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Structure, Conformations, and Internal Hydrogen Bonding in Gaseous 4-Fluorobutan-1-ol. Gas-Phase Electron Diffraction and Ab Initio Study

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Excluding enantiomers, there are 14 possible rotomeric conformations of 4-fluorobutan-1-ol, of which two are capable of forming an internal O−H···F hydrogen bond. The composition of the gaseous system is of special interest because it is determined by the energies of the conformers which reflect the energies of the hydrogen bonds. We have investigated the conformational composition of the gaseous system and the molecular structures of the conformers at 83 °C by gas-phase electron diffraction (GED) augmented by molecular orbital calculations. Because of the complexity of the 4-fluorobutan-1-ol system, the parameters of the several models tested were simplified by various constraints taken from the theoretical work. With these constraints, the best agreement with the GED data was obtained with a model consisting of about equal amounts of hydrogen-bonded and non-hydrogen-bonded conformers. Because the curled-up shape of the two forms capable, in principle, of forming internal hydrogen bonds is expected to be energetically unfavorable in the absence of such bonding, the experimental results are interpreted as strong evidence for its existence. Weighted average values, with estimated 2σ uncertainties, of the more important bond distances (r_a/Å) and bond angles ($\angle_a$/deg) for the preferred model are $r(C_O-C) = 1.529(2)$, $r(C_C-C_C) = 1.537(2)$, $r(C-C_F) = 1.520(2)$, $r(C-O) = 1.430(5)$, $r(C-F) = 1.401(5)$, $\angle(C_O-C-C) = 112.5(33)$, $\angle(C-C-O)_{H\ bond} = 112.3(55)$, $\angle(C-C-O)_{no\ H\ bond} = 108.2(45)$, and $\angle(C-C-C_F) = 109.8(12)$. The two hydrogen-bonded conformers comprise 48.5% of the mixture with an estimated 2σ uncertainty of 14.0%. A rough estimate of the energy of the O−H···F hydrogen bond is 3 kcal mol^{-1}. The average O···F separation in this bond for the H-bonded conformers is 2.46(4) Å, about 0.3 Å less than the sum of the van der Waals radii.

Introduction

The 1,2-disubstituted ethanols consist of a mixture of gauche and anti conformers in proportions that depend on the nature of the substituents. In general, the dominant form of these molecules is anti; however, when the possibility of internal hydrogen bonding exists, the gauche form may be the more abundant. An interesting special case is 1,2-difluoroethane; despite the absence of hydrogen-bonding capability, it is nearly all gauche in the gas phase, whereas the dichloro and dibromo compounds are mostly anti. This effect arising from the high electronegativity of the fluorine atoms has been termed the "gauche effect".[1]

Because strong hydrogen bonds are formed between donor and acceptor groups of high electronegativity (e.g., OH and F, or NH_2 and F), where in the ethane derivatives the gauche effect is known from the example of 1,2-difluoroethane to be present as well, the question of the relative roles played by the gauche effect and internal hydrogen bonding presents itself. Because the gauche effect appears to operate only when the ligands are separated by three bonds, as in the 1,2-disubstituted ethanes, one way to investigate the problem is to study the composition of systems in which the substituents are farther apart. In previous work, we have discovered that gaseous butan-1,4-diol consists of about 40% H-bonded forms at 144 °C,[2] but gaseous 1,4-difluorobutane[3] has scarcely any forms with the fluorine atoms in close proximity. As expected, the results for the latter show that the gauche effect plays no role in the stabilization of the "curled-up" forms of the 1,4-disubstituted butanes. The set of results from the series ethane-1,2-diol (glycol),[4] 2-fluoroethanol,[5] and 1,2-difluoroethane[6] (all primarily gauche) and the pair of butanes, butane-1,4-diol[1] and 1,4-difluorobutane,[2] suggests a similar investigation of 4-fluorobutan-1-ol (hereafter 4-FB; Figure 1) to shed more light on the strength of the (possible) internal hydrogen bond in this molecule. This paper is a report of our results.

Experimental Section

The sample of 4-FB was prepared at Portland State University by the transesterification of 4-fluorobutyl acetate, which in turn had been made from 4-bromobutyl acetate.[7] The NMR spectrum of the 4-FB sample obtained just after its preparation and again from the residue after the diffraction experiments showed the purity of the sample to be very high.

4-Fluorobutyl Acetate. 4-Bromobutyl acetate (36.12 g, 0.185 mol) was treated with KF (26 g, 0.45 fw, spray dried) at 160 °C in an evacuated 300 mL Carius tube. After 2 weeks of continuous reaction, a sample was withdrawn and GC−MS

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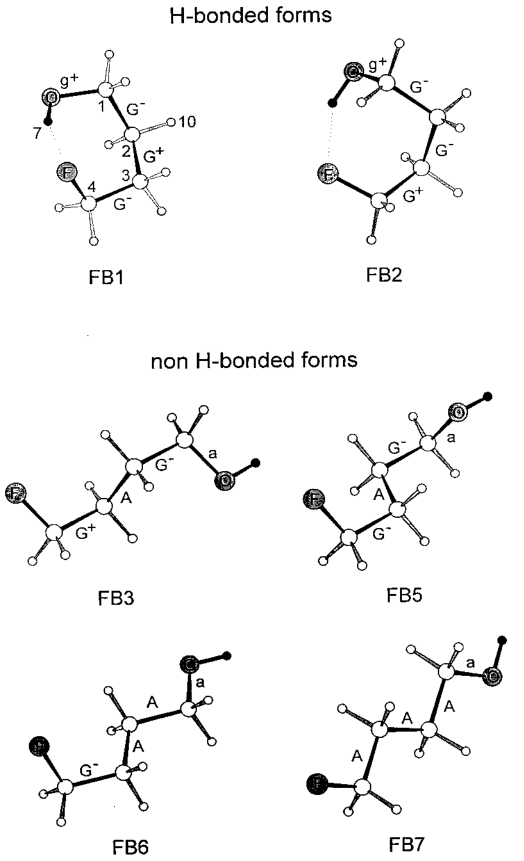

Figure 1. Diagrams of some of the more important conformers of 4-fluorobutan-1-ol. These conformers comprise the preferred model A.

analysis showed a conversion of ~60%; the product was removed by repeated washing with CH_2Cl_2, and after distillative removal of the solvent, the partially fluorinated product was again subjected to fluorination with 16.20 g of KF. After another 2 weeks, the contents of the Carius tube was diluted with 200 mL of light petroleum ether and then stirred with 14.2 g of finely ground $CaCl_2$ for 2 weeks. This was done to remove an impurity ($R_t = 6.17$ min, 25 m DB5 column, 50 → 200 °C at 10 °C min^{-1}) which was surmised to be 4-hydroxybutyl acetate by GC−MS analysis. After this contaminant had been largely removed by the above treatment, the liquor was filtered off, the petroleum ether was distilled at atmospheric pressure, and the residue was subjected to simple distillation at 29−32 Torr, 71−79 °C, giving a purity of >95% by GC−MS (13.82 g, 56% of theory; bp 56−57 °C at 12 Torr).[8]

4-Fluorobutan-1-ol. A total of 8.10 g of 4-fluorobutyl acetate, 40 mL of absolute ethanol, and 4 drops of concentrated H_2SO_4 were refluxed for 9 h; because the composition had changed little after 4 h, the solvent was largely distilled off (33 mL), and the residue was refluxed for another 4.5 h with 28 mL of fresh ethanol. At that time, GC−MS analysis showed 4-FB to be the sole product. After cooling, solid $NaHCO_3$ was added (≈100 mg), the mixture was stirred vigorously for 1 h and filtered, and ethyl acetate was distilled away through a 12 cm Vigreux column. The residue was then vacuum distilled with the same apparatus, and a clear, colorless liquid (2.4 g, 43%), which was free of any contaminants according to GC−MS analysis, was collected at 66.5−69 °C (22−26 Torr); the reported boiling points are 57.5−58 °C at 15 Torr[7] and 56 °C at 15 Torr.[9]

Electron Diffraction. The diffraction experiments were made with the Oregon State apparatus using an r^3 sector and Kodak projector slide plates (medium contrast) developed for 10 min in a D19 developer diluted 1:1. The temperature of the nozzle tip was 83 °C during the experiments. The nominal accelerating voltage was 60 kV (electron wavelength, 0.049 Å) calibrated against CO_2 in separate experiments [r_a(C=O) = 1.1646 Å; r_a(O···O) = 2.3244 Å]. The nominal nozzle-to-plate distances were 750 (long camera, LC) and 300 mm (middle camera, MC). Three out of four plates were selected for analysis from the LC/MC experiments. The procedures for obtaining the total scattered intensities ($s^4I_t(s)$) and the molecular intensities ($sI_m(s)$) have been described.[10,11] To reduce the level of noise in the data, all of the plates were traced several times. The background for each trace was then subtracted, and the resulting molecular intensities were averaged to yield a data set for each plate. These data sets were averaged in turn to give average intensities for each of the two camera distances. Ranges of these average modified molecular intensities ($sI_m(s)$) were $2.00 \leq s/Å^{-1} \leq 16.00$ (LC) and $8.00 \leq s/Å^{-1} \leq 40.00$ (MC), with $\Delta s/Å^{-1} = 0.25$. The experimental intensity curves are shown in Figure 2 and the corresponding radial distribution (RD) curves in Figure 3. The complex scattering factors used in these and other calculations were taken from tables.[12] The average intensity data from each of the camera distances is available as Supporting Information.

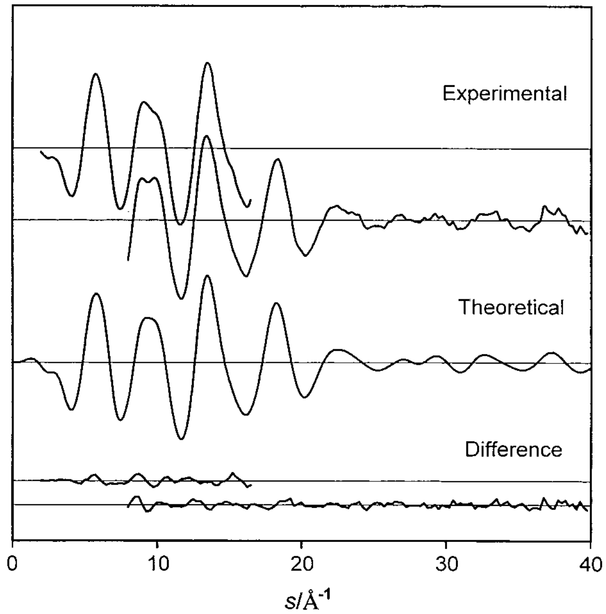

Figure 2. Intensity ($sI_m(s)$) curves. Experimental curves are averages of data from three plates at the long camera distance and four plates at the middle distance. The theoretical curve is for the preferred model A.

Theoretical Calculations

Ab Initio Optimizations. If one assumes 3-fold potentials for rotation about the C−O and C−C bonds in 4-FB, there are 81 possible conformations for the molecule. However, those conformations, differing only by rotations around the C−O bond (i.e., essentially in the position of the hydroxyl hydrogen atom), are not distinguishable by gas-phase electron diffraction (GED). Moreover, mirror image structures give identical scattering patterns in a GED experiment. These circumstances reduce the number of distinguishable conformers to 14, equal to (81/3 − 1)/2 + 1, where the 1 refers to the unique extended form. These conformers have similar bond lengths and valence angles which are not separately measurable by GED. The average values are

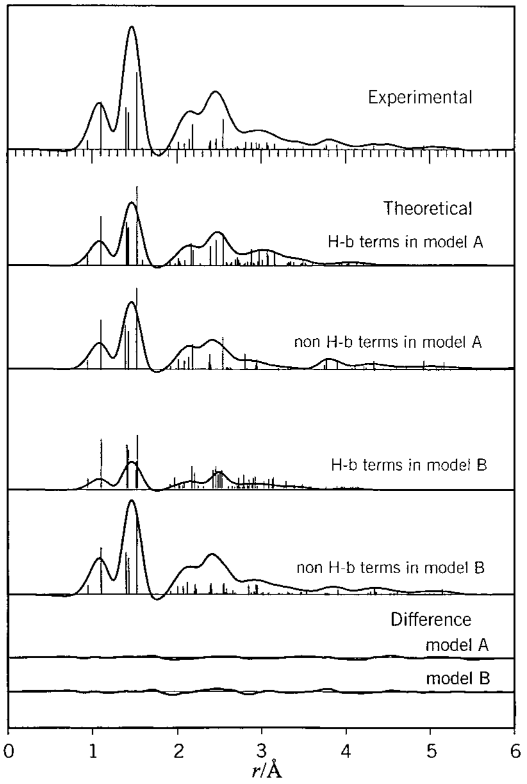

Figure 3. Radial distribution curves. Theoretical curves are for the models of Tables 5 and 6 and in each case show contributions from the groups of hydrogen-bonded species and non-hydrogen-bonded species. The vertical bars indicate the positions and the relative weights of the distances within each group.

TABLE 1: Theoretical Free-Energy Differences (kcal mol^{-1}) and Estimated Conformational Composition for 4-Fluorobutan-1-ol

		HF/6-31G*		MP2/6-31G*		B3LYP/6-31G*	
	conformer	$\Delta G°$	%	$\Delta G°$	%	$\Delta G°$	%
FB1[a]	$G^-G^+G^-g^+$	0.67	9.5	0.00	35.3	0.00	49.1
FB2[a]	$G^+G^-G^-g^+$	0.86	7.3	0.22	26	0.84	15
FB3	G^+AG^-a	0.00	24.5	0.75	12.3	1.11	10.3
FB4	GGGa	0.89	7.1	1.35	5.3	1.94	3.2
FB5	G^-AG^-a	0.62	10.2	1.39	5.0	1.75	4.2
FB6	G^-AAa	0.71	9.0	1.87	2.5	1.90	3.4
FB7	AAAa	0.70	4.6	2.23	0.8	2.13	1.2
FB8	AG^+G^-a	1.08	5.4	1.71	3.2	2.13	2.4
FB9	G^+G^-Aa	1.20	4.6	1.86	2.6	1.99	3.0
FB10	AAG^-a	0.66	9.6	1.76	3.0	1.87	3.5
FB11	$G^+G^+G^-a$	1.69	2.3	2.02	2.1	2.46	1.6
FB12	AG^-G^-a	1.75	2.1	2.75	0.7	2.72	1.1
FB13	GGAa	1.72	2.2	2.73	0.8	2.66	1.2
FB14	AG^-Aa	1.94	1.6	3.18	0.4	3.09	0.6
$\Delta G° = G°(\mathrm{FB}n') - G°(\mathrm{FB}n)$							
FB1′	$G^-G^+G^-g^-$	4.24		4.75			
FB2′	$G^+G^-G^-a$	0.52		1.14			
FB4′	GGGg	0.08		−0.02			
FB7′	AAAg	0.27		0.07			

[a] Hydrogen-bonded conformers.

measurable with high accuracy, however. In such cases, useful information about the deviations from the average bond-length, valence-angle, and torsion-angle parameters for each of the conformers can be obtained from ab initio calculations. By introducing the calculated parameter differences, one obtains a more realistic model for refinement and presumably more accurate structural results. The calculated energies of the conformers also give an indication about the composition of the conformational mixture.

Full geometry optimizations at the ab initio HF, MP2, and B3LYP levels of theory with the 6-31G* basis set were carried out for the 14 conformers listed in Table 1 using the program Gaussian98.[13] In the following symbolism for individual conformers, capital letters indicate (A) anti or (G) gauche torsions of the heavy atom skeleton given in the order $-C_3-C_4-$, $-C_2-C_3-$, and $-C_1-C_2-$, and the small letter (a or g) symbolizes torsion about the $-C_1-O$ bond showing the orientation of the O−H bond. The sense of the rotation is positive for the counterclockwise motion of the near bond looking along the connecting bond to the far bond; the zero of rotation is with the near and far bonds eclipsed. For these calculations, the orientation of the O−H bond was in all of the cases but two taken as anti on the assumption that the energy of this conformer was lower than that of the corresponding g^+ or g^- forms, an assumption generally consistent with the results for FB4′ and FB7′ versus those for FB4 and FB7 (seen in Table 1). The two exceptions are FB1 and FB2, each representing a molecule with internal hydrogen bonding where the hydrogen atom is pointed toward the fluorine as seen in Figure 1. For these conformers, the calculated energies are substantially lower than those of the other conformers, indicating that the formation of O−H···F hydrogen bonds is an important factor in determining the conformational composition of the mixture. We had hoped to be able to form a rough estimate of the magnitude of the stabilization energy due to the hydrogen bonding by optimizations of the conformations having the FB1 and FB2 skeletal arrangements but with orientations of the O−H bonds incompatible with hydrogen-bond formation. These forms are labeled FB1′ and FB2′ in Table 1. The results from the MP2 calculations seem to indicate that the hydrogen-bond stabilization of the two conformers amounts to about 4.8 and 1.1 kcal mol^{-1}, respectively.

The HF/6-31G* energies indicate that the two hydrogen-bonded conformers together comprise about 17% of the conformational mixture. The situation is decidedly different according to the results of higher level calculations (Table 1). For the MP2/6-31G* optimizations of the same set of conformers, the hydrogen-bonded pair FB1 and FB2 dominate the mixture to the extent of 61%; for the B3LYP/6-31G* optimizations, the value is 64%. In the B3LYP/6-31G* calculations, but not the MP2/6-31G*, the ratio of the amounts of the two hydrogen-bonded forms is also changed substantially in favor of FB1.

Normal Coordinate Analyses. To obtain estimates of vibrational amplitudes and possibly other corrections involved in the formulation of a 4-FB model for refinement, it was necessary to carry out normal coordinate analyses. This was done with the program ASYM40 in a new version[14] that permits the symmetrization of the Cartesian force constants obtained from ab initio calculations. The force constants for each conformer were taken from the results of the HF/6-31G* calculations. Theoretical vibrational amplitudes were calculated for all of the distances, except for the H···H in all of the conformers included in the model of the system to be refined. Values for the most prominent distances in conformers comprising one of the models are seen in Table 2. The force fields are of no special significance, and no further use was made of them.

Structure Analysis. *Model Definitions.* Because it is impossible to measure the structures of the complex 4-FB system from GED data alone, it was necessary to introduce a number of assumptions and constraints to reduce the large number of structural parameters to a manageable level for refinement. (Because these assumptions involved distances and angles, they were drawn from the theoretical results at the HF/6-31G* level,

TABLE 2: Calculated[a] (Upper) and Experimental (Lower) Average Root-Mean-Square Amplitudes (RMS, *l*/Å) for Some Important Distances in Conformers of 4-Fluorobutan-1-ol[b,c]

	conformer					
	FB1 $G^-G^+G^-g^+$	FB2 $G^+G^-G^-g^+$	FB3 G^+AG^-a	FB5 G^-AG^-a	FB6 G^-AAa	FB7 AAAa
C−H	0.077	0.077	0.078	0.078	0.078	0.078
	0.081^A	0.081^A	0.082^A	0.082^A	0.082^A	0.082^A
C_1-C_2	0.051	0.052	0.050	0.051	0.050	0.050
	0.057^B	0.057^B	0.056^B	0.056^B	0.056^B	0.056^B
$C_1\cdots C_3$	0.074	0.074	0.075	0.075	0.078	0.078
	0.080^C	0.079^C	0.081^C	0.081^C	0.084^C	0.084^C
$C\cdots H_{10}$	0.108	0.108	0.107	0.107	0.107	0.107
	0.092^D	0.092^D	0.091^D	0.091^D	0.091^D	0.091^D
$C_1\cdots C_4$	0.142	0.123	0.075	0.076	0.077	0.078
	0.155^E	0.135^E	0.073^F	0.074^F	0.075^F	0.076^F
$C_2\cdots F$	0.127	0.123	0.147	0.150	0.149	0.071
	0.139^E	0.135^E	0.159^E	0.162^E	0.161^E	0.069^F
$C_3\cdots O$	0.127	0.132	0.145	0.146	0.072	0.072
	0.139^E	0.144^E	0.157^E	0.159^E	0.070^F	0.070^F
$C_1\cdots F$	0.198	0.153	0.155	0.150	0.158	0.096
	0.210^E	0.165^E	0.164^G	0.159^G	0.167^G	0.375^H
$C_4\cdots O$	0.211	0.162	0.154	0.149	0.096	0.099
	0.223^E	0.174^E	0.163^G	0.158^G	0.375^H	0.364^H
$F\cdots O$	0.144	0.210	0.068	0.284	0.204	0.085
	0.156^E	0.223^E	0.417^H	[0.284]	0.448^H	[0.104]

[a] Force field from HF/6-31G* theory. [b] Quantities in square brackets were assumed. [c] Same upper case superscript letters indicate experimental amplitudes refined in groups with 2σ uncertainties (least significant figures of items) as follows: $A = 5$, $B = 3$, $C = 8$, $D = 13$, $E = 25$, $F = 27$, $G = 95$, $H = 585$.

TABLE 3: Theoretical (HF/6-31G*) Values of Nonbond Heavy-Atom Distances (Å) in Conformers of 4-Fluorobutan-1-ol

	conformer	$C_2\cdots F_5$	$C_3\cdots O_6$	$C_1\cdots O_4$	$C_1\cdots F_5$	$C_4\cdots O_6$	$F_4\cdots O_6$
FB1[a]	$G^-G^+G^-g^+$	3.06	3.18	3.09	2.89	3.00	2.49
FB2[a]	$G^+G^-G^-g^+$	3.00	2.91	2.97	2.70	3.37	2.72
FB3	G^+AG^-a	2.93	2.95	3.90	4.33	4.34	5.14
FB4	GGGa	2.91	2.91	3.08	3.46	3.47	4.29
FB5	G^-AG^-a	2.93	2.95	3.91	4.35	4.35	4.61
FB6	G^-AAa	2.94	3.77	3.90	4.33	4.94	5.17
FB7	AAAa	3.75	3.77	3.89	4.92	4.92	6.11
FB8	AG^+G^-a	3.77	3.07	3.24	4.53	3.01	4.35
FB9	G^+G^-Aa	3.07	3.79	3.21	2.99	4.52	4.37
FB10	AAG^-a	3.75	3.02	3.90	4.94	4.41	5.24
FB11	$G^+G^+G^-a$	2.97	3.02	3.34	3.97	3.10	3.72
FB12	AG^-G^-a	3.77	2.93	3.17	4.45	3.67	4.69
FB13	GGAa	2.92	3.75	3.16	3.63	4.45	4.67
FB14	AG^-Aa	3.77	3.78	3.19	4.46	4.47	5.79

[a] Hydrogen bonded.

but when they involved conformational composition, they were taken from the MP2/6-31G* results.)[15] The constraints were the following: (1) As in the cases of butane-1,4-diol and 1,4-difluorobutane already cited,[1,2] the conformers were divided into two groups, one of which comprised the (potentially) hydrogen-bonded pair FB1 and FB2, and the other various conformers were chosen from the non-hydrogen-bonded group FB3−FB10, depending on the model of interest. In all of the cases, the forms FB11−FB14 were omitted on grounds that together they are predicted to total only a small proportion of the mixture (about 8% from HF and less than 5% for MP2 and B3LYP) and that, in any event, their distance distributions are similar (Table 3) to those of other species that are already included. (2) For most models, the *relative* amounts of the conformers in both the hydrogen-bonded and non-hydrogen-bonded groups were pegged at values obtained from an assumed Boltzmann distribution based on the theoretical energies, but variations of these ratios were also tested. (3) The values of the C−O, C−C, and C−F bond distances of the conformers in both groups were tied to those of FB1 via the theoretical differences. The C−H and O−H bond lengths in all of the conformers were assumed equal. (4) The C−C−O, $C_1-C_2-C_3$, $C_2-C_3-C_4$, and C−C−F bond angles in FB2 were constrained to be smaller than those in FB1 by the theoretical amounts and fixed at the theoretical values for the other conformers. The difference between $C_1-C_2-C_3$ and $C_2-C_3-C_4$ in FB1 was constrained to the theoretical value. All of the C−C−H angles were tied to the FB1 value through the theoretical differences, and all of the C−O−H bond angles were assumed equal.

The results of these simplifications were several. First, the $n - 1$ mole fraction parameters were reduced to just one, which permitted an experimental evaluation of the relative amounts of H-bonded and non-H-bonded forms in the system. Second, the very large number of structural parameters was reduced to 18: five bond lengths, five bond angles, and eight torsion angles. The first 14 of the following set of parameters are designed to apply to the reference conformer FB1 and the last four to apply to FB2: r(C−O), r(C−C), r(C−F), r(O−H), r(C−H), $\angle$(C−O−H), $\angle$(C−C−O), $\angle(C_1-C_2-C_3)$, $\angle(C_2-C_1-H_8)$, $\angle$(C−C−F), $\angle$(C−C−C−F), $\angle$(C−C−C−C), $\angle$(C−C−C−O), $\angle$(C−C−O−H), $\angle(C-C-C-F)_{FB2}$, $\angle(C-C-C-C)_{FB2}$, $\angle(C-C-C-O)_{FB2}$, $\angle(C-C-O-H)_{FB2}$. If all of the H···H distances are omitted, there are 62 distances in each 4-FB conformer leading to a total of 620 different distances in a 10-conformer-system model, for each of which there is an associated vibrational amplitude parameter.

We tested several types of trial models of which two were investigated in depth. All of the models were based on r_a distances.[16] In all of the models, attempts at the accurate determination of the dihedral angles in both the hydrogen-bonded and non-hydrogen-bonded groups of the conformers failed, and we chose to fix them at the theoretical values shown in Table 4 for the HF/6-31G* calculations. (The refined values of these angles were actually not much different from the calculated ones, but they had very large standard deviations. Fortunately, the values of the other parameters were only marginally influenced by reasonable changes in the dihedral angles.)

In the first type of model (model B), the relative amounts of the conformers within both the hydrogen-bonded (FB1 and FB2) and the non-hydrogen-bonded (FB3−FB10) groups were kept at the values determined by the MP2/6-31G* calculations; these relative amounts are seen in Figure 4. The bond distances, the heavy-atom bond angles, and the C−C−H angles in both groups were tied to those of FB1 by the theoretical differences; the C−O−H bond angle was kept at the theoretical value. The fit to the experiment given by model B is certainly not bad, but it has a few small, disquieting features which can be seen in its RD-difference curve in Figure 3. An example is the small peak in this curve at about 3.8 Å, which implies an insufficient contribution from distances near this value, presumably those between heavy atoms. As is seen from Figure 4, the hydrogen-bonded group has no distance near 3.8 Å, whereas all of the conformers except the $G^+G^+G^+a$ in the non-hydrogen-bonded group have at least one such distance. Figure 4 also shows that the 3.8 Å peak is due to X(1)···Y(4) skeletal distances arising from anti dihedral angles.

The problems with model B led us to formulate a second type of model (model A) intended to remedy the defects of the first by inclusion of more of these forms than is suggested by theory. Conformers FB3, FB5, FB8, and FB9 have one anti dihedral skeletal angle (Figure 4), FB6 and FB10 have two such

TABLE 4: Theoretical Values of Bond Lengths (Å) and Valence and Dihedral Angles (deg) in the Conformers of 4-Fluorobutan-1-ol[a]

		$r(C_1-C_6)$			$r(C_1-C_2)$			$r(C_2-C_3)$			$r(C_3-C_4)$			$r(C_4-F_5)$		
	conformer	HF	MP2	DFT	HF	MP2	DFT	HF	MP2	DFT	HF	MP2	DFT	HF	MP2	DFT
FB1	G$^-$G$^+$G$^-$g	1.340	1.425	1.418	1.529	1.526	1.536	1.535	1.531	1.539	1.516	1.513	1.520	1.386	1.418	1.413
FB2	G$^+$G$^-$G$^-$g$^+$	1.401	1.425	1.420	1.529	1.528	1.538	1.534	1.530	1.539	1.515	1.512	1.519	1.384	1.416	1.410
FB3	G$^+$AG$^-$a	1.405	1.430	1.426	1.518	1.515	1.522	1.529	1.525	1.533	1.514	1.511	1.518	1.376	1.404	1.397
FB4	GGGa	1.406	1.432	1.427	1.520	1.518	1.525	1.532	1.530	1.537	1.515	1.512	1.519	1.377	1.406	1.399
FB5	G$^-$AG$^-$a	1.404	1.429	1.425	1.519	1.516	1.524	1.529	1.525	1.533	1.515	1.512	1.519	1.374	1.402	1.396
FB6	G$^-$AAa	1.403	1.428	1.423	1.518	1.516	1.523	1.529	1.526	1.532	1.515	1.513	1.520	1.373	1.402	1.395
FB7	AAAa	1.403	1.428	1.423	1.518	1.516	1.524	1.529	1.527	1.533	1.519	1.513	1.520	1.372	1.401	1.393
FB8	AG$^+$G$^-$a	1.406	1.431	1.427	1.520	1.51 7	1.525	1.533	1.530	1.537	1.518	1.517	1.523	1.377	1.406	1.398
FB9	G$^+$G$^-$Aa	1.406	1.431	1.426	1.521	1.519	1.526	1.532	1.528	1.536	1.515	1.513	1.520	1.376	1.405	1.399
FB10	AAG$^-$a	1.403	1.429	1.424	1.525	1.524	1.532	1.529	1.526	1.533	1.515	1.513	1.519	1.372	1.400	1.393

		$\angle(O_6-C_1-C_2)$			$\angle(C_1-C_2-C_3)$			$\angle(C_2-C_3-C_4)$			$\angle(C_3-C_4-F_5)$		
	conformer	HF	MP2	DFT	HF	MP2	DFT	HF	MP2	DFT	HF	MP2	DFT
FB1	G$^-$G$^+$G$^-$g	113.7	113.0	113.9	116.8	116.1	116.6	116.6	116.0	116.8	110.4	109.9	110.8
FB2	G$^+$G$^-$G$^-$g$^+$	112.9	112.2	113.0	115.3	114.0	114.7	115.5	115.0	115.7	110.1	110.0	110.5
FB3	G$^+$AG$^-$a	108.6	107.4	108.2	113.1	112.5	113.2	112.7	112.2	112.8	110.0	109.4	110.0
FB4	GGGa	108.8	107.6	108.5	114.7	113.4	114.4	114.3	113.0	113.9	110.1	109.6	110.2
FB5	G$^-$AG$^-$a	108.7	107.4	108.3	113.2	112.7	113.4	112.8	112.3	112.9	110.0	109.4	110.1
FB6	G$^-$AAa	108.0	107.2	107.9	112.6	112.4	112.9	112.9	112.3	112.9	109.9	109.2	109.9
FB7	AAAa	107.9	107.1	107.8	112.6	112.3	112.7	112.3	111.9	112.4	109.5	109.4	109.8
FB8	AG$^+$G$^-$a	109.0	107.8	108.8	115.6	115.0	115.6	115.3	114.9	115.1	108.3	108.0	108.6
FB9	G$^+$G$^-$Aa	107.1	106.2	107.0	115.1	114.5	114.9	115.4	114.7	115.3	110.5	109.9	110.7
FB10	AAG$^-$a	113.0	112.6	113.3	113.0	112.4	113.1	112.3	112.2	112.7	109.6	109.5	109.9

		$\angle(C_2-C_3-C_4-F)$			$\angle(C_1-C_2-C_3-C_4)$			$\angle(O_6-C_1-C_2-C_3)$			$\angle(C_2-C_1-O_6-H_7)$		
	conformer	HF	MP2	DFT	HF	MP2	DFT	HF	MP2	DFT	HF	MP2	DFT
FB1	G$^-$G$^+$G$^-$g	−74.0	−75.7	−73.5	63.2	58.5	63.0	−76.1	−74.6	−74.6	75.7	78.4	71.3
FB2	G$^+$G$^-$G$^-$g$^+$	71.1	71.7	70.0	−55.7	−55.5	−55.2	−52.0	−51.4	−49.4	81.2	80.1	77.8
FB3	G$^+$AG$^-$a	60.5	59.4	59.6	180.2	180.6	180.3	−62.2	−61.0	−61.9	180.2	180.0	177.7
FB4	GGGa	54.0	52.1	53.4	55.7	51.0	54.8	54.4	53.1	54.5	178.9	179.3	180.4
FB5	G$^-$AG$^-$a	−60.1	−59.1	−59.6	181.5	180.9	179.0	−61.7	−60.4	−61.8	179.7	179.3	178.4
FB6	G$^-$AAa	−61.7	−60.6	−61.0	178.6	178.1	177.7	179.0	179.1	179.2	178.7	178.7	178.8
FB7	AAAa	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
FB8	AG$^+$G$^-$a	171.5	170.8	173.8	68.5	65.6	68.9	−68.8	−69.4	−68.9	179.1	177.7	177.0
FB9	G$^+$G$^-$Aa	68.6	68.7	67.4	−65.9	−62.6	−66.0	−172.6	−171.1	−173.6	−176.7	−176.1	−176.3
FB10	AAG$^-$a	179.8	180.1	180.0	178.8	178.0	177.4	−60.4	−58.5	−59.1	180.0	176.8	176.1

[a] Basis set was 6-31G* in all cases.

angles, and FB7 has three. Although it is likely that all of the conformers are present, a study of the torsion-dependent distances suggested that the makeup of the second model could be simplified by including only one or two forms to represent each of the three angle groups. Grounds for such an assumption are that conformers with the same number of anti dihedral angles have roughly similar distance distributions. Conformers FB3 and FB5 were taken to represent the group with one anti dihedral angle when tests showed that the combination was better than either one alone. FB6 and FB7 were chosen to represent the groups with two and three anti angles, respectively. FB3 and FB5 differ mainly in the positions of the OH and F groups that are either on the same side (FB5) or on opposite sides (FB3) of the plane of the carbon skeleton. Because these two functional groups are too far away to interact strongly, it seemed reasonable to incorporate FB3 and FB5 in equal amounts. The hydrogen-bonded group of conformers in this second model type was represented by FB1 and FB2 as before in relative amounts determined by test refinements. As Figure 3 shows, the fit provided by model A is considerably better than that from model B.

The vibrational amplitudes in all of the refinements were refined in groups defined largely by regions or peaks of the RD curve in which the associated interatomic distances were found. Most of the vibrational amplitudes within such groups have calculated amplitudes of similar magnitude. The groups may be identified from Tables 3 and 6.

Refinement Results. The parameter values obtained for model B are found in Table 5. Models of type A are much more flexible than the model B types, and it was first necessary to establish the relative amounts of FB3 + FB5, FB6, and FB7 in the non-hydrogen-bonded group and those of FB1 and FB2 in the hydrogen-bonded group that gave the best fit. These relative amounts were studied systematically in trial refinements. The best results were obtained with about 75% FB1 and 25% FB2 in the hydrogen-bonded group and 20% FB3 + FB5, 50% FB6, and 30% FB7 in the non-hydrogen-bonded group. Refinement results for this model are listed in Table 5 as model A.

The results of our investigation of the 4-FB system are found in Tables 5 and 6. The values of Table 5 are weighted averages (i.e., the contributions of the conformers were weighted according to the conformational compositions). The entries of this table are limited to bond distances and bond angles because the averaging of gauche and anti dihedral angles is meaningless. The data of Table 6 deals only with the important H-bonded conformer FB1 and is thus more detailed. Values of the parameters in the other conformers may be deduced from those in Table 6 by applying the differences available from the values of Table 4. Model A is our preferred model because of the better fit to the experimental data that it provides; this is evident from the value of the quality-of-fit factor R (Table 5) which is significantly smaller for model A than for model B and from the difference curves of Figure 3 which show a better match between the experiment and the theory for model A. Figure 3 also

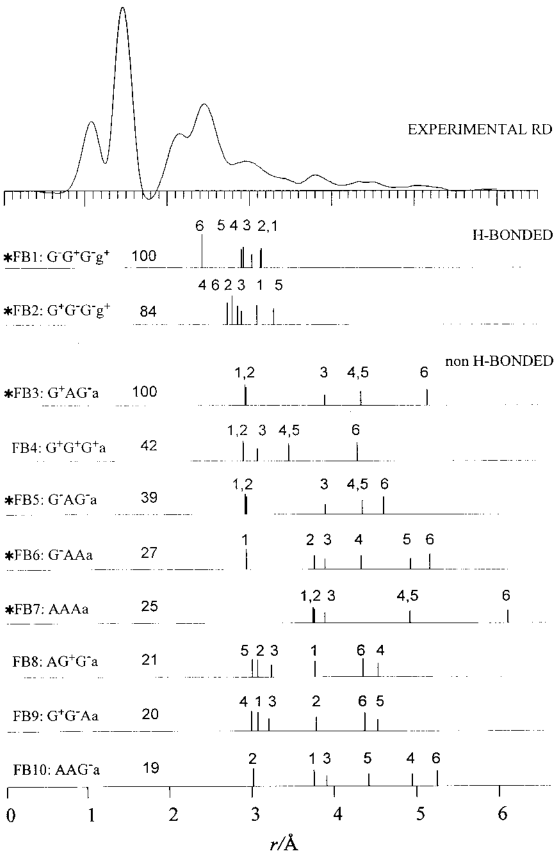

Figure 4. Distribution of torsion-sensitive distances in the 10 most abundant conformers. Distance identification: (1) $r(C_2\cdots F)$, (2) $r(C_3\cdots O)$, (3) $r(C_1\cdots C_4)$, (4) $r(C_1\cdots F)$, (5) $r(C_4\cdots O)$, (6) $r(O\cdots F)$. For each conformer the lengths of the vertical bars are proportional to the weights of the distances Z_iZ_j/r_{ij}. Starred conformers comprise model A; all of the conformers comprise model B (see text). The *relative* abundances in the hydrogen-bonded group (FB1 and FB2) and non-hydrogen-bonded group (FB3−FB10) are listed by the conformer labels.

shows the relative contributions to each model from the hydrogen-bonded and non-hydrogen-bonded groups. The correlation matrix for the parameters of model A is given in Table 7.

Discussion

The most important result of our study of gaseous 4-FB is the finding of substantial amounts of conformers with internal O−H···F hydrogen bonds. Although there is no doubt that non-hydrogen-bonded conformers also contribute significantly to the conformational mixture, neither is there doubt that the hydrogen-bonded conformers play a very important role; we were unable to obtain a good fit to the experiment with the models that did not contain substantial amounts of each. For a large number of models, the refined values of the total contribution of the hydrogen-bonded conformers was found to lie in the range of 48−62%. At 48(14)% in our preferred model A, the contribution of the hydrogen-bonded forms is larger than that found for butane-1,4-diol[1] of 40(4)% at 144 °C. The difference seems to suggest that the energy of the O−H···F hydrogen bond may be larger than that of the O−H···O one, but the uncertainties on the amounts and the host of (different) approximations applied in each analysis make such a conclusion very risky.

The contribution of the hydrogen-bonded conformers to the mixture comprising 4-FB, predicted at 61% from the MP2/6-31G* optimizations, is in good agreement with the experimental result for our model A. This is not the case for the results from the HF theory, which predicts that hydrogen-bonded conformers should be present only to the extent of about 17%. Clearly, the conformational stabilization of 4-FB resulting from O−H···F hydrogen bonding is underestimated by the latter with the 6-31G* basis. Although the matter has not been checked, results from other work suggest that these predictive failures likely are due to the small basis set rather than to the theoretical levels.

The theoretical results for the relative amounts of each hydrogen-bonded conformer are also interesting. All three sets of calculations led to a lower energy for FB1 than for the alternative FB2. The calculated energy difference between the two forms is modest at the HF and MP2 levels of theory, but as Table 1 shows, the B3LYP calculations predict about 3 times as much FB1. This theoretical prediction of the FB1/FB2 ratio at the B3LYP level received support on the experimental side when a systematic variation of the ratio led to a best fit that agreed with the theoretical prediction. The reason for the greater stability of FB1 is reflected by the structures of the O−H···F groups: the O···F distance in FB1 is shorter than that in FB2 (2.46 vs 2.71 Å; the van der Waals distance is about 2.75 Å), and the O−H···F angle is larger (151° vs 133°). The dominant role played by FB1 (i.e., the $G^-G^+G^-g^+$ conformer) in the hydrogen-bonded group of 4-FB is consistent with the observation that the hydrogen-bonded conformers in butane-1,4-diol[2] are best represented by the same form (or its mirror image) for the $-OB(CH_2)_4-O-H$ moiety.

Bond Lengths and Vibrational Amplitudes. Table 8 shows the values of the bond distances and bond angles for 4-FB and the related compounds 1,4-difluorobutane and 1,4-butanediol. The average C−C bond in the two compounds with internal hydrogen bonding, 4-FB and 1,4-butanediol, is found to be about 0.01 Å longer than that in 1,4-difluorobutane where hydrogen bonding is absent. The average length of the C−F bond in 4-FB, like the average C−C bond, is again slightly greater than that in non-hydrogen-bonded 1,4-difluorobutane. These observations may be partly understood by an analysis of the theoretical results. Although ab initio bond-length values are not available for 1,4-butanediol, they have been calculated for 1,4-difluorobutane.[2] It is seen that, for 4-FB itself (Table 4), the average C−C bond length is increased mainly by contributions from the central bond (C_2-C_3) in all of the non-hydrogen-bonded conformers and by contributions from the bond nearest the OH group (C_1-C_2) in the hydrogen-bonded conformers FB1 and FB2. In 1,4-difluorobutane, the central C_2-C_3 bond is also the longest (by about 0.015 Å) throughout the list of conformers, but the C_1-C_2 bond is not elongated as in 4-FB. The average C−C bond in 4-FB is thus longer than it is in 1,4-difluorobutane because about 50% of the conformational weight accrues to the hydrogen-bonded group of its conformers. A similar picture applies to the C−F bonds in that the theoretical values of these bonds in the hydrogen-bonded conformers of 4-FB are slightly larger than those in conformers of the non-hydrogen-bonded group, which are like those in 1,4-difluorobutane. It is not surprising that the C−O bonds, which occur only in hydrogen-bonded 4-FB and 1,4-butanediol, are experimentally the same because both the structures of the molecules and the strengths of the O−H···O and O−H···F hydrogen bonds are similar.

The experimental vibrational amplitudes (Table 3) of the bond distances in 4-FB are in good agreement with the calculated ones, but those for conformationally similar 1,4-butanediol were found to be 0.01−0.02 Å larger than calculated. The differing levels of agreement for these molecules probably reflect the differing assumptions applied to the structural analyses. For the 1,4-butanediol study, the various bond lengths were assumed

TABLE 5: 4-Fluorobutan-1-ol. Some Average Bond Lengths and Bond Angles[a]

	bond lengths (r_a/Å)			bond angles ($\angle_a$/deg)	
parameter	model A[b]	model B[c]	parameter	model A[b]	model B[c]
C−O	1.430(5)	1.430(6)	C−O−H	[106.1]	[106.1]
C_1-C_2	1.529(2)	1.528(2)	C−C−O (H-bond)	112.3(55)	111.8(45)
C_2-C_3	1.537(2)	1.537(2)	C−C−O (non-H-bond)	108.2(45)	108.9(45)
C_3-C_4	1.520(2)	1.521(2)	$C_1-C_2-C_3$	112.5(33)	112.9(39)
C−F	1.401(5)	1.402(7)	$C_2-C_3-C_4$	112.4(32)	112.7(37)
O−H	[0.947]	[0.947]	C−C−F	109.8(12)	111.2(59)
C−H	1.102(4)	1.103(5)			
compositions and agreement factors					
% (H-bond)	48.5 } (140)	22.7 } (196)			
% (non-H-bond)	51.6	77.4			
R^d	0.072	0.086			

[a] Values are weighted averages with weights according to conformational composition. Quantities in parentheses are estimated 2σ uncertainties; those in square brackets were assumed. [b] Preferred model containing six conformers. [c] Contains 10 conformers. [d] Goodness of fit factor. $R = [\Sigma_i w_i \Delta_i^2/\Sigma_i I_i(\text{obsd})^2]^{1/2}$ where $\Delta_i = I_i(\text{obsd}) - I_i(\text{calcd})$ with $I_i = s_i I_i$.

TABLE 6: 4-Fluorobutan-1-ol. Some Interatomic Distances (*r*/Å), Bond Angles (∠/deg), and RMS Amplitudes of Vibration (*l*/Å) for the Principal Hydrogen-Bonded Conformer, $G^-G^+G^-g^+$ (FB1)[a]

	model A[b]			model B				model A[b]			model B		
parameters[c]	r_a; $\angle_a$	l		r_a; $\angle_a$	l		parameters	r_a; $\angle_a$	l		r_a; $\angle_a$	l	
C−O	1.428(5)	0.052	(3)	1.425(6)	0.035	(4)	C···H	2.14−2.20(20)	0.090(13)		2.15−2.22(23)	0.090(18)	
C_1-C_2	1.533(3)	0.057		1.535(3)	0.058		$C_1\cdots C_3$	2.556(12)	0.080	(8)	2.535(64)	0.074	(8)
C_2-C_3	1.540(3)	0.057		1.541(3)	0.058		$C_2\cdots C_4$	2.542(12)	0.080		2.521(64)	0.074	
C_3-C_4	1.520(3)	0.056		1.522(3)	0.057		$C_3\cdots F$	2.397(27)	0.076		2.488(115)	0.070	
C−F	1.408(6)	0.052		1.410(7)	0.053		$C_2\cdots O$	2.463(29)	0.077		2.457(173)	0.070	
O−H	[0.947]	0.072	(5)	[0.947]	0.072	(5)	$C_1\cdots C_4$	3.083(29)	0.155	(25)	3.026(164)	0.187	(39)
C−H	1.102(4)	0.081		1.103(5)	0.081		$C_2\cdots F$	3.067(33)	0.139		3.146(111)	0.172	
C−O−H	[106.1]			[106.1]			$C_3\cdots O$	3.159(31)	0.139		3.126(193)	0.171	
C−C−O	112.5(20)			112.1(120)			$C_1\cdots F$	2.882(51)	0.210		2.925(188)	0.242	
$C_1-C_2-C_3$	112.5(8)			111.0(43)			$C_4\cdots O$	2.974(43)	0.223		2.889(277)	0.255	
$C_2-C_1-H_8$	109.5(16)			110.5(18)			O···F	2.463(49)	0.156		2.416(238)	0.189	
C−C−F	109.8(18)			116.1(85)									

[a] Quantities in parentheses are estimated 2σ uncertainties; those in square brackets were assumed. All dihedral angles are set equal to those from optimized HF/6-31G* calculations (Table 4). [b] Preferred model. [c] For atom numbering, see Figure 1.

TABLE 7: Correlation Matrix (×100) for Parameters of 4-Fluorobutan-1-ol[a]

		$100\sigma_{LS}$[b]	r_1	r_2	r_3	r_4	$\angle_5$	$\angle_6$	$\angle_7$	$\angle_8$	l_9	l_{10}	l_{11}	l_{12}	l_{13}	l_{14}	l_{15}	l_{16}	$\alpha_{\text{H bond}}$
1	r(C−O)	0.17	100																
2	$r(C_1-C_2)$	0.07	−14	100															
3	r(C−F)	0.19	−76	42	100														
4	r(C−H)	0.14	−4	5	3	100													
5	∠C−C−O	71.0	−17	16	25	3	100												
6	$\angle C_1-C_2-C_3$	27.7	2	−16	−7	14	−37	100											
7	$\angle C_2-C_1-H_8$	57.1	−6	1	11	−13	12	33	100										
8	∠C−C−F	64.1	5	16	<1	15	−38	−5	−1	100									
9	l(C−H)	0.13	<1	19	8	−1	−3	6	4	−1	100								
10	l(C−C)	0.09	−31	7	30	11	6	12	7	3	13	100							
11	$l(C_1\cdots C_3)$	0.27	−1	3	−1	−1	−28	−32	−48	49	4	10	100						
12	$l(C_1\cdots C_4)$	0.86	2	−18	−12	−5	−11	1	30	−14	2	<1	−33	100					
13	l(C···H)	0.43	3	12	−1	19	−4	−26	−85	13	5	8	54	−26	100				
14	$l(C_1\cdots C_4)^c$	0.95	−8	31	25	5	28	−8	4	23	<1	10	<1	−25	3	100			
15	$l(C_1\cdots F)^c$	3.35	−6	15	14	7	14	9	20	10	3	8	−9	−15	−15	8	100		
16	$l(F\cdots O)^c$	20.7	−1	3	3	<1	4	−3	−2	2	−1	<1	1	−2	2	1	17	100	
17	$\alpha_{\text{H bond}}{}^d$	5.0	12	−49	−39	−11	−39	6	−11	−38	<1	−13	3	42	<1	−64	−36	−7	100

[a] For preferred model A, Table 6. [b] Standard deviations from least-squares refinement. Distances (Å), angles (deg). [c] Conformers containing A-type distances. [d] Mole fraction of H-bonded conformers (FB1 + FB2).

to be the same in all of the conformers, while in 4-FB, the bond-length differences from ab initio calculations have been incorporated into the GED model. In any case, the accuracy of the measured amplitudes must be viewed with caution because the results depend heavily on the many assumptions made to allow their refinement. These include the amplitude differences imposed on the members of the amplitude groups and the arbitrary makeup of the groups themselves.

Matters are only slightly different for the amplitudes of the nonbond distances. All of the values except those connected to the RD peak at 5.1 Å are in satisfactory agreement with the theoretical prediction, but the experimental amplitudes for distances under this peak are nominally much larger. The distances contributing to the area of the RD peak at about 5.1 Å from several conformers are the following: FB3, $F_5\cdots O$; FB6, $C_4\cdots O$ and $F_5\cdots O$; FB7, $C_1\cdots F$ and $C_4\cdots O$. When the theoretical amplitudes for these distances, which range between 0.0676 and 0.2043 Å, are used in the calculations of theoretical RD curves, the peak at 5.1 Å is considerably sharper than that seen experimentally. The large experimental amplitudes for the

TABLE 8: Bond Lengths (Å) and Bond Angles (deg) for 4-Fluorobutan-1-ol and Some Related Compounds[a,b]

parameter	1,4-difluorobutane	4-fluorobutan-1-ol	1,4-butanediol
$r(\mathrm{C-H})$	1.106(3)	1.108(4)	1.116(12)
$r(\mathrm{C_1-C_2})$	1.516 (2)[b]	1.531 (3)[b]	1.531 (2)[c]
$r(\mathrm{C_2-C_3})$	1.532	1.539	1.531
$r(\mathrm{C_3-C_4})$	1.516	1.522	1.531
$r(\mathrm{C-F})$	1.398(2)	1.40110(5)	C
$r(\mathrm{C-O})$	C	1.432(5)	1.429(2)
$\angle\mathrm{C-C-O}$	C	110.1(43)	110.9(10)
$\angle\mathrm{C-C-F}$	110.1(19)	109.7(12)	C
$\langle\angle\mathrm{C-C-C}\rangle$	113.8(22)	112.4(31)	114.3(22)
$\langle r(\mathrm{C-C})\rangle$	1.521(2)[d]	1.531(3)[d]	1.530(2)
ref	2	this work	1

[a] Values are conformational averages. Distances, r_g; angles, $\angle_g$. [b] The magnitudes of the C−C distances were held at the theoretical differences. [c] Distances were assumedequal. [d] Uncertainties do not reflect the error in calculated differences.

distances in this region that are required to give good agreement are not easily understood, but we believe they are due to the inadequacies in our models of the system structure. Fortunately, the geometrical parameter values of the models were not appreciably influenced by the changes in these amplitude values, but the use of refined values for distances in the 5.1 Å region led to a change, still not significant as judged by the associated uncertainties, in the percentage of hydrogen-bonded conformers from 58.3 to 48.5%.

Bond Angles. As Table 8 shows, the experimental value of the average C−C−C angle in 4-FB is about the same as it is in 1,4-difluorobutane, where hydrogen bonding does not exist, and somewhat smaller than that in butane-1,4-diol, where it does. These comparative values are mildly surprising. It seems likely that the reason the 4-FB value is smaller than that in butane-1,4-diol lies in the structural constraints applied to our model A, where the angles in the non-hydrogen-bonded conformers were fixed at theoretical values instead of being tied to those in conformer FB1. However, any error in this angle value would likely lie within the range of the attached uncertainty.

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Supporting Information Available: Table of the averaged experimental molecular intensities from each camera distance. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) This arrangement was one of timing and convenience. Much of the work in setting up the models was completed before it was decided to carry out the calculations at higher theoretical levels. In any case, the bond-length and bond-angle differences are not much different for calculations at different theoretical levels.

(16) Because of the complexity of the system and the many approximations being applied, it was deemed of no consequence whether the geometry of the conformers was calculated on the basis of r_a or r_α parameters; it was therefore decided to use the r_a approach, ignoring corrections for shrinkage effects.