

A Microwave and *Ab Initio* Quantum Chemical Study of Intramolecular Hydrogen Bonding and Conformational Properties of 2-(Methylthio)ethanol

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The microwave spectra of $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OD}$ have been investigated at 0°C . One conformer with all-*gauche* atomic arrangements, denoted *gGG*, was assigned and shown to be at least 3 kJ mol^{-1} more stable than any other rotameric form of the molecule. This rotamer is stabilized with an intramolecular hydrogen bond formed between the hydroxyl group hydrogen atom and the sulfur atom. *Ab initio* quantum chemical calculations at the 3–21 G level have been made for four selected conformations whose structures were fully optimized. These calculations predict the *gGG* conformer to be the more stable, in agreement with the microwave findings.

Ethanol derivatives of the form $\text{XCH}_2\text{CH}_2\text{OH}$ are capable of forming intramolecular hydrogen bonds in cases where X is an electronegative atom or group. Many such compounds have been studied by microwave (MW) spectroscopy in recent years. These studies include $\text{X} = \text{F}$,¹ Cl ,² Br ,² $\text{C}\equiv\text{N}$,³ OH ,⁴ NH_2 ,⁵ SH ,⁶ $\text{HC}=\text{CH}_2$,⁷ $\text{C}\equiv\text{C}-\text{H}$,⁸ OCH_3 ,⁹ $\text{NH}(\text{CH}_3)$,¹⁰ $\text{CH}_2-\text{CH}_2-\text{N}$ ¹¹ and $\text{N}(\text{CH}_3)_2$.¹² In all these molecules, one conformer, or in the cases of $\text{HOCH}_2\text{CH}_2\text{OH}$ ^{4d} and $\text{HOCH}_2\text{CH}_2\text{NH}(\text{CH}_3)$,¹⁰ two rotamers, with heavy-atom *gauche* atomic arrangements and internal hydrogen bonds have been found to predominate in the gaseous state. In only one of these compounds, namely $\text{HSCH}_2\text{CH}_2\text{OH}$,⁶ has a sulfur atom participated in intramolecular hydrogen bonding as proton acceptor. This molecule was found to adopt the all-*gauche* conformation with the hydroxyl group as proton donor and the thiol group as acceptor. No further conformations were identified for free $\text{HSCH}_2\text{CH}_2\text{OH}$.⁶

2-(Methylthio)ethanol was chosen for study because we wanted to investigate the ability of the sulfur atom to act as acceptor for internal hydrogen bonds, as well as to extend the list of 2-substituted ethanol derivatives for which this interaction is a major factor in determining the conformational properties of the molecule.

In $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$ there are three internal rotation axes; consequently, as many as 17 all-staggered conformations are possible for this compound. Fig. 1 shows four selected rotamers. These conformations are believed to be the four with the lowest energies for the following reasons: The *gGG* and *gGA* rotamers each possess an intramolecular hydrogen bond, just as in the case of $\text{HSCH}_2\text{CH}_2\text{OH}$.⁶

Both *gGG* and *gGA* on the one hand were therefore expected to be more stable than *aAG* and *aAA* on the other, because *aAG* and *aAA* lack this stabilizing interaction.

The only conformational difference between the hydrogen-bonded *gGG* and *gGA* forms is the orientation of the methyl group, which is *gauche* to the C–C bond in *gGG* and *anti* to the same bond in *gGA*. The same conformational difference as that between *gGG* and *gGA* is also found for $\text{CH}_3\text{SCH}_2\text{CH}_3$.¹³ The enthalpy difference between the *gauche* and *anti* conformers of $\text{CH}_3\text{SCH}_2\text{CH}_3$ is only $0.13(20)\text{ kJ mol}^{-1}$, with the *gauche* rotamer being the slightly more stable.^{13a} If conformational properties were

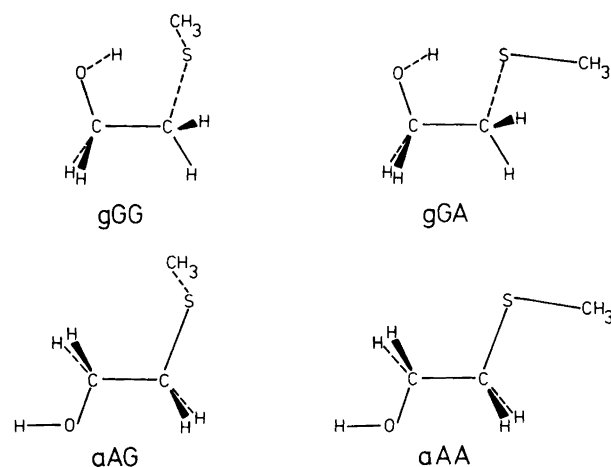


Fig. 1. Four selected conformations of $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$. Intramolecular hydrogen bonding is possible in *gGG* and *gGA*, while this interaction is not possible in *aAG* and *aAA*. Only the all-*gauche* rotamer *gGG* was identified in the MW spectrum.

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transferable, it would thus be expected that the *gGG* and *gGA* rotamers would have very similar energies, by analogy with the findings for CH₃SCH₂CH₃. This, however, was *not* found to be the case. It turned out in the course of this work that there is a remarkable preference for *gGG*, just as for the all-*gauche* counterpart of HSCH₂CH₂OH.⁶

It was also believed worthwhile to examine the spectrum for evidence of two of the heavy-atom *anti* conformations of the title molecule, which perhaps might have sufficiently low energies to be observable. The best candidates for such a search are presumably the *aAG* and *aAA* conformations shown in Fig. 1. There is of course no internal hydrogen bond in any of these two forms. Moreover, the O–H bond is *anti* to the C–C bond in both *aAG* and in *aAA*. This conformation for the hydroxyl group was selected instead of *gauche* because the *anti* conformer of ethanol is 2.9(2) kJ mol⁻¹ more stable than the *gauche*.¹⁴ The methyl group conformation is *gauche* in *aAG* and *anti* in *aAA*. Neither *aAG* nor *aAA* were assigned in this work, presumably because they have higher energies than the identified *gGG* conformer.

Ab initio computations are often found to mimic gas-phase conformational equilibria rather well. It was therefore decided to perform such calculations for the four selected conformations shown in Fig. 1. These computations also predicted the *gGG* conformer to be considerably more stable than the other three conformations depicted in Fig. 1, as will be shown below.

Experimental

Experimental conditions. A commercial sample of 2-(methylthio)ethanol was employed in this work. The sample was purified by gas chromatography before use. The absorption cell was cooled to about 0°C. Lower temperatures could not be used due to insufficient vapour pressure of the compound. The pressure was about 2 Pa when the spectra were recorded. The spectrometer used is an improved version of the one described briefly in Ref. 15, employing klystrons as radiation sources. The radio frequency–microwave frequency double resonance technique (RFMWDR) was used as described in Ref. 16, employing the equipment mentioned in Ref. 17. The 26.5–38.0 GHz spectral region was studied extensively. Some measurements were also made in the 18–24 GHz range. The deute-

riated species CH₃SCH₂CH₂OD was produced by exchange with heavy water in the absorption cell. The degree of deuteration obtained in this way was roughly 50%.

Method of calculation. The *ab initio* quantum chemical computations were performed using the GAMESS¹⁸ program package. The program used in the present calculations is a revised version prepared by M. W. Schmidt of North Dakota State University and S. Elbert of Iowa State University. The computations were made using a FPS-164 computer. The basis set 3–21 G (Ref. 19) was chosen, and the geometries of the four conformations of Fig. 1 were optimized at the Hartree-Fock theoretical level by calculating the analytical energy gradients. More elaborate basis sets could not be used for financial reasons.

Results

Predictions. *Ab initio* calculations are helpful in making predictions about energy differences between various conformations, as well as their dipole moments and structures. In Table 1, energy differences between the four conformations as well as principal axis dipole moment components obtained from the *ab initio* computations are collected. It is seen that the *gGG* conformation is predicted to be more than 5 kJ mol⁻¹ more stable than any other of the four forms for which computations were made. This conformer is also predicted to possess sizable dipole moment components along all three principal inertial axes (Table 1).

The *ab initio* optimized structural parameters given in Table 2 appear to be reasonable, apart from the C–S bond lengths and the C–C–S–C dihedral angles of the *gGG* and *aAG* conformations. The C–S bond lengths are roughly 8 pm greater, while the C–C–S–C dihedral angles are approximately 10° smaller than the substitution values found for the corresponding bond lengths and dihedral angle in *gauche* CH₃SCH₂CH₃^{13d} (see also Table 7). This kind of overestimation of C–S bond lengths is known to occur when use is made of the 3–21 G basis set.²⁰

The rather long bond lengths and small C–C–S–C dihedral angles obtained by the theoretical calculations in the cases of *gGG* and *aAG* will predict rotational constants which will be too small. Therefore, preliminary rotational constants were computed by combining structural parameters for related compounds (see Table 7). Principal axis

Table 1. Relative energies and principal axis dipole moment components calculated by *ab initio* for the four conformations of Fig. 1.

| Conformation | Relative energy/kJ mol ⁻¹ | Dipole moment comp./10 ⁻³⁰ C m | | |
|--------------|--------------------------------------|-------------------------------------------|----------------|----------------|
| | | <i>a</i> -axis | <i>b</i> -axis | <i>c</i> -axis |
| <i>gGG</i> | 0.0 | 5.3 | 7.9 | 2.6 |
| <i>gGA</i> | 5.2 | 6.6 | 5.9 | 0.5 |
| <i>aAG</i> | 9.2 | 2.6 | 7.3 | 3.5 |
| <i>aAA</i> | 11.6 | 1.4 | 0.4 | 0.0 |

Table 2. Selected optimized structural parameters obtained by *ab initio* calculations for the four conformations shown in Fig. 1.

| | <i>gGG</i> | <i>gGA</i> | <i>aAG</i> | <i>aAA</i> |
|---------------------------|------------|------------|------------|------------|
| Bond lengths/pm | | | | |
| S-CH ₃ | 188.7 | 188.5 | 188.8 | 188.4 |
| S-CH ₂ - | 189.1 | 189.2 | 188.3 | 188.7 |
| O-C | 143.3 | 143.3 | 144.3 | 144.1 |
| C-C | 152.7 | 152.7 | 151.9 | 152.2 |
| Bond angles/° | | | | |
| ∠C-S-C | 100.2 | 100.2 | 100.3 | 99.8 |
| ∠C-C-S | 111.7 | 108.8 | 112.0 | 108.7 |
| ∠O-C-C | 111.7 | 112.2 | 105.4 | 108.7 |
| Dihedral angles/° | | | | |
| ∠O-C-C-S from <i>syn</i> | 61.5 | 68.7 | 179.4 | 180.0 |
| ∠C-C-S-C from <i>anti</i> | 103.1 | 4.6 | 100.8 | 0.0 |
| ∠H-O-C-C from <i>syn</i> | 57.3 | 63.7 | 177.4 | 180.0 |

Table 4. Microwave spectrum of the *gGG* conformer of CH₃SCH₂CH₂OH.

| Transition | Observed frequency ^a /MHz | Obs. - Calc. frequency/MHz |
|-------------------------------------|--------------------------------------|----------------------------|
| 5 _{0,5} ← 4 _{0,4} | 22861.90 | 0.05 |
| 5 _{1,4} ← 4 _{1,3} | 23008.59 | -0.07 |
| 5 _{1,5} ← 4 _{1,4} | 22731.17 | -0.08 |
| 5 _{2,3} ← 4 _{2,2} | 22881.43 | -0.11 |
| 5 _{2,4} ← 4 _{2,3} | 22871.18 | -0.05 |
| 6 _{0,6} ← 5 _{0,5} | 27428.01 | -0.03 |
| 6 _{1,5} ← 5 _{1,4} | 27608.48 | 0.09 |
| 6 _{1,6} ← 5 _{1,5} | 27275.66 | 0.07 |
| 6 _{2,4} ← 5 _{2,3} | 27462.00 | 0.00 |
| 6 _{2,5} ← 5 _{2,4} | 27444.07 | 0.08 |
| 7 _{0,7} ← 6 _{0,6} | 31990.81 | -0.10 |
| 7 _{1,6} ← 6 _{1,5} | 32207.05 | 0.05 |
| 7 _{1,7} ← 6 _{1,6} | 31818.98 | 0.06 |
| 7 _{2,4} ← 6 _{2,3} | 32044.84 | 0.14 |
| 7 _{2,5} ← 6 _{2,4} | 32015.95 | 0.00 |
| 8 _{0,8} ← 7 _{0,7} | 36550.00 | 0.05 |
| 8 _{1,7} ← 7 _{1,6} | 36804.23 | -0.05 |
| 8 _{1,8} ← 7 _{1,7} | 36361.06 | -0.03 |
| 8 _{2,6} ← 7 _{2,5} | 36629.85 | -0.08 |
| 8 _{2,7} ← 7 _{2,6} | 36586.95 | -0.01 |

^a ±0.15 MHz.Table 3. Predicted rotational constants and principal axis dipole moment components for the four conformations of Fig. 1.^a

| Conformation | Rotational constants/GHz | | | Dipole moment comp./10 ⁻³⁰ C m | | |
|--------------|--------------------------|------|------|-------------------------------------------|--------|--------|
| | A | B | C | a-axis | b-axis | c-axis |
| <i>gGG</i> | 6.76 | 2.32 | 2.23 | 3.7 | 4.8 | 4.0 |
| <i>gGA</i> | 10.23 | 2.04 | 1.86 | 5.6 | 4.4 | 1.0 |
| <i>aAG</i> | 9.11 | 1.88 | 1.68 | 2.2 | 7.0 | 2.4 |
| <i>aAA</i> | 13.85 | 1.63 | 1.50 | 1.0 | 0.0 | 0.0 |

^aSee text.

dipole moment components were predicted using the bond-moment method,²¹ which is often quite accurate in cases such as the present one. The results are summarized in Table 3. The *total* dipole moments of the four conformations of Fig. 1 can be calculated from the values shown in Tables 1 and 3. The total dipole moments predicted by the bond-moment method are roughly 20% smaller than those predicted using the *ab initio* method.

Spectrum. The spectrum of CH₃SCH₂CH₂OH is very dense, with absorptions occurring every few MHz throughout the entire investigated MW region. It is also comparatively very weak. The strongest absorptions of the spectrum are the high-*K*₋₁ pile-ups of the *a*-type *R*-branch transitions of the *gGG* conformation. The ground-state *J* = 8 ← 7 pile-up has a peak absorption coefficient of roughly 1.5 × 10⁻⁷ cm⁻¹. This is the strongest transition in the spectrum. The intensities of the resolved low-*K*₋₁ lines of the *J* = 8 ← 7 transitions corresponded to peak absorption coefficients of roughly 5 × 10⁻⁸ cm⁻¹.

Assignment. A search was first made for the *gGG* form based on the predictions discussed above. This rotamer has a value for Ray's asymmetry parameter²² of $\kappa \approx -0.97$. High-*K*₋₁ pile-ups were predicted for the *a*-type *R*-branch transitions of this conformer. These pile-ups were readily observed since they are the strongest lines in the spectrum. They were also found very close to their predicted frequencies. Their assignments were confirmed by RFMWDR experiments.¹⁶ The low-*K*₋₁ lines which are resolved from these pile-ups were found after some searching. They are listed in Table 4. The spectroscopic constants given in Table 5 were derived from the transitions listed in Table 4.

According to the predicted dipole moments in Tables 1 and 3, the *gGG* conformer would be expected to display *b*- and *c*-type transitions in addition to the *a*-type lines listed in Table 2. Extensive searches were made in an attempt to find these *b*- and *c*-type transitions, but they were not identified, presumably because of the weakness and density of the spectrum. Without these *b*- or *c*-type lines it is not possible to obtain an accurate value for the *A*₀ rotational constant, since *gGG* is nearly a symmetrical top with $\kappa = -0.975354$ and the *aR*-transitions of Table 2 are insufficient for an accurate determination of said constant in

Table 5. Spectroscopic constants for the ground vibrational states of the *gGG* conformer of CH₃SCH₂CH₂OH and CH₃SCH₂CH₂OD.^a

| Species | CH ₃ SCH ₂ CH ₂ OH | CH ₃ SCH ₂ CH ₂ OD |
|-------------------------------|-----------------------------------------------------|-----------------------------------------------------|
| Number of transitions | 20 | 9 |
| R.m.s deviation / MHz | 0.080 | 0.113 |
| <i>A</i> ₀ / MHz | 6762.7(76) | 6468(27) |
| <i>B</i> ₀ / MHz | 2315.0640(69) | 2280.037(21) |
| <i>C</i> ₀ / MHz | 2259.5705(69) | 2244.212(26) |
| Δ_J / kHz ^b | 2.028(48) | 2.03(18) |
| Δ_{JK} / kHz | -5.4(12) | -6.1(24) |
| χ^c | -0.975354 | -0.983040 |

^aA-reduction *I'*-representation.²³ Uncertainties represent one standard deviation. ^bFurther quartic centrifugal distortion constants were preset at zero. ^cRay's asymmetry parameter.²²

such cases. Only two of Watson's centrifugal distortion constants²³ were used in the least-squares fitting of the spectroscopic constants (*A*-reduction *I'*-representation) due to the limited experimental data at hand.

Table 5 also contains the spectroscopic constants⁸ for the deuteriated species CH₃SCH₂CH₂OD. This species was studied in order to establish beyond doubt the position of the hydroxyl group hydrogen atom. This atom cannot be located accurately by the use of Kraitchman's equations²⁴ because the *A*₀'s for the parent and deuteriated species are rather inaccurate (Table 5). However, the *B*₀'s and *C*₀'s for said species are very accurate and can be used to obtain unambiguous information concerning the position of the hydroxyl group hydrogen atom. From Table 5 it is seen that *B*₀ changes by -35.03 MHz and *C*₀ by -15.36 MHz, respectively, upon substitution. The changes calculated using the plausible structure (see below) are -36.55 MHz and -18.56 MHz, respectively. There is thus quite good agreement between experimental and calculated changes in *B*₀ and *C*₀ upon substitution. This is conclusive evidence that an intramolecular hydrogen bond exists in the preferred *gGG* conformation of free 2-(methylthio)ethanol.

Vibrationally excited states. The ground-state transitions were accompanied by transitions belonging to several vibrationally excited states. Four of these were assigned. In two cases the low-*K*₋₁ transitions were so strong that assignments could be made. Their spectroscopic constants are given in Table 6. It is presumed that these two excited states result from successive excitation of the torsion around the -CH₂-SCH₃ bond. In the two other cases only the pile-ups were assigned, and approximate values for *B*_v + *C*_v of 4600.85(10) MHz were determined for what is

⁸The transitions used to derive these constants, as well as the spectra of the vibrationally excited states, are available from the authors upon request, or from the Molecular Spectra Data Center, Bldg. 221, Room B 268, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A., where they have been deposited.

Table 6. Spectroscopic constants for vibrationally excited states of the *gGG* conformer of CH₃SCH₂CH₂OH.^a

| Vibrational state | First ex. -CH ₂ -S torsional vib. | Second ex. -CH ₂ -S torsional vib. |
|-------------------------------|----------------------------------------------|-----------------------------------------------|
| Number of transitions | 17 | 11 |
| R.m.s deviation / MHz | 0.128 | 0.182 |
| <i>A</i> _v / MHz | 6765(11) | 6835(23) |
| <i>B</i> _v / MHz | 2323.717(13) | 2327.690(23) |
| <i>C</i> _v / MHz | 2264.786(11) | 2269.478(25) |
| Δ_J / kHz ^b | 2.260(91) | 3.32(19) |
| Δ_{JK} / kHz | -5.9(22) | -14.1(34) |
| χ^c | -0.973811 | -0.974501 |

^{a, b, c}Comments as for Table 5.

presumed to be the third excited state of the same torsional mode. A value of *B*_v + *C*_v ≈ 4561.86(10) MHz was found for the fourth pile-up which is presumed to be the first excited state of the -CH₂-CH₂- torsional vibration. It is also possible that this is a low-frequency bending mode.

An accurate determination of the two torsional frequencies could not be made due to the weakness of the spectrum. However, the -CH₂-SCH₃ torsion is estimated to have a frequency of ca. 70 cm⁻¹. This mode appears to be quite anharmonic, since the spectral shifts of the pile-up of successively excited states are not equidistant. The approximate sums of *B* + *C* derived from the pile-ups are thus 4574.95 MHz for the ground state, 4588.84 MHz for the first excited torsional state, 4597.52 MHz for the second, and 4600.85 MHz for the third excited state of this torsional vibration.

The -CH₂-CH₂- torsional vibration is estimated to have a frequency of ca. 130 cm⁻¹. These two values for the two torsional vibrations are not very different from what have been observed by IR spectroscopy^{13a} in condensed phases for ethyl methyl sulfide. The *ab initio* values for these two torsional vibrations were computed to be 77 cm⁻¹ and 157 cm⁻¹, respectively. It has been noted that vibrational frequencies calculated with a 3-21 G basis are generally 5-10 % too large.²⁰

Searches for further conformations. As mentioned above, the hypothetical *gGA* (Fig. 1) conformation was believed to be a good candidate to search for. The *ab initio* calculations (Table 1) predict this conformer to be 5.2 kJ mol⁻¹ less stable than *gGG*. As can be seen in Tables 1 and 3, a rather large μ_a was predicted for this conformer, which was also predicted to be very prolate with $\chi \approx -0.95$. Easily identifiable pile-ups similar to those assigned for *gGG* were thus predicted for *gGA*. Searches were made for these pile-ups using ordinary Stark effect spectroscopy as well as the RFMWDR technique.¹⁶ Moreover, *b*-type lines were also searched for since μ_b is predicted to be sizable (Tables 1 and 3), but *gGA* was not found.

Table 7. Plausible molecular structure^a (bond lengths in pm, angles in degrees) of CH₃SCH₂CH₂OH.

| Structural parameters kept fixed | | | |
|-----------------------------------------|-------------------------|--------------------------------------|--------------------|
| H ₃ S–C | 180.2 ^b | ∠C–C–S | 114.7 ^b |
| H ₃ S–C | 180.4 ^d | ∠C–C–S | 109.5 ^d |
| –S–CH ₂ – | 180.6 ^b | ∠C–S–C | 100.2 ^b |
| –S–CH ₂ – | 180.4 ^d | ∠C–S–C | 99.0 ^d |
| C–C | 152.4 ^b | ∠O–C–C | 112.5 |
| C–C | 153.0 ^d | ∠H–O–C | 104.0 |
| C–O | 141.5 | ∠H–C–C | 109.47 |
| O–H | 95.0 | ∠H–C–S | 109.47 |
| C–H | 109.3 | | |
| Fitted ^e | | | |
| ∠C–C–S–C | 113(3) from <i>anti</i> | (67(3)) from <i>syn</i> | |
| ∠O–C–C–S | 61(3) from <i>syn</i> | | |
| Hydrogen bond parameters | | | |
| H...S | 271 | ∠O–H...S | 113 |
| O...S | 321 | ∠H...S–CH ₂ – | 65 |
| | | ∠O–H, S–CH ₃ ^f | 104 |
| | | ∠H...S–CH ₃ | 98 |
| Sum of van der Waals radii ^g | | | |
| H...S | 305 | | |
| O...S | 325 | | |

^aSee text. ^b*gGG* and *aAG* conformations. ^cTaken from Refs. 13c and 13d. ^d*gGA* and *aAA* conformations. ^eSee text. Dihedral angle. ^fAngle between O–H and S–C bond. ^gTaken from Ref. 25.

The bond-moment method²¹ is generally found to yield quite accurate dipole moments in cases such as the present molecule. It is therefore concluded that there must be a considerable energy difference between the *gGG* and the hypothetical *gGA* conformation, since the latter could not be identified. Conservative estimates lead us to conclude that *gGG* is a least 3 kJ mol⁻¹ more stable than the hypothetical *gGA* form. This is in accord with the *ab initio* value of 5.2 kJ mol⁻¹ (Table 1).

The two O–C–C–S *anti* rotamers *aAG* and *aAA* were also searched for in vain. The *ab initio* computations of Table 1 predict these two conformations to have considerably higher energies than the identified *gGG* conformer.

Although the above assignments account for the strongest lines of the spectrum, there is a very large number of

weak or very weak unassigned transitions left. Many of these are suspected to be high-*J* *Q*-branch transitions of the *b*- or *c*-type varieties of the ground and vibrationally excited states of the identified *gGG* conformer. Unfortunately, it was not possible for us to assign them, as mentioned above. The existence of small fractions of conformations other than *gGG* is considered to be quite possible. However, intensity considerations lead us to conclude rather conservatively that *gGG* must be at least 3 kJ mol⁻¹ more stable than any other form of the molecule.

Structure. Rotational constants have been derived for only two isotopomers (Table 5). There are thus insufficient data to perform a complete structure determination for the *gGG* conformer of 2-(methylthio)ethanol. Assumptions have to be made in order to derive important structural parameters. The C–C–S–C and O–C–C–S dihedral angles were selected for fitting, because they are chemically interesting and because the rotational constants depend strongly on these dihedral angles. The two dihedral angles were varied in steps of 1°, with the other structural parameters kept at the values shown in Table 7. The entries in this table have been selected from recent, accurate studies of closely related compounds. The fit yielded 113° from *anti* (67° from *syn*) for the C–C–S–C dihedral angle and 61° from *syn* for O–C–C–S dihedral angle. The uncertainty limit corresponding approximately to three standard deviations is estimated to be 3° in each of these cases. The C–C–S–C dihedral angle (113(3)°) is rather close to 110.57(83)° found for the corresponding dihedral angle in *gauche* CH₃CH₂SCH₃^{13d}, while the O–C–C–S angle of 61(3)° from *syn* is rather typical for this kind of hydrogen-bonded molecules in the *gauche* conformation.^{1–12} The rotational constants calculated employing the structural parameters of Table 7 are to be found in Table 8.

Discussion

It is believed that the intramolecular hydrogen bond is a decisive factor for the conformational properties of 2-(methylthio)ethanol and the major cause of the *gGG* conformation being preferred to any other form of the molecule. The hydrogen bond in the *gGG* conformation of CH₃SCH₂CH₂OH is of rather moderate strength, as can be inferred from the fact that the non-bonded distance be-

Table 8. Observed and calculated rotational constants^{a, b} for CH₃SCH₂CH₂OH and CH₃SCH₂CH₂OD.

| Constant / MHz | CH ₃ SCH ₂ CH ₂ OH | | | CH ₃ SCH ₂ CH ₂ OD | | |
|----------------|-----------------------------------------------------|--------|-----------|-----------------------------------------------------|--------|-----------|
| | Obs. | Calc. | Diff. / % | Obs. | Calc. | Diff. / % |
| A ₀ | 6762 | 6763 | 0.0 | 6469 | 6603 | 2.07 |
| B ₀ | 2315.1 | 2320.6 | 0.24 | 2280.0 | 2284.1 | 0.17 |
| C ₀ | 2259.6 | 2232.9 | 1.18 | 2244.2 | 2214.3 | 1.33 |

^aSee text. ^bStructural parameters used in the calculations are found in Table 7.

tween the hydroxyl group hydrogen atom and the sulfur atom is approximately 34 pm shorter than the sum of the van der Waals radii of hydrogen and sulfur²⁵ (Table 7). The non-bonded distance of 321 pm between the oxygen and sulfur atoms is almost the same as the sum of the van der Waals distances of said atoms, as revealed in the same table. The O–H and S–CH₂– bonds are about 5° from being parallel. This is a favourable arrangement for electrostatic interaction between the corresponding two bond dipoles.

Interestingly, the closely related compound CH₃CH₂SCH₂CH₂OH is known to possess a moderately strong intramolecular hydrogen bond in carbon tetrachloride solution,²⁶ as reflected by a shift of the O–H stretching frequency of 92 cm⁻¹.

The hydrogen bond in the title molecule is very similar to that in 2-mercaptoethanol.⁶ The conformational choices of CH₃SCH₂CH₂OH and HSCH₂CH₂OH⁶ are also strikingly similar. In both these compounds the all-*gauche* conformer is strongly preferred. No other forms have been found.

The reason why the all-*gauche* conformers are preferred both in the case of the title compound and for 2-mercaptoethanol⁶ is difficult to answer. Perhaps electrons of the sulfur atom become more easily available for hydrogen bonding in this conformation than in other forms such as *gGA*. Other factors may also be of importance.

It is also of interest to compare the conformational preference of the CH₃S– group with the corresponding preference of the CH₃O– group in cases where intramolecular hydrogen bonding is present. Several studies⁹ have shown that the methyl group is *anti* to the C–C bond in the hydrogen-bonded conformer of CH₃OCH₂CH₂OH, while the rotamer in which the methyl group is *gauche* with respect to the C–C bond has not been identified by MW spectroscopy.⁹ The conformational situation in CH₃OCH₂CH₂OH is thus remarkably different from what is found in this work for CH₃SCH₂CH₂OH, where the methyl group is *gauche* to the C–C bond.

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