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Microwave Spectrum, Conformational Equilibria, Intramolecular Hydrogen Bonding, Dipole Moment and Centrifugal Distortion of 3-Hydroxypropanenitrile

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The microwave spectra of 3-hydroxypropanenitrile, $HOCH_2CH_2C{\equiv}N$, and one deuterated species, $DOCH_2CH_2C{\equiv}N$, have been investigated in the 18.0–39.6 GHz spectral region at room temperature. Three conformations of the molecule were assigned.

The heavy-atom *gauche* conformation is stabilized by a weak, internal hydrogen bond formed between the hydroxyl group hydrogen atom and the π-electrons of the cyano group.

The second assigned conformation denoted *anti I* has a heavy-atom *anti* arrangement and C_s-symmetry, and the third identified conformation called *anti II* has the hydroxyl group hydrogen atom rotated approximately 120° out of the plane formed by the heavy atoms.

The internal energy difference was found to be 2.7(4) kJ/mol by relative intensity measurements between *anti I* and *gauche*, with the latter as the more stable conformation. *Anti II* was likewise found to be 7.4(24) kJ/mol less stable than the *gauche*.

The strength of the intramolecular hydrogen bond is taken to be approximately equal to the energy difference between the *gauche* and *anti II* conformations, *viz.* 7.4(24) kJ/mol.

3-Hydroxypropanenitrile is the first example of a 2-substituted ethanol derivative for which both a hydrogen-bonded *gauche* as well as two *anti* conformations have been assigned by microwave spectroscopy.

It is well established that the cyano group may act as proton acceptor for hydrogen bonds. Its ability to form internal hydrogen bonds with amino, thiol and phosphino groups has recently been studied by microwave spectroscopy in this laboratory in the cases of $H_2NCH_2CH_2C{\equiv}N$,[1] $HSCH_2CH_2C{\equiv}N$,[2] and $H_2PCH_2CH_2C{\equiv}N$.[3] Weak intramolecular hydrogen bonding was found to be important in all these three cases.

In 3-hydroxypropanenitrile, $HOCH_2CH_2CN$, internal hydrogen bonding between a fourth proton donor, the hydroxyl group, and the cyano group is possible. The hydrogen-bonded heavy atom *gauche* conformation is depicted in Fig. 1. In addition, *anti I* with a symmetry plane, and *anti II* which has the hydroxyl group rotated 120° out of this plane, are both likely conformations of the molecule. (See Fig. 1).

3-Hydroxypropanenitrile has previously been studied by a variety of methods. Krueger and Mettee[4] using IR spectroscopy studied the compound in carbon tetrachloride solution, and found that the hydrogen-bonded *gauche* conformation is more stable than *anti* by

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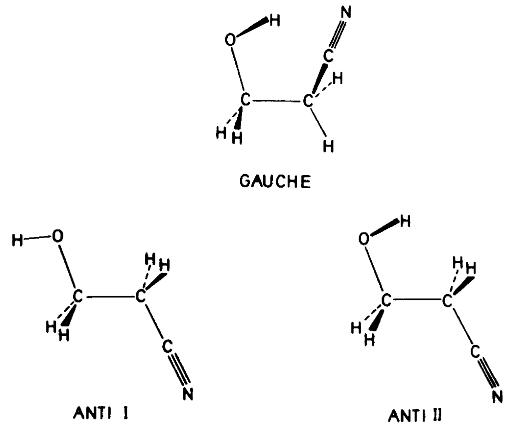

Fig. 1. The three conformations of $HOCH_2CH_2CN$ assigned in this work. The hydrogen-bonded heavy-atom *gauche* conformation was found to be 2.7(4) kJ/mol more stable than *anti I* and to be 7.4(24) kJ/mol more stable than *anti II*. The uncertainties represent one standard deviation in the first case, and the uncertainty limit, which is approximately three standard deviations, in the second case.

0.59(13) kJ/mol. These workers did not differentiate between *anti I* and *anti II,* which may be of importance as will be shown in this work.

In the gaseous state, an enthalpy difference of 2.9(13) kJ/mol between *anti* (no distinction between the two *anti* forms being made) and *gauche* was determined by IR spectroscopy.[5] A normal-coordinate analysis of $HOCH_2CH_2CN$ has also been made.[6] Moreover, in an old electron-diffraction study,[7] only *anti* was found. A microwave study of $HOCH_2CH_2CN$ has been referred to[8] in which the assignment of *anti* (no specification of which one of them) and a tentative assignment of the *gauche* conformation was claimed. It was therefore felt that it would be of value to reinvestigate the microwave spectrum of $HOCH_2CH_2CN$ and compare these results to those of $H_2NCH_2CH_2CN$,[1] $HSCH_2CH_2CN$,[2] and $H_2PCH_2CH_2CN$.[3]

In this work it is found that the hydrogen-bonded heavy-atom *gauche* conformation is the most stable form of the molecule. It is more stable than *anti I* by 2.7(4) kJ/mol, and more stable than *anti II* by 7.4(24) kJ/mol. As pointed out in the Discussion, the hydrogen bond strength is taken to be the energy difference between the *anti II* and the *gauche* conformations, and is thus 7.4(24) kJ/mol.

EXPERIMENTAL

3-Hydroxypropanenitrile *puriss* was purchased from Fluka, A. G., Buchs, Switzerland and used as received. The compound has low volatility and the spectra were therefore recorded at room temperature by flowing it slowly through the absorption cell at a pressure of roughly 1.0 Pa. The spectrum was investigated extensively in the 18.0–31.5 GHz region. Many measurements were also made in the 31.5–39.6 GHz region. A conventional microwave spectrometer equipped with free-running klystrons was used. The deuterated species was produced by exchange with heavy water in the absorption cell.

Table 1. Selected transitions for the ground vibrational state of the heavy-atom *gauche* conformation of $HOCH_2CH_2CN$.

Transition	Observed frequency[a] (MHz)	Obs.−calc. Frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
a-type				
$3_{0,3}\leftarrow 2_{0,2}$	18594.33	0.01	−0.44	
$3_{1,2}\leftarrow 2_{1,1}$	19644.07	0.00	−0.56	
$4_{0,4}\leftarrow 3_{0,3}$	24624.04	0.01	−0.96	
$4_{1,3}\leftarrow 3_{1,2}$	26144.23	−0.06	−1.39	
$4_{1,4}\leftarrow 3_{1,3}$	23686.98	0.04	−0.47	
$4_{2,2}\leftarrow 3_{2,1}$	25328.68	0.11	−0.55	
$5_{0,5}\leftarrow 4_{0,4}$	30526.91	−0.02	−1.68	
$5_{1,5}\leftarrow 4_{1,4}$	29547.05	−0.04	−1.08	
b-type				
$2_{2,0}\leftarrow 2_{1,1}$	21919.45	0.12	−0.58	
$2_{2,1}\leftarrow 2_{1,2}$	23731.68	−0.06	−0.80	
$3_{2,2}\leftarrow 3_{1,3}$	24679.76	−0.06	−0.52	
$3_{1,3}\leftarrow 2_{0,2}$	24510.97	0.01	0.09	
$5_{1,5}\leftarrow 4_{0,4}$	34526.64	0.00	−0.05	
$5_{0,5}\leftarrow 4_{1,4}$	25547.47	0.09	−2.71	
$6_{2,4}\leftarrow 6_{1,5}$	19121.77	−0.04	2.39	
$7_{1,6}\leftarrow 7_{0,7}$	19226.13	0.05	−7.13	
$8_{2,7}\leftarrow 8_{1,8}$	34385.17	0.00	−3.68	0.01
$9_{2,7}\leftarrow 8_{3,6}$	25235.16	0.03	−28.94	0.01
$9_{2,7}\leftarrow 9_{1,8}$	20401.34	−0.06	−2.83	0.01
$10_{2,8}\leftarrow 10_{1,9}$	22082.43	0.10	−9.38	0.01
$10_{3,7}\leftarrow 10_{2,8}$	31143.96	0.13	18.59	0.02
$11_{2,9}\leftarrow 11_{1,10}$	24498.69	0.07	−19.70	0.01
$12_{3,9}\leftarrow 12_{2,10}$	29127.96	0.06	19.33	0.04
$14_{4,11}\leftarrow 13_{5,8}$	20794.84	0.02	−61.74	0.08
$17_{5,13}\leftarrow 16_{6,10}$	25171.17	0.01	−117.74	0.20
$17_{5,12}\leftarrow 16_{6,11}$	25911.32	−0.03	−132.77	0.19
$22_{7,16}\leftarrow 21_{8,13}$	26475.97	−0.01	−243.97	0.70
$22_{7,15}\leftarrow 21_{8,14}$	26536.01	0.02	−246.91	0.70
$24_{8,17}\leftarrow 23_{9,14}$	23681.16	−0.01	−293.98	1.04
Coalescing K_{-1}-doublet lines[b]				
$15_{9}\leftarrow 16_{8}$	28328.60	−0.02	−54.57	0.26
$19_{10}\leftarrow 20_{9}$	18107.15	0.10	5.32	0.11
$22_{10}\leftarrow 21_{11}$	20695.12	−0.03	1.86	0.21
$27_{14}\leftarrow 28_{13}$	28443.91	−0.02	−19.37	0.93
$31_{14}\leftarrow 30_{15}$	24661.96	−0.03	67.66	0.42
$36_{13}\leftarrow 35_{14}$	22992.40	−0.08	−854.19	7.28
$38_{17}\leftarrow 37_{18}$	26104.78	−0.04	207.11	−0.23
$46_{17}\leftarrow 45_{18}$	24767.10	0.08	−1694.51	24.09
$49_{23}\leftarrow 50_{22}$	26629.72	0.03	729.65	−8.11
$56_{21}\leftarrow 55_{22}$	26143.00	0.05	−2943.06	63.13
$57_{26}\leftarrow 58_{25}$	22207.35	0.05	1508.70	−30.02
$65_{25}\leftarrow 64_{26}$	20886.85	−0.08	−4227.46	125.14
$67_{30}\leftarrow 68_{29}$	20819.07	0.02	2734.04	−81.34
$71_{27}\leftarrow 70_{28}$	27296.64	−0.02	−5727.08	202.77
$73_{28}\leftarrow 72_{29}$	24343.53	−0.04	−6037.41	227.64
$76_{29}\leftarrow 75_{30}$	27406.98	0.03	−6927.09	283.62

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[a] ±0.10 MHz. [b] The K_{-1}-energy doublets coalesce for high values of K_{-1}. Subscripts of J-quantum numbers refer only to K_{-1}, and not to K_{+1}.

RESULTS

Assignment of the ground vibrational state of the hydrogen-bonded gauche conformation. Based on the findings of the IR-gas phase work[4] as well as the fact that only hydrogen-bonded *gauche* conformations were found for 3-aminopropanenitrile,[1] it was presumed that 3-hydroxypropanenitrile would also prefer the hydrogen-bonded heavy-atom *gauche* conformation shown in Fig. 1.

Preliminary rotational constants were computed for this conformation. Its dipole moment components along the principal axes were predicted to be μ_a=1.8 D, μ_b=2.3 D, and μ_c=0.1 D, respectively, using the bond-moment method.[9] The molecule was thus predicted to have a relatively strong and dense spectrum dominated by *b*-type *Q*-branch transitions.

This was also found to be the case. The strongest lines of the spectrum are of the *b*-type *Q*-branch variety with *J* in the 10–17 range. These lines have peak absorption coefficients of roughly about 5×10^{-7} cm^{-1} at room temperature. The assignments of these transitions were made readily. Soon, low-*J*, *R*-branch *a*- and *b*-type transitions were found. Medium *J*, *P*- and *R*-branch lines which are of moderate intensities were now predicted and found using a trial and error procedure. Spectral positions of high *J*, *P*- and R-branch lines, none of which are very strong, were next predicted and identified by their 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 $67_{30,38} \leftarrow 68_{29,39}$ and $67_{30,37} \leftarrow 68_{29,40}$ pair of transitions, and *R*-branch lines including the $76_{29,47} \leftarrow 75_{30,46}$ and $76_{29,48} \leftarrow 75_{30,45}$ coalescing pair were identified. The peak intensities of both these pairs were roughly 2×10^{-8} cm^{-1}. *P*- and *R*-branch lines with even higher *J* quantum numbers were searched for but not identified with certainty presumably because of too low intensities.

A total of about 240 transitions were ultimately assigned; 45 of which are shown in Table 1. The complete spectra of $HOCH_2CH_2CN$ and $DOCH_2CH_2CN$ are available from the authors upon request, or from the Molecular Spectra Data Center, National Bureau of

Table 2. Spectroscopic constants of the ground vibrational states of the heavy-atom *gauche* conformation of $HOCH_2CH_2CN$ and $DOCH_2CH_2CN$.[a]

Species	$HOCH_2CH_2CN$	$DOCH_2CH_2CN$
Number of transitions	220	35
Root-mean-square (MHz)	0.056	0.078
A_0(MHz)	10726.4535(36)	10237.154(18)
B_0(MHz)	3432.3084(11)	3419.491(14)
C_0(MHz)	2815.6078(15)	2771.972(14)
Δ_J(kHz)	4.8684(54)	4.81(22)
Δ_{JK}(kHz)	−29.091(46)	−27.37(15)
Δ_K(kHz)	80.212(24)	75.2(18)
δ_J(kHz)	1.4939(34)	1.5490(58)
δ_K(kHz)	10.61(12)	10.40(22)
H_J(Hz)	0.0434(41)	–[c]
H_{JK}(Hz)	0.397(72)	–[c]
H_{KJ}(Hz)	−0.369(53)	–[c]
H_K(Hz)[b]	2.698(36)	–[c]

[a] Uncertainties represent one standard deviation. [b] Further sextic constants preset at zero. [c] Preset at zero.

Table 3. Spectroscopic constants of vibrationally excited states of the heavy-atom *gauche* conformation of $HOCH_2CH_2CN$[a]

Vibrational state	First ex. C–C tors.	Second ex. C–C tors.	Third ex. C–C tors.	Fourth ex. C–C tors.	First ex. C–O tors.	First ex. lowest bending[g]
N.o.t.[b]	124	29	14	14	28	14
Rms (MHz)[c]	0.065	0.166	0.164		0.116	0.093
A_v (MHz)	10810.3568(55)	10895.768(26)	10983.190(51)	11073.682(68)	10728.787(36)	10813.995(21)
B_v (MHz)	3423.7073(17)	3415.2056(66)	3406.621(11)	3398.153(17)	3436.310(14)	3419.2307(61)
C_v (MHz)	2808.8807(22)	2802.2276(70)	2795.590(11)	2789.528(16)	2817.695(11)	2808.5013(57)
Δ_J (kHz)	4.780(11)	–[e]	–[e]	–[e]	4.70(21)	–[e]
Δ_{JK} (kHz)	−28.507(98)	−28.53(20)	−28.51(33)	−27.28(49)	−25.8(10)	−31.62(17)
Δ_K (kHz)	83.902(40)	–[e]	–[e]	–[e]	57(11)	–[e]
δ_J (kHz)	1.4597(50)	1.4109(99)	1.392(13)	1.4098(89)	1.562(29)	1.1139(38)
δ_K (kHz)	10.82(19)	–[e]	–[e]	–[e]	8.0(13)	–[e]
H_J (Hz)	0.120(25)	–[f]	–[f]	–[f]	–[f]	–[f]
H_{JK} (Hz)	1.61(43)	–[f]	–[f]	–[f]	–[f]	–[f]
H_{KJ} (Hz)	0.94(32)	–[f]	–[f]	–[f]	–[f]	–[f]
H_K (Hz)[d]	2.61(15)	–[f]	–[f]	–[f]	–[f]	–[f]

[a] Uncertainties represent one standard deviation. [b] Number of transitions. [c] Root-mean-square deviation. [d] Further sextic constants preset at zero. [e] Preset at ground-state value. [f] Preset at zero. [g] Tentative assignments of *R*-branch lines. See text.

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Centrifugal distortion is prominent, as can be seen from this table. It amounts to about 7 GHz for the highest J-transition. The spectroscopic constants in I^r-representation displayed in Table 2 were obtained from 220 selected transitions.

These constants predict the positions of the strongest of the hypothetical c-type lines to within the measurement accuracy of our instrument. However, no c-type lines were identified with certainty. This is in keeping with the fact that μ_c=0.387(4) D (see below) producing insufficient intensities for these transitions.

The ^{14}N nucleus may produce quadrupole splittings of the transitions. However, no splittings were seen. It is assumed that the strong components are split by less than about 0.5 MHz, which is the resolution power of our instrument.

Vibrationally excited states of the gauche conformation. The ground state lines were accompanied by a rich satellite spectrum presumably belonging to vibrationally excited states. Six such states were assigned as shown in Table 3. The most intense of these vibrational satellites is the first excited state of the C–C torsional mode which has about 55 % of the ground-state intensity at room temperature. About 135 a- and b-type transitions were assigned for this state in the same manner as described for the ground state. Maximum

Table 4. Assumed diagonal force field,[a] centrifugal distortion constants and torsional frequency for the heavy-atom *gauche* conformation of $HOCH_2CH_2CN$.

Stretching (10^2 N m^{-1})			
C≡N	17.7	H_2C-CH_2	4.4
C–CN	5.3	C–O	5.2
O–H	7.4	C–H	4.7
Bending (aJ rad^{-2})			
O–C–C	1.02	C–O–H	0.835
O–C–H	0.765	H–C–CN	0.657
C–C–C	2.14	C–C–H	0.61
H–C–H	0.53	C–C≡N	0.11
Torsion (aJ rad^{-2})			
C–O	0.25		
C–C	0.131[b]		
Centrifugal distortion constants (kHz)			
	Obs.	Calc.	
Δ_J	4.8684	4.6145	
Δ_{JK}	−29.091	−25.653	
Δ_K	80.212	81.186	
δ_J	1.4939	1.4529	
δ_K	10.61	11.06	
C–C torsional frequency (cm^{-1})			
From relative intensities[a]	108(15)		
From force-field calculations[a,c]	102(10)		

[a] See text. [b] Obtained from least-squares fit of centrifugal distortion constants keeping all the other force constants fixed at the values shown in this table. [c] Calculated from the force constants shown in this table.

J for the P-branch transitions were found for the $58_{26} \leftarrow 59_{25}$ coalescing K_{-1}-pair, while the $63_{27} \leftarrow 62_{28}$ coalescing pair of transitions represents the maximum J identified for the R-branch lines. The spectroscopic constants of this excited state (Table 3) were derived from 124 transitions.

Relative intensity measurements made largely as described in Ref. 10 were used to determine the C–C torsional frequency. A value of 108(15) cm^{-1} was obtained. This is similar to 128 cm^{-1} calculated by Giguère and Schneider.[6] It is also similar to the frequencies determined for this mode for the *gauche* forms of $H_2NCH_2CH_2CN$,[1] $HSCH_2CH_2CN$,[2] and $H_2PCH_2CH_2CN$,[3] as expected.

A rough, diagonal force field (Table 4) was assumed in order to compute the C–C-torsional frequency using the quartic centrifugal distortion constants in the manner described previously.[11] A frequency of 102 cm^{-1} was obtained as shown in Table 4, compared to 108(15) cm^{-1} found by relative intensity measurements. It is difficult to estimate uncertainty limits of the C–C torsional frequency calculated from the centrifugal distortion constants, but ± 10 cm^{-1} appears reasonable. There are acceptable differences between the calculated and observed centrifugal distortion constants as shown in Table 4.

Attempts were also made to reproduce the changes of the rotational constants upon excitation of this mode by opening up the OCCC dihedral angle by 1.5° with the other structural parameters (Table 9) kept fixed. $\Delta A = 63.55$ MHz, $\Delta B = -25.73$ MHz, and $\Delta C = -8.32$ MHz, respectively, were computed from the plausible structure of Table 9. This is fairly close, at least for ΔA and ΔC, to the observed values: $\Delta A = 83.903$ MHz, $\Delta B = -8.601$ MHz, and $\Delta C = -6.727$ MHz, found from Tables 2 and 3, and it is independent evidence for assigning this mode as the C–C torsional mode. The second, third, and fourth excited states of the H_2C-CH_2 torsional mode were also assigned, as shown in Table 3. These excited states are so weak that assignments were restricted to b-type Q-branch lines up to $J=17$ at most and a- and b-type R-branch transitions with $J \leqslant 5$. Changes of the rotational constants upon successive excitation of the C–C torsional mode are fairly constant as can be seen from Table 2 and 3. This is typical of a harmonic mode, and also reminiscent of the findings for *gauche* $HSCH_2CH_2CN$[2].

Another excited state having approximately 40 % of the intensity of the ground state was also assigned (Table 3). Q-branch transitions with $J \leqslant 15$ and a- and b-type lines with $J \leqslant 7$ were assigned for this excited state. None of the lines were detectably split. Relative intensity measurements[10] yielded 183(30) cm^{-1} for this fundamental. We believe that this is the C–O torsional fundamental for the following reasons: The rotational constants change little from the ground state values as can be seen from Table 2 and 3. This is typical for a mode involving little reduced mass as is the case for the C–O torsional fundamental. Moreover, the C–O torsional frequencies of *gauche* and *anti* ethanol[12] are close to 200 cm^{-1} and thus similar to 183(30) cm^{-1} found for the title compound. Our finding of 183(30) cm^{-1} is in disagreement with 296 cm^{-1} assigned for this mode in the IR-work.[5,6]

The second excited state of this C–O torsional mode was searched for. If the C–O torsional potential were harmonic, this excited state would be expected to have about 16 % of the intensity of the ground state, and its rotational transitions should be found approximately twice as far from the ground state lines as the corresponding first excited state transitions. Such a spectral pattern was not seen. It is concluded that the second vibrationally excited state of the C–O torsional mode is perturbed either by an interaction with another normal mode, or because the C–O torsional potential is significantly anharmonic. It is remembered that the C–O torsional potential of ethanol is quite

Table 5. Stark coefficients [a] and dipole moment of the heavy-atom *gauche* conformation of $HOCH_2CH_2CN$.

Transition		$\Delta\nu/E^2$, (MHz V^{-2} cm^2)$\times 10^5$ Obs.	Calc.
$4_{2,3}\leftarrow 4_{1,4}$	$\|M\|=4$	−21.8(2)	−22.7
$5_{1,5}\leftarrow 4_{0,4}$	$M=0$	0.661(6)	0.666
	$\|M\|=1$	0.954(9)	0.958
	$\|M\|=2$	1.82(2)	1.83
	$\|M\|=3$	3.31(4)	3.29
$2_{2,0}\leftarrow 1_{1,1}$	$M=0$	0.727(6)	0.707
$2_{2,1}\leftarrow 1_{1,0}$	$M=0$	3.26(4)	3.13
$8_{2,7}\leftarrow 8_{1,8}$	$\|M\|=7$	−0.979(10)	−0.971
	$\|M\|=8$	−1.27(2)	−1.30

Dipole moment
$\mu_a=1.844(14)$ D[b] $\mu_b=2.544(17)$ D $\mu_c=0.387(4)$ D $\mu_{tot.}=3.166(18)$ D

[a] Uncertainties represent one standard deviation. [b] 1 D=3.33564 · 10^{-30} Cm.

anharmonic.[12] The behaviour of this C−O torsion is actually similar to the findings made for the C−S torsional mode of *gauche* $HSCH_2CH_2CN$[2].

Searches were made for the simultaneously excited C−O and C−C torsional states, however, with negative result. Perturbation of some kind is suggested as the explanation for this.

12 *Q*-branch lines with $J\leq 17$ having approximately 20 % of the intensities of their ground state counterparts were next assigned and $A-C=8005.494(22)$ MHz and Ray's asymmetry parameter[13] $\kappa=-0.847422$ was determined. *R*-branch lines were difficult to find for this excited state, but tentative assignments were made for two such lines and the *tentative* spectroscopic constants shown in the last column of Table 3 were derived. Because the value of $A-C$ differs relatively much from the corresponding ground state value, this excited state presumably involves large-amplitude motions of heavy atoms. It is therefore assigned as the first excited state of the lowest bending mode of the molecule. Relative intensity measurements yielded 340(50) cm^{-1} for this mode. Perhaps the frequency at 296 cm^{-1} observed in the IR work[5] and assigned as the C−O torsional mode[5,6] should rather be assigned as the lowest bending mode in accordance with the present finding.

Dipole moment of the gauche conformation. The Stark coefficients shown in Table 5 were used to determine the dipole moment employing standard procedure.[14] The results are also shown in Table 5. The dipole moment and its components along the principal axes are quite similar, but a bit larger than the values computed by the bond-moment method and reported above.

Assignment of the ground vibrational state of anti I. A set of preliminary rotational constants of both *anti I* and *anti II* of Fig. 1 were predicted in the same manner as described above for the heavy-atom *gauche* conformation. Both these *anti* rotamers were predicted to be nearly symmetrical tops with Ray's asymmetry parameter[13] $\kappa=-0.99$. The dipole moment components along the principal axes were predicted to be $\mu_a=3.5$ D, $\mu_b=0.2$ D, and $\mu_c=0$ D (for symmetry reasons) for *anti I*, and $\mu_a=2.7$ D, $\mu_b=0.1$ D, and $\mu_c=1.2$ D, respectively, for *anti II* using the bond-moment method.[9] Both these conformations were thus predicted to have relatively strong, simple *a*-type *R*-branch spectra characterized by

Table 6. Microwave spectrum of the ground vibrational state of the *anti I* conformation of $HOCH_2CH_2CN$.

Transition	Observed frequency[a] (MHz)	Obs.−calc. frequency (MHz)	Centrifugal distortion (MHz)
$5_{0,5}\leftarrow4_{0,4}$	22716.90	0.05	−0.22
$5_{1,4}\leftarrow4_{1,3}$	23044.16	−0.01	−0.07
$5_{1,5}\leftarrow4_{1,4}$	22405.47	−0.08	−0.07
$5_{2,3}\leftarrow4_{2,2}$	22736.43	−0.02	0.39
$5_{2,4}\leftarrow4_{2,3}$	22726.42	0.02	0.39
$6_{0,6}\leftarrow5_{0,5}$	27254.54	−0.05	−0.39
$6_{1,5}\leftarrow5_{1,4}$	27651.53	0.05	−0.20
$6_{1,6}\leftarrow5_{1,5}$	26885.20	0.03	−0.20
$6_{2,4}\leftarrow5_{2,3}$	27288.17	−0.05	0.35
$6_{2,5}\leftarrow5_{2,4}$	27270.70	0.06	0.35
$7_{0,7}\leftarrow6_{0,6}$	31789.22	−0.03	−0.62
$7_{1,6}\leftarrow6_{1,5}$	32257.93	−0.03	−0.40
$7_{1,7}\leftarrow6_{1,6}$	31364.06	0.06	−0.40
$7_{2,6}\leftarrow6_{2,5}$	31814.33	0.01	0.25
$8_{0,8}\leftarrow7_{0,7}$	36320.31	−0.04	−0.92
$8_{1,7}\leftarrow7_{1,6}$	36863.48	0.04	−0.67
$8_{1,8}\leftarrow7_{1,7}$	35841.94	0.03	−0.67
$8_{2,6}\leftarrow7_{2,5}$	36399.44	−0.02	0.07
$8_{2,7}\leftarrow7_{2,6}$	36357.31	−0.02	0.07

[a] ±0.10 MHz.

strong pile-ups of all the medium- and high- K_{-1} transitions. These pile-ups should also have very fast Stark effects. Low-K_{-1} transitions are displaced somewhat from these pile-ups, with the two $K_{-1}=1$ transitions displaced the most.

At low Stark voltages, several K_{-1}-pile-up series belonging to the ground and vibrationally excited states of both *anti* forms were immediately noted. The strongest of these series belonged to the ground vibrational state of *anti I*. The $K_{-1}=1$ transitions, so important for the determination of the individual rotational constants, were then found after some searching, because they are relatively weak. The low-K_{-1} lines which were resolved from the pile-ups and used to determine the spectroscopic constants in I^r representation (Table 7), are shown in Table 6. The peak absorption coefficients of the strongest transitions listed in Table 6 were roughly 6×10^{-8} cm^{-1} at room temperature. $I_a+I_b-I_c=6.472(17)\times10^{-20}$ u m^2 as shown in Table 7, is very similar to the corresponding value found for *anti* ethanol[15] (6.40924 (15)$\times10^{-20}$ u m^2) which is known to have C_s-symmetry.[15]

No dipole moment could be determined for this conformation because the lines are so weak. No searches were made for *b*-type transitions since μ_b is predicted to be much smaller than μ_a by the bond-moment method. (See above).

Vibrationally excited states of Anti I. The ground state spectrum was accompanied by a relatively strong satellite spectrum presumably belonging to vibrationally excited state. These spectral features were similar to the observations made for the *anti* forms of $HSCH_2CH_2CN$[2] and $H_2PCH_2CH_2CN$.[3] Due to low intensities, only the high-K_{-1} pile-ups were assigned. Five such lumps of lines were identified; four of which are found on the high-frequency sides of the ground-state pile-ups, and one on the low frequency side. They are assigned as successively excited states of the H_2C-CH_2 torsional mode. $B+C\approx$

Table 7. Spectroscopic constants of the ground vibrational states of the *anti I* conformation of $HOCH_2CH_2CN$ and $DOCH_2CH_2CN$.[a]

Species	$HOCH_2CH_2CN$	$DOCH_2CH_2CN$
Number of transitions	19	17
Root-mean-square (MHz)	0.0449	0.121
A_0 (MHz)	26627.8(243)	26003.8(504)
B_0 (MHz)	2336.5773(39)	2250.0038(99)
C_0 (MHz)	2208.8476(39)	2128.274(12)
Δ_J (kHz)	0.449(27)	0.314(65)
Δ_{JK} (kHz)[b]	−15.46(70)	−9.8(17)
κ[c]	−0.989538	−0.989803
$I_a+I_b-I_c$ (10^{-20} u m^2)[d]	6.472(17)	6.588(38)

[a] Uncertainties represent one standard deviation. [b] Further quartic centrifugal distortion constants kept at zero in the least-squares fit. [c] Ray's asymmetry parameter. [d] Conversion factor 505376×10^{-20} u m^2 MHz.

4551.67(10) MHz (not included in Table 7) for the first excited state of the C−C torsional vibration; $B+C\approx4557.59(10)$ MHz for the second and $B+C\approx4564.11(12)$ MHz, for the third; and $B+C\approx4571.21(15)$ MHz for the fourth vibrationally excited state of this mode. The fact that $B+C$ increases almost linearly upon excitation is typical for a harmonic mode.

The intensity of the K_{-1} pile-up of the first excited state of this mode is about 60 % of that of the ground-state pile-up at room temperature. The C−C torsional frequency is then calculated to be *ca.* 105 cm^{-1}, which is similar to the values found for the *gauche* conformation and reported above.

Another pile-up series found on the low-frequency side of the ground-state pile-ups, was determined to have $B+C\approx4542.66(10)$ MHz. The intensities of these pile-ups are roughly 25 % of the intensities of the corresponding ground-state lumps of lines. This is presumed to be the first excited state of the lowest bending mode, because $B+C$ is somewhat different from the ground state value [4545.4249(55) MHz; Table 7] which is typical for large-amplitude motions involving heavy atoms. Moreover, its relative intensity yields a frequency of *ca.* 290 cm^{-1} which is similar to the value found for the corresponding normal frequency of the *gauche* conformation as mentioned above.

It is remembered (see above) that an excited state having about 40 % of the intensity of the ground state was found for the *gauche* conformation and assigned as the first excited state of the C−O torsional frequency. Small changes of the rotational constants from the ground-state values were found for this excited state. No corresponding excited state was seen for *anti I*, and it is believed that overlapping with the ground state pile-ups is the reason for this because the changes of the rotational constants upon excitation are expected to be small for this excited state. Hence, insufficient resolution from the ground state lines is expected.

Assignment of anti II. A series of high-K_{-1} pile-ups with $B+C\approx4530.18(10)$ MHz (see Table 8) was noted at the same time as *anti I* was assigned. It is most unlikely that this series is a vibrationally excited state of *anti I*, because this would have required an enormous – and highly unexpected – vibrational amplitude. Rather, this series is assigned as belonging to the heavy-atom *anti II* conformation depicted in Fig. 1. The spectrum of the deuterated species which will be discussed below, supports this assignment.

The intensities of these pile-ups were about 40 % of the intensities of the corresponding lumps of lines belonging to the ground vibrational state of *anti I*. Only a tentative assignment of very weak low-K_{-1} lines could be made and the following *tentative* rotational constants which are not included in Table 8, were derived: A=25625.7(3036) MHz, B=2322.167(51) MHz, C=2207.360(48) MHz. The fit had a root-mean-square deviation of 0.755 MHz for 12 transitions, which is not sufficiently convincing to be certain that correct assignment has been achieved.

There could be two major reasons why the low-K_{-1} lines were not found. The first one is obvious, namely the low intensities of these transitions. The other one is splittings or perturbations caused by tunneling between the two mirror-image forms of *anti II*, similar to the ones already observed for *gauche* ethanol.[12]

Two vibrationally excited state pile-ups were assigned for *anti II* in analogy with the findings made for *anti I*. The first excited state of the C–C torsional vibration has $B+C\approx4537.32(15)$ MHz (not included in Table 8), while the lowest heavy-atom bending mode has $B+C\approx4528.03(15)$ MHz.

Energy differences. Unfortunately, no dipole moment could be obtained for the two heavy-atom *anti* conformations, and the dipole moment calculated by the bond-moment method and reported above had to be used in the internal energy difference calculations. $K_{-1}=1$ lines of *anti I* were compared with low-J b-type lines of the hydrogen-bonded *gauche* conformation. Harrington's technique of power saturating the transitions[16] as well as the ordinary use of completely unsaturated lines were employed.[17] The statistical weight of the *gauche* conformation was assumed to be twice that of *anti I*. In this manner, the hydrogen-bonded *gauche* rotamer was found to be 2.7 kJ/mol more stable than the *anti I* conformation. One standard deviation was estimated to be 0.4 kJ/mol. The fact that μ_a of *anti I* is not known experimentally, but calculated by the bond-moment method, is taken into consideration in the quoted one standard deviation.

The internal energy difference between *anti I* and *anti II* were determined by comparing the peak intensities of pile-ups involving the same J quantum number in the limit of no power saturation. The statistical weight of *anti II* was assumed to be twice that of *anti I*. Thus, it was found that *anti I* is more stable than *anti II* by 4.7 kJ/mol. The total uncertainty limit which is approximately equal to three standard deviations is estimated to be a liberal ±2 kJ/mol. The hydrogen-bonded heavy-atom *gauche* conformation is thus more stable than *anti II* by 7.4(24) kJ/mol, where the uncertainty limit of ±2.4 kJ/mol represents approximately three standard deviations.

Table 8. Microwave spectrum and approximate values of $B+C$ for the *anti II* conformation of $HOCH_2CH_2CN$ and $DOCH_2CH_2CN$.

Species Transition	$HOCH_2CH_2CN$ Observed frequency[a] (MHz)	≈B+C (MHz)	$DOCH_2CH_2CN$ Observed frequency[a] (MHz)	≈B+C (MHz)
$6\leftarrow5^b$	27180.91	4530.15	26324.67	4387.45
$7\leftarrow6^b$	31711.22	4530.17	30712.74	4387.53
$8\leftarrow7^b$	36241.83	4530.23	35100.90	4387.61
$9\leftarrow8^b$	–[c]		39490.63	4387.85
Average		4530.18(10)		4387.61(15)

[a] ±0.15 MHz. [b] Centre frequencies of high-K_{-1} pile ups. [c] Not measured.

Table 9. Plausible molecular structure[a] (bond lengths in *pm*; angles in *degrees*) of the *gauche*, *anti I* and *anti II* conformations of $HOCH_2CH_2CN$.

Structural parameters kept fixed

C≡N	115.7	∠CCN	180.00	
C–O	141.5	∠CCH	109.47	
C–C	153.8	∠HCH	109.47	
C–CN	147.4	∠COH	104.00	
C–H	109.3	∠OCC	108.00	for *anti I*
O–H	97.0	∠OCC	112.50	for *gauche* and *anti II*
		∠HOCC[b]	0.00	for *anti I*
		∠HOCC[b]	120.00	for *gauche* and *anti II*
		∠OCCC[c]	180.00	for *anti* forms

Fitted structural parameters

Conformation	*gauche*	*anti I*	*anti II*
∠CCC	109.5(15)	109.0(15)	109.0(15)
∠OCCC from *syn*[c]	59(3)	–[d]	–[d]

Rotational constants (MHz) of the *gauche* conformation

	$HOCH_2CH_2CN$			$DOCH_2CH_2CN$		
	Obs.	Obs.–calc.	Diff. (%)	Obs.	Obs.-calc.	Diff. (%)
A	10726.4535	−7.31	0.07	10237.154	−71.12	0.69
B	3432.3084	−13.89	0.40	3419.491	−13.28	0.39
C	2815.6078	−0.25	0.01	2771.972	−4.94	0.18

Kraitchman's coordinates[e] of the hydroxyl group hydrogen atom of the *gauche* conformation

	$\|a\|$	$\|b\|$	$\|c\|$
From rotational constants	0.74457(37)	1.51463(20)	imaginary
From plausible structure	0.753	1.404	0.007

Hydrogen bond parameters of the *gauche* conformation

$H\cdots C_N$	246	$H\cdots N$	295
$O\cdots C_N$	290	$O\cdots N$	364
$\angle O{-}H\cdots C$	107	$\angle O{-}H\cdots N$	129
∠O–H, C≡N[f]	5		

Sum of van der Waals radii[g]

$H\cdots C$[h]	290	$H\cdots N$	270
$O\cdots C$[h]	310	$O\cdots N$	290

Rotational constants (MHz) of the *anti I* conformation

	$HOCH_2CH_2CN$			$DOCH_2CH_2CN$		
	Obs.	Obs.-calc.	Diff. (%)	Obs.	Obs.-calc.	Diff. (%)
A	26627.8	552.9	2.07	26003.8	599.8	2.31
B	2336.5773	1.84	0.08	2250.0038	−1.26	−0.06
C	2208.8476	6.00	0.27	2128.274	4.47	0.21

Kraitchman's coordinates[e] of the hydroxyl group hydrogen atom of the *anti I* conformation

	$\|a\|$	$\|b\|$	$\|c\|$
From rotational constants	2.8827(39)	0.645(16)	0.250(45)
From plausible structure	2.8080	0.694	0.0

B+C (MHz) for the *anti II* conformation

	$HOCH_2CH_2CN$			$DOCH_2CH_2CN$		
	Obs.	Obs.-calc.	Diff. (%)	Obs.	Obs.-calc.	Diff. (%)
B+C	≈4530.18	4.69	0.10	≈4387.61	−18.09	0.41

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[a] See text. [b] H−O−C−C dihedral angle. [c] O−C−C−C dihedral angle. [d] Not fitted; kept at 180°. [e] Ref. 33. [f] Angle between O−H and C≡N bonds. [g] Ref. 35. [h] van der Waals radius of carbon assumed to be 170 pm as in aromatic systems.[35]

Three comments are in order: The internal energy difference between *anti II* and *anti I* of 4.7(20) kJ/mol is similar to the most recent and accurate enthalpy difference of 2.9(2) kJ/mol found for the corresponding *gauche-anti* conformational equilibrium of ethanol.[18] The internal energy difference between the *anti I* and *gauche* conformations of $HOCH_2CH_2CN$ is similar to the value (2.9(13) kJ/mol) found in the IR-work between *gauche* and the unspecified *anti* form.[4] Moreover, in recent years, 2-ethanol derivatives of the form XCH_2CH_2OH, where X=F,[19] Cl,[20] Br,[20] OH,[21] NH_2,[22] SH,[23] $HC=CH_2$,[24] C≡C−H,[25] OCH_3,[26] $NH(CH_3)$,[27] $\overline{CH_2-CH_2N}$,[28] and $N(CH_3)_2$,[29] have been studied in the gaseous state by microwave spectroscopy. In all these cases, the hydrogen-bonded *gauche* conformations have been found to predominate to such an extent that no further rotamers have been identified by this method. $HOCH_2CH_2CN$ is thus the first example of a 2-substituted ethanol derivative where a hydrogen-bonded *gauche,* as well as the two possible *anti* conformations, have been assigned by microwave spectroscopy.

Deuterated species. The deuterated species, $DOCH_2CH_2CN$, was studied in order to obtain information about the hydroxyl group hydrogen atom position. 35 transitions were readily assigned for the heavy-atom hydrogen-bonded *gauche* conformation and the spectroscopic constants shown in Table 2 were determined. Likewise, 17 transitions were assigned for *anti I,* and the spectroscopic constants shown in Table 7 were derived. The fact that the values of $I_a+I_b-I_c$ (Table 7) of the parent and the deuterated species are so similar shows that the deuterium substitution has taken place in the symmetry plane of the *anti I* conformation.

From the plausible structure of *anti II* to be discussed below, a shift of −119.79 MHz was calculated for $B+C$ upon deuteration. As seen from Table 8, a shift of $B+C$ of −142.57 MHz was observed. The rather large discrepancy of 22.78 MHz is believed to be caused by the large amplitude C−O and C−C torsional motions.

Structure of the three conformations. Only two isotopic species were studied for the three rotamers assigned in this work. A complete geometrical structure cannot, therefore, be determined for each one of the three conformations. The structural parameters kept fixed are shown in Table 9. They are taken from recent accurate, structural studies of related compounds. Two of these parameters need additional comments: the C−C≡N chain of atoms was assumed to be linear although it is known that small deviations from linearity do occur. The CCO angle was assumed to be 108° for *anti I,* close to the substitution structure value found for *anti* ethanol.[15] In hydrogen-bonded molecules such as $HOCH_2CH_2Cl$[20,30]

and $HOCH_2CH_2CH=CH_2$[31] as well as in *gauche* ethanol[32] a large CCO angle of 112–113° has been found in accurate structural studies, and this angle was assigned a value of 112.5° in the *gauche* and *anti II* conformations.

The CCC angles were the only parameters fitted for the two *anti* forms, while the CCC angle and the OCCC dihedral angle were fitted for the heavy-atom hydrogen-bonded *gauche* conformation. These parameters were selected because they are chemically interesting and because the rotational constants are sensitive to variations in them.

The CCC angles were fitted in steps of 0.5° and the OCCC dihedral angle in steps of 1°. The CCC angle was found to be 109.5° in the *gauche* conformation and 109.0° in the two *anti* forms. The error limit is estimated to be ±1.5°, which is approximately three standard deviations. The inherent uncertainties of the assumed structural parameters are taken into account in this error limit. The OCCC dihedral angle of the *gauche* conformation was found to be 59° with an uncertainty limit (about three standard deviations) of ±3° (Table 9).

Rotational constants of the deuterated species are available for the *gauche* and *anti I* conformations and Kraitchman's coordinates[33] for the hydroxyl hydrogen atom are shown in Table 9 for these two rotamers. Initially, attempts were made to fit structural parameters of the hydroxyl group, but once more[22b,24,2] unacceptable structural parameters were found, especially for the *gauche* and the *anti II* conformations. In the case of *anti II,* for example, a fit of the HOCC dihedral angle to the changes of $B+C$ caused by deuteration led to an angle about 20° less than the presumed 120° *gauche* angle. Moreover, an unacceptably long O–H bond length resulted in the case of the *gauche* conformation.

van Eick[34] has recently discussed the difficulties of determining structural parameters of hydrogen atoms attached to heavy atoms involved in large-amplitude motions. His conclusions were rather pessimistic as to the accuracy of structural parameters obtained by deuterium substitutions of such hydrogen atoms. Such a situation seems to be the case for $HOCH_2CH_2CN$ too, especially for the *gauche* and *anti II* conformations.

In the final fits, the O–H bond lengths were therefore kept at the plausible 97.0 pm and the COH angle at 104° for all three conformations as shown in the top of Table 9. The HOCC dihedral angles were likewise chosen to be fixed at 120° from *anti* positions in the *gauche* and *anti II* conformations, and to be fixed at 0° in *anti I.* There is reasonably good over-all agreement between the observed and calculated rotational constants, and between Kraitchman's coordinates[33] of the hydroxyl group hydrogen atom and its structural coordinates calculated from the plausible structure as shown in Table 9.

DISCUSSION

The present work agrees with the IR-finding[5] in that the heavy-atom *gauche* conformation is the most stable form of the molecule. It appears that some sort of weak attraction, presumably a hydrogen bond, is formed between the hydroxyl group hydrogen atom and the cyano group. This stabilization is probably mainly electrostatic in origin, since the O–H and C≡N bonds are about 5° from being parallel (Table 9) which is ideal for dipole-dipole interaction. In addition, covalent forces formed between the hydroxyl group hydrogen atom and the π electrons of the cyano group may play a small role in stabilizing the *gauche* conformation, because the $H\cdots C_N$ distance is about 44 pm shorter than the sum of the van der Waals radii[35] of hydrogen and carbon. (Table 9) (The van der Waals radius of carbon has here been taken to be 170 pm as in aromatic molecules.[35]) Similar results have been found for $H_2NCH_2CH_2CN$,[1] $HSCH_2CH_2CN$,[2] and $H_2PCH_2CH_2CN$.[3]

Microwave data of four 3-substituted propanenitrile derivatives, XCH_2CH_2CN, with X=OH, NH_2, SH, and PH_2 are now available. Selected conformtional and energy difference data are collected in Table 10. It is seen from this table that the XCCC dihedral angles of the heavy-atom hydrogen-bonded *gauche* forms are close to 60° in all cases. The energy differences between *anti* and *gauche* conformations follow the usual trend in that the hydroxyl and amino groups on the one hand are capable of forming considerably stronger hydrogen bonds than the thiol and phosphino groups on the other hand.

Table 10 also reveals that it is important to specify what is actually meant by intramolecular hydrogen-bond strength. *E.g.*, the *gauche* conformation of $HOCH_2CH_2CN$ is transformed into the *anti II* form by rotation about the central C−C bond by approximately 120°. Another rotation of some 120° about the C−O bond is again needed to reach the *anti I* conformation. *Anti II* is less stable than *gauche* by 7.4(24) kJ/mol, and *anti I* less stable than *gauche* by 2.7(4) kJ/mol. (The uncertainties of these two numbers are the uncertainty limit which is approximately equal to three standard deviations in the former case, and one standard deviation in the latter, respectively). The molecule thus relaxes from the *anti II* into the *anti I* conformation with a gain in energy of about 4.7 kJ/mol.

Should the strength of the intramolecular hydrogen bond, to be compared with other molecular systems, be taken to be approximately the internal energy difference between *anti I* and *gauche,* or between *anti II* and *gauche?* We are in favour of the latter, because *only* rotation about the central C−C bond and no further relaxations are involved. An approximate value for the intramolecular hydrogen-bond strength is then 7.4(24) kJ/mol for $HOCH_2CH_2CN$. Likewise, the hydrogen-bond strength is taken to be 1.3(20) kJ/mol for $HSCH_2CH_2CN$, equal to the energy difference between *anti II* and *gauche* of this molecule.[2]

Conformation *V* (see Fig. 1 of Ref. 3) of $H_2PCH_2CH_2CN$[3] is transformed into conformation *II* by rotation about the central C−C bond. The energy difference between these two forms[3] (Table 10) is 0.3(20) kJ/mol which is then taken to be the internal hydrogen-bond strength. Another pair, *viz.* conformations *I* and *IV* (see Fig. 1 of Ref. 3) of $H_2PCH_2CH_2CN$, are also related to each other by a rotation about the C−C bond, but in this case conformation *I* was not assigned and this hydrogen-bond strength thus remains unknown.

Table 10. Selected conformational and internal energy difference data for four XCH_2CH_2CN-type molecules.

Molecule	∠X−C−C−C[a] (degrees)	$\Delta E_0^\circ = E^\circ_{0\,anti} - E^\circ_{0\,gauche}$ (kJ/mol)
$HOCH_2CH_2CN$[b]	59(3)	2.7(12)[i] 7.4(24)[j]
$H_2NCH_2CH_2CN$[c]	63(3)[f]	>4[k]
$H_2NCH_2CH_2CN$[c]	59(3)[g]	>4[k]
$HSCH_2CH_2CN$[d]	65(3)	1.3(20)[l] >2.3[k,m]
$H_2PCH_2CH_2CN$[e]	66(3)[h]	0.3(20)[n] 3(2)[o]

[a] Dihedral angle of *gauche* measured from *syn*=0°. [b] This work. [c] Ref. 1. [d] Ref. 2. [e] Ref. 3. [f] Conformation I. [g] Conformation II. [h] Conformation II. [i] *Anti I;* uncertainties of this table are error limits approximately equal to three standard deviations. [j] *Anti II.* [k] Estimated; *anti* conformation not assigned. [l] *Anti II.* [m] *Anti I.* [n] Conformation *V.* [o] Conformation *IV.*

$H_2NCH_2CH_2CN$ (see Fig. 1 of Ref. 1) resembles $H_2PCH_2CH_2CN$ in its conformational properties. However, no *anti* forms were seen for the former molecule. Such conformations were estimated to be more than 4 kJ/mol[1] (Table 10) less stable than the two assigned heavy-atom hydrogen-bonded *gauche* conformations denoted *I* and *II*.[1] The intramolecular hydrogen-bond strengths are thus more than 4 kJ/mol for each of conformation *I* and *II* of $H_2NCH_2CH_2CN$. Presumably, they are less than 7.4(24) kJ/mol found for $HOCH_2CH_2CN$, because the hydroxyl group is generally a better proton donor than the amino group.

The results found for the four molecules considered in Table 10 are in harmony with the usual presumption that the proton donating ability decreases in the order $OH > NH_2 > SH \geq PH_2$.

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