

A Microwave and Quantum Chemical Study of the Conformational Properties and Intramolecular Hydrogen Bonding of 1-Fluorocyclopropanecarboxylic Acid

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The structural and conformational properties of 1-fluorocyclopropanecarboxylic acid have been explored by microwave spectroscopy and a series of ab initio (MP2/6-311++G(d,p) level), density functional theory (B3LYP/aug-cc-pVTZ level), and G3 quantum chemical calculations. Four “stable” conformers, denoted conformers I–IV, were found in the quantum chemical calculations, three of which (conformers I–III) were predicted to be low-energy forms. Conformer I was in all the quantum chemical calculations predicted to have the lowest energy, conformer III to have the second lowest energy, and conformer II to have the third lowest energy. Conformers II and III were calculated to have relatively large dipole moments, while conformer I was predicted to have a small dipole moment. The microwave spectrum was investigated in the 18–62 GHz spectral range. The microwave spectra of conformers II and III were assigned. Conformer I was not assigned presumably because its dipole moment is comparatively small. Conformer II is stabilized by an intramolecular hydrogen bond formed between the fluorine atom and the hydrogen atom of the carboxylic acid group. Conformer III has a *synperiplanar* orientation for the F–C–C=O and H–O–C=O chains of atoms. Its dipole moment is: $\mu_a = 3.4(10)$, $\mu_b = 10.1(13)$, and $\mu_c = 0.0$ (assumed) and $\mu_{\text{tot}} = 10.6(14) \times 10^{-30}$ C m [3.2(4) D]. Several vibrationally excited states of the lowest torsional mode of each of II and III were also assigned. The hydrogen-bonded conformer II was found to be 2.7(2) kJ/mol *less* stable than III by relative intensity measurements. Absolute intensity measurements were used to show that the unassigned conformer I is the most abundant form present at a concentration of roughly 65% at room temperature. Conformer I was estimated to be ca. 5.0 kJ/mol more stable than the hydrogen-bonded rotamer (conformer II) and ca. 2.3 kJ/mol more stable than conformer III. The best agreement with the theoretical calculations is found in the MP2 calculations, which predict conformer I to be 5.1 kJ/mol more stable than III and 1.7 kJ/mol more stable than II.

Introduction

The carboxyl group normally prefers a *synperiplanar* (sp) arrangement for the O=C–O–H chain of atoms (dihedral angle = 0°). This conformation is for example found to be 16.3(4) kJ/mol more stable than the *antiperiplanar* (ap) (dihedral angle = 180°) in formic acid (HCOOH).¹ If an electronegative group or atom is placed on a carbon atom adjacent to the carboxyl group, intramolecular hydrogen (H) bonding may change the conformational preference within this group. Examples are glyoxylic acid (O=C(H)COOH)^{2–4} and pyruvic acid (CH₃COCO(H)COOH),^{5–7} in which the COOH groups prefer an ap conformation. An internal H bond between the hydrogen atom of the acid group and the carbonyl group of the adjacent carbon atom stabilizes this unusual conformation of the acid group.

A fluorine atom on an adjacent carbon atom may act in a manner similar to that of a carbonyl group. This has been seen in gaseous fluoroacetic acid (CH₂FCOOH).^{8,9} Two rotamers were assigned by microwave (MW) spectroscopy for this compound. The high-energy form is stabilized by a

F...H–O–C=O hydrogen bond. This rotamer is 2.47(12) kJ/mol *less* stable than the form which has a “normal” sp conformation of the carboxyl group. The situation in the closely related 1-fluoropropionic acid (CH₃CHF₂COOH) is reversed. The H-bonded form is preferred by 0.5(2) kJ/mol in this case,¹⁰ indicating that the electronic environment of the fluorine atom is of considerable importance for this type of H bonds. The fact that no H-bonded rotamer has been found either in CHF₂-COOH¹¹ or in CF₃COOH¹² is additional evidence that the H-bonding acceptor ability of the fluorine atom is influenced significantly by its neighbors.

1-Fluorocyclopropanecarboxylic acid (FCCA) differs from the other examples by having the fluorine atom attached to the cyclopropyl moiety. The strained cyclopropyl ring has pseudo π electrons along the edges of the ring according to Walsh.¹³ The bonding situation in FCCA is thus quite different from those found in the four other fluorine-containing acids referred to previously.^{8–12} The influence the cyclopropyl group might have on the internal H bonding and conformational properties of this compound was the major reason it was chosen for this study.

The conformational behavior of FCCA is complicated because rotation around the two single bonds FH₄C₃–COOH and OC–OH bonds may give rise to rotational isomerism. Models of four rotameric forms denoted conformers I–IV, respectively,

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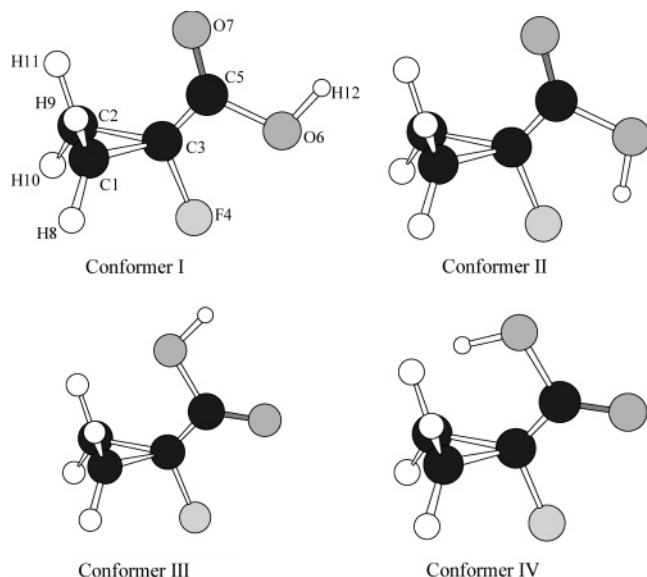


Figure 1. The four stable rotamers of 1-fluorocyclopropanecarboxylic acid. Atom numbering is indicated on conformer I. Conformers I–III are low-energy forms of the molecule, whereas conformer IV is a high-energy conformer. Conformer II is stabilized with an internal hydrogen bond. Conformer I is the most stable form, but this rotamer was not assigned by MW spectroscopy, presumably because it has a comparatively small dipole moment. Conformers II and III are much more polar and were assigned. Intensity measurements have been used to show that the unassigned conformer I is ca. 5.0 kJ/mol more stable than II and ca. 2.3 kJ/mol more stable than III.

are drawn in Figure 1, where the atom numbering is also given. Each of these four rotamers has a symmetry plane (C_s symmetry). The carboxyl group has the usual sp conformation in conformers I and III. These two forms are interchangeable by a 180° rotation around the C3–C5 bond. Conformers II and IV can also be interchanged by a 180° rotation around the same bond, but the acid group has an ap conformation in these two cases.

There is already some information about cyclopropyl compounds related to FCCA. Cyclopropanecarboxylic acid is one such molecule, which has been studied by MW spectroscopy, electron diffraction, and quantum chemical calculations.¹⁴ One rotamer similar to conformer I was found to be preferred in this acid. This form was assigned by MW spectroscopy.¹⁴ The electron-diffraction pattern indicated that an additional second form similar to III is also present in the gas phase with an energy that is 3–5 kJ/mol higher than that of the conformer identified by MW spectroscopy. The MW spectrum of the second form was not assigned, presumably because it is a high-energy form present in low concentration in the gas phase.

This work represents a continuation of our investigations of intramolecular H bonding. Recent studies of this laboratory are found in refs 4 and 15–27. Reviews are also available.^{28,29} MW spectroscopy and high-level quantum chemical calculations are the methods chosen for this study. The former spectroscopic method is characterized by its unique specificity, whereas modern high-level quantum chemical calculations are useful in guiding and supplementing the experiments.

Experimental Section

Synthesis. FCCA was prepared by bromoform reaction of the known 1-(1-fluorocyclopropyl)ethanone³⁰ as mentioned in footnote 21 of ref 15. It was purified by short-path distillation, bp 120–125 °C/100 Torr, mp 63–67 °C. ^1H NMR (250 MHz, CDCl_3): δ = 1.42–1.49 (m, 4 H), 11.40 (bs, 1 H, COOH).

^{13}C NMR (62.9 MHz, CDCl_3 , DEPT): δ = 15.25 (d, $^2J_{\text{CF}}$ = 10.5 Hz), 74.00 (C_{quat} , d, $^1J_{\text{CF}}$ = 226.4 Hz), 177.5 (C_{quat} , d, $^2J_{\text{CF}}$ = 24.5 Hz, COOH).

Spectrometer. The 50-kHz Stark-modulated spectrometer used in this work operates in the 7–62 GHz spectral range. The home-built Stark generator is based on thyristor technology. The MW signals are processed using a Perkin-Elmer 5209 lock-in amplifier. The home-built brass cells are 2 or 3 m long. The microwave source is a Systron Donner 1730B microwave synthesizer, which covers the 2–26.5 GHz spectral region. The 26.5–40 GHz frequency range is covered using this synthesizer together with the Accurel 220 millimeter frequency extender. Microwave radiation in the 40–62 GHz frequency region is provided using the same synthesizer together with a Millitech FEX-19-07FBI frequency quadrupler. Hewlett-Packard MW detectors are used in the 7–40 GHz range. A Millitech DXP-19-RPFW0 detector is employed in the 40–62 GHz range. The spectrometer is run under PC control. The LabView programming tool has been used to write the necessary programs. The programming was carried out by Grønås.³¹ The spectra are finally processed using the Grams A17 or LabView programs.

Radio frequency microwave double resonance (RFMWDR) experiments were carried out as described in ref 32. The radio frequency source is a Rohde & Schwarz SML01 signal generator operating in the 9 kHz–1.1 GHz spectral region. This frequency source is controlled by another LabView program by Grønås.³¹ An EIN Model 503L amplifier provides 3 W linear amplification of the radio signals between 2 and 510 MHz. Mixing of the radio signal with the Stark modulation signal is provided using a Hewlett-Packard 10514 mixer.

The spectrum of FCCA was investigated in the 18–62 GHz spectral region. The vapor pressure of this compound is only a few Pascal at room temperature. It was therefore not possible to study the spectrum at lower temperatures, which would have increased the intensity of the spectrum. The accuracy of the spectral measurements is better than ± 0.12 MHz, and the resolution is about 0.5 MHz.

Results

Quantum Chemical Calculations. A series of quantum chemical calculations were carried out using the Gaussian 03 program package³³ running on the HP superdome in Oslo. It is known that Møller–Plesset second-order perturbation calculations (MP2)³⁴ employing a large basis set yield structures that are close to the equilibrium structure.³⁵ Rotational constants obtained from such structures are therefore expected to be close to the effective rotational constants obtained from MW spectroscopy and should therefore be a good starting point for assigning the MW spectrum.

MP2 calculations were first carried out for the four conformers of FCCA shown in Figure 1 employing the 6-311++G(d,p) basis set. This basis set is of triple- ζ quality augmented with diffuse functions. The starting geometries, which did not possess a symmetry plane, were fully optimized with no geometrical restrictions imposed. The refined geometry of each of the conformers I–IV was found to have a symmetry plane (C_s symmetry) and to represent a minimum on the potential-energy hypersurface, since all vibrational frequencies were calculated to be positive in each case.³⁶

The energies of the four conformers were corrected for zero-point vibrational energies and compared. Conformer I was found to have the lowest energy of the four forms. The energies relative to conformer I were +5.1, +1.7, and +34.7 kJ/mol for

TABLE 1: MP2/6-311++G(d,p) Structures (Bond Distances in pm, Angles in Degree) of Three Conformers of 1-Fluorocyclopropanecarboxylic Acid

conformer	I	II	III
	Distance		
C1–C2	151.3	151.6	151.5
C1–C3	150.2	149.7	150.3
C3–F4	136.8	138.7	136.6
C3–C5	149.0	149.9	150.0
C5–O6	134.5	134.8	136.0
C5–O7	121.3	120.6	120.7
C1–H8	108.4	108.4	108.4
C1–H9	108.3	108.3	108.3
O6–H12	96.9	96.7	96.8
	Angles		
C2–C1–H8	117.1	117.1	117.1
C2–C1–H9	118.1	118.2	118.3
C3–C1–H8	114.8	115.3	114.5
C3–C1–H9	117.0	116.7	117.8
C1–C3–F4	116.7	116.6	116.2
C1–C3–C5	118.2	119.8	121.3
F4–C3–C5	115.4	113.5	112.2
C3–C5–O6	112.8	115.5	110.5
C3–C5–O7	122.6	121.7	125.4
C5–O6–H12	105.5	108.5	105.8
	Dihedral Angles		
H8–C1–C3–F4	1.2	0.7	1.5
H9–C1–C3–F4	144.6	144.3	145.0
C1–C3–C5–O6	145.2	144.3	–36.1
C1–C3–C5–O7	–34.8	–35.7	143.8
F4–C3–C5–O6	0.0	0.0	180.0
F4–C3–C5–O7	180.0	180.0	0.0
O7–C5–O6–H12	0.0	180.0	0.0

conformers II–IV, respectively. Interestingly, conformer I is similar to the most stable form of cyclopropanecarboxylic acid.¹⁴

The fact that the energy of conformer IV is considerably higher than the energy of the remaining three forms makes it highly unlikely that this rotamer can be identified by MW spectroscopy since its population must be negligible at room temperature. This rotamer was therefore not considered further. The structures of conformer I–III are listed in Table 1. The rotational constants calculated from these structures are displayed in Table 2, where the relative energies obtained in the MP2 calculations are displayed. The MP2 dipole moments are listed in Table 9S in the Supporting Information.

Energy differences calculated by the G3 method³⁷ tend to be more accurate than the ones calculated by the MP2 procedure. G3 calculations were therefore carried out next. These calculations were again found to predict conformer I to be the most stable form, being 2.6 kJ/mol more stable than conformer II and 2.8 kJ/mol more stable than III. These results are listed in Table 2.

It is our experience that density functional theory (DFT) calculations normally yield dipole moments and vibrational frequencies that are more accurate than those obtained using the MP2 procedure provided that the same basis set has been employed. B3LYP calculations³⁸ were performed using Dunning's triple- ζ correlation consistent basis set³⁹ with diffuse functions and polarized valence electrons (aug-cc-pVTZ). The resulting dipole moment and quartic centrifugal distortion constants in the *A* representation⁴⁰ are listed in Table 2. The B3LYP/aug-cc-pVTZ structure and rotational constants are displayed in Table 8S in the Supporting Information. B3LYP energy differences were also calculated. Conformer I was predicted to be 2.1 kJ/mol more stable than II and 3.7 kJ/mol more stable than III (Table 2). These results resemble the G3 calculations more closely than the MP2 calculations.

TABLE 2: MP2/6-311++G(d,p) Rotational Constants (MHz), B3LYP/aug-cc-pVTZ Quartic Centrifugal Distortion Constants (kHz) and Principal-Axes Dipole Moments (10^{-30} C m) and Relative Energies (kJ/mol)

conformer	I	II	III
	Rotational Constants (MP2)		
A	4108.9	4058.1	4056.3
B	2621.7	2640.8	2644.3
C	1834.4	1834.3	1835.3
	Quartic Centrifugal Distortion Constants (B3LYP) ^a		
Δ_J	0.268	0.278	0.284
Δ_{JK}	0.213	0.143	0.0452
Δ_K	0.202	0.246	0.362
δ_J	0.0872	0.0914	0.0949
δ_K	–0.142	–0.072 9	–0.133
	Dipole Moments (B3LYP) ^b		
μ_a	2.00	9.44	3.66
μ_b	0.83	5.51	10.82
μ_c	0.0 ^c	0.0 ^c	0.0 ^c
	Energy Difference ^d		
MP2	0.0	5.1	1.7
B3LYP	0.0	2.1	3.7
G3	0.0	2.6	2.8
experiment	0.0	ca. 5.0 ^e	ca. 2.3 ^e

^a *A*, reduction; *F*, representation.⁴⁰ ^b 1 D = 3.3356×10^{-30} C m. ^c For symmetry reasons. ^d Relative to conformer I. ^e See text.

Conformer I is transformed into II essentially by rotation around the C5–O6 bond. The transition state (TS) for this transformation (one negative vibrational frequency³⁶) was completely optimized using the MP2 procedure. The full structure of this TS is not given here except for two parameters of special interest, viz., the F4–C3–C5–O7 and C3–C5–O6–H12 dihedral angles, which were found to be –172.1 and 93.7°, respectively. The energy of the TS was calculated to be 45.5 kJ/mol higher than the energy of conformer I.

The TS for the transformation of conformer I into III is likewise characterized by having the F4–C3–C5–O7 and C3–C5–O6–H12 dihedral angles equal to –81.3 and –177.7°, respectively. The energy of this TS is 24.6 kJ/mol higher than the energy of conformer I. This is about one-half of the value of the other TS, which seems likely.

Microwave Spectrum and Assignment of Conformer III.

The quantum chemical calculations above indicate that the major constituents of FCCA in the gas phase are the three rotamers I–III. The rotational constants are accidentally about $A = 4.1$, $B = 2.6$, and $C = 1.8$ GHz for each of them (Table 2). They all have eight normal vibrational modes below 700 cm^{-1} according to the B3LYP calculations (not listed in Tables 1 or 2). Relatively large partition functions are therefore predicted at room temperature. Each quantum state will consequently have a low population resulting in comparatively weak spectra.

a- and b-type spectra are predicted for all three forms. No c-type spectra were expected since the μ_c is zero by symmetry. The a-type spectra will consist exclusively of R-branch transitions and are consequently not particularly rich. A different situation exists for b-type spectra. Numerous relatively strong *Q*-transitions would occur in this case resulting in a very crowded spectrum.

The observed MW spectrum was found to be very dense with absorption lines occurring every few MHz. The lines were all remarkably weak. The peak absorption coefficients of the strongest transitions were roughly $5 \times 10^{-7} \text{ cm}^{-1}$. The crowded nature of the spectrum revealed that most of the lines had to be b-type transitions. None of the transitions displayed a resolved Stark effect. Most lines were modulated at low Stark voltages.

TABLE 3: Rotational Constants (MHz),^a Quartic (kHz),^a and Sextic (Hz)^a Centrifugal Distortion Constants and Δ^b (10^{-20} m² u) of Conformer III of 1-Fluorocyclopropanecarboxylic Acid

vib. state	ground	1st ex. C3–C5 tors.	2nd ex. C3–C5 tors.
A	4069.8264(21)	4067.7207(24)	4065.7389(36)
B	2643.1538(21)	2636.2853(23)	2629.3680(35)
C	1838.5651(21)	1841.1897(23)	1843.7977(35)
Δ_J	0.2932(64)	0.3012(75)	0.283(11)
Δ_{JK}	0.0111(12)	0.0107(30)	0.0034(36)
Δ_K	0.3804(20)	0.3836(29)	0.3893(34)
δ_J	0.09643(16)	0.09616(35)	0.09554(46)
δ_K	-0.0946(13)	-0.1007(33)	-0.0880(39)
Φ_{JK}	0.00061(12)	<i>g</i>	<i>g</i>
ϕ_J^c	0.000198(14)	<i>g</i>	<i>g</i>
Δ^b	-40.50321(11)	-41.45747(13)	-42.41061(18)
max J^d	80	50	45
no. trans. ^e	605	370	306
rms ^f	0.128	0.114	0.129

^aA, reduction; *F*, representation.⁴⁰ Uncertainties represent one standard deviation. ^b $\Delta = I_c - I_a - I_b$ (I_a , I_b , and I_c are the principal-axis moments of inertia). Conversion factor $505379.05 \times 10^{-20}$ m² u MHz. ^cFurther sextic constants preset at zero. ^dMaximum value of the *J* quantum number. ^eNumber of transitions in fit. ^fRoot-mean-square deviation (MHz). ^gPreset at zero.

This behavior is typical for a conformer having a large μ_b . Inspection of Table 2 reveals that this is the case for conformer III. It was therefore decided to attempt to assign the spectrum focusing on this rotamer.

Model calculations using the rotational constants in Table 2 indicate that numerous comparatively strong ^bQ-branch transitions appear throughout the investigated spectral range. These lines were first searched for using a trial-and-error procedure. The first successful assignments were made after many combinations of lines had been tested. The assignments were then gradually extended to include further ^bQ-branch lines up to $J = 80$. Further Q-branch lines involving even higher values of *J* were searched for but not found, presumably because they are too weak owing to unfavorable Boltzmann factors.

The b-type R-branch transitions were now searched for and soon found. Finally, the much weaker a-type R-branch lines were identified using ordinary Stark as well as RFWDR spectroscopy. A total of about 650 transitions were ultimately assigned for the ground vibrational state of conformer III. The full spectrum is listed in the Supporting Information Table 1S. The fitting procedure was carried out using the program ROTFIT by Sørensen.⁴¹ The spectroscopic constants (*A* reduction *F* representation⁴⁰) calculated from 605 transitions are gathered in Table 3. Two of the sextic centrifugal distortion constants (Φ_{JK} and ϕ_J) had to be employed in order to get at fit with a root-mean-square deviation similar to the experimental uncertainty of ± 0.12 MHz.

Comparison of the experimental and theoretical spectroscopic constants is of interest. There is very good agreement between the experimental rotational constants (Table 3) and the MP2 rotational constants (Table 2). The differences are only +0.3, -0.05, and +0.18% in the cases of *A*, *B*, and *C*, respectively. The differences are considerably larger for the quartic centrifugal distortion constants, viz., +4.5, -311, +4.7, +0.9, and +29% for Δ_J , Δ_{JK} , Δ_K , δ_J and δ_K , respectively.

The value of $\Delta = I_c - I_a - I_b = -40.50327(14) \times 10^{-20}$ u m² (Table 3) is typical for cyclopropyl derivatives possessing a symmetry plane formed by the bisector of the cyclopropyl ring and the carboxyl group.⁴² The corresponding value in cyclopropanecarboxylic acid for the conformer corresponding to *I* is, e.g., -39.595758(48).¹⁴

TABLE 4: Second-Order Stark Coefficient^a and Dipole Moment^{a,b} of Conformer III of 1-Fluorocyclopropanecarboxylic Acid

transition		$\Delta\nu$ E ⁻² /10 ⁻⁶ MHz V ⁻² cm ²	
		obsd	calcd
29 _{13,14} ← 29 _{12,17}	[M] = 29	15.9(20)	12.1
31 _{14,17} ← 31 _{13,18}	[M] = 31	6.5(15)	7.9
36 _{15,21} ← 36 _{14,22}	[M] = 36	12.4(20)	16.0
37 _{15,22} ← 37 _{14,23}	[M] = 37	9.5(15)	6.9

^aUncertainties represent one standard deviation. ^b $\mu_a = 3.4(10)$, $\mu_b = 10.1(13)$, and $\mu_c = 0.0$ (assumed) and $\mu_{\text{tot}} = 10.6(14) \times 10^{-30}$ C m [3.2(4) D]; 1 D = 3.33564×10^{-30} C m.

Vibrationally Excited States of Conformer III. Several transitions accompanying the ground-state lines were seen to have lower intensities than the ground-state lines and almost identical Stark effects. These lines were assigned to vibrationally excited states of conformer III. It is seen from the data in Table 3 that two excited states have been assigned. The spectra, which consist exclusively of b-type lines, are found in the Supporting Information, Tables 2S and 3S. These excited states are assumed to be successively excited states of the C3–C5 torsional vibration, which is predicted to have a wavenumber of 70 cm⁻¹ according to the B3LYP calculations. Relative intensity measurements for the first excited state of this mode were made following the procedure described in ref 43, which yielded 68-(20) cm⁻¹ in good agreement with the theoretical predictions.

It is seen in Table 3 that the rotational constants vary almost linearly through the first and second excited state. This near-linear behavior is typical for an almost harmonic vibration.⁴⁴ Furthermore, it is seen that the numerical values of $\Delta = I_c - I_a - I_b$ increase upon excitation of this torsional mode. This was also found in cyclopropanecarboxylic acid¹⁴ and is typical for an out-of-symmetry plane vibration.⁴⁴

The wavenumbers of the next three vibrational modes are 233, 257, and 349 cm⁻¹, respectively, according to the B3LYP calculations (not given in Table 2). Excited states belonging to these vibrational modes could not be assigned, presumably because of the weakness of the MW spectrum.

Dipole Moment of Conformer III. As was pointed out above, the rotational constants of the three low-energy forms (conformers I–III) are accidentally very similar. The rotational constants alone, therefore, cannot be used to differentiate between them. However, the dipole moment components can be used for this purpose, since they are very different, as seen in Table 2. Conformer III is the only rotamer that is predicted to have a large μ_b and a small μ_a , which is consistent with the observations made in the two previous paragraphs.

Accurate values of the dipole moment have traditionally been obtained from resolved Stark effects. This method cannot be used here because no lines could be resolved into their individual *M* components in an electric field. It has recently been pointed out that a less accurate determination of the dipole moment can be obtained even from unresolved Stark effects.⁴⁵ A variant of this method was used here to determine the dipole moment of conformer III. The intensities of the Stark components are proportional to M^2 .⁴⁶ The most intense component therefore has $M = J$. Rough values of the second order $M = J$ Stark coefficients of four of the strongest Q-branch lines involving *J* between 29 and 37 were used to determine the dipole moment as shown in Table 4. The cell was calibrated using OCS whose dipole moment was taken to be 2.38568(67) $\times 10^{-30}$ C m.⁴⁷

The dipole moment components in Table 4 [$\mu_a = (3.4(10)$ and $\mu_b = 10.1(13) \times 10^{-30}$ C m)] are in satisfactory agreement with the B3LYP values in Table 2 (3.66 and 10.82×10^{-30} C

TABLE 5: Rotational Constants (MHz),^a Centrifugal Distortion Constants (kHz),^a and Inertial Defect^b (10⁻²⁰ m² u) of Conformer II of 1-Fluorocyclopropanecarboxylic Acid

vib. state	ground	1st ex. C3–C5 tors.	2nd ex. C3–C5 tors.	3rd ex. C3–C5 tors.
A	4074.5544(19)	4071.2946(35)	4068.1788(84)	4061.6(14)
B	2642.3510(16)	2636.6942(26)	2631.0266(55)	2624.87(17)
C	1839.1157(16)	1841.8601(26)	1844.5925(36)	1847.82(18)
Δ_J	0.3012(52)	0.2914(89)	0.314(11)	0.307(41)
Δ_{JK}	0.0273(47)	0.0167(84)	0.0273 ^f	0.0273 ^f
Δ_K	0.3482(48)	0.3470(72)	0.340(14)	0.3482 ^f
δ_J	0.09727(54)	0.0971(10)	0.1045(43)	0.09727 ^f
δ_K	-0.0973(50)	-0.0939(87)	-0.0973 ^f	-0.0973 ^f
Δ^b	-40.49950(12)	-41.41859(22)	-42.33300(73)	-43.463(83)
max J^c	50	49	28	13
no. trans. ^d	283	146	78	20
rms ^e	0.110	0.118	0.113	0.125

^a A, reduction; F , representation.⁴⁰ Uncertainties represent one standard deviation. ^b $\Delta = I_c - I_a - I_b$. Conversion factor = 505379.05 $\times 10^{-20}$ m² u MHz. ^c Maximum value of the J quantum number. ^d Number of transitions in fit. ^e Root-mean-square deviation (MHz). ^f Fixed.

m, respectively). It is concluded that the spectra in Tables 1S–3S undoubtedly belong to conformer III.

Assignment of the Ground Vibrational State of Conformer II. The assignments reported previously for conformer III include the majority of the strongest lines of the spectrum. The quantum chemical calculations above indicate that conformer I is somewhat more stable than II. Conformer II was nevertheless guessed to have a significantly more intense MW spectrum than conformer I because the intensities of MW transitions are proportional to the square of the dipole moment components. In the case of the a -axis dipole moment component this ratio is, e.g., expected to be about $(9.44/2.00)^2 = 22$ using the predictions in Table 2.

The fact that conformer II is predicted to have a rather large μ_a and a smaller μ_b (Table 2) indicates that the ^aR-branch transitions are the strongest ones in its MW spectrum. The RFMWDR technique is quite effective in making assignments of this type of spectra and was therefore employed.

The first assignments were indeed made using this technique. They were gradually extended to include further ^aR-lines using ordinary Stark spectroscopy. Many b-type lines were ultimately identified. The majority of these transitions were relatively high- J high- K_{-1} Q-branch lines. Comparison of the intensities of the ^aR- and ^bQ-lines leaves no doubt that $\mu_a > \mu_b$ in this case. Unfortunately, no quantitative Stark effect studies could be made for this rotamer owing to insufficient intensities. However, the modulation patterns of the ^aR-lines show that μ_a is comparatively large. This is consistent with the predictions for conformer II. Confusion with conformer I, which is predicted to have small μ_a and an even smaller μ_b (Table 2), is definitely ruled out.

A total of about 300 transitions were ultimately assigned for the ground vibrational state, 283 of which were used to determine the spectroscopic constants appearing in Table 5. The maximum value of the J quantum number was 50. The spectrum could be fitted satisfactorily using only quartic centrifugal distortion constants. The full spectrum is shown in Table 4S in the Supporting Information.

The rotational constants in Table 5 are very similar to the MP2 constants in Table 2. The differences are +0.4, +0.06, and +0.26% in the cases of A, B, and C, respectively. The differences seen for the quartic centrifugal distortion constants are +8.3, -432, +29, +6.1, and +24% for Δ_J , Δ_{JK} , Δ_K , δ_J , and δ_K , respectively. $\Delta = -40.50327(14) \times 10^{-20}$ u m², which is almost the same as that of conformer III (Table 3) as expected.

Vibrationally Excited States of Conformer II. It is seen in Table 5 that three vibrationally excited states of this rotamer have been assigned. The first assignments of these states were

made using the RFMWDR technique. The corresponding spectra are displayed in the Supporting Information, Tables 5S–7S. These states are assigned to successively excited states of the torsion around the C3–C5 bond for similar reasons as those described for the corresponding excited states of conformer III. Relative intensity measurements⁴³ made for the first excited state yielded 71(20) cm⁻¹, compared to the B3LYP value of 76 cm⁻¹.

Searches for Conformer I. Conformers II and III both have remarkably weak spectra although each of them has a relatively large dipole moment. This is one indication that one or more unassigned rotamers coexist with I and II. Dimers held together with *intermolecular* H bonds could also contribute to the composition of the gas phase, but such species are considered to contribute little owing to the low pressure (a few Pa). All the theoretical calculations above indicate that conformer I is the most stable form of the molecule. Conformer IV contributes practically nothing to the gaseous composition. The weakness of the spectra of II and III could hence be explained if conformer I is indeed the major component in the gas phase.

The a - and b -axis dipole moment components of conformer I are predicted to be comparatively small with μ_a larger than μ_b (Table 2). A RFMWDR search for the ^aR-branch lines of this form was therefore made, but no assignments could be made. It is concluded that the gas phase may well contain a large fraction of conformer I, but its low dipole moment made it impossible to assign its MW spectrum. A semiquantitative estimate of the concentration of conformer I at room temperature is given below.

Internal Energy Difference Between Conformers II and III. The internal energy difference between two conformers have been derived using a variant of eq 3 of Esbitt and Wilson.⁴³ According to Wilson,⁴⁸ the internal energy difference is given by

$$E''_{v''} - E'_{v'} = E'_{J'} - E''_{J''} + RT \ln L \quad (1)$$

where $E''_{v''}$ and $E'_{v'}$ are the internal energies of the two conformers in the v'' and v' vibrational states, respectively, $E'_{J'}$ and $E''_{J''}$ are the lowest energy levels of the two rotational transitions under investigations, R is the universal gas constant, and T is the absolute temperature. L is given by

$$L = \frac{S'}{S} \frac{g}{g'} \left(\frac{\nu\mu}{\nu'\mu'} \right)^2 \frac{l}{l'} \frac{\Delta\nu}{\Delta\nu'} \frac{\lambda}{\lambda'} \frac{(2J' + 1)}{(2J + 1)} \quad (2)$$

where S is the peak signal amplitude of the radiation unsaturated line, g is the degeneracy other than the rotational degeneracy, which is $2J + 1$, ν is the frequency of the transition, μ is the

principal-axis dipole moment component, l is the radiation wavelength in the Stark cell,⁴⁹ $\Delta\nu$ is the line breadth at half-height, λ is the line strength, and J is the principal rotational quantum number.

The internal energy difference between the ground vibrational states of conformers II and III were determined by comparing the intensities of four selected ground-state ^aR-branch transitions of conformer II with the intensities of four ^bQ-branch lines of III. The lines employed in this comparison procedure were relatively strong and not detectably overlapped by other lines. The differences in frequencies in the pairs of transitions that were compared were less than 50 MHz. The intensity comparison was performed as described by Esbitt and Wilson.⁴³ The statistical weight (g) of each of the two rotamers was taken to be the same. The radiation wavelengths (l) were assumed to be identical. The line breadths ($\Delta\nu$) were assumed to be proportional to the principal-axis dipole moment component. The ratio of the dipole moment components of the two forms was calculated using the B3LYP predictions in Table 2.

The internal energy difference, $E_{\text{III}} - E_{\text{II}}$, obtained this way varied between -2.4 and -2.9 kJ/mol (conformer III more stable than II). The average value was found to be $E_{\text{III}} - E_{\text{II}} = -2.7$ kJ/mol. There are several sources of errors in this procedure. One standard deviation has conservatively been estimated to be ± 0.2 kJ/mol by taking plausible uncertainties of the many parameters of eq 2 into account.

The fact that conformer III is 2.7(2) kJ/mol more stable than II should be compared with the theoretical results. The MP2 prediction of this energy difference (Table 2) is best (3.4 kJ/mol), followed by G3 (-0.2 kJ/mol), and finally by B3LYP (-1.6 kJ/mol).

Conformational Composition. The absolute intensity of a peak absorption coefficient, α , of an absorption line of a conformer contains information about the mole fraction of that rotamer. This has been used to get a rough idea about the conformational composition of FCCA in the gas phase at room temperature.

Gordy and Cook⁵⁰ give the following expression for α (in cm^{-1})

$$\alpha = 3.85 \times 10^{-14} F_v(ABC)^{1/2} \mu^2 \lambda \nu^2 (\Delta\nu^{-1}) T^{-5/2} g \exp(-E_{J,\tau}/kT) \quad (3)$$

μ , λ , ν , $\Delta\nu$, g , and T have same definitions as above (eq 2). A , B , and C are the rotational constants, and F_v is the fraction of molecules in a given vibrational state, k is Boltzmann's constant, and $E_{J,\tau}$ is the energy of the lowest energy level involved in the MW transition. The units used to derive the constant 3.85×10^{-14} are given in ref 50.

In eq 3, it is assumed that there is only one species present in the gas phase. The peak intensity of one conformer in a conformational mixture is denoted α' . We have assumed that α' is proportional to its mole fraction (x) multiplied by α ($\alpha' = \alpha \times x$).

With this in mind, an estimate of the conformational composition of FCCA at room temperature was given as follows: The values of α' of selected ground-state lines of conformer III were determined by comparison with peak intensities of OCS using the values compiled by Kisiel and Millen.⁵¹ Two OCS lines in close proximity with two transitions belonging to conformer III were compared.

The values of α were calculated next for the same lines using eq 3. F_v was assumed to be the inverse of the vibrational partition function of the ground vibrational state. The value of

the partition function of the ground vibrational state at 298 K given in the B3LYP calculations (0.065) was used. The line breadths ($\Delta\nu$) were estimated by comparison with the known value of OCS (6.25 MHz/133 Pa).⁵¹ The rotational constants in Table 3 and μ_b (Table 4) were used. The line strengths were calculated from the rotational constants. The mole fraction of conformer III at room temperature was estimated to be roughly 0.25 in this manner.

The mole fraction of conformer II was calculated next using the energy difference of 2.7 kJ/mol and assuming a Boltzmann distribution. This fraction was hence found to be roughly 0.10. Conformers II and III together therefore make up roughly 35% of the gas at room temperature, while conformer I make up ca. 65%; if it is assumed that dimers contribute only marginally to the composition of the gas phase. A mixture of roughly 25% of conformer III and 65% of conformer I and assuming a Boltzmann distribution yields an energy difference of ca. 2.3 kJ/mol with conformer I as the more stable. The energy difference between II and I is then ca. 5.0 kJ/mol. These results are summarized in Table 2. It is seen in this table that the estimate of the energy differences between the three rotamers is in best agreement with the MP2 predictions.

Structures. The fact that the experimental (Tables 3 and 5) and theoretical rotational constants (Table 2) are very similar is thought not to be fortuitous but reflects that the MP2 structures of conformers II and III in Table 2 are indeed close to the equilibrium structures as expected.³⁵

The values of Δ in Tables 3 and 5 can be used to calculate the C1–C2 bond lengths in conformers II and III following a procedure reported by Penn and Boggs⁴² using their eq 3. The C1–C2 bond lengths are calculated to be 151.0 pm both in conformers II and in III employing this equation. This compares well with the corresponding MP2 values of 151.6 and 151.5 pm, respectively (Table 2).

Comparison of the approximate r_e structures of the three forms of the title compound (Table 2) with the r_g structure of cyclopropanecarboxylic acid¹⁴ shows that the highly electronegative fluorine atom has a significant influence. The largest deviations are found for the bond lengths of the cyclopropyl ring and for the carbon–carbon bond adjacent to the ring (C3–C5 in the present case). If one compares the *average* values of the said bond lengths of the three rotameric forms of FCCA calculated from the entries in Table 1, it is seen that the average C1–C2 bond length (151.1 pm) and the average C3–C5 bond length (149.6) are both about 2 pm longer than their counterparts in cyclopropanecarboxylic acid ((149.3(6) and 147.8(5) pm, respectively). The average C1–C3 bond length (150.1 pm) is approximately 2 pm shorter than the corresponding bond length in cyclopropanecarboxylic acid (152.4(3) pm).¹⁴ The other corresponding bond lengths in these two compounds are almost the same. The influence of the fluorine atom is hence limited to the ring and to bonds adjacent to the ring.

Discussion

The conformational preferences of FCCA are certainly a complicated compromise of several effects. A striking feature is the prediction that all four stable conformers have a symmetry plane (C_s symmetry). An sp arrangement for the F4–C3–C5–O6 sequence of atoms is found in rotamers I and II. The F4–C3–C5=O7 link is sp in III and IV. This brings the highly electronegative oxygen and fluorine atoms into the shortest possible proximity in each of the four conformers, but it will not result in steric repulsion because the distance between the F4 (Figure 1) and the nearest oxygen atom (O6 or O7) is nearly

the same as the sum of the van der Waals radii of oxygen and fluorine (275 pm) in each of the four rotamers.⁵²

There must be a significant dipole–dipole repulsion between the C3–F4 and C5–O6 bonds in conformers I and II and between the C3–F4 and C5=O7 bonds in III and IV, because the relevant bond moments are comparatively large.⁵³ This repulsion must be counterbalanced by electronic and other effects because the C_s symmetry is retained.

The intramolecular H bond in conformer II formed between the fluorine atom (F4) and the hydrogen atom (H12) is calculated from the structure in Table 2 to have the following characteristics: The nonbonded F4···H12 distance of 202.6 pm is significantly shorter than 260 pm, which is the sum of the van der Waals radii of hydrogen and fluorine.⁵² This indicates that covalent forces are of importance in this H bond. A linear or near-linear arrangement for the F4···H12–O6 atomic orientation would probably have to be preferred, but the actual F4–H12–O6 angle is 118.8°, far away from linearity (180°). This deviation from linearity is caused by the bonded forces.

Electrostatic forces must be important for this H bond too, since the C3–F4 and H12–O6 bonds are 22.4° from being parallel. The corresponding bond moments are sizable⁵³ and have a nearly antiparallel configuration, which is ideal.

It is difficult to estimate the strength of the H bond quantitatively in this case. A value of 16.4(3) kJ/mol was found for the energy difference between the ap and sp forms of formic acid.¹ A H bond strength of roughly 15 kJ/mol therefore appears plausible in the present case.

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Supporting Information Available: MP2 dipole moments, B3LYP/aug-cc-pVTZ structure and rotational constants, and the full vibrational spectra of conformers I–IV. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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