A Microwave and *Ab Initio* Study of the Conformational Properties and Intramolecular Hydrogen Bonding of Cyclopropanemethanethiol

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Marstokk, K.-M. and Møllendal, H., 1991. A Microwave and *Ab Initio* Study of the Conformational Properties and Intramolecular Hydrogen Bonding of Cyclopropanemethanethiol. – Acta Chem. Scand. 45: 354–360.

The microwave spectra of three isotopomers of cyclopropanemethanethiol ($C_3H_5CH_2SH$, $C_3H_5CH_2SD$ and $C_3H_5CH_2{}^{34}SH$) have been investigated. One heavy-atom *gauche* conformation was assigned. This conformation is stabilized with a weak hydrogen bond formed between the thiol group hydrogen atom and the 'quasi-π' electrons of the cyclopropyl ring. The dipole moment is (in units of 10^{-30} C m): μ_a = 5.199(88), μ_b = 0.82(28), μ_c = 0.39(40) and μ_{tot} = 5.28(18). *Ab initio* calculations at the 3-21G* level were made for six selected conformations, with results in good agreement with the experimental findings.

The question of whether the thiol group may participate in intramolecular hydrogen (H) bonding as a proton donor has been investigated in several recent studies of gaseous molecules. In allyl mercaptan, $H_2C{=}CH{-}CH_2SH$, the preferred conformation appears to be stabilized by a very weak internal H bond, as shown by a microwave (MW) study.[1] The thiol group is the H donor and the double-bond π-electrons are the acceptor.

Two conformations were identified in the MW spectrum of $H_2NCH_2CH_2SH$.[2] One of these, the less stable one, possesses a H bond in which the thiol group is the donor and the amino group lone-pair is the H acceptor. In an electron-diffraction study[3] it was shown that one or more heavy-atom *anti* conformers, for which internal hydrogen bonding is impossible, are also present with energies slightly higher than those of the two heavy-atom *gauche* conformations identified in the MW studies.[2]

3-Mercaptopropionitrile, $HSCH_2CH_2C{\equiv}N$,[4] takes a heavy-atom *gauche* conformation as its preferred form. A weak intramolecular H bond between the thiol group H atom and the π-electrons of the cyano group stabilizes this rotamer. In addition, one heavy-atom *anti* conformation not possessing an internal H bond was found to be present with an energy 1.3(20) kJ mol^{-1} higher.[4]

Three rotamers, two high-energy forms without a H bond and one that is more stable and possesses this kind of bonding, was found in the MW study of 3-butene-1-thiol, $HSCH_2CH_2CH{=}CH_2$.[5] The H bond is formed between the thiol-group hydrogen atom and the π-electrons belonging to the double bond.

There are very similar internal H bonds in the preferred conformers of $HOCH_2CH_2SH$[6] and $CH_3CH(OH)CH_2SH$.[7] However, in these two compounds the hydroxyl group is the H donor and the thiol group is the acceptor in the one conformation identified for these two molecules.[6,7] This H bond is not among the weakest, as judged by its geometry and the frequency of its O–H stretching vibration.[7] One reason why a conformation having the thiol group as H donor and the hydroxyl group as H acceptor was not seen in 2-mercaptoethanol and 1-mercapto-2-propanol[7] is perhaps the rather unfavourable geometry that would exist for the intramolecular H bond in such a case,[7] as well as the fact that the thiol group is a better acceptor than donor for H bonds in general.

The cyclopropyl group possesses 'quasi-π' electrons according to the Walsh model[8] for cyclopropane. These electrons may act as proton acceptors for H bonds. It has recently been shown in MW studies that intramolecular hydrogen bonds are present both in (hydroxymethyl)cyclopropane,[9a,b] 1-cyclopropylethanol[9c] and (aminomethyl)-cyclopropane.[10] In the last-mentioned case, two H-bonded conformers were identified.[10]

It was thus felt worthwhile to investigate whether the thiol group might be capable of forming an internal H bond with the cyclopropyl 'quasi-π' electrons. Cyclopropanemethanethiol is the natural choice for such a study.

Five possible conformations for the title compound are sketched in Fig. 1. The atom numbering is given in Fig. 2. In the three *gauche* conformations given in Fig. 1, the S–C1–C2–H2 chain of atoms takes a *gauche* orientation (60° from *syn*), whereas this orientation is *anti* in the two forms denoted *Anti I* and *Anti II*. In *Gauche I* and

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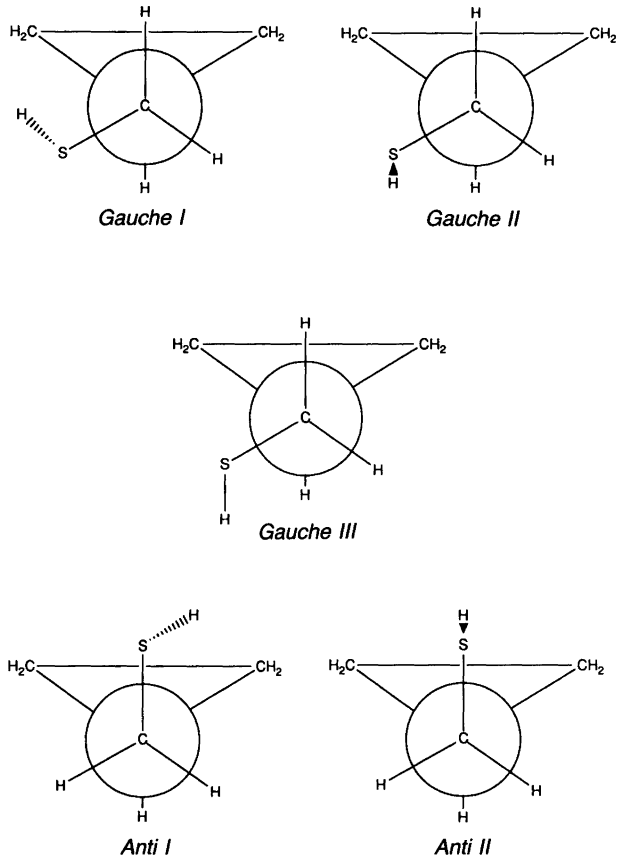

Fig. 1. Newman projections of five conformations of cyclopropanemethanethiol viewed along the C1–C2 bond.

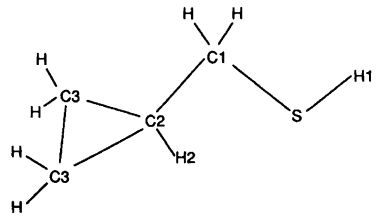

Fig. 2. Atom numbering. The C–C bond distances of the cyclopropyl ring were assumed to be identical.

Gauche III the H1–S–C1–C2 dihedral angle is *gauche*, 60 or −60°, respectively, whereas this angle is *anti* (180°) in *Gauche II*. The H1–S–C1–C2 dihedral angle is 60° in *Anti I* and 180° in *Anti II*.

Very weak H bonds might thus exist for both *Gauche I* and *Anti I*, while this kind of interaction is not possible in the three other conformers shown in Fig. 1. It was found in this work that *Gauche I* is clearly the more stable form of the molecule, and it is suggested that internal H bonding is one of the reasons why the free molecule prefers this conformation.

Experimental

The sample used in this work was purchased from Lancaster Synthesis Ltd., Bischheim, France. It was purified by gas chromatography before use. The spectrum was studied extensively in the 18.0–29.0 GHz spectral region. Many measurements were also made in the 29.0–38.0 GHz spectral range. The temperature was approximately −40 °C during the spectral measurements, and the pressure was about 1 Pa. The spectrometer is an improved version of the one described briefly in Ref. 11 employing klystrons as radiation sources. The radiofrequency – microwave fre-

Table 1. MW spectrum of the ground vibrational state of the *Gauche I* conformer of cyclopropanemethanethiol.

Transition	Observed frequency[a]/MHz	Obs. − calc. frequency/MHz	Centrifugal distortion/MHz
$5_{0,5}\leftarrow4_{0,4}$	19 409.26	0.06	−0.25
$5_{1,4}\leftarrow4_{1,3}$	19 843.40	0.16	−0.21
$5_{1,5}\leftarrow4_{1,4}$	19 038.69	−0.01	−0.21
$5_{2,3}\leftarrow4_{2,2}$	19 485.92	−0.19	−0.12
$5_{2,4}\leftarrow4_{2,3}$	19 445.40	−0.06	−0.12
$5_{4,1}\leftarrow4_{4,0}$	19 454.82	−0.08	0.26
$5_{4,2}\leftarrow4_{4,1}$	19 454.82	−0.08	0.26
$6_{0,6}\leftarrow5_{0,5}$	23 268.83	0.10	−0.42
$6_{1,5}\leftarrow5_{1,4}$	22 806.04	0.14	−0.39
$6_{1,6}\leftarrow5_{1,5}$	22 841.08	0.12	−0.39
$6_{2,4}\leftarrow5_{2,3}$	23 401.68	0.04	−0.27
$6_{2,5}\leftarrow5_{2,4}$	23 330.73	0.05	−0.27
$6_{3,3}\leftarrow5_{3,2}$	23 351.52	−0.19	−0.08
$6_{4,2}\leftarrow5_{4,1}$	23 347.20	−0.04	0.19
$6_{4,3}\leftarrow5_{4,2}$	23 347.20	−0.04	0.19
$6_{5,1}\leftarrow5_{5,0}$	23 345.71	−0.04	0.53
$6_{5,2}\leftarrow5_{5,1}$	23 345.71	−0.04	0.53
$7_{0,7}\leftarrow6_{0,6}$	27 116.45	0.04	−0.67
$7_{1,6}\leftarrow6_{1,5}$	27 765.21	0.06	−0.63
$7_{1,7}\leftarrow6_{1,6}$	26 640.44	0.09	−0.63
$7_{2,5}\leftarrow6_{2,4}$	27 327.02	0.17	−0.50
$7_{2,6}\leftarrow6_{2,5}$	27 213.75	−0.05	−0.50
$7_{3,4}\leftarrow6_{3,3}$	27 247.86	0.02	−0.27
$7_{4,3}\leftarrow6_{4,2}$	27 240.28	−0.06	0.04
$7_{4,4}\leftarrow6_{4,3}$	27 240.28	−0.05	0.04
$7_{5,2}\leftarrow6_{5,1}$	27 237.74	−0.08	0.44
$7_{5,3}\leftarrow6_{5,2}$	27 237.74	−0.08	0.44
$7_{6,1}\leftarrow6_{6,0}$	27 236.84	0.06	0.94
$7_{6,2}\leftarrow6_{6,1}$	27 236.84	0.06	0.94
$8_{0,8}\leftarrow7_{0,7}$	30 950.68	0.02	−1.00
$8_{1,7}\leftarrow7_{1,6}$	31 720.16	−0.14	−0.95
$8_{1,8}\leftarrow7_{1,7}$	30 436.50	−0.05	−0.95
$8_{2,6}\leftarrow7_{2,5}$	31 263.03	0.10	−0.81
$8_{2,7}\leftarrow7_{2,6}$	31 094.45	−0.02	−0.80
$8_{3,5}\leftarrow7_{3,4}$	31 146.11	−0.02	−0.55
$8_{3,6}\leftarrow7_{3,5}$	31 142.00	−0.07	−0.55
$8_{4,4}\leftarrow7_{4,3}$	31 134.23	−0.07	−0.19
$8_{4,5}\leftarrow7_{4,4}$	31 134.23	−0.04	−0.19
$8_{5,3}\leftarrow7_{5,2}$	31 130.36	−0.04	0.27
$8_{5,4}\leftarrow7_{5,3}$	31 130.36	−0.04	0.27
$8_{6,2}\leftarrow7_{6,1}$	31 128.73	0.05	0.83
$8_{6,3}\leftarrow7_{6,2}$	31 128.73	0.05	0.83
$8_{7,1}\leftarrow7_{7,0}$	31 128.06	0.06	1.49
$8_{7,2}\leftarrow7_{7,1}$	31 128.06	0.06	1.49

[a] ±0.10 MHz.

Table 2. Ground-state spectroscopic constants[a,b] of the *Gauche I* conformer of cyclopropanemethanethiol.

Species:	$C_3H_5CH_2SH$	$C_3H_5CH_2SD$	$C_3H_5CH^{34}SH$
No. of transitons:	44	39	29
R.m.s. deviation/MHz:	0.087	0.054	0.074
A_0/MHz	11 481.2(31)	11 002.3(12)	11 452.9(41)
B_0/MHz	2 025.4979(61)	2 008.4118(34)	1 971.0656(69)
C_0/MHz	1 864.5225(61)	1 839.2003(44)	1 818.0716(65)
Δ_J/kHz	0.491(38)	0.504(21)	0.509(44)
Δ_{JK}[c]/kHz	−3.188(71)	−3.200(38)	−3.239(91)

[a] *A*-reduction, *I*^{r}-representation.[22] [b] Uncertainties represent one standard deviation. [c] Further centrifugal distortion constants preset at zero.

quency double-resonance technique (RFMWDR) was used, as described in Ref. 12, employing the equipment mentioned in Ref. 13. The ^{34}S species, $C_3H_5CH_2{}^{34}SH$, was studied in natural abundance (4.4 %). The partially deuterated species, $C_3H_5CH_2SD$, was produced by conditioning the cell with D_2O and then introducing the normal sample.

Results

Ab initio *calculations*. The *ab initio* calculations were performed using the Gaussian 88 program package.[14] The 3-21G* basis set[15,16] with *d*-polarization functions on sulfur[17] was utilized. The computations were initially made for the five conformations sketched in Fig. 1 with full geometry optimization. The reason for selecting *gauche* and *anti* conformations for computation is that similar molecules, such as $C_3H_5CH_2Br$[18] and $C_3H_5CH_2Cl$[19] (where there is of course no H bonding), prefer these conformations.

Stable conformations were predicted for all three *gauche* conformations and for *Anti I*, whereas *Anti II*, which has a symmetry plane, was found to represent a saddle point. When the requirement of possessing a symmetry plane was lifted for *Anti II*, a stable conformation (referred to as 'near-*Anti II*') was predicted to have a S–C1–C2–H2 dihedral angle of 172.6° and a H1–S–C1–C2 dihedral angle of 164.4°.

Moreover, *Gauche I* was predicted to be the more stable form, with a total energy of −1446 277.2 kJ mol^{-1}. Its S–C1–C2–H2 dihedral angle was calculated to be 57.9°, and the H1–S–C1–C2 dihedral angle was found to be 58.8°. The remaining geometry seemed to be rather normal and close to the values used below (Table 6) in the structure determination. *Gauche II* and *Gauche III* were calculated to be 2.9 and 2.8 kJ mol^{-1}, respectively, less stable than *Gauche I*. It is noted that the S–C1-C2–H2 dihedral angle was computed to be 62.8° for *Gauche II* and 63.7° in *Gauche III*. These values are 4.0 and 4.9° larger than in *Gauche I* (58.8°). A decrease of the S–C1–C2–H2 dihedral angle would increase the H bond interaction presumed to be present in *Gauche I*.

Not unexpectedly, the *Anti* conformations were predicted to be considerably less stable than the *Gauche* rotamers, as has been seen in other cases.[9,10,18–21] *Anti I* was predicted to be 8.3 kJ mol^{-1} less stable than *Gauche I*, while the stable near-*Anti II* (see above) was predicted to be 13.7 kJ mol^{-1} less stable than *Gauche I*. The saddle point encountered for *Anti II* was predicted to be only 0.1 kJ mol^{-1} above the energy of the near-*Anti II* conformation.

Microwave spectrum and assignment of the Gauche I *conformer*. Model calculations indicated that the three *gauche* conformations should be rather prolate tops with a Ray's asymmetry parameter[22] κ of ca. −0.97. Characteristic *a*-type high-K_{-1} *R*-branch pile-ups should thus appear at frequencies given approximately by $(B + C) \times (J+1)$ provided that the molecule possesses a dipole moment along the *a*-inertial axis.

Such strong lumps of lines were immediately recognized, and the assignments of the *a*-type *R*-branch transitions were easily made. The assignments were confirmed by the RFMWDR method.[12] Only ^aR-transitions were identified, owing to the fact that components of the dipole moment along the *b*- and *c*-principal inertial axes are very small (see below). The ground vibrational spectrum is shown in Table 1,* and the spectroscopic constants (*A*-reduction *I*^{r}-representation)[23] are given in Table 2.

The rotational constants predicted for *Gauche II* and *Gauche III* are rather similar to those predicted for *Gauche I*. However, the shifts of the rotational constants upon deuteration of the thiol group H atom would be very different in these three cases. The assignment of the spectrum of the $C_3H_5CH_2SD$ species was straightforward. The shifts of the rotational constants thus obtained were very close to those predicted for *Gauche I* and confirmed beyond doubt that the spectrum indeed belonged to *Gauche I* and that no confusion with the other two *gauche* conformations has been made.

The assignment of the spectrum of the $C_3H_5CH_2{}^{34}SH$

* The complete spectra are available from the authors upon request, or from the National Institute of Standards and Technology, Molecular Spectroscopy Division, Rm. 268/Bldg. 221, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 3. Spectroscopic constants[a,b] of successively excited states of the C1–C2 torsional vibration of the *Gauche I* conformer of cyclopropanemethanethiol.

Vibrational state:	1st excited	2nd excited	3rd excited	4th excited
No. of transitions:	40	40	38	29
R.m.s. deviation/MHz:	0.074	0.070	0.064	0.125
A_v/MHz	11 456.3(31)	11 431.4(26)	11 424.4(29)	11 272.3(68)
B_v/MHz	2 021.3197(52)	2 017.1333(50)	2 012.9921(46)	2 008.905(11)
C_v/MHz	1 862.3537(52)	1 860.1721(50)	1 858.0113(47)	1 855.853(10)
Δ_J/kHz	0.650(34)	0.434(32)	0.471(31)	0.430(74)
Δ_{JK}[c]/kHz	−2.990(81)	−2.811(71)	−2.828(70)	−2.15(16)

[a,b]Comments as for Table 2.

species was then made. These transitions lie far away from the ground- and vibrationally excited-state transitions. Moreover, the intensities of these lines were about 4 % of the intensities of their ground-state counterparts. There is thus no risk that the ^{34}S species has been confused with a vibrationally excited state. The ground-state rotational constants of the three isotopomers are given in Table 2.

Vibrationally excited states. According to the *ab initio* calculations reported above the four lowest fundamental vibrations of *Gauche I* are predicted at 112, 217, 256 and 373 cm^{-1}, and should have Boltzmann factors of 0.50, 0.26, 0.19 and 0.10, respectively, at −40 °C. Relatively strong spectra were thus expected for the first excited states of the three lowest fundamentals.

As seen in Tables 3 and 4, five excited states of two of the low-frequency fundamentals were assigned. Relative intensity measurements[24] yielded 135(20) cm^{-1} for the lowest vibration, in reasonably good agreement with the theoretical value of 112 cm^{-1}. This fundamental is presumed to be the C1–C2 torsional vibration. As seen in Table 3, four vibrationally excited states were ultimately assigned for this vibration, which is presumed to be rather harmonic, since the rotational constants vary fairly linearly upon excitation.[25]

The vibrationally excited state whose rotational constants are displayed in Table 4 was found to have a frequency of 195(25) cm^{-1}, as determined by the method of Esbitt and Wilson.[24] This compares well with the *ab initio* values of 217 cm^{-1}. This vibration is presumed to be the S–H torsional vibration, but it could also be the lowest bending vibration. The reason why the first excited states of the next two low-frequency vibrations (calculated as 256 and 373 cm^{-1}, respectively) were not found can presumably be ascribed to the crowded nature of the pile-ups, making overlaps a likely possibility.

Table 4. Spectroscopic constants[a–c] of the first excited state of the S–H torsional vibration[d] of the *Gauche I* conformer of cyclopropanemethanethiol.

No. of transitons:	27
R.m.s. deviation/MHz:	0.096
A_v/MHz	11 479.5(35)
B_v/MHz	2 026.0476(77)
C_v/MHz	1 864.6876(77)
Δ_J/kHz	0.479(53)
Δ_{JK}[c]/kHz	−2.70(17)

[a–c]Comments as for Table 2. [d]Could alternatively be the first excited state of the lowest bending vibration.

Dipole moment. The dipole moment was determined by Stark effect measurements in the usual manner.[26] The results are given in Table 5. The principal-axes dipole moments calculated by the *ab initio* method for *Gauche I* were (in units of 10^{-30} C m) $\mu_a = 6.26$, $\mu_b = 0.24$ and $\mu_c = 1.54$. The values calculated using the bond-moment method[27] were $\mu_a = 4.12$, $\mu_b = 0.03$ and $\mu_c = 1.49$, respectively. There is thus reasonably good agreement between these theoretical dipole moment components and the experimental ones shown in Table 5.

The dipole moment components were also calculated for the hypothetical rotamers *Gauche II* and *Gauche III* both by *ab initio* as well as by the bond-moment method. The *ab initio* values for the three dipole moment components were

Table 5. Stark coefficients[a] and dipole moment[a] of the *Gauche I* conformer of cyclopropanemethanethiol.

Transition	$\|M\|$	$\Delta\nu E^{-2}/10^{-6}$ cm² MHz V^{-2}	
		Obs.	Calc.
$4_{0,4}\leftarrow3_{0,3}$	0	−1.91(3)	−1.88
	2	0.785(10)	0.774
$4_{1,3}\leftarrow3_{1,2}$	0	−0.940(20)	−0.870
$5_{1,5}\leftarrow4_{1,4}$	1	0.299(5)	0.296
$5_{1,4}\leftarrow4_{1,3}$	0	−0.526(7)	−0.546
	1	−1.06(2)	−1.08
$6_{1,6}\leftarrow5_{1,5}$	2	0.612(9)	0.621

Dipole moment/10^{-30} C m[b]

$\mu_a = 5.199(88)$ $\mu_b = 0.82(28)$ $\mu_c = 0.39(40)$ $\mu_{tot} = 5.28(18)$

[a]Uncertainties represent one standard deviation. [b]1 debye = 3.33564×10^{-30} C m.

Table 6. Plausible molecular structure[a] of the *Gauche I* conformer of cyclopropanemethanethiol.

Structural parameters kept fixed[b]			
Bond distances / pm		Angles / °	
C_{ring}–C_{ring}	151.2	C_{ring}–C_{ring}–C_{ring}	60.0
C1–C2	152.0	H–C3–H	116.0
C1–C2	133.9	H2–C2–C1	116.0
C1–S	181.4	C2–C1–H	109.47
S–H1	134.0	C1–S–H	96.5
C1–H	109.3		
C_{ring}–H	108.3		
Fitted dihedral angles / °			
S–C1–C2–H2	60(1)[c]		
H1–S–C1–C2	57(1)		

[a]See text. Atom numbering given in Fig. 2. [b]The H–C_{ring}–H planes and the H2–C2–C1 plane are perpendicular to the ring. [c]The H2–C2–C1–H dihedral angles will be 60 and 180°, respectively.

(same units as above) 4.94, 2.73 and 2.70, respectively, for *Gauche II*. For *Gauche III* values of 3.20, 4.77 and 1.50, respectively, were obtained. The values of the principal-axes dipole moment components calculated by the bond-moment method[27] were similar. It is seen that a better agreement between the calculated dipole moment components and the experimentally determined ones (Table 5) is found for *Gauche I*. This is one piece of independent evidence that the assigned spectra can correctly be ascribed to the H-bonded *Gauche I* conformer.

Searches for further conformations. After the assignment of the spectrum of *Gauche I* was complete there remained many lines that had not been assigned. These lines were much weaker that the ^aR-spectrum of *Gauche I*. It is possible that these absorptions belong to impurities, but we were not able to identify any such impurities. The possibility that they belong to high-energy forms of cyclopropanemethanethiol was therefore considered next.

According to the *ab initio* computations reported above, the hypothetical *Gauche II* and *Gauche III* conformations should both be less stable than *Gauche I* by approximately 3 kJ mol^{-1}. Both *Gauche II* and *Gauche III* were calculated to possess sizable dipole moments both by the *ab initio* and the bond-moment method.[27] Many attempts were made to assign them to *Gauche II* or *Gauche III* using both the ordinary Stark method as well as the RFMWDR technique.[12] However, these attempts were unsuccessful.

Table 7. Rotational constants, substitution coordinates and hydrogen-bond parameters for the *Gauche I* conformer of cyclopropanemethanethiol.

Rotational constants[a] / MHz	$C_3H_5CH_2SH$		$C_3H_5CH_2SD$		$C_3H_5CH_2{}^{34}SH$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A	11481.2	11468.5	11002.3	10992.7	11452.9	11458.1
B	2025.5	2031.2	2008.4	2013.4	1971.1	1976.5
C	1864.5	1872.9	1839.2	1846.6	1818.1	1826.1

Substitution coordinate[b] / pm	Thiol group H atom			Sulfur atom		
	|a|	|b|	|c|	|a|	|b|	|c|
Calculated from rotational constants	140.04(23)	133.26(22)	41.02(86)	187.35(14)	19.5(13)	14.0(19)
From structure[c]	143.4	134.0	37.7	187.7	14.3	3.1

Hydrogen bond parameters[c]			
Distances / pm		Angles / °	
H1 ··· C2	288	S–H1 ··· C2	73
H1 ··· C3	309	S–H1 ··· C3	101
S ··· C3	359	H1 ··· C2–C3	83
		H1 ··· C3–C2	68
		S–H1 ··· C2–C3[d]	15
Sum of van der Waals radii[e] / pm			
H ··· C[f]	290	S ··· C[f]	375

[a]The rotational constants were calculated using the structure in Table 6. [b]Calculated using Kraitchman's equations.[28] [c]Structure of Table 6. [d]Angle between S–H1 bond and the nearest C2–C3 bond. [e]Taken from Ref. 29. [f]van der Waals radius of carbon taken to be 190 pm, as for aromatic carbon atoms.[29]

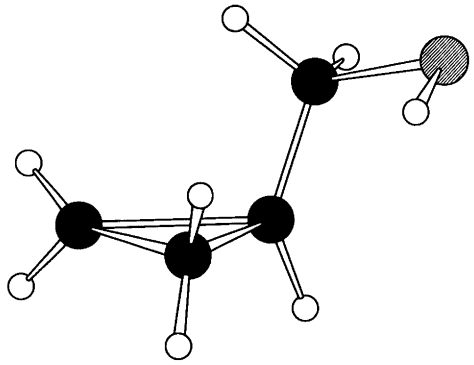

Fig. 3. Model of the identified *Gauche I* conformer. This rotamer, which is stabilized by a very weak H bond formed between the thiol group H atom and the 'quasi-π' electrons of the cyclopropyl ring, is at least 3 kJ mol^{-1} more stable than any other hypothetical conformation.

Attempts to assign these unidentified lines to the *anti* conformations that were predicted to have rather high energies (see *ab initio* section above) were also futile. Considerations based on intensities and dipole-moment predictions lead us to conclude that *Gauche I* is at least 3 kJ mol^{-1} more stable than any other hypothetical form of the molecule.

Structure. The nine rotational constants determined for *Gauche I* furnish insufficient information for a full structure determination: certain assumptions have to be made. The S–C1–C2–H2 and H1–S–C1–C2 dihedral angles were fitted in steps of 1°, while the remaining structural parameters shown in Table 6 were kept fixed. These fixed parameters were taken from recent, accurate structural studies,[20] and are presumed to be slightly more accurate than the values obtained above in the *ab initio* computation. It is seen in Table 6 that the S–C1–C2–H2 dihedral angle is found to be 60(1)° from *syn,* and the H1–S–C1–C2 dihedral angle to be 57(1)° (the uncertainties represent one standard deviation), a value close to the *ab initio* values reported above. The rotational constants are well reproduced, as can be seen in Table 7. The substitution coordinates calculated using Kraitchman's equations[28] are also close to the values found for the plausible structure displayed in Table 7. A model of *Gauche I* is shown in Fig. 3.

Discussion

The conformational choices of $C_3H_5CH_2OH$,[9a,b] $C_3H_5CH(OH)CH_3$,[9c] $C_3H_5CH_2NH_2$[10] and $C_3H_5CH_2SH$ are very similar. The more stable conformers of these compounds all prefer heavy-atom *gauche* conformations apparently stabilized with internal hydrogen bonds. These H bonds are rather weak. In the case of the title molecule it is seen that the non-bonded distance between H1 and C2 in *Gauche I* is rather close to the sum of the van der Waals radii of hydrogen and aromatic carbon,[29] as shown in Table 7. A very weak H bond interaction between the thiol group H atom and the 'quasi-π' electron of the nearest C2–C3 edge can thus be one factor that stabilizes *Gauche I* as compared to the hypothetical conformations *Gauche II* and *Gauche III* (Fig. 1), for which this kind of interaction is not possible. In addition to the H bond, repulsive forces between the cyclopropyl ring electrons and the thiol group electrons could stabilize *Gauche I.*

A H bond very similar to that found for *Gauche I* should exist in *Anti I.* Yet, *Anti I* is much less stable than *Gauche I,* as indicated in the *ab initio* calculations made above. The reason for this stability difference, which appears to be general,[9,10,18–21] is perhaps that repulsive forces are more prominent in the *anti* than in the *gauche* forms in methyl derivatives of cyclopropane.

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Received August 30, 1990.