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Microwave Spectrum, Conformational Equilibria, Intramolecular Hydrogen Bonding, Dipole Moments, ^{14}N Nuclear Quadrupole Coupling Constants and Centrifugal Distortion Constants of 2,2-Difluoroethylamine

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The microwave spectrum of 2.2-difluoroethylamine, $CHF_2CH_2NH_2$, has been investigated in the 17.9 – 28.5 GHz spectral range. The three conformations denoted I, II and III and shown in Fig. 1 were assigned. Conformations I and II are stabilized by one and III by two weak intramolecular hydrogen bonds. The enthalpy difference between I and III is 1.0(7) kJ/mol with III as the more stable. III is also more stable than II by 1.5(7) kJ/mol. The two hypothetical rotamers IV and V (Fig. 1) are at least 2 kJ/mol less stable than any one of the three assigned conformations.

The FCCN dihedral angle of the hydrogen bond is 60.0(10)° in both I and II. The CCN angle has a "normal" value of 109.0(10)° in I, while this angle opens up to 114.0(10)° in both II and III.

Two vibrationally excited states were assigned for I and III, while one such excited state was identified for II. The vibrational frequencies of these excited states were determined by relative intensity measurements. Force field calculations using the centrifugal distortion constants were made as an independent method of determining the C – C torsional frequencies. The values found by this method were 107(10) cm^{-1} for I, 119(10) cm^{-1} for II, and 127(10) cm^{-1} for III, respectively.

The dipole moments are $\mu_a = 2.042(15)$ D, $\mu_b = 1.101(29)$ D, $\mu_c \sim 0$ D, and $\mu_{tot.} = 2.320(27)$ D, for I, $\mu_a = 1.073(14)$ D, $\mu_b = 0.22(23)$ D, $\mu_c = 1.483(26)$ D, and $\mu_{tot.} = 1.844(57)$ D for II, and $\mu_a = 0.090(28)$ D, $\mu_b = 0$ D (for symmetry reasons), $\mu_c = 1.427(28)$ D, and $\mu_{tot.} = 1.430(30)$ D for III, respectively.

^{14}N quadrupole coupling constants of conformation I are $\chi_{aa} = 3.1(10)$ MHz, and $\chi_{bb} = 2.5(6)$ MHz. No determination of these constants was made for II, whereas $\chi_{aa} = -3.77(17)$ MHz, and $\chi_{bb} = 2.78(17)$ MHz were found for III.

Extensive centrifugal distortion analyses were carried out for both the ground and excited states of all three rotamers and accurate values were found for the centrifugal distortion constants of the ground states of all the three rotamers assigned in this work.

Several amines with weak intramolecular hydrogen bonds have been studied by microwave spectroscopy in recent years. These studies include $CF_3CH_2NH_2$,[1] $CH_2NH_2CH_2NH_2$,[2] $CH_3OCH_2CH_2NH_2$ [3] and $CH_2FCH_2NH_2$.[4] Amines may use both amino group hydrogen atoms for forming hydrogen bonds. More than one hydrogen-bonded conformation is thus possible in most cases. Two hydrogen-bonded rotamers have been assigned for $CH_2NH_2CH_2NH_2$ [2] and for $CH_2FCH_2NH_2$,[4] while only one conformation has been found for each of $CF_3CH_2NH_2$ [1] and $CH_3OCH_2CH_2NH_2$.[3]

2,2-Difluoroethylamine, $CHF_2CH_2NH_2$, may possess four weakly hydrogen-bonded rotamers as shown in Fig. 1. Conformations I, II, and IV each have one hydrogen bond, whereas III has two such bonds. Only one conformation having no hydrogen bonds is possible for $CHF_2CH_2NH_2$, *viz.* V. It is believed to be less stable than hydrogen-bonded conformations because it lacks this stabilizing interaction.

The object of this work has been to study the role of hydrogen bonding and other forces for the conformational preferences of $CHF_2CH_2NH_2$. Three rotamers, namely I, II, and III of Fig. 1 were

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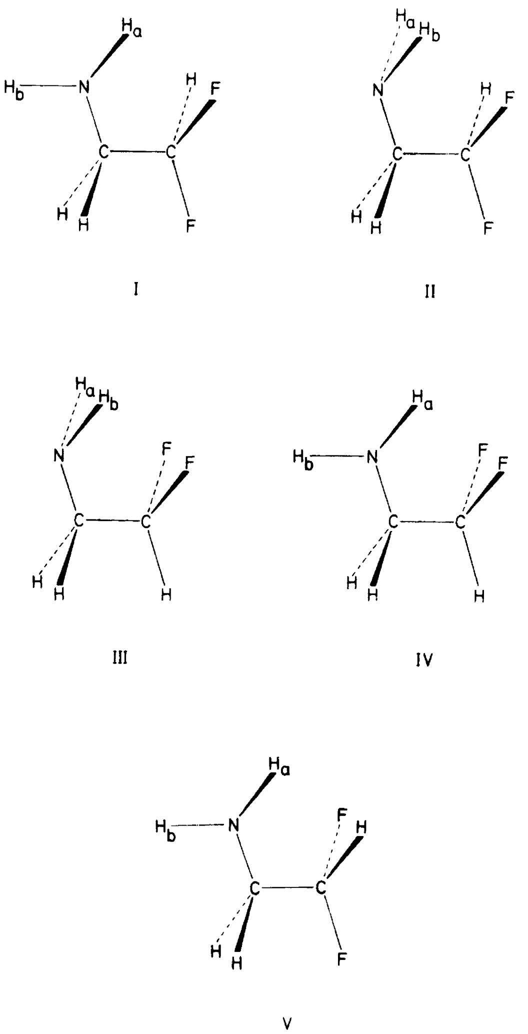

Fig. 1. Possible conformations of $CHF_2CH_2NH_2$ with all-staggered atomic arrangements. All but V contain hydrogen bonds. I, II, and III were assigned and each found to be at least 2 kJ/mol more stable than IV and/or V.

assigned, while no assignments could be made for IV and V which are presumed to be at least 2 kJ/mol less stable than any one of these three identified rotamers.

EXPERIMENTAL

The hydrochloride of 2,2-difluoroethylamine was donated by Professor R.W. Taft of the University of California at Irvine. This compound was mixed with solid powdered sodium hydroxide, heated gently and distilled. The pure amine was then obtained by gas chromatography of the water-containing distillate.

The microwave spectrum was recorded in the 17.9 – 28.5 GHz spectral region using a conventional microwave spectrometer equipped with free-running klystrons. With this equipment, quadrupole fine-structure splittings larger than about 0.6 MHz were resolved. The spectrum was recorded at pressures of about 1.3 Pa. Nearly all spectral measurements were made at −65(5) °C. A few recordings of relative intensities were also made at room temperature.

RESULTS

Microwave spectrum and assignment of the ground vibrational state of conformation I. The microwave spectrum of $CHF_2CH_2NH_2$ is dense with absorptions occurring practically everywhere. The most intense lines are of moderate strengths. The peak absorption coefficients of the strongest transitions observed were roughly 3×10^{-7} cm^{-1} at about −65 °C.

The dipole moment components along the principal axes were predicted to be $\mu_a=2.1$ D, $\mu_b=0.4$ D, and $\mu_c=0$ D, respectively, for conformation I using the bond-moment method.[5] A comparatively simple spectrum dominated by strong *a*-type *R*-branch transitions was thus predicted for this rotamer. The $J=2\rightarrow3$ *a*-type *R*-branch transitions were consequently searched for and readily assigned by their spectral positions, strengths, well-resolved Stark effects and rigid-rotor fit. The preliminary rotational constants thus obtained were used to predict the spectral positions of further *a*-type *R*-branch lines as well as the relatively strong *b*- and *c*-type *Q*-branch series. The *b*-type *Q*-branch series and additional *R*-branch *a*-type lines were found with ease. No *c*-type absorptions were seen. This is in keeping with the small μ_c being very close to zero as shown in a later section.

In addition to low *J a*- and *b*-type *R*-branch and low and medium *J b*-type *Q*-branch lines, the spectrum of conformation I also contains medium and high *J a*-type *Q*-branch transitions of considerable strengths since μ_a is 2.042(15) D (see below) in addition to moderate or low intensity medium and high *J P*- and *R*-branch *b*-type absorptions. These strong *Q*-branch lines have unresolved, comparatively slow Stark effects, whereas the *b*-type *P*- and *R*-branch lines in question have very rapid Stark effects because of the μ_a-connection between the coalescing K_{-1}-doublet energy levels.

The preliminary centrifugal distortion constants obtained from the strong low and medium *J* transitions were not very accurate. The spectral positions of the high *J* transitions could therefore not be predicted very precisely. The initial searches for these lines were, therefore, not conclusive because several alternatives were found in most cases in this dense spectrum. Their definite assignments were first made after the completion of the assignments of the ground vibrational states of conformations II and III which reduced the number of possibilities very much. The maximum *J* transitions identified were the coalescing pair of $35_{22}\rightarrow34_{23}$ for the *P*-branch, the $65_{17,49}\rightarrow65_{17,48}$ transition for the *Q*-branch and the coalescing K_{-1} energy level doublets $38_{21}\rightarrow39_{20}$ for the *R*-branch transitions. Even higher *J* transitions were searched for but no identifications could be made presumably because of insufficient intensities of these lines.

A total of about 90 transitions were assigned for the ground vibrational state of conformation I. A portion of the spectrum* is shown in Table 1. The spectroscopic constants shown in Table 2 were derived using 78 well-resolved transitions. Fairly accurate quartic centrifugal distortion constants were obtained, while the two sextic distortion constants are of a rather poor quality. However, their inclusion was necessary in order to get a good fit.

Some of the transitions were split by quadrupole coupling between the nitrogen nucleus and the overall rotation. These lines 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.

Vibrationally excited states of I. The ground state transitions were accompanied by a satellite spectrum presumably belonging to vibrationally excited states of conformation I. The strongest of these satellites had about 35 % of the intensity of the ground state at −65(5) °C. Relative intensity measurements performed largely as prescribed by Esbitt and Wilson[6] yielded 141(30) cm^{-1} for this vibration. Force-field calculations as described below yielded 107(10) cm^{-1}; a considerable improvement of accuracy in comparison with the relative intensity method. The vibrational frequency is close to 124(10) cm^{-1} determined for the corresponding mode of the closely related molecule CHF_2CH_2OH.[7] The rotational constants as well as their variations upon excitation are close to their counterparts of CHF_2CH_2OH[7] which has a conformation and mass distribution quite similar to conformation I of $CHF_2CH_2NH_2$.

The transitions assigned for this excited state were the low *J a*-type *R*-branch lines, through which the initial identifications were made; and the high *J a*-type *Q*-branch lines with a maximum value of *J* of

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*The complete microwave spectrum of all three rotamers assigned as well as their vibrationally excited states is available from the authors upon request or from Molecular Spectra Data Center, Bldg. 221, Room B 265, National Bureau of Standards, Washington D.C. 20234, U.S.A. where it has been deposited.

Table 1. Selected transitions for the ground vibrational state of conformation I of $CHF_2CH_2NH_2$.

Transition	Observed frequency[a] (MHz)	Obs. − calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
a-type				
$2_{1,2}\rightarrow3_{1,3}$	18221.07	−0.10	−0.08	
$2_{0,2}\rightarrow3_{0,3}$	19198.49	−0.11	−0.07	
$2_{2,1}\rightarrow3_{2,2}$	19586.18	0.06	−0.28	
$2_{2,0}\rightarrow3_{2,1}$	19973.84	0.02	−0.31	
$2_{1,1}\rightarrow3_{1,2}$	20826.83	−0.04	−0.18	
$3_{1,3}\rightarrow4_{1,4}$	24194.65	0.01	−0.17	
$3_{3,1}\rightarrow4_{3,2}$	26292.85	−0.01	−0.81	
$3_{1,2}\rightarrow4_{1,3}$	27636.17	0.00	−0.34	
$10_{2,9}\rightarrow10_{2,8}$	24365.69	0.07	−3.91	
$19_{5,15}\rightarrow19_{5,14}$	18790.03	0.07	−14.61	0.01
$27_{7,21}\rightarrow27_{7,20}$	24156.87	0.03	−38.44	0.06
$46_{12,35}\rightarrow46_{12,34}$	25928.75	0.07	−137.38	1.13
$57_{15,43}\rightarrow57_{15,42}$	21524.99	0.07	−195.39	3.05
$65_{17,49}\rightarrow65_{17,48}$	23305.61	0.16	−239.04	6.51
b-type				
$2_{0,2}\rightarrow3_{1,3}$	22736.47	−0.09	−0.10	
$3_{1,3}\rightarrow4_{0,4}$	21655.81	0.11	−0.12	
$4_{1,4}\rightarrow5_{0,5}$	28421.56	−0.05	−0.24	
$8_{4,4}\rightarrow9_{3,7}$	19017.72	−0.06	0.99	
$14_{7,7}\rightarrow15_{6,10}$	26925.96	0.05	2.77	
$6_{0,6}\rightarrow6_{1,5}$	18759.30	0.06	−1.07	
$7_{0,7}\rightarrow7_{1,6}$	23634.51	−0.11	−1.58	
$6_{1,6}\rightarrow6_{2,5}$	26794.50	0.09	−1.46	
$10_{1,9}\rightarrow10_{2,8}$	26594.24	−0.08	−4.34	
$5_{2,3}\rightarrow5_{3,2}$	26526.33	0.10	−1.09	
$8_{2,6}\rightarrow8_{3,5}$	22343.96	−0.07	−2.51	
$12_{2,10}\rightarrow12_{3,9}$	25463.56	0.04	−6.81	
Coalescing lines[b]				
$35_{22}\rightarrow34_{23}$	25338.17	0.01	−25.71	0.99
$24_{13}\rightarrow25_{12}$	24298.88	0.06	14.69	−0.15
$28_{15}\rightarrow29_{14}$	28176.35	−0.06	22.96	−0.32
$33_{18}\rightarrow34_{17}$	26988.42	−0.06	36.93	−0.72
$38_{21}\rightarrow39_{20}$	25834.56	0.03	55.07	−1.45

[a] ±0.10 MHz. Transitions with resolved quadrupole splittings have been corrected for this effect. [b] The K_{-1}-energy doublets coalesce for high values of K_{-1}. Subscripts of J-quantum number refer only to K_{-1}.

49 belonging to the $49_{13,37}\rightarrow49_{13,36}$ transition. In addition, the low J R- and Q-branch b-type lines were assigned. The high J P- and R-branch b-type lines were too weak to be assigned. A total of 41 transitions were identified for this mode and the spectroscopic constants shown in Table 2 were derived.

The second excited state lines of this normal mode should have about 10% of the intensities of the corresponding ground state transitions. These lines should thus have sufficient intensities to be observed. A search was made for them and tentative assignments were made for 7 a-type R-branch lines yielding $A=8928.9(26)$ MHz, $B=3687.84(13)$ MHz and $C=2823.89(12)$ MHz (not included in Table 2).

The first excited state of what is assumed to be the lowest heavy-atom bending mode was also assigned with the spectroscopic constants displayed in Table 2. The types of transitions assigned were the same as for the first excited heavy-atom torsional mode.

Table 2. Spectroscopic constants for conformation I of $CHF_2CH_2NH_2$.[a]

Vibrational state	Ground	First ex. C – C tors.	First ex. lowest bending mode
Number of transitions	78	41	22
rms (MHz)	0.068	0.095	0.138
A_v (MHz)	8987.2718(51)	8947.288(15)	8987.217(50)
B_v (MHz)	3699.8821(19)	3692.383(11)	3692.988(21)
C_v (MHz)	2828.9179(18)	2826.230(11)	2823.580(21)
Δ_J (kHz)	0.9455(49)	−0.04(35)	1.47(60)
Δ_{JK} (kHz)	7.294(15)	6.28(21)	7.86(67)
Δ_K (kHz)	0.838(14)	1.4(13)	−25.8(43)
δ_J (kHz)	0.2089(16)	0.1779(68)	0.332(37)
δ_K (kHz)	4.793(61)	4.58(19)	4.29(75)
H_J (Hz)	−0.00258(58)	–[b]	–[b]
H_{JK}	−0.0092(10)	−0.0127(53)	–[b]

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

Maximum J was 19 for the $19_{5,15} \rightarrow 19_{5,14}$ transition.

The intensities of the lines of this mode are about 20% of the corresponding ground state transitions. A frequency of 228(40) cm^{-1} was determined for this normal mode by relative intensity measurements. This corresponds well with 243(20) cm^{-1} found for the lowest bending mode of CHF_2CH_2OH.[7] However, the changes of the rotational constants upon excitation of this mode are not very similar in the two molecules. The reason for this dissimilarity is perhaps that somewhat different coupling schemes exist for the heavy-atom bending modes in each of the two molecules.

In the case of CHF_2CH_2OH [7] the second lowest bending mode having a frequency of 309(40) cm^{-1} was also assigned. A similar frequency for the corresponding mode of conformation I of $CHF_2CH_2NH_2$ should yield excited state transitions with about 10% of the intensities of their ground-state counterparts. Searches were made for such an excited state, but an assignment was not reached possibly because of the richness – and frequent overlaps – occurring in the spectrum of $CHF_2CH_2NH_2$.

Dipole moment of I. Stark coefficients of low J transitions were used to determine the dipole moment. Comparatively large Stark splittings were measured in order to minimize possible quadrupole coupling effects. A d.c. voltage was applied between the Stark septrum and the cell with the modulating square wave voltage superimposed. The d.c. field strength was calibrated using the OCS $J = 1 \rightarrow 2$ transition with $\mu_{OCS} = 0.71521$ D.[8] Each second order coefficient shown in Table 3 was assigned a standard deviation presumed to take into account

Table 3. Stark coefficients[a] and dipole moment of conformation I of $CHF_2CH_2NH_2$.

Transition		$\Delta\nu/E^2$ (MHz V^{-2} cm^2) × 10^5 Obs.	Calc.
$2_{0,2} \rightarrow 3_{0,3}$	M = 0	−0.464(5)	−0.463
	|M| = 2	1.74(2)	1.73
$2_{2,1} \rightarrow 3_{2,2}$	M = 0	0.781(9)	0.766
	|M| = 1	105(2)	112.6
$2_{1,1} \rightarrow 3_{1,2}$	|M| = 1	−1.00(1)	−0.981
	|M| = 2	−3.98(4)	−4.05

[a] Uncertainties represent one standard deviation. [b] $\mu_a = 2.042(15)$ D; $\mu_b = 1.101(29)$ D; $\mu_c = 0.0$ D[c]; $\mu_{tot} = 2.320(27)$ D. [c] Assumed, see text.

the additional uncertainty arising from quadrupole coupling. A least squares fit using a diagonal weight matrix was performed. The weights were chosen as the inverse squares of the standard deviations of the Stark coefficients appearing in Table 3. An imaginary and small value of the c-axis dipole moment component was found when all three dipole moment components were varied in the least-squares fit. In the final fit, μ_c was assumed to be zero. The results thus obtained are shown in Table 3. From the dependency of the Stark coefficients of this table on μ_c, it is estimated that this dipole moment component is definitely less than 0.2 D.

There is reasonably good agreement between the observed dipole moment components and those predicted by the bond moment method as seen above. This is independent evidence for the fact that the assigned rotamer is indeed conformation I.

The total dipole moment was calculated to be 2.1 D by the bond moment method. The experimental value of 2.320(27) D may perhaps indicate some enhancement of the dipole moment as a result of hydrogen bonding, but this is quite uncertain because of the rather rough approximation used in the bond-moment method.

^{14}N quadrupole coupling constants of I. Several low and medium J b-type transitions were split due to quadrupole coupling of the ^{14}N nucleus with the molecular rotation. In order to determine the two independent quadrupole coupling constants χ_{aa} and χ_{bb} the following procedure was employed: Only lines with no resolved quadrupole fine structure were used in a least squares fit to predict the hypothetical unsplit frequencies of the relatively few remaining transitions exhibiting a resolved quadrupole fine structure. The splittings from these hypothetical unperturbed frequencies were then least squares fitted using eqn. (1). The symbols of this equation are defined in Ref. 9.

$$E_q = [2f(I,J,F)]/J(J+1)\sum_g \chi_{gg}\langle P_g^2\rangle \qquad (1)$$

The quadrupole splittings are relatively small for a nitrogen-containing molecule and normally overlap each other to lesser or greater extent. The data to be fitted to eqn. (1) are thus correlated and a symmetrical weight matrix applies to such cases. Application of this kind of weight matrix is not easy and the simpler method using diagonal weight matrix was chosen. This choice is not expected to have influenced the final results in any significant manner. The weights of the diagonal matrix were taken as the inverse squares of the standard deviations of the observed splittings, E_q, shown in Table 4. The entries of this table are the best resolved quadrupole components found for this molecule and consist basically of only one quadrupole component. Inclusion of lines consisting of basically two quadrupole components in the least-squares fit was attempted but yielded somewhat less accurate values for χ_{aa} and χ_{bb} than those reported in Table 4.

After this least-squares determination of the quadrupole coupling constants had been performed, the split lines were corrected for quadrupole effects and used in the final determination of the spectroscopic constants shown in Table 2.

Assignments of the ground vibrational state of conformation II. Many strong lines remained in the spectrum after the initial assignments had been made for the ground and the vibrationally excited states of conformation I. These so-far unidentified transitions were too numerous and too strong to be attributed to unassigned vibrationally excited states

Table 4. ^{14}N quadrupole splittings and diagonal elements of the quadrupole coupling tensor of conformation I of $CHF_2CH_2NH_2$.[a]

Transition	$F \rightarrow F'$	E_q (obs.)[b,c] (MHz)	E_q (obs.) $-$ E_q (calc.) (MHz)
$6_{0,6} \rightarrow 6_{1,5}$	$6 \rightarrow 6$	$-1.63(3)$	0.06
$7_{0,7} \rightarrow 7_{1,6}$	$7 \rightarrow 7$	$-1.67(3)$	-0.04
$6_{0,6} \rightarrow 6_{2,5}$	$6 \rightarrow 6$	$-1.20(3)$	-0.11
$5_{1,5} \rightarrow 5_{2,4}$	$5 \rightarrow 5$	$-1.24(3)$	0.08
$8_{1,7} \rightarrow 8_{2,6}$	$8 \rightarrow 8$	$-0.85(3)$	-0.02
$10_{1,9} \rightarrow 10_{2,8}$	$10 \rightarrow 10$	$-1.12(3)$	-0.04
$12_{2,10} \rightarrow 12_{3,9}$	$12 \rightarrow 12$	$-0.48(4)$	0.09

[a] $\chi_{aa} = 3.1(10)$ MHz; $\chi_{bb} = 2.5(6)$ MHz. [b] Uncertainties represent one standard deviation. [c] See text.

Table 5. Selected transitions for the ground vibrational state of conformation II of $CHF_2CH_2NH_2$.

Transition	Observed frequency[a] (MHz)	Obs. − calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
a-type				
$2_{1,2}\rightarrow 3_{1,3}$	18049.15	−0.04	−0.08	
$2_{0,2}\rightarrow 3_{0,3}$	18999.64	0.11	−0.06	
$2_{2,0}\rightarrow 3_{2,1}$	19726.55	−0.06	−0.28	
$2_{2,1}\rightarrow 3_{2,2}$	19363.10	0.11	−0.25	
$3_{1,3}\rightarrow 4_{1,4}$	23971.38	0.07	−0.15	
$3_{0,3}\rightarrow 4_{0,4}$	24951.10	−0.09	−0.14	
$3_{3,0}\rightarrow 4_{3,1}$	26023.01	0.04	−0.73	
$16_{4,13}\rightarrow 16_{4,12}$	20184.56	−0.07	−9.44	0.01
$24_{6,19}\rightarrow 24_{6,18}$	26083.65	0.01	−28.30	0.05
$27_{7,21}\rightarrow 27_{7,20}$	21255.12	−0.16	−32.12	0.10
$38_{10,29}\rightarrow 38_{10,28}$	18847.36	−0.11	−64.48	0.56
c-type				
$1_{0,1}\rightarrow 2_{1,1}$	19841.20	−0.03	−0.10	
$2_{0,2}\rightarrow 3_{1,2}$	27585.67	0.07	−0.24	
$5_{1,4}\rightarrow 6_{0,6}$	22136.17	−0.08	0.14	
$8_{1,7}\rightarrow 9_{0,9}$	24891.80	0.03	0.53	
$10_{5,6}\rightarrow 11_{4,8}$	21935.80	0.11	1.03	
$12_{1,11}\rightarrow 13_{0,13}$	26865.62	−0.03	1.54	
$12_{6,6}\rightarrow 13_{5,8}$	24968.40	−0.07	1.00	
$16_{8,9}\rightarrow 17_{7,11}$	28126.76	−0.01	3.48	
$3_{1,3}\rightarrow 3_{2,1}$	20049.69	0.02	−0.37	
$5_{2,3}\rightarrow 5_{3,3}$	26216.44	−0.09	−0.94	
$8_{2,6}\rightarrow 8_{3,6}$	19718.30	−0.04	−1.65	
$14_{3,11}\rightarrow 14_{4,11}$	18351.47	−0.06	−4.62	−0.01
$18_{4,14}\rightarrow 18_{5,14}$	23007.89	0.16	−9.48	−0.02
$27_{6,21}\rightarrow 27_{7,21}$	26285.76	−0.06	−23.73	−0.15
$32_{7,25}\rightarrow 32_{8,25}$	23874.02	−0.05	−29.92	−0.34
$45_{10,35}\rightarrow 45_{11,35}$	27123.64	0.01	−63.56	−2.04
$50_{11,39}\rightarrow 50_{12,39}$	22935.77	−0.09	−65.94	−3.09
$55_{12,43}\rightarrow 55_{13,43}$	18922.49	0.08	−66.08	−4.33
$63_{14,49}\rightarrow 63_{15,49}$	23667.06	−0.05	−103.53	−10.05
$68_{15,53}\rightarrow 68_{16,53}$	19144.58	0.05	−99.03	−12.51
Coalescing lines[b]				
$18_{12}\rightarrow 17_{13}$	24072.98	−0.09	−2.37	0.01
$26_{17}\rightarrow 25_{18}$	28371.20	0.05	−9.11	0.04
$30_{19}-29_{20}$	24731.83	−0.08	−16.60	0.06
$36_{22}\rightarrow 35_{23}$	19238.94	0.06	−32.66	0.09
$22_{12}\rightarrow 23_{11}$	21538.75	−0.04	10.19	0.02
$28_{15}-29_{14}$	27139.65	−0.05	20.63	0.06
$35_{19}-36_{18}$	27714.84	−0.03	40.02	0.16
$40_{22}\rightarrow 41_{21}$	26451.75	0.07	59.27	0.27
$48_{27}-49_{26}$	22108.50	−0.04	100.34	0.51

[a] ±0.10 MHz. [b] Comments as for Table 1.

of this conformation. Several of these transitions even displayed resolved Stark splittings, while others were suspected to be split by quadrupole coupling. The intensity patterns of the lines perturbed by presumed quadrupole interaction could in no way be predicted from χ_{aa} and χ_{bb} determined for conformation I.

In our work on 2-fluoroethylamine[4] it was found that a rotamer similar to conformation II of Fig. 1 was almost as stable as the conformation corresponding to rotamer I of this figure. Assignment of conformation II of Fig. I thus became the next goal.

The dipole moment components of II were predicted as $\mu_a = 1.1$ D, $\mu_b = 0.2$ D, and $\mu_c = 1.6$ D, respectively, using the bond-moment method. A spectrum dominated by strong and numerous *c*-type *Q*-branch transitions and some few relatively intense *a*-type *R*-branch lines was expected for this rotamer. The existence of a μ_a-dipole moment component produces very rapid Stark effects for the low *J* *c*-type *Q*-branch lines. This property was exploited to achieve the initial assignment of the *Q*-branch series. The *a*-type *R*-branch lines were then easily found. Extension of the assignment to high *J* *Q*-branch transitions was not difficult, since the *c*-type *Q*-branch series are relatively strong and numerous. No *b*-type lines were definitely assigned although their frequencies could be predicted very accurately. This is in agreement with the fact that $\mu_b = 0.23(23)$ D as shown below. The *b*-type lines thus have insufficient intensities to be definitely identified. Finally, the medium and high *J* *R*-branch *c*-type lines were found by a trial and error procedure amongst medium-intensity lines with very rapid Stark effects produced by the μ_a-connection between the K_{-1}-doublets.

A total of about 130 transitions were assigned for the ground vibrational state of conformation II. 40 selected lines are shown in Table 5. The derived spectroscopic constants using 114 transitions are shown in Table 6. Very accurate values were derived for the quartic centrifugal distortion constants while the sextic constants hardly have much physical significance. Their inclusion was necessary, however, in order to produce a good fit. In this case, the highest *J* value assigned was the *c*-type $68_{15,53}\rightarrow68_{16,53}$ *Q*-branch transition. Maximum *J* *P*- and *R*-branch lines were the $30_{19}\rightarrow29_{20}$ and $48_{27}\rightarrow49_{26}$ transitions, respectively.

Low *J* lines were scrutinized for quadrupole splittings. Some transitions were definitely broader by this effect while the shape of others deviated from the usual Lorentzian form. However, no obvious splittings were observed. It is therefore assumed that χ_{aa} and χ_{bb} in this case take values which do not produce splittings larger than about 0.6 MHz for intense components.

Vibrationally excited states of II. A strong satellite spectrum having about 1/3 of the intensity of the ground state spectrum was assigned as the first excited state of the C–C torsional mode. Relative intensity measurements yielded 160(30) cm^{-1} for this fundamental frequency. A value of 119(10) cm^{-1} is found by the force-field calculations described below. This is similar to the values determined for I, as one would expect. The changes of the rotational constants upon excitation also closely resemble the findings for I as expected.

The spectroscopic constants for this excited state are reported in Table 6. They were derived from 45 selected transitions. *c*-Type *Q*-branch lines up to the $58_{13,45}\rightarrow58_{14,45}$ transition and *R*-branch lines with a maximum *J* value of 31 for the $31_{17}\rightarrow32_{16}$ coalescing K_{-1}-doublets were identified for this excited state. No assignments could be made for the

Table 6. Spectroscopic constants for conformation II of $CHF_2CH_2NH_2$.[a]

Vibrational state Number of transitions rms (MHz)	Ground 114 0.072	First ex. C–C tors. 45 0.087
A_v (MHz)	8900.8048(46)	8863.8060(95)
B_v (MHz)	3646.8396(18)	3641.9421(36)
C_v (MHz)	2807.5735(13)	2806.0888(29)
Δ_J (kHz)	0.8440(10)	0.738(26)
Δ_{JK} (kHz)	6.576(11)	6.409(68)
Δ_K (kHz)	0.8284(37)	0.122(84)
δ_J (kHz)	0.19209(68)	0.2039(37)
δ_K (kHz)	3.979(15)	2.18(29)
H_J (Hz)	0.00042(14)	0.0092(23)
H_{JK} (Hz)	−0.01393(37)	0.0047(33)

[a] Comments as for Table 2.

Table 7. Stark coefficients[a] and dipole moment of conformation II of $CHF_2CH_2NH_2$.[b]

		$\Delta\nu/E^2$ (MHzV^{-2} cm^2) × 10^6	
		Obs.	Calc.
$3_{2,2}\rightarrow4_{2,3}$	|M|=1	15.0(1)	14.5
	|M|=2	60.9(7)	60.4
$2_{1,2}\rightarrow3_{1,3}$	|M|=1	−23.0(2)	−22.9
$1_{0,1}\rightarrow2_{1,1}$	|M|=1	36.8(3)	37.8
$3_{1,3}\rightarrow3_{2,1}$	|M|=2	61.1(6)	56.8
	|M|=3	89.2(7)	95.3
$2_{1,1}\rightarrow3_{1,2}$	|M|=1	−0.785(10)	−0.766

[a] Uncertainties represent one standard deviation. [b] $\mu_a = 1.073(14)$ D; $\mu_b = 0.22(23)$ D; $\mu_c = 1.483(26)$ D; $\mu_{tot.} = 1.844(57)$ D.

second excited state of this normal mode, despite intensive searching.

Tentative assignments (not reported in Table 6) were made for 13 medium J and high J Q-branch transitions of what might be the first exited state of the lowest bending mode. $A-C$ was found to be 6100.66(76) MHz and Ray's asymmetry parameter[10] κ was determined as −0.723982. The intensities of these tentatively assigned transitions were about 20% of their presumed ground state counterparts.

Dipole moment of II. The dipole moment of this rotamer was determined in the same manner as described for I. The results are seen in Table 7. There is good agreement between the above-mentioned bond-moment computations and the experimental findings. This is independent evidence for the fact that the identified conformation is indeed rotamer II.

Assignment of the ground vibrational state of conformation III. After the assignments of conformations I and II had been made, many strong lines remained in the spectrum. Two intense so-far unassigned transitions, at 24940.94 and 28465.82 MHz, respectively, had well-resolved Stark effects. Intensity patterns of the Stark components indicated that they had to be a $J=1\rightarrow2$ and a $J=2\rightarrow3$ transition, respectively. Moreover, several of the strong hitherto unassigned lines displayed partially resolved Stark effects typical for Q-branch transitions. In addition, lines with presumed quadrupole splittings remained unidentified. It was thus obvious that conformations I and II could not account for the entire microwave spectrum of $CHF_2CH_2NH_2$.

The existence of conformation III seemed quite probable since the related molecule $CF_3CH_2NH_2$ is known to possess a conformation similar to III as its most stable rotamer.[1] This is a conformation with two weak hydrogen bonds. The dipole moment components for III were predicted to be $\mu_a = 0.10$ D and $\mu_c = 0.82$ D. μ_b is zero for this conformation since the $a-c$-principal axes plane is also its symmetry plane. Conformation III was thus predicted to have a moderately strong c-type spectrum and a very weak a-type spectrum.

It was then assumed that the line at 24940.94 MHz was either the $1_{1,0}\rightarrow2_{2,0}$ (which turned out to be correct) or the $1_{1,1}\rightarrow2_{2,1}$ transition, while the absorption at 28465.82 MHz had to be the $2_{0,2}\rightarrow3_{1,2}$ transition since this was predicted from the rotational constants found using a probable molecular model. The initial assignments were readily made using the two above-mentioned lines together with lines presumed to be medium J c-type Q-branch transitions as judged by their Stark effects. The assignments of the c-type Q-branch lines were easily extended up to the $64_{18,46}\rightarrow64_{19,46}$ transition. Only the low J c-type R-branch lines were identified. The high J, P and R-branch lines were not sufficiently strong to be assigned. No a-type transitions were seen although their hypothetical frequencies could be very exactly predicted. This was expected since μ_a is 0.090(28) D (see below). About 50 transitions were assigned for this conformation. Some of them were resolvably split by quadrupole effects while others were distorted from the ordinary Lorentzian shape. The split lines were "corrected" for quadrupole coupling effects in the same manner as described for conformation I. (See also later section.) The 47 lines shown in Table 8 were used to derive the spectroscopic constants shown in Table 9.

For molecules possessing an $a-c$-axes symmetry plane the following relation exists for the principle moments of inertia, *viz.* $I_a+I_c-I_b=\Sigma m_i b_i^2+\Delta$

Table 8. Microwave spectrum of the ground vibrational state of conformation III of $CHF_2CH_2NH_2$.

Transition	Observed frequency[a] (MHz)	Obs. – calc. frequency (MHz)	Centrifugal distortion Total (MHz)	Centrifugal distortion Sextic (MHz)
$6_{2,5}\rightarrow 6_{3,3}$	19448.76	0.03	–1.60	
$7_{2,6}\rightarrow 7_{3,4}$	22038.31	0.05	–2.39	
$8_{2,7}\rightarrow 8_{3,5}$	25848.05	–0.04	–3.38	
$5_{3,2}\rightarrow 5_{4,2}$	22608.17	–0.02	–0.61	
$6_{3,3}\rightarrow 6_{4,3}$	21994.55	–0.04	–1.33	
$7_{3,4}\rightarrow 7_{4,4}$	20899.46	–0.06	–2.14	
$8_{3,5}\rightarrow 8_{4,5}$	19229.33	–0.04	–3.00	
$5_{3,3}\rightarrow 5_{4,1}$	22970.71	0.09	–0.64	
$6_{3,4}\rightarrow 6_{4,2}$	23039.98	–0.11	–1.42	
$7_{3,5}\rightarrow 7_{4,3}$	23336.97	–0.12	–2.34	
$8_{3,6}\rightarrow 8_{4,4}$	24067.68	–0.06	–3.40	
$9_{3,7}\rightarrow 9_{4,5}$	25507.10	–0.08	–4.60	
$10_{3,8}\rightarrow 10_{4,6}$	27960.88	0.12	–5.95	
$9_{4,5}\rightarrow 9_{5,5}$	27855.29	0.05	–4.53	
$10_{4,6}\rightarrow 10_{5,6}$	26514.70	–0.01	–6.06	
$11_{4,7}\rightarrow 11_{5,7}$	24535.51	0.07	–7.65	
$12_{4,8}\rightarrow 12_{5,8}$	21917.98	–0.01	–9.17	–0.01
$13_{4,9}\rightarrow 13_{5,9}$	18793.05	0.08	–10.45	–0.01
$15_{5,10}\rightarrow 15_{6,10}$	27006.08	0.05	–18.19	–0.02
$16_{5,11}\rightarrow 16_{6,11}$	23463.79	–0.09	–20.32	–0.03
$19_{6,13}\rightarrow 19_{7,13}$	28384.94	0.15	–35.35	–0.07
$20_{6,14}\rightarrow 20_{7,14}$	23993.83	0.01	–37.66	–0.08
$21_{6,15}\rightarrow 21_{7,15}$	19376.06	0.08	–38.42	–0.10
$24_{7,17}\rightarrow 24_{8,17}$	23642.30	–0.04	–62.02	–0.21
$25_{7,18}\rightarrow 25_{8,18}$	18521.94	–0.06	–60.73	–0.23
$27_{8,19}\rightarrow 27_{9,19}$	28237.28	–0.01	–94.54	–0.41
$28_{8,20}\rightarrow 28_{9,20}$	22558.72	–0.07	–93.50	–0.45
$31_{9,22}\rightarrow 31_{10,22}$	26950.71	0.01	–137.49	–0.82
$32_{9,22}\rightarrow 32_{10,23}$	20907.51	–0.02	–131.18	–0.86
$35_{10,25}\rightarrow 35_{11,25}$	25052.15	0.07	–188.21	–1.48
$36_{10,26}\rightarrow 36_{11,26}$	18862.64	0.03	–172.96	–1.48
$39_{11,28}\rightarrow 39_{12,28}$	22710.35	–0.03	–244.16	–2.47
$42_{12,30}\rightarrow 42_{13,30}$	26937.29	–0.12	–334.68	–3.92
$43_{12,31}\rightarrow 43_{13,31}$	20101.48	0.06	–301.44	–3.79
$46_{13,33}\rightarrow 46_{14,33}$	23995.64	0.00	–410.12	–5.91
$49_{14,35}\rightarrow 49_{15,35}$	28273.52	–0.02	–544.78	–8.91
$53_{15,38}\rightarrow 53_{16,38}$	24814.13	0.01	–638.48	–12.46
$57_{16,41}\rightarrow 57_{17,41}$	21328.66	0.05	–720.18	–16.48
$60_{17,43}\rightarrow 60_{18,43}$	25208.92	0.03	–936.88	–23.74
$61_{17,44}\rightarrow 61_{18,44}$	17973.24	–0.02	–782.68	–20.72
$64_{18,46}\rightarrow 64_{19,46}$	21401.19	–0.03	–1021.39	–29.76
$1_{0,1}\rightarrow 2_{1,1}$	19682.70	–0.05	–0.09	
$1_{1,0}\rightarrow 2_{2,0}$	24940.94	–0.06	–0.12	
$1_{1,1}\rightarrow 2_{2,1}$	25561.31	0.03	–0.12	
$2_{0,2}\rightarrow 3_{1,2}$	28465.82	0.09	–0.25	
$3_{1,2}\rightarrow 4_{0,4}$	23367.84	–0.01	–0.05	
$3_{2,1}\rightarrow 4_{1,3}$	23318.57	–0.02	–0.18	

[a] ±0.10 MHz. Transitions with resolved quadrupole splittings have been corrected for this effect.

Table 9. Spectroscopic constants for conformation III of $CHF_2CH_2NH_2$.[a]

Vibrational state	Ground	First ex. C – C tors.	First ex. lowest bending mode
Number of transitions	47	34	22
rms (MHz)	0.069	0.090	0.147
A_v (MHz)	7125.170(12)	7142.150(26)	7158.743(31)
B_v (MHz)	4185.890(13)	4179.324(27)	4184.917(28)
C_v (MHz)	3441.172(13)	3429.070(27)	3435.758(45)
Δ_J (kHz)	1.0(5)	−1.5(20)	–[b]
Δ_{JK} (kHz)	8.34(10)	9.32(15)	8.76(84)
Δ_K (kHz)	−6.59(36)	−7.87(55)	−7.7(29)
δ_J (kHz)	0.2420(58)	0.2521(94)	0.232(37)
δ_K (kHz)	1.53(15)	1.56(25)	0.39(68)
H_{JK} (Hz)	−0.02252(49)	−0.0200(16)	–[b]

[a,b] Comments as for Table 2.

where b_i is the b-principle axis coordinate of the out-of-plane atoms. The m_i's are their masses and Δ is the inertial defect. In the case of conformation III of $CHF_2CH_2NH_2$ $I_a+I_c-I_b$ is found to be 97.05663(68) uÅ^2. In the identified conformation of $CF_3CH_2NH_2$ the corresponding value was found as 96.9(3) uÅ^2. The close resemblance of the two values of $I_a+I_c-I_b$ is expected because each of the two conformations of the two molecules possesses two out-of-plane fluorine atoms, two methylene group hydrogen atoms, and two amino group hydrogen atoms.

Vibrationally excited states of III. Two vibrationally excited states were assigned for conformation III as indicated in Table 9. The strongest of these two excited state spectra had about 40 % of the intensity of the ground state spectrum. This state is assigned as the first excited state of the C – C torsional mode both because of its strength and because $I_a+I_c-I_b$ increases[11] upon excitation to 97.2166(14) uÅ^2. This is expected for an out-of- plane torsional mode. Low J c-type R-branch transitions and Q-branch lines with a maximum J value of 54 (for the $54_{15,39}\rightarrow54_{16,39}$ transition) were assigned for this excited state. The frequency of this torsional mode was determined as 141(30) cm^{-1} by relative intensity measurements. A value of 127(10) cm^{-1} was found by the force-field calculations described below.

The second excited state which was identified for this conformation had about 20 % of the intensity of the ground state. Relative intensity measurements yielded 234(40) cm^{-1} for this normal vibration which is presumed to be the lowest heavy-atom bending mode. $I_a+I_b-I_c$ takes the value of 96.9274(21) uÅ^2 which is smaller than the corresponding ground state value. A reduction of $I_a+I_b-I_c$ upon excitation is predicted[11] for a bending mode of an A' vibrational species fundamental in agreement with the present finding.

The spectroscopic constants for this excited state (Table 9) were derived from 22 transitions with a maximum value of $J=43$ for the $43_{12,13}\rightarrow43_{13,31}$ transition.

Table 10. Stark coefficients[a] and dipole moment of conformation III of $CHF_2CH_2NH_2$.[b]

Transition		$\Delta\nu/E^2$(MHzV^{-2} cm^2)$\times10^6$ Obs.	Calc.
$1_{1,0}\rightarrow2_{2,0}$	M = 0	−6.79(7)	−7.48
	|M| = 1	7.30(7)	7.32
$2_{0,2}\rightarrow3_{1,2}$	M = 0	1.26(2)	1.37
	|M| = 1	19.0(1)	17.9
	|M| = 2	74.5(7)	78.2

[a] Uncertainties represent one standard deviation. [b] $\mu_a=0.090(28)$ D; $\mu_c=1.427(28)$ D; $\mu_{tot.}=1.430(30)$ D.

Table 11. ^{14}N quadrupole splittings and diagonal elements of the quadrupole coupling tensor of conformation III of $CHF_2CH_2NH_2$.[a]

Transition	$F \rightarrow F'$	E_q(obs.)[b,c] (MHz)	E_q(obs.) $-$ E_q(calc.) (MHz)
$1_{1,1} \rightarrow 2_{2,1}$	$2 \rightarrow 3$	$-0.17(3)$	-0.04
	$0 \rightarrow 1$	$0.48(5)$	0.03
$3_{2,1} \rightarrow 4_{1,3}$	$4 \rightarrow 5$	$0.34(3)$	0.04
	$3 \rightarrow 4$	$-0.87(5)$	-0.07
$5_{3,3} \rightarrow 5_{4,1}$	$6 \rightarrow 6$	$-0.19(4)$	0.07
	$5 \rightarrow 5$	$0.73(3)$	0.06
$5_{3,2} \rightarrow 5_{4,2}$	$6 \rightarrow 6$	$-0.30(4)$	-0.02
	$5 \rightarrow 5$	$0.65(3)$	-0.08
$6_{3,3} \rightarrow 6_{4,3}$	$7 \rightarrow 7$	$-0.14(4)$	0.09
	$6 \rightarrow 6$	$0.58(3)$	0.00

[a] $\chi_{aa} = -3.77(17)$ MHz; $\chi_{bb} = 2.78(17)$ MHz. [b,c] Comments as for Table 4.

Dipole moment of III. The dipole moment of III was determined in the same manner as described above for the two other rotamers. The results are shown in Table 10. The total dipole moment is 1.430(30) D as compared to 0.83 D calculated by the bond-moment method. The relatively large difference of 0.6 D may indicate that an enhancement of the dipole moment actually occurs in this conformation which has two contributing hydrogen bonds.

^{14}N quadrupole coupling constants of III. Several low J transitions were split by quadrupole coupling. The lines found to have a resolved quadrupole fine structure are shown in Table 11. χ_{aa} and χ_{bb} shown in this table were determined in the same manner as described for conformation I. Inclusion of lines consisting of more than one quadrupole component was made for conformation III. The standard deviations of E_q for such components were judiciously increased as compared with a line consisting of only one quadrupole component.

Searches for conformations IV and V. The assignments made as described above include about 430 transitions. Approximately 30 more lines were tentatively assigned. Every strong line of the spectrum has been identified. The great majority of intermediate intensity and many weak transitions have also been accounted for. Careful Stark effect studies have been made for the majority of the remaining unassigned lines of intermediate intensities. In none of these cases was a well-resolved Stark pattern seen.

Simulation of the spectra of conformations IV and V were made. These two hypothetical rotamers are the only two additional conformations with all-staggered atomic arrangements possible for $CHF_2CH_2NH_2$. The rotational constants of IV were predicted to be roughly $A = 7.2$ GHz $B = 4.2$ GHz, and $C = 3.4$ GHz. The principal axes dipole moment components were computed as $\mu_a = 1.6$ D, $\mu_b = 1.2$ D, and $\mu_c = 2.0$ D, using the bond-moment method. The corresponding molecular constants for V were computed as: $A = 9.0$ GHz, $B = 3.6$ GHz, $C = 2.8$ GHz, $\mu_a = 2.3$ D, $\mu_b = 1.7$ D, and $\mu_c = 1.7$ D. IV and V are thus each predicted to possess dipole moment components of about 2 D. They would then have as strong spectra as the identified forms provided they were present in the same amounts.

Typically, the most intense unassigned lines had roughly 15 % of the intensities of the strongest (and identified) lines of the spectrum. If these unidentified transitions were indeed the spectra of IV and/or V they could not for intensity reasons be present in concentrations exceeding about 15 % of each of I, II or III. It is thus concluded that conformations I, II and III each are at least 2 kJ/mol more stable than IV or V.

Furthermore, it is believed that the unidentified lines of medium strengths are high J transitions as judged by their Stark effects. More probably, they are weakly populated vibrationally excited state transitions of one or more of the three identified rotamers.

Force-field determination of the C–C torsional frequency of the three conformations. Accurate centrifugal distortion constants were determined for all the three rotamers. As shown in Table 12, these molecular constants may be used to determine the torsional frequency. The reasons for using

Table 12. Assumed force field, centrifugal distortion constants and torsional frequencies for conformations I, II, and III of $CHF_2CH_2NH_2$.[a]

Force constants common for I, II and III

Stretching (10^{-2} N m^{-1})			
C–C	4.2	C–H	4.7
C–N	5.1	N–H	6.4
C–F	4.9		

Bending (aJ rad^{-2})			
C–C–N	1.3	N–C–H	0.90
C–C–F	1.5	H–C–H	0.50
C–C–H	0.65	C–N–H	0.85
F–C–F	1.7	H–N–H	0.47
F–C–H	0.70		

Torsion (aJ rad^{-2})	
C–N	0.25
C–C	0.0987 (conformation I)[b]
C–C	0.1228 (conformation II)[b]
C–C	0.1786 (conformation III)[b]

Centrifugal distortion constants (kHz)

Conformation	I		II		III	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
Δ_J	0.9455(49)	1.06	0.8440(10)	0.992	1.0(5)	2.07
Δ_{JK}	7.294(15)	7.54	6.576(11)	6.92	8.34(10)	8.23
Δ_K	0.838(14)	1.00	0.8284(37)	1.25	−6.59(36)	−6.68
δ_J	0.2089(16)	0.245	0.19209(68)	0.220	0.2420(58)	0.239
δ_K	4.793(61)	4.56	3.979(15)	3.99	1.53(15)	1.06

C–C torsional frequency (cm^{-1})

Conformation	I	II	III
Force-field calculations[b]	107(10)	119(10)	127(10)
Relative intensity[a]	141(30)	160(30)	141(30)

[a] See text. [b] Obtained from least-squares fit.

centrifugal distortion constants for this purpose have been given previously.[12]

The simple diagonal force field shown in Table 12 was partly selected from related molecules or partly estimated. The centrifugal distortion constants depend primarily on the C–C torsional force constant. The C–C–F, C–C–N, and F–C–F bending force constants were also seen to contribute considerably to the centrifugal distortion constants. Only the C–C torsional force constant was varied in the least-squares fit. The remaining force constants were kept at the values shown in Table 12. Unit weights were given to the centrifugal distortion constants in the fitting procedure. The programme used was NCA written by Christen.[13]

The torsional frequencies were found to be 107 cm^{-1} for I, 119 cm^{-1} for II and 127 cm^{-1} for III. The uncertainties of these frequencies are difficult to estimate since several assumptions are involved in their derivation. However, it is felt that ± 10 cm^{-1} is a realistic error limit. The torsional frequencies obtained by this method are considerably more accurate than those obtained by the completely independent relative intensity method as shown in Table 12. The two methods yield results which agree within their estimated uncertainty limits.

It is satisfactory to note that the C–C torsional frequency of III obtained by the force-field method [127(10) cm^{-1}] is higher than those of I [107(10) cm^{-1}] and II [119(10) cm^{-1}], respectively. This is expected since two hydrogen bonds exist in III. They would tend to make the torsional motion more rigid than in I or II where only one such bond exists.

Energy differences between the three conformers. Relative intensity measurements were made at −65(5) °C and room temperature to determine Gibbs free energy difference between the three conformers. The peak intensities were taken by slowly scanning the spectral lines. The carefully selected lines were strong and, hopefully, not seriously perturbed by overlapping lines or Stark components. Lines with unresolved quadrupole fine structure were used in order to avoid complications from this effect. In some cases high J lines with coalescing K_{-1}-doublet energy levels were utilized. The peak intensities of these lines were assumed to be equal to the sum of the intensities of the individual transitions of which these lines were composed. The equilibrium constant K for the $\mathrm{II} \rightleftarrows \mathrm{I}$ conformational equilibrium was calculated from[4,14] eqn. (2). The symbols of eqn. (2) have been

$$K = \frac{[\mathrm{I}]}{[\mathrm{II}]} = \frac{\alpha_{\mathrm{I}}}{\alpha_{\mathrm{II}}}\left(\frac{v_{\mathrm{II}}}{v_{\mathrm{I}}}\right)^2 \left(\frac{A_{\mathrm{II}}B_{\mathrm{II}}C_{\mathrm{II}}}{A_{\mathrm{I}}B_{\mathrm{I}}C_{\mathrm{I}}}\right)^{\frac{1}{2}} \times \frac{\sum\limits_{\mathrm{g}}(\lambda_{\mathrm{II}}\mu_{\mathrm{gII}}\exp(-E^{\mathrm{J}}_{\tau\mathrm{II}})/kT)}{\sum\limits_{\mathrm{g}}(\lambda_{\mathrm{I}}\mu_{\mathrm{gI}}\exp(-E^{\mathrm{J}}_{\tau\mathrm{I}})/kT)} \tag{2}$$

defined previously.[4,14] This equation is based on many assumptions discussed elsewhere.[4,14] There are also many sources of errors in the measurements of peak absorption coefficients as discussed in Ref. 6. However, by using a rather large number of intensity observations as shown in Table 13, it was hoped that accurate values might be obtained for the thermodynamic parameters. The relatively small standard deviations of ΔG° (Table 13) calculated using $\Delta G^\circ = -RT\ln K$ are reassuring. The standard deviations of ΔG° are seen to be higher for the measurements made at 22(1) °C than at −65(5) °C. This is caused by the fact that the transitions measured at room temperature have rougly 1/6 of the intensity at −65(5) °C. Measurements of ΔG° at two temperatures were made for all three equilibria in attempting to derive accurate values not only for ΔH° but for ΔS° as well. These two thermodynamic parameters were calculated from the Gibbs-Helmholtz equation.

Unfortunately, no accurate value of ΔS° could be found using the values of ΔG° shown in Table 13, as the standard deviation of ΔS° was found to be larger than ΔS° itself in all three cases. ΔS° was therefore estimated using another, and presumable more accurate, procedure. In the case of the $\mathrm{II} \rightleftarrows \mathrm{I}$ equilibrium, there are great structural similarities between the two rotamers. The vibrational partition functions of the two conformers are also presumed to be very similar. The quartic contrifugal distortion constants are quite similar for I and II. This is evidence for the assumption that the harmonic force fields of the two conformations are indeed similar. ΔS° for the $\mathrm{II} \rightleftarrows \mathrm{I}$ equilibrium is thus presumed to be very nearly zero. Using this value for ΔS° in eqn. (3), ΔH° is estimated to be −0.5(7) kJ/mol for this equilibrium. Conformation I is thus more stable than II by 0.5(7) kJ/mol.

ΔS° for the $\mathrm{III} \rightleftarrows \mathrm{I}$ and $\mathrm{III} \rightleftarrows \mathrm{II}$ equilibria was presumed to be $R \ln 2 = 5.8$ J/(mol K) since the statistical weight of I and II in each case is 2 as compared to conformation III. It is thus assumed that the vibrational partition functions are very similar and thus contribute insignificantly to the entropy difference for these two equilibria.

Table 13. Thermodynamic parameters for conformational equilibria of $CHF_2CH_2NH_2$.

Conformational equilibrium	Temp. (K)	Number of obs.	ΔG° (kJ/mol)[a]	Selected thermodynamic parameters[b] ΔH° (kJ/mol)[c]	ΔS° (J/mol K)
$\mathrm{II} \rightleftarrows \mathrm{I}$	208±5	13	−0.32(62)	−0.5(7)	~0
	295±1	24	−0.69(84)		
$\mathrm{III} \rightleftarrows \mathrm{I}$	208±5	23	0.07(62)	1.0(7)	~5.8
	295±1	32	−0.70(79)		
$\mathrm{III} \rightleftarrows \mathrm{II}$	208±5	26	0.30(43)	1.5(7)	~5.8
	295±1	48	−0.09(75)		

[a] Calculated using eqn. (2) and $\Delta G^\circ = -RT\ln K$. Uncertainties represent one standard deviation obtained from the least-squares fit. [b] See text. Uncertainties are estimated standard deviations. [c] Estimated uncertainties.

Table 14. Plausible structural parameters[a] (bond lengths in *pm*, angles in *degrees*) and observed and calculated rotational constants of conformations I, II, and III of $CHF_2CH_2NH_2$.

Assumed structural parameters common for I, II and III

C–F	135.0	∠CCF	110.0	∠HNCC[b] 0.0 or 60.0
C–N	146.9	∠FCF	108.94	
C–C	153.0	∠CCH	109.48	
C–H	109.3	∠HCH	109.48	
N–H	101.7	∠HNC	109.48	
		∠HNH	109.48	
		∠FCH	109.20	

Fitted structural parameters

Conformation	I	II	III
∠FCCN[c] from *syn*	60.0(20)	60.0(20)	60[d]
∠CCN	109.0(10)	114.0(10)	114.0(10)

Hydrogen bond parameters

	I	II	III
N···F	281	290	290
N···H	247	260	260
∠N–H···F[e]	98.4	96.4	96.4
∠C–F, N–H[e,f]	0.3	3.1	3.1

Sum of van der Waals radii[g]

N···F	285	H···F	255

Rotational constants (MHz)

	Obs.	Obs. – Cal.	Diff. (%)
		I	
A	8987.27	–34.51	0.38
B	3699.88	1.29	0.03
C	2828.92	9.84	0.35
		II	
A	8900.80	–16.09	0.18
B	3646.84	4.78	0.13
C	2807.57	1.76	0.06
		III	
A	7125.17	2.76	0.04
B	4185.89	–4.75	0.11
C	3441.17	11.08	0.32

[a] See text. [b] Dihedral angle assumed to be exactly staggered. [c] Dihedral angle involving the fluorine atom engaged in hydrogen bonding. [d] This angle is exactly 60° due to symmetry. [e] Hydrogen atom involved in hydrogen bonding. [f] Angle between C–F and N–H bonds involved in hydrogen bonding. [g] Taken from Ref. 15.

Conformation III is then found to be the most stable of the three conformers. It is favored by enthalpy by 1.0(7) kJ/mol as compared to I and by 1.5(7) kJ/mol as compared to conformation II.

Structures of the three conformations. Only one isotopic species was studied for the three rotamers and only three rotational constants are thus available for each rotamer. A complete geometrical structure cannot, therefore, be determined for each of the three conformations. A selection of parameters to be fitted must be made. The CCN angle and the FCCN dihedral angle where the fluorine atom is involved in hydrogen bonding, were varied for conformations I and II. Only the CCN angle was fitted for III. These structural parameters were selected because the rotational constants are very sensitive to variations in these angles, because they are chemically interesting, and finally because they are presumed to be among the structural parameters of this molecule most likely to vary from one conformation to another. Further parameters expected to vary in different conformations, namely the HNCC dihedral angle, the HNC and HNH angles, *etc.*, cannot be meaningfully fitted because the rotational constants are relatively insensitive to these angles as a result of the small mass of the amino group hydrogen atoms. The amino group hydrogens were therefore assumed to be in exactly staggered positions. The remaining bond lengths and angles which were kept constant in the fit, were selected from recent accurate structural studies of related compounds. They are shown in Table 14.

The FCCN dihedral angle was varied in steps of 1° and the CCN angle in steps of 0.5°. As shown in Table 14, the rotational constants are reproduced better than 0.4 % by this procedure. The error limits of the FCCN dihedral angles and the CCN angles are assumed to encompass possible differences between the assumed structural parameters and the real ones.

DISCUSSION

2,2-Difluoroethylamine is another example of an amine which takes hydrogen-bonded conformations as its preferred forms. The intramolecular hydrogen bonds are rather weak in all the three conformations as seen by their structural characteristics given in Table 14. The hydrogen bonds are presumably mainly electrostatic in origin since the C – F and N – H bonds are nearly parallel and the corresponding bond dipoles are thus almost antiparallel which is favourable for electrostatic attraction. Covalent forces are hardly of much significance for the hydrogen bonds as the non-bonded distances between the hydrogen and fluorine atoms are approximately equal to the sum of the van der Waals radii of these two atoms.[15]

The fact that the NCCF dihedral angles are 60.0(20)° in both I and II comes as no surprise. Similar values have been found in all hydrogen-bonded amines so far studied.

Important differences exist in the CCN angles of the three conformations. As shown in Table 14, this angle is 109.0(10)° in conformation I and 114.0(10)° in both II and III. Similar findings were made for the two assigned forms of $CH_2FCH_2NH_2$.[4] The identified rotamer of $CF_3CH_2NH_2$ [1] was also found to have a CCN angle of $113^\circ 50' \pm 1^\circ$. This conformation is similar to III of this work. In another related hydrogen-bonded amine, *viz.* ethylenediamine,[2] the average CCN angle of the conformation denoted II was also larger than in rotamer I of this molecule. There is no obvious explanation for these observations. Perhaps repulsion of the 1,3-type is more prevalent in those conformations having the larger CCN angle.

The fact that conformation III of $CHF_2CH_2NH_2$ is the most stable rotamer of the molecule can presumably be explained by the existence of two hydrogen bonds in this form. The slightly higher stability of I as compared to II is paralleled by the findings made for the similar two conformations of $CH_2FCH_2NH_2$.[4]

The three identified rotamers were each found to be more stable than the hypothetical conformations IV and V by at least 2 kJ/mol. Conformation IV has one hydrogen bond, but the probable direction of the amino group lone pair and the other C – F bond not involved in hydrogen bonding are nearly parallel. The resulting repulsion may perhaps explain the instability of IV as compared to the identified rotamers. In V, no hydrogen bonds exist and this may be the reason why this conformation is also less stable than the three rotamers assigned for $CHF_2CH_2NH_2$.

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Note added in proof. A more accurate method of calculating ΔH_0° has now been derived by E. B. Wilson, Jr. and will be presented in a forthcoming paper.

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