

# Microwave Spectrum, Conformational Equilibrium, Intramolecular Hydrogen Bonding, Dipole Moments, $^{14}\text{N}$ Nuclear Quadrupole Coupling Constants and Centrifugal Distortion Constants of 2-Fluoroethylamine

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The microwave spectrum of 2-fluoroethylamine  $\text{CH}_2\text{FCH}_2\text{NH}_2$  has been investigated in the 18.0–30.0 GHz spectral range. The two F–C–C–N *gauche* conformers denoted I and II and shown in Fig. 1, were assigned. Both conformers are stabilized by an intramolecular hydrogen bond. The enthalpy difference is  $0.1 \pm 0.3$  kcal/mol\* with conformer I as the more stable. Conformer II is favoured by entropy by  $0.2 \pm 0.2$  cal/(mol K). The existence of large fractions of further conformers is ruled out.

The F–C–C–N dihedral angles are  $64 \pm 2^\circ$  in I, and  $63 \pm 2^\circ$  in II, respectively. The CCN angle has a "normal" value of  $110 \pm 1^\circ$  in I, while this angle opens up to  $114.5 \pm 1^\circ$  in conformer II possibly because of a 1,3-repulsive interaction between two hydrogen atoms.

Five vibrationally excited states belonging to three different normal modes were assigned for conformer I, whereas three excited states of two normal vibrations were identified for II. The vibrational frequencies of the normal modes were determined by relative intensity measurements.

The dipole moments are  $\mu_a = 1.148 \pm 0.003$  D,  $\mu_b = 1.380 \pm 0.008$  D,  $\mu_c = 0.332 \pm 0.021$  D, and  $\mu_{\text{rot}} = 1.826 \pm 0.012$  D for conformer I, and  $\mu_a < 0.03$  D,  $\mu_b = 1.337 \pm 0.008$  D,  $\mu_c = 1.002 \pm 0.005$  D, and  $\mu_{\text{rot}} = 1.671 \pm 0.010$  D for II, respectively. The  $^{14}\text{N}$  quadrupole coupling constants of I are  $\chi_{aa} = 2.02 \pm 0.13$  MHz, and  $\chi_{bb} = 2.49 \pm 0.10$  MHz. For II the following values were found:  $\chi_{aa} = -2.78 \pm 0.14$  MHz, and  $\chi_{bb} = 2.34 \pm 0.08$  MHz.

Accurate quartic centrifugal distortion constants were determined for the ground and first excited state of the C–C torsional mode of both conformers.

\* 1 kcal = 4.184 kJ.

The structure and conformational preferences of 2-haloethanols have in recent years attracted great interest. The free molecules have been studied by electron diffraction, microwave, IR, and Raman spectroscopy.<sup>1,2</sup> These investigations have shown that the preferred form by the 2-haloethanols is the heavy-atom *gauche* conformation with an intramolecular hydrogen bond in all cases.

An amino group may replace the hydroxyl group as proton donor. When this is done, both hydrogen atoms may be used for hydrogen bond formation. Such hydrogen bonds have been shown to exist in ethylenediamine<sup>3</sup> and in trifluoroethylamine.<sup>4</sup> In the case of 2-fluoroethylamine, the fact that both hydrogens of the amino groups may be used for

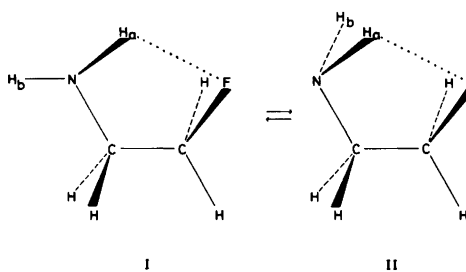


Fig. 1. The most stable conformations of 2-fluoroethylamine. I is more stable than II by  $0.1 \pm 0.3$  kcal/mol. I is changed into II by an approximately  $240^\circ$  clock-wise rotation about the C–N bond as viewed from N to C. Both conformers are stabilized by weak hydrogen bonds.

hydrogen bonding leads one to expect that the two heavy-atom *gauche* conformers of Fig. 1 will be the preferred forms of the molecule. Conformer I may be changed into II by an approximately 240° clock-wise rotation of the amino group as viewed along the N–C bond.

No experimental work on the structure of this molecule has been found in the literature, but Pople *et al.*<sup>5</sup> have made *ab initio* MO calculations. They found that the two conformers shown in Fig. 1 were the energetically favoured ones with I 0.63 kcal/mol more stable than II. These researchers did not optimize the geometry in their computations.

As will be shown later, there are some structural differences between the two rotamers which might have influenced the *ab initio* result.

IR and Raman work on this compound has now been initiated in this department.<sup>6</sup>

## EXPERIMENTAL

2-Fluoroethylamine hydrochloride was purchased from Aldrich-Europe Division, Beerse, Belgium. The hydrochloride was mixed with excess solid sodium hydroxide and distilled. The product was then purified by gas chromatography. Studies were made in the 18–30 GHz spectral region with the cell cooled with dry ice to about –60 °C. Lower temperatures could not be utilized because of insufficient vapour pressure. Vapour pressures of 5–25 microns were employed. The spectra were recorded on a conventional spectrometer with free-running klystrons. In favourable cases this equipment made it possible to resolve quadrupole coupling components spaced by less than 0.5 MHz.

## RESULTS

### *Microwave spectrum and assignment of conformer I.*

Preliminary rotational constants were computed by combining structural parameters taken from related compounds. The rotational constants were quite similar because of the small structural difference of the two rotamers. Bond moment calculations of the dipole moments were then performed using the values of Ref. 7. The results for conformer I were:  $\mu_a = 1.1$  D,  $\mu_b = 0.9$  D and  $\mu_c = 0.5$  D. For II the following values were computed:  $\mu_a = 0.1$  D,  $\mu_b = 0.9$  D, and  $\mu_c = 1.9$  D. The agreement between bond moment calculations and experiment is often quite good, and conformer I was thus expected to

exhibit a relatively strong *a*- and *b*-type spectrum, whereas comparatively strong *b*- and *c*-type lines were expected for II. A dense spectrum was expected since many transitions of *b*- and *c*-type fall in the investigated spectral range.

The microwave spectrum of 2-fluoroethylamine was compatible with these predictions. It is relatively strong and dense with absorptions occurring every few megahertz throughout the entire microwave spectral range. The 18–22 GHz region was first investigated because several low *J* lines of both conformers were predicted to appear here. Several such lines were readily identified by their Stark effects, positions in the spectrum, intensities, and characteristic quadrupole splittings caused by the <sup>14</sup>N nucleus. After a few trials the unrefined rotational constants of conformer I were derived from low *J* *a*- and *b*-type lines. These were used to predict several more transitions which were subsequently measured and included in the least squares fit in which centrifugal distortion was also taken into account. The molecular constants thus derived allowed the frequencies of more transitions of still higher *J* to be predicted. They were then measured and included in the least squares procedure. By repeating this process several times, a total of about 150 transitions of the *a*-, *b*- and *c*-type varieties were ultimately assigned. The highest *J* *c*-type line was the  $59_{9,50} \rightarrow 59_{10,50}$  while a  $J = 46 \rightarrow 47$  *R*-branch and a  $J = 48 \rightarrow 47$  *P*-branch transition were the highest values of *J* identified for perpendicular transitions. At such high values of *J*, intensities are quite low. Still higher *J*-transitions were searched for but could not be positively identified because of insufficient intensities. Table 1 lists 41 selected lines.\* As shown in this table centrifugal distortion is a prominent feature of the spectrum. In fact, it amounts to as much as 9690.01 MHz for the highest *J* transition. Several of the entries of Table 1 have been "corrected" for resolved quadrupole splittings in a manner to be described in the section on the determination of the quadrupole coupling constants of the nitrogen nucleus.

The spectroscopic constants derived from 134 transitions are shown in Table 2. Because of the large centrifugal distortion perturbation accurate values were found for the quartic centrifugal

\* The complete microwave spectra of two conformers are available from the authors upon request, or from the Microwave Data Center, Molecular Spectroscopy Section, National Bureau of Standards, Washington D.C. 20234, U.S.A., where they have been deposited.

Table 1. Selected transitions for the ground vibrational state of conformer I of CH<sub>2</sub>FCH<sub>2</sub>NH<sub>2</sub>.

Transition	Observed frequency <sup>a</sup> (MHz)	Obs. - calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
<i>a</i> -type				
1 <sub>1,1</sub> → 2 <sub>1,2</sub>	18 621.03	0.02	0.05	
1 <sub>0,1</sub> → 2 <sub>0,2</sub>	19 430.80	-0.04	-0.21	
1 <sub>1,0</sub> → 2 <sub>1,1</sub>	20 346.45	-0.04	-0.21	
2 <sub>1,2</sub> → 3 <sub>1,3</sub>	27 899.25	0.05	-0.21	
2 <sub>2,1</sub> → 3 <sub>2,2</sub>	29 225.94	0.08	0.11	
<i>b</i> -type				
0 <sub>0,0</sub> → 1 <sub>1,1</sub>	19 877.23	0.05	-0.01	
1 <sub>0,1</sub> → 2 <sub>1,2</sub>	28 756.41	0.11	0.07	
2 <sub>1,2</sub> → 3 <sub>0,3</sub>	19 689.74	-0.06	-0.95	
5 <sub>0,5</sub> → 5 <sub>1,4</sub>	18 416.61	-0.08	-2.46	
7 <sub>0,7</sub> → 7 <sub>1,6</sub>	26 848.36	-0.07	-10.44	
3 <sub>1,2</sub> → 3 <sub>2,1</sub>	29 408.41	-0.05	0.30	
5 <sub>1,4</sub> → 5 <sub>2,3</sub>	27 250.57	0.00	2.54	
9 <sub>1,8</sub> → 9 <sub>2,7</sub>	28 412.43	-0.07	-4.73	0.01
11 <sub>6,5</sub> → 10 <sub>7,4</sub>	29 444.38	0.11	-36.43	0.09
9 <sub>4,5</sub> → 10 <sub>3,8</sub>	24 156.90	0.01	-28.55	
9 <sub>4,6</sub> → 10 <sub>3,7</sub>	27 344.64	0.05	-42.44	0.01
15 <sub>7,8</sub> → 16 <sub>6,11</sub>	20 651.30	0.05	-103.23	0.08
15 <sub>7,9</sub> → 16 <sub>6,10</sub>	20 681.63	0.11	-103.96	0.08
<i>c</i> -type				
3 <sub>1,2</sub> → 3 <sub>2,2</sub>	29 145.90	-0.11	0.44	
6 <sub>1,5</sub> → 6 <sub>2,5</sub>	23 131.08	0.05	7.22	
7 <sub>1,6</sub> → 7 <sub>2,6</sub>	20 529.32	0.07	11.14	
13 <sub>2,11</sub> → 13 <sub>3,11</sub>	28 197.28	0.00	86.12	0.03
22 <sub>3,19</sub> → 22 <sub>4,19</sub>	19 044.83	0.04	376.64	0.30
33 <sub>5,28</sub> → 33 <sub>6,28</sub>	29 427.39	-0.03	1747.00	2.48
40 <sub>6,34</sub> → 40 <sub>7,34</sub>	25 465.23	-0.07	2911.30	5.68
47 <sub>7,40</sub> → 47 <sub>8,40</sub>	21 617.32	-0.03	4252.29	10.95
53 <sub>8,45</sub> → 53 <sub>9,45</sub>	23 456.93	-0.04	6522.79	20.18
59 <sub>9,50</sub> → 59 <sub>10,50</sub>	25 677.15	-0.03	9690.01	35.34
0 <sub>0,0</sub> → 1 <sub>1,10</sub>	20 740.01	0.04	-0.09	
7 <sub>2,6</sub> → 8 <sub>1,8</sub>	29 386.90	-0.08	-4.57	
13 <sub>6,7</sub> → 14 <sub>5,9</sub>	22 349.42	-0.03	-77.61	0.04
13 <sub>6,8</sub> → 14 <sub>5,10</sub>	22 193.10	-0.01	-75.23	0.04
Coalescing <i>b</i> - and <i>c</i> -type <sup>b</sup>				
16 <sub>8</sub> → 15 <sub>9</sub>	22 482.03	-0.07	-24.10	0.17
25 <sub>12</sub> → 24 <sub>13</sub>	18 495.08	0.01	55.23	0.36
31 <sub>15</sub> → 30 <sub>16</sub>	22 983.03	-0.01	106.02	0.92
39 <sub>19</sub> → 38 <sub>20</sub>	29 003.15	-0.06	212.27	2.47
48 <sub>23</sub> → 47 <sub>24</sub>	25 402.70	-0.04	705.53	-1.40
24 <sub>11</sub> → 25 <sub>10</sub>	24 471.64	0.05	-351.87	0.80
31 <sub>14</sub> → 32 <sub>13</sub>	29 710.49	-0.09	-723.97	2.85
39 <sub>18</sub> → 40 <sub>17</sub>	23 223.16	0.10	-1203.31	8.18
46 <sub>21</sub> → 47 <sub>20</sub>	28 072.00	-0.09	-1974.26	19.20

<sup>a</sup> ±0.10 MHz. Transitions with resolved quadrupole splittings have been corrected for this effect. <sup>b</sup> The K-doublets coalesce for high values of K<sub>-1</sub>. Subscripts refer to K<sub>-1</sub>.

Table 2. Spectroscopic constants for conformer I of  $\text{CH}_2\text{FCH}_2\text{NH}_2$ .<sup>a</sup>

Vibrational state	Ground	First ex. C—C torsion
Number of transitions	134	72
rms (MHz)	0.073	0.108
$A_v$ (MHz)	$15\,437.6657 \pm 0.0082$	$15\,579.291 \pm 0.018$
$B_v$ (MHz)	$5\,302.3944 \pm 0.0028$	$5\,263.6823 \pm 0.0063$
$C_v$ (MHz)	$4\,439.5230 \pm 0.0021$	$4\,421.1920 \pm 0.0059$
$\Delta_J$ (kHz)	$7.305 \pm 0.015$	$6.990 \pm 0.040$
$\Delta_{JK}$ (kHz)	$-37.544 \pm 0.077$	$-35.74 \pm 0.26$
$\Delta_K$ (kHz)	$91.494 \pm 0.038$	$97.26 \pm 0.17$
$\delta_J$ (kHz)	$2.1469 \pm 0.0031$	$2.106 \pm 0.013$
$\delta_K$ (kHz)	$15.54 \pm 0.31$	$10.4 \pm 1.1$
$H_J$ (Hz)	$0.0176 \pm 0.068$	$0.09 \pm 0.14$
$H_{JK}$ (Hz)	$0.60 \pm 0.14$	$4.2 \pm 2.0$
$H_{KJ}$ (Hz)	$-2.40 \pm 0.30$	$13.5 \pm 1.3$
$H_K$ (Hz)	$4.44 \pm 0.27$	$-1.7 \pm 2.4$
$h_J$ (Hz)	$0.0006 \pm 0.0022$	$0.246 \pm 0.015$
$h_{JK}$ (Hz)	$0.42 \pm 0.14$	$-8.9 \pm 2.4$
$h_K$ (Hz)	$3.4 \pm 1.4$	$-69.6 \pm 11.6$

<sup>a</sup>Uncertainties represent one standard deviation. rms is the root-mean-square deviation. The rotational constants are those obtained directly from the least squares fit without correcting for centrifugal distortion.

distortion constants. The sextic coefficients are of a much poorer quality. However, the inclusion of these constants was necessary in order to obtain a fit with a root-mean-square deviation comparable to the experimental uncertainty.

*Vibrationally excited states.* The ground vibrational state transitions were accompanied by a rich satellite spectrum. The strongest of these absorption lines were about 30% as intense as the corresponding ground state transitions. They are assigned as the first excited state of the C—C torsional mode. The spectroscopic constants for this state are shown in Table 2. They were derived from 72 transitions. Maximum value of  $J$  was 41 for the  $c$ -type  $Q$ -branch transition,  $40_{18} \rightarrow 41_{17}$  for the  $R$ -branch and  $29_{14} \rightarrow 28_{15}$  for the  $P$ -branch coalescing  $b$ - and  $c$ -type  $K_{-1}$ -doublets. Accurate quartic centrifugal distortion constants were found for this state whereas the sextic coefficients are very uncertain as shown in Table 2.

Our reason for assigning this state as the first excited state of the C—C torsion is, apart from its low frequency, the fact that a  $2^\circ$  opening of the NCCF dihedral angle of our molecular model (see below) reasonably well reproduces the observed changes of the rotational constants. These changes were calculated to be  $\Delta A = 131.7$  MHz,  $\Delta B = -52.9$  MHz and  $\Delta C = -13.0$  MHz, respectively. This is acceptably close to the observed values:  $\Delta A = 141.63$

MHz,  $\Delta B = -38.72$  MHz and  $\Delta C = -18.33$  MHz, respectively. The reason for the discrepancy between the observed and calculated changes is presumably that the torsional motion is more complicated than a simple rotation about the C—C bond.

Relative intensity measurements were made following most of the precautions of Esbitt and Wilson.<sup>8</sup> Lines with unresolved quadrupole fine structure were utilized and  $195 \pm 15$   $\text{cm}^{-1}$  was derived for the C—C torsional frequency. This is close to  $152 \pm 10$   $\text{cm}^{-1}$  determined for 2-fluoroethanol,<sup>9</sup>  $181 \pm 20$   $\text{cm}^{-1}$  found for conformation II of ethylenediamine<sup>3</sup> and the IR-value of 148  $\text{cm}^{-1}$  seen in 1,2-difluoroethane.<sup>10</sup> These compounds are isoelectronic to and prefer very similar conformations to those of 2-fluoroethylamine.

The second excited state of the C—C torsional motion was also assigned and the rotational constants appearing in Table 3 were determined from low  $J$   $b$ -type  $Q$ - and  $R$ -branch lines as well as from one  $a$ -type  $R$ -branch transition. Only  $\Delta_{JK}$  was varied in the fitting procedure but the resulting value for this coefficient is too uncertain to warrant its publication.

15 transitions of the lowest bending mode were assigned and the rotational constants of Table 3 determined. These transitions are about 20% as intense at 215 K as their ground-state counterparts. The quartic constants were also varied in the least

Table 3. Rotational constants<sup>a</sup> for vibrationally excited states of conformer I of CH<sub>2</sub>FCH<sub>2</sub>NH<sub>2</sub>.

Vibrational state	A <sub>v</sub> (MHz)	B <sub>v</sub> (MHz)	C <sub>v</sub> (MHz)
Second ex. C–C torsional state <sup>b</sup>	15 716.82 ± 0.29	5225.778 ± 0.075	4403.780 ± 0.074
First ex. CCN bending state <sup>c</sup>	15 470.01 ± 0.21	5273.061 ± 0.091	4425.575 ± 0.065
First ex. C–N torsional state <sup>d</sup>	15 397.21 ± 0.14	5305.652 ± 0.047	4436.164 ± 0.045
Combination of C–C tors. and CCN bending <sup>e</sup>	15 609.10 ± 0.33	5235.10 ± 0.22	4408.01 ± 0.22

<sup>a</sup> Uncertainties represent one standard deviation. <sup>b</sup> 10 transitions. <sup>c</sup> 15 transitions. <sup>d</sup> 9 transitions. <sup>e</sup> 8 transitions. In all cases were one or more centrifugal distortion constants varied in the least squares fit, but the results were too inaccurate to warrant their publication.

squares fit, but the results were quite inaccurate and are therefore not reported here. Relative intensity measurements yielded  $227 \pm 25 \text{ cm}^{-1}$  for this fundamental frequency.

In order to assign this mode to either the CCN or the CCF bending mode, the two angles were opened up by  $0.5^\circ$  each in our model calculations. Very similar results for the changes of the rotational constants were found in both cases. These changes were also close to the experimentally determined ones. It is thus not possible to determine unambiguously from the microwave data alone whether this is the CCN or the CCF bending mode or some combination mode of the two. The last-mentioned possibility is probably correct, but it is nevertheless felt that this mode is closer to the pure CCN bending mode than to the pure CCF bending mode. This is believed since the lowest bending mode of the isoelectronic *gauche* 1,2-difluoroethane,  $\nu_9$ , is reported<sup>10</sup> at  $327 \text{ cm}^{-1}$ , which is  $100 \text{ cm}^{-1}$  higher than found in our case.

8 transitions of a combination mode of the C–C torsion and CCN bending mode were also identified. The intensity of this spectrum is about 5% of the ground state spectrum. Due to its weakness only one *R*-branch line was tentatively assigned, while the *Q*-branch transitions were ascertained by their Stark effect in several cases. It is seen from Tables 2 and 3 that the rotational constants of this combination mode are about exactly that calculated from the changes of the rotational constants upon excitation of these two normal vibrations.

The final excited state which was assigned for conformer I was the first excited state of what is believed to be the torsional motion of the amino group. These lines have about 10% of the intensity of the corresponding ground state transitions at

215 K. Attempts to reproduce the observed changes of the rotational constants upon excitation by twisting the amino group  $2^\circ$  in the model calculations failed. In spite of this, the small changes of the rotational constants of this state as compared with the ground state are expected for the CN-torsional motion since little mass is involved in this rotation. It is thus quite probable that this mode is somewhat more complex than a simple torsion about the CN bond. Relative intensity measurements yielded  $350 \pm 30 \text{ cm}^{-1}$  for this fundamental frequency. This is roughly  $90 \text{ cm}^{-1}$  higher than the corresponding frequency of methylamine<sup>11</sup> ( $263.9 \text{ cm}^{-1}$ ). An increase of the torsional frequency of 2-fluoroethylamine as compared to that of methylamine is expected because of the hydrogen bond which is present in the former molecule. This bond is presumed to "hold" the proton more firmly in 2-fluoromethylamine while no hydrogen bond exists in methylamine. This should lead to a higher C–N-torsional frequency in the former molecule in agreement with the present finding.

*Dipole moment.* Stark coefficients of low *J* transitions were used to determine the dipole moment. In those cases where a quadrupole fine structure was more or less resolved, comparatively large Stark shifts were measured in order to minimize coupling effects. A d.c. voltage was applied between the Stark septum and the cell with the modulating square wave voltage superimposed. The d.c. voltage was calibrated using the OCS  $J=1 \rightarrow 2$  transitions with  $\mu_{\text{OCS}} = 0.71521 \text{ D}$ .<sup>12</sup> Each second order coefficient shown in Table 4 was assigned a standard deviation which is presumed to take into account the additional uncertainty arising from quadrupole coupling. A least squares fit using a diagonal weight matrix was performed. The weights were chosen as

Table 4. Stark coefficients and dipole moment of conformer I of CH<sub>2</sub>FCH<sub>2</sub>NH<sub>2</sub>.

Transition		$\Delta\nu/E^2$ (MHz V <sup>-2</sup> cm <sup>2</sup> ) × 10 <sup>6</sup>	
		Obs.	Calc.
1 <sub>0,1</sub> → 2 <sub>0,2</sub>	M =1	15.8 ± 0.2 <sup>a</sup>	16.0
1 <sub>1,1</sub> → 2 <sub>1,2</sub>	M=0	1.92 ± 0.02	1.93
2 <sub>1,1</sub> → 3 <sub>0,3</sub>	M =2	12.4 ± 0.2	12.5
4 <sub>1,3</sub> → 4 <sub>2,2</sub>	M =2	14.0 ± 0.2	13.9
	M =3	34.0 ± 0.3	34.0
	M =4	63.1 ± 0.6	62.3
$\mu_a = 1.148 \pm 0.003$ D		$\mu_b = 1.380 \pm 0.008$ D	
$\mu_c = 0.332 \pm 0.021$ D		$\mu_{rot} = 1.826 \pm 0.012$ D	

<sup>a</sup> Uncertainties represent one standard deviation.

the inverse squares of the standard deviations of the Stark coefficients appearing in Table 4. This table also gives the total dipole moment and its components along the principal inertial axes. There is good agreement between the observed dipole moment components and those obtained by the bond-moment method (p. 16). This is independent evidence for the fact that the observed rotamer is indeed conformer I.

The total dipole moment was calculated to be 1.5 D by the bond-moment method. The experimental value of 1.826 ± 0.012 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 approximations used in the bond-moment method.

<sup>14</sup>N quadrupole coupling constants. Several of the low and medium *J* transitions were split due to quadrupole coupling of the <sup>14</sup>N nucleus with the molecular rotation. In order to determine  $\chi_{aa}$  and  $\chi_{bb}$  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,  $E_q$ , from the "unperturbed" frequencies were then least squares fitted using eqn. (1)

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

The symbols of this equation are defined in Ref. 13.

The splittings are relatively small in a nitrogen containing molecule and normally overlap to lesser or greater extent. The data to be fitted to eqn. (1) are thus correlated and a symmetrical weight matrix should have been used. Application of this kind of weight matrix is not easy and the simpler method using a 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 5. In those rather frequent cases where two or more quadrupole components were unresolved, the measured peak was presumed to be most representative for the strongest of these components and only this one was then used in the least squares procedure. The standard deviation of  $E_q$  for this component was judiciously increased as compared with a corresponding line consisting of only one quadrupole component. The results are shown in Table 5. After the least squares determination of  $\chi_{aa}$  and  $\chi_{bb}$  were performed, the split lines were corrected for quadrupole effects and used in the least squares fit to determine the final values for the spectroscopic constants shown in Table 2.

Assignment of conformer II. Many strong lines remained in the spectrum after the assignment of conformer I had been accomplished. These transitions were too intense to be attributed to unidentified vibrationally excited states of this rotamer. A search was therefore made for conformer II shown in Fig. 1. The strongest low *J* lines of its spectrum were, on the basis of the bond-moment calculations described above, predicted to be the *b*-type *Q*-branch  $J_{1,J-1} \rightarrow J_{2,J-2}$  and the *c*-type *Q*-branch  $J_{1,J-1} \rightarrow J_{2,J-1}$ . These transitions were predicted to fall in the 25–30 GHz-range. They were then searched for and readily assigned. Low *J* *b*-type *R*-branch lines were next found close to their predicted frequencies. The full assignment of the spectrum of the ground vibrational state of II was then derived in the same step-wise manner as described for conformer I. A total of about 150 transitions were ultimately assigned. Table 6 lists 42 selected lines of the *b*- and the *c*-type. No *a*-type lines were identified because of the small  $\mu_a$ -component which is less than 0.03 D producing insufficient intensities for these transitions.

The highest *J* value assigned was the *c*-type  $66_{10,56} \rightarrow 66_{11,56}$  *Q*-branch transition. Centrifugal distortion is as large as 13 609.71 MHz for this

Table 5.  $^{14}\text{N}$  quadrupole splittings and diagonal elements of the quadrupole coupling tensor.

Transition	$F \rightarrow F$	$E_q(\text{obs})$ (MHz)	$E_q(\text{obs}) - E_q(\text{calc.})$ (MHz)
$1_{1,0} \rightarrow 2_{1,1}$	2→3	$-0.01 \pm 0.03^a$	0.04
	1→2	$0.46 \pm 0.04$	-0.04
	0→1	$-1.56 \pm 0.03$	0.07
$2_{2,1} \rightarrow 3_{2,2}$	3→4	$-0.06 \pm 0.03$	0.08
	2→3	$0.61 \pm 0.03$	0.11
$2_{2,0} \rightarrow 3_{2,1}$	3→4	$0.02 \pm 0.03$	0.13
	2→3	$0.41 \pm 0.03$	0.01
$5_{0,5} \rightarrow 5_{1,4}$	5→5	$-1.37 \pm 0.03$	-0.10
	6→6	$0.43 \pm 0.05$	-0.06
$6_{0,6} \rightarrow 6_{1,5}$	6→6	$-1.36 \pm 0.03$	-0.01
	7→7	$0.46 \pm 0.05$	-0.08
$7_{0,7} \rightarrow 7_{1,6}$	7→7	$-1.57 \pm 0.03$	-0.17
	8→8	$0.53 \pm 0.05$	-0.05
$9_{1,8} \rightarrow 9_{2,7}$	9→9	$-0.56 \pm 0.03$	-0.14
	10→10	$-0.03 \pm 0.04$	-0.21
$0_{0,0} \rightarrow 1_{1,1}$	1→2	$-0.08 \pm 0.03$	0.05
	1→1	$0.48 \pm 0.05$	-0.14
	1→0	$-1.20 \pm 0.03$	0.05
$1_{0,1} \rightarrow 2_{1,2}$	2→3	$-0.08 \pm 0.03$	0.14
	1→2	$0.67 \pm 0.04$	0.05
$3_{1,2} \rightarrow 3_{2,2}$	4→4	$-0.23 \pm 0.04$	-0.07
	3→3	$0.36 \pm 0.03$	-0.12
$5_{1,4} \rightarrow 5_{2,4}$	6→6	$-0.26 \pm 0.04$	-0.01
	5→5	$0.66 \pm 0.04$	0.00
$6_{1,5} \rightarrow 6_{2,5}$	7→7	$-0.19 \pm 0.04$	0.08
	6→6	$0.74 \pm 0.03$	0.07
$7_{1,6} \rightarrow 7_{2,6}$	8→8	$-0.14 \pm 0.03$	0.13
	7→7	$0.75 \pm 0.03$	0.10
$0_{0,0} \rightarrow 1_{1,0}$	1→2	$0.26 \pm 0.03$	0.04
	1→1	$-1.03 \pm 0.03$	0.10
$3_{1,2} \rightarrow 4_{0,4}$	5→5	$-0.36 \pm 0.04$	0.09
	3→4	$1.24 \pm 0.03$	-0.04
$\chi_{aa} = 2.02 \pm 0.13$		$\chi_{bb} = 2.49 \pm 0.10$ MHz	

<sup>a</sup> Uncertainties represent one standard deviation.

line. *b*- and *c*-, *P*- and *R*-branch lines were identified up to the  $46_{2,2} \rightarrow 45_{2,3}$  and the  $45_{2,1} \rightarrow 46_{2,0}$  transitions. As shown in Table 7 accurate rotational and quartic distortion constants have been determined from 134 transitions. The sextic constants are of a poorer quality, but it was necessary to include them in order to obtain a good fit.

Comparison of the spectroscopic constants of Tables 2 and 7 shows that the rotational constants as well as the quartic coefficients centrifugal distortion are fairly similar. The entries for conformer II are all a little bit smaller than the corresponding values for I. This is expected because of the great structural similarity of the two rotamers. The

sextic constants, however, of the two forms differ radically. This indicates that little physical significance should be attached to them.

*Vibrationally excited states.* A strong satellite spectrum having about 1/3 of the intensity of the ground state was assigned as the first excited state of the C-C torsional mode. Relative intensity measurements performed on unsplit lines yielded  $162 \pm 15 \text{ cm}^{-1}$  for this fundamental frequency. This is definitely lower by about  $30 \text{ cm}^{-1}$  than the corresponding frequency of the other conformer.

A  $2^\circ$  opening of the NCCF torsional angle of our geometrical model reproduces satisfactorily, albeit not perfectly, the observed changes of the rotational

Table 6. Selected transitions for the ground vibrational state of conformer II of CH<sub>2</sub>FCH<sub>2</sub>NH<sub>2</sub>.

Transition	Observed frequency <sup>a</sup> (MHz)	Obs. - calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
<i>b</i> -type				
0 <sub>0,0</sub> → 1 <sub>1,1</sub>	19 587.21	-0.03	-0.01	
1 <sub>0,1</sub> → 2 <sub>1,2</sub>	28 388.88	0.06	0.05	
2 <sub>1,2</sub> → 3 <sub>0,3</sub>	19 482.13	0.09	-0.90	
3 <sub>1,3</sub> → 4 <sub>0,4</sub>	29 888.11	-0.05	-2.10	
7 <sub>3,4</sub> → 8 <sub>2,7</sub>	22 605.47	0.06	-10.77	0.02
13 <sub>6,7</sub> → 14 <sub>5,10</sub>	22 476.60	-0.07	-70.80	0.12
13 <sub>6,8</sub> → 14 <sub>5,9</sub>	22 612.49	-0.13	-72.80	0.11
18 <sub>8,11</sub> → 19 <sub>7,12</sub>	29 652.45	-0.10	-176.66	0.41
18 <sub>8,10</sub> → 19 <sub>7,13</sub>	29 643.54	0.05	-176.31	0.42
6 <sub>0,6</sub> → 6 <sub>1,5</sub>	21 374.18	0.14	-4.95	
7 <sub>0,7</sub> → 7 <sub>1,6</sub>	25 789.36	0.04	-9.53	
2 <sub>1,1</sub> → 2 <sub>2,0</sub>	29 941.52	0.05	-0.53	
3 <sub>1,2</sub> → 3 <sub>2,1</sub>	28 935.37	-0.02	0.26	
4 <sub>1,3</sub> → 4 <sub>2,2</sub>	27 835.96	0.02	1.30	
7 <sub>1,6</sub> → 7 <sub>2,5</sub>	25 932.83	0.01	2.93	-0.01
10 <sub>1,9</sub> → 10 <sub>2,8</sub>	29 795.01	-0.07	-12.06	-0.03
<i>c</i> -type				
0 <sub>0,0</sub> → 1 <sub>1,10</sub>	20 408.50	0.02	-0.08	
3 <sub>1,2</sub> → 4 <sub>0,4</sub>	24 963.08	0.03	-1.21	
7 <sub>2,6</sub> → 8 <sub>1,8</sub>	29 848.05	0.02	-4.71	0.01
11 <sub>5,6</sub> → 12 <sub>4,8</sub>	24 398.21	0.00	-53.31	0.05
11 <sub>5,7</sub> → 12 <sub>4,9</sub>	23 744.23	-0.03	-47.83	0.07
2 <sub>1,1</sub> → 2 <sub>2,1</sub>	29 892.76	-0.02	-0.51	
4 <sub>1,3</sub> → 4 <sub>2,3</sub>	27 117.03	-0.01	1.78	
6 <sub>1,5</sub> → 6 <sub>2,5</sub>	22 952.05	-0.13	6.65	
13 <sub>2,11</sub> → 13 <sub>3,11</sub>	28 538.60	-0.07	80.23	-0.02
20 <sub>3,17</sub> → 20 <sub>4,17</sub>	29 931.98	0.01	330.13	-0.08
29 <sub>4,25</sub> → 29 <sub>5,25</sub>	18 467.47	0.07	813.29	-0.15
41 <sub>6,35</sub> → 41 <sub>7,35</sub>	22 906.47	0.00	2740.13	-0.47
48 <sub>7,41</sub> → 48 <sub>8,41</sub>	19 858.04	-0.09	3995.10	-0.86
54 <sub>8,46</sub> → 54 <sub>9,46</sub>	22 044.98	0.11	6184.65	-1.81
61 <sub>9,52</sub> → 61 <sub>10,52</sub>	19 407.23	0.01	8089.98	-3.92
66 <sub>10,56</sub> → 66 <sub>11,56</sub>	27 877.95	-0.01	13609.71	-9.18
Coalescing <i>b</i> - and <i>c</i> -type <sup>b</sup>				
13 <sub>7</sub> → 12 <sub>8</sub>	29 668.70	-0.01	-45.07	0.07
20 <sub>10</sub> → 19 <sub>11</sub>	23 921.76	-0.06	-28.85	
27 <sub>13</sub> → 26 <sub>14</sub>	18 208.75	-0.04	66.01	-0.69
33 <sub>16</sub> → 32 <sub>17</sub>	22 304.29	-0.08	121.26	-1.54
41 <sub>20</sub> → 40 <sub>21</sub>	27 801.40	-0.01	234.94	-3.81
46 <sub>22</sub> → 45 <sub>23</sub>	20 989.27	0.07	600.42	-12.19
24 <sub>11</sub> → 25 <sub>10</sub>	25 292.15	0.01	-331.05	1.41
32 <sub>15</sub> → 33 <sub>14</sub>	19 519.00	0.06	-623.92	4.92
37 <sub>17</sub> → 38 <sub>16</sub>	26 370.57	0.00	-1007.25	10.20
45 <sub>21</sub> → 46 <sub>20</sub>	20 381.37	0.10	-1554.48	26.20

<sup>a</sup> ±0.10 MHz. Transitions with resolved quadrupole splittings have been corrected for this effect. <sup>b</sup> The  $K_{-1}$ -doublets coalesce for high values of  $K_{-1}$ . Subscripts refer to  $K_{-1}$ .



Table 7. Spectroscopic constants for conformer II of CH<sub>2</sub>FCH<sub>2</sub>NH<sub>2</sub>.<sup>a</sup>

Vibrational state	Ground	First ex. C—C torsion
Number of transitions	134	66
rms (MHz)	0.070	0.077
<i>A<sub>v</sub></i> (MHz)	15 186.4940 ± 0.0077	15 303.333 ± 0.013
<i>B<sub>v</sub></i> (MHz)	5 222.0616 ± 0.0028	5 192.3159 ± 0.0045
<i>C<sub>v</sub></i> (MHz)	4 400.7600 ± 0.0023	4 385.4414 ± 0.0040
$\Delta_J$ (kHz)	6.943 ± 0.013	6.716 ± 0.017
$\Delta_{JK}$ (kHz)	-34.775 ± 0.068	-34.75 ± 0.11
$\Delta_K$ (kHz)	86.028 ± 0.036	91.965 ± 0.039
$\delta_J$ (kHz)	1.9911 ± 0.0027	1.9061 ± 0.0032
$\delta_K$ (Hz)	13.17 ± 0.27	14.72 ± 0.21
<i>H<sub>J</sub></i> (Hz)	-0.0008 ± 0.0065	-0.052 ± 0.011
<i>H<sub>JK</sub></i> (Hz)	-1.57 ± 0.17	0.192 ± 0.022
<i>H<sub>KJ</sub></i> (Hz)	2.91 ± 0.33	-4.10 ± 0.50
<i>H<sub>K</sub></i> (Hz)	-0.68 ± 0.34	6.69 ± 0.65
<i>h<sub>J</sub></i> (Hz)	-0.0118 ± 0.0021	<sup>b</sup>
<i>h<sub>JK</sub></i> (Hz)	0.481 ± 0.083	<sup>b</sup>
<i>h<sub>K</sub></i> (Hz)	-22.0 ± 1.5	<sup>b</sup>

<sup>a</sup> Uncertainties represent one standard deviation. rms is the root-mean-square deviation. The rotational constants are those obtained directly from the least squares fit without correcting for centrifugal distortion. <sup>b</sup> Fixed at zero in least-squares fit.

Table 8. Rotational constants<sup>a</sup> for vibrationally excited states of conformer II of CH<sub>2</sub>FCH<sub>2</sub>NH<sub>2</sub>.

Vibrational state	<i>A<sub>v</sub></i> (MHz)	<i>B<sub>v</sub></i> (MHz)	<i>C<sub>v</sub></i> (MHz)
Second ex. C—C torsional state <sup>b</sup>	15 403.98 ± 0.79	5163.74 ± 0.14	4369.41 ± 0.13
First ex. C—N torsional state <sup>c</sup>	15 176.01 ± 0.19	5230.49 ± 0.11	4404.34 ± 0.12

<sup>a</sup> Uncertainties represent one standard deviation. <sup>b</sup> 6 transitions. <sup>c</sup> 12 transitions. Centrifugal distortion constants were varied in the least squares fit, but the results were too inaccurate to warrant their publication.

constants upon excitation. The spectroscopic constants of this state derived from 66 transitions are shown in Table 7. *J*-values up to 49 were used to compute these parameters.

The second excited state of this mode was also assigned and its rotational constants are shown in Table 8.

This table also includes what is assigned as the first excited state of the C—N torsional mode. As in the case of conformer I an opening of the torsional angle of the amino group in our calculations did not reproduce satisfactorily the observed changes of the rotational constants upon excitation. A frequency of 324 ± 30 cm<sup>-1</sup> was found for this mode by relative intensity measurements. This frequency too, is higher than that of methylamine, a finding that can be rationalized in the same way as discussed for conformer I.

It was not possible to assign the first excited state of the CCN-bending vibration despite several thousand attempts using various procedures including also a restricted form of the method described by van Eijck.<sup>14</sup> The most likely explanation for this is perhaps that several low *J* *b*-type *Q*-branch lines which are the most intense ones and therefore the prime target for these attempts, overlapped with other stronger lines. Alternatively, this bending mode could fall at a considerable higher frequency in this rotamer than in conformation II. This would have decreased intensities so much that it was impossible to make assignments. Coriolis resonance is another rather remote possibility.

Inversion tunneling of the amino group has been found in several amines. This feature is absent from the microwave spectra of the two conformers. A prerequisite for tunneling is the fact that there are

Table 9. Stark coefficients<sup>a</sup> and dipole moment of conformer II of CH<sub>2</sub>FCH<sub>2</sub>NH<sub>2</sub>.

Transition		$\Delta\nu/E^2$ (MHz V <sup>-2</sup> cm <sup>2</sup> ) × 10 <sup>6</sup>	
		Obs.	Calc.
0 <sub>0,0</sub> → 1 <sub>1,1</sub>	M = 0	13.9 ± 0.2	13.2
7 <sub>0,7</sub> → 7 <sub>1,6</sub>	M  = 5	25.4 ± 0.3	24.9
	M  = 6	35.6 ± 0.4	35.9
	M  = 7	48.9 ± 0.3	48.8
6 <sub>1,5</sub> → 6 <sub>2,4</sub>	M  = 5	4.22 ± 0.05	4.15
	M  = 6	5.42 ± 0.06	5.58
8 <sub>1,7</sub> → 8 <sub>2,6</sub>	M  = 8	10.3 ± 0.1	10.4
3 <sub>1,2</sub> → 3 <sub>2,1</sub>	M  = 2	-43.9 ± 0.5	-44.9
	M  = 2	-6.05 ± 0.07	-6.02
$\mu_a < 0.03$ D		$\mu_b = 1.337 \pm 0.008$ D	
$\mu_c = 1.002 \pm 0.005$ D		$\mu_{rot} = 1.671 \pm 0.010$ D	

<sup>a</sup>  $\mu_a$  assumed to be zero in the least squares fit  
Uncertainties represent one standard deviation.

two identical forms of the molecule with an associated double-minimum potential. This is indeed the case for both I and II which each possesses two identical mirror image forms. For rotamer II a simple rotation of approximately 120° about the C–C bond transforms the one heavy-atom *gauche* rotamer into its mirror image. In conformer I rotations about the C–C as well as the C–N bonds have the same effect. The direction of the *c*-axis dipole moment component is expected to be reversed for both conformers by this kind of transformation motion. This should result in a splitting of the *c*-type transitions into doublets, but these were not resolved. The reason for this is presumed to be the fact that heavy atoms are involved in the transformation motion making the splittings very small even if the barrier is reasonably low.

**Dipole moment.** The dipole moment of conformer II was determined in the same manner as for I. If all dipole moment components were varied, the component along the *a*-axis was found to be imaginary. Transitions which are very sensitive to  $\mu_a$  were employed, and it was therefore found that this component is less than 0.03 D. The result obtained by assuming that  $\mu_a$  is equal to zero is shown in Table 9.

There is quite good agreement between the bond moment calculations mentioned above and  $\mu_a$  and  $\mu_b$  determined experimentally.  $\mu_c$  is, however, found to be too big by these calculations as is the total dipole moment which was computed as 2.1 D. There is thus no evidence for enhancement of the dipole moment as a result of the hydrogen bond in this conformer.

**Quadrupole coupling constants.** The <sup>14</sup>N-nucleus quadrupole coupling constants were determined as described for conformer I. The results are shown in Table 10.

The fact that  $\chi_{aa}$  is changed from +2.02 ± 0.13 MHz in I to -2.78 ± 0.14 MHz in conformer II is evidence for a large rotation of the amino group upon conversion of the two forms. This is, of course, in agreement with the existence of the two conformers assigned in this work.

**Search for anti conformations.** The assignments made as described above include about 400 transitions. 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 among the majority of the remaining unassigned medium intensity lines. In a few cases partial resolution of the Stark effect was achieved for these transitions which seem to be *Q*-branch lines.

Three explanations seem plausible for these rather few unassigned lines. They might, for example, belong to one and/or both the two *anti* conformers denoted III or IV and shown in Fig. 2. These forms were computed to be 1.06 kcal/mol and 1.61 kcal/mol, respectively, less stable than I by the *ab initio* method.<sup>5</sup> Rotational constants were predicted to be *A* = 29.8 GHz, *B* = 3.82 GHz and *C* = 3.57 GHz and the dipole moment components were predicted<sup>7</sup> as  $\mu_a = 2.5$  D,  $\mu_b = 0.6$  D, and  $\mu_c = 1.0$  D for III. For conformer IV the following predictions were made: *A* = 28.3 GHz, *B* = 3.89 GHz, *C* = 3.65 GHz, with  $\mu_a = 1.3$  D,  $\mu_b = 2.0$  D, and  $\mu_c = 0$  D for symmetry reasons. Searches for these forms were negative, and from the spectral positions of the unidentified lines it is concluded that they most likely belong to neither III nor IV.

The second possibility is that the unidentified transitions belong to a third heavy-atom *gauche* rotamer, a conformer calculated to be less stable than I by 4.02 kcal/mol by Pople *et al.*<sup>5</sup> The rotational constants for this conformer are predicted to be rather close to those of the two identified

Table 10.  $^{14}\text{N}$  quadrupole splittings and diagonal elements of the quadrupole coupling tensor.

Transition	$F \rightarrow F'$	$E_q(\text{obs.})$ (MHz)	$E_q(\text{obs.}) - E_q(\text{calc.})$ (MHz)
$7_{0,7} \rightarrow 7_{1,6}$	8 $\rightarrow$ 8	$0.15 \pm 0.03^a$	0.01
	7 $\rightarrow$ 7	$-0.33 \pm 0.03$	0.02
$2_{1,1} \rightarrow 2_{2,0}$	3 $\rightarrow$ 3	$-0.32 \pm 0.03$	0.04
	4 $\rightarrow$ 4	$-0.28 \pm 0.03$	-0.05
$3_{1,2} \rightarrow 3_{2,1}$	3 $\rightarrow$ 3	$0.76 \pm 0.03$	0.06
	5 $\rightarrow$ 5	$-0.15 \pm 0.03$	0.01
$4_{1,3} \rightarrow 4_{2,2}$	4 $\rightarrow$ 4	$0.52 \pm 0.03$	0.07
	1 $\rightarrow$ 2	$-0.10 \pm 0.03$	0.02
$0_{0,0} \rightarrow 1_{1,1}$	1 $\rightarrow$ 1	$0.52 \pm 0.03$	-0.06
	2 $\rightarrow$ 3	$-0.07 \pm 0.04$	0.04
$1_{0,1} \rightarrow 2_{1,2}$	1 $\rightarrow$ 2	$0.66 \pm 0.03$	0.08
	0 $\rightarrow$ 1	$-1.20 \pm 0.03$	0.08
	3 $\rightarrow$ 4	$0.26 \pm 0.04$	0.08
$2_{1,2} \rightarrow 3_{0,3}$	2 $\rightarrow$ 3	$-0.47 \pm 0.03$	0.06
	4 $\rightarrow$ 5	$-0.04 \pm 0.03$	-0.17
$3_{1,3} \rightarrow 4_{0,4}$	3 $\rightarrow$ 4	$-0.38 \pm 0.03$	-0.05
	3 $\rightarrow$ 3	$-0.41 \pm 0.03$	-0.04
$2_{1,1} \rightarrow 2_{2,1}$	2 $\rightarrow$ 2	$1.25 \pm 0.03$	-0.03
	1 $\rightarrow$ 1	$-1.34 \pm 0.04$	-0.06
	5 $\rightarrow$ 5	$-0.17 \pm 0.04$	0.03
$4_{1,3} \rightarrow 4_{2,3}$	4 $\rightarrow$ 4	$0.55 \pm 0.04$	0.01

$$\chi_{aa} = -2.78 \pm 0.14 \text{ MHz}$$

$$\chi_{bb} = 2.34 \pm 0.08 \text{ MHz}$$

<sup>a</sup> Uncertainties represent one standard deviation.

rotamers, but the facts that this form will have no hydrogen bond and that the probable direction of the amino group lone electron pair is nearly parallel to the C-F bond indicate a high energy for this conformer in agreement with the *ab initio* result.

Thus, the third possibility that remains, namely that these transitions are unassigned, vibrationally

excited state lines presumably for rotamer II, seems most probable both because of their intensities, Stark effects, and spectral positions.

It is thus concluded that the presence of any *anti* form would have been noticed if its concentration had exceeded 10% of the total. Conformer I and II are thus conservatively estimated to be more stable by at least 0.75 kcal/mol than any other form of the molecule.

Absolute intensity measurements have also been made for some spectral lines of both I and II. Although this method is rather crude,<sup>15</sup> it gives independent evidence pointing in the same direction.

*Energy difference between the two conformers.* Relative intensity measurements<sup>8</sup> were made to determine Gibbs free energy difference between the two conformers. The peak intensities were taken by slowly scanning over the spectral lines. The carefully selected transitions 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 several cases high  $J$  lines with coalescing  $K_{-1}$  doublets of

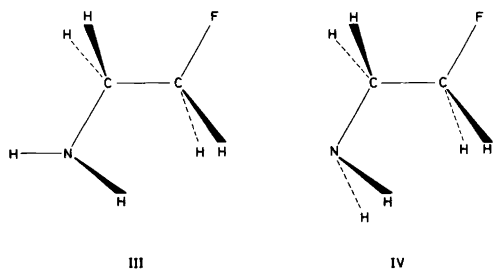


Fig. 2. Heavy-atom *anti* conformers of 2-fluoroethylamine. No hydrogen bond is possible in these cases. Neither of these were identified in the microwave spectrum.

Table 11. Intensity measurements,<sup>a</sup> equilibrium constants, and Gibbs' free energy difference of conformers I and II of CH<sub>2</sub>FCH<sub>2</sub>NH<sub>2</sub> at 215 ± 5 K.<sup>a</sup>

Conformation	Transition	$\alpha_I/\alpha_{II}$	$K = \frac{[I]}{[II]}$	$\Delta G^\circ$ (kcal/mol)
I II	14 <sub>2,12</sub> → 14 <sub>3,12</sub> 20 <sub>10</sub> → 19 <sub>11</sub>	1.2	1.3	-0.11
I II	14 <sub>2,12</sub> → 14 <sub>3,12</sub> 11 <sub>5,7</sub> → 12 <sub>4,8</sub>	1.2	1.0	0.0
I II	28 <sub>13</sub> → 29 <sub>12</sub> 6 <sub>0,6</sub> → 6 <sub>1,5</sub>	0.75	1.4	-0.14
I II	4 <sub>1,3</sub> → 4 <sub>2,2</sub> 11 <sub>6</sub> → 10 <sub>7</sub>	2.4	1.1	-0.04
I II	13 <sub>2,11</sub> → 13 <sub>3,11</sub> 11 <sub>6</sub> → 10 <sub>7</sub>	1.4	1.2	-0.08
I II	13 <sub>2,11</sub> → 13 <sub>3,11</sub> 40 <sub>6,34</sub> → 40 <sub>7,34</sub>	0.59	1.1	-0.04
I II	4 <sub>1,3</sub> → 4 <sub>2,2</sub> 40 <sub>6,34</sub> → 40 <sub>7,34</sub>	0.99	1.0	0.0
I II	4 <sub>1,3</sub> → 4 <sub>2,2</sub> 35 <sub>16</sub> → 36 <sub>15</sub>	1.5	0.8	0.10
I II	13 <sub>2,11</sub> → 13 <sub>3,11</sub> 35 <sub>16</sub> → 36 <sub>15</sub>	0.84	0.8	0.10
I II	2 <sub>1,2</sub> → 3 <sub>1,3</sub> 35 <sub>16</sub> → 36 <sub>15</sub>	1.6	1.1	-0.04
I II	5 <sub>1,4</sub> → 5 <sub>2,3</sub> 35 <sub>16</sub> → 36 <sub>15</sub>	1.7	0.7	0.30
I II	8 <sub>1,7</sub> → 8 <sub>2,6</sub> 22 <sub>10</sub> → 23 <sub>9</sub>	2.5	1.2	-0.08
I II	8 <sub>1,7</sub> → 8 <sub>2,6</sub> 24 <sub>12</sub> → 23 <sub>13</sub>	3.6	1.0	0.0
I II	6 <sub>1,5</sub> → 6 <sub>2,4</sub> 24 <sub>12</sub> → 23 <sub>13</sub>	2.6	1.0	0.0
I II	6 <sub>1,5</sub> → 6 <sub>2,4</sub> 22 <sub>10</sub> → 23 <sub>9</sub>	1.8	1.2	-0.08
$K_{av.} = \frac{[I]}{[II]} = 1.06 \pm 0.19$		$\Delta G^\circ = -0.07 \pm 0.10$ kcal/mol		

<sup>a</sup> Uncertainties represent one standard deviation.

both *b*- and *c*-type 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 composited. The equilibrium constant *K* was calculated from eqn. (2) which is a slight modification of eqn. (2) of Ref. 16.

$$K = \frac{[I]}{[II]} = \frac{\alpha_I}{\alpha_{II}} \left( \frac{v_{II}}{v_I} \right)^2 \left( \frac{A_{II} B_{II} C_{II}}{A_I B_I C_I} \right)^{\frac{1}{2}} \times \frac{\sum_g [\lambda_{II} \mu_{gII} \exp(-E_{gII}^I/kT)]}{\sum_g [\lambda_I \mu_{gI} \exp(-E_{gI}^I/kT)]} \quad (2)$$

The symbols of eqn. (2) are defined in Ref. 16 except for the sum symbols (the capital-letter sigmas).

Eqn. (2), as well as the relative intensity measurements, is based on many assumptions and there are several sources of errors both systematic and random.<sup>16,17</sup> However, by using a large number of measurements including both high and low values of  $J$ , it was hoped that these may, to a large extent, cancel. This optimism is in fact strengthened by the findings of Table 11 which show remarkably consistent values for the equilibrium constant. A precise value of  $-0.07 \pm 0.10$  kcal/mol is found for the free energy difference between I and II.

The entropy difference between these two rotamers was approximated from eqn. (3).<sup>16</sup>

$$\Delta S^\circ = R \ln \frac{1 - \exp(-1.44 \times 162/215)}{1 - \exp(-1.44 \times 195/215)} \quad (3)$$

which yields  $\Delta S^\circ = -0.2 \pm 0.2$  cal/(mol K), where the error limit is assumed to be representative for systematic and random errors.

Application of eqn. (4)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

gives the enthalpy difference as  $\Delta H^\circ = -0.11$  kcal/mol. Error bounds are difficult to estimate, and  $\pm 0.3$  kcal/mol is judiciously chosen. It is thus concluded that conformer I is slightly more stable than II by  $0.1 \pm 0.3$  kcal/mol. However, II is favoured by entropy by  $0.2 \pm 0.2$  kcal/(mol K), mainly because the torsional frequency of this rotamer is lower by about  $30 \text{ cm}^{-1}$ .

*Potential function for the rotation of the amino group.* There are insufficient data for constructing a full potential function for the rotation of the amino group keeping the rest of the molecule in a fixed heavy-atom *gauche* position. The only information that is available comes from the bottoms of the potential wells of the two conformers. The regions between them are quite uncertain. In fact, it is not known at all whether the third *gauche* conformer with staggered atomic positions is stable. A typical potential function is sketched in Fig. 3. The  $\text{CCNH}_a$  dihedral angle is taken to be  $0^\circ$  for I and  $240^\circ$  for II.  $120^\circ$  corresponds to the third *gauche* conformer. The full line in this region corresponds to a stable conformer, while the dotted line corresponds to an unstable form. Peak heights are probably in the 3–6 kcal/mol range. This is somewhat higher than in methylamine,<sup>11</sup> where the three-fold rotational barrier is 1.95 kcal/mol. The reason for assuming that the barrier is higher for the title compound than for methylamine is the hydrogen bond which restricts motion about the C–N bond. This is also reflected in the torsional frequencies as discussed above.

*Structure of the two conformers.* Only one isotopic species was studied for both rotamers and only three rotational constants are thus available for each conformer. A complete geometrical structure cannot, therefore, be determined for the two forms. A selection of parameters to be fitted must be made. The FCCN dihedral angle and the CCN angle were chosen because the rotational constants are sensitive to variation in these parameters and because they are chemically interesting. Further important

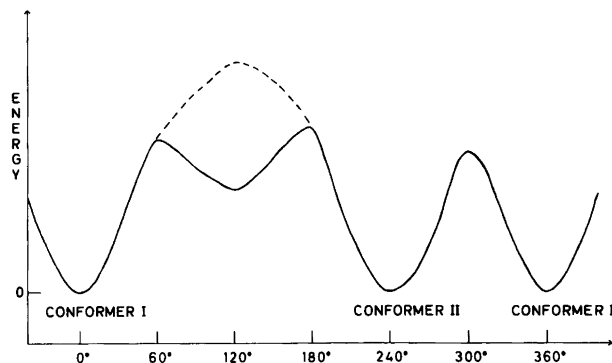


Fig. 3. Plausible shape of the potential function for rotation of the amino group about the C–N bond for the heavy-atom *gauche* conformers. Full line corresponds to the existence of a stable third *gauche* conformer. Dotted line indicates the probable shape for an unstable form.

Table 12. Plausible structural parameters<sup>a</sup> and observed and calculated rotational constants of the two conformers of CH<sub>2</sub>FCH<sub>2</sub>NH<sub>2</sub>.

Assumed structural parameters common for conformer I and II					
C-F (Å)	1.398	CCF (°)	109.70	HNCC (°) <sup>b</sup>	60 or 180
C-N (Å)	1.469	HNH (°)	109.48		
C-C (Å)	1.510	CCH (°)	109.48		
C-H (Å)	1.093	HCH (°)	109.48		
N-H (Å)	1.017	CNH (°)	109.48		
Fitted structural parameters					
Conformer I			Conformer II		
FCCN (°)	64 ± 2 from <i>syn</i>		FCCN (°)	63 ± 2 from <i>syn</i>	
CCN (°)	110 ± 1		CCN (°)	114.5 ± 1	
Hydrogen bond parameters					
N...F (Å)	2.87		2.94		
N-H <sub>a</sub> ...F (Å)	2.55		2.63		
∠N-H <sub>a</sub> ...F (°)	99		97		
∠C-F, N-H <sub>a</sub> (°) <sup>c</sup>	4		5		
∠C-F, N-H <sub>b</sub> (°) <sup>c</sup>	70		68		
Sum of van der Waals' radii <sup>d</sup>					
N...F	2.85 Å		H...F		
Rotational constants (MHz)					
Obs.	Calc.	Diff. (%)	Obs.	Calc.	Diff. (%)
15437.67	15414.38	0.15	15186.49	15197.49	0.07
5302.39	5302.92	0.00	5222.06	5216.61	0.11
4439.52	4426.45	0.29	4400.76	4415.85	0.52

<sup>a</sup> See text. <sup>b</sup> Amino groups assumed to be in exactly staggered positions. <sup>c</sup> Angles between C-F and N-H bonds. <sup>d</sup> Taken from Pauling, L., *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, N.Y., 1960, p. 260.

structural parameters as, for example, the HNCC dihedral angles cannot be meaningfully fitted because the rotational constants are relatively insensitive to these angles as a result of the small masses involved. The amino group hydrogens were then assumed to be in exactly staggered positions. The remaining bond lengths and angles which were kept constant in the fit, were selected from accurate structural studies of related compounds. They are shown in Table 12.

This table also shows that good agreement exists between the observed and calculated rotational constants. The error limits of the FCCN dihedral angle and the CCN angle are assumed to encompass differences between the assumed structural parameters and the real ones.

The FCCN dihedral angles were found to be slightly larger than 60° from *syn*. This was also

found for the two corresponding conformers of ethylenediamine.<sup>3</sup> The CCN angle takes the normal value of 110° in conformer I, but is about 4.5° larger in II. The opening of this angle is perhaps a result of non-bonded repulsion between the amino group hydrogen not involved in hydrogen bonding, H<sub>b</sub>, and the nearest hydrogen atom of the CH<sub>2</sub>F-group.

The hydrogen bond structural parameters, though somewhat more uncertain than the two fitted angles, indicate that the geometry is unfavourable for strong hydrogen bonding. Electrostatic interaction, however, seems to be nearly ideal as the C-F and N-H<sub>a</sub> bonds are about 5° from being parallel.

## DISCUSSION

There are probably several reasons why 2-fluoroethylamine prefers two *gauche* conformers I and II.

Hydrogen bonding is undoubtedly an important factor for this preference. The hydrogen bonds in these two conformers are very similar. The  $H_a-N$  and  $C-F$  bonds are nearly parallel as shown in Table 12. This is very favourable for an electrostatic stabilization of the observed conformer. Covalent bonding between the  $H_a$  and fluorine atoms is probably of little importance in this case because the distance between these two atoms is roughly as large as the sum of their van der Waals radii. It is, therefore, concluded that the hydrogen bonds are mainly electrostatic in origin in both conformers.

Unfortunately, it was not possible to find any sign of a heavy-atom *anti* conformation and thereby determine the energy difference between *gauche* and *anti* conformations. However, in the isoelectronic molecules  $CH_2(OH)CH_2F$ <sup>18</sup> and  $CH_2(NH_2)CH_2NH_2$ <sup>19</sup> high temperature electron diffraction experiments have shown that the *gauche* conformations are so stable that hydrogen bonding alone can hardly account for this preference. It is quite likely that the hydrogen bonds in these cases are augmented by a rather large dispersion force between the proton acceptor and the proton donor. This significant dispersion-force stabilization seems to be present in all  $CH_2XCH_2Y$ -molecules provided that X and Y are the electronegative atoms or groups F, OH, or  $NH_2$ . Even  $CH_2FCH_2F$  exists with *gauche* more stable than *anti* by 0.93 kcal/mol.<sup>20</sup> In this molecule there is, of course, no hydrogen bond. Thus, it will come as no surprise if future electron diffraction experiments indeed show that the *anti* conformers of  $CH_2FCH_2NH_2$  are less stable than *gauche* by several kcal/mol.

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