

# The Conformational Composition of 4-Fluoro-1-butene as Studied by Microwave Spectroscopy and *Ab initio* Computations

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The microwave spectrum of 4-fluoro-1-butene has been reinvestigated in the 10–26.5 GHz spectral range. The ground and several vibrationally excited states have been assigned for two 'new' rotamers denoted *Skew-Gauche I* and *Skew-Gauche II*. The dipole moments of the 'new' conformers have been determined. Additional data have been obtained for the already assigned conformer denoted *Skew-Anti*. The energy differences between the three conformers have been established. *Skew-Gauche II* is the more stable rotamer. It is 1.9(2) kJ mol<sup>-1</sup> more stable than *Skew-Anti*, and *Skew-Gauche II* is 2.1(2) kJ mol<sup>-1</sup> more stable than *Skew-Gauche I*. Further conformers are at least 4 kJ mol<sup>-1</sup> less stable than *Skew-Gauche II*. *Ab initio* calculations with the 3-21G\* basis were made for five selected conformations in order to assist the microwave work.

Several conformations are possible for 4-fluoro-1-butene. In Fig. 1, five forms which are presumed to be low-energy rotamers of the molecule are depicted. In the three *skew* conformers (*Skew-Anti*, *Skew-Gauche I*, and *Skew-Gauche II*) the C1–C2–C3–C4 chain of atoms forms a dihedral angle that is approximately 120° from *syn*. In the two *syn* conformations (*Syn-Anti* and *Syn-Gauche*), this angle is about 0°. The *anti* notation indicates that the C2–C3–C4–F atoms are in *anti* position (180° from *syn*), whereas *gauche* indicates that this angle is 60° (or –60°) from *syn*.

In a previous microwave (MW) investigation by Li *et al.*,<sup>1</sup> the *Skew-Anti* conformer of 4-fluoro-1-butene was assigned. It was noted that many transitions were unassigned in this spectrum. The question as to whether some of these lines might belong to further unidentified conformers of the molecule prompted this investigation.

## Experimental

The sample used in this work was synthesized as described in Ref. 1. Its purity was confirmed by gas chromatography. The spectra were studied using the Oslo spectrometer. The 10–26.5 GHz spectral region was investigated with the microwave absorption cell cooled to dry-ice temperature (195 K). The pressure was about 1 Pa during the spectral measurements.

The spectrometer used in this work employs 50 kHz Stark modulation obtained from a home-built generator. The brass absorption cells are about 3 m long. The microwave source is a Systron Donner 1730B microwave

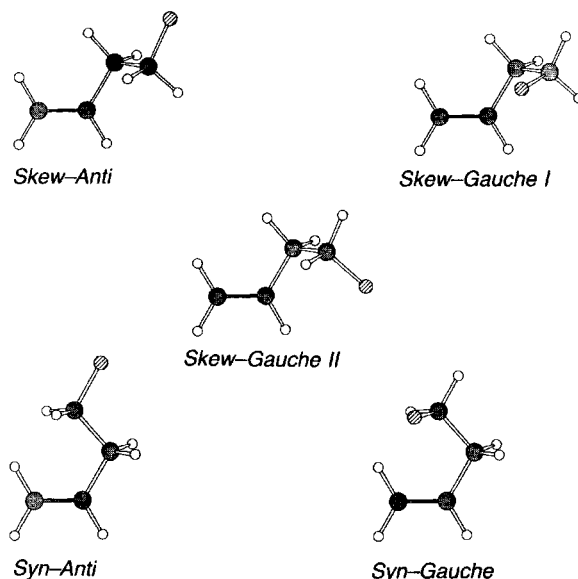


Fig. 1. Typical rotameric forms of 4-fluoro-1-butene. Note that the fluorine atom is closer to the double bond in *Skew-Gauche I* than in *Skew-Gauche II*.

synthesizer which covers the 2–26.5 GHz spectral region. The frequency range 26.5–40 GHz is covered using this synthesizer together with the Acurrel 2200 millimeter extender. In the 40–60 GHz interval microwave radiation is provided using the same synthesizer with the U-2X doubler and the U-3X tripler from Spacek Labs, Inc. Computer control of the microwave synthesizer is now being implemented employing a Hewlett-Packard Vectra 486 personal computer.

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Table 1. Optimized dihedral angles calculated by *ab initio*<sup>a-c</sup> methods.

Conformation	$\angle C1=C2-C3-C4$ <sup>a</sup>	$\angle C2-C3-C4-F$ <sup>b</sup>
<i>Skew-Anti</i>	111.1	177.1
<i>Skew-Gauche I</i>	119.0	-61.8
<i>Skew-Gauche II</i>	127.9	55.8
<i>Syn-Anti</i>	0.0	180.0
<i>Syn-Gauche</i>	25.7	-65.2

<sup>a</sup>Atom numbering H<sub>2</sub>C1=C2H-C3H<sub>2</sub>-C4H<sub>2</sub>F. <sup>b</sup>Measured from *syn* = 0°. <sup>c</sup>3-21G\* basis set. <sup>a</sup>A negative value indicates that the fluorine atom is near to the double bond.

## Results

*Ab initio calculations.* The *ab initio* calculations were performed using the Gaussian 88 program package.<sup>2</sup> The 3-21G\* basis set<sup>3,4</sup> was chosen. Computations were made for the five selected conformations sketched in Fig. 1 with full geometry optimization. The reason for selecting these five forms for study by the theoretical calculations is that closely related molecules prefer *syn* and/or *skew* forms. For example, H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>3</sub> prefers the *skew* conformation.<sup>5</sup> The *syn* form is also present at a higher energy.<sup>5</sup> One *skew* form has been assigned by MW spectroscopy for H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>Br.<sup>6</sup> An electron-diffraction study claims that two rotamers are present in the case of H<sub>2</sub>C=CH-CH<sub>2</sub>CH<sub>2</sub>OH,<sup>7a</sup> while only one form was found in a MW work.<sup>7b</sup> MW spectroscopy revealed the existence of several *skew* rotamers in each of the cases of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>NH<sub>2</sub><sup>8</sup> and H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>SH.<sup>9</sup> Stable rotamers in which the C1=C2-C3-C4 chain of atoms are arranged in conformations other than *syn* and/or *skew* have to our knowledge not been seen in the free state.

The *ab initio* computations predict that all five forms shown in Fig. 1 are stable. The bond angles and bond distances obtained in the computations appear to be normal 'contaminated' with the usual basis set deficiencies. For that reason, a full listing of them is not given. However, in Table 1 the dihedral angles that determine the conformation of each of the five rotamers are collected. All these angles, apart from the C1-C2-C3-C4 dihedral angle of *Syn-Gauche*, take their usual values close to 0, 60, 120 and 180°, respectively. In the said conformation this angle deviates by 25.7° from the normal 0° value, a prediction

Table 2. Rotational constants calculated by *ab initio* methods.

Conformation	A/MHz	B/MHz	C/MHz
<i>Skew-Anti</i>	19782	2143	2129
<i>Skew-Gauche I</i>	9752	3123	2650
<i>Skew-Gauche II</i>	12350	2786	2477
<i>Syn-Anti</i>	15429	2519	2225
<i>Syn-Gauche</i>	8184	3993	2932

Table 3. Principal-axes dipole moment components calculated by *ab initio* methods.

Conformation	$\mu_a/10^{-30}$ C m	$\mu_b/10^{-30}$ C m	$\mu_c/10^{-30}$ C m
<i>Skew-Anti</i>	6.73	2.91	0.83
<i>Skew-Gauche I</i>	0.68	7.35	0.75
<i>Skew-Gauche II</i>	2.13	6.44	1.84
<i>Syn-Anti</i>	7.00	0.70	0.00
<i>Syn-Gauche</i>	0.56	6.76	3.12

that might perhaps indicate repulsion between the fluorine atom and the double-bond  $\pi$  electrons.

The predicted rotational constants are shown in Table 2. It is shown below that they deviate from the experimental ones in the cases of three *skew* rotamers by less than a few percent.

The principal-axes dipole moment components are shown in Table 3. The energy differences between the five conformations, which are predicted to be small, as listed in Table 4.

*Microwave spectrum and extension of the assignments for Skew-Anti.* The MW spectrum of 4-fluoro-1-butene is very dense, with absorptions occurring every few MHz throughout the entire MW region. The spectrum is also comparatively strong at dry-ice temperature. In Ref. 1, *a*-type *R*-branch transitions of the ground vibrational state were assigned in the 26.5–40 GHz spectral region. This conformer is a near-prolate asymmetric rotor ( $\kappa = -0.998$ ). Therefore, the *A* rotational constant was poorly determined from the '*R*' transitions.<sup>1</sup> The accuracy of the *A* rotational constant is very much dependent on the assignment of *b*- or *c*-type transitions. The dipole moment component along the *b*-axis is<sup>1</sup>  $2.3(2) \times 10^{-30}$  C m. The dipole moment component along the *c*-axis is even smaller.<sup>1</sup> <sup>b</sup>*Q*-transitions might thus be strong enough to be possible to assign. A successful search for the  $J_{1,J-1} \leftarrow J_{0,J}$  *Q*-branch series of lines was performed and assignments were made from  $J = 5$  to  $J = 37$  for the ground vibrational state. Accurate predictions of <sup>b</sup>*R*-, <sup>c</sup>*Q*- and <sup>c</sup>*R*-transitions could now be made, but none of them was found, presumably owing to insufficient intensities caused by the small dipole-moment components along the *b*- and *c*-axes.<sup>1</sup> Selected

Table 4. Energies relative to *Skew-Gauche II*<sup>a</sup> as calculated by *ab initio* methods.

Conformation	Relative energy/kJ mol <sup>-1</sup>
<i>Skew-Anti</i>	1.6
<i>Skew-Gauche I</i>	7.5
<i>Skew-Gauche II</i>	0.0
<i>Syn-Anti</i>	6.6
<i>Syn-Gauche</i>	3.1

<sup>a</sup>The total energy computed for this conformer with the 3-21G\* basis is -665685.86 kJ mol<sup>-1</sup>.

Table 5. Selected transitions of the ground-state MW spectrum of the *Skew-Anti* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F.

Transition	Observed frequency <sup>a</sup> /MHz	Obs.-calc. frequency/MHz	Centrifugal distortion/MHz
<b><sup>a</sup>R-transitions</b>			
3 <sub>0,3</sub> ← 2 <sub>0,2</sub>	12 734.91	0.01	-0.08
3 <sub>1,3</sub> ← 2 <sub>1,2</sub>	12 705.24	-0.01	0.06
4 <sub>1,3</sub> ← 3 <sub>1,2</sub>	17 019.91	0.04	0.05
4 <sub>1,4</sub> ← 3 <sub>1,3</sub>	16 940.19	-0.03	-0.02
5 <sub>0,5</sub> ← 4 <sub>0,4</sub>	21 224.39	0.02	-0.38
5 <sub>1,4</sub> ← 4 <sub>1,3</sub>	21 274.71	0.01	-0.05
5 <sub>1,5</sub> ← 4 <sub>1,4</sub>	21 175.09	0.01	-0.18
6 <sub>0,6</sub> ← 5 <sub>0,5</sub>	25 468.90	0.04	-0.65
6 <sub>1,5</sub> ← 5 <sub>1,4</sub>	25 529.43	0.00	-0.23
6 <sub>1,6</sub> ← 5 <sub>1,5</sub>	25 409.83	0.01	-0.45
6 <sub>4,2</sub> ← 5 <sub>4,1</sub>	25 474.64	0.12	4.37
6 <sub>4,3</sub> ← 5 <sub>4,2</sub>	25 474.64	0.12	4.37
<b><sup>b</sup>Q-transitions</b>			
5 <sub>1,4</sub> ← 5 <sub>0,5</sub>	18 117.63	0.03	0.90
7 <sub>1,6</sub> ← 7 <sub>0,7</sub>	18 249.03	-0.03	1.87
8 <sub>1,7</sub> ← 8 <sub>0,8</sub>	18 330.43	0.03	2.56
9 <sub>1,8</sub> ← 9 <sub>0,9</sub>	18 422.31	0.01	3.41
10 <sub>1,9</sub> ← 10 <sub>0,10</sub>	18 524.96	0.06	4.47
11 <sub>1,10</sub> ← 11 <sub>0,11</sub>	18 638.39	0.02	5.75
12 <sub>1,11</sub> ← 12 <sub>0,12</sub>	18 762.87	0.00	7.31
14 <sub>1,13</sub> ← 14 <sub>0,14</sub>	19 045.77	0.01	11.40
15 <sub>1,14</sub> ← 15 <sub>0,15</sub>	19 204.52	-0.05	14.04
16 <sub>1,15</sub> ← 16 <sub>0,16</sub>	19 375.24	-0.03	17.14
17 <sub>1,16</sub> ← 17 <sub>0,17</sub>	19 558.10	-0.02	20.77
18 <sub>1,17</sub> ← 18 <sub>0,18</sub>	19 753.40	0.02	25.01
19 <sub>1,18</sub> ← 19 <sub>0,19</sub>	19 961.33	-0.26	29.91
20 <sub>1,19</sub> ← 20 <sub>0,20</sub>	20 182.33	-0.01	35.56
21 <sub>1,20</sub> ← 21 <sub>0,21</sub>	20 416.60	-0.06	42.05
22 <sub>1,21</sub> ← 22 <sub>0,22</sub>	20 664.63	-0.02	49.47
23 <sub>1,22</sub> ← 23 <sub>0,23</sub>	20 926.66	-0.01	57.92
24 <sub>1,23</sub> ← 24 <sub>0,24</sub>	21 203.02	-0.07	67.51
25 <sub>1,24</sub> ← 25 <sub>0,25</sub>	21 494.32	0.03	78.35
26 <sub>1,25</sub> ← 26 <sub>0,26</sub>	21 800.70	0.02	90.56
27 <sub>1,26</sub> ← 27 <sub>0,27</sub>	22 122.71	0.03	104.29
28 <sub>1,27</sub> ← 28 <sub>0,28</sub>	22 460.75	0.03	119.66
29 <sub>1,28</sub> ← 29 <sub>0,29</sub>	22 815.25	0.01	136.83
30 <sub>1,29</sub> ← 30 <sub>0,30</sub>	23 186.72	0.01	155.96
31 <sub>1,30</sub> ← 31 <sub>0,31</sub>	23 575.63	0.04	177.21
32 <sub>1,32</sub> ← 32 <sub>0,32</sub>	23 982.41	0.02	200.76
33 <sub>1,32</sub> ← 33 <sub>0,33</sub>	24 407.60	0.01	226.81
34 <sub>1,33</sub> ← 34 <sub>0,34</sub>	24 851.71	0.02	255.54
35 <sub>1,34</sub> ← 35 <sub>0,35</sub>	25 315.21	-0.02	287.16
36 <sub>1,35</sub> ← 36 <sub>0,36</sub>	25 798.71	0.00	321.89
37 <sub>1,36</sub> ← 37 <sub>0,37</sub>	26 302.62	-0.05	359.95

<sup>a</sup> ± 0.05 MHz.

transitions not previously published<sup>1</sup> are shown in Table 5.\* The spectroscopic constants in *A*-reduction *I*'-representation<sup>10</sup> are displayed in Table 6. It was found that only three quartic (and no sextic) centrifugal distortion constants were

\* The complete spectra are available from the authors upon request, or from the National Institute of Standards and Technology, Molecular Spectroscopy Division, Rm. 268/Bldg. 221, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 6. Spectroscopic constants<sup>a-c</sup> of the *Skew-Anti* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F in the ground vibrational state.

No. of transitions:	71
R.m.s. deviation/MHz:	0.038
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A <sub>0</sub> /MHz	20089.510(16)
B <sub>0</sub> /MHz	2132.4569(15)
C <sub>0</sub> /MHz	2112.5589(15)
Δ <sub>J</sub> /kHz	0.755(12)
Δ <sub>JK</sub> /kHz	-26.165(29)
δ <sub>J</sub> /kHz	-0.128432(40)

<sup>a</sup>A-reduction, *I*'-representation.<sup>10</sup> <sup>b</sup>Uncertainties represent one standard deviation. <sup>c</sup>Δ<sub>K</sub> and δ<sub>K</sub> preset at zero in the least-squares fit: see text.

necessary in the fitting procedure in order to obtain a root-mean-square deviation comparable to the experimental uncertainty.

*Vibrationally excited states of Skew-Anti.* No assignments were given for vibrationally excited states in Ref. 1. According to the *ab initio* calculations reported above, the three lowest normal modes are predicted at 88, 126 and 267 cm<sup>-1</sup>, respectively. (These values are not included in Tables 1-4.) The first of these normal modes is presumably the torsion around the C2-C3 bond, the second is the torsion around the C3-C4 bond, whereas the last frequency is the lowest bending vibration. The Boltzmann factors of these three normal modes are predicted to be 0.52, 0.39 and 0.14 at 195 K. The intensities of the corresponding three first excited-state spectra were thus predicted to be about 50, 40 and 15 % of the intensities of the ground-state spectrum. (The relative intensity of the first excited state of the fourth lowest normal vibrational mode is predicted by *ab initio* to be much less than 14 % of that of the ground vibrational state. For this reason it is not given herein.)

Satellite spectra belonging to the first excited states of the two lowest vibrations were found with relative intensities approximately 50 and 40 %, respectively, of the intensity of the ground vibrational state. These are close to the values predicted in the theoretical computations. <sup>b</sup>Q lines were assigned in addition to the strong <sup>a</sup>R transitions. The spectroscopic constants of these excited states are shown in Table 7. Relative intensity measurements<sup>11</sup> yielded 95(15) cm<sup>-1</sup> for the lowest vibration, in good agreement with the theoretical value of 88 cm<sup>-1</sup>. This vibration is probably the torsion around the C2-C3 bond. The frequency of the second lowest vibration, which is probably the torsion around the C3-C4 bond, was found to be 124(15) cm<sup>-1</sup> by relative intensity measurements,<sup>11</sup> in good agreement with the *ab initio* value of 126 cm<sup>-1</sup>. The frequencies of these two torsional modes are quite similar to their counterparts in the isoelectronic compounds 3-butene-1-ol<sup>7</sup> [84(20) and 172(15) cm<sup>-1</sup>, respectively] and 1-amino-3-butene<sup>8</sup> [95(20) and 130(30) cm<sup>-1</sup> for *Gauche I*; and 83(20) and 148(30) cm<sup>-1</sup> for *Gauche II*].

Table 7. Spectroscopic constants<sup>a,b</sup> of the *Skew-Anti* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F in vibrationally excited states.

Vibrational state:	First excited lowest torsional vibration <sup>c</sup>	Second excited lowest torsional vibration <sup>c</sup>	First excited second lowest torsional vibration <sup>d</sup>
No of transitions:	40	8	35
R.m.s. deviation <sup>e</sup> /MHz	0.022	0.047	0.046
$A_v$ /MHz	19 675.068(10)	19 261 <sup>f</sup>	20 299.135(24)
$B_v$ /MHz	2 137.7744(35)	2 143.5491(40)	2 133.8504(64)
$C_v$ /MHz	2 121.6423(36)	2 130.3268(43)	2 115.7920(67)
$\Delta_J$ /kHz	0.938(57)	0.755 <sup>g</sup>	0.80(11)
$\Delta_{JK}$ /kHz	-23.35(19)	-26.16 <sup>g</sup>	-28.56(40)
$\delta_J$ /kHz	-0.132 861(35)	-0.128 <sup>g</sup>	-0.129 666(83)

<sup>a,b</sup>Comments as for Table 6. <sup>c</sup>Presumably torsion around the C2-C3 bond: see text. <sup>d</sup>Presumably torsion around the C3-C4 bond: see text. <sup>e</sup>Root-mean-square deviation. <sup>f</sup>Fixed. <sup>g</sup>Fixed at ground-state value.

The *a*-type *R*-branch transitions of the second excited state of the C2-C3 torsional vibration were also assigned. Its spectroscopic constants are found in Table 7. The *A* rotational constant was preset at 19 261 MHz, a value extrapolated from the ground and first excited states of this mode.

The lowest bending mode, predicted to have a relative intensity of about 14 %, was not identified. One reason for this might be the prominent overlappings seen for the <sup>a</sup>*R*-lines, which have to be used as the starting point in the assignments.

*Assignment of Skew-Gauche II.* The *ab initio* calculations indicate that this conformer is the more stable one (Table 4). Searches were first made for the *b*-type  $J_{1,J-1} \leftarrow J_{0,J}$  transitions in the 10–20 GHz range. These transitions were soon identified, as were the <sup>b</sup>*R*-transitions. The assignments were gradually extended to high values of *J*, with a maximum value of 73. Transitions involving even higher *J* values were searched for but not found, presumably because of insufficient intensities caused by an unfavourable Boltzmann factor. The much weaker <sup>a</sup>*R*- and <sup>c</sup>*Q*-transitions were also found with ease. A total of about 200 transitions were measured, some of which are displayed in Table 8. The spectroscopic constants obtained using 182 transitions are found in Table 9. Three sextic centrifugal distortion constants had to be used in the fitting procedure in order to get the best fit.

The vibrational force field of the various conformers of 4-fluoro-1-butene is not expected to vary widely. The C2-C3 and C3-C4 torsional vibrations are thus expected to be the two lowest normal modes. Indeed, four vibrationally excited states, presumably belonging to torsions around C2-C3 and C3-C4, were identified, as indicated in Tables 9 and 10. Relative intensity measurements<sup>11</sup> yielded 90(15) cm<sup>-1</sup> for the torsion around C2-C3 and 131(15) cm<sup>-1</sup> for the torsion around the C3-C4 bond. The *ab initio* values were 106 and 148 cm<sup>-1</sup>, respectively. Note the similarity with the results obtained for *Skew-Anti* above.

The dipole moment was determined following standard procedure.<sup>12</sup> The results are shown in Table 11. These

experimental values are in fair agreement with the computed ones shown in Table 3.

*Assignment of Skew-Gauche I.* After the numerous lines belonging to *Skew-Gauche II* and *Skew-Anti* had been assigned, there remained several fairly intense absorptions that could hardly be ascribed to unidentified vibrationally excited states of any of these two conformers. After some searching the *b*-type *Q*-branch  $J_{2,J-2} \leftarrow J_{1,J-1}$  series of *Skew-Gauche I* was identified. The <sup>b</sup>*R* transitions were found next, and the assignments were gradually extended up to *J* = 67. Higher-*J* transitions were too weak to be assigned with certainty for reasons mentioned above. A total of about 150 *b*-type transitions were ultimately assigned for the ground vibrational state, a few of which are shown in Table 12. No *a*-type or *c*-type transitions could be identified with certainty, owing to the small dipole moment components along these two inertial axis (see below). 137 transitions were used to obtain the spectroscopic constants displayed in Table 13.

*Q*- and *R*-branch transitions were assigned for the first excited state of the C2-C3 torsional vibration, while only *Q*-branch lines were identified for the first excited state of the C3-C4 torsional motion. The *R*-branch transitions were too weak to be identified with certainty. Thus only *A*-*C* and  $\kappa$  can be determined in this case. The spectroscopic constants of these two excited states are found in Tables 13 and 14.

The vibrational frequencies of the two lowest torsional vibrations were determined to be 76(15) and 140(20) cm<sup>-1</sup>, respectively, by relative intensity measurements.<sup>11</sup> The *ab initio* results for these two vibrations were 70 and 124 cm<sup>-1</sup>, respectively.

The dipole moment determined in the ordinary manner<sup>12</sup> is shown in Table 15. The principal-axes dipole moment components in this table are in fair agreement with those obtained by the theoretical computations (Table 3).

*Searches for further conformations.* The assignments reported above include some 800 transitions. All the strongest lines of the spectrum, the large majority of the lines of

Table 8. Selected transitions of the ground-state MW spectrum of the *Skew-Gauche II* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F.

Transition	Observed frequency <sup>a</sup> /MHz	Obs. - calc. frequency/MHz	Centrifugal distortion/MHz	
			Total	Sextic
1 <sub>1,1</sub> ← 0 <sub>0,0</sub>	15 454.39	0.00	-0.14	
2 <sub>1,2</sub> ← 1 <sub>0,1</sub>	20 267.12	0.00	-0.04	
2 <sub>1,2</sub> ← 2 <sub>0,2</sub>	10 875.79	0.02	-0.06	
3 <sub>1,2</sub> ← 3 <sub>0,3</sub>	11 233.89	0.05	0.05	
4 <sub>0,4</sub> ← 3 <sub>1,3</sub>	10 279.81	0.00	-0.75	
5 <sub>1,4</sub> ← 4 <sub>1,3</sub>	25 771.60	0.05	-0.82	
5 <sub>2,4</sub> ← 4 <sub>2,3</sub>	25 205.82	0.00	0.29	
6 <sub>0,6</sub> ← 5 <sub>1,5</sub>	21 216.57	0.01	-2.66	
8 <sub>1,7</sub> ← 8 <sub>0,8</sub>	15 258.46	-0.05	0.09	
10 <sub>1,9</sub> ← 9 <sub>2,7</sub>	23 645.10	0.00	-14.06	0.01
10 <sub>1,9</sub> ← 10 <sub>0,10</sub>	18 178.93	-0.02	-1.45	
12 <sub>2,10</sub> ← 11 <sub>3,9</sub>	10 482.86	0.09	-22.65	0.02
14 <sub>2,12</sub> ← 13 <sub>3,11</sub>	22 394.28	-0.07	-42.97	0.04
15 <sub>2,14</sub> ← 15 <sub>1,14</sub>	18 964.58	-0.14	30.06	-0.03
17 <sub>3,14</sub> ← 16 <sub>4,13</sub>	13 814.53	0.01	-60.45	0.10
19 <sub>3,17</sub> ← 18 <sub>4,14</sub>	22 355.44	0.01	-81.27	0.18
21 <sub>4,18</sub> ← 20 <sub>5,15</sub>	12 006.91	0.08	-99.55	0.26
22 <sub>4,18</sub> ← 21 <sub>5,17</sub>	17 660.40	0.04	-128.54	0.35
25 <sub>5,21</sub> ← 24 <sub>6,18</sub>	11 264.59	0.00	-162.55	0.61
27 <sub>5,23</sub> ← 26 <sub>6,20</sub>	21 636.79	-0.07	-230.65	0.98
27 <sub>3,25</sub> ← 27 <sub>2,25</sub>	24 916.48	-0.04	202.51	-0.50
30 <sub>6,24</sub> ← 29 <sub>7,23</sub>	15 607.41	0.05	-290.47	1.56
31 <sub>3,29</sub> ← 31 <sub>2,29</sub>	16 654.66	0.03	248.82	-0.74
34 <sub>7,28</sub> ← 33 <sub>8,25</sub>	14 686.27	-0.14	-407.80	2.85
36 <sub>7,29</sub> ← 35 <sub>8,28</sub>	25 018.76	-0.02	-532.86	4.05
40 <sub>4,37</sub> ← 40 <sub>3,37</sub>	26 319.42	-0.01	709.28	-3.44
43 <sub>4,40</sub> ← 43 <sub>3,40</sub>	18 957.86	-0.02	731.23	-3.95
53 <sub>5,49</sub> ← 53 <sub>4,49</sub>	25 935.36	0.06	1689.37	-13.53
55 <sub>5,51</sub> ← 55 <sub>4,51</sub>	20 595.40	-0.07	1634.42	-13.88
Coalescing <i>P</i> - and <i>R</i> -branch transitions <sup>b</sup>				
25 <sub>8</sub> ← 26 <sub>7</sub>	26 226.65	-0.16	22.23	-0.31
30 <sub>9</sub> ← 31 <sub>8</sub>	21 953.25	-0.08	110.73	-1.03
34 <sub>10</sub> ← 35 <sub>9</sub>	22 784.15	-0.03	178.21	-1.97
38 <sub>11</sub> ← 39 <sub>10</sub>	23 634.86	-0.03	266.48	-3.51
43 <sub>9</sub> ← 42 <sub>10</sub>	17 922.79	0.12	-819.60	9.20
47 <sub>10</sub> ← 46 <sub>11</sub>	16 921.93	0.05	-1044.23	14.15
47 <sub>13</sub> ← 48 <sub>12</sub>	20 385.84	0.01	636.72	-11.25
52 <sub>11</sub> ← 51 <sub>12</sub>	20 954.72	0.02	-1439.21	23.78
55 <sub>12</sub> ← 54 <sub>13</sub>	14 820.23	-0.06	-1603.49	30.28
56 <sub>15</sub> ← 57 <sub>14</sub>	17 330.08	0.01	1210.16	-28.56
59 <sub>16</sub> ← 60 <sub>15</sub>	23 322.44	-0.06	1294.28	-35.24
64 <sub>14</sub> ← 63 <sub>15</sub>	17 551.55	-0.01	-2527.36	64.89
67 <sub>18</sub> ← 68 <sub>17</sub>	25 458.24	-0.07	191.36	-66.67
70 <sub>15</sub> ← 69 <sub>16</sub>	26 249.26	-0.08	-3453.79	104.91
72 <sub>19</sub> ← 73 <sub>18</sub>	21 709.00	0.08	2552.46	-99.45

<sup>a</sup> ±0.05 MHz. <sup>b</sup>The *K*<sub>-1</sub> doublets coalesce for high values of *J* and *K*<sub>-1</sub>. Subscripts of *J* quantum number refer to *K*<sub>-1</sub>.

intermediate intensities, and many weak transitions have been assigned. The remaining, relatively few unassigned lines of intermediate intensity could arise from unassigned, vibrationally excited states of the three *skew* conformations reported above, or they could arise from the hypothetical *Syn-Anti* and/or *Syn-Gauche* conformations. These two rotamers are predicted to possess sizeable dipole moments, as indicated in Table 3, and they are predicted to be rather close in energy to the *skew* conformers (Table 4). In the

extensive searches for *Syn-Anti* and *Syn-Gauche* amongst the remaining unassigned intermediate-intensity lines, the rotational constants of Table 2 were used as starting points. The strongest transitions predicted for the hypothetical *syn* conformations were searched for; however, no assignments could be made. The fact that the unassigned lines are much less intense than the strongest assigned lines, and the fact that a large dipole moment is computed for each of the two hypothetical *syn* forms (Table 3), lead us to conclude that

Table 9. Spectroscopic constants<sup>a,b</sup> of the *Skew-Gauche II* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F in the ground vibrational state and in vibrationally excited states of the torsion around the C2-C3 bond.

Vibrational state:	Ground	First excited C2-C3 torsional vibration	Second excited C2-C3 torsional vibration
No of transitions:	182	101	18
R.m.s. deviation <sup>c</sup> /MHz:	0.064	0.059	0.045
$A_v$ /MHz	13 048.2161(61)	12 913.8630(91)	12 797.8717(62)
$B_v$ /MHz	2 636.4673(12)	2 645.9577(18)	2 655.2823(26)
$C_v$ /MHz	2 406.3153(11)	2 418.1765(20)	2 429.8259(25)
$\Delta_J$ /kHz	1.9979(23)	2.1449(60)	1.530(18)
$\Delta_{JK}$ /kHz	-31.813(30)	-31.182(83)	-31.813 <sup>d</sup>
$\Delta_K$ /kHz	206.370(45)	182.57(12)	206.37 <sup>d</sup>
$\delta_J$ /kHz	0.21429(33)	0.2228(19)	0.2369(13)
$\delta_K$ /kHz	5.158(98)	4.88(15)	5.158 <sup>d</sup>
$\Phi_J$ /Hz	0.00802(22)	0.0359(41)	- <sup>e</sup>
$\Phi_{JK}$ /Hz	-0.1804(53)	0.508(97)	- <sup>e</sup>
$\Phi_{KJ}$ /Hz	0.8095(47)	0.427(11)	- <sup>e</sup>

<sup>a,b</sup>Comments as for Table 6. <sup>c</sup>Root mean-square deviation. <sup>d</sup>Fixed at ground-state value. <sup>e</sup>Preset at zero. <sup>f</sup>Further sextic constants preset at zero.

the hypothetical *syn* forms are at least 4 kJ mol<sup>-1</sup> less stable than *Skew-Gauche II*, which is the more stable of the *skew* forms (see next section).

**Energy differences.** The energy differences between the three *skew* conformers were determined from relative intensity measurements observing the precautions of Ref. 11. It was found that *Skew-Gauche II* is the more stable conformer. This rotamer is 1.9(2) kJ mol<sup>-1</sup> more stable than *Skew-Anti*, while *Skew-Gauche I* is less stable than *Skew-Gauche II* by 2.1(2) kJ mol<sup>-1</sup>. The uncertainties represent one standard deviation. *Skew-Anti* and *Skew-Gauche I* are thus almost equally stable; the energy difference being only 0.2(3) kJ mol<sup>-1</sup> favouring *Skew-Anti*.

The energy differences found in the *ab initio* calculations (Table 4) correctly predicts the energy difference between *Skew-Gauche II* and *Skew-Anti*. However, the energy dif-

Table 11. Stark coefficients and dipole moment of the *Skew-Gauche II* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F.<sup>a</sup>

Transition	$M$	$\Delta\nu E^{-2}/10^{-5}$ MHz V <sup>-2</sup> cm <sup>2</sup>	
		Obs.	Calc.
2 <sub>1,2</sub> ← 1 <sub>0,1</sub>	0	-0.619(10)	-0.621
4 <sub>1,3</sub> ← 4 <sub>0,4</sub>	4	4.11(4)	4.02
	3	1.99(3)	1.95
5 <sub>1,4</sub> ← 5 <sub>0,5</sub>	5	3.61(4)	3.72
	4	2.06(3)	2.09
	3	0.805(20)	0.813
8 <sub>1,7</sub> ← 8 <sub>0,8</sub>	8	3.01(3)	2.96
	7	2.21(3)	2.26
Dipole moment/10 <sup>-30</sup> C m			
$\mu_a = 2.806(54)$ $\mu_b = 4.865(73)$ $\mu_c = 2.43(13)$ $\mu_{tot} = 6.12(11)$			

<sup>a</sup>Uncertainties represent one standard deviation. 1 D = 3.335 64 × 10<sup>-30</sup> C m.

Table 10. Spectroscopic constants<sup>a,b</sup> of the *Skew-Gauche II* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F in vibrationally excited states.

Vibrational state:	First excited C3-C4 torsional vibration	Combined excited C2-C3 and C3-C4 torsional vibration
No. of transitions:	72	18
R.m.s. deviation <sup>c</sup> /MHz	0.093	0.045
$A_v$ /MHz	13 239.988(18)	13 074.980(42)
$B_v$ /MHz	2 625.5706(37)	2 635.1449(38)
$C_v$ /MHz	2 398.0820(38)	2 410.1090(38)
$\Delta_J$ /kHz	1.941(25)	2.104(37)
$\Delta_{JK}$ /kHz	-34.19(32)	-33.57(24)
$\Delta_K$ /kHz	241.12(48)	206.37 <sup>d</sup>
$\delta_J$ /kHz	0.2154(48)	0.2185(29)
$\delta_K$ /kHz	5.40(45)	5.158 <sup>d</sup>
$\Phi_J$ /Hz	0.008(10)	- <sup>e</sup>
$\Phi_{JK}$ /Hz	-0.20(25)	- <sup>e</sup>
$\Phi_{KJ}$ /Hz	0.814(36)	- <sup>e</sup>

<sup>a-f</sup>Comments as for Table 9.

Table 12. Selected transitions of the ground-state MW spectrum of the *Skew-Gauche I* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F.

Transition	Observed frequency <sup>a</sup> /MHz	Obs. - calc. frequency/MHz	Centrifugal distortion/MHz	
			Total	Sextic
2 <sub>1,2</sub> ← 1 <sub>0,1</sub>	17 830.68	0.10	0.06	
3 <sub>1,2</sub> ← 2 <sub>0,2</sub>	22 828.07	0.12	0.14	
2 <sub>2,0</sub> ← 2 <sub>1,1</sub>	21 015.63	0.08	-1.12	
3 <sub>2,2</sub> ← 3 <sub>1,3</sub>	22 923.96	0.03	-0.80	
4 <sub>0,4</sub> ← 3 <sub>1,3</sub>	16 308.45	0.09	-1.73	
5 <sub>0,5</sub> ← 4 <sub>1,4</sub>	22 456.83	0.03	-3.25	
5 <sub>2,4</sub> ← 5 <sub>1,5</sub>	24 896.92	0.02	0.07	-0.02
7 <sub>1,6</sub> ← 6 <sub>2,5</sub>	23 263.68	0.03	-13.64	
8 <sub>1,7</sub> ← 8 <sub>0,8</sub>	17 396.82	0.03	-11.00	-0.03
10 <sub>2,9</sub> ← 9 <sub>3,6</sub>	17 731.68	0.06	-16.73	-0.02
10 <sub>1,9</sub> ← 10 <sub>0,10</sub>	23 822.39	-0.02	-27.68	-0.07
12 <sub>2,10</sub> ← 12 <sub>1,11</sub>	21 321.17	0.01	-18.57	-0.28
14 <sub>2,12</sub> ← 14 <sub>1,13</sub>	25 852.05	0.06	-58.35	-0.28
17 <sub>5,13</sub> ← 16 <sub>6,10</sub>	17 674.85	-0.03	-113.31	0.48
20 <sub>6,15</sub> ← 19 <sub>7,12</sub>	20 323.84	-0.02	-184.26	1.11
23 <sub>7,17</sub> ← 22 <sub>8,14</sub>	22 919.40	-0.14	-278.18	2.25
26 <sub>8,19</sub> ← 25 <sub>9,16</sub>	25 481.77	-0.02	-398.52	4.15
26 <sub>8,18</sub> ← 25 <sub>9,17</sub>	25 484.65	-0.21	-398.85	4.17
Coalescing <i>P</i> - and <i>R</i> -branch transitions <sup>b</sup>				
14 <sub>8</sub> ← 15 <sub>7</sub>	23 198.57	-0.03	-80.47	0.26
16 <sub>9</sub> ← 17 <sub>8</sub>	26 270.40	0.04	-116.70	0.48
19 <sub>10</sub> ← 20 <sub>9</sub>	23 651.45	-0.05	-114.55	0.56
26 <sub>9</sub> ← 25 <sub>10</sub>	10 659.92	0.10	-275.18	3.33
24 <sub>12</sub> ← 25 <sub>11</sub>	24 102.01	-0.07	-142.65	0.87
30 <sub>10</sub> ← 29 <sub>11</sub>	18 968.77	-0.02	-501.10	7.60
30 <sub>14</sub> ← 31 <sub>13</sub>	18 918.51	0.00	-45.39	-0.99
35 <sub>12</sub> ← 34 <sub>13</sub>	18 245.92	0.06	-733.16	15.62
37 <sub>13</sub> ← 36 <sub>14</sub>	15 029.19	-0.02	-787.39	19.40
36 <sub>16</sub> ← 37 <sub>15</sub>	13 816.54	-0.12	154.51	-7.37
40 <sub>14</sub> ← 39 <sub>15</sub>	17 477.41	0.10	-1020.08	29.15
43 <sub>15</sub> ← 42 <sub>16</sub>	19 886.97	0.02	-1292.35	42.42
45 <sub>20</sub> ← 46 <sub>19</sub>	20 520.11	0.12	159.63	-17.39
50 <sub>18</sub> ← 49 <sub>19</sub>	15 776.86	-0.06	-1771.68	82.73
51 <sub>22</sub> ← 52 <sub>21</sub>	15 654.75	-0.08	603.70	-47.95
56 <sub>20</sub> ← 55 <sub>21</sub>	20 313.20	0.08	-2593.26	150.31
61 <sub>22</sub> ← 60 <sub>23</sub>	19 243.21	-0.08	-3189.40	224.02
67 <sub>24</sub> ← 66 <sub>25</sub>	23 443.48	-0.05	-4346.19	366.69

<sup>a</sup> ±0.05 MHz. <sup>b</sup>The *K*<sub>-1</sub> doublets coalesce for high values of *J* and *K*<sub>-1</sub>. Subscripts of *J* quantum number refer to *K*<sub>-1</sub>.

ference between *Skew-Gauche II* and *Skew-Gauche I* is calculated to be too high, as the calculated value is 7.5 kJ mol<sup>-1</sup> (Table 4) compared to the experimental value of 2.1(2) kJ mol<sup>-1</sup>. We also suspect the energy difference computed for the hypothetical *Syn-Gauche* and *Skew-Gauche II* (3.1 kJ mol<sup>-1</sup>; Table 4) to be too small.

**Structure.** The three rotational constants determined for each of the three *skew* conformers of 4-fluoro-1-butene furnish insufficient information for a full structure determination. Assumptions have to be made. In our case only the C1=C2-C3-C4 and the C2-C3-C4-F dihedral angles were fitted in steps of 1°, keeping the rest of the structural parameters fixed at the values shown in Table 16. These

structural parameters were taken from related molecules for which accurate structures have been determined.<sup>13</sup> This choice of parameters is considered to be slightly more accurate than the alternative choice of the *ab initio* structure.

The fitted dihedral angles are shown in Table 16, where the uncertainty limit of 3° represents approximately three standard deviations. The *ab initio* results (Table 1) differ from the experimental values by a few degrees. It is seen in Table 17 that the rotational constants are well reproduced with the structural parameters given in Table 16. This agreement is generally much better than that found in the *ab initio* calculations listed in Table 2.

Table 13. Spectroscopic constants<sup>a,b</sup> of the *Skew-Gauche I* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F in the ground and first excited state of the C2-C3 torsional vibration.

Vibrational state:	Ground	First excited C2-C3 torsional vibration
No. of transitions:	137	25
R.m.s deviation <sup>c</sup> /MHz:	0.069	0.092
<i>A<sub>v</sub></i> /MHz	10 026.3189(69)	10 042.509(17)
<i>B<sub>v</sub></i> /MHz	3 027.0373(19)	3 045.2495(69)
<i>C<sub>v</sub></i> /MHz	2 601.3400(24)	2 606.8392(71)
$\Delta_J$ /kHz	5.025(14)	5.490(51)
$\Delta_{JK}$ /kHz	-41.44(12)	-41.83(30)
$\Delta_K$ /kHz	130.727(37)	130.73 <sup>d</sup>
$\delta_J$ /kHz	1.5184(44)	1.6805(47)
$\delta_K$ /kHz	7.84(22)	7.84 <sup>d</sup>
$\Phi_J$ /Hz	-0.3367(96)	- <sup>e</sup>
$\Phi_{JK}$ /Hz	-7.70(17)	- <sup>e</sup>
$\Phi_{KJ}$ /Hz	-4.38(15)	- <sup>e</sup>

<sup>a-d</sup>Comments as for Table 9.Table 14. Spectroscopic constants<sup>a,b</sup> of the *Skew-Gauche I* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F in the first excited state of the C3-C4 torsional vibration.

No. of transitions:	14
R.m.s. deviation MHz:	0.133
( <i>A<sub>v</sub></i> , <i>C<sub>v</sub></i> )/MHz	7462.536(14)
$\kappa$	-0.885895
$\Delta_{JK}$	-40.20(22)
$\Delta_K$	130.73 <sup>c</sup>
$\delta_J$	1.5274(30)
$\delta_K$	7.84 <sup>c</sup>

<sup>a,b</sup>Comments as for Table 6. <sup>c</sup>Preset at ground-state value shown in Table 12.Table 15. Stark coefficients and dipole moment of the *Skew-Gauche I* conformer of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F.

Transition	<i>M</i>	$\Delta v E^{-2}/10^{-6}$ MHz V <sup>-2</sup> cm <sup>2</sup>	
		Obs.	Calc.
8 <sub>2,6</sub> → 8 <sub>1,7</sub>	8	15.9(2)	15.5
	7	12.0(2)	12.0
5 <sub>2,4</sub> ← 5 <sub>1,4</sub>	6	9.02(20)	8.94
	5	3.89(4)	4.10
6 <sub>2,4</sub> ← 6 <sub>1,5</sub>	4	-0.874(10)	-0.894
	6	2.75(3)	2.68
7 <sub>2,5</sub> ← 7 <sub>1,6</sub>	5	-3.87(5)	-3.69
	6	7.94(9)	7.80
5 <sub>2,3</sub> ← 5 <sub>1,4</sub>	5	-3.61(4)	-3.58

Dipole moment/10<sup>-30</sup> C m $\mu_a = 1.108(20)$   $\mu_b = 6.248(39)$   $\mu_c = 0.30(10)$   $\mu_{tot} = 6.352(45)$ <sup>a</sup>Comments as for Table 11.

## Discussion

The finding that 4-fluoro-1-butene takes the three *skew* conformations as its stable forms is typical. Similar results have been observed in all other H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>X-type molecules, where X is H,<sup>5</sup> Br,<sup>6</sup> OH,<sup>7</sup> NH<sub>2</sub><sup>8</sup> and SH.<sup>9</sup> In the last three cases the preferred conformers are stabilized by intramolecular hydrogen bonds formed between the hydroxyl,<sup>7</sup> amino<sup>8</sup> and thiol<sup>9</sup> group hydrogen atom and the  $\pi$  electrons of the double bond.

The reason why *Skew-Gauche II* is the more stable of the

Table 16. Plausible molecular structure<sup>a</sup> of HC=CH-CH<sub>2</sub>-CH<sub>2</sub>FStructural parameters kept fixed for all three stable rotamers<sup>b</sup>

Bond distances/pm		Angles/°	
C1=C2	133.1	C1=C2-C3	127.8
C2-C3	149.6	C2-C3-C4	111.6
C3-C4	153.0	H-C1=C2	121.5
C4-F	139.3	H-C2=C1	121.5
C1-H	109.0	C3-C4-F	111.0
C2-H	109.0	C3-C4-H	109.47
C3-H	109.3	C4-C3-H	109.47
C4-H	109.3	H-C3-H	109.47
		H-C4-H	109.47

Fitted dihedral angles/°

	<i>Skew-Anti</i>	<i>Skew-Gauche I</i>	<i>Skew-Gauche II</i>
C1=C2-C3-C4	114	125	125
C2-C3-C4-F <sup>d</sup>	-179	-57	63

<sup>a</sup>See text. <sup>b</sup>The vinyl group has been assumed to be planar. Atom numbering: C1=C2-C3-C4-F. <sup>c</sup>The uncertainty limit (approximately three standard deviations) is  $\pm 3^\circ$  for these dihedral angles. <sup>d</sup>A negative value of this angle indicates that the fluorine atom approaches the double bond.



Table 17. Observed and calculated<sup>a</sup> rotational constants of the three stable conformers of H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>2</sub>F.

	<i>Skew-Anti</i>			<i>Skew-Gauche I</i>			<i>Skew-Gauche II</i>		
	Obs.	Calc.	Diff./%	Obs.	Calc.	Diff./%	Obs.	Calc.	Diff./%
A	20 089.51	20 075.73	0.07	10 026.32	10 003.79	0.22	13 048.22	13 015.00	0.25
B	2 132.46	2 101.82	1.43	3 027.04	3 031.23	0.14	2 625.57	2 620.51	0.19
C	2 112.56	2 087.71	1.18	2 601.34	2 591.80	0.37	2 406.32	2 380.96	1.06

<sup>a</sup>Using the structural parameters shown in Table 16.

three *skew* forms is difficult to explain. One reason might be the general tendency to prefer *gauche* conformations over *anti*. This should make the *Skew-Gauche II* rotamer more stable than *Skew-Anti*, in agreement with the present findings [energy difference 1.9(2) kJ mol<sup>-1</sup>].

The *Skew-Gauche II* conformer is 2.1(2) kJ mol<sup>-1</sup> more stable than *Skew-Gauche I*. The double-bond  $\pi$  electrons and the fluorine atom are much closer to one another in *Skew-Gauche I* than in *Skew-Gauche II*. This may perhaps give an electrostatic repulsion that destabilizes *Skew-Gauche I* in comparison with the *Skew-Gauche II*, thus making the latter conformer the more stable.

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