Microwave Spectrum, Conformational Equilibria and Intramolecular Hydrogen Bonding of 1-Amino-3-butene

K.-M. Marstokk and Harald Møllendal

Department of Chemistry, The University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3, Norway


The microwave spectrum of H₂NCH₂CH₂CH=CH₂ has been investigated in the 22.0–38.0 GHz spectral region at ~50°C. Five low-energy conformers are believed to exist for this compound, four of which were assigned in this work. The rotamers denoted Gauche I and Gauche II each possess an intramolecular hydrogen bond formed between one of the amino group hydrogen atoms and the π electrons of the double bond, while Extended I and Extended II do not have this kind of stabilizing interaction. Gauche I is the most stable, being 0.8(3) kJ mol⁻¹ more stable than Gauche II, 1.9(5) kJ mol⁻¹ more stable than Extended I, and 2.1(5) kJ mol⁻¹ more stable than Extended II.

The hydrogen-bond strength in Gauche I and in Gauche II is compared with those in HOCH₂CH₂CH=CH₂ and HSCNCH₂CH=CH₂. The hydrogen-bond strength in Gauche I and in Gauche II of H₂NCH₂CH₂CH=CH₂ are each nearly the same as in HSCNCH₂CH=CH₂, but considerably weaker than in HOCH₂CH₂CH=CH₂.

Dedicated to Professor Otto Bastiansen on his 70th birthday

A large number of conformations produced by rotation around the C2–C3, C3–C4 and C4–N single bonds (see Fig. 1) is possible for 1-amino-3-butene. Figs. 2 and 3 show Newman projections of six selected rotamers.

It is known that ethylamine derivatives of the type H₂NCH₂CH₂X, where X is some proton-accepting atom or group, prefer two heavy-atom gauche conformations, each with an intramolecular hydrogen bond (H bond) formed between one of the amino group hydrogen atoms and the substituent X, as their most stable conformers. This has been found in recent microwave (MW) studies of H₂NCH₂CH₂F, H₂NCH₂CH₂CN, H₂NCH₂CH₂C≡N, H₂NCH₂CH₂C≡CH, H₂NCH₂CH₂NH₂, and H₂NCH₂CH₂OCH₃. The two heavy-atom gauche rotamers which are capable of forming intramolecular H bonds between one of the amino group hydrogen atoms and the π electrons of the double bond are denoted Gauche I and Gauche II, respectively, and are shown in Figs. 2 and 3. Gauche III of the same figures cannot have an internal H bond. It was found in this work that the H-bonded conformers Gauche I and Gauche II are the two preferred forms of 1-amino-3-butene, with Gauche I slightly more stable than Gauche II. This is in accord with findings for the other H₂NCH₂CH₂X-type molecules.

In addition to the H-bonded Gauche I and Gauche II conformers, further rotamers might coexist with them. A MW study of the closely related alcohol, HOCH₂CH₂CH=CH₂, led to the conclusion that its H-bonded conformer, which was the only one found, is at least 3 kJ mol⁻¹ more stable than any further hypothetical form of this molecule. However, the corresponding thiol, HSCNCH₂CH₂CH=CH₂, revealed the existence of two extended conformers in addition to the more stable H-bonded gauche conformer. The internal H bond in amines is generally somewhat weaker than in the corresponding alcohols.

*To whom correspondence should be addressed.
Fig. 1. Atom numbering and dihedral angles 
\[ \alpha = \angle C1C2C3C4, \ \beta = \angle C2C3C4N, \]
\[ \gamma = \angle C3C4NH2. \] The conformation shown has 
\[ \alpha = \beta = \gamma = 0^\circ. \] Rotation around \( \alpha \) by about 60°, \( \beta \) by approximately 120° and \( \gamma \) by about 0° in the 
direction indicated by the arrows produces the 
H-bonded Gauche I conformer. Keeping \( \alpha \) and \( \beta \) 
constant at these values, a further rotation around 
\( \gamma \) by approximately 120° yields the other 
H-bonded Gauche II, while a rotation by 240° 
produces the non-H-bonded Gauche III rotamer. 
Rotation about \( \alpha \) by 60°, \( \beta \) by 0° and \( \gamma \) by 0° yields 
Extended I. If a 120° rotation around \( \gamma \) is then 
made, Extended II will result, whereas a 240° 
rotation around \( \gamma \) results in Extended III.

It was therefore presumed that extended conformations might also be observable in the case of 1-amino-3-butene. This was found to be the case, as elucidated below.

1-Amino-3-butene, \( \text{H}_2\text{NCH}_2\text{CH}_2\text{CH} = \text{CH}_2 \), was chosen for study because we wanted to investigate the possible H bond interaction between the amino group and the \( \pi \) electrons of the double bond. As mentioned above, it is generally found that alcohols form stronger internal H bonds than do the corresponding amines. Whether amines form stronger bonds than their thiol counterparts is not yet entirely clear. Comparison of intramolecular H bonding in \( \text{H}_2\text{NCH}_2\text{CH}_2\text{CH} = \text{CH}_2 \) with that in 
\( \text{HOCH}_2\text{CH}_2\text{CH} = \text{CH}_2 \) and \( \text{HSCH}_2\text{CH}_2\text{CH} = \text{CH}_2 \) might therefore shed light on this question.

**Experimental**

1-Amino-3-butene was donated by Professor G. Courtois, Laboratoire de Synthèse Organique, Université de Poitiers, France. The synthesis is described by him and his coworkers in Ref. 9. The sample was purified by gas chromatography before use. The spectrometer is an improved version of the one described briefly in Ref. 10 employing klystrons as microwave sources. With this equipment, quadrupole fine-structure splittings larger than approximately 0.6 MHz were resolved in favourable cases. The radio frequency microwave double resonance technique (RFMWDR) was used, as described by Wodarczyk and Wilson.11 A Hewlett-Packard 8660A synthesized-signal generator with an ENI 503L RF power amplifier and a Hewlett-Packard 10514A mixer were utilized in the double resonance ex-

![Microwave Spectrum of H₂NCH₂CH₂CH=CH₂](image)

**Fig. 2.** Newman projections of the gauche and extended conformations of 1-amino-3-butene viewed along the C3–C4 bond.

![Extended Forms](image)

**Fig. 3.** Newman projections of the gauche and extended conformations of 1-amino-3-butene viewed along the N–C4 bond.

375
periments. Measurements were made in the 22.0–38.0 GHz spectral region with the cell cooled with dry ice to about −50°C. A study at lower temperatures could not be made because of insufficient vapour pressure of the compound. The pressure was 0.5–2 Pa during the spectral measurements. Relative intensity measurements were made largely as described in Ref. 12.

**Results**

**Spectrum.** The MW spectrum of 1-amino-3-butene is very dense, with absorptions occurring every few MHz throughout the entire investigated MW region. It is also comparatively weak. The strongest lines, which turned out to be the ground-state $Q$-branch $c$-type transitions of *Gauche I* with $J$ between 15 and 40, have peak absorption coefficients somewhat less than $3 \times 10^{-7}$ cm$^{-1}$. The $J = 6 \leftrightarrow 5$ $R$-branch $a$-type transitions of *Gauche II*, which were the strongest ones observed for this rotamer, are even somewhat weaker than this. The strongest transitions of *Extended I* and *Extended II* have peak absorption intensities less than $1 \times 10^{-7}$ cm$^{-1}$.

**Assignment of Gauche I.** Preliminary rotational constants of the three *gauche* as well as of the three *extended* conformations shown in Figs. 2 and 3 were computed by combining structural parameters taken from related molecules (see Table 14 below). Principal axis dipole moment components predicted by the bond-moment method$^{13}$ are useful for making definite assignments in cases like this. A computation of these parameters was therefore carried out, and the results are collected in Table 1. Likewise, the diagonal elements of the principal axis $^{14}$N-quadrupole coupling tensor of the nitrogen nucleus can be used to help identify the various conformers possessing similar rotational constants or dipole moments. The values shown in Table 2 have been computed as described in Ref. 14 assuming the principal quadrupole coupling constant of the $^{14}$N nucleus to be $\chi = -4.1$ MHz, the value found for NH$_3$,$^{15}$ and to be oriented 109.4°$^{16}$ with respect to the three bonds to the nitrogen nucleus.

A preliminary set of rotational constants was calculated for *Gauche I*. This conformer was predicted (Table 1) to have its predominant principal axis dipole moment component along the $c$-axis. For a prolate asymmetrical rotor with Ray’s asymmetry parameter$^{16}$ close to −0.84, as in the present case, strong $Q$-branch $c$-type transitions will dominate throughout the investigated spectral range (22–38 GHz). The quadrupole coupling constants of Table 2 predict most of these transitions to be split into three strong components with a characteristic intensity pattern. Two

---

**Table 1.** Predicted principal axes bond-moment components calculated by the bond-moment method$^{*}$ for H$_2$NCH$_2$CH$_2$CH=CH$_2$.

<table>
<thead>
<tr>
<th>Conformation</th>
<th>$\mu_a$/10$^{-30}$ C m</th>
<th>$\mu_b$/10$^{-30}$ C m</th>
<th>$\mu_c$/10$^{-30}$ C m</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Gauche I</em></td>
<td>0.4</td>
<td>1.2</td>
<td>4.1</td>
</tr>
<tr>
<td><em>Gauche II</em></td>
<td>3.6</td>
<td>1.0</td>
<td>1.8</td>
</tr>
<tr>
<td><em>Gauche III</em></td>
<td>3.4</td>
<td>0.3</td>
<td>2.3</td>
</tr>
<tr>
<td><em>Extended I</em></td>
<td>0.8</td>
<td>0.2</td>
<td>4.0</td>
</tr>
<tr>
<td>*Extended II</td>
<td>1.2</td>
<td>3.3</td>
<td>2.0</td>
</tr>
<tr>
<td>*Extended III</td>
<td>1.9</td>
<td>2.3</td>
<td>3.1</td>
</tr>
</tbody>
</table>

$^{*}$Ref. 13. 1 Debye = 3.33564×10$^{-30}$ C m.

**Table 2.** Predicted$^{*}$ diagonal elements of the $^{14}$N-quadrupole coupling tensor for H$_2$NCH$_2$CH$_2$CH=CH$_2$.

<table>
<thead>
<tr>
<th>Conformation</th>
<th>$\chi_{aa}$/MHz</th>
<th>$\chi_{bb}$/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Gauche I</em></td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td><em>Gauche II</em></td>
<td>-2.9</td>
<td>1.8</td>
</tr>
<tr>
<td><em>Gauche III</em></td>
<td>-1.2</td>
<td>0.6</td>
</tr>
<tr>
<td><em>Extended I</em></td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>*Extended II</td>
<td>-0.6</td>
<td>-0.3</td>
</tr>
<tr>
<td>*Extended III</td>
<td>2.0</td>
<td>-1.2</td>
</tr>
</tbody>
</table>

$^{*}$See text.
### Table 3. Selected transitions of the ground vibrational state of the hydrogen-bonded gauche I conformer of H$_2$NCH$_2$CH$_2$CH=CH$_2$.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed frequency$^{a,b}$/MHz</th>
<th>Obs-calc frequency/MHz</th>
<th>Centrifugal distortion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total/MHz</td>
<td>Sextic/MHz</td>
<td></td>
</tr>
<tr>
<td><strong>b-type</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10$<em>{3,7}$ ← 10$</em>{2,8}$</td>
<td>25537.11</td>
<td>-0.03</td>
<td>17.68</td>
</tr>
<tr>
<td>12$<em>{3,9}$ ← 12$</em>{2,10}$</td>
<td>23993.95</td>
<td>-0.04</td>
<td>17.53</td>
</tr>
<tr>
<td>13$<em>{3,10}$ ← 13$</em>{2,11}$</td>
<td>23909.03</td>
<td>0.00</td>
<td>10.99</td>
</tr>
<tr>
<td>14$<em>{3,11}$ ← 14$</em>{2,12}$</td>
<td>24431.62</td>
<td>-0.02</td>
<td>-1.81</td>
</tr>
<tr>
<td>15$<em>{3,12}$ ← 15$</em>{2,13}$</td>
<td>25637.23</td>
<td>-0.06</td>
<td>-22.23</td>
</tr>
<tr>
<td>16$<em>{3,13}$ ← 16$</em>{2,14}$</td>
<td>27571.46</td>
<td>0.11</td>
<td>-51.32</td>
</tr>
<tr>
<td>15$<em>{4,11}$ ← 15$</em>{3,12}$</td>
<td>34830.24</td>
<td>-0.03</td>
<td>71.08</td>
</tr>
<tr>
<td>16$<em>{4,12}$ ← 16$</em>{3,13}$</td>
<td>33434.07</td>
<td>0.03</td>
<td>74.57</td>
</tr>
<tr>
<td>17$<em>{4,13}$ ← 17$</em>{3,14}$</td>
<td>32216.38</td>
<td>-0.03</td>
<td>68.90</td>
</tr>
<tr>
<td>18$<em>{4,14}$ ← 18$</em>{3,15}$</td>
<td>31610.57</td>
<td>-0.03</td>
<td>51.23</td>
</tr>
<tr>
<td>19$<em>{4,15}$ ← 19$</em>{3,16}$</td>
<td>31654.96</td>
<td>-0.12</td>
<td>19.16</td>
</tr>
<tr>
<td>20$<em>{4,16}$ ← 20$</em>{3,17}$</td>
<td>32434.87</td>
<td>-0.15</td>
<td>-29.15</td>
</tr>
<tr>
<td>21$<em>{4,17}$ ← 21$</em>{3,18}$</td>
<td>34035.24</td>
<td>-0.01</td>
<td>-94.73</td>
</tr>
<tr>
<td>22$<em>{4,18}$ ← 22$</em>{3,19}$</td>
<td>36448.13</td>
<td>0.19</td>
<td>-177.17</td>
</tr>
<tr>
<td><strong>c-type</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4$<em>{3,2}$ ← 4$</em>{2,2}$</td>
<td>31063.31</td>
<td>0.04</td>
<td>-1.86</td>
</tr>
<tr>
<td>6$<em>{3,4}$ ← 6$</em>{2,4}$</td>
<td>29990.93</td>
<td>-0.01</td>
<td>2.75</td>
</tr>
<tr>
<td>8$<em>{3,6}$ ← 8$</em>{2,6}$</td>
<td>27337.48</td>
<td>0.01</td>
<td>11.80</td>
</tr>
<tr>
<td>10$<em>{3,8}$ ← 10$</em>{2,8}$</td>
<td>23508.90</td>
<td>-0.03</td>
<td>26.68</td>
</tr>
<tr>
<td>12$<em>{3,10}$ ← 12$</em>{2,11}$</td>
<td>37232.05</td>
<td>-0.13</td>
<td>58.81</td>
</tr>
<tr>
<td>13$<em>{4,11}$ ← 13$</em>{3,12}$</td>
<td>32140.91</td>
<td>0.04</td>
<td>104.72</td>
</tr>
<tr>
<td>14$<em>{5,12}$ ← 14$</em>{3,13}$</td>
<td>22633.83</td>
<td>-0.03</td>
<td>186.01</td>
</tr>
<tr>
<td>21$<em>{5,17}$ ← 21$</em>{4,18}$</td>
<td>37477.42</td>
<td>0.09</td>
<td>338.41</td>
</tr>
<tr>
<td>23$<em>{5,19}$ ← 23$</em>{4,20}$</td>
<td>29633.92</td>
<td>0.08</td>
<td>452.98</td>
</tr>
<tr>
<td>26$<em>{6,23}$ ← 26$</em>{5,24}$</td>
<td>37290.63</td>
<td>-0.10</td>
<td>927.02</td>
</tr>
<tr>
<td>30$<em>{6,26}$ ← 30$</em>{5,27}$</td>
<td>27970.20</td>
<td>0.13</td>
<td>1082.36</td>
</tr>
<tr>
<td>35$<em>{7,29}$ ← 35$</em>{6,30}$</td>
<td>35106.50</td>
<td>-0.07</td>
<td>1957.41</td>
</tr>
<tr>
<td>36$<em>{7,30}$ ← 36$</em>{6,31}$</td>
<td>29951.57</td>
<td>0.05</td>
<td>2029.60</td>
</tr>
<tr>
<td>2$<em>{2,1}$ ← 1$</em>{1,1}$</td>
<td>30870.28</td>
<td>0.01</td>
<td>-0.67</td>
</tr>
<tr>
<td>3$<em>{2,2}$ ← 2$</em>{1,2}$</td>
<td>37269.17</td>
<td>0.06</td>
<td>-0.51</td>
</tr>
<tr>
<td>8$<em>{1,7}$ ← 7$</em>{2,5}$</td>
<td>32474.39</td>
<td>0.02</td>
<td>-11.33</td>
</tr>
<tr>
<td>10$<em>{1,6}$ ← 9$</em>{1,8}$</td>
<td>31800.29</td>
<td>0.09</td>
<td>9.56</td>
</tr>
<tr>
<td>12$<em>{2,11}$ ← 11$</em>{3,9}$</td>
<td>32376.57</td>
<td>-0.14</td>
<td>-17.34</td>
</tr>
<tr>
<td>14$<em>{4,11}$ ← 13$</em>{5,9}$</td>
<td>27101.98</td>
<td>-0.02</td>
<td>-59.47</td>
</tr>
<tr>
<td>16$<em>{5,12}$ ← 15$</em>{6,10}$</td>
<td>33557.14</td>
<td>0.01</td>
<td>-127.71</td>
</tr>
<tr>
<td>17$<em>{5,13}$ ← 16$</em>{6,11}$</td>
<td>32860.47</td>
<td>-0.08</td>
<td>-112.87</td>
</tr>
<tr>
<td>21$<em>{7,14}$ ← 20$</em>{6,12}$</td>
<td>31243.42</td>
<td>0.04</td>
<td>-187.29</td>
</tr>
<tr>
<td>21$<em>{7,15}$ ← 20$</em>{6,13}$</td>
<td>31210.40</td>
<td>-0.04</td>
<td>-185.72</td>
</tr>
<tr>
<td>26$<em>{9,17}$ ← 25$</em>{10,15}$</td>
<td>35643.70</td>
<td>-0.05</td>
<td>-333.81</td>
</tr>
<tr>
<td>26$<em>{9,18}$ ← 25$</em>{10,16}$</td>
<td>35641.43</td>
<td>0.01</td>
<td>-333.59</td>
</tr>
</tbody>
</table>

$^a$±0.10 MHz. $^b$Corrected for $^{14}$N quadrupole interaction; see text. $^c$The $K_{-1}$-energy doublets coalesce for high values of $K_{-1}$. Subscripts of $J$ quantum number refer to $K_{-1}$.  

*377*
Table 4. Spectroscopic constants* for the hydrogen-bonded Gauche I conformer of H₂NCH₂CH₂=CH₂.

<table>
<thead>
<tr>
<th>Vib. state</th>
<th>Ground</th>
<th>First ex.</th>
<th>First ex.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N.o.t. c</td>
<td>112</td>
<td>74</td>
<td>32</td>
</tr>
<tr>
<td>R.m.s. MHz</td>
<td>0.072</td>
<td>0.096</td>
<td>0.105</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
A₂/\text{MHz} & = 9223.866(9) & 9289.447(10) & 9249.250(27) \\
B₂/\text{MHz} & = 3199.339(20) & 3193.927(36) & 3191.267(69) \\
C₂/\text{MHz} & = 2668.286(18) & 2662.872(32) & 2662.497(84) \\
\Deltaₐ/\text{kHz} & = 4.425(70) & 4.140(13) & 4.4255^a \\
\Delta_{\text{a,a}}/\text{kHz} & = -28.581(22) & -27.452(47) & -28.92(29) \\
\Deltaₙ/\text{kHz} & = 75.891(87) & 75.504(35) & 78.8(28) \\
\deltaₐ/\text{kHz} & = 1.4216(15) & 1.3200(15) & 1.437(12) \\
\deltaₙ/\text{kHz} & = 6.704(65) & 7.54(21) & 7.19(90) \\
\Phiₐ/\text{Hz} & = 0.063(11) & -0.0050(23) & \_h \\
\Phi_{\text{a,a}}/\text{Hz} & = -0.571(35) & -0.2124(61) & -0.772(61) \\
\Phiₙ/\text{Hz} & = 2.97(69) & -1.21(10) & 6.4(13) \\
\Phiₙ/\text{Hz} & = -3.5(12) & 3.13(14) & \_h \\
\end{align*}

*Uncertainties represent one standard deviation. ^aA-reduction l'-representation. ^bNumber of transitions.

Table 5. ¹⁴N-quadrupole splittings (\(E_q\)) and diagonal elements of the quadrupole coupling tensor of the Gauche I conformer of H₂NCH₂CH₂=CH₂.

<table>
<thead>
<tr>
<th>Transition</th>
<th>(F' \leftarrow F)</th>
<th>(E_q\text{(obs)/MHz})</th>
<th>(E_q\text{(obs)} - E_q\text{(calc)/MHz})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2₁,₁ \leftarrow 1₁,₁</td>
<td>3 \leftarrow 2</td>
<td>0.29(3)</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>2 \leftarrow 1</td>
<td>-1.05(3)</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>1 \leftarrow 0</td>
<td>1.67(4)</td>
<td>0.08</td>
</tr>
<tr>
<td>4₁,₃ \leftarrow 3₀,₃</td>
<td>5 \leftarrow 4</td>
<td>0.34(3)</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>4 \leftarrow 3</td>
<td>-0.90(3)</td>
<td>0.08</td>
</tr>
<tr>
<td>6₃,₃ \leftarrow 6₂,₅</td>
<td>7 \leftarrow 7</td>
<td>0.18(4)</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>5 \leftarrow 5</td>
<td>-0.43(4)</td>
<td>-0.04</td>
</tr>
<tr>
<td>1₆,₁₃ \leftarrow 1₆,₃,₁₃</td>
<td>1₇ \leftarrow 1₇</td>
<td>-0.28(3)</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>1₅ \leftarrow 1₅</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1₆ \leftarrow 1₆</td>
<td>0.41(3)</td>
<td>-0.10</td>
</tr>
<tr>
<td>1₇,₁₄ \leftarrow 1₇,₃,₁₄</td>
<td>1₈ \leftarrow 1₈</td>
<td>-0.24(3)</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>1₆ \leftarrow 1₆</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1₇ \leftarrow 1₇</td>
<td>0.63(3)</td>
<td>0.12</td>
</tr>
<tr>
<td>1₈,₁₅ \leftarrow 1₈,₃,₁₅</td>
<td>1₉ \leftarrow 1₉</td>
<td>-0.30(3)</td>
<td>-0.07</td>
</tr>
<tr>
<td></td>
<td>1₇ \leftarrow 1₇</td>
<td>-0.03(3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1₈ \leftarrow 1₈</td>
<td>0.45(3)</td>
<td>-0.05</td>
</tr>
<tr>
<td>2₃₁₉ \leftarrow 2₃₄,₁₉</td>
<td>2₄ \leftarrow 2₄</td>
<td>-0.14(3)</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>2₂ \leftarrow 2₂</td>
<td>-0.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2₃ \leftarrow 2₃</td>
<td>0.54(3)</td>
<td>0.06</td>
</tr>
</tbody>
</table>

¹⁴N quadrupole coupling constants/MHz

\(\chi_{xx} = 2.07(40)\) \(\chi_{yy} = 2.14(24)\)

*Uncertainties represent one standard deviation.
of these components lie so close together that it is not possible to resolve them with our instrument. However, these two components are in most cases split from the third by 0.4–0.7 MHz, which is approximately the limit of our resolution. The observed split lines (or “shoulders”) were quite useful in making the first assignments of the strong c-type Q-branch lines of this conformer. These assignments were gradually extended to include c-type R-branch as well as the rather weak b-type Q-branch transitions. No a- or b-type R-branch lines were assigned with certainty, presumably because of insufficient intensities caused by small dipole moment components, as demonstrated below in the section on dipole moment determination. A total of approximately 130 transitions were ultimately assigned for Gauche I. Some selected transitions are listed in Table 3 (the complete spectra are available from the authors upon request, or from the Molecular Spectra Data Center, Bldg. 221, Room B268, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A., where they have been deposited). 112 transitions were used to determine the spectroscopic constants shown in Table 4. Sextic centrifugal distortion constants had to be employed in order to obtain a good fit. Four of them were sufficient to obtain a root-mean-square deviation comparable to the experimental uncertainty (see Table 4). However, these sextic constants are quite uncertain and also highly correlated.

Some of the transitions appearing in Table 3 were split by quadrupole interaction of the 14N nucleus, while “shoulders” were observed on others. Small frequency shifts of the peaks which were measured occur for still other transitions. In order to arrive at as accurate spectroscopic constants as possible, the transitions in question were “corrected” for quadrupole interaction. The quadrupole coupling constants shown in Table 5 were used for this purpose. The transitions appearing in Table 3 have been “corrected” in some cases and the frequencies shown there may deviate slightly from the observed frequencies.

A problem was encountered during the fitting of high-J ‘Q’-branch lines to the ordinary Watson A-reduction I-representation Hamiltonian. Several such lines, starting with the 37,2,1 ⩞ 37,6,1 transition, were found to deviate from their predicted frequencies (there is no doubt about the assignments of these transitions). The reason for these deviations, which vary from about 0.5 MHz up to a few MHz, is difficult to say. Perhaps some kind of Coriolis interaction with low-lying levels in the potential surface can account for this behaviour. Interestingly, the high-J, high-K-branch lines do not display this kind of interaction, as shown by a few examples listed in Table 3.

14N-nuclear quadrupole coupling constants. The selected transitions appearing in Table 5 were used to determine the quadrupole coupling constants of the 14N nucleus following the procedure of Ref. 18. The resulting constants χₐₐ = 2.07(40) MHz and χₐₜ = 2.14(24) MHz (Table 5) compare favourably with the predicted values of χₐₐ = 2.0 MHz and χₐₜ = 1.9 MHz of Table 2. This is independent evidence that the assigned conformer is indeed Gauche I.

Vibrationally excited states. The ground state transitions were accompanied by a satellite spectrum presumably belonging to vibrationally excited states of Gauche I. Two such states were assigned, as shown in Table 4. The strongest of these satellites had approximately 50% of the intensity of the ground state at about −50°C. The Q-transitions were too weak to be assigned with certainty for this excited state. Several of the measured transitions were split or perturbed a little by quadrupole interaction, just as in the case of the ground vibrational state. It was not possible to determine the 14N-quadrupole coupling constants with high precision. The ground state values of the quadrupole coupling constants were therefore utilized in “correcting” some of the 74 transitions used to determine the spectroscopic constants listed in Table 4. Interestingly, there were no problems similar to those found for the ground state, with the least-squares fitting of the high-J Q-branch of both the two excited states shown in Table 4.

Relative intensity measurements32 yielded a frequency 95(20) cm⁻¹ for this vibration, which was assumed to be the first excited state of the torsion around the C2–C3 bond. This is close to 93(4) cm⁻¹ determined from the corresponding frequency of skew-1-butene.19 84(20) cm⁻¹ found for 3-butene-1-ol,7 and 85(20) cm⁻¹ found for 3-butene-1-thiol,8 as expected.

The second strongest satellite spectrum had about 40% of the ground-state intensity. Un-
fortunately, it was not possible for us to make
definite assignments of the c-type R-branch transitions
of this excited state, because there were
only some few comparatively weak low-j-
transitions of this kind in the spectrum. The spectro-
scopic constants of Table 4 have been derived
using only one 'R-line, namely the $8_{1,7} \leftrightarrow 7_{2,5}$ at
32290.86 MHz. However, from the many 'Q-
branch transitions assigned in this case, $A_{r} - C_{r} =
6586.753(28)$ MHz and $x = -0.839444$ were de-
termined. "Correction" for quadrupole interaction
was made in the same manner as above.

A frequency of 139(30) cm$^{-1}$ was determined by
relative intensity measurements$^{12}$ for this funda-
mental, which is presumed to be the C3$-$C4
torsional vibration or perhaps the lowest heavy-
atom bending mode. 172(15) cm$^{-1}$ was found by
relative intensity measurements for this funda-
mental mode in 3-buten-1-ol, while 137(30) cm$^{-1}$
was determined for 3-buten-1-thiol.$^{8}$

**Dipole moment.** It is necessary to know the dipole
moment in order to determine energy differ-
ces between conformers. It is also useful to
know the dipole moment in order to differenti-
ate between conformations with very similar rota-
tional constants. Unfortunately, we were only
able to find transitions with resolved Stark effects
which were practically independent of $\mu_p$. There-
fore, only $\mu_x$ and $\mu_y$ could be determined. The
results found following the standard procedure of
Ref. 18 are shown in Table 6. In order to cal-
culate the total dipole moment of this conformer, $\mu_b$
was assigned the value 1.18×10$^{-30}$ C m calculated
by the bond-moment method.$^{13}$

Comparison of the experimental a- and c-axis
dipole moment components of Table 6 with those
predicted$^{13}$ (Table 1) for Gauche I show good
agreement. This too is evidence for the assign-
ment of this spectrum to the said conformer.

**Assignment of Gauche II.** In analogy with the
other ethylamine derivatives referred to in the
introductory section,$^{1,4}$ the H-bonded Gauche II
conformer was presumed to have nearly the same
internal energy as Gauche I. A large fraction of
Gauche II was therefore presumed to be present.
As shown in Table 1, this conformer was estimated to
possess a relatively large a-axis dipole moment
component. A search was therefore first made for
the strong low-J R-branch transitions, which
were soon found. Some of the assignments were
confirmed using the RIFMWD technique.$^{11}$ The
considerably weaker b- and c-type lines were sub-
sequently assigned. Selected transitions are listed
in Table 7. No transitions displayed quadrupole
splittings. The predicted quadrupole coupling
constants shown in Table 2 for this rotamer pre-
dict splittings which are considerably less than the
resolution of our spectrometer. About 90 transitions
were assigned for Gauche II, 82 of which
were used to determine the spectroscopic con-
stants listed in Table 8. High-J c-type transitions
(Table 7) were employed in the least-squares de-
terminations of the entries of Table 8. No prob-
lems were encountered in the fitting procedure
for these transitions, as opposed to the situation
for the ground vibrational state of Gauche I, as
described above.

**Table 6.** Stark coefficients$^{a}$ and dipole moment$^{b}$ of the Gauche I conformer of H$_2$NCH$_2$CH$_2$CH=CH$_2$.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\Delta v$ E$^{-2}/10^{-5}$ MHz V$^{-2}$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6_{3,4} \leftrightarrow 6_{2,4}$</td>
<td>$M = 6$</td>
</tr>
<tr>
<td></td>
<td>$M = 5$</td>
</tr>
<tr>
<td></td>
<td>$M = 4$</td>
</tr>
<tr>
<td>$8_{3,5} \leftrightarrow 8_{2,7}$</td>
<td>$M = 8$</td>
</tr>
<tr>
<td>$9_{3,6} \leftrightarrow 9_{2,8}$</td>
<td>$M = 9$</td>
</tr>
<tr>
<td>Dipole moment/10$^{-30}$ C m</td>
<td>$\mu_x = 0.751(6)$</td>
</tr>
<tr>
<td></td>
<td>$\mu_{tot} = 3.92(4)$</td>
</tr>
</tbody>
</table>

$^{a}$Uncertainties represent one standard deviation. $^{b}$Assumed; see text. 1 Debye = 3.33564×10$^{-30}$ C m.

380
**Table 7.** Selected transitions of the ground vibrational state of the hydrogen-bonded Gauche II conformer of H\(_2\)NCH\(_2\)CH=CH\(_2\).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed frequency(^{a,b})/MHz</th>
<th>Obs-calc frequency/MHz</th>
<th>Centrifugal distortion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total/MHz</td>
</tr>
<tr>
<td><strong>a-type</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4(<em>{0.4}) ← 3(</em>{0.3})</td>
<td>22835.40</td>
<td>-0.07</td>
<td>-0.88</td>
</tr>
<tr>
<td>4(<em>{3.3}) ← 3(</em>{1.2})</td>
<td>24077.32</td>
<td>-0.03</td>
<td>-1.22</td>
</tr>
<tr>
<td>4(<em>{1.4}) ← 3(</em>{1.3})</td>
<td>22069.60</td>
<td>-0.05</td>
<td>-0.42</td>
</tr>
<tr>
<td>4(<em>{2.2}) ← 3(</em>{2.1})</td>
<td>23410.77</td>
<td>0.10</td>
<td>-0.40</td>
</tr>
<tr>
<td>4(<em>{2.3}) ← 3(</em>{2.2})</td>
<td>23111.75</td>
<td>0.09</td>
<td>-0.17</td>
</tr>
<tr>
<td>5(<em>{0.5}) ← 4(</em>{0.4})</td>
<td>26337.66</td>
<td>-0.01</td>
<td>-1.53</td>
</tr>
<tr>
<td>5(<em>{1.5}) ← 4(</em>{1.4})</td>
<td>27536.70</td>
<td>-0.05</td>
<td>-0.97</td>
</tr>
<tr>
<td>5(<em>{2.4}) ← 4(</em>{2.3})</td>
<td>28850.78</td>
<td>0.10</td>
<td>-0.91</td>
</tr>
<tr>
<td>5(<em>{2.2}) ← 4(</em>{2.1})</td>
<td>29037.33</td>
<td>-0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>6(<em>{1.5}) ← 5(</em>{1.4})</td>
<td>35932.73</td>
<td>-0.07</td>
<td>-4.16</td>
</tr>
<tr>
<td>6(<em>{2.4}) ← 5(</em>{2.3})</td>
<td>35526.34</td>
<td>-0.03</td>
<td>-3.51</td>
</tr>
<tr>
<td>6(<em>{3.4}) ← 5(</em>{3.3})</td>
<td>34839.93</td>
<td>-0.12</td>
<td>-0.85</td>
</tr>
<tr>
<td>6(<em>{3.3}) ← 5(</em>{4.2})</td>
<td>34808.60</td>
<td>0.07</td>
<td>1.51</td>
</tr>
<tr>
<td>6(<em>{3.2}) ← 5(</em>{5.1})</td>
<td>34784.69</td>
<td>0.13</td>
<td>4.52</td>
</tr>
<tr>
<td><strong>b-type</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7(<em>{3.5}) ← 7(</em>{2.6})</td>
<td>32050.60</td>
<td>0.10</td>
<td>1.35</td>
</tr>
<tr>
<td>9(<em>{3.7}) ← 9(</em>{2.8})</td>
<td>33473.84</td>
<td>-0.03</td>
<td>2.09</td>
</tr>
<tr>
<td>11(<em>{1.10}) ← 11(</em>{0.11})</td>
<td>30622.32</td>
<td>0.00</td>
<td>-31.73</td>
</tr>
<tr>
<td>12(<em>{3.10}) ← 12(</em>{2.10})</td>
<td>23829.76</td>
<td>-0.03</td>
<td>19.20</td>
</tr>
<tr>
<td>15(<em>{3.12}) ← 15(</em>{2.13})</td>
<td>24902.54</td>
<td>-0.16</td>
<td>-15.87</td>
</tr>
<tr>
<td>16(<em>{4.13}) ← 16(</em>{3.13})</td>
<td>33427.63</td>
<td>-0.02</td>
<td>77.91</td>
</tr>
<tr>
<td>20(<em>{4.16}) ← 23(</em>{3.20})</td>
<td>31666.46</td>
<td>-0.09</td>
<td>-7.75</td>
</tr>
<tr>
<td>23(<em>{4.19}) ← 23(</em>{3.20})</td>
<td>37605.37</td>
<td>0.11</td>
<td>-237.79</td>
</tr>
<tr>
<td>6(<em>{1.6}) ← 5(</em>{0.5})</td>
<td>36249.81</td>
<td>0.03</td>
<td>-0.27</td>
</tr>
<tr>
<td>7(<em>{0.7}) ← 6(</em>{1.6})</td>
<td>36535.40</td>
<td>-0.05</td>
<td>-5.35</td>
</tr>
<tr>
<td><strong>c-type</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5(<em>{3.2}) ← 5(</em>{2.4})</td>
<td>31382.77</td>
<td>-0.05</td>
<td>-1.04</td>
</tr>
<tr>
<td>9(<em>{3.6}) ← 9(</em>{2.8})</td>
<td>34473.68</td>
<td>-0.02</td>
<td>-1.84</td>
</tr>
<tr>
<td>13(<em>{4.10}) ← 13(</em>{3.10})</td>
<td>37377.67</td>
<td>-0.02</td>
<td>56.60</td>
</tr>
<tr>
<td>17(<em>{4.14}) ← 17(</em>{3.14})</td>
<td>26779.67</td>
<td>0.05</td>
<td>156.73</td>
</tr>
<tr>
<td>22(<em>{5.18}) ← 22(</em>{4.18})</td>
<td>35009.25</td>
<td>-0.06</td>
<td>389.44</td>
</tr>
<tr>
<td>24(<em>{5.20}) ← 24(</em>{4.20})</td>
<td>27300.14</td>
<td>-0.10</td>
<td>502.21</td>
</tr>
<tr>
<td>30(<em>{6.25}) ← 30(</em>{5.25})</td>
<td>30509.11</td>
<td>0.02</td>
<td>1096.68</td>
</tr>
<tr>
<td>31(<em>{6.26}) ← 31(</em>{5.26})</td>
<td>26071.43</td>
<td>0.06</td>
<td>1154.71</td>
</tr>
<tr>
<td>36(<em>{7.30}) ← 36(</em>{6.30})</td>
<td>33447.67</td>
<td>-0.09</td>
<td>2081.65</td>
</tr>
<tr>
<td>38(<em>{7.32}) ← 38(</em>{6.32})</td>
<td>23846.11</td>
<td>-0.02</td>
<td>2145.60</td>
</tr>
<tr>
<td>42(<em>{8.35}) ← 42(</em>{7.35})</td>
<td>36315.09</td>
<td>-0.05</td>
<td>3587.23</td>
</tr>
<tr>
<td>43(<em>{8.36}) ← 43(</em>{7.36})</td>
<td>30929.85</td>
<td>0.15</td>
<td>3633.15</td>
</tr>
<tr>
<td>50(<em>{9.42}) ← 50(</em>{8.42})</td>
<td>28081.64</td>
<td>-0.04</td>
<td>5638.41</td>
</tr>
</tbody>
</table>

\(^{a}\pm 0.10\) MHz.
Vibrationally excited states. Two vibrationally excited states were assigned for this conformer, as indicated in Table 8. The spectroscopic constants of the first excited state of the C2–C3 torsional vibration were determined from 39 low-J $^3R$- and medium-J $^4Q$-branch transitions; no c-type $Q$-branch lines were strong enough to be identified beyond doubt. The frequency of this vibration was determined to be 83(20) cm$^{-1}$ by relative intensity measurements, which is close to the value found for Gauche I above, as expected.

Only $^3R$-branch lines were sufficiently strong to be identified with certainty for what is probably the first excited state of the C3–C4 torsional vibration, or the lowest bending vibration. 11 transitions were used to determine the spectroscopic constants displayed in Table 8. The vibrational frequency is 148(30) cm$^{-1}$ for this mode, as determined by relative intensity measurements.

Assignment of Extended I. The assignments reported above include all the strongest lines of the spectrum, as well as a majority of lines of intermediate intensities and many weak transitions too. However, a rich spectrum of comparatively weak lines remained. Many of these last-mentioned transitions are undoubtedly associated with vibrationally excited states of the two gauche conformers which we were not able to assign, although many attempts were made with this in mind. From our work on HSC$^2$H$_2$CH$_2$CH=CH$_2$ it was known that extended conformers (see Figs. 2 and 3) might exist in such high concentrations that they could be detectable provided the H bonds of the two gauche conformers assigned above were not too strong. The asymmetry parameter $\kappa$ for the three highly prolate extended conformers is about $-0.995$ in all three cases. The spectra of such highly prolate molecules are relatively easy to assign, provided that they have a sizable dipole moment component along the $a$-axis. This will give rise to characteristic $^3R$-branch $K_{\perp}$-pile-ups. Unfortunately, none of the three extended rotamers are predicted to possess a large $\mu_a$, as can be inferred from Table 1. A search for such pile-ups was futile, as expected.

It can be seen from Table 1 that $\mu_a$ of Extended I is predicted to be comparatively large. Attempts to find this rotamer were therefore made next. The strongest transitions predicted for this
Table 9. Stark coefficients* and dipole moment* of the Gauche II conformer of \( \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}:=\text{CH}_2 \).

| Transition | \( |M| = 1 \) | \( |M| = 2 \) | \( |M| = 3 \) | \( \Delta v \) (Obs) | \( \Delta v \) (Calc) |
|------------|-----------|-----------|-----------|-------------|-------------|
| \( 5_{1,5} \leftrightarrow 4_{1,4} \) | \( 1.69(2) \) | \( 2.27(2) \) | \( 4.17(5) \) | \( 8.00(10) \) | \( -0.820(10) \) | \( -0.821 \) |
| \( 6_{2,5} \leftrightarrow 5_{2,4} \) | \( 0.247(3) \) | \( 0.415(6) \) | \( 0.248 \) |
| \( 5_{2,3} \leftrightarrow 4_{2,2} \) | \( 1.20(2) \) | \( 1.61 \) | \( 2.30 \) | \( 4.30 \) | \( 7.66 \) | \( -1.22 \) |

Dipole moment/10\(^{-30}\) C m

| \( \mu_a = 3.199(50) \) | \( \mu_c = 1.211(93) \) | \( \mu_c = 2.019(45) \) | \( \mu_{\text{tot}} = 3.972(75) \) |

*Comments as for Table 6.

Conformer are the c-type Q-branch \( K_{-1} = 2 \leftrightarrow 1 \) series starting in the upper frequency end of the spectrum and extending towards lower frequencies as the \( J \) quantum number increases. The starting value for \( J \) was predicted to be about 40 at 38 GHz, the upper end of the investigated frequency range. Moreover, the quadrupole coupling constants of Extended I (Table 2) predicted these transitions to be split by 0.7–0.9 MHz in a typical 1:2 intensity pattern. With this in mind, a search for the said Q-branch series was carried out. A search among the remaining, so far unassigned medium-intensity transitions displaying apparent quadrupole splittings was soon successful. The observed transitions are to be found in Table 10. There is no doubt about the assignment of these transitions as a c-type \( K_{-1} = 2 \leftrightarrow 1 \) series. The predicted quadrupole coupling constants (Table 2) conclusively demonstrate that this series indeed belongs to Extended I, because the quadrupole coupling constants predicted for the other two extended forms (Table 2) yield fine-structures completely different from those in Table 10.

However, a problem associated with the assignment of the \( J \) quantum numbers remains. The fact that Extended I is almost an accidental symmetrical top makes it difficult to decide whether a correct assignment of \( J \) has been made in Table 10. Several values of \( J \) can be successfully assumed for each transition, as judged by the least-squares fit. In an attempt to confirm the \( J \) assignments, searches were made for low-\( J \) c-type R-branch transitions. Unfortunately, there are only a few such transitions in the spectrum. They are considerably weaker than the identified Q-branch series and they are predicted to be split by quadrupole interactions in most cases. Our searches for them were therefore in vain. Attempts to find \( ^4Q \)-branch transitions which might confirm the \( J \) assignments were also made, in spite of the fact that \( \mu_a \) is predicted to be very small (Table 1). Not surprisingly, such series were not found.

The reason for selecting the tentative \( J \) assignments shown in Table 10 is that these values give the most reasonable values for the quartic and sextic centrifugal distortion constants shown in Table 11. Other values for the \( J \)'s yield much less realistic values for the centrifugal distortion constants than those shown in Table 11. With only one \( Q \)-branch series assigned, only \( A_e-C_0 \) and the asymmetry parameter \( \chi \) can be determined (see Table 11). Only one quartic and one sextic centrifugal distortion constant were needed in order to obtain a root-mean-square deviation of the fit comparable to the experimental uncertainty. The "corrected" frequencies estimated using Rudolph's formula were used in fitting these transitions to Watson's \( A \)-reduction \( F \)-representation Hamiltonian. No problems were encountered with this Hamiltonian, even with such a prolate asymmetric rotor as this one.

No accurate values of both \( \chi_{aa} \) and \( \chi_{bb} \) can be
Table 10. Microwave spectrum of the ground vibrational state of the Extended I conformer of H₂NCH₂CH₂CH=CH₂.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$F' \leftarrow F''$</th>
<th>Observed frequency/MHz</th>
<th>&quot;Corrected&quot; frequency/MHz</th>
<th>Obs$^a$–Calc frequency/MHz</th>
<th>Centrifugal distortion Total/MHz</th>
<th>Sextic/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>39$<em>{2,37}$ $\leftarrow$ 38$</em>{1,37}$</td>
<td>39 $\leftarrow$ 39</td>
<td>37898.68</td>
<td>37898.94</td>
<td>-0.07</td>
<td>-185.35</td>
<td>1.38</td>
</tr>
<tr>
<td>38 $\leftarrow$ 38</td>
<td>37899.76</td>
<td>37244.58</td>
<td>37244.83</td>
<td>0.03</td>
<td>-203.76</td>
<td>1.53</td>
</tr>
<tr>
<td>39 $\leftarrow$ 39</td>
<td>37245.48</td>
<td>36577.98</td>
<td>36578.25</td>
<td>0.08</td>
<td>-223.31</td>
<td>1.68</td>
</tr>
<tr>
<td>40$<em>{2,39}$ $\leftarrow$ 40$</em>{1,39}$</td>
<td>41 $\leftarrow$ 41</td>
<td>35209.47</td>
<td>35209.70</td>
<td>0.02</td>
<td>-265.90</td>
<td>2.03</td>
</tr>
<tr>
<td>39 $\leftarrow$ 39</td>
<td>35210.44</td>
<td>34508.67</td>
<td>34508.90</td>
<td>-0.01</td>
<td>-288.92</td>
<td>2.22</td>
</tr>
<tr>
<td>42$<em>{2,41}$ $\leftarrow$ 42$</em>{1,41}$</td>
<td>43 $\leftarrow$ 43</td>
<td>33797.66</td>
<td>33797.89</td>
<td>-0.04</td>
<td>-313.08</td>
<td>2.42</td>
</tr>
<tr>
<td>42 $\leftarrow$ 42</td>
<td>33798.59</td>
<td>33077.18</td>
<td>33077.40</td>
<td>0.03</td>
<td>-338.37</td>
<td>2.64</td>
</tr>
<tr>
<td>43$<em>{2,42}$ $\leftarrow$ 43$</em>{1,42}$</td>
<td>44 $\leftarrow$ 44</td>
<td>32347.58</td>
<td>32347.81</td>
<td>-0.10</td>
<td>-364.76</td>
<td>2.87</td>
</tr>
<tr>
<td>42 $\leftarrow$ 42</td>
<td>32348.52</td>
<td>30865.01</td>
<td>30865.25</td>
<td>0.10</td>
<td>-420.64</td>
<td>3.36</td>
</tr>
<tr>
<td>43$<em>{2,43}$ $\leftarrow$ 43$</em>{1,43}$</td>
<td>45 $\leftarrow$ 45</td>
<td>30113.10</td>
<td>30113.34</td>
<td>-0.05</td>
<td>-450.04</td>
<td>3.63</td>
</tr>
<tr>
<td>44 $\leftarrow$ 44</td>
<td>30113.92</td>
<td>29355.58</td>
<td>29355.78</td>
<td>-0.02</td>
<td>-480.33</td>
<td>3.91</td>
</tr>
<tr>
<td>45$<em>{2,44}$ $\leftarrow$ 45$</em>{1,44}$</td>
<td>46 $\leftarrow$ 46</td>
<td>28593.02</td>
<td>28593.22</td>
<td>0.00</td>
<td>-511.31</td>
<td>4.20</td>
</tr>
<tr>
<td>45 $\leftarrow$ 45</td>
<td>28593.37</td>
<td>27826.34</td>
<td>27826.65</td>
<td>-0.01</td>
<td>-543.22</td>
<td>4.51</td>
</tr>
</tbody>
</table>

contd
Table 10. contd

<table>
<thead>
<tr>
<th>Transition</th>
<th>$F' \leftarrow F'$</th>
<th>Observed frequency/MHz</th>
<th>&quot;Corrected&quot; frequency/MHz</th>
<th>Obs$^c$-Calc frequency/MHz</th>
<th>Centrifugal distortion Total/MHz</th>
<th>Sextic/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$53_{2,52} \leftarrow 53_{1,52}$</td>
<td>$54 \leftarrow 54$</td>
<td>27056.73</td>
<td>27056.85</td>
<td>0.11</td>
<td>-576.63</td>
<td>4.83</td>
</tr>
<tr>
<td></td>
<td>$52 \leftarrow 52$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$53 \leftarrow 53$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$54_{2,55} \leftarrow 54_{1,53}$</td>
<td>$55 \leftarrow 55$</td>
<td>26284.39</td>
<td>26284.65</td>
<td>-0.07</td>
<td>-608.54</td>
<td>5.16</td>
</tr>
<tr>
<td></td>
<td>$53 \leftarrow 53$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$54 \leftarrow 54$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$59_{2,58} \leftarrow 59_{1,58}$</td>
<td>$60 \leftarrow 60$</td>
<td>22426.59</td>
<td>22426.77</td>
<td>0.00</td>
<td>-775.96</td>
<td>6.97</td>
</tr>
<tr>
<td></td>
<td>$58 \leftarrow 58$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$An ambiguity exists with regard to the quantum numbers involved in these transitions; see text. $^b\pm0.10$ MHz. $^c$"Corrected" frequency shown in preceding column used for least-squares fitting.

derived from the quadrupole splittings shown in Table 10 because the members of this $Q$-branch series have almost the same splittings for all transitions. There is thus not enough independent information to allow a determination of both $\chi_{ab}$ and $\chi_{ac}$. However, the quadrupole coupling constants shown in Table 2 predict splittings and intensity patterns very close to the observed ones.

Assignment of Extended II. It is seen from Table 1 that $\mu_b$ is predicted to be the largest principal axes dipole moment component for this conformer. This should result in a comparatively strong $b$-type $Q$-branch $K_{\perp} = 1 \leftarrow 0$ series spreading out towards higher frequencies as $J$ increases. $J$ was predicted to be approximately 30 at 22 GHz and increasing with increasing frequency. The quadrupole coupling constants shown in Table 2 predicted unresolvable quadrupole splittings for this series provided it belonged to Extended II, whereas comparatively large splittings were predicted if it belonged to Extended I, and somewhat smaller splittings were predicted for this series in case it belonged to Extended III. The transitions displayed in Table 12 are undoubtedly a $b$-type $K_{\perp} = 1 \leftarrow 0$ series, but because no further $Q$-branch series or $R$-branch lines were identified, the same ambiguity with respect to the $J$ quantum number exists for this conformation as in the case of Extended I, as reported above. The transitions of Table 12 were scrutinized for quadrupole splittings, but no such splittings were noted. This is one reason why the spectrum of this table is assigned to Extended II.

The derived spectroscopic constants are listed in Table 13. The tentative $J$ quantum numbers selected for the assignments shown in Table 12 were those that gave the most reasonable values for the centrifugal distortion constants, exactly as described above for Extended I. No determination of the dipole moment could be made for any of the two extended conformers assigned in this work due to the low intensity of the spectral lines as well as to the high-$J$ transitions assigned for both of them.

Table 11. Spectroscopic constants$^{a,b,c}$ of the ground vibrational state of the Extended I conformer of $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH} = \text{CH}_2$.

<table>
<thead>
<tr>
<th>N.o.t.</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.m.s. dev./MHz</td>
<td>0.067</td>
</tr>
</tbody>
</table>

| $(A_0-C_0)/$MHz | 16992.95(41) |
| $\chi$ | -0.995737 |
| $\delta_\nu$/kHz | -0.0943(11) |
| $\Phi_{\omega}$/Hz | 0.21(20) |

$^a$A-reduction $l$-representation. $^b$Using the quantum numbers shown in Table 10; see text. $^c$Further centrifugal distortion constants preset at zero.

Internal energy differences. The internal energy differences were determined by comparison of spectral intensities. The principal axes dipole mo-
Table 12. Microwave spectrum* of the ground vibrational state of the Extended II conformer of H₂NCH₂CH₂CH=CH₂.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed frequency/MHz</th>
<th>Obs–calc frequency/MHz</th>
<th>Centrifugal distortion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total/MHz</td>
</tr>
<tr>
<td>30₁,30 ← 30₀,30</td>
<td>22166.11</td>
<td>0.04</td>
<td>112.46</td>
</tr>
<tr>
<td>31₁,31 ← 31₀,31</td>
<td>22581.62</td>
<td>0.00</td>
<td>129.63</td>
</tr>
<tr>
<td>32₁,32 ← 32₀,32</td>
<td>23016.42</td>
<td>-0.06</td>
<td>148.84</td>
</tr>
<tr>
<td>33₁,33 ← 33₀,33</td>
<td>23471.24</td>
<td>0.04</td>
<td>170.26</td>
</tr>
<tr>
<td>34₁,34 ← 34₀,34</td>
<td>23946.24</td>
<td>-0.05</td>
<td>194.08</td>
</tr>
<tr>
<td>35₁,35 ← 35₀,35</td>
<td>24442.35</td>
<td>0.04</td>
<td>220.51</td>
</tr>
<tr>
<td>36₁,36 ← 36₀,36</td>
<td>24959.73</td>
<td>-0.07</td>
<td>249.73</td>
</tr>
<tr>
<td>37₁,37 ← 37₀,37</td>
<td>25499.33</td>
<td>0.03</td>
<td>281.97</td>
</tr>
<tr>
<td>39₁,39 ← 39₀,39</td>
<td>26646.44</td>
<td>-0.03</td>
<td>356.40</td>
</tr>
<tr>
<td>40₁,40 ← 40₀,40</td>
<td>27255.26</td>
<td>0.04</td>
<td>399.05</td>
</tr>
<tr>
<td>41₁,41 ← 41₀,41</td>
<td>27888.15</td>
<td>0.05</td>
<td>445.64</td>
</tr>
<tr>
<td>42₁,42 ← 42₀,42</td>
<td>28545.61</td>
<td>-0.01</td>
<td>496.42</td>
</tr>
<tr>
<td>43₁,43 ← 43₀,43</td>
<td>29228.27</td>
<td>0.00</td>
<td>551.63</td>
</tr>
<tr>
<td>44₁,44 ← 44₀,44</td>
<td>29936.57</td>
<td>0.04</td>
<td>611.54</td>
</tr>
<tr>
<td>45₁,45 ← 45₀,45</td>
<td>30670.85</td>
<td>0.02</td>
<td>676.37</td>
</tr>
<tr>
<td>47₁,47 ← 47₀,47</td>
<td>33219.37</td>
<td>0.04</td>
<td>821.86</td>
</tr>
<tr>
<td>49₁,49 ← 49₀,49</td>
<td>33876.67</td>
<td>-0.13</td>
<td>902.99</td>
</tr>
<tr>
<td>50₁,50 ← 50₀,50</td>
<td>34747.22</td>
<td>0.02</td>
<td>990.03</td>
</tr>
<tr>
<td>51₁,51 ← 51₀,51</td>
<td>35645.74</td>
<td>-0.01</td>
<td>1083.20</td>
</tr>
<tr>
<td>52₁,52 ← 52₀,52</td>
<td>36572.71</td>
<td>0.06</td>
<td>1182.71</td>
</tr>
</tbody>
</table>

*Comments as for Table 10.

The two extended forms with regard to this quantum number. The statistical weight was assumed to be 2 for all four conformers.

The intensities of many transitions were compared in the limit of no power saturation.²¹ Gauche I was found to be the most stable of them all. Gauche I is 0.8 kJ mol⁻¹ more stable than Gauche II. One standard deviation is liberal estimated to be ±0.3 kJ mol⁻¹. Gauche I is 1.9 kJ mol⁻¹ more stable than Extended I. One standard deviation is in this case liberal estimated to be ±0.5 kJ mol⁻¹. The uncertainties resulting from the unknown μ₀-dipole moment component of Extended I as well as from the tentative J quantum number assignment are taken into account. In an identical manner, Gauche I is found to be 2.1(5) kJ mol⁻¹ more stable than Extended II. These results are summarized in Table 17 and discussed below.

In addition to 1-amino-3-butene, the energy difference between the H-bonded gauche conformers and non-H-bonded conformers has been determined in one other case for the

Table 13. Spectroscopic constants*⁶ of the ground vibrational state of the Extended II conformer of H₂NCH₂CH₂CH=CH₂.

<table>
<thead>
<tr>
<th>N.o.t.</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.m.s. dev./MHz</td>
<td>0.061</td>
</tr>
</tbody>
</table>

| (A₀⁻C₀)/MHz | 16629.34(72) |
| x | -0.997462 |
| δ₀/kHz | -0.12008(29) |
| Φ₀/KHz | -16.5(14) |

*Comments as for Table 11. *Using the quantum numbers shown in Table 12; see text.
H$_2$NCH$_2$CH$_2$X-type molecules in the free state, viz. for ethylenediamine, where an energy difference of 1.9(5) kJ mol$^{-1}$ was determined using electron diffraction. However, this result is difficult to interpret because it represents some mean over two H-bonded gauche and several anti conformers.

**Searches for further conformers.** After these assignments had been made, there were only a few unassigned medium intensity transitions left in the spectrum. There is no reason to believe that Extended III has a much higher energy than the two other extended forms which were assigned. However, searches for this fifth rotamer were futile. One reason for this failure may perhaps be that none of its principal axes dipole moment components are as large as $\mu_\nu$ for Extended I, or $\mu_\alpha$ for Extended II (see Table 1).

A search was also made for the hypothetical Gauche III, which has no H bond. A large $\mu_\alpha$ is predicted for this conformation, as inferred from Table 1. However, no assignments could be made for this rotamer. This is not surprising, because Gauche III has no stabilizing H bond. In addition, the lone electron pair of the nitrogen nu-

---

**Table 14. Plausible molecular structure* [bond lengths (pm), angles (*)] of H$_2$NCH$_2$CH$_2$CH=CH$_2$.**

<table>
<thead>
<tr>
<th>Structural parameters kept fixed</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N−C4</td>
<td>147.5</td>
</tr>
<tr>
<td>C1−C2</td>
<td>133.1</td>
</tr>
<tr>
<td>C2−C3</td>
<td>149.6</td>
</tr>
<tr>
<td>C3−C4</td>
<td>152.8</td>
</tr>
<tr>
<td>C1−H</td>
<td>109.0</td>
</tr>
<tr>
<td>C2−H</td>
<td>109.0</td>
</tr>
<tr>
<td>C3−H</td>
<td>109.3</td>
</tr>
<tr>
<td>C4−H</td>
<td>109.3</td>
</tr>
<tr>
<td>N−H</td>
<td>101.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fitted</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha(\angle C1=C2−C3−C4)$</td>
<td>66(3) for both Gauche I and Gauche II</td>
</tr>
<tr>
<td>$\beta(\angle C2−C3−C4−N)$</td>
<td>116(3) [64(3) from syn] for both Gauche I and Gauche II</td>
</tr>
</tbody>
</table>

**Hydrogen bond parameters**

<table>
<thead>
<tr>
<th>Conformer:</th>
<th>Gauche I</th>
<th>Gauche II</th>
</tr>
</thead>
<tbody>
<tr>
<td>H−H′...C2</td>
<td>257</td>
<td>270</td>
</tr>
<tr>
<td>H−H′...C1</td>
<td>297</td>
<td>313</td>
</tr>
<tr>
<td>N...C2</td>
<td>297</td>
<td>306</td>
</tr>
<tr>
<td>N...C1</td>
<td>357</td>
<td>369</td>
</tr>
<tr>
<td>$\angle N−H′...C2$</td>
<td>103</td>
<td>101</td>
</tr>
<tr>
<td>$\angle N−H′...C1$</td>
<td>118</td>
<td>116</td>
</tr>
<tr>
<td>$\angle N−H′,C1=C2$</td>
<td>51</td>
<td>51</td>
</tr>
</tbody>
</table>

**Sum of van der Waals radii**

| H−C                    | 290      |
| N−C                    | 320      |

---

*aSee text. bKept at this value for Gauche I, Gauche II, Extended I, and Extended III. cKept at this value for Gauche II and Extended II. dThis dihedral angle was not fitted for Extended I and Extended II; see text. eThese two dihedral angles were fitted only for Gauche I and Gauche II. fAmino group hydrogen atom involved in intramolecular hydrogen bonding. gAngle between N−H bond involved in hydrogen bonding and C1−C2 bond. hTaken from Ref. 24. iRadius of aromatic carbon atom assumed to be 170 pm according to Ref. 24.
ucleus of this conformation is oriented so that it is probably repelled by the π electrons of the double bond. *Gauche III* may thus perhaps represent a local maximum in the potential surface of 1-amino-3-butene. If this is the case, then there is no such thing as a stable *Gauche III* conformer.

Conformations other than the three *gauche* and three *extended* forms drawn in Figs. 2 and 3 are of course possible. *Syn* conformations (not shown in Figs. 2 and 3) which have a planar heavy-atom skeleton with \( \alpha = 0^\circ \), \( \beta = 180^\circ \), and \( \gamma = 0^\circ \) or \( \gamma = 120^\circ \) (see Fig. 1) were looked for, because it is known that a similar conformation occurs in large abundance in 1-butene.\(^{19}\) These hypothetical *syn* conformations are predicted\(^{13}\) to possess sizeable principal axes dipole moment components, and to be very crowded. However, no identification of them was made among the remaining unassigned, mostly rather weak transitions. It is impossible that large fractions of *syn* forms coexist with the two *gauche* and two *extended* conformers identified above for 1-amino-3-butene. It is concluded that the conformational make-up of 1-amino-3-butene primarily consists of two *gauche* conformers which are about 2 kJ mol\(^{-1}\) more stable than the three *extended* rotamers.

**Table 15.** Observed and calculated rotational constants\(^a\) of the *Gauche I* and *Gauche II* conformers of \( \text{H}_2\text{NCH}_2\text{CH}_2\text{CH} = \text{CH}_2 \).

<table>
<thead>
<tr>
<th></th>
<th><em>Gauche I</em></th>
<th></th>
<th><em>Gauche II</em></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_0 / \text{MHz} )</td>
<td>9223.86</td>
<td>9244.87</td>
<td>0.22</td>
<td>9109.93</td>
</tr>
<tr>
<td>( B_0 / \text{MHz} )</td>
<td>3199.34</td>
<td>3210.38</td>
<td>0.34</td>
<td>3143.89</td>
</tr>
<tr>
<td>( C_0 / \text{MHz} )</td>
<td>2668.29</td>
<td>2671.06</td>
<td>0.10</td>
<td>2640.02</td>
</tr>
</tbody>
</table>

\(^a\)See text. \(^b\)Structural parameters used in the calculations are found in Table 14.

**Table 16.** Observed and calculated spectroscopic constants\(^a,b\) of the *Extended I* and *Extended II* conformers of \( \text{H}_2\text{NCH}_2\text{CH}_2\text{CH} = \text{CH}_2 \).

<table>
<thead>
<tr>
<th></th>
<th><em>Extended I</em></th>
<th></th>
<th><em>Extended II</em></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs</td>
<td>Calc</td>
<td>Obs</td>
<td>Calc</td>
</tr>
<tr>
<td>((A_0 - C_0) / \text{MHz} )</td>
<td>16992.95</td>
<td>17126.29</td>
<td>16629.34</td>
<td>17189.01</td>
</tr>
<tr>
<td>( \chi )</td>
<td>-0.99574</td>
<td>-0.995117</td>
<td>-0.99746</td>
<td>-0.99689</td>
</tr>
</tbody>
</table>

\(^a\)\(^b\)Comments as for Table 15.

388
Table 17. Selected results for three XCH₂CH₂CH=CH₂-type molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>α°/degrees</th>
<th>(∆E° = E° Extended - E° Gauche)/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOCH₂CH₂CH=CH₂</td>
<td>75(3)</td>
<td>&gt;3</td>
</tr>
<tr>
<td>H₂NCH₂CH₂CH=CH₂</td>
<td>66(3)</td>
<td>1.9(5)*</td>
</tr>
<tr>
<td>HSC₂H₂CH₂CH=CH₂</td>
<td>57(3)</td>
<td>2.1(5)*</td>
</tr>
</tbody>
</table>

*Diherdral angle as defined in Fig. 1. †Ref. 7. ‡Ref. 23. §This work. †Energy difference between Gauche II and Gauche I is 0.8(3) kJ mol⁻¹; see text. ††Gauche II. ‡‡E Extended - E Gauche = E Extended - E Gauche I.

Due to the fact that the J quantum numbers are only tentative for Extended I and Extended II (see above), the spectroscopic constants also become uncertain. A fit of the dihedral angles α, β and γ was therefore not considered to be worthwhile. However, only small adjustments of the said dihedral angles would reproduce A₂₂C₀ and A₀ rather well. The spectroscopic constants computed using the structural parameters of Table 14 assuming completely staggered atomic arrangements are listed in Table 16.

Discussion

It was expected at the beginning of this work that the two H-bonded conformers Gauche I and Gauche II would be the most stable forms of 1-amino-3-butene, with Gauche I as the slightly more stable in accord with the findings made for the other H₂NCH₂CH₂X-type molecules.¹⁶ This was indeed found, as demonstrated above. It is suggested that intramolecular H-bonding is the major cause of these conformational preferences. The H-bonds in Gauche I and Gauche II are rather weak, however, as can be inferred from the structural parameters and sums of the van der Waals radii given in Table 14. It can also be seen from this table that the geometry of the H bond in Gauche I is only marginally different from that in Gauche II. The energy difference is, as expected, very small, being only 0.8(3) kJ mol⁻¹ in favour of Gauche I.

In order to compare the H-bond strengths in 3-butenes, selected data for the alcohol,⁷,²³ the thiol,⁸ as well as for 1-amino-3-butene are collected in Table 17. The strength of the H bond is expected to manifest itself in at least two important parameters, viz. the C1C2C3C4 (α) dihedral angle (see Fig. 1), and the energy difference between extended and gauche conformers. The H bond in the three compounds of Table 17 is undoubtedly strongest in HOCH₂CH₂CH=CH₂. This shows up in a large α-angle of 75(3)° which brings the hydroxyl hydrogen atom and the π electrons into close proximity, enhancing the hydrogen-bond interaction, as well in the fact that the energy difference between the H-bonded gauche conformer and any extended form is so large (over 3 kJ mol⁻¹) that the latter escaped being detected by electron diffraction and MW spectroscopy.⁷

The strength of the H bond in Gauche HSC₂H₂CH=CH₂ as compared to the H bonds in Gauche I and in Gauche II of the title compound is more difficult to decide. The α-angles are both about 9° larger in the two gauche rotamers of 1-amino-3-butene than in the H-bonded conformer of HSC₂H₂CH=CH₂ (Table 17). By this criterion, one would expect the H bond to be slightly stronger in both the gauche forms of H₂NCH₂CH₂CH=CH₂ than in Gauche HSC₂H₂CH=CH₂. However, the energy differences between the two extended forms and gauche conformer are both slightly larger in HSC₂H₂CH=CH₂ than in the corresponding three cases of H₂NCH₂CH₂CH=CH₂, as shown in Table 17. This fact should indicate the opposite
of what is found from the $\alpha$ dihedral angle, namely that the internal H bond is somewhat stronger in gauche HSCH$_2$CH$_2$CH=CH$_2$ than in both gauche I and gauche II of 3-amino-1-butene. These findings make it impossible to say definitely whether the hydrogen bonds in the two gauche forms of the amine are stronger than in the thiol. It is then concluded that the H-bond strengths in gauche I and in gauche II are each nearly the same as in the H-bonded gauche conformer of HSCH$_2$CH$_2$CH=CH$_2$.$^8$

Acknowledgments. We are most grateful to Professor G. Courtois, Laboratoire de Synthese Organique, University of Poitiers, France, for the donation of the sample used in this work.

We would like to thank Otto for his interest in, and encouragement and support of MW spectroscopy over many years. Without his support there would hardly have been any MW spectroscopy in Norway.

References


Received October 25, 1987.