Synthesis, Microwave Spectrum, and Conformational Properties of 2-Fluoroethyl Azide (FCH₂CH₂N₃)

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Ⓢ Supporting Information

ABSTRACT: A novel synthesis producing neat 2-fluoroethyl azide (FCH₂CH₂N₃) is described. A conformational analysis using microwave spectroscopy augmented by quantum chemical calculations at the CCSD(T)/cc-pVTZ, B3LYP/aug-cc-pVTZ, and B3LYP/cc-pVTZ levels of theory has been performed for this compound. The spectra of the ground vibrational state and two vibrationally excited states of one rotameric form were assigned. A large number of transitions was assigned, and very accurate values were obtained for the rotational and quartic centrifugal distortion constants. The identified conformer has synclinal orientations for the F−C−C−N and C−C−N−N chains of atoms bringing the fluorine atom and the azido group into close proximity. It is concluded from consideration of absolute intensities that this conformer is indeed the preferred form of the molecule in accord with the theoretical calculations. The experimental and CCSD(T) rotational constants are in very good agreement, whereas much larger discrepancies were seen for the experimental and B3LYP quartic centrifugal distortion constants.
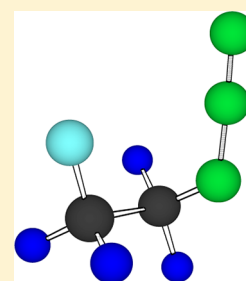
INTRODUCTION

1,2-Ethane derivatives, XCH₂CH₂Y, generally exist as a mixture of X−C−C−Y antiperiplanar (ap) and synclinal (sc) conformers. It is well-known that such ethane derivatives with highly electronegative substituents (atoms or groups) often prefer sc conformers in spite of significant electrostatic repulsion between the substituents.[1] The most prominent example displaying this so-called gauche effect is FCH₂CH₂F, for which an experimental energy difference of a few kJ/mol favoring the sc rotamer was found.[2,3] Recently, a density functional study[4] indicates that hyperconjugation between σ-bonding orbitals of the C−H bonds and the σ-antibonding orbitals of the C−F fluorine bonds is largely responsible for the sc preference of 1,2-difluoroethane.

We have recently studied two ethane derivatives containing the fluorine atom and the very polar nitrile and isocyanide groups, namely, FCH₂CH₂CN[5] and FCH₂CH₂NC,[6] using microwave (MW) spectroscopy and high-level quantum chemical calculations. The MW spectra of an ap and a sc form were assigned for each of these compounds and the energy differences were determined by comparison of intensities of MW transitions. It was found that the ap form is 1.4(5) kJ/mol more stable than the sc conformer in the case of FCH₂CH₂CN.[5] The opposite was found for FCH₂CH₂NC[6] where the sc form was more stable than the ap rotamer by 0.7(5) kJ/mol. It was assumed that several effects contribute to the energy differences in these two cases, but it was concluded that the gauche effect is of considerable importance in each of these two molecules.[5,6]

This time, our synthetic, MW, and quantum chemical investigations are extended to include yet another ethyl fluoride derivative, namely, 2-fluoroethyl azide (FCH₂CH₂N₃), which we have succeeded to prepare in pure form for the first time, allowing the first experimental study of the interaction between a fluorine atom and an azido group on adjacent atoms to be performed.

The gauche effect might be expected to have an effect on the conformational properties of the title compound because the nitrogen atom is the third most electronegative atom having a Pauling electronegativity value of 3.04.[7] The polarized C−N bond can therefore accommodate σ(C−H) → σ*(C−N) hyperconjugation, which should contribute stabilization to the F−C−C−N sc conformers.

The conformational properties of FCH₂CH₂N₃ are more complicated than in the cases of FCH₂CH₂CN and FCH₂CH₂NC, because of the azido group geometry. The fact that the C−N−N link of atoms is bent may result in rotational isomerism about the C−N bond in addition to the isomerism about the C−C bond. Five different conformers, instead of just two, as for FCH₂CH₂CN and FCH₂CH₂NC, can therefore be envisaged. These five forms are depicted in Figure 1 and given Roman numerals for reference. Atom numbering is shown on rotamer **I**. The N6−C1−C2−F3 and the C2−C1−N6−N7 dihedral angles can conveniently be used to describe the geometry of the five conformers. The N6−C1−C2−F3 link of
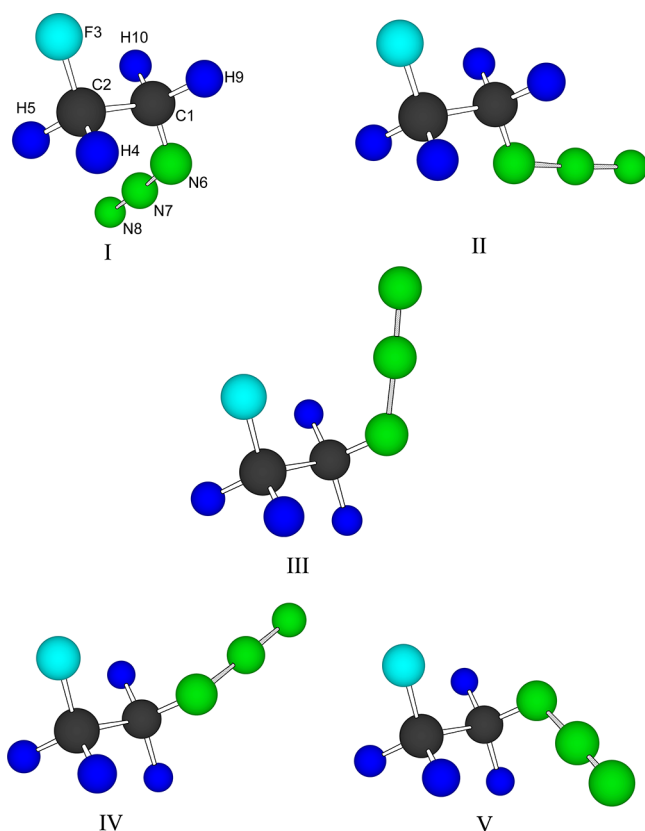
Figure 1. Five conformers of $FCH_2CH_2N_3$. The MW spectrum of **III** was assigned. The N6−C1−C2−F3 chain of atoms is +sc and the C2−C1−N6−N7 link is −sc in this conformer.

atoms is ap in **I** and **II**, and +sc in **III**−**V**. The C2−C1−N6−N7 chain is ap in **II** and **IV**, +sc in **I** and **V**, and −sc in **III**. Mirror-image forms exist for conformers **I** and **III**−**V**.

There are not many studies of conformational properties of azides in the literature, which is presumably due to the fact that some members of this class of compounds are explosive. However, studies by Nielsen and co-workers[8] of a selection of azides demonstrated that more than one conformer is found in several cases. 2-Fluoroethyl azide has been subject to a quantum chemical investigation at the B3LYP/6-311+G(d,p) level of theory,[4] and some results for conformer **III** were reported.[4] This compound has also been used to synthesize drugs of interest for PET (positron emission tomography) investigations.[9−11]

The fact that so little information exists on the interesting interaction between a fluorine atom and an azido group on adjacent carbon atoms motivated us to synthesize $FCH_2CH_2N_3$ to investigate its conformational properties by MW spectroscopy and very high-level quantum chemical calculations. MW spectroscopy was chosen because it is ideal for a conformational analysis due to its superior accuracy and resolution. The quantum chemical calculations were conducted with the purpose of obtaining information for use in assigning the MW spectrum and investigating properties of the potential-energy hypersurface.

■ EXPERIMENTAL SECTION

Synthesis of 2-Fluoroethyl Azide. Caution! 2-Fluoroethyl azide is potentially explosive[10] and all the experiments should be performed behind a safety screen and in a well-ventilated hood. Only small amounts of substrate (2.3 mmol) were used to prepare the product, which was never heated beyond room temperature.

The synthesis was performed in two steps starting from the commercially available 2-fluoroethanol and via the formation of the corresponding tosylate prepared as previously reported (Scheme 1).[9] To a solution of (2-fluoroethyl)-4-toluenesulfo-

Scheme 1
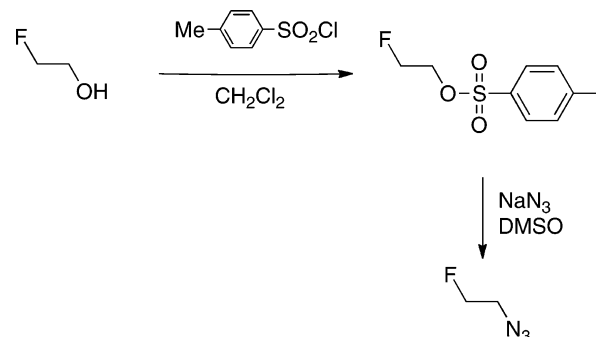
nate (0.5 g, 2.3 mmol) in triethylene glycol (15 mL) was added sodium azide (0.5 g, 0.77 mmol), and the resulting mixture was stirred at ambient temperature for 48 h. The reaction mixture was distilled at 0.1 mbar at room temperature using a vacuum line. The high boiling impurities were separated in a trap cooled at −20 °C and 2-fluoroethyl azide was selectively separated in a second trap cooled at −60 °C. The pure compound was transferred in vacuo to a cell cooled in a liquid nitrogen bath. It can be kept for months at −80 °C. Yield: 150 mg, 73%. Although this compound has already been synthesized[10] and used as reagent in several studies, to the best of our knowledge, 2-fluoroethyl azide has never been isolated and characterized by NMR spectroscopy.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.51 (dt, 2H, $^3J_{HF}$ = 27.3 Hz, $^3J_{HH}$ = 4.6 Hz, CH$_2$N), 4.60 (dm, 2H, $^2J_{HF}$ = 47.1 Hz, $^3J_{HH}$ = 4.6 Hz, CH$_2$F). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 51.2 ($^2J_{CF}$ = 20.3 Hz (d), $^1J_{CH}$ = 141.5 Hz (t), CH$_2$N), 82.2 ($^1J_{CF}$ = 171.5 Hz (d), $^1J_{CH}$ = 151.9 Hz (t), CH$_2$F). ^{19}F NMR (CDCl$_3$, 374.4 MHz): δ −222.3 (tt, $^2J_{HF}$ = 47.1 Hz, $^3J_{HF}$ = 27.3 Hz).

Spectroscopic Experiments. The MW spectra were recorded at room temperature, or with the cell cooled to about −30 °C using small portions of dry ice to cool the waveguide. The pressure was roughly 7 Pa. The MW spectrum was studied with Stark-modulation spectroscopy using the microwave spectrometer of the University of Oslo. Details of the construction and operation of this device have been given elsewhere.[12−14] This spectrometer has a resolution of about 0.5 MHz and measures the frequency of isolated transitions with an estimated accuracy of ≈0.10 MHz. The spectrum was investigated in the whole 18−75 GHz frequency interval. Selected measurements were performed in the 75−100 GHz region. Radio-frequency microwave double-resonance experiments (RFMWDR), similar to those performed by Wodarczyk and Wilson,[15] were also conducted to unambiguously assign particular transitions, using the equipment described elsewhere.[12] No splittings of the spectral lines produced by quadrupole interaction of the three ^{14}N nuclei were observed, but a few lines were broad possibly as a result of this effect.

Quantum Chemical Methods. The present ab initio calculations were performed employing the Gaussian 09[16] and Molpro[17] programs, running on the Titan cluster in Oslo.

Becke's three-parameter hybrid functional employing the Lee, Yang, and Parr exchange–correlation functional (B3LYP)[18] was employed in the density functional theory (DFT) calculations using Peterson and Dunning's[19] correlation-consistent aug-cc-pVTZ basis set, which is of triple-ζ quality and augmented with diffuse functions. Selected B3LYP calculations employing the simpler cc-pVTZ basis set were also undertaken. Coupled-cluster calculations with singlet and doublet excitations including noniterative triplet excitations, CCSD(T),[20] were performed employing the latter basis set.

■ RESULTS

Quantum Chemical Calculations. B3LYP/aug-cc-pVTZ calculations of the structures, dipole moments, vibrational frequencies, and Watson's A-reduction quartic centrifugal distortion constants[21] were first performed for the five conformers **I–V**. All structural parameters were varied freely in these calculations with no symmetry restrictions. No imaginary harmonic normal vibrations were obtained, which is an indication that these rotamers are minima on the potential-energy hypersurface. Selected results of these calculations are found in Tables 1S–5S in the Supporting Information.

The MW spectrum of the ground and vibrationally excited states of rotamer **III** was assigned and sextic centrifugal distortion constants as well as vibration–rotation constants (the α's) were obtained (see below). B3LYP/aug-cc-pVTZ calculations of these parameters are considerably more costly than B3LYP/cc-pVTZ calculations, which were therefore undertaken to compare experiment and theory. Calculation of centrifugal distortion constants and the α constants is not straightforward using Gaussian 09.[22] These constants were obtained from an optimized structure using the principal inertial axes coordinates as recommended by McKean et al.[22] The results of these calculations for **III** are listed in Table 6S of the Supporting Information.

The very comprehensive CCSD(T)/cc-pVTZ calculations of optimized structures, dipole moments, and electronic energies of forms **I–V** were finally performed using the B3LYP structures in Tables 1S–5S (Supporting Information) as starting points. The optimizations were done without symmetry restrictions employing the default convergence criteria of Molpro. The resulting structures are listed in Table 1, and the principal inertial coordinates of the atoms are listed in Table 7S of the Supporting Information. The rotational constants calculated from these structures are shown in Table 2. The dipole moment components of the Molpro calculations were transferred to the principal-axes dipole moment components using Bailey's program Axis[23] with the results listed in Table 2. Calculation of the centrifugal distortion constants by the CCSD(T) method is beyond our computational resources. The B3LYP/aug-cc-pVTZ quartic centrifugal distortion constants in the A-reduction form[21] are therefore included in Table 2.

Some of the results in Tables 1 and 2 warrant further comments. The calculation of the C–F bond length is critical in quantum chemistry due to its extreme electronegativity. The equilibrium C–F bond length is for example 138.3(1) pm in CH_3F,[24] about the same as found for the five forms in Table 1 (138.2–138.7 pm).

The geometry of the azido group is interesting. The N6–N7 bond lengths vary between 123.9 and 124.3 pm in the different conformers, whereas the N7–N8 distances are shorter

Table 1. CCSD(T)/cc-pVTZ Structures of Five Conformers of $FCH_2CH_2N_3$

	I	II	III[a]	IV	V
Bond Length (pm)					
C1–C2	152.1	151.6	**151.4**	151.0	151.6
C1–N6	147.8	147.9	**147.6**	147.8	147.9
C1–H9	108.8	109.4	**109.4**	109.4	108.8
C1–H10	109.3	109.4	**109.0**	109.6	109.6
C2–F3	138.4	138.4	**138.7**	138.2	138.2
C2–H4	109.1	109.1	**109.1**	109.2	109.4
C2–H5	109.3	109.1	**109.3**	109.2	109.3
N6–N7	124.2	123.9	**124.3**	123.9	124.0
N7–N8	114.0	114.0	**113.8**	114.0	114.1
Angle (deg)					
C2–C1–N6	110.2	106.2	**112.0**	108.5	113.3
C2–C1–H9	109.8	109.8	**109.8**	109.5	109.6
C2–C1–H10	110.2	109.8	**109.1**	108.8	108.9
N6–C1–H9	106.4	111.1	**111.2**	111.2	105.6
N6–C1–H10	111.6	111.1	**106.1**	110.0	110.7
H9–C1–H10	108.5	108.8	**108.5**	108.8	108.5
C1–C2–F3	108.8	108.6	**109.2**	110.0	110.2
C1–C2–H4	110.5	110.6	**110.7**	110.5	111.2
C1–C2–H5	110.9	110.6	**110.5**	109.9	109.7
F3–C2–H4	108.8	108.8	**108.1**	108.3	108.2
F3–C2–H5	108.4	108.8	**108.3**	108.3	108.5
H4–C2–H5	109.3	109.3	**110.0**	109.8	109.0
C1–N6–N7	113.4	113.4	**113.6**	113.6	113.1
N6–N7–N8	173.3	173.8	**172.6**	173.7	173.7
Dihedral Angle (deg)					
N6–C1–C2–F3	177.7	180.0	**66.6**	70.6	64.6
N6–C1–C2–H4	58.2	60.7	**−52.3**	−48.9	−55.4
N6–C1–C2–H5	−63.2	−60.7	**−174.3**	−170.2	−176.1
H9–C1–C2–F3	60.7	59.8	**−57.4**	−50.9	−53.1
H9–C1–C2–H4	−58.7	−59.5	**−176.3**	−170.4	−173.0
H9–C1–C2–H5	179.9	179.1	**61.6**	68.3	66.3
H10–C1–C2–F3	−58.8	−59.8	**−176.2**	−169.6	−171.7
H10–C1–C2–H4	−178.2	−179.1	**64.9**	70.8	68.4
H10–C1–C2–H5	60.4	59.3	**−57.2**	−50.4	−52.3
C2–C1–N6–N7	81.5	180.0	**−80.4**	−159.0	66.6
H9–C1–N6–N7	−159.4	−60.6	**42.8**	−38.6	−173.4
H10–C1–N6–N7	−41.2	60.6	**160.6**	82.0	−56.2
C1–N6–N7–N8	175.0	180.0	**−172.9**	178.1	179.3

[a]The MW spectrum of this conformer was assigned.

(113.8–114.1 pm; Table 1). This is consistent with a resonance hybrid description of the azido group consisting of the FCH_2CH_2—N≡N^+=N^- and FCH_2CH_2—N^-—N^+≡N canonical structures as the main contributors. Interestingly, the r_s length of the longer N—N bond in CH_3N_3 is 123.1 pm, whereas the terminal N—N bond length is 113.7 pm,[25] very similar to the CCSD(T) values of the present investigation. The azido group of **I–V** is nonlinear, deviating by 6–7° from linearity in the five forms (Table 1), in good agreement with 173.1° found for their counterpart in CH_3N_3.[25]

The C2–C1–N6 angles are a few degrees smaller when the C2–C1–N6–N7 chain of atoms has an ap conformation (rotamers **II** and **IV**) than a sc conformation (**I, III, IV**), which may reflect a repulsive interaction or a slight rehybridization of the C1 atom in the sc forms.

The N6–C1–C2–F3 dihedral angle is 180°, or close to this value in the two ap forms **I** and **II**, but larger than 60° by approximately 4–11° in the sc forms **III–IV**. The C2–C1–

Table 2. CCSD(T)/cc-pVTZ and B3LYP/aug-cc-pVTZ Parameters of Spectroscopic Interest of Five Conformers[a] of FCH$_2$CH$_2$N$_3$

	I	II	III	IV	V
			Rotational Constants (MHz)		
A	11513.7	23803.8	**6582.7**	12202.8	8040.1
B	1699.6	1396.6	**2774.2**	1711.4	2115.4
C	1576.4	1341.5	**2084.8**	1606.8	1953.0
		Quartic Centrifugal Distortion Constants[b] (kHz)			
Δ_J	1.87	0.0973	**5.87**	2.89	5.75
Δ_{JK}	−80.9	−6.94	**−29.0**	−117	−89.3
Δ_K	11.3	501	**59.6**	1843	434
δ_J	0.499	0.00951	**2.04**	0.573	1.46
δ_K	25.7	−1.12	**9.64**	3.82	30.6
		Dipole Moment[c] (10^{-30} C m)			
μ_a	0.33	0.77	**7.11**	2.00	1.58
μ_b	0.10	0.25	**6.08**	8.89	3.83
μ_c	0.13	0.0[d]	**2.61**	3.10	9.01
μ_{tot}	0.37	0.81	**9.72**	9.62	9.92
		Energy Difference[e] (kJ/mol)			
ΔE	4.70	4.56	**0.0[f]**	4.69	5.81

[a]Minima on the potential energy hypersurface. [b]A-reduction.[21] [c]1 debye = 3.33564 × 10^{-30} C m. [d]By symmetry. [e]CCSD(T) electronic energy difference relative to I. [f]CCSD(T) electronic energy: −898 286.20 kJ/mol.

N6−N7 dihedral angle has its canonical value (180°) in **II** but deviates by as much as 7−22° from normality in the remaining four conformers.

The CCSD(T) electronic energy differences between the various conformers that are listed in Table 2 indicates that conformer **III** is the most stable form of the molecule, being more stable than **I**, **II**, **IV**, and **V** by 4.70, 4.56, 4.69, and 5.81 kJ/mol, respectively. The corresponding B3LYP/aug-cc-pVTZ energy differences corrected for harmonic zero-point vibrational energies can be obtained from entries in Tables 1S−5S of the Supporting Information as 4.36, 2.57, 1.67, and 4.87 kJ/mol, respectively.

Microwave Spectrum and Assignment of the Ground Vibrational State of Conformer III. The microwave spectrum of 2-fluoroethyl azide is relatively strong and very rich with absorption lines occurring every few MHz. The quantum chemical calculations above indicate that **III** is a few kJ/mol more stable than the remaining four forms and searches for this rotamer were therefore first undertaken. This conformer has sizable dipole moment components of $\mu_a \approx$ 7.1, $\mu_b \approx$ 6.1, and $\mu_c \approx$ 2.6 × 10^{-30} C m (1 debye = 3.33564 × 10^{-30} C m) according to the CCSD(T) calculations (Table 2). The *a*-type *R*-branch lines were first searched for using the RFMWDR technique. Several candidates were soon found close to the predicted frequencies and they were least-squares fitted to Watson's *A*-reduction *I*^{r}-representation Hamiltonian[21] using the computer program Rotfit by Sørensen.[26] Additional *a*R-branch lines were then found with ease and included in the fit. The approximate frequencies of the relatively strong *b*-type *Q*-branch lines were now predicted and readily assigned. The fit was gradually extended to include 646 transitions with J_{max} = 55 and K_{-1max} = 19. *c*-type lines were searched for, but no definite assignments could be made, in spite of the fact that their hypothetical frequencies can be very accurately predicted from the spectroscopic constants derived from the 646 transitions. This finding is assumed to be caused by a comparatively small

μ_c, which is in accord with the CCSD(T) calculations (Table 2). The spectrum is listed in Table 8S of the Supporting Information, and the spectroscopic constants are shown in Table 3. All the five quartic centrifugal distortion constants

Table 3. Spectroscopic Constants[a] of Conformer III of 2-Fluoroethyl Azide

vibrational state	ground	first ex C1−N6 tors[b]	first ex C1−C2 tors[c]
A (MHz)	6598.7095(31)	6682.1560(38)	6611.3308(82)
B (MHz)	2764.01151(80)	2722.0506(12)	2760.1772(18)
C (MHz)	2075.86147(69)	2058.4479(12)	2071.7712(22)
Δ_J (kHz)	5.4148(14)	6.1506(33)	6.2098(40)
Δ_{JK} (kHz)	−22.1582(67)	−29.223(10)	−26.599(21)
Δ_K (kHz)	40.785(20)	57.825(30)	52.21(21)
δ_J (kHz)	1.93091(39)	2.17120(48)	2.2636(15)
δ_K (kHz)	7.7308(74)	8.6638(95)	9.302(64)
Φ_J (Hz)	−0.07086(77)	−0.0525(23)	−0.07086[d]
Φ_{JK} (Hz)	0.3769(54)	0.5009(74)	0.589(41)
Φ_{KJ} (Hz)	−1.423(26)	−2.500(45)	−3.618(71)
Φ_K (Hz)	2.447(35)	3.54(12)	22.2(14)
ϕ_J (Hz)	−0.02511(27)	−0.03231(30)	−0.02511[d]
ϕ_{JK} (Hz)	−0.2146(66)	−0.2483(81)	−0.60(11)
ϕ_K (Hz)	0.0[d]	0.0[d]	0.0[d]
$\Lambda_J{}^e$ (Hz)	0.000064(11)	0.000203(25)	0.0[d]
rms[f]	1.356	1.509	1.475
rms[g] (MHz)	0.16	0.18	0.16
N[h]	646	624	324

[a]A-reduction *I*^{r}-representation.[21] Spectra listed in Tables 8S−10S of the Supporting Information. [b]First excited state of the torsion about the C1−N6 bond. [c]First excited state of the torsion about the C1−C2 bond. [d]Fixed at this value in the least-squares fit. [e]Further octic constants preset at zero in the least-squares fit. [f]Root-mean-square deviation of a weighted fit defined by rms^2 = $\Sigma[(\nu_{obs} - \nu_{calc})/u]^2/(N - P)$, where ν_{obs} and ν_{calc} are the observed and calculated frequencies, u is the uncertainty of the observed frequency, N is the number of transitions used in the least-squares fit, and P is the number spectroscopic constants used in the fit. [g]Calculated putting u = 1. [h]Number of transitions used in the least-squares fit.

were accurately determined. It was also possible to determine six of the seven sextic centrifugal distortion constants. The ϕ_K constant could not be obtained and was preset at zero in the least-squares fit. One octic centrifugal distortion constant, Λ_J, was also determined.

Interestingly, the CCSD(T) rotational constants (Table 2) and their experimental counterparts (Table 3) are in very good agreement (within better than 0.5%). The CCSD(T) rotational constants are derived from an approximate equilibrium structure, whereas the experimental rotational constants are *effective* constants. Differences of the magnitude found in the present case are therefore to be expected. However, the good agreement between the two set of constants is a strong indication that the CCSD(T) structure is very close to the equilibrium structure, which was expected because of the very high level of theory involved in these calculations.

The agreement between the B3LYP/aug-cc-pVTZ (Table 2) and experimental quartic centrifugal distortion constants (Table 3) are not good. Δ_K represents the worst case. This B3LYP constant deviates by 46% from the experimental value. The theoretical δ_J is in best agreement with experiment deviating by about 6% from its experimental counterpart. All experimental constants are smaller than the B3LYP constants, which may

reflect that the molecule is more rigid than indicated in the B3LYP calculations.

There is only an order of magnitude agreement between the experimental and B3LYP/cc-pVTZ sextic centrifugal distortion constants, as seen from Table 3 and Table 6S (Supporting Information).

Vibrationally Excited States. The B3LYP calculations (Table 3S, Supporting Information) predict that conformer **III** has five normal modes below 500 cm^{-1}. The harmonic frequencies of these vibrations are 58, 115, 256, 318, and 494 cm^{-1}, respectively. The ground state spectrum should therefore be accompanied by a rich satellite spectrum belonging to vibrationally excited states. This was also observed, and the spectra of two excited states were assigned in the same manner as described for the ground state. The strongest of these excited-state spectra is due to the first excited state of the torsion about the C1−N6 bond, whereas the second spectrum belongs to the first excited state of the torsion about the C1−C2 bond. 624 transitions (Table 9S of the Supporting Information) were assigned for the torsion about the C1−N6 bond, whereas 324 transitions (Table 10S, Supporting Information) were assigned for the first excited state of the torsion of the CH$_2$F group. The spectroscopic constants obtained from these two spectra are shown in Table 3.

Relative intensity measurements yielded 74(25) cm^{-1} for the C1−N6 torsional vibration compared to the B3LYP value of 58 cm^{-1}. It is possible to compare the experimental and theoretical vibration−rotation constants defined by $\alpha_{ex} = X_0 - X_{ex}$, where X_0 is the rotational constants of the ground state and X_{ex} are the rotational constants of the excited state under consideration. The experimental vibration−rotation constants derived from the entries in Table 3 are $\alpha_A = -83.4465(49)$, $\alpha_B = 41.9609(14)$, and $\alpha_C = 17.4136(14)$ MHz, compared to the B3LYP/cc-pVTZ values of −86.0, +24.5, and +10.0 MHz, respectively (Table 6S, Supporting Information).

The frequency of the C1−C2 torsion is 155(25) cm^{-1} according to relative intensity measurements, whereas B3LYP yielded 115 cm^{-1} (Table 3S, Supporting Information). The experimental vibration−rotation constants are (from Table 3) $\alpha_A = -12.6213(88)$, $\alpha_B = 3.8343(20)$, and $\alpha_C = 4.0903(23)$ MHz, compared to the B3LYP/cc-pVTZ values of −1.29, +4.01, and +4.06 MHz, respectively (Table 6S, Supporting Information). The difference between the observed and calculated values for α_A is comparatively large (about 10.4 MHz) in this case, whereas the corresponding differences for α_B and α_C are less than 0.3 MHz. This demonstrates that B3LYP/cc-pVTZ calculations are not sufficient in the present case.

Searches for Further Conformers. Conformers **I** and **II** have very small dipole moments according to the CCSD(T) calculations and their MW spectra would be very hard to assign under any circumstances. However, we attempted to find their spectra using the RFMWDR method but did not succeed. Conformers **IV** and **V** are both quite polar (Table 2), but searches for them were also negative. It is therefore concluded that both these forms are present in relatively small concentrations.

The assignments described in the two previous paragraphs include the vast majority of the lines of comparatively strong and intermediate intensities. The *absolute* intensities of the spectrum indicate whether *more* than one conformer is present. Rough intensity estimates made in the present case demonstrated that **III** must indeed be the predominant species. Our observations are in accord with the CCSD(T) predictions

that **III** is 4−6 kJ/mol more stable than any further rotamer (Table 2).

■ DISCUSSION

Hyperconjugation, electrostatic interactions, and steric forces seem to be needed to explain the conformational properties of 2-fluoroethyl azide. The azido group and the fluoromethyl group are relatively close to one another in conformers **I** and **III**; see Figure 1. This may result in steric repulsion, which manifests itself in the C2−C1−N6−N7 dihedral angle, which is +81.5° in **I** and −80.4° in **III** (Table 1), about 20° larger than normal.

The C−F bond is very polar with a bond moment of 4.70×10^{-30} C m.[27] The group moment of the C−N$_3$ group is not known but is presumed to be sizable because the dipole moment of hydrazoic acid, HN$_3$, is as large as $5.67(17) \times 10^{-30}$ C m.[28] Electrostatic repulsion should therefore favor the N6−C1−C2−F3 ap forms **I** and **II** over the three remaining rotamers, because the azido group and the fluorine atom have a maximum separation in these two forms. This electrostatic repulsion is countered by the gauche effect operating in the sc forms **III**−**V**. Interestingly, the CCSD(T) calculations indicate that **IV** and **V** have about the same energy as **I** and **II**, whereas **III** is more stable than any other form (Table 2). This added stability of **III** may have an electrostatic origin, because the resonance structures discussed above indicate that N6 and N8 have extra negative charges, whereas N7 has an extra positive charge. This is also found in the CCSD(T) calculations where the N7 atom Mulliken charge of +0.319 (not given in Table 2), whereas N6 and N8 have charges of −0.347 and −0.124, respectively. The Mulliken charge of F3 is −0.311. The CCSD(T) nonbonded distance between the F3 and N7 is as short as 288.6 pm in **III**, and much longer in the other conformers. It is therefore likely that a significant electrostatic attraction exists uniquely in this rotamer, tipping the energy balance in its favor.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Results of the theoretical calculations, including electronic energies, molecular structures and structural parameters, dipole moments, harmonic and anharmonic vibrational frequencies, rotational and centrifugal distortion constants, and rotation-vibration constants. Microwave spectra of the ground and vibrationally excited states. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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