

Microwave Spectrum, Conformation, Intramolecular Hydrogen Bonding and *Ab Initio* Computations for 2,2,3,3-Tetrafluoro-1-propanol

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The microwave spectra of 2,2,3,3-tetrafluoro-1-propanol, HOCH₂CF₂CF₂H, and one deuterated species, DOCH₂CF₂CF₂H, have been investigated in the 25.5–39.5 GHz spectral region at –25°C. Conformations with five- or six-membered OH...F hydrogen bonds are possible for this compound. One conformer was assigned. This rotamer is stabilized by a five-membered intramolecular hydrogen bond formed between the hydroxyl-group hydrogen atom and one of the fluorine atoms attached to the carbon in the 2-position. The microwave work has been assisted by *ab initio* computations at the 6-31G** level of theory and the gas-phase IR spectrum.

The ability of the fluorine atom to form intramolecular hydrogen (H) bonds with the hydroxyl-group H atom has been thoroughly studied and reported in several publications.^{1–10} Gas-phase studies of both five-^{1–4,6–8} and six-membered¹⁰ H...F bonds have been made.

The simplest five-membered H...F bond is found in 2-fluoroethanol, HOCH₂CH₂F, whose H-bonded conformation is rather stable in the gas phase, as shown by infrared¹ and microwave (MW) spectroscopy,² and by electron diffraction.³ In fact, in the latest electron-diffraction study^{3b} this rotamer was found to be about 11 kJ mol^{–1} more stable than the heavy-atom *anti* conformer. *Ab initio* computations⁴ at the high CID/6-31G** level of theory found this energy difference to be 6.00 kJ mol^{–1}, while 8.4 kJ mol^{–1} was computed more recently.⁵ Moreover, the only conformers of CH₃CH(OH)CH₂F⁶ and CH₃CHFCH₂OH⁷ identified in MW investigations also possess five-membered internal H...F bonds very similar to that found in 2-fluoroethanol.

In 2,2-difluoroethanol, HOCH₂CF₂H, two different conformations stabilized with five-membered H bonds are possible.⁸ In the first of these, the C–O bond is *gauche* to one of the C–F bonds and *anti* to the other C–F bond. In the second rotamer, the C–O bond is + or –*gauche* to the two C–F bonds, respectively. Only the former conformer was identified by MW spectroscopy.⁸ This rotamer was estimated to be at least 6 kJ mol^{–1} more stable than the latter conformation.⁸ *Ab initio* computations⁴ and matrix-isolation IR studies⁹ corroborate this conclusion.

Studies of free molecules with six-membered OH...F

bonds are rare, and only one (of HOCH₂CH₂CH₂F)¹⁰ has been found in the literature. In this elegant work,¹⁰

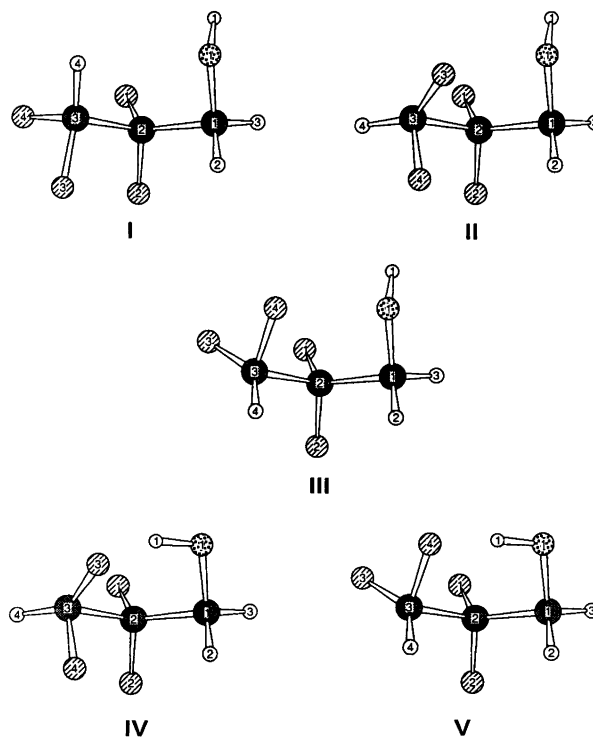


Fig. 1. Selected conformations of HOCH₂CF₂CF₂H with atom numbering (H1–O1–C1–H2, H3–C2–F1, F2–C3–F3, F4, H4). Rotamers I, II and III have five-membered intramolecular OH...F hydrogen bonds formed by the H1–O1–C1–C2–F1 chain of atoms, while IV and V have six-membered OH...F hydrogen bonds formed by the H1–O1–C1–C2–C3–F3 (rotamer IV) or F4 (rotamer V) chains of atoms. Conformer I with a five-membered H bond was assigned in this work.

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three conformers, one with and two without H...F bonds, were found by MW spectroscopy. Interestingly, the one stabilized with an internal six-membered H...F bond was *not* found to be the most stable form of the molecule.

2,2,3,3-Tetrafluoro-1-propanol, HOCH₂CF₂CF₂H, differs from the compounds above in that *two* different types of internal H bonding may exist for this molecule. The hydroxyl-group H atom may form a *five*-membered H bond with one of the fluorine atoms in the 2-position, or a *six*-membered H bond with one of the fluorine atoms in the 3-position, as illustrated in Fig. 1 for five selected conformations. The competitive situation between rotamers having five- or six-membered H...F bonds that exists for this compound has been the main motivation to carry out this work. It will be shown below that a five-membered internal H...F bond is preferred by the most stable conformer of this molecule.

Experimental

The sample used in this work was purchased from Aldrich Chemie, Steinheim, Germany. The sample was purified by preparative gas chromatography. The MW spectrum was studied employing the Oslo spectrometer which is described in Ref. 11. The 26.5–39.5 GHz spectral region was investigated, with the microwave absorption cell cooled to about –25°C. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 3–6 Pa, and the accuracy of the spectral measurements is presumed to be better than ±0.10 MHz. The deuteration of the hydroxyl group was achieved by conditioning the MW well with heavy water and then introducing the normal species.

The gas-phase IR spectrum in the 500–4000 cm⁻¹ region was taken at room temperature using a Bruker IFS 88 spectrometer equipped with a multiple-reflection cell. The pressure was ca. 100 Pa, the path length was ca. 3 m, and the resolution 2 cm⁻¹.

Results

Ab initio calculations. The calculations were made using the Gaussian 90 program package¹² running on the Cray-Y-MP/464 computer in Trondheim. The 6-31G** basis set was chosen. 2,2,3,3-Tetrafluoro-1-propanol has three axes of internal rotation. Consequently, a large number of rotamers is possible for this molecule. It has not been possible to make computations for all of them. Calculations were restricted to the five conformations shown in Fig. 1, because previous results^{1–10} indicate that these conformations might be the ones with the lowest energies.

Note that the O1–C1–C2–F1 dihedral angle is *-gauche* (–60° from *syn*), while the O1–C1–C2–F2 is *anti* (180° from *syn*) in all five rotamers, just as in the case (see above) of the most stable conformer of HOCH₂CF₂H.^{4,8,9} Conformations I–III are each stabi-

lized by a five-membered internal H bond, and differ only in the orientation of the CF₂H group, which has the C1–C2–C3–H4 chain of atoms in the *-gauche* (–60°) position in rotamer I, in the *anti* position in II, and in the *+gauche* (+60°) position in III.

In conformation IV the hydroxyl group has been rotated 120° from its position in II, while in V the said group has been rotated 120° from its position in III to allow *six*-membered H bonds to be formed in each of IV and V.

The geometries of the five rotamers in Fig. 1 were fully optimized. They were all found to be stable, as no imaginary vibrational frequencies were computed for any of them.^{13a} The predicted geometries, rotational constants, principal-axes dipole moment components and energy differences for I–V are listed in Table 1. Some further results of the computations are given in the text below.

MW spectrum and assignment of conformer I. According to the theoretical predictions (Table 1) rotamer I was predicted to have the lowest energy and a rather large *a*-axis dipole moment component. This is a fortunate situation for such a 'heavy' molecule as the present one, because the strongest transitions expected for this prolate top were the *a*-type *R*-branch lines, which are much easier to assign than *b*- or *c*-type transitions.

The high-*K*₋₁ *aR*-transitions were first identified using a low Stark voltage. Low-*K*₋₁ *aR*-transitions were then readily assigned. A portion of the spectrum* is shown in Table 2. The spectrum is rather weak (see discussion below), but only very weak lines remained unassigned. No *b*- or *c*-type transitions were found, presumably because μ_b and μ_c are considerably less than μ_a , as predicted (Table 1). The spectroscopic constants (*A*-reduction, *I'*-representation)¹⁴ are collected in Table 3. Note that the rotational constants given there agree to within a few percent with those listed for rotamer I in Table 1. Much larger discrepancies between the experimental rotational constants (Table 3) and the *ab initio* values (Table 1) are seen for the other four rotamers II–V. This is one important reason for assigning the spectrum to conformer I.

The ground-state transitions were accompanied by many satellite lines presumably originating from vibrationally excited states of this conformer. Two such states were assigned. They are assumed to be the first excited states of the C2–C3 and C1–C2 torsions, respectively. Their spectroscopic constants are listed in Table 4. The assignment of rotational constants to fundamental modes in this table is somewhat uncertain, and the two sets of excited-state rotational constants there should possibly be

* The complete spectra of the parent and deuterated species are available from the authors upon request, or from The National Institute of Standards and Technology, Microwave Data Center, Molecular Physics Division, Bldg. 221, Rm. B265, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 1. Structure, rotational constants, principal-axes coordinates of the hydroxyl-group H atom and dipole moments of rotamers I–V^a of HOCH₂CF₂CF₂H as calculated by *ab initio* methods using the 6-31 G** basis set.

Conformation:	I	II	III	IV	V
Distances/pm					
H1–O1	94.4	94.4	94.4	94.3	94.3
C1–O1	139.3	138.7	138.6	138.7	138.5
H2–C1	108.0	108.0	108.2	108.6	108.9
H3–C1	108.6	108.7	108.7	108.2	108.1
C1–C2	151.3	151.5	151.6	151.9	152.1
C2–F1	134.9	134.8	134.4	133.8	133.2
C2–F2	133.7	134.4	134.3	134.5	134.8
C2–C3	151.8	151.9	152.1	151.9	152.0
C3–F3	133.9	133.1	133.5	134.2	132.8
C3–F4	133.5	133.7	133.3	133.6	134.7
C3–H4	107.8	108.0	108.0	107.9	108.0
Angles/°					
H1–O1–C1	109.7	110.0	110.1	110.9	110.9
O1–C1–H2	108.0	107.9	107.7	112.9	112.7
O1–C1–H3	112.7	112.6	112.7	107.5	107.5
O1–C1–C2	110.5	112.4	112.8	113.1	113.5
C1–C2–F1	108.8	109.3	108.9	110.8	110.4
C1–C2–F2	109.3	108.4	107.8	108.3	107.9
C1–C2–C3	114.8	117.8	116.9	116.5	115.3
C2–C3–F3	108.4	110.4	108.6	109.5	110.1
C2–C3–F4	109.1	108.8	109.7	108.9	109.3
C2–C3–H4	111.9	110.4	111.8	111.6	111.2
Dihedral angles ^b /°					
H1–O1–C1–H2	–168.8	–178.9	–180.1	56.3	60.8
H1–O1–C1–H3	–48.7	–59.2	–61.0	175.7	179.5
H1–O1–C1–C2	71.6	60.9	59.4	–67.0	–63.1
O1–C1–C2–F1	–59.6	–59.0	–60.8	–52.8	–49.6
O1–C1–C2–F2	183.0	184.3	181.4	189.3	192.6
O1–C1–C2–C3	60.2	63.2	60.9	69.9	74.5
C1–C2–C3–F3	60.0	–67.0	174.4	–58.2	190.7
C1–C2–C3–F4	177.8	52.0	–67.7	59.2	–50.7
C1–C2–C3–H4	–60.0	171.9	54.0	180.5	69.2
Rotational constants ^c /MHz					
A	2720.3	2281.4	2695.0	2295.4	2631.3
B	1732.9	1978.3	1912.9	2011.6	1936.1
C	1499.3	1637.4	1428.6	1601.5	1432.5
Principal axis coordinates of hydroxyl-group H atom/pm					
a	242.2	188.8	208.9	102.6	162.3
b	20.3	142.9	97.6	194.0	162.3
c	112.5	47.9	83.9	25.4	8.9
Dipole moments ^d /10 ^{–30} C m					
μ _a	7.76	2.34	4.85	4.39	0.50
μ _b	0.04	3.97	1.95	0.02	2.22
μ _c	2.19	1.93	3.75	1.90	9.96
Energy difference ^{e,f} /kJ mol ^{–1}					
	0.0	2.2	10.6	3.3	13.3

^a See Fig. 1 for definition. ^b Measured from *syn* = 0°. ^c Calculated from the structures given above in this table. ^d 1 D = 3.335 64 × 10^{–30} C m. ^e The total energy of conformer I was calculated to be –1545 152.9 kJ mol^{–1}. ^f Energy difference between I and each of the other four conformations.

Table 2. MW spectrum of the ground vibrational state of conformer I of HOCH₂CF₂CF₂H.

Transition	Observed frequency ^a /MHz	Obs. – calc. frequency/MHz
$J''_{K''-1, K''+1} \leftarrow J'_{K'-1, K'+1}$		
8 _{4,5} ← 7 _{4,4}	25 705.41	–0.01
9 _{0,9} ← 8 _{0,8}	27 038.80	–0.02
9 _{1,9} ← 8 _{1,8}	27 028.37	0.04
9 _{3,6} ← 8 _{3,5}	29 649.75	0.02
9 _{4,6} ← 8 _{4,5}	28 938.32	0.05
9 _{7,2} ← 8 _{7,1}	28 813.79	–0.01
9 _{7,3} ← 8 _{7,2}	28 813.79	0.01
10 _{0,10} ← 9 _{0,9}	29 980.16	–0.09
10 _{2,8} ← 9 _{2,7}	32 398.47	0.00
10 _{3,8} ← 9 _{3,7}	31 799.70	0.03
10 _{5,5} ← 9 _{5,4}	32 219.32	–0.01
10 _{6,4} ← 9 _{6,3}	32 097.61	–0.10
10 _{6,5} ← 9 _{6,4}	32 094.79	0.07
10 _{8,2} ← 9 _{8,1}	32 008.32	–0.03
10 _{8,3} ← 9 _{8,2}	32 008.32	–0.03
11 _{0,11} ← 10 _{0,10}	32 923.20	–0.12
11 _{3,8} ← 10 _{3,7}	36 249.92	–0.12
11 _{4,7} ← 10 _{4,6}	36 066.41	0.06
11 _{6,5} ← 10 _{6,4}	35 357.30	–0.06
11 _{10,1} ← 10 _{10,0}	35 181.95	0.04
11 _{10,2} ← 10 _{10,1}	35 181.95	0.04
12 _{1,11} ← 11 _{1,10}	36 949.12	0.01
12 _{2,10} ← 11 _{2,9}	38 207.10	0.08
12 _{5,8} ← 11 _{5,7}	38 678.73	0.02
12 _{8,4} ← 11 _{8,3}	38 466.90	–0.03
12 _{8,5} ← 11 _{8,4}	38 466.90	0.02
12 _{11,1} ← 11 _{11,0}	38 378.38	0.03
12 _{11,2} ← 11 _{11,1}	38 378.38	0.03

^a ±0.10 MHz.

interchanged. Crude relative intensity measurements made largely as described in Ref. 15 yielded ca. 105 cm^{–1} for the C2–C3 torsional mode and ca. 135 cm^{–1} for the C1–C2 torsional vibration. *Ab initio* calculations (not reported in Table 1) predicted 76 cm^{–1} for the C2–C3 torsion and 128 cm^{–1} for the C1–C2 torsion, values which are in fair agreement with the experimental ones.

The hydroxyl-group deuterated species was studied in order to locate exactly the position of the H atom of the said group using Kraitchman's equations.¹⁶ The assign-

Table 3. Ground-state spectroscopic constants^{a,b} of the parent and hydroxyl-group deuterated species of conformer I of 2,2,3,3-tetrafluoro-1-propanol.

Species:	HOCH ₂ CF ₂ CF ₂ H	DOCH ₂ CF ₂ CF ₂ H
No. of transitions:	65	30
R.m.s. deviation ^c /MHz	0.051	0.091
<i>A</i> ₀ /MHz	2638.178(28)	2620.157(64)
<i>B</i> ₀ /MHz	1710.798 6(50)	1667.514 3(64)
<i>C</i> ₀ /MHz	1472.487 5(48)	1445.693 3(62)
Δ _{<i>J</i>} /kHz	0.343 2(73)	0.341(23)
Δ _{<i>K</i>} /kHz	–0.596(10)	–0.405(33)
δ _{<i>J</i>} ^d /kHz	0.101(11)	– ^e

^a *A*-reduction, *J'*-representation.¹⁶ ^b Uncertainties represent one standard deviation. ^c Root-mean-square deviation. ^d Further centrifugal distortion constants preset at zero. ^e Kept at zero in least-squares fit.

Table 4. Spectroscopic constants^{a,b} of conformer I of HOCH₂CF₂CF₂H in vibrationally excited states.

Vibrational state:	C2–C3 torsion ^c	C1–C2 torsion ^c
No. of transitions:	61	49
R.m.s. deviation ^d /MHz:	0.072	0.080
<i>A</i> _{<i>v</i>} /MHz	2642.684(38)	2634.092(48)
<i>B</i> _{<i>v</i>} /MHz	1709.839 0(68)	1711.843 9(92)
<i>C</i> _{<i>v</i>} /MHz	1469.436 1(64)	1472.730 9(74)
Δ _{<i>J</i>} /kHz	0.327(10)	0.319(15)
Δ _{<i>K</i>} ^e /kHz	–0.559(15)	–0.560(22)
δ _{<i>J</i>} ^f /kHz	0.094(13)	0.041(17)

^{a,b} Comments as for Table 3. ^c The assignment of these excited states may perhaps be interchanged; see text.

^{d-f} Comments as for ^{c-e} in Table 3.

ments were again made in a straightforward manner for the ^a*R* transitions. The spectroscopic constants are collected in Table 3.

Kraitchman's substitution coordinates¹⁶ of the H1 atom were then calculated as $|a| = 251.174(61)$, $|b| = 7.4(20)$ and $|c| = 117.01(13)$ pm using the rotational constants shown in Table 3. This is in reasonably good agreement with $|a| = 242.1$, $|b| = 20.3$ and $|c| = 112.5$ pm found for conformer I in the *ab initio* calculations (Table 1). The corresponding coordinates of H1 of rotamers II–V are widely different from those of I, as seen in the same table. It can therefore be concluded beyond doubt that I has indeed not been confused with any other rotameric form.

The dipole moment could not be determined because the transitions were too weak.

The existence of further rotamers. The *ab initio* computations predict that conformer I is only a few kJ mol^{–1} more stable than II and IV. However, the assignments reported above include all the strongest lines of the spectrum, and it was not possible to assign II or IV to any of the very few, weak lines (which could be impurities) that still remained after the assignment of I was completed.

The fact that the assigned lines are all quite weak in spite of a rather large dipole moment (Table 1) is not an indication in itself that large fractions of conformations other than I are present. The spectral weakness is rather a result of a large partition function, as the following argument will show: For example, the 10_{4,7} ← 9_{4,6} transition at 32 155.98 MHz has a peak absorption coefficients of roughly 6 × 10^{–8} cm^{–1}. This value can be compared with the calculated peak absorption coefficient using the formula given in Ref. 17, assuming that 100% of the gas is rotamer I. The following values were used in this formula: the line breadth (Δ*v*)₁ was estimated to be roughly 40 MHz Torr^{–1}; *F*_{*v*} was found to be 0.031 using the harmonic vibrational frequencies calculated by *ab initio* methods (not listed in Table 1) and reduced by 10%;^{13b} the dipole moment, μ_{*a*}, shown in Table 1 was reduced by 10%;^{13c} the line strength for the said transition was calculated to be 8.4 using the rotational constants shown in Table 3; the temperature was about 250 K; and

$\exp(-E_{J_i}/kT)$ was assumed to be 1. With these values, the peak absorption coefficient was calculated to be $8.4 \times 10^{-8} \text{ cm}^{-1}$ using the formula in Ref. 17. Given the rather large uncertainties encountered in this case, this value is not significantly different from the experimental value of $6 \times 10^{-8} \text{ cm}^{-1}$.

The intensity of the spectrum thus indicates that most of the gas phase is made up of conformer **I**. It can thus be concluded that this rotamer is the most stable form of the molecule, in agreement with the *ab initio* result in Table 1. Further conformations, such as the hypothetical rotamers **II** or **IV**, may of course be present in the gas in small fractions, but the fact that much smaller dipole moments are predicted for them than for **I** (Table 1) would make their assignments difficult.

IR spectrum. The gas-phase IR spectrum in the region of the O–H stretching vibration is shown in Fig. 2. The band is seen to have its maximum at 3657 cm^{-1} with shoulders at 3663 and 3650 cm^{-1} . The structure of this band is presumably due to the *P*-, *Q*- and *R*-rotational fine structure, and not to rotational isomerism, since many other bands (not reported herein) were seen to have similar fine structures. There is thus no obvious indication from the IR spectrum of the existence of several conformers.

Structure. A full structure of **I** cannot be determined on the basis of the six rotational constants shown in Table 3. The *ab initio* structures of rotamers **I–V** (Table 1) are similar to experimental structures for closely related compounds.¹⁸ The fact that the theoretical structure of **I** reproduces the rotational constants and the principal-

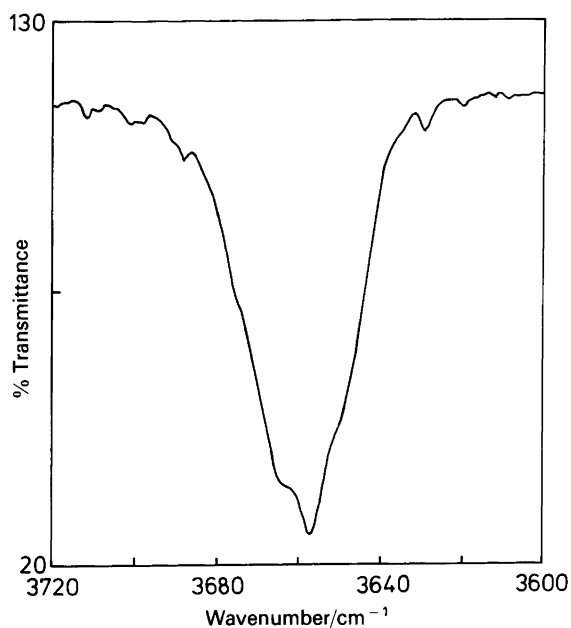


Fig. 2. Gas-phase infrared spectrum in the O–H stretching region. The shoulders at 3663 and 3650 cm^{-1} and the maximum at 3657 cm^{-1} are ascribed to the rotational fine structure, and not to rotational isomerism.

axes coordinates of the hydroxyl-group H atom rather well leads us to suggest that this structure is the best available approximation to the real structure. No data are at hand that could improve the *ab initio* structure.

The structural parameters of **I** (Table 1) are all rather normal, with one exception. The H1–O1–C1–C2 dihedral angle of 71.6° instead of 60° indicates that the hydroxyl-group H atom is rotated *away* from F1. This is not expected to increase the H-bond interaction.

Discussion

The reason why $\text{HOCH}_2\text{CF}_2\text{CF}_2\text{H}$ prefers conformation **I**, which has a five-membered OH...F bond, to a conformation such as **IV**, which has a six-membered OH...F bond, is probably quite complex. A comparison of the internal H bonds in **I** and **IV** using the results in Table 1 reveals some interesting traits: The contribution from electrostatic forces to the H bond in **I** is favourable because the O1–H1 and C2–F1 bonds are about 11° from being parallel. The dipoles of these two bonds are thus almost antiparallel, which is favourable for electrostatic stabilization. Covalent forces contribute little to the H bond in rotamer **I**; the non-bonded H1...F1 distance is 252 pm , which is almost the same as the sum of the van der Waals radii of hydrogen and fluorine (255 pm),¹⁹ and the O1...F1 distance is 275 pm , which is the same as the sum of the van der Waals radii of oxygen and fluorine.¹⁹ Moreover, the O1–H...F1 angle is 93° , while approximately 180° is generally preferred²⁰ when the covalent contribution to the H bond is at a maximum. The H bond in **I** is very similar to that in 2-fluoroethanol, whose strength has recently been estimated to be 7.9 kJ mol^{-1} (a remarkably large value) in high-level *ab initio* computations,⁵ while the *gauche* effect²¹ was estimated to be only 0.4 kJ mol^{-1} .

The geometry of **I** should be compared with a H1...F3 distance of 229 pm , a O1...F3 distance of 286 pm and an O1–H1...F3 angle of 118° calculated for the hypothetical conformation **IV**, which is predicted to be the most stable rotamer with a six-membered H...F bond (Table 1). Covalent contributions to the H bond should thus be somewhat more important in **IV** than in **I**. On the other hand, the electrostatic contribution to the H bond is probably of less importance in **IV** than in **I**, as the O1–H1 and C3–F3 bond dipoles in **IV** are 56° from being antiparallel.

The rather long H...F distances in both **I** and **IV** imply that the H bonds are rather *weak* in both conformers. In fact, the H bond in **I** represents a borderline case by this criterion. It is suggested that **I** is preferred to **IV** because the electrostatic interaction between the O1–H1 and C2–F1 dipoles in **I** is more efficient than the covalent forces between H1 and F3 and the O1–H1, C3–F3 dipole interaction in **IV**.

Finally it remains to be explained why **I** is preferred to the other five-membered H-bonded conformations **II** and **III**, and why **IV** is probably more stable than the other

conformer with a six-membered H bond, viz. V. The strongly polar C1–O1 and C–F bonds undoubtedly repel each other strongly. It is thought that this interaction is of great importance for the conformational preferences, especially around the C1–C2 and C2–C3 bonds, and might explain why I is preferred to II and III, and why IV is preferred to V.

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