Microwave Spectrum, Conformational Equilibrium, Intramolecular Hydrogen Bonding, ^{14}N Nuclear Quadrupole Coupling Constants and Centrifugal Distortion Constants of 1-Amino-3-butyne

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The microwave spectrum of 1-amino-3-butyne, $H_2NCH_2CH_2C\equiv CH$, has been investigated in the 18.0−32.0 GHz spectral region at −40 °C. Two C−C−C−N *gauche* conformations denoted I and II were assigned. Both these rotamers are stabilized by an intramolecular hydrogen bond formed between the amino group hydrogen atom and the C≡CH group. The energy difference between I and II is 1.5(20) kJ/mol with I as the more stable conformation. I is also estimated to be at least 3 kJ/mol more stable than any further rotamer.

The C−C−C−N dihedral angles are 63(3)° from *syn* in I and 60(3)° from *syn* in II. The C−C−N angle has a "normal" value of 108.3(15)° in I, while this angle opens up to 113.5(15)° in II. The angle between the N−H bond involved in hydrogen bonding and the C≡C bond is about 4° from being parallel in I and about 6° from being parallel in II.

Two vibrationally excited states were found for I, while only one such state was identified for II. Accurate centrifugal distortion constants were determined for I and II and used to determine the C−C torsional frequency as 111(10) cm^{-1} for I and 115(10) cm^{-1} for II.

^{14}N nuclear quadrupole coupling constants of conformation I are χ_{aa}=1.94(47) MHz and χ_{bb}=2.34(17) MHz. No determination of these constants was possible for II.

Molecules possessing intramolecular hydrogen bonds have received considerable attention by microwave spectroscopists in recent years. Ethylamine derivatives, $H_2NCH_2CH_2X$, where X is some proton accepting or donating group have been found to possess varied conformational properties. *E.g.*, $H_2NCH_2CH_2F$,[1] $H_2NCH_2CH_2CN$,[2] and $H_2NCH_2CH_2NH_2$[3] all prefer *two* heavy-atom *gauche* conformations stabilized by intramolecular hydrogen bonds while $H_2NCH_2CH_2OCH_3$[4] has *one* such form. The most stable form of $H_2NCH_2CH_2OH$[5] is again the *gauche,* but in this case the hydroxyl group is proton donor and the amino group is acceptor. Two N−C−C−S *gauche* conformations were found for $H_2NCH_2CH_2SH$.[6] In one of these, the less stable one, the amino group is proton acceptor and the mercapto group is proton donor in a very weak intramolecular hydrogen bond.

$H_2NCH_2CH_2C\equiv CH$ was chosen for study because we wanted to investigate the possible hydrogen-bond interaction between the amino and acetylene groups thereby extending the list of ethylamine derivatives investigated by microwave spectroscopy. Five all-staggered
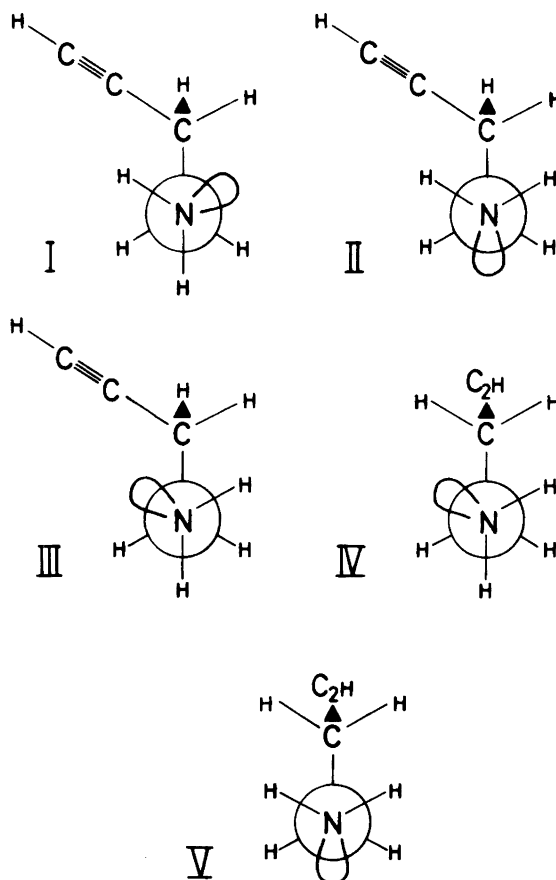
Fig. 1. Possible conformations of $H_2NCH_2CH_2C\equiv CH$ with all-staggered atomic arrangements. I and II, both containing intramolecular hydrogen bonds, were assigned and the energy difference between them determined to be 1.5(20) kJ mol^{-1} with I as the more stable. I is furthermore at least 3 kJ mol^{-1} more stable than any one of III, IV or V.

conformations are possible for this molecule as shown in Fig. 1. Intramolecular hydrogen bonds are possible for the N$-$C$-$C$-$C *gauche* conformations I and II, while this kind of interaction is not possible for the other three conformations III, IV and V.

It is found in this work that I and II are preferred conformations of the molecule, but the stable coexistence of considerable fractions of further conformations, *e.g.* N$-$C$-$C$-$C *anti* forms cannot be ruled out.

EXPERIMENTAL

1-Amino-3-butyne was donated by Professor Björn Lindeke, Department of Pharmaceutical Chemistry, Biomedical Center, University of Uppsala, Sweden, and purified by gas chromatography before use. Thorough studies were made in the 18.0$-$30.0 GHz spectral region. Selected spectral ranges above 30.0 GHz were also searched, particularly for possible *a*-type, *R*-branch $K_{-1} \neq 1$ pile-ups of the two hypothetical N$-$C$-$C$-$C *anti*

conformations. The cell was cooled with dry ice to about -40 °C. Lower temperatures could not be used because of insufficient vapour pressure of the compound. The spectrum was recorded at pressures in the $2-6$ Pa range. Free-running klystrons were employed as radiation sources. With this equipment, quadrupole fine-structure splittings larger than about 0.6 MHz were resolved.

RESULTS

Spectrum. The microwave spectrum of 1-amino-3-butyne is very dense and relatively weak. About 420 lines with peak absorption coefficients between roughly 2×10^{-8} and 2×10^{-7} cm^{-1} at -40 °C, were observed and measured in the $18.0-30.0$ GHz region. The Stark effects of all these lines were studied, but not a single one of them was found to be resolved. The Stark effects were of two categories. One type of lines had relatively slow Stark effects which is typical for high-J Q-branch lines of a prolate rotor. The other type had very fast Stark effects typical for high-J P-and R-branch lines of a prolate rotor possessing a non-zero μ_a. The fact that there were so many Q-branch lines made us conclude that most of them had to be c-type transitions.

The lack of resolved Stark effects, as well as the fact that assignments had to be made *via* high J-transitions, made the assignments of the two conformations a bit difficult as elucidated below.

Assignment of the ground vibrational state of conformation I. Preliminary rotational constants of I were computed by combining structural parameters taken from related compounds (see Table 7), and from these constants a rigid-rotor spectrum was calculated. Bond moment calculations were performed using the values of Ref. 7, but with one important difference. The method of Ref. 7 does not include any bond-moments for bonds between sp- and sp^3-hybridized carbon atoms, and because of this it can not reproduce the dipole moment of about 0.8 D found for propyne;[8] in fact it yields a dipole moment of 0 D for this compound. In addition to the usual bond moments, it was therefore necessary to include a bond moment of 0.8 D in the $C-CCH$ bond with positive end at the sp^3-hybridized carbon atom. This procedure reproduces the dipole moment of propyne, and therefore it is believed that this is the best way to predict the dipole moments of the conformations of the title compound. The dipole moment components were then predicted to be μ_a=0.6 D, μ_b=0.4 D, and μ_c=0.8 D for I.

Searches were therefore first made for relatively strong low-J a- and c-type lines. However, no such lines were initially found due to their absolute weakness.

The next step was then to search for c-type Q-branch K_{-1}=3$\leftarrow$2 and K_{-1}=4$\leftarrow$3 transitions with J between 12 and 25. These lines were predicted to be among the strongest ones of conformation I. However, due to the inherent uncertainty of the model rotational constants, their spectral positions were uncertain by about ± 3 GHz. Moreover, centrifugal distortion was presumed to be prominent for these transitions, which complicates the rigid rotor fit which must be employed initially.

A large number of different combinations had to be tried out before it was possible to identify these transitions by their unresolved, slow Stark effects and near rigid-rotor fit. Assignments were then successively extended to include higher and higher values of J for the various c-type Q-branch series transitions occurring in the investigated spectral range. Allowance had to be made for centrifugal distortion in this process. The maximum J value definitely assigned was 77 for the $77_{13,65} \leftarrow 77_{12,65}$ transition (see Table 1). Its peak intensity was roughly 3×10^{-8} cm^{-1}. Transitions with even higher values of J were searched for, but

Table 1. Selected transitions for the ground vibrational state of conformation I of $H_2NCH_2CH_2C{\equiv}CH$.

Transition	Observed frequency[a] (MHz)	Obs.−calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
$3_{2,2} \leftarrow 3_{1,2}$	20313.02	−0.21	−0.03	
$4_{2,2} \leftarrow 4_{1,4}$	25545.27	0.17	−0.67	
$7_{1,6} \leftarrow 6_{2,4}$	25009.87	−0.07	−6.32	
$12_{3,9} \leftarrow 11_{4,7}$	25908.28	0.06	−41.38	0.01
$12_{3,10} \leftarrow 11_{4,8}$	20887.31	0.03	−22.34	0.01
$13_{3,11} \leftarrow 13_{2,11}$	20090.16	−0.08	41.64	−0.02
$14_{1,14} \leftarrow 13_{2,12}$	28637.64	0.16	4.71	
$15_{4,11} \leftarrow 14_{5,9}$	28287.00	−0.03	−71.69	0.04
$15_{4,12} \leftarrow 14_{5,10}$	25832.37	−0.05	−50.90	0.03
$17_{5,12} \leftarrow 16_{6,10}$	24291.24	−0.06	−82.12	0.06
$18_{4,15} \leftarrow 18_{3,15}$	28434.31	0.16	133.93	−0.11
$19_{4,16} \leftarrow 19_{3,16}$	24658.30	−0.10	154.00	−0.13
$20_{4,17} \leftarrow 20_{3,17}$	20929.14	−0.11	171.04	−0.15
$25_{5,21} \leftarrow 25_{4,21}$	28472.85	0.13	401.39	−0.53
$26_{5,22} \leftarrow 26_{4,22}$	24035.95	0.07	426.04	−0.57
$27_{5,23} \leftarrow 27_{4,23}$	19854.16	−0.11	437.45	−0.61
$32_{6,27} \leftarrow 32_{5,27}$	26702.83	0.00	878.76	−1.69
$33_{6,28} \leftarrow 33_{5,28}$	21998.20	0.09	877.03	−1.73
$38_{7,32} \leftarrow 38_{6,32}$	29090.04	0.18	1600.91	−4.15
$39_{7,33} \leftarrow 39_{6,33}$	23928.58	−0.19	1565.43	−4.15
$40_{7,34} \leftarrow 40_{6,34}$	19300.18	−0.08	1484.41	−4.03
$45_{8,38} \leftarrow 45_{7,38}$	25770.08	−0.01	2575.49	−8.84
$46_{8,39} \leftarrow 46_{7,39}$	20801.63	0.01	2409.89	−8.45
$51_{9,43} \leftarrow 51_{8,43}$	27638.54	−0.12	3993.90	−17.20
$52_{9,44} \leftarrow 52_{8,44}$	22349.72	0.03	3702.19	−16.26
$58_{10,49} \leftarrow 58_{9,49}$	24042.47	−0.08	5461.28	−29.35
$64_{11,54} \leftarrow 64_{10,54}$	25982.91	0.05	7817.92	−50.40
$65_{11,55} \leftarrow 65_{10,55}$	20837.88	−0.01	7006.08	−45.96
$70_{12,59} \leftarrow 70_{11,59}$	28283.97	0.16	10945.35	−83.31
$77_{13,65} \leftarrow 77_{12,65}$	25228.56	−0.09	13547.81	−121.83

Coalescing K_{-1}-doublet lines[b]

Transition	Observed frequency[a] (MHz)	Obs.−calc. frequency (MHz)	Total (MHz)	Sextic (MHz)
$15_9 \leftarrow 16_8$	28005.24	0.07	−60.97	0.29
$20_{11} \leftarrow 21_{10}$	26988.44	−0.10	−77.37	0.67
$25_{13} \leftarrow 26_{12}$	25962.11	−0.04	−83.25	1.32
$32_{16} \leftarrow 33_{15}$	27495.74	−0.01	−99.40	3.34
$36_{13} \leftarrow 35_{14}$	21071.04	−0.01	−480.38	1.73
$38_{14} \leftarrow 37_{15}$	18377.29	−0.10	−524.06	1.99
$37_{18} \leftarrow 38_{17}$	26487.26	−0.02	−66.98	5.28
$42_{15} \leftarrow 41_{16}$	28171.22	−0.13	−809.11	4.12
$40_{19} \leftarrow 41_{18}$	22939.18	−0.10	18.33	5.77
$44_{16} \leftarrow 43_{17}$	25446.14	0.05	−874.41	4.74
$42_{20} \leftarrow 43_{19}$	25500.99	−0.06	−6.11	7.88
$49_{18} \leftarrow 48_{19}$	26208.34	−0.07	−1172.11	7.78
$54_{20} \leftarrow 53_{21}$	26914.13	−0.01	−1529.10	12.15

[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}.

Table 2. Spectroscopic constants of the ground state of conformation I of $H_2NCH_2CH_2C\equiv CH$.[a]

	Vibrational state	Ground state
	N.o.t.[b]	111
	Rms (MHz)[c]	0.111
A_0 (MHz)		10349.460(11)
B_0 (MHz)		3293.3850(35)
C_0 (MHz)		2708.4104(30)
Δ_J (kHz)		3.329(13)
Δ_{JK} (kHz)		$-19.449(79)$
Δ_K (kHz)		63.923(22)
δ_J (kHz)		1.0144(11)
δ_K (kHz)		8.49(14)
H_J (Hz)		$-0.0016(14)$
H_{JK} (Hz)		$-0.0753(43)$
H_{KJ} (Hz)		$-0.728(94)$
H_K (Hz)[d]		2.28(17)

[a] Uncertainties represent one standard deviation. [b] Number of transitions. [c] Root-mean-square deviation. [d] Further sextic constants preset at zero.

not identified, presumably because of insufficient intensities.

A new effort was now made to identify the low-J a- and c-type R-branch lines, in order to determine all three rotational constants, but again these lines were not found because of their weakness.

The strongest c-type R-branch lines in the spectrum are the coalescing K_{-1}-transitions with $30<J<45$. These lines have fast Stark effects provided $\mu_a\neq0$. A trial and error search among relatively strong lines with such Stark effects finally led to the complete assignment. Maximum values of J and K_{-1} (for the coalescing K_{-1}-doublets) were $54_{20}\leftarrow53_{21}$ for the R-, and $44_{21}\leftarrow45_{20}$ for the P-branch transitions. A total of about 120 c-type transitions were assigned for the ground vibrational state of conformation I; 56 of these are shown in Table 1. (The complete spectra of conformations I and II are available from the authors upon request, or from the Molecular Spectra Data Center, National Bureau of Standards, Bld. 221, Rno. B265, Washington D.C. 20234, U.S.A., where they have been deposited.) 111 of these were used to derive the spectroscopic constants (I^r representation) shown in Table 2.

The lines which were split by quadrupole coupling between the ^{14}N nucleus and the overall rotation, were included in the final fit after allowance had been made for this effect in the manner to be described in the section on quadrupole coupling.

As shown in Table 2, accurate values were found for the quartic, while the four sextic constants used are of a rather poor quality and they were only included to give a good fit.

The spectroscopic constants of Table 2 very accurately predict the frequencies of hypothetical a- and b-type transitions. However, none of these were definitely identified, presumably because of insufficient intensities caused by small a- and b-axis dipole moment components. Small values for these two dipole moment components were also predicted by the procedure outlined above.

Vibrationally excited states of I. Two vibrationally excited states of I were assigned. The strongest of these excited states had approximately 50 % of the ground state intensity at about -40 °C, and is assumed to be the first excited state of the C$-$C torsional vibration. For this excited state, it was only possible to assign about 25 transitions of the c-type

Table 3. Assumed diagonal force field, centrifugal distortion constants and torsional frequency for conformations I and II of $H_2NCH_2CH_2C\equiv CH$.

Stretching 10^2 Nm^{-1})	$C\equiv C$	15.22	N−C	5.10
	N−H	6.40	C−H	4.71
	CC−H	5.98	C−C	4.42
	C−CC	5.14		

Bending (aJ rad^{-2})	C−C−C	2.14	CC−C−H	0.67
	C−C−N	1.30	H−C−C	0.66
	H−C−N	0.90	H−C−H	0.53
	C−N−H	0.85	H−N−H	0.47

	Conformation I		Conformation II	
	H−C≡C	0.13[b]	H−C≡C	0.19[b]
	C−C≡C	0.17[b]	C≡C−C	0.15[b]

Torsion (aJ rad^{-2})	C−N	0.10		

	Conformation I		Conformation II	
	C−C	0.173[c]	C−C	0.215[c]

Centrifugal distortion constants (kHz)	Conformation I		Conformation II	
	Obs.	Calc.	Obs.	Calc.
Δ_J	3.329	3.349	3.324	3.184
Δ_{JK}	−19.499	−19.465	−19.814	−18.322
Δ_K	63.923	63.963	62.098	62.626
δ_J	1.014	1.065	1.020	0.991
δ_K	8.490	8.324	7.441	7.085

C−C torsional frequency (cm^{-1})		I	II
	From relative intensities[a]	82(30)	90(30)
	From force-field calculation[a,d]	111(10)	115(10)

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

Q-branch series with maximum value of *J* for the $65_{11,55} \leftarrow 65_{10,55}$ transition. 22 of these transitions were used to determine the spectroscopic constants. However, since no *P*- or *R*-branch transitions were assigned, only $A-C$ and κ could be derived. The values were: $A-C=7729.767(63)$ MHz and $\kappa=-0.850049$ (not included in Table 2).

Relative intensity measurements yielded 82(30) cm^{-1} for this vibration. A rough diagonal force field was estimated for I in order to calculate the C−C torsional frequency utilizing the quartic centrifugal distortion constants in the manner described previously.[9] A torsional frequency of 111 cm^{-1} was obtained. Its uncertainty is estimated to be ± 10 cm^{-1}, a

Table 4. [14]N quadrupole splittings[a] and diagonal elements of the quadrupole coupling tensor of conformation I of $H_2NCH_2CH_2C\equiv CH$.

Transition	$F' \leftarrow F$	E_q (obs.) (MHz)	E_q (obs.)$-E_q$ (calc.) (MHz)
$9_{3,7} \leftarrow 9_{2,7}$	$8 \leftarrow 8$	$-0.34(6)$	-0.05
	$9 \leftarrow 9$	$0.38(4)$	-0.11
	$10 \leftarrow 10$	$-0.34(5)$	-0.13
$10_{3,8} \leftarrow 10_{2,8}$	$9 \leftarrow 9$	$-0.28(6)$	0.03
	$10 \leftarrow 10$	$0.55(4)$	0.02
	$11 \leftarrow 11$	$-0.28(5)$	-0.05
$11_{3,9} \leftarrow 11_{2,9}$	$10 \leftarrow 10$	$-0.30(6)$	0.01
	$11 \leftarrow 11$	$0.49(4)$	-0.06
	$12 \leftarrow 12$	$-0.30(5)$	-0.06
$12_{3,10} \leftarrow 12_{3,9}$	$11 \leftarrow 11$	$-0.28(6)$	0.03
	$12 \leftarrow 12$	$0.55(4)$	0.01
	$13 \leftarrow 13$	$-0.28(5)$	-0.04
$2_{2,1} \leftarrow 1_{1,1}$	$2 \leftarrow 1$	$-1.06(4)$	-0.04
	$3 \leftarrow 2$	$0.11(3)$	-0.14
$3_{1,2} \leftarrow 2_{0,2}$	$4 \leftarrow 3$	$0.21(3)$	-0.08
$4_{1,3} \leftarrow 3_{0,3}$	$4 \leftarrow 3$	$-1.08(4)$	-0.13
	$5 \leftarrow 4$	$0.27(3)$	-0.06
$7_{0,7} \leftarrow 6_{1,5}$	$7 \leftarrow 6$	$1.32(4)$	-0.01
	$8 \leftarrow 7$	$-0.57(5)$	-0.03

Quadrupole coupling constants
$\chi_{aa}=1.94(47)$ MHz, $\chi_{bb}=2.14(27)$ MHz

[a] Uncertainties represent one standard deviation.

considerable improvement of accuracy as compared to $82(30)$ cm^{-1} obtained by relative intensity measurements.

In addition to its frequency, changes of $A-C$ upon excitation also indicate that this is indeed the first excited state of the C–C torsional vibration. The observed values were $\Delta(A-C)=88.7$ MHz as compared to $\Delta(A-C)=75.6$ MHz found by increasing the C–C–C–N dihedral angle of the plausible structure (see below) by $1.5°$ from *syn*.

It was not possible to assign the second excited state of the C–C torsional vibration, presumably because of too low intensities.

14 c-type Q-branch transitions for another excited state were also assigned, with maximum value of J for the $64_{11,54} \leftarrow 64_{10,54}$ transition. $A-C$ was determined to be $7656.66(12)$ MHz and $\kappa=-0.847167$.

For this vibration, the value of κ is very similar to the ground state value, and $A-C$ has only increased by 15.6 MHz as compared to that of the ground state. This implies that little reduced mass is involved in this vibration which is therefore assumed to be the C–N torsional vibration. Relative intensity measurements yielded $182(50)$ cm^{-1} for this vibration which is close to the values found for $H_2NCH_2CH_2CN$[2] and CH_3NH_2[10].

[14]N *quadrupole coupling constants of I.* The quadrupole coupling constants of I were predicted by assuming that the principal axis quadrupole coupling constant of NH_3, $\chi_z=-4.1$ MHz, could be used in the present case and oriented along the "lone-pair" symmetry axis. The results were $\chi_{aa}=1.9$ MHz and $\chi_{bb}=2.0$ MHz.

For this conformation many lines were split due to quadrupole coupling of the [14]N

Table 5. Selected transitions for the ground vibrational state of conformation II of $H_2NCH_2CH_2C\equiv CH$.

Transition	Observed frequency[a] (MHz)	Obs.−calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
$7_{1,6}\leftarrow6_{2,4}$	25261.21	−0.03	−6.35	
$8_{3,6}\leftarrow8_{2,6}$	31308.68	−0.02	7.79	
$9_{3,7}\leftarrow9_{2,7}$	29381.79	0.04	12.60	−0.01
$12_{3,9}\leftarrow11_{4,7}$	27007.41	0.05	−42.43	0.01
$12_{3,10}\leftarrow12_{2,10}$	21892.32	0.04	33.35	−0.02
$15_{4,11}\leftarrow14_{5,9}$	29692.29	0.04	−74.22	0.04
$17_{5,12}\leftarrow16_{6,10}$	25967.12	−0.03	−85.57	0.08
$18_{4,15}\leftarrow18_{3,15}$	26806.27	−0.03	133.88	−0.13
$19_{4,16}\leftarrow19_{3,16}$	23089.12	0.01	152.85	−0.15
$20_{6,14}\leftarrow19_{7,12}$	29698.06	−0.08	−132.61	0.17
$20_{6,15}\leftarrow19_{7,13}$	29426.51	−0.01	−126.05	0.16
$22_{7,15}\leftarrow21_{8,13}$	27057.10	−0.04	−156.32	0.26
$25_{5,21}\leftarrow25_{4,21}$	26295.03	−0.01	395.44	−0.60
$26_{5,22}\leftarrow26_{4,22}$	21994.49	0.00	415.44	−0.65
$28_{10,19}\leftarrow27_{11,17}$	19799.24	0.13	−242.25	0.73
$32_{6,27}\leftarrow32_{5,27}$	24059.56	−0.04	848.14	−1.90
$38_{7,32}\leftarrow38_{6,32}$	25806.55	0.10	1528.58	−4.62
$39_{7,33}\leftarrow39_{6,33}$	20968.80	−0.02	1471.63	−4.56
$44_{8,37}\leftarrow44_{7,37}$	27378.81	−0.13	2525.09	−9.91
$45_{8,38}\leftarrow45_{7,38}$	22217.91	0.07	2390.86	−9.60
$50_{9,42}\leftarrow50_{8,42}$	28907.28	0.06	3916.22	−19.36
$51_{9,43}\leftarrow51_{8,43}$	23456.40	−0.05	3662.41	−18.47

Coalescing K_{-1}-doublet lines.[b]

Transition	Observed frequency[a] (MHz)	Obs.−calc. frequency (MHz)	Centrifugal distortion	
$15_9\leftarrow16_8$	25162.43	−0.05	−55.45	0.21
$17_{10}\leftarrow18_9$	27395.48	0.07	−74.44	0.36
$19_{11}\leftarrow20_{10}$	29624.06	0.07	−97.22	0.58
$22_{12}\leftarrow23_{11}$	25753.57	0.09	−87.14	0.71
$27_{14}\leftarrow28_{13}$	24107.08	0.04	−85.41	1.20
$30_{15}\leftarrow31_{14}$	20236.36	0.07	−43.02	1.24
$33_{12}\leftarrow32_{13}$	21343.46	−0.03	−380.78	1.62
$34_{12}\leftarrow33_{13}$	27606.30	0.02	−463.41	2.05
$32_{16}\leftarrow33_{15}$	22468.54	−0.01	−63.16	1.82
$36_{13}\leftarrow35_{14}$	25221.34	0.00	−512.97	2.59
$38_{14}\leftarrow37_{15}$	22850.34	−0.01	−563.11	3.20
$36_{18}\leftarrow37_{17}$	26919.33	−0.10	−115.70	3.60
$40_{15}\leftarrow39_{16}$	20490.34	0.05	−613.49	3.87
$38_{19}\leftarrow39_{18}$	29137.75	0.12	−148.67	4.91
$41_{15}\leftarrow40_{16}$	26688.28	0.04	−733.09	4.85
$43_{16}\leftarrow42_{17}$	24311.54	0.07	−794.95	5.81
$41_{20}\leftarrow42_{19}$	25305.43	−0.07	−62.82	4.85
$45_{17}\leftarrow44_{18}$	21943.52	−0.06	−856.91	6.86
$43_{21}\leftarrow44_{20}$	27526.91	0.03	−93.79	6.55
$50_{19}\leftarrow49_{20}$	23342.01	0.01	−1156.43	11.46
$51_{19}\leftarrow50_{20}$	29465.15	0.09	−1340.74	13.87
$53_{20}\leftarrow52_{21}$	27069.06	−0.01	−1429.17	16.00

[a,b] Comments as for Table 1.

Table 6. Spectroscopic constants of the ground state of conformation II of $H_2NCH_2CH_2C\equiv CH^a$.

	Vibrational state	Ground state
	N.o.t.[b]	84
	Rms (MHz)[c]	0.090
A_0 (MHz)		10128.449(15)
B_0 (MHz)		3273.6146(52)
C_0 (MHz)		2690.3158(53)
Δ_J (kHz)		3.324(25)
Δ_{JK} (kHz)		−19.81(14)
Δ_K (kHz)		62.098(32)
δ_J (kHz)		1.0199(25)
δ_K (kHz)		7.44(31)
H_J (Hz)		−0.0016(14)
H_{JK} (Hz)		−0.0923(94)
H_{KJ} (Hz)		−0.702(92)
H_K (Hz)[d]		1.94(16)

[a,b,c,d] Comments as for Table 2.

nucleus with the molecular rotation. The resolved, strong components of these lines were measured, and χ_{aa} and χ_{bb} were calculated as described in Ref. 1, with the results: χ_{aa}=1.94(47) MHz and χ_{bb}=2.14(27) MHz. The fact that the experimental values are so similar to the predicted ones, is another evidence that this conformation is indeed conformation I.

The centre frequencies of the split lines were calculated using these quadrupole coupling constants and included in the final least squares fit of the transitions, as mentioned above with the results shown in Tables 1 and 2.

Assignment of the ground vibrational state of conformation II. After the assignment of conformation I had been completed, it was evident that at least one more conformation had to be present, and therefore a search for conformation II was begun because this conformation also has the possibility of forming an intramolecular hydrogen bond.

Preliminary rotational constants and bond moments were calculated as described for conformation I. Again μ_c=1.0 D was predicted to be the larger dipole moment component, with μ_a and μ_b both predicted as 0.2 D.

The spectrum, which is even a bit weaker than that of I, was assigned in the same manner as described for conformation I. Only c-type transitions (see Table 5) were found in a totality of about 95; 84 of which were used to derive the spectroscopic constants of Table 6. Maximum J-values were 44 for P-, 51 for Q-, and 53 for R-branch transitions. Only one R-type line with J values lower than 10 could be assigned, *viz.* the $7_{1,6}\leftarrow 6_{2,4}$ transition, due to low intensities. Again, no a- or b-type transitions were found presumably because of too low intensities.

The principal axis quadrupole coupling constants of II were predicted to be χ_{aa}=−2.1 MHz and χ_{bb}=1.3 MHz in the same manner as described above. These values imply that no splittings of the assigned lines of II are large enough to be observed with the equipment used, as was indeed found experimentally.

Vibrationally excited states of II. Only one excited state of II with about 55 % of the ground state intensity at about −40 °C, were assigned, and as in the case of conformation I,

Table 7. Plausible molecular structure[a] (bond lengths in *pm*, angles in *degrees*) of conformations I and II of $H_2NCH_2CH_2C\equiv CH$.

Structural parameters kept fixed

$C\equiv C$	120.7	$\angle C-C\equiv C$	180.00
$CC-H$	106.0	$\angle H-C\equiv C$	180.00
$CC-C$	145.9	$\angle C-C-H$	109.47
$C-C$	154.8	$\angle C-C-C$	111.70
$C-N$	147.5	$\angle C-N-H$	111.00
$C-H$	109.1	$\angle CCNH^b$	60 or
$N-H$	101.7		180 from *syn*

Fitted structural parameters	Conformation I	Conformation II
$\angle CCN$	108.3(15)	113.5(15)
$\angle CCCN$ (from *syn*)	63(3)	60(3)

Rotational constants (MHz)

	Conformation I			Conformation II		
	Obs.	Obs.−calc.	Diff %	Obs.	Obs.−Calc.	Diff %
A	10349.460	−0.71	0.01	10128.449	−48.29	0.48
B	3293.3850	2.12	0.06	3273.6146	8.84	0.27
C	2708.4104	−2.81	0.10	2690.3158	−6.34	0.24

Hydrogen bond parameters	I	II
$H\cdots C_\alpha{}^c$	310	319
$H\cdots C_\beta{}^c$	259	269
$N\cdots C_\alpha{}^c$	373	379
$N\cdots C_\beta{}^c$	293	300
$\angle N-H\cdots C_\alpha{}^c$	122	119
$\angle N-H\cdots C_\beta{}^c$	99	97
$\angle N-H, C\equiv C^d$	4	6

Sum of van der Waals radii[e]	$H\cdots C^f$ 290	$N\cdots C^f$ 320

[a] See Text. [b] C−C−N−H dihedral angle. [c] $H-C_\alpha\equiv C_\beta-$. [d] Angle between N−H and C≡C bonds. [e] Ref. 11. [f] van der Waals radius of carbon assumed to be 170 ppm as in aromatic systems.[15]

this vibration is assumed to be the first excited state of the C−C torsional vibration. It was only possible to assign about 12 transitions of the *c*-type *Q*-branch series for this excited state, 10 of which were used to derive the spectroscopic constants. The maximum value of *J* for the assigned lines were 39 for the $39_{7,33}\leftarrow 39_{6,33}$ transition. No *P*- or *R*-branch transitions were assigned, and therefore only $A-C$ and κ could be determined. The results were: $A-C=7608.52(19)$ MHz and $\kappa=-0.845361$.

Relative intensity measurements yielded 90(30) cm^{-1} for this vibration which is believed to be the C−C torsional vibration for similar reasons as for I. Force field calculations[9] using the centrifugal distortion constants yielded a frequency of 115(10) cm^{-1} as shown in Table 3.

Searches for further conformations. At this point, about 200 lines had been assigned and 25 more tentatively identified, while another 200 relatively strong and intermediate intensity

lines had not been accounted for. Many of these lines of intermediate intensity are believed to belong to vibrationally excited states of I and II, which could not be assigned. The strongest unassigned lines, which are just as intense as the strongest identified ones, could be due to impurities, which can never be completely ruled out, but a literature search did not reveal any likely sources of impurity. The compound was carefully purified by gas chromatography, and it is therefore presumed that many of the strongest lines of the spectrum belong to either conformations III, IV, or V. Searches for these conformations were therefore made.

Conformation III was predicted in the manner described above, to have a large dipole moment of 1.8 D along the a-axis, and much smaller μ_b and μ_c. No spectrum compatible with these predictions were seen, and from intensity considerations it is concluded that III is at least 3 kJ/mol less stable than conformation I.

The heavy-atom *anti* conformations IV and V are nearly prolate rotors with $\kappa \approx -0.99$. IV is predicted to have $\mu_a=1.3$ D, $\mu_b=0.1$ D, and $\mu_c=1.1$ D. Strong, easily identifiable $K_{-1}\mp1$ pile-ups are expected for this conformation, but no such characteristic spectral feature was seen. This led us to estimate that I is at least 3 kJ/mol more stable than conformation IV.

Conformation V has $\frac{1}{2}$ the statistical weight of the remaining four conformations shown in Fig. 1. Its dipole moment components were predicted to be $\mu_a=0.6$ D, $\mu_b=1.5$ D, and $\mu_c=0$ D (for symmetry reasons). The unidentified, strong lines can hardly all belong to this conformation because they also occur in spectral regions not predicted by the large b-axis dipole moment component of V.

In all likelihood, there is a small energy difference between IV and V, and I is then at least 3 kJ/mol more stable than V as well.

Provided that the unidentified lines do not belong to impurities, only one possibility remains. They could be c-type transitions of conformation IV because μ_c is predicted to be about 1 D (see above). There are two identical forms of IV, and tunnelling of the amino group could result in the kind of spectrum observed. Presumably, rather high J values and a large tunnelling frequency are involved. Such a spectrum is very complicated, and no analysis was attempted.

Energy difference between I *and* II. Intensities of high J c-type Q-branch transitions of conformations I and II were compared. These transitions were chosen because they are not expected to be split by quadrupole coupling. However, in order to derive the energy difference between I and II, the values of the dipole moments calculated by the bond-moment method (see above) had to be used for both conformations, since the dipole moments could not be determined.

The energy difference was found to be 1.5(20) kJ/mol with I as the more stable conformation. The uncertainty of ±2 kJ/mol is estimated to represent three standard deviations.

Structure. Since no isotopic substitutions were carried out, only three rotational constants could be determined for each conformation. This means that a complete structure cannot be determined, and that a maximum of three parameters could be fitted in each case. However, only two parameters were fitted, namely the C−C−C−N heavy-atom dihedral angle and the C−C−N angle. The reasons for choosing these parameters are that they are chemically interesting, and that variations of their values lead to pronounced variations of the rotational constants. The bond lengths and angles shown in Table 7 and kept fixed in the fitting procedure, were taken from recent accurate studies of related compounds.

Table 8. Selected parameters for some $H_2NCH_2CH_2X$-type molecules.

X	Assigned conformations	$\Delta E_0^{\circ a}$ (kJ mol^{-1})	$\angle$X–C–C–N (Degrees)	$\angle$N–C–C (Degrees)	Ref.
H[b]	I[c] and II	−1.3(6)	–	109.5 for I; 115.2 for II	12
F	I and II	0.4(12)	64(2) for I; 63(2) for II	110(1) for I; 114.5(10) for II	1
OH	gauche[d]	–	55.4(20)	108.1(20)	5
SH	Two gauche[e]	−1.1(3)[f]	63.8(20) for A, 67.0(20) f. B	110.9(10) f. A; 109.6(10) f. B	6
CN	I and II	0(2)	63(3) for I; 59(3) f. II	108.0(15) f. I; 114.0(15) f. II	2
NH₂	I and II	1.2(8)	63(2) for I and II	109(1) f. I; 111.5(1) f. II[g]	3
OCH₃	II	<−7.2	61.5(12)	112.2(12)	4
CCH	I and II	1.5(20)	63(3) for I; 60(3) f. II	108.3 f. I; 113.5(15) f. II	–[h]

[a] Positive value for ΔE° means that I is more stable than II. [b] No possibility of forming internal hydrogen bonds. [c] For $H_2NCH_2CH_3$, there is no difference between I and III. [d] One gauche conformation with a O–H···N hydrogen bond. [e] Two different gauche conformations, one with a S–H···N hydrogen bond (A) and one without hydrogen bonds (B). [f] The hydrogen-bonded conformer is the less stable. [g] Average value. [h] Present work.

In order to determine the values of these two parameters that gave the best fit of the rotational constants, the heavy-atom dihedral angle was first varied in steps of 1°. The value that gave the best fit was 63(3)° for I and 60(3)° for II, respectively. The dihedral angle was then kept fixed at the "best" value, and the $C-C-N$ bonding angle was varied in steps of 0.5°. The results were 108.3(15)° for I and 113.5(15)° for II. With these values of the two parameters, the rotational constants can be well reproduced for both conformations, as can be seen in Table 7. The error limits have been derived taking into account the inherent uncertainties of the assumed structural parameters and are approximately three standard deviations.

DISCUSSION

In Table 8, selected structural and thermodynamic parameters for seven 2-substituted ethylamine derivatives as well as for ethylamine[12] itself are collected.

The structural parameters found for $H_2NCH_2CH_2C\equiv CH$ is typical for this type of molecules. *E.g.,* the $N-C-C-C$ dihedral angle is near 60° from *syn,* as found for all the other $N-C-C-X$ dihedral angles of the molecules shown in Table 8. Likewise, the $N-C-C$ angle is about 5° larger in II than in conformation I, which is also characteristic as evidenced in this table. 1,3-Repulsion may perhaps explain this angle opening.[1,2]

The $N-H$ bond involved in hydrogen bonding and the acetylene group are nearly parallel (Table 7) in both I and II. This is ideal for dipole-dipole stabilization. Covalent forces are hardly of much significance for the weak internal hydrogen bonds of I and II as can be inferred from the rather unfavourable structural parameters shown in Table 7. Similar findings have also been made for the other molecules of Table 8 for their conformations possessing intramolecular hydrogen bonds.

The energy difference of 1.5(20) kJ/mol between II and I is similar to what has been found for $H_2NCH_2CH_2F$,[1] $H_2NCH_2CH_2CN$,[2] and $H_2NCH_2CH_2NH_2$,[3] but quite different from the value estimated for $H_2NCH_2CH_2OCH_3$, *viz.* less than -7.2 kJ/mol[4] (Table 8).

It has been suggested[13] that the internal hydrogen bond strength can be approximated as the internal energy difference between one *gauche* conformation with a hydrogen bond and the *anti* conformation which can be made from the *gauche* with only *one* rotation about the central $C-C$ bond and no further relaxations. This means that the energy difference between I and IV, and between II and V (Fig. 1), are approximately equal to the intramolecular hydrogen bond strengths.

As no identifications of *anti* forms have been made, no precise value for the hydrogen bond strength can be given. However, it was estimated above that conformation I is more stable than IV by more than 3 kJ/mol, and it is believed that a lower limit of 3 kJ/mol is valid for the internal hydrogen bond strength of both I and II. For comparison, the intramolecular hydrogen bond strength was found to be about 7.4(24) kJ/mol in $HOCH_2CH_2CN$.[13]

A lower limit of 4 kJ/mol was estimated for both conformations of $H_2NCH_2CH_2CN$,[2] while *ab initio* calculations[14] yielded even smaller energy differences between *gauche* and *anti* forms of this molecule.

REFERENCES

1. Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. A 34* (1980) 15.
2. Braathen, O.-A., Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. A 37* (1983) 493.
3. Marstokk, K.-M. and Møllendal, H. *J. Mol. Struct. 49* (1978) 221.
4. Caminati, W. and Wilson, E.B. *J. Mol. Spectrosc. 81* (1980) 356.
5. a. Penn, R.E. and Curl, R.F., Jr. *J. Chem. Phys. 55* (1971) 651; b. Penn, R.E. and Olsen, R.J. *J. Mol. Spectrosc. 62* (1976) 423.
6. Nandi, R.N., Boland, M.F. and Harmony, M.D. *J. Mol. Spectrosc. 92* (1982) 419.
7. Smith, C.P. *Dielectric Behavior and Structure,* McGraw-Hill, New York 1955, p. 244.
8. Burrell, P.M., Bjarnov, E. and Schwendeman, R.H. *J. Mol. Spectrosc. 82* (1980) 193.
9. Braathen, O.-A., Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. A 36* (1982) 173.
10. Tamagake, K., Tsuboi, M. and Hirakawa, A.Y. *J. Chem. Phys. 48* (1968) 5536.
11. Pauling, L. *The Nature of the Chemical Bond,* 3rd Ed., Cornell University Press, New York 1960, p. 260.
12. a. Fischer, E. and Botskor, I. *J. Mol. Spectrosc. 91* (1982) 116; b. Fischer, E. and Botskor, I. *J. Mol. Spectrosc. 104* (1984) 226.
13. Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. A 39* (1985) 15.
14. Skancke, P.N. *Acta Chem. Scand. A 38* (1984) 95.