Acta Chemica Scandinavica A 37 (1983) 477–486

Microwave Spectrum, Conformational Equilibrium, Intramolecular Hydrogen Bonding and Centrifugal Distortion of 3-Mercaptopropionitrile

K.-M. MARSTOKK and HARALD MØLLENDAL

Department of Chemistry, The University of Oslo, P.O.Box 1033, Blindern, Oslo 3, Norway

The microwave spectra of 3-mercaptopropionitrile, CH_2SHCH_2CN, and one deuterated species, CH_2SDCH_2CN, have been investigated in the 12.0–18.0 GHz and 20.3–28.5 GHz spectral regions at −5 °C. Two conformations were assigned. The heavy atom *gauche* conformation has a very weak hydrogen bond formed between the mercapto group hydrogen atom and the cyano group. The other identified conformation, which has no hydrogen bond, has the heavy atoms in *anti* position and the mercapto group is *gauche* to the plane formed by the heavy atoms. The hydrogen-bonded conformation is the more stable of the two by 1.3(20) kJ/mol. The two conformations together make up at least 90 % of the gas at −5 °C.

The SCCC dihedral angle is 65(3)° from *syn*, and the C≡N and S–H bonds are about 7° from being parallel in the *gauche* form. The CCS angle is 114.0(15)° in this rotamer, while the CCS angle takes the value of 111.5(10)° in the *anti* conformation.

Five vibrationally excited states belonging to two different normal modes were assigned for the hydrogen-bonded *gauche* rotamer. The C–C torsional frequency was determined to be 118(20) cm^{-1} by relative intensity measurements in fair agreement with 97(10) cm^{-1} found using the quartic centrifugal distortion constants in a force field calculation. The C–S torsional frequency was found to be 178(30) cm^{-1} by relative intensity measurements.

Three vibrationally excited states of the C–C torsional mode was found for the *anti* conformation, and this frequency was determined to be 121(20) cm^{-1} by relative intensity measurements.

An extensive centrifugal analysis was carried out for the ground vibrational state of the *gauche* form and accurate values were determined for the quartic and four sextic centrifugal distortion constants.

Intramolecular hydrogen bonding of free molecules has in recent years been studied for many alcohols and amines. However, only few reports exist for thiols. In allyl mercaptan,[1] $CH_2=CHCH_2SH$, the preferred conformation has what could perhaps be called a very weak intramolecular hydrogen bond. In CH_2OHCH_2SH [2] the one identified conformation has an internal hydrogen bond with the hydroxyl group acting as proton donor and the mercapto group as proton acceptor. Two rotamers were identified for $CH_2NH_2CH_2SH$;[3] one of these, which is also the less stable, has a hydrogen bond with the −SH group being proton donor. Only one heavy-atom *anti* form without a hydrogen bond was assigned in the case of CH_2SHCH_2Cl.[3] This molecule possesses a weak, but crowded microwave spectrum and the stable coexistence of a hydrogen-bonded heavy-atom *gauche* conformation as well as a second *anti* form was by no means ruled out in this study.

3-Mercaptopropionitrile, CH_2SHCH_2CN, was chosen for study because hydrogen bonding might exist between the mercapto and the cyano groups. In addition, the existence of *anti* conformations without hydrogen bonds was considered to be quite probable, because the mercapto group is a weak proton donor. The three most probable conformations are shown in Fig. 1. The hydrogen-bonded heavy-atom *gauche* conforma-

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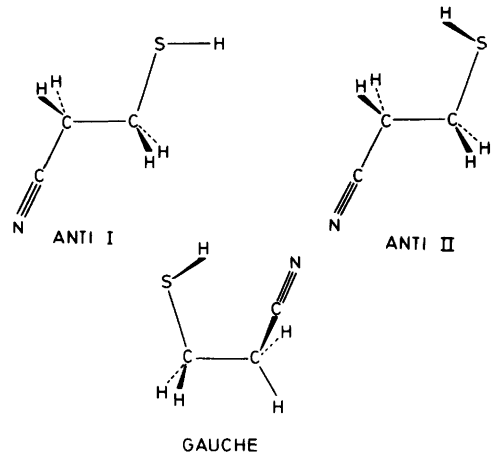

Fig. 1. Selected conformations of CH_2SHCH_2CN. The hydrogen-bonded heavy-atom *gauche* conformation was found to be more stable than *anti II* by 1.3(20) kJ/mol. *Anti I* was not identified and shown to be less stable than *anti II* by at least 1 kJ/mol.

tion as well as *anti II* were assigned. The former is more stable than the latter by 1.3(20) kJ/mol. *Anti I* was not identified and it is estimated to be at least 2.3 kJ/mol less stable than the *gauche* rotamer if it exists at all as a stable conformation of the molecule.

EXPERIMENTAL

CH_2SHCH_2CN was purchased from Parish Chemical Company, Orem, Utha, U.S.A. The sample was checked by gas chromatography and found to be pure. The deuterated species, CH_2SDCH_2CN, was produced by direct exchange by heavy water in the wave guide. In this manner, about 30 % deuteration was achieved. Measurements were made on a conventional microwave spectrometer in the 12.0–18.0 and 20.3–28.5 GHz spectral regions. A few spectral measurements were also made above 28.5 GHz. A pressure of roughly 20 Pa was used. The spectra were measured at about −5 °C. Lower temperatures could not be utilized due to insufficient vapour pressure of the compound.

RESULTS

Assignment of the ground vibrational state of anti II. The rotational constants of both *anti I* and *anti II* were predicted using structural parameters taken from related molecules (see later section). Both these conformations were predicted to be very nearly symmetrical tops with the asymmetry parameter $\kappa \approx -0.99$. The dipole moment components along the principal axes were predicted to be μ_a=2.8 D, μ_b=0.2 D and μ_c=0.0 D (for symmetry reasons) for *anti I*, and μ_a=2.4 D, μ_b=1.1 D and μ_c=0.6 D for *anti II*, respectively, using the bond-moment method.[4] Both these

Table 1. Microwave spectrum of the ground vibrational state of *anti II* of CH_2SHCH_2CN.

Transition	Observed frequency [a] (MHz)	Obs.−calc. frequency (MHz)	Centrifugal distortion (MHz)
$5_{0,5} \rightarrow 6_{0,6}$	17643.34	−0.02	−0.10
$5_{1,4} \rightarrow 6_{1,5}$	17790.42	0.03	−0.10
$5_{1,5} \rightarrow 6_{1,6}$	17500.54	0.06	−0.10
$6_{1,5} \rightarrow 7_{1,6}$	20755.13	0.01	−0.15
$6_{1,6} \rightarrow 7_{1,7}$	20416.93	0.04	−0.15
$7_{0,7} \rightarrow 8_{0,8}$	23521.36	−0.14	−0.23
$7_{1,6} \rightarrow 8_{1,7}$	23719.74	0.04	−0.23
$7_{1,7} \rightarrow 8_{1,8}$	23333.26	0.10	−0.23
$8_{0,8} \rightarrow 9_{0,9}$	26459.60	−0.06	−0.32
$8_{1,7} \rightarrow 9_{1,9}$	26249.21	−0.04	−0.32
$8_{2,6} \rightarrow 9_{2,7}$	26476.66	−0.09	−0.32
$9_{0,9} \rightarrow 10_{0,10}$	29397.12	0.02	−0.44
$9_{1,8} \rightarrow 10_{1,9}$	29648.40	0.11	−0.44
$9_{1,9} \rightarrow 10_{1,10}$	29165.17	0.02	−0.44

[a] ±0.10 MHz.

Table 2. Spectroscopic constants for *anti II* of CH_2SHCH_2CN.[a]

Vibrational state	Ground	First ex. C−C tors.	Second ex. C−C tors.
Number of transitions	15	13	6
rms (MHz) [b]	0.078	0.106	0.132
A_v (MHz)	24200.6(1107)	22514.5(2092)	22176.0(3643)
B_v (MHz)	1494.6723(54)	1495.9761(83)	1497.289(16)
C_v (MHz)	1446.3525(54)	1449.5251(77)	1452.709(15)
Δ_J (kHz) [c]	0.111(30)	0.034(45)	−0.156(85)
$I_a+I_b-I_c$ [u(nm)^2]	0.09587(96)	0.1162(21)	0.1243(37)

[a] Uncertainties represent one standard deviation. [b] rms is the root-mean square deviation. [c] Further quartic centrifugal distortion constants were kept at zero in the least squares fit.

conformations were thus predicted to have relatively strong, simple *R*-branch *a*-type spectra characterized by strong pile-ups of all the $K_{-1}\neq1$ transitions. These pile-ups should also have very rapid Stark effects. The $K_{-1}=1$ transitions, however, are placed almost symmetrical on the high and low frequency sides of the $K_{-1}\neq1$ pile-ups.

The observed microwave spectrum of CH_2SHCH_2CN was found to be very dense and of moderate intensity. The strongest lines observed had peak absorption coefficients of roughly 4×10^{-7} cm^{-1}. Despite its density, one series of *R*-branch *a*-type $K_{-1}\neq1$ pile-ups was readily assigned due to their strengths, spectral positions, and rapid Stark effects. The $K_{-1}=1$ transitions were then found after some searching and identified by their spectral positions and Stark effects. The spectrum is shown in Table 1.* Only the well-resolved low-K_{-1} lines have been included in this table. The derived spectroscopic constants are shown in Table 2.

A search was made for *b*- and *c*-type lines, but none was identified. This was expected, because both μ_b and μ_c were predicted to be much smaller than μ_a by the bond-moment method as discussed above. Very low intensities are thus predicted for the *b*- and *c*-type lines.

There is no great difference between the predicted values of the rotational constants for each of the conformations *anti I* and *anti II*. However, *anti I* should have $\mu_c=0$ D, while μ_c of *anti II* is different from zero. Unfortunately, attempts to resolve the Stark effect of several $K_{-1}=1$ transitions and thereby determine the dipole moment were futile because of the absolute weakness of these transitions. No determination of the dipole moment could thus be made.

Another method which may be used to differentiate between *anti I* and *anti II* is based on the value of $I_a+I_b-I_c$. The calculated value for *anti I*, which has two out-of-plane hydrogen atoms, is 0.0642 u(nm)^2 while 0.0887 u(nm)^2 is computed for *anti II*. (See structure section below). The latter is quite close to the observed value of 0.09587(96) u(nm)^2 as shown in Table 2. Moreover, the study of the deuterated species, CH_2SDCH_2CN, as discussed below also strongly indicates that the assigned *anti* form is undoubtedly *anti II* and not *anti I*.

There are two identical forms of *anti II*. The mercapto group proton might be expected to tunnel between these two identical forms. The *c*-type transitions would then be expected to occur between (+) and (−)-states with resulting large splittings, whereas the *a*- and *b*-type transitions would be of the (+)→(+) or (−)→(−) type. These last-mentioned transitions should then have small splittings which would not perhaps be resolved. Such spectral features have been observed for other thiols, *e.g.* ethyl mercaptan,[5,6] isopropyl mercaptan,[7] propargyl mercaptan [8,9] and in *anti-gauche* propyl mercaptan.[10–12] However, in the case of *anti II*, no splittings were observed for the assigned *a*-type transitions. The $K_{-1}=1$ lines were especially scrutinized for this effect, however, with negative result. It is concluded that these lines are split by 0.6 MHz at most. This resembles the findings for propyl mercaptan [11,12] where only a

* The complete microwave spectra of CH_2SHCH_2CN and CH_2SDCH_2CN are available from the authors upon request or from the Molecular Spectra Data Center, National Bureau of Standards, Bld. 221, Rno. B 265, Washington D.C. 20234, USA, where they have been deposited.

few *a*-type lines were seen to be split by a small amount, due to accidental degeneracy between the (+) and (−) states, whereas ethyl mercaptan,[5,6] isopropyl mercaptan [7] and propargyl mercaptan [8,9] typically displayed splittings of a few megahertz for the majority of this kind of transition.

Vibrationally excited states of anti II. Three vibrationally excited states presumably belonging to successively excited states of the C−C torsional mode were assigned for *anti II*. The spectroscopic constants of the first and the second excited states are shown in Table 2. Only the high $K_{-1}\neq1$ pile-ups were identified for the third excited state of this motion and $B+C\approx2954.98(10)$ MHz was determined using the peak absorption frequencies of the pile-ups. The fourth excited state of this fundamental was tentatively assigned. This state was found to have $B+C\approx2959.45(20)$ MHz. No splittings were observed for any of these excited state transitions.

The B and C rotational constants increase almost linearly with increasing excitation as can be seen from Table 2. The values of $I_a+I_b-I_c$ also increase upon excitation. This is typical for a harmonic mode. Relative intensity measurements were made for this C−C torsional mode following the prescription of Esbitt and Wilson.[13] A value of 121(20) cm^{-1} was found.

As will be shown below, a C−S torsional frequency of 178(30) cm^{-1} was found for the hydrogen-bonded heavy-atom *gauche* conformation. Searches were made for the corresponding excited state of *anti II* which was expected to have roughly 1/3 of the intensity of the ground state lines. No identifications could be made for this excited state. One explanation for this could be that the rotational transitions of this state are split which would result in intensities of only about 1/6 of the corresponding ground state lines. Such weak lines would be very difficult to identify in this dense spectrum. This is especially true for the $K_{-1}=1$ transitions. The first excited state lines of the C−S torsion are furthermore expected to lie close to their ground state counterparts since little reduced mass is involved in this mode. Overlapping by ground state lines is thus considered to be quite likely.

Assignment of the ground vibrational state of the gauche *conformation.* A large number of unassigned lines remained in the spectrum after *anti II* had been assigned. Search for the hydrogen-bonded *gauche* rotamer was therefore made. The dipole moment components of this conformation were predicted using the bond-moment method [4] as $\mu_a=1.3$ D, $\mu_b=3.6$ D and $\mu_c=0.3$ D, respectively. Searches were then initiated for the $K_{-1}=1\rightarrow2$ and $K_{-1}=2\rightarrow3$ *b*-type *Q*-branch series whose high-*J* members are among the strongest lines of the spectrum. The low *J* members of these series were not so strong that well-resolved Stark effects were observed. The initial assignments were made for the $K_{-1}=1\rightarrow2$ *Q*-branch series in the 12−18 GHz spectral region and readily extended to the $K_{-1}=2\rightarrow3$ and $K_{-1}=3\rightarrow4$ *Q*-branch series. The *b*-type low *J* *R*-branch lines were then found after some searching. None of these transitions displayed well-resolved Stark splitting due to insufficient intensities and crowded neighbourhoods. Medium *J*-, *P*- and *R*-branch lines which are of moderate intensities were then predicted and found using a trial and error procedure. Spectral positions of high *J*-, *P*- and *R*-branch lines, none of which are strong, were now predicted and identified by their spectral positions and fit to a centrifugally distorted asymmetric rotor. Their very rapid Stark effects produced by a non-zero value of μ_a were also a considerable aid for their assignments. In this manner, *P*-branch lines up to the coalescing $70_{29,41}\rightarrow69_{30,40}$ and $70_{29,42}\rightarrow69_{30,39}$ pair of transitions, and *R*-branch lines including the $75_{28,47}\rightarrow76_{27,50}$ and $75_{28,48}\rightarrow76_{27,49}$ pair were identified. *P*- and *R*-branch lines with even higher *J* quantum numbers were searched for but not identified presumably because of too low intensities. A total of about 290 *b*-type transitions were assigned in this manner for the ground state. 50 selected transitions are shown in Table 3. 251 transitions, of which 35 are *Q*-branch and 216 *P*- or *R*-branch, were used to determine the spectroscopic constants shown in Table 4.

These constants predict the frequencies of *a*- and *c*-type transitions very accurately. However, no such transitions were identified with certainty, presumably because μ_a and μ_c are too small and thus produce lines of insufficient intensities.

The Stark effects of many low and medium *J*-lines were studied in an attempt to determine the dipole moment of the *gauche* conformation. Unfortunately, no lines with adequately resolved Stark effects were found, and thus no dipole moment could be measured.

Vibrationally excited states of the gauche *con-*

Table 3. Selected transitions for the ground vibrational state of the hydrogen-bonded *gauche* conformation.

Transition	Observed frequency[a] (MHz)	Obs.−calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
$1_{1,0} \rightarrow 2_{2,1}$	25280.65	0.11	−0.40	
$1_{1,1} \rightarrow 2_{2,0}$	25752.77	−0.06	−0.42	
$2_{0,2} \rightarrow 3_{1,3}$	17357.76	0.18	0.06	
$4_{1,4} \rightarrow 5_{0,5}$	17623.37	−0.12	−1.41	
$5_{0,5} \rightarrow 6_{1,6}$	27635.72	−0.03	−0.08	
$5_{2,3} \rightarrow 5_{3,2}$	27316.11	−0.06	−0.14	−0.01
$6_{1,6} \rightarrow 6_{2,5}$	21615.52	−0.14	−0.08	−0.01
$7_{2,5} \rightarrow 7_{3,4}$	26012.46	−0.03	3.38	−0.02
$7_{0,7} \rightarrow 7_{1,6}$	13968.53	0.01	−3.39	
$7_{1,7} \rightarrow 7_{2,6}$	23260.86	−0.08	−0.50	−0.01
$7_{2,6} \rightarrow 8_{1,7}$	25042.81	−0.02	−9.41	
$8_{0,8} \rightarrow 8_{1,7}$	16808.28	−0.02	−5.94	
$8_{1,7} \rightarrow 8_{2,6}$	14237.67	0.21	1.01	−0.01
$9_{1,9} \rightarrow 9_{2,8}$	27245.45	−0.16	−2.71	−0.02
$9_{2,7} \rightarrow 9_{3,6}$	24030.80	0.05	8.44	−0.04
$10_{1,9} \rightarrow 10_{2,8}$	16111.87	0.03	−3.80	−0.02
$10_{2,8} \rightarrow 10_{3,7}$	22996.13	0.15	10.82	−0.06
$11_{1,10} \rightarrow 11_{2,9}$	17823.35	−0.05	−8.92	−0.02
$11_{2,9} \rightarrow 11_{3,8}$	22099.09	−0.14	12.30	−0.08
$12_{2,10} \rightarrow 12_{3,9}$	21471.45	0.01	12.12	−0.10
$12_{4,8} \rightarrow 13_{3,11}$	17174.50	−0.08	−22.32	−0.02
$13_{2,11} \rightarrow 13_{3,10}$	21229.77	0.07	9.44	−0.12
$14_{1,13} \rightarrow 14_{2,12}$	26111.66	0.06	−37.65	−0.01
$15_{2,13} \rightarrow 15_{3,12}$	22260.50	−0.05	−6.67	−0.13
$17_{2,15} \rightarrow 17_{3,14}$	25666.30	0.09	−41.68	−0.09
$18_{3,15} \rightarrow 18_{4,14}$	28310.93	0.12	39.75	−0.66
$18_{8,10} \rightarrow 17_{9,9}$	15599.27	−0.03	−5.89	0.03
$18_{8,11} \rightarrow 17_{9,8}$	15599.27	−0.10	−5.90	0.03
$19_{3,16} \rightarrow 19_{4,15}$	28045.20	−0.03	25.33	−0.68
$20_{3,17} \rightarrow 20_{4,16}$	28368.85	0.08	2.00	−0.65
$23_{8,15} \rightarrow 24_{7,18}$	23835.29	−0.06	−190.24	0.32
$23_{8,16} \rightarrow 24_{7,17}$	23965.66	−0.04	−195.33	0.37
$27_{12,15} \rightarrow 26_{13,14}$	20579.66	0.08	4.02	0.08
$27_{12,16} \rightarrow 26_{13,13}$	20579.66	0.08	4.02	0.08
$36_{16,20} \rightarrow 35_{17,19}$	25577.29	−0.01	36.44	0.04
$36_{16,21} \rightarrow 35_{17,18}$	25577.29	−0.01	36.44	0.04
$44_{19,25} \rightarrow 43_{20,24}$	23812.05	0.00	217.69	−1.94
$44_{19,26} \rightarrow 43_{20,23}$	23812.05	0.00	217.69	−1.94
$49_{18,31} \rightarrow 50_{17,34}$	25957.06	0.03	−1387.27	13.31
$49_{18,32} \rightarrow 50_{17,33}$	25957.06	0.03	−1387.27	13.31
$54_{23,31} \rightarrow 53_{24,30}$	24549.88	0.00	538.39	−7.87
$54_{23,32} \rightarrow 53_{24,29}$	24549.88	0.00	538.39	−7.87
$61_{23,38} \rightarrow 62_{22,41}$	22037.48	0.01	−2391.80	37.92
$61_{23,39} \rightarrow 62_{22,40}$	22037.48	0.01	−2391.80	37.92
$66_{28,38} \rightarrow 65_{29,37}$	27879.64	0.13	1075.13	−23.84
$66_{28,39} \rightarrow 65_{29,36}$	27879.64	0.13	1075.13	−23.84
$72_{27,45} \rightarrow 73_{26,48}$	24785.28	0.09	−3866.73	84.85
$72_{27,46} \rightarrow 73_{26,47}$	24785.28	0.09	−3866.73	84.85
$75_{28,47} \rightarrow 76_{27,50}$	26481.54	−0.02	−4391.67	103.70
$75_{28,48} \rightarrow 76_{27,49}$	26481.54	−0.02	−4391.67	103.70

[a] ±0.10 MHz.

Table 4. Spectroscopic constants of the ground vibrational state of the *gauche* conformation of CH_2SHCH_2CN and CH_2SDCH_2CN.[a]

Species	CH_2SHCH_2CN	CH_2SDCH_2CN
Number of transitions	251	31
rms (MHz) [b]	0.076	0.115
A_v (MHz)	7773.9116(41)	7521.020(24)
B_v (MHz)	2404.9015(13)	2401.280(19)
C_v (MHz)	1959.2031(15)	1941.588(18)
Δ_J (kHz)	2.4141(44)	2.55(24)
Δ_{JK} (kHz)	−17.855(34)	−17.50(18)
Δ_K (kHz)	48.232(18)	52.3(27)
δ_J (kHz)	0.7696(23)	0.7473(67)
δ_K (kHz)	3.502(79)	4.44(23)
H_J (Hz)	−0.0475(49)	– [d]
H_{JK} (Hz)	−0.865(86)	– [d]
H_{KJ} (Hz)	−1.137(60)	– [d]
H_K (Hz) [c]	1.070(43)	– [d]

[a,b] Comments as for Table 2. [c] Further sextic constants preset at zero. [d] Sextic constants preset at zero.

Table 5. Spectroscopic constants of vibrationally excited states of the *gauche* conformation of CH_2SHCH_2CN.[a]

rms (MHz) [b]	First ex. C−C tors. 0.15	Second ex. C−C tors. 0.19	Third ex. C−C tors. 0.69	First ex. C−S tors. 0.15	Comb. C−C and C−S tors. 0.01
A_v (MHz)	7852.945(24)	7933.925(63)	8015.04(42)	7768.266(45)	7846.000(11)
B_v (MHz)	2392.848(14)	2381.217(38)	2369.42(19)	2405.846(30)	2393.246(14)
C_v (MHz)	1952.030(13)	1944.993(35)	1937.66(18)	1959.788(31)	1952.915(20)
Δ_J (kHz)	2.30(16)	2.83(45)	[c]	1.30(37)	[c]
Δ_{JK} (kHz)	−18.80(41)	−18.90(39)	[c]	−17.06(24)	[c]
Δ_K (kHz)	64.9(50)	38.6(72)	[c]	48.3(33)	[c]
δ_J (kHz)	0.723(10)	0.731(14)	[c]	0.778(11)	[c]
δ_K (kHz)	4.27(51)	5.07(55)	[c]	3.04(37)	[c]
No. of Q-branch lines	28	21	9	25	8
No. of R-branch lines	9	4	2	3	1
J_{max} Q-branch	19	18	18	20	19
J_{max} R-branch	8	7	7	7	7

[a,b] Comments as for Table 2. [c] Fitted, but too inaccurate to be reported.

formation. Five vibrationally excited states were assigned for this conformation as shown in Table 5. The most intense of these vibrational satellites is the first excited state of the C−C torsional mode which has about 50 % of the ground state intensity. Low J,R-branch and low medium J,Q-branch lines were assigned for this mode as seen in Table 5. Many attempts were made to assign the medium and high J,P- and R-branch lines for this excited state in the same manner as described for the ground vibrational state. However, these attempts were unsuccessful presumably because P- and R-branch lines with J between 10 and 25 are quite weak and also overlap with other lines in many cases.

Relative intensity measurements yielded 118(20) cm^{-1} for this C−C torsional fundamental. This is close to 121(20) cm^{-1} found for the *anti II* conformation as expected.

A rough force field (Table 6) was constructed

Table 6. Assumed diagonal force field,[a] centrifugal distortion constants and torsional frequency for the heavy-atom *gauche* conformation of CH_2SHCH_2CN.

Stretching (10^2 N m^{-1})			
C≡N	17.4	H_2C-CH_2	4.6
C–CN	5.5	C–S	1.7
S–H	3.5	C–H	4.8
Bending (aJ rad^{-2})			
S–C–C	1.0	C–S–H	0.58
S–C–H	0.76	H–C–CN	0.67
C–C–C	1.1	C–C–H	0.61
H–C–H	0.50	C–C≡N	0.16
Torsion (aJ rad^{-2})			
C–S	0.25		
C–C	0.270 [b]		

Centrifugal distortion constants (kHz)	Obs.	Calc.
Δ_J	2.414	2.664
Δ_K	−17.86	−17.65
Δ_K	48.23	48.23
δ_J	0.7696	0.7796
δ_K	3.50	4.30

[a] See text. [b] Obtained from least-squares fit yielding a C–C torsional frequency of 97 cm^{-1} as compared to 118(20) cm^{-1} found by relative intensity measurements.

for *gauche* CH_2SHCH_2CN in order to calculate the torsional frequency utilizing the quartic centrifugal distortion contants in the manner described previously.[14]

A value of 97 cm^{-1} was found as compared to 118(20) cm^{-1} obtained by relative intensity measurements. It is difficult to estimate uncertainty limits with this method, but ±10 cm^{-1} appears reasonable. All quartic centrifugal distortion constants, with the exception of δ_K, are well reproduced as can be seen in Table 6.

No similar calculation could be made for *anti II* because no accurate centrifugal distortion constants are available.

Attempts were also made to reproduce the changes of the rotational constants upon excitation by opening up the SCCC dihedral angle by 3° with the other structural parameters kept fixed. The calculated values were ΔA=+165.83 MHz, ΔB=−51.59 MHz and ΔC=−19.94 MHz as compared to ΔA=+79.04 MHz, ΔB=−12.06 MHz and ΔC=−7.17 MHz, respectively, found experimentally (Tables 4 and 5). The agreement is not very good. This presumably means that the C–C torsional motion is considerably more complex than just a simple rotation about the central C–C bond. Further torsional motions or bending vibrations seem to be involved.

The second and third excited states of the heavy-atom torsional motion were also assigned as shown in Table 5. The successive changes of the rotational constants upon progressive excitation are very constant. This is typical for a harmonic mode.

Another excited state having approximately one third of the intensity of the ground state was also identified. Relative intensity measurements [13] yielded 178(30) cm^{-1} for this fundamental. This state is assigned as the first excited state of C–S torsional motion because the changes of the rotational constants upon excitation are small as compared to the C–C torsional motion (Tables 4 and 5). Moreover, its frequency of 178(30) cm^{-1} is typical for the C–S torsion of thiols.[15] Splitting of any of its lines was searched for, but not observed. Attempts to assign the second excited state of this normal mode were futile.

The fifth excited state assigned (Table 5) is presumably a combinational mode where both the C–C and C–S torsional modes simultaneously are excited, because its rotational constants are very close to what is found when both the changes of the rotational constants upon excitation of each of the C–C and C–S torsions are added to the ground vibrational state rotational constants.

Further excited vibrational states were searched for. In particular, a search was made for the first excited state of the heavy atom bending mode. In the isoelectronic compound 2-chloro propionitrile [16] the lowest of these modes is found at 307 cm^{-1}. The Boltzmann factor at −5 °C would then be 0.19 for the first excited state of this bending mode of 2-chloro propionitrile. It is likely that a similar situation exists for 3-mercaptopropionitrile. However, no excited state of about 20 % of the ground state intensity could be identified.

Searches for further conformations. A total of about 600 transitions making up about 400 well-resolved lines were assigned for the two

conformations. All "strong" lines, *i.e.* lines with peak absorption coefficients larger than roughly 1×10^{-7} cm^{-1}, were assigned. The great majority of "medium" intensity (peak absorption coefficients between approximately 5×10^{-8} and 1×10^{-7} cm^{-1}) were also identified. Many "weak" lines with absorption coefficients less than about 5×10^{-8} cm^{-1} were also assigned. Stark effect studies were made for the remaining unassigned lines of medium intensity, but no resolution was seen.

In particular, attempts were made to find the coalescing $K_{-1}\neq1$ pile-ups of the hypothetical *anti I* conformation. However, no assignments could be made.

There are probably small differences between the rotational constants of the *anti II* and the hypothetical *anti I* conformations. If the $K_{-1}\neq1$ pile-ups were well-separated for these two rotamers, identification would probably have been made provided that the intensities of the *anti I* pile-ups were 20 % or more of the corresponding transitions of *anti II*. If overlap does occur, the presence of *anti I* would probably have been noted provided that the concentration of this rotamer were 1/3 of that of *anti II*. *Anti I*, which has half the statistical weight of *anti II*, is then conservatively estimated to be at least 1.0 kJ/mol less stable than the latter assigned conformation if it exists at all as a stable conformation.

3-Mercaptopropionitrile is not the only thiol which prefers the *gauche* form for the HSCC dihedral angle. Ethyl mercaptan has the *gauche* form more stable than *anti* by about 1.7 kJ/mol.[5] The *anti–gauche* conformation of propyl mercaptan is also more stable than the *anti–anti* rotamer by 1.8 kJ/mol.[12]

The majority of the unassigned lines of the spectrum are believed to belong to unidentified vibrationally excited states of the heavy-atom hydrogen-bonded *gauche* conformation. Presumably, *anti II* and the *gauche* form together make up at least 90 % of the gaseous composition of CH_2SHCH_2CN at −5 °C.

Energy differences between the heavy-atom gauche *and* anti II *conformations*. Relative intensity measurements were made following the procedure of Ref. 17 in order to determine the energy difference between the two conformers. Strong lines of the heavy-atom *gauche* conformation lying relatively close to $K_{-1}\neq1$-lines of *anti II* were selected. The lines were checked for overlap with other lines or Stark components and were presumably not significantly contaminated by such effects. Unfortunately, the dipole moments of the two conformations were not available, and the bond–moment values cited above were assumed in order to derive an energy difference. ΔH°_3 was thus found to be 1.3(20) kJ/mol with the hydrogen-bonded form as the more stable. Uncertainties resulting from the fact that the principal axes dipole moment components have to be assumed, are included in the above uncertainty limit of 2.0 kJ/mol.

Deuterated species. The deuterated species, CH_2SDCH_2CN, was studied to obtain information about the mercapto group hydrogen position. 31 transitions were readily assigned for the hydrogen-bonded conformation and the spectroscopic constants shown in Table 4 were determined. Kraitchman's coordinates [18] were then calculated for the mercapto group hydrogen atom. They are reported in Table 7.

In the case of *anti II*, only the $K_{-1}\neq1$ pile-ups were assigned and $B+C\approx2895.55(5)$ MHz was determined. The $K_{-1}=1$-lines were too weak to be assigned with certainty.

The changes of $B+C$ upon deuteration were calculated to be −65.74 MHz for *anti I* and −42.77 MHz for *anti II* using the plausible structure discussed later. The observed value was −45.47 MHz. Deuteration thus clearly shows that assignment has been made for *anti II* and not for *anti I*.

^{34}S is present in about 4 % concentration. The spectrum is relatively weak and dense, and assignment of this isotopic species of both rotamers would therefore be very difficult and no attempts were made to this end.

Structure of the two conformations. Only two isotopic species were studied for the two rotamers. A complete geometrical structure cannot, therefore, be determined for each of the two conformations. A selection of geometrical parameters to be fitted must be made. The S−H bond length, the CCS angle and the SCCC dihedral angle were fitted for the heavy-atom hydrogen-bonded *gauche* conformation, while only the CCS angle was fitted for *anti II*. The remaining bond lengths and angles were kept fixed as shown in Table 7. These structural parameters were selected from recent accurate studies. The CCN angle was assumed to be 180°, although it is realized that small deviations from linearity have

Table 7. Plausible structural parameters [a] (bond lengths in *pm*, angles in *degrees*) of *anti II* and of the hydrogen-bonded *gauche* conformation of CH_2SHCH_2CN.

Assumed structural parameters common for both conformations

C–S	182.0	∠CCC	110.5
C–C	153,0	∠CSH	96.2
C–CN	147.4	∠CCN	180.00
C≡N	115.7	∠CCH	109.48
C–H	109.3	∠HCH	109.48
		∠HSCC	120.00 from *anti*

Fitted structural parameters

Conformation	*Gauche*	*Anti II*
S–H	137(10)	132.2 [b]
∠CCS	114.0(15)	111.5(10)
∠SCCC from *syn*	65(3)	180.00 [b]

Hydrogen bond parameters of the *gauche* conformation

$H\cdots C_N$	267	H···N	301
$S\cdots C_N$	324	S···N	394
∠S–H···N	124	∠S–H···C	101
∠S–H,CN	7		

Sum of van der Waals radii [c]

H···C	290 [d]	H···N	270
S···C	355 [d]	S···N	335

Rotational constants (MHz) of the *gauche* conformation

	CH_2SHCH_2CN			CH_2SDCH_2CN		
	Obs.	Obs.-calc.	Diff (%)	Obs.	Obs.-calc.	Diff(%)
A	7773.9116	5.04	0.06	7521.020	−4.17	0.06
B	2404.9015	5.18	0.22	2401.280	6.84	0.24
C	1959.2031	3.57	0.18	1941.588	4.69	0.24

Kraitchman's coordinates of mercapto group hydrogen atom of the *gauche* form

	|*a*|	|*b*|	|*c*|
From rotational constants	48.31(15)	145.448(53)	29.23(27)
From plausible structure	65.1	144.4	19.6

Rotational constants (MHz) of the *anti II* conformation of CH_2SHCH_2CN

	Obs.	Obs.-calc.	Diff(%)
A	24200.6(1107)	−889.8	3.7
B	1494.6723(54)	−1.30	0.08
C	1446.3525(54)	−1.28	0.09

B+*C* for *anti II* of CH_2SDCH_2CN

	Obs.	Calc.
B+*C*	2895.55(5)	2900.83

[a] See text. [b] Not fitted, held fixed. [c] Taken from Ref. 21. [d] van der Waals radius of carbon assumed to be 170 pm as for aromatic carbon atoms.

been found for several molecules containing the cyano groups.

The CCS angle of *anti II* was fitted in steps of 0.5°. The A rotational constant is much less accurately determined than B and C, and the fit was made using only these two constants. A value of 111.5(10)° was found for the CCS angle (see Table 7).

The SCCC angle of the heavy-atom *gauche* conformation was fitted in steps of 1° and the CCS angle in steps of 0.5°. The best values were found to be 65(3)° from *syn* and 114.0(15)°, respectively, for these two angles (Table 7).

A rough reproduction of the Kraitchmann coordinates of the mercapto group hydrogen atom shown in Table 7 was attempted by varying the S–H bond length. However, a reproduction of the *a*-axis coordinate would have required an abnormally long S–H bond length as well as an unrealistically small CSH angle.

A similar situation was found for $CH_2OHCH_2NH_2$.[19] This anomaly was explained [20] as resulting from a shortening of the non-bonded O···N distance upon deuteration of the hydroxyl hydrogen atom. It seems that a similar situation exists for 3-mercaptopropionitrile. The S–H bond length becomes very uncertain as a result of this effect.

DISCUSSION

The present work demonstrates that the mercapto group is capable of forming some sort of weak attractive interaction to the cyano group leaving the heavy-atom *gauche* conformation more stable than *anti II* by 1.3(20) kJ/mol. This stabilization is presumably mainly electrostatic in origin, as the S–H and C≡N bonds are about 7° from being parallel (Table 7) which is ideal for dipole–dipole interaction. Covalent forces may play a small role in stabilizing the *gauche* conformation. If the van der Waals radius of the carbon atom of the cyano group is taken to be 170 pm, which is the value often quoted for aromatic carbon atoms,[21] the non-bonded H···C distance is about 20 pm shorter than the sum of the van der Waals radii of hydrogen and carbon. Likewise, the S···C distance is shorter than the sum of the van der Waals radii [21] by about 30 pm.

No explanation can be offered for the finding that *anti II* is more stable than *anti I* by at least 1 kJ/mol. It should be pointed out, however, that molecules of the type $X-CH_2SH$ have a propensity for forming stable *gauche* rotameric forms. This has been found for ethyl mercaptan,[5] propyl mercaptan [10–12] and propargyl mercaptan [8,9] in addition to the title compound.

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Received October 11, 1982.