gFixed. ^hSextic centrifugal distortion constants preset at zero.

pm; values that are fairly close to the predicted ones (Table 1). This is corroborative evidence that the rotational constants in Table 4 are correctly assigned to *H bond outer 2*.

Assignment of H bond inner. This conformer was predicted (Table 1) to have a large b -axis dipole moment component. Searches for bQ -branch lines among the strongest transitions that so far had not been assigned, were soon successful. Numerous transitions of this type exist in the accessible spectral range, and about 170 of them with a maximum of $J=62$ were assigned. Low- J bR -lines were found next in a trial-and-error procedure. Unfortunately, high- J bR -transitions were so weak that no definite assignments could be made. No a - or c -type lines were identified, presumably because the corresponding dipole moment components are so small, as indicated in Table 1. The spectroscopic constants determined from 180 transitions are listed in Table 6. Two sextic centrif-

Table 5. Spectroscopic constants^{a,b} of the first excited state of the C1–C2 torsional vibration of *H bond outer 2* of thiiranemethanethiol.

No. of transitions:	141
R.m.s. dev. ^c /MHz:	0.032
$J_{Q_{\max}}^d$	43
$J_{P,R_{\max}}^e$	84
A_v /MHz	10605.1237(28)
B_v /MHz	1423.28001(39)
C_v /MHz	1323.65418(43)
Δ_J /kHz	0.17772(23)
Δ_{JK} /kHz	0.0361(35)
Δ_K /kHz	6.371(12)
δ_J /kHz	0.015174(32)
δ_K /kHz	0.7559(66)
Φ_J /Hz	-0.000443(36)
Φ_{JK}^f /Hz	-0.01885(96)

^{a-f}Comments as for Table 2.

Table 6. Ground-state spectroscopic constants^{a,b} of *H bond inner* of thiiranemethanethiol.

No. of transitions:	180
R.m.s. dev. ^c /MHz:	0.052
$J_{Q_{\max}}$ ^d	62
$J_{P,R_{\max}}$ ^e	12
A_0 /MHz	6 134.450 3(44)
B_0 /MHz	1 948.820 8(28)
C_0 /MHz	1 818.389 7(28)
Δ_J /kHz	0.685(15)
Δ_{JK} /kHz	-1.465 5(58)
Δ_K /kHz	2.32(28)
δ_J /kHz	0.103 609(38)
δ_K /kHz	1.9534(50)
Φ_{KJ} /Hz	2.88(25)
Φ_K /Hz	-96.7(89)

^{a-f}Comments as for Table 2.

ugal distortion constants had to be included in order to get a fit with a root mean-square deviation comparable to the experimental uncertainty.

Q-branch *b*-type transitions of the first excited state of the C1–C2 torsional fundamental were also assigned. The strongest *R*-branch lines of this excited state were searched for, but not identified. Therefore, only A_v – C_v , and the asymmetry parameter κ could be determined from 54 transitions. The result is found in Table 7. Two sextic centrifugal distortion constants had to be used for the same reason as mentioned above for the ground vibrational state of this conformer. Relative intensity measurements yielded 116(30) cm⁻¹ for this fundamental vibration, in good agreement with 122 cm⁻¹ obtained in *ab initio* computations. The deuterated species of this conformer was not identified presumably because of low intensity.

Assignment of Conformer IV. When the spectral region around 33 GHz was searched with a low Stark voltage (about 60 V cm⁻¹), a typical high- K_{-1} *aR*-branch pile-up showed up. It was soon found that this rather weak

Table 7. Spectroscopic constants^{a,b} of the first excited state of the C1–C2 torsional vibration of *H bond inner* of thiiranemethanethiol.

No. of transitions:	54
R.m.s. dev. ^c /MHz:	0.064
$J_{Q_{\max}}$ ^d	63
$(A_v - C_v)$ /MHz	4 328.688 3(86)
κ	-0.939 335
Δ_J /kHz	0.685 ^e
Δ_{JK} /kHz	-1.436(11)
Δ_K /kHz	2.32 ^e
δ_J /kHz	0.101 63(12)
δ_K /kHz	1.979(11)
Φ_{KJ} /Hz	3.58(38)
Φ_K /Hz	111(13)

^{a-d,f}Comments as for Table 2. ^eFixed.

Table 8. Ground-state spectroscopic constants^{a,b} of *Conformer IV* of thiiranemethanethiol.

No. of transitions:	69
R.m.s. dev. ^c /MHz:	0.061
$J_{P,R_{\max}}$ ^d	14
A_0 /MHz	10 645.2(17)
B_0 /MHz	1 424.169 2(27)
C_0 /MHz	1 331.302 1(29)
Δ_J /kHz	0.176 8(60)
Δ_{JK} ^e /kHz	0.026 6(94)

^{a-c}Comments as for Table 2. ^dComments as for ^e in Table 2.

^eFurther quartic centrifugal distortion constants preset at zero in the least-squares fit.

pile-up had to be identified with the $J = 13 \leftarrow 12$ series of transitions. With this starting point, the frequencies of additional *aR*-lines were predicted, identified and included in the least-squares fit. Searches for *b*- and *c*-type transitions were futile. This is in accord with the *ab initio* computations (Table 1), which predict small values for the two dipole moment components in question. 69 transitions were used to determine the spectroscopic constants shown in Table 8. Only two quartic centrifugal distortion constants (Δ_J and Δ_{JK}) could be obtained in this case owing to the rather limited selection of transitions that were assigned. No assignments were made for the deuterated species because they were too weak under the experimental conditions which were employed.

The good agreement between the calculated rotational constants (Table 1) and the agreement with regard to the principal-axes components of the dipole moments are taken as proofs that both *Conformer IV* as well as *H bond inner* have indeed been assigned and not confused with other rotamers which have the same heavy-atom conformations, but different orientation of the mercapto group. A different orientation would not have influenced the rotational constants to a great extent, but would have produced widely different dipole moments (and spectra) than the observed ones. It is therefore considered beyond doubt that *Conformer IV* and *H bond inner* have indeed been assigned.

Searches for further rotamers. The assignments reported above include all the strongest transitions of the MW spectrum, most of the transitions with intermediate intensity and many weak ones too. However, this spectrum has a rich background of mostly weak or very weak transitions which have not been assigned. A majority of these belong in all likelihood to unassigned vibrationally excited states of the four identified conformers. It is of course possible that some of these weak signals belong to one (or more) additional unassigned forms present in low concentrations. Such forms, which in most cases should possess rather sizable dipole moments, were searched for, but no assignments could be made. On this basis it is thus concluded that *H bond outer 2*, which is the most stable conformer (see below), is at least 3 kJ mol⁻¹ more

stable than any fifth hypothetical conformation of thiiranemethanethiol.

Energy difference. The internal energy differences between the four conformers were obtained from relative intensity measurements²⁰ made on carefully selected transitions. The ratio between the calculated dipole-moment components given in Table 1 were used, as no experimental dipole moments of the four rotamers have been obtained. It is rather difficult to measure half-breadths of the transitions accurately, especially in a spectrum as crowded as this, and these quantities were assumed to be proportional to the dipole moment²² of the transitions being employed. This assumption is of course rather drastic. In this manner, *H bond outer 2* was found to be the most stable form of thiiranemethanethiol. The internal energy difference between this rotamer and *H bond outer 1* is 0.9(3) kJ mol⁻¹. Moreover, *H bond outer 2* was found to be 1.4(3) kJ mol⁻¹ more stable than *H bond inner*, and 3.5(4) kJ mol⁻¹ more stable than *Conformer IV*. The quoted uncertainties represent one standard deviation which has been estimated by taking into account the uncertainties of the calculated dipole moment components (less than 10%), as well as other sources of error such as the assumption that the half-breadth is proportional to the dipole moment (less than 25%).

The energy differences obtained in the MP2/6-31G* computations (Table 1) are in remarkably good agreement with the experimental values.

Conformational analysis in solution. To ensure the existence of only monomers, the NMR spectra were recorded using dilute solutions (3 mM) of CDCl₃. The analysis based on coupling constants was performed as described in Ref. 23 at ambient temperature. However, with sulfur substituting oxygen, more accurate coupling constants for the J_{60} and the J_{180} were needed. More refined Karplus equations, which also take into consideration the electronegativity values of the substituents, are given in the literature.^{24,25} From these equations it was found that $J_{60} = 3.1$ Hz and the $J_{180} = 13.1$ Hz, respectively. Putting these values into eqns. (1) and (2) of Ref. 23 the ratio of *H bond outer 2*:*H bond outer 1*:*H bond inner* was found to be 43:23:34. This is in reasonable agreement with the gas-phase results, and in particular it indicates that the *H bond outer 2* conformer is the most stable of the three.

Structure. It is seen from Tables 2, 4, 6 and 8 that the experimental rotational constants of the four conformers are close to those calculated from the MP2/6-31G* structure (Table 1). In fact, in no case is the deviation larger than about 2%. Moreover, the structural parameters of the thiirane ring and the -CH₂SH substituent are very similar to their experimental counterparts in thiirane¹⁶ and methanethiol,¹⁷ as already mentioned. There is also good agreement between the substitution coordinates of the H atom of the mercapto group and those obtained in the *ab initio* computations. No experimental data are at

hand that could really improve the MP2/6-31G* structures of these four conformers. For example, a fit of the H1-S1-C1-C2 and S1-C1-C2-C3 dihedral angles to the rotational constants taking the other structural parameters from the best available experimental structures of similar molecules and keeping them fixed in this fitting procedure, would not yield results significantly different from those in Table 1. The *ab initio* structures shown in Table 1 are therefore adopted as *plausible* structures for the four assigned conformers of thiiranemethanethiol. It is presumed that the *plausible* structures are close to the equilibrium structures. It is guessed that the bond lengths are no more than 0.5 pm, bond angles no more than 1°, and dihedral angles no more than 3° from the equilibrium values.

Discussion

The reason why thiiranemethanethiol prefers the four conformers shown in Fig. 1 is probably quite complex. Steric conditions in its most stable form, *H bond outer 2*, are rather ideal. The formation of an intramolecular H bond between the H1 atom and the pseudo- π electrons along the C2-C3 edge of the thiirane ring presumably stabilizes this form to such an extent that it makes it the most stable form of the molecule.

Conformer IV, which is similar to *H bond outer 2* but has the H1-S1 bond *anti* to the C1-C2 bond, has a completely relaxed conformation. Yet it is 3.5(4) kJ mol⁻¹ less stable than *H bond outer 2*. Some, perhaps most, of this energy difference probably stems from the H bond in the latter form. The *H bond strength* is thus suggested to have a strength of roughly 3.5 kJ mol⁻¹ in *H bond outer 2*, since the major difference between the two forms involves only a rotation around the C1-S1 axis and no further significant relaxation (see Ref. 26 for a discussion).

In *H bond outer 1* the H1-S1 and C2-S2 bonds are only 8.2° (calculated from the structure; Table 1) from being parallel. The bond dipoles are thus almost antiparallel, which is very favourable, and this stabilizing effect may be of importance. In addition, the pseudo- π electron along the C2-S2 edge of the thiirane is helpful in strengthening the H bond. Apparently, the lone pairs on the S2 atom are not very effective in forming a H bond since the H1...S2 distance is slightly longer (313.9 pm; Table 1) than the sum of the van der Waals radii of hydrogen and sulfur¹⁸ (305 pm; Table 1). All this makes this rotamer 0.9(3) kJ mol⁻¹ less stable than the most stable conformer, *H bond outer 2*.

The H bond in *H bond inner* is an ordinary S-H...S hydrogen bond, and it is weak since the H1...S2 distance is only 13 pm shorter than the sum of the van der Waals radii of hydrogen and sulfur¹⁸ (Table 1). In addition the S1-H1...S2 angle is 54.1°, which is far from the ideal linear shape. The requirements of the *bonded* atoms thus make it impossible for *H bond inner* to form as strong a

H bond as it could have made if this restriction did not exist. This is guessed to be the major reason why *H bond inner* is 1.4(3) kJ mol⁻¹ less stable than *H bond outer 2*.

The conformational make-up of thiiranemethanethiol is strikingly different from that of its oxygen analogue, oxiranemethanol (glycidol), where the *H bond inner* conformer is the most stable one and *H bond outer 2* is a high-energy form of the molecule not found experimentally,²⁷ but predicted to be stable in *ab initio* computations.^{27c} The reason for this difference between oxiranemethanol and the title compound is presumed to be different geometries of the *H bond inner* conformer in the two molecules (less favourable in thiiranemethanethiol), different electronegativities of oxygen and sulfur (again less favourable in thiiranemethanethiol) and different electronic environments on oxygen and sulfur. The 'unfortunate' circumstances in thiiranemethanethiol raise the relative energy of *H bond inner* to such an extent that it becomes less stable than *H bond outer 2*.

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