Microwave Spectrum, Conformation and Intramolecular Hydrogen Bonding of 1-Mercapto-2-propanol

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Marstokk, K.-M., Møllendal, H. and Samdal, S., 1990. Microwave Spectrum, Conformation and Intramolecular Hydrogen Bonding of 1-Mercapto-2-propanol. – Acta Chem. Scand. 44: 339–345.

The microwave spectrum of $CH_3CH(OH)CH_2SH$ has been investigated in the 26.5–38.0 GHz spectral range at $-10\,°C$. One conformer, which is at least 3 kJ mol^{-1} more stable than any further hypothetical form, was assigned. The identified conformer has the methyl group and the C–S bond in the *anti* position relative to each other, while the C–O and C–S bonds are *gauche*. An intramolecular hydrogen bond is formed between the hydroxyl group and the thiol group, with the hydroxyl group acting as proton donor and the thiol group as acceptor. The S–H bond is *gauche* with respect to the C1–C2 bond. *Ab initio* calculations made for three selected conformations are in agreement with the microwave findings. The infrared spectrum shows no indication of the presence of several conformers.

In 1977 Sung and Harmony[1] reported the microwave (MW) spectrum of 2-mercaptoethanol, $HOCH_2CH_2SH$. They found that this compound prefers a heavy-atom *gauche* conformation stabilized with an OH···S intramolecular hydrogen bond. The conformation of the mercapto group was determined to be *gauche* to the C–C bond. No further conformers were detected.

The related title compound, $CH_3CH(OH)CH_2SH$, can have as many as 27 different *all-staggered* conformations. Two of these, denoted I and II in Fig. 1, are very similar to the stable conformation found for 2-mercaptoethanol.[1] Both rotamer I and rotamer II are stabilized with an OH···S internal hydrogen bond which is practically identical with that found in 2-mercaptoethanol.[1] The difference between I and II is that in conformation I the methyl group is *anti* to the C–S bond, whereas the methyl group is *gauche* with respect to the C–S bond in II. The S–H bond is
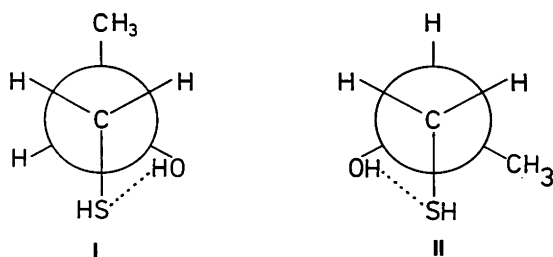

Fig. 1. Newman projections viewed along the C1–C2 bond of possible hydrogen-bonded conformations of $CH_3CH(OH)CH_2SH$ where the hydroxyl group acts as proton donor and the mercapto group as acceptor. Dots indicate intramolecular hydrogen bonds. Only conformation I was identified and shown to be at least 3 kJ mol^{-1} more stable than any other hypothetical rotamer.

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of course *gauche* with respect to the C1–C2 bond in both I and II, just as in 2-mercaptoethanol.[1]

No gas-phase structural studies appear to have been made for 1-mercapto-2-propanol, but in a ^{1}H NMR study by Alcudia *et al.*[2] it was concluded that the molecule prefers conformation I in dilute $CDCl_3$ solutions.

1-Mercapto-2-propanol is the sixth of a series of hydrogen-bonded 1,2-propanols which have been studied by MW spectroscopy in the gaseous state in recent years. In $CH_3CH(NH_2)CH_2OH$[3] and $CH_3CH(OH)CH_2OH$[4] conformers similar to both I and II were identified; II being the slightly less stable in each case. In $CH_3CH(OH)CH_2NH_2$,[5] $CH_3CH(OH)CH_2F$[6] and CH_3CHFCH_2OH,[7] however, only one rotamer similar to I was assigned for each of them. Our motivation for carrying out this work has been the lack of data on the structure of the free title molecule. Moreover, in the five previously investigated propanols[3-7] only first- and second-row elements have been involved, while in 1-mercapto-2-propanol the third-row element sulfur may influence the conformational choices the compound will make. In addition to the microwave investigation, infrared (IR) spectroscopy and *ab initio* calculations were employed in order to shed light on this problem.

Experimental

The sample used in this work was purchased from Parish Chemical Company, Orem, Utah, U.S.A. and purified by gas chromatography before use. The spectrum was studied in the 26.5–38.0 GHz spectral region at a temperature of about $-10\,°C$. Lower temperatures could not be used owing to insufficient vapour pressure of the compound. The pressure was between 1 and 2 Pa during the recording of the spectra. The spectrometer is an improved version of the

Table 1. Selected transitions of the ground-state MW spectrum of conformer I of 1-mercapto-2-propanol.

Transition	Observed frequency/MHz	Obs.-calc. freq./MHz	Centrifugal dist./MHz	
			Total	Sextic
b-Type				
$3_{3,1} \leftarrow 3_{2,2}$	31439.25	0.14	-0.43	
$5_{3,2} \leftarrow 5_{2,3}$	31111.04	-0.05	-0.66	
$8_{3,5} \leftarrow 8_{2,6}$	29796.48	-0.17	-1.11	
$11_{3,8} \leftarrow 11_{2,9}$	27245.88	-0.15	-1.62	
$14_{1,13} \leftarrow 14_{0,14}$	31461.30	0.01	-3.79	
$18_{4,14} \leftarrow 18_{3,15}$	36342.75	0.04	-5.04	
$21_{3,18} \leftarrow 21_{2,19}$	28705.29	-0.07	-9.98	
$24_{4,20} \leftarrow 24_{3,21}$	31616.78	0.00	-10.77	-0.01
$28_{4,24} \leftarrow 28_{3,25}$	36473.07	0.04	-23.20	
$2_{2,1} \leftarrow 1_{1,0}$	26757.99	0.00	-0.13	
$5_{2,4} \leftarrow 4_{1,3}$	37375.10	0.07	-0.44	
$8_{1,8} \leftarrow 7_{0,7}$	33624.53	-0.07	-0.57	
$14_{2,12} \leftarrow 13_{3,11}$	35286.12	0.05	-2.97	
$19_{3,17} \leftarrow 18_{4,14}$	29118.27	-0.01	0.57	0.01
$23_{5,18} \leftarrow 22_{6,17}$	27369.62	-0.05	-3.07	0.02
$28_{6,22} \leftarrow 27_{7,21}$	35654.37	0.02	-5.90	0.05
$36_{9,28} \leftarrow 35_{10,25}$	29167.35	-0.02	1.14	0.19
$40_{10,31} \leftarrow 39_{11,28}$	33145.25	0.11	1.05	0.32
$44_{11,34} \leftarrow 43_{12,31}$	37123.04	0.15	0.86	0.52
$44_{11,33} \leftarrow 43_{12,32}$	37125.02	0.01	0.84	0.52
c-Type				
$6_{3,4} \leftarrow 6_{2,4}$	30794.54	0.04	-0.79	
$9_{3,7} \leftarrow 9_{2,7}$	28773.93	-0.12	-1.19	
$12_{3,9} \leftarrow 12_{2,11}$	35834.05	0.07	-3.49	
$17_{4,14} \leftarrow 17_{3,14}$	36527.78	0.04	-3.95	
$21_{4,18} \leftarrow 21_{3,18}$	27648.74	0.03	-2.32	-0.01
$27_{5,23} \leftarrow 27_{4,23}$	36561.68	-0.08	-4.03	-0.04
$37_{6,32} \leftarrow 37_{5,32}$	31516.88	-0.04	6.93	-0.16
$46_{7,40} \leftarrow 46_{6,40}$	27471.65	0.02	27.58	-0.43
$52_{8,45} \leftarrow 52_{7,45}$	35082.88	-0.03	47.38	-0.92
$60_{9,52} \leftarrow 60_{8,52}$	33595.23	0.02	90.09	-1.86
$68_{10,59} \leftarrow 68_{9,59}$	31477.64	-0.07	147.22	-3.37
$76_{11,66} \leftarrow 76_{10,66}$	28940.92	0.02	216.54	-5.62
$2_{2,0} \leftarrow 1_{1,0}$	26770.71	-0.06	-0.13	
$5_{1,4} \leftarrow 4_{0,4}$	28994.71	0.04	-0.34	
Coalescing *b*- and *c*-type transitions[b]				
$13_8 \leftarrow 14_7$	37585.13	0.00	-7.07	
$17_9 \leftarrow 18_8$	33860.37	-0.01	-10.48	-0.01
$21_{10} \leftarrow 22_9$	30099.72	0.02	-14.62	-0.02
$27_{12} \leftarrow 28_{11}$	30783.56	0.01	-25.74	-0.08
$36_{15} \leftarrow 37_{14}$	31779.48	-0.01	-50.93	-0.29
$45_{18} \leftarrow 46_{17}$	32747.76	-0.02	-88.51	-0.84
$52_{20} \leftarrow 53_{19}$	29215.77	0.01	-120.14	-1.65
$61_{23} \leftarrow 62_{22}$	30139.52	-0.02	-183.44	-3.58
$67_{25} \leftarrow 68_{24}$	30742.84	0.10	-236.27	-5.65
$48_{13} \leftarrow 47_{14}$	27655.20	0.00	16.78	0.83
$55_{15} \leftarrow 54_{16}$	31264.67	0.01	26.41	1.64
$62_{17} \leftarrow 61_{18}$	34879.28	-0.06	39.31	3.00
$68_{19} \leftarrow 67_{20}$	34195.10	-0.08	62.74	4.80
$73_{21} \leftarrow 72_{22}$	29248.03	-0.03	99.99	6.96
$77_{22} \leftarrow 76_{23}$	33204.50	0.09	110.78	9.04

[a] ± 0.10 MHz. [b] The K_{-1}-energy doublets coalesce for high values of K_{-1}. Subscripts on *J* quantum numbers refer to K_{-1}.

Table 2. Spectroscopic constants[a,b] for conformer I of 1-mercapto-2-propanol in the ground and first excited state of the C(1)–C(2) torsional vibration.

Vibrational state:	Ground	First ex. C–C torsion
No. of transitions:	252	176
R.m.s. deviation/MHz:	0.065	0.076
A_v/MHZ	8302.0364(21)	8248.8903(31)
B_v/MHz	2179.37792(63)	2177.12006(94)
C_v/MHz	1852.01215(57)	1850.73549(87)
Δ_J/kHz	0.33659(48)	0.34014(71)
Δ_{JK}/kHz	2.7011(60)	2.7380(79)
Δ_K/kHz	4.1013(48)	3.0992(79)
δ_J/kHz	0.04953(21)	0.04837(34)
δ_K/kHz	1.512(20)	1.491(26)
Φ_J/Hz	0.000204(22)	0.00070(15)
Φ_{JK}/Hz	−0.00452(37)	0.0013(27)
Φ_{KJ}/Hz	−0.01119(97)	−0.0122(32)

[a]Uncertainties represent one standard deviation. [b]A-reduction I'-representation.[16]

one described briefly in Ref. 8, employing klystrons as radiation sources. The radiofrequency–microwave-frequency double resonance technique (RFMWDR) was used as described in Ref. 9, employing the equipment mentioned in Ref. 10.

The gas-phase IR spectrum in the 500–4000 cm⁻¹ region was taken at room temperature using a Bruker model IFS 88 spectrometer equipped with a multiple reflexion cell. The path length was about 8 m, the vapour pressure about 150 Pa and the resolution 1 cm⁻¹.

The *ab initio* computations were performed using the GAMESS[11] program package. The program utilized 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 program was slightly modified to run on PRIME computers. The present computations were made employing PRIME 750 and PRIME 9950 computers. The 3-21G*basis set[12,13] with d-polarization functions on the sulfur[14] atom was used. The calculated equilibrium geometry was optimized at the Hartree–Fock level of theory by calculating the analytical energy gradients.

Results

Microwave spectrum and assignment of the ground vibrational state. Survey spectra revealed a relatively weak and very dense MW spectrum for 1-mercapto-2-propanol. The strongest lines of the spectrum have peak absorption coefficients of roughly 2.5×10^{-7} cm⁻¹ at −10 °C. It turned out later that these transitions are the high-J b-type Q-branch transitions.

A preliminary set of rotational constants was predicted for both conformer I and for II using the structural parameters shown later in Table 5. The dipole moment components (in units of 10^{-30} C m) were predicted using the bond-moment method.[15] The results for I were $\mu_a = 0.7$, μ_b

= 3.4 and μ_c = 4.3, respectively, while μ_a = 0.5, μ_b = 5.3 and μ_c = 1.1, respectively, were predicted for conformation II.

As mentioned in the introduction, conformers similar to I have been found to be the more stable in all cases which have so far been investigated.[3-7] Searches were thus made first for the high-J b-type Q-branch transitions of I. These lines were soon identified. The strongest low-J ^bR-transitions were identified next. The assignments were then gradually extended to include higher and higher b-type P- and R-branch and c-type Q-branch transitions. The maximum value for J was 77 for the R-branch lines and 76 for the Q-branch transitions. Even higher-J transitions were searched for, but no definite assignments could be made, presumably because of too low intensities caused by unfavourable Boltzmann factors. A total of about 270 transitions were assigned for the ground vibrational state; a portion of these transitions are shown in Table 1. 252 of the ground-state transitions were used to determine the spectroscopic constants (A-reduction, I'-representation[16]) shown in Table 2.* Inclusion of three sextic centrifugal distortion constants had to be made in order to get the best fit.

The strongest of the hypothetical ^aR-branch transitions were searched for using both ordinary Stark effect spectroscopy as well as the RFMWDR technique,[9] but no such transitions were assigned, presumably because of insufficient intensities caused by a very small component of the dipole moment along the a-inertial axis. The small μ_a also manifested itself in the fact that the coalescing high-J R-branch transitions invariably displayed slow Stark effects towards lower frequencies. Even a small μ_a would have caused a much more rapid Stark effect owing to the almost complete degeneracies which exist for the energy levels involved in these transitions. It is therefore concluded that μ_a is practically zero. Unfortunately, the dipole moment could not be determined for this molecule, because the low-J transitions were so weak that no quantitative Stark effect measurements could be made, although many attempts were made with this in mind. The *ab initio* computations reported below yielded (in 10^{-30} C m) 0.207, 5.407 and 4.550, respectively, for the components of the dipole moment along the a-, b- and c-inertial axes. These values appear to be quite plausible.

Vibrationally excited states. The ground-state transitions were accompanied by a satellite spectrum presumably belonging to vibrationally excited states of conformer I. Four such states were assigned, as shown in Tables 2 and 3. The strongest of these satellite spectra had approximately 50 % of the intensity of the ground-state spectrum at −10 °C.

Table 3. Spectroscopic constants[a,b] for conformer I of 1-mercapto-2-propanol in vibrationally excited states.

Vib. state:	Second excited C–C tors. vib.	First ex. lowest bending vib.	First ex. methyl or C–S tors. vib.
No. of trans.:	25	37	35
R.m.s. deviation/MHz:	0.089	0.088	0.100
A_v/MHz	8202.339(12)	8323.1948(87)	8304.134(10)
B_v/MHz	2174.9044(28)	2180.4938(36)	2178.7823(31)
C_v/MHz	1849.3662(21)	1852.0108(34)	1851.7175(30)
Δ_J/kHz[c]	0.33659	0.33659	0.33659
Δ_{JK}/kHz	2.767(81)	2.737(32)	2.771(39)
Δ_K/kHz[c]	4.1013	4.1013	4.1013
δ_J/kHz	0.0490(33)	0.0501(11)	0.0451(13)
δ_K/kHz	1.38(20)	1.594(64)	1.775(78)

[a,b]Comments as for Table 2. [c]Fixed at ground-state value. See text.

About 190 transitions were measured for this spectrum; 176 of which were used to determine the spectroscopic constants shown in Table 2. The maximum value of J was 63 in this case.

Relative intensity measurements made largely as described in Ref. 17 yielded 131(20) cm^{-1} for this vibration which is assumed to be the first excited state of the torsion around the C1–C2 bond. This value is rather close to 139(15) cm^{-1} found for the corresponding vibration in 1-amino-2-propanol,[5] 109(10) cm^{-1} in 1-fluoro-2-propanol,[6] 147(7) cm^{-1} in 2-fluoropropanol, 126(10) cm^{-1} in conformer I of 2-amino-1-propanol[3] and 105(10) cm^{-1} in conformer I of 1,2-propanediol.[4]

The second excited state of the C1–C2 torsional vibration was also assigned as shown in Table 3. It is seen from Tables 2 and 3 that the rotational constants change almost linearly upon excitation. This is characteristic for a harmonic vibration. The intensity of the second excited torsional state is roughly 25 % of the intensity of the ground vibrational state spectrum, as expected. In this case, as well as for the two other vibrationally excited states shown in Table 3, the spectroscopic constants were determined from low-J b-type R-branch transitions and ^bQ-branch lines with a maximum value of $J = 28$. Accurate values for the Δ_J and the Δ_K centrifugal distortion constants could not be determined from these transitions. Δ_J and Δ_K were therefore preset to the values found for the ground state (Table 2) in the final fit.

The second strongest vibrationally excited state has approximately 37 % of the intensity of the ground state. This corresponds to a frequency of 183(30) cm^{-1} as determined by relative intensity measurements.[17] This excited state is presumed to be the first excited state of the lowest bending mode. The changes of the rotational constants upon excitation (Tables 2 and 3) are relatively large. It is therefore presumed that heavy atoms are much involved in this normal mode, as is probably the case for the lowest bending mode.

The final excited state is presumed to be a torsional vibration. Little reduced mass can be involved in this mode since the changes of the rotational constants upon excita-

tion are relatively small, as can be inferred from Tables 2 and 3. We suspect that this is the C–CH$_3$, or perhaps the C–S torsional vibration. No splittings were seen for any of the transitions belonging to this excited state, whose intensity is about 25 % of that of the ground vibrational state. A frequency of 255(30) cm^{-1} was determined for this mode by relative intensity measurements.[17] This value is close to 221 cm^{-1} calculated for the C–CH$_3$ torsional vibration from the barrier in 1-amino-2-propanol,[5] and 208 cm^{-1} calculated in the same manner from the methyl barrier of 1-fluoro-2-propanol.[6]

Searches for further conformations. A total of about 550 transitions were assigned for conformer I. This includes all the strongest lines of the spectrum, practically all lines of intermediate intensities and a large number of weak absorptions. The Stark effects of the strongest of the unassigned transitions were investigated and RFMWDR studies[9] were also made in attempts to find further conformations. In particular, conformation II was looked for. The rotational constants for this hypothetical rotamer were predicted to be approximately $A = 6.09$, $B = 2.61$ and $C = 2.38$ GHz (using the structural parameters given later in Table 5) with a large component of the dipole moment along the b inertial axis, as predicted above[11] and from the *ab initio* calculations reported below. The strongest lines of this spectrum are thus predicted to be numerous b-type Q-branch transitions. Searches for these lines were made, however, with negative results.

Rotational constants and dipole moment components have also been predicted in the same manner for many of the remaining 25 *all-staggered* conformations which were considered to be probable forms of 1-mercapto-2-propanol. Invariably, these conformers were predicted to have sizable dipole moments.[15] However, no such forms were identified. From the microwave spectrum it is thus conservatively concluded that conformer I is at least 3 kJ mol^{-1} more stable than any other rotameric form of 1-mercapto-2-propanol.

The gas-phase IR spectrum supports this conclusion regarding the conformational composition. The O–H stretch-
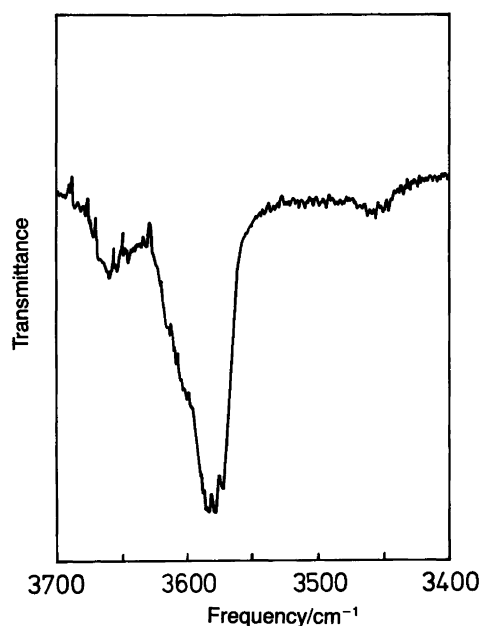
Fig. 2. Gas-phase infrared spectrum in the O–H stretching fundamental region.

Fig. 3. Model of the identified conformer I of 1-mercapto-2-propanol.

ing fundamental band is shown in Fig. 2. The band is broad and complex, with small absorption maxima at 3584, 3578 and 3573 cm⁻¹. There is no obivous doubling of this band or any other bands in the 500–4000 cm⁻¹ spectral region that can be ascribed to the presence of more than one conformer.

Ab initio *results.* Owing to the limited computational resources at our disposal, the *ab initio* computations were restricted to only three out of the 27 possible conformations of 1-mercapto-2-propanol. In addition to conformations I and II (cf. Figs. 1 and 3), the third conformer selected (denoted III in the following), has a conformation that is identical with that of I with one exception. The hypothetical rotamer III (not shown in Figs. 1 or 3) differs from I in having the S–H bond *anti* to the C1–C2 bond. Conformation III was selected because it is believed that this form is perhaps more stable than any of the remaining 24 *all-staggered* rotamers of this molecule. Table 4 summarizes important findings made in these computations. It is seen that conformer I is calculated to be the most stable form; 3.7 kJ mol⁻¹ more stable than II and 6.1 kJ mol⁻¹ more stable than III. These results are consistent with the MW findings of the preceding section. The rotational constants obtained from the *ab initio* optimized structure of I are shown in Table 5. It is seen to be close to the experimentally determined rotational constants.

Structure. Only three rotational constants were determined for conformer I of 1-mercapto-2-propanol, which is also drawn in Fig. 3. Consequently, a full molecular structure
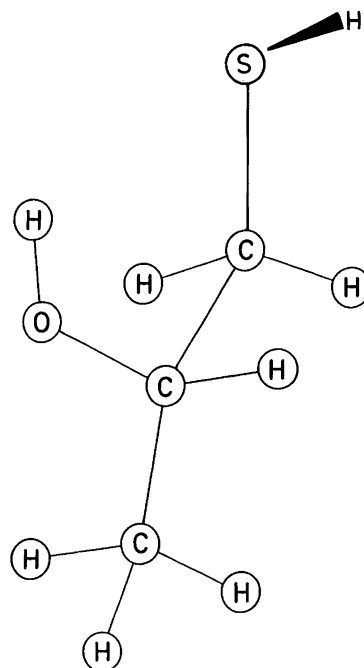
cannot be determined. Instead, we restricted ourselves to fitting the S–C–C–O dihedral angle, because this angle is sensitive to the rotational constants, and because it is chemically interesting. The remaining bond lengths and bond angles were kept constant at the values shown in Table 5. These parameters were selected from recent, accurate experimental studies of related compounds. The experimental parameters were chosen for fitting instead of the parameters obtained in the *ab initio* computations because it is felt that they are probably slightly more accurate.

The S–C–C–O dihedral angle was fitted in steps of 1° until a satisfactory agreement between the observed and calculated rotational constants was found. This occurred with 58(2)°, which is close to 59.4° obtained in the *ab initio* study (Table 4). The error limit of 2° is assumed to encompass not only random errors but also uncertainties originating from the assumed structural parameters. It should be taken to be approximately three standard deviations.

Discussion

The intramolecular hydrogen bond undoubtedly plays an important role in stabilizing conformer I of Figs. 1 and 3. The hydrogen bond is of moderate strength, as can be inferred from its geometry and shift of the O–H stretching frequency. The OH⋯S non-bonded distance of 266 pm (Table 5) is thus about 29 pm shorter than the sum of the van der Waals radii of sulfur and hydrogen.[18] The O–H stretching frequency was found to be shifted 66 cm⁻¹ towards lower frequency in dilute carbon tetrachloride solutions.[2]

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Table 4. Results of ab initio calculations with a 3-21G* basis.

Conformation	I	II	III
Structural parameters[a]			
Distances			
C1–C2	153.6	153.9	153.8
C2–O	143.7	143.7	143.8
C2–C3	152.6	153.1	152.6
C1–S	182.7	182.7	183.4
O–H	96.7	96.8	96.7
S–H	132.8	132.6	132.6
O···S	315.4	318.5	320.8
O–H···S	268.0	275.8	278.1
Angles			
$\angle$C1–C2–O	110.6	110.7	110.7
$\angle$C2–C1–S	113.0	114.3	110.0
$\angle$C1–C2–C3	111.0	113.4	110.8
$\angle$C2–O–H	110.3	109.8	110.8
$\angle$C1–S–H	97.4	98.2	98.3
$\angle$O–H,S–H[b]	94.8	99.8	103.4
Dihedral angles[c]			
$\angle$S–C1–C2–O	59.4	59.6	69.4
$\angle$S–C1–C2–C3	176.3	66.1	173.8
$\angle$H–O–C2–C1	54.9	61.3	58.0
$\angle$H–S–C1–C2	68.2	79.2	153.1
Absolute energies/Hartree	−587.71461	−587.71320	−587.71228
Energy differences[d]/kJ mol^{-1}	0	3.7	6.1
Total dipole moment/10^{-30} C m	7.07	8.03	5.63

[a] Bond lengths in pm; angles in degrees. Atom numbering: $H_3C3–C2H(OH)C1H_2SH$. [b] Angle between O–H and S–H bonds. [c] Measured from syn position. [d] Relative to conformer I.

Table 5. Plausible molecular structure[a] (bond lengths/pm; angles/°) of conformer I of 1-mercapto-2-propanol.

Structural parameters kept fixed[b]

C–S	180.6	$\angle$C–S–H	96.5
C–O	141.5	$\angle$C–O–H	104.0
C–C	153.0	$\angle$C–C–S	113.5
S–H	134.0	$\angle$C–C–O	112.5
O–H	95.0	$\angle$C–C–C	110.0
C–H	109.3	$\angle$C–C–H	109.47
		$\angle$C–C–O–H	60.0 from syn
		$\angle$H–S–C–C	60.0 from syn

Fitted

$\angle$O–C–C–S[c] 58(2) from syn

Rotational constants/MHz

Observed:	A = 8302.04	B = 2179.38	C = 1852.01
Calculated:[d]	A = 8210.95	B = 2184.64	C = 1850.97
Calculated:[e]	A = 8277.74	B = 2154.14	C = 1834.50

Hydrogen-bond parameters

O···S	316	$\angle$O–H···S	113
S···H	266	$\angle$O–H,C–S[f]	6
		$\angle$O–H,S–H[g]	77

Sum of van der Waals radii[h]

O···S	325	S···H	305

[a] See text. [b] Dihedral angles around the carbon atoms are 120°. [c] Dihedral angle. [d] Calculated from the structure shown in this table. [e] Calculated from the optimized ab initio structure partly shown in Table 4. [f] Angle between O–H and C–S bonds. [g] Angle between O–H and S–H bonds. [h] Taken from Ref. 18.

The reason why I is at least 3 kJ mol^{-1} more stable than the hypothetical conformation II of Fig. 1 is difficult to explain. Repulsion between the nearest of the methyl-group hydrogen atoms and the mercapto-group hydrogen atom may perhaps account for this finding. The fact that the H–S–C1–C2 angle opens up by about 11° in the ab initio computations (Table 4) is in accord with this view. Non-bonded repulsion similar to this was used to explain the absence of conformation II in the case of 1-amino-2-propanol,[5] while this effect can hardly explain the absence of II in the cases of 1-fluoro-2-propanol[6] as well as 2-fluoropropanol.[7] The lack of conformation II in these two fluorine-containing molecules is difficult to understand.[6,7]

A noteworthy finding both for 2-mercaptoethanol[1] and for the title compound is the absence of conformations having a SH···O hydrogen bond. Model calculations employing the structure of Table 5 indicate that this kind of hydrogen bond would have a rather long H···O non-bonded distance owing to the long C–S bond. Consequently, a weak hydrogen bond would exist in these hypothetical conformations. The geometrical requirements of the bonded atoms thus seem to preclude low-energy conformations stabilized by SH···O hydrogen bonds.

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