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# Structure and conformation of 1,4-difluorobutane as determined by gas-phase electron diffraction, and by molecular mechanics and *ab initio* calculations<sup>☆</sup>

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## Abstract

Gas-phase electron diffraction data at 23°C together with molecular mechanics (MM3) and *ab initio* (HF/6-31G\*, GAUSSIAN 86) calculations have been used to determine the structure and conformations of 1,4-difluorobutane. The object was to ascertain whether effects similar to the gauche effect in 1,2-difluoroethane, which serves to stabilize the gauche form with the fluorine atoms in close proximity, could also operate in 1,4-difluorobutane. It was found both theoretically and experimentally that the proportion of those conformers having close fluorine atoms was small, implying the absence of effects similar to the gauche effect. The conformational composition estimated from the theoretical calculations is in good agreement with the experimental data. The experimental electron diffraction results constrained by assumptions drawn from the theoretical calculations, ED/MM3 [ED/*ab initio*], for the principal distances ( $r_g/\text{\AA}$ ) and angles ( $\angle_\alpha/\text{deg}$ ) with estimated  $2\sigma$  uncertainties are as follows:  $r(\text{C-H}) = 1.105(3)$  [1.106(3)],  $r(\text{C-F}) = 1.398(2)$  [1.398(2)],  $r(\text{C}_1-\text{C}_2) = 1.513(2)$  [1.516(2)],  $r(\text{C}_2-\text{C}_3) = 1.537(2)$  [1.532(2)],  $\angle\text{F-C-C} = 110.9(3)$  [111.1(3)],  $\angle\text{C-C-C} = 112.9(4)$  [112.9(4)], and  $\angle\text{H-C-H} = 100(3)$  [100(3)].

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## 1. Introduction

The relative stabilities of the rotational conformers of 1,2-disubstituted ethanes in the gas phase are highly dependent on the electronegativities of the substituents and on whether they comprise a donor–acceptor pair for the formation of internal hydrogen bonds. Thus, the anti forms of 1,2-dichloro- and 1,2-dibromoethane are more stable than the gauche [1], whereas in

1,2-difluoroethane [2], glycol [3], ethylenediamine [4], 2-fluoro- [5] and 2-chloroethanol [6] the gauche form is predominant. The effect tending to stabilize the gauche form of 1,2-difluoroethane, where internal hydrogen bonding is non-existent and the substituent electronegativities are very high, has been termed the “gauche effect” [7].

In addition to determining the molecular structures of the components of gaseous mixtures, gas-phase electron diffraction (GED) provides measurements of the composition of the mixtures, and from experiments done at different temperatures the energy and entropy differences of the components may then be determined. In cases where internal hydrogen bonding exists, the

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<sup>☆</sup> Dedicated to Professor Yonezo Morino on his 87th birthday.

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energy of the bond will be a major contributor to the energy difference of the conformers. A chemical question of interest concerns the relative importance of hydrogen bonding and of the gauche effect when *both* may play a role — as in glycol and 2-fluoroethanol. In an effort to obtain experimental evidence that bears on this problem we are carrying out some GED studies of 1,4-disubstituted *n*-butanes: the idea is that by separating the two functional groups the gauche effect would likely not be operational, and the “coiled up” forms that position these groups for mutual interaction would owe their stabilities in good part to the formation of internal hydrogen bonds. An earlier GED study of 4-chlorobutanol [8] suggested that internal hydrogen bonding was present, as does a recent one of 1,4-butanediol [9].

If the OH groups in 1,4-butanediol are replaced by fluorine atoms, i.e. by substituents of comparable size and electronegativity, one obtains 1,4-difluorobutane (Fig. 1), a molecule which in many ways is similar to 1,4-butanediol but one in which the possibility of internal hydrogen bonding has been removed. We decided to undertake a GED investigation of this molecule. The results would remove any doubt about the possible operation of a gauche effect when the functional groups are separated, and a comparison of the results for 1,4-difluorobutane with 1,4-butanediol should provide valuable information about effects such as internal hydrogen bonding which are important for establishing the conformational composition of molecules like these.

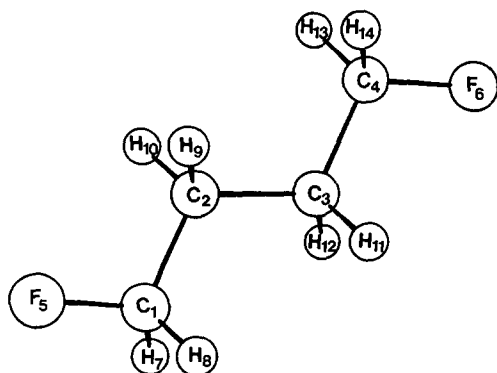


Fig. 1. Diagrams of the AAA conformer of 1,4-difluorobutane with atom numbering.

Some information about the conformation of 1,4-difluorobutane is available. Matsuura et al. [10] concluded from IR and Raman spectra that the molecule has a center of symmetry in the solid state; normal coordinate calculations indicated it to be the  $C_i$  and not the  $C_{2h}$  form. In the liquid state many conformers were present. No study of 1,4-difluorobutane in the gas phase has yet been published.

## 2. Experimental and data reduction

1,4-Difluorobutane was prepared as described earlier [11] and purified by preparative GC (purity > 99%). Diffraction photographs were made in the Oregon State apparatus using an  $r^3$  sector and  $8 \times 10''$  Kodak projector slide plates (medium contrast), developed for 10 min in D-19 developed diluted 1:2. The nominal nozzle-to-plate distances were 750 mm (long camera) and 300 mm (middle camera) and the nominal electron wavelength was  $0.048 \text{ \AA}$  (calibrated in separate experiments with  $\text{CS}_2$ ;  $r_a(\text{C}=\text{S}) = 1.577 \text{ \AA}$  and  $r_a(\text{S} \cdot \text{S}) = 3.109 \text{ \AA}$ ). Exposure times of 90–180 s were used with beam currents of  $0.35\text{--}0.46 \mu\text{A}$ . The ambient apparatus pressure during experiments was  $(1.1\text{--}1.4) \times 10^{-5}$  Torr. The nozzle temperature was  $23^\circ\text{C}$  and the sample reservoir was kept at  $0^\circ\text{C}$ . Four plates from each of the two camera distances were used in the analysis. The ranges of data were  $2.00 \leq s/\text{\AA}^{-1} \leq 15.50$  and  $7.00 \leq s/\text{\AA}^{-1} \leq 36.75$ , and the data interval was  $\Delta s = 0.25 \text{ \AA}^{-1}$ . The procedures for obtaining the total scattered intensities ( $s^4 I_t(s)$ ) and the molecular intensities ( $s I_m(s)$ ) have been described elsewhere [12–14]. In order to reduce the level of noise in the data, the middle camera plates were traced twice and the results averaged. Curves of the intensity data superimposed on their computer generated backgrounds are shown in Fig. 2; the data are available from the authors. Fig. 3 shows the final experimental radial distribution (RD) curve calculated in the usual way from the modified molecular intensity  $I'(s) = s I_m(s) Z_C^2 A_C^{-2} \cdot \exp(-0.002s^2)$ , where  $A = s^2 F$  and  $F$  is the absolute value of the complex electron-scattering

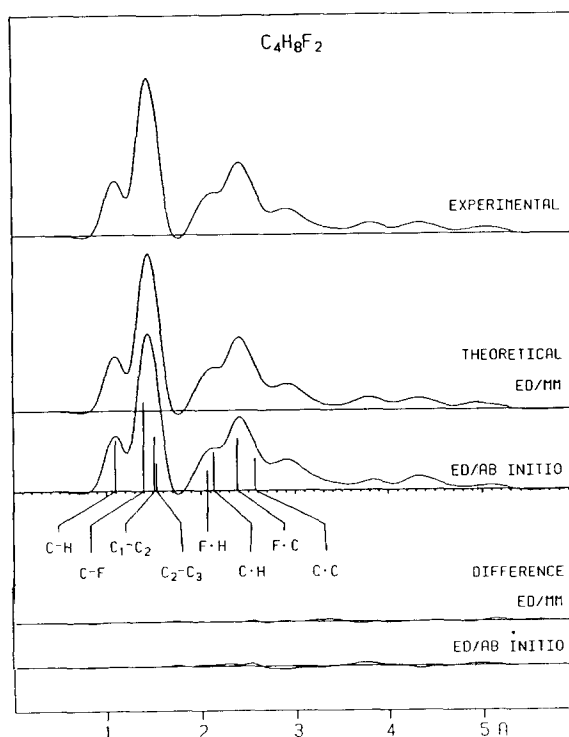
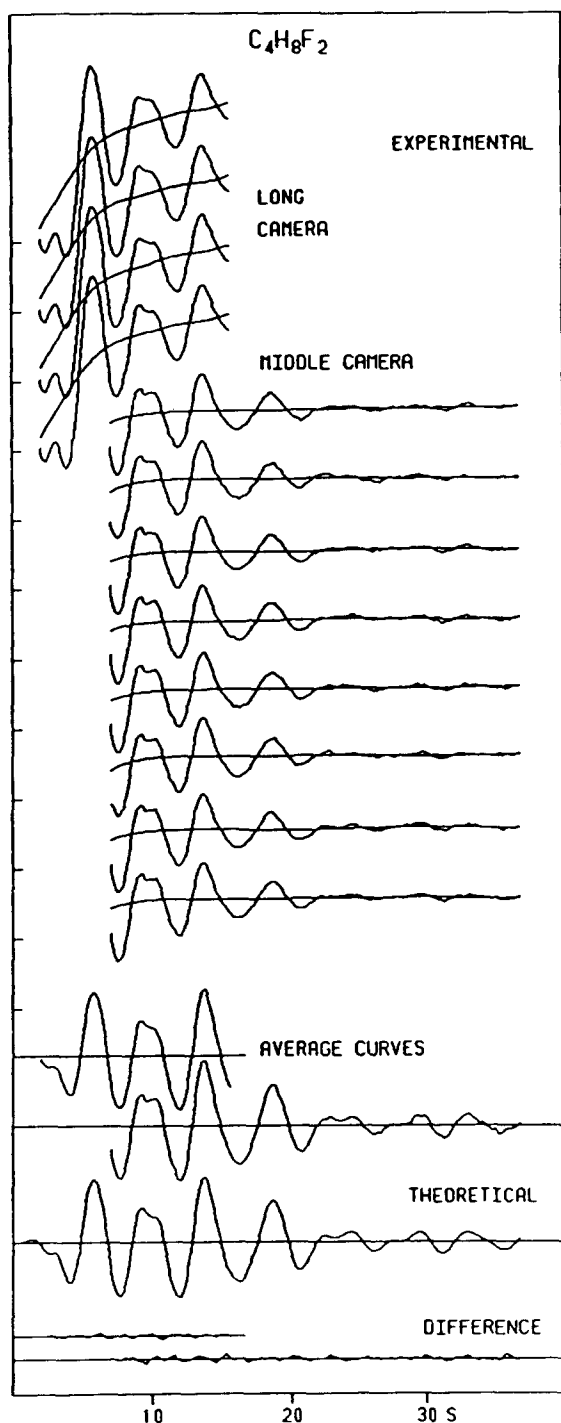


Fig. 3. Radial distribution curves for 1,4-difluorobutane. The experimental curve was calculated from the composite of the two average intensity curves with use of theoretical data for the region  $0 \leq s/\text{\AA}^{-1} \leq 1.75$ , and  $B/\text{\AA}^2 = 0.0020$ . The theoretical curves are calculated from the two sets of parameter values given in Table 3. The vertical lines indicate the interatomic distances which do not change with the C–C torsion angles; lengths are proportional to the distance weights.

amplitude. The scattering amplitudes and phases were taken from tables [15].

### 3. Theoretical calculations

Gaseous 1,4-difluorobutane may in principle exist as a mixture of up to ten distinct conformers with similar bond distances and bond angles. Electron diffraction with its limited resolving power can provide only average values for these parameters. In order to obtain more reliable

Fig. 2. Intensity curves for 1,4-difluorobutane. The  $s^4 I_t$  experimental curves are shown magnified seven times with respect to the backgrounds on which they are superimposed; each of the four middle distance plates was traced twice. The average curves are  $s(s^4 I_t - \text{bkgd})$ . The theoretical curve is calculated from parameter values given in Table 3.

structural results, as well as information about the conformational composition of the gaseous mixture, we have carried out molecular mechanics and ab initio calculations to provide information to be incorporated as constraints in our electron diffraction analysis.

Assuming local three-fold torsional potentials at each carbon atom in 1,4-difluorobutane, there are  $3^3 = 27$  different conformers for 1,4-difluorobutane of which several are enantiomers with identical interatomic distances. If we use the symbols A,  $G^+$  and  $G^-$  to represent torsion angles of 180, +60 and  $-60^\circ$  for torsion about a C–C bond, the ten groups of distinguishable conformers and their multiplicities are the following. AAA, 1 (illustrated in Fig. 1); AAG, 4 ( $AAG^+$ ,  $AAG^-$ ,  $G^+AA$ ,  $G^-AA$ );  $G^+AG^-$ , 2 ( $G^+AG^-$ ,  $G^-AG^+$ );  $G^+AG^+$ , 2 ( $G^+AG^+$ ,  $G^-AG^-$ ); AGA, 2 ( $AG^+A$ ,  $AG^-A$ );  $AG^+G^+$ , 4 ( $AG^+G^+$ ,  $AG^-G^-$ ,  $G^+G^+A$ ,  $G^-G^-A$ );  $AG^+G^-$ , 4 ( $AG^+G^-$ ,  $AG^-G^+$ ,  $G^+G^-A$ ,  $G^-G^+A$ );  $G^+G^+G^+$ , 2 ( $G^+G^+G^+$ ,  $G^-G^-G^-$ );  $G^+G^+G^-$ , 4 ( $G^+G^+G^-$ ,  $G^-G^-G^+$ ,  $G^-G^+G^+$ ,  $G^+G^-G^-$ );  $G^+G^-G^+$ , 2 ( $G^+G^-G^+$ ,  $G^-G^+G^-$ ). The structure of each of these conformers was optimized by molecular mechanics (MM3 [16]) and by ab initio methods (HF/6-31G\*; GAUSSIAN 86 [17]). The results for the relative energies, and for the corresponding amounts of the conformers determined on the basis of Boltzmann weighting, are shown in Table 1.

Table 1

Relative energy, multiplicity and population for the different conformers of 1,4-difluorobutane at 298 K determined from molecular mechanics (MM3) and ab initio (6-31G\*) calculations

Conformer <sup>a</sup>	Mult.	E <sup>b</sup>		MM3 (%)	Ab initio (%)
		MM3 <sup>b</sup>	6-31G*		
AAA	1	0.17	1.35	9.5	2.0
AAG	4	0.30	1.04	29.5	13.0
$G^+AG^-$	2	0	0	24.5	37.5
$G^+AG^+$	2	0.36	0.57	13.6	14.3
AGA	2	1.40	2.72	2.3	0.3
$AG^+G^+$	4	1.39	2.22	4.7	1.8
$AG^+G^-$	4	1.23	1.13	6.1	11.1
$G^+G^+G^+$	2	0.82	0.71	6.2	11.1
$G^+G^+G^-$	4	1.59	1.29	3.4	8.5
$G^+G^-G^+$	2	2.83	2.72	0.2	0.4

<sup>a</sup> The letters stand for anti or gauche, the superscripts for a clockwise (+) or an anticlockwise (–) rotation. The first letter indicates the conformation of the  $F_5-C_1-C_2-C_3$  group, the second the  $C_1-C_2-C_3-C_4$  group, and the last the  $C_2-C_3-C_4-F_6$  group; see text.

<sup>b</sup> Energies are in kcal mol<sup>-1</sup> relative to the conformer with the lowest calculated energy ( $G^+AG^-$ ).

Theoretical values of the important geometrical parameters are given in Table 2.

We took account of the effects of vibrational averaging (“shrinkage”) by defining the structures in the geometrically consistent  $r_\alpha$  space and calculating the corrections to  $r_a$  from the usual formula  $r_a = r_\alpha + \delta r + K - l^2/r = r_g - l^2/r$ . The normal coordinate program ASYM20 [18] was used to calculate the quantities in this formula (centrifugal distortions  $\delta r$ , perpendicular amplitude corrections  $K$ , root-mean-square amplitudes of vibration  $l$ ) for each conformer. The values of the force constants (stretches, bends, torsions, and interactions) were those used for 1,4-butanediol [9] slightly modified as necessary by the replacement of OH with F; the same force field was used for all conformers.

#### 4. Structure analysis

Refinements of the  $r_\alpha$ -type structure were carried out by the least squares method [19], adjusting a theoretical  $sI_m(s)$  curve simultaneously to the two average experimental curves (one from each nozzle-to-plate experiment). A unit weight matrix was used. It is obviously not possible to determine the structures of individual conformers in a

Table 2

Theoretical values of selected structural parameters for conformers of 1,4-difluorobutane<sup>a,b</sup>

	AAA	AAG	G <sup>+</sup> AG <sup>-</sup>	G <sup>+</sup> AG <sup>+</sup>	AGA	AG <sup>+</sup> G <sup>+</sup>	AG <sup>+</sup> G <sup>-</sup>	G <sup>+</sup> G <sup>+</sup> G <sup>+</sup>	G <sup>+</sup> G <sup>+</sup> G <sup>-</sup>	G <sup>+</sup> G <sup>-</sup> G <sup>+</sup>
$r(\text{C}_1\text{C}_2)$	1.515 <i>1.514</i>	1.515 <i>1.514</i>	1.514 <i>1.514</i>	1.515 <i>1.514</i>	1.518 <i>1.514</i>	1.516 <i>1.514</i>	1.519 <i>1.515</i>	1.516 <i>1.514</i>	1.518 <i>1.515</i>	1.518 <i>1.516</i>
$r(\text{C}_2\text{C}_3)$	1.530 <i>1.538</i>	1.529 <i>1.538</i>	1.529 <i>1.539</i>	1.529 <i>1.539</i>	1.532 <i>1.540</i>	1.532 <i>1.540</i>	1.532 <i>1.540</i>	1.532 <i>1.540</i>	1.534 <i>1.542</i>	1.533 <i>1.541</i>
$r(\text{C}_3\text{C}_4)$	1.515 <i>1.514</i>	1.515 <i>1.514</i>	1.514 <i>1.514</i>	1.515 <i>1.514</i>	1.518 <i>1.514</i>	1.518 <i>1.515</i>	1.515 <i>1.515</i>	1.516 <i>1.514</i>	1.516 <i>1.515</i>	1.518 <i>1.516</i>
$r(\text{C}_1\text{F}_6)$	1.371 <i>1.382</i>	1.371 <i>1.382</i>	1.375 <i>1.382</i>	1.373 <i>1.382</i>	1.371 <i>1.382</i>	1.372 <i>1.382</i>	1.375 <i>1.382</i>	1.376 <i>1.381</i>	1.376 <i>1.382</i>	1.373 <i>1.382</i>
$r(\text{C}_4\text{F}_6)$	1.371 <i>1.382</i>	1.373 <i>1.382</i>	1.375 <i>1.382</i>	1.373 <i>1.382</i>	1.371 <i>1.382</i>	1.372 <i>1.381</i>	1.376 <i>1.381</i>	1.376 <i>1.381</i>	1.376 <i>1.380</i>	1.373 <i>1.382</i>
$\angle\text{C}_2\text{C}_1\text{F}_5$	109.4 <i>110.3</i>	109.5 <i>110.4</i>	109.8 <i>110.8</i>	109.9 <i>110.9</i>	109.0 <i>110.3</i>	109.0 <i>110.4</i>	108.4 <i>110.1</i>	109.9 <i>110.8</i>	109.1 <i>110.8</i>	109.7 <i>111.0</i>
$\angle\text{C}_3\text{C}_4\text{F}_6$	109.4 <i>110.3</i>	109.7 <i>110.8</i>	109.8 <i>110.8</i>	109.9 <i>110.9</i>	109.0 <i>110.3</i>	109.8 <i>110.8</i>	110.2 <i>111.3</i>	109.9 <i>110.8</i>	110.9 <i>111.6</i>	109.7 <i>111.0</i>
$\angle\text{C}_1\text{C}_2\text{C}_3$	112.1 <i>112.6</i>	112.2 <i>112.6</i>	112.7 <i>113.0</i>	112.8 <i>113.0</i>	114.1 <i>114.0</i>	114.2 <i>114.1</i>	114.2 <i>114.8</i>	114.3 <i>114.6</i>	114.3 <i>115.1</i>	115.9 <i>115.8</i>
$\angle\text{C}_2\text{C}_3\text{C}_4$	112.1 <i>112.6</i>	112.8 <i>113.0</i>	112.7 <i>113.0</i>	112.8 <i>113.0</i>	114.1 <i>114.0</i>	114.6 <i>114.6</i>	115.1 <i>114.9</i>	114.3 <i>114.6</i>	114.8 <i>114.8</i>	115.9 <i>115.8</i>
$\phi(\text{F}_5\text{C}_1\text{C}_2\text{C}_3)$	180.0 <i>180.0</i>	180.0 <i>180.6</i>	59.9 <i>62.2</i>	59.9 <i>61.5</i>	176.8 <i>177.6</i>	175.3 <i>176.0</i>	171.8 <i>174.5</i>	54.1 <i>57.2</i>	62.0 <i>60.1</i>	76.0 <i>76.3</i>
$\phi(\text{F}_6\text{C}_4\text{C}_3\text{C}_2)$	180.0 <i>180.0</i>	60.1 <i>62.8</i>	-59.9 <i>-62.2</i>	59.9 <i>61.5</i>	176.8 <i>177.6</i>	63.4 <i>58.1</i>	-67.0 <i>-68.9</i>	54.1 <i>57.2</i>	-61.2 <i>-65.7</i>	76.0 <i>76.3</i>
$\phi(\text{C}_1\text{C}_2\text{C}_3\text{C}_4)$	180.0 <i>180.0</i>	179.8 <i>179.8</i>	180.0 <i>180.0</i>	179.9 <i>177.6</i>	69.6 <i>67.5</i>	54.8 <i>63.8</i>	66.3 <i>67.4</i>	60.5 <i>60.5</i>	79.9 <i>73.1</i>	-51.2 <i>-58.5</i>

<sup>a</sup> Distances ( $r$ ) are in Ångströms, bond angles ( $\angle$ ) and torsion angles ( $\phi$ ) are in degrees.<sup>b</sup> Values in normal type from HF/6-31G\*; values in italics from MM3.

conformational mixture of ten species, each defined by a large number of geometrical parameters. Constraints and assumptions drawn from the results of the theoretical calculations (molecular mechanics or ab initio in separate refinements) were therefore introduced as follows. The differences between  $r(\text{C}_1\text{C}_2)$  and  $r(\text{C}_2\text{C}_3)$  were assumed to have the calculated values. All C–H, all C–F, and all peripheral C–C bonds ( $\text{C}_1\text{C}_2$  and  $\text{C}_3\text{C}_4$ ) were assumed to be equal, and all torsion angles in the different conformers were kept constant at the calculated values. The differences between corresponding valence angles in different conformers were also kept constant at the calculated values, but the average values for

$\angle\text{C}-\text{C}-\text{C}$ ,  $\angle\text{C}-\text{C}-\text{F}$  and  $\angle\text{H}-\text{C}-\text{H}$  were allowed to refine. In 1,4-butanediol [9] it was clear that the amount of the two conformers where internal hydrogen bonding was possible (forms in which the ends of the molecule tended to be near each other) was much larger than that predicted by the molecular mechanics and ab initio calculations. Tests for a similar effect in 1,4-difluorobutane were negative: when the amount of the “curled up” forms  $\text{G}^+\text{G}^+\text{G}^-$  and  $\text{G}^+\text{G}^-\text{G}^+$  was allowed to refine against the amount of the other eight conformers, the ED/MM3 result was  $4 \pm 6\%$  (calculated from MM3: 3.6%) and the ED/ab initio result was  $14 \pm 7\%$  (calculated value: 8.9%). Lacking any

Table 3

Molecular structure of 1,4-difluorobutane obtained from electron diffraction with parameter constraints drawn from molecular mechanics (MM3) and ab initio (HF/6-31G\*) calculations<sup>a</sup>

Parameter	ED/MM3		ED/ab initio	
	$r_g; \angle_\alpha$	$l_\alpha$	$r_g; \angle_\alpha$	$l_\alpha$
$r(\text{C-H})$	1.105 (3)	0.086 (4)	1.106 (3)	0.086 (4)
$r(\text{C-F})$	1.398 (2)	0.057 (3)	1.398 (2)	0.057 (3)
$r(\text{C}_1\text{-C}_2)$	1.513 (2)	0.060	1.516 (2)	0.061
$r(\text{C}_2\text{-C}_3)$	1.537 (2)	0.059	1.532 (2)	0.061
$\angle\text{F-C-C}$	110.9 (3)	} (3)	111.1 (3)	} (3)
$\angle\text{C-C-C}$	112.9 (4)		112.9 (4)	
$\angle\text{H-C-H}$	100 (3)		100 (3)	
<i>Dependent distances for the AAA conformer</i>				
$r(\text{C}_2\text{-F}_5)$	2.383 (4)	0.073	2.388 (4)	0.072
$r(\text{C}_1\text{-C}_3)$	2.537 (6)	0.080	2.533 (7)	0.080
$r(\text{C}_1\text{-C}_4)$	3.872 (9)	0.127	3.873 (9)	0.088
$r(\text{C}_2\text{-F}_6)$	3.738 (7)	0.122	3.735 (7)	0.084
$r(\text{C}_4\text{-F}_5)$	4.899 (10)	[0.100]	4.900 (10)	[0.100]
$r(\text{F}_5\text{-F}_6)$	6.055 (11)	[0.094]	6.056 (11)	[0.094]
$r(\text{C}_1\text{-H}_{10})$	2.150 (7)	0.133	2.144 (7)	0.136
$r(\text{C}_3\text{-H}_{14})$	2.161 (7)	0.132	2.154 (7)	0.135
$r(\text{F}_5\text{-H}_7)$	2.051 (7)	0.130	2.041 (7)	0.133
$r(\text{C}_1\text{-H}_{14})$	4.170 (11)	[0.167]	4.163 (11)	[0.167]
$r(\text{C}_1\text{-H}_{11})$	2.764 (6)	[0.171]	2.749 (6)	[0.171]
$r(\text{C}_2\text{-H}_{14})$	2.771 (8)	[0.171]	2.757 (8)	[0.171]
$r(\text{F}_5\text{-H}_{10})$	2.630 (5)	[0.164]	2.635 (8)	[0.164]
$r(\text{F}_5\text{-H}_{14})$	5.035 (10)	[0.206]	5.036 (10)	[0.206]
$r(\text{F}_5\text{-H}_{11})$	4.032 (9)	[0.165]	4.028 (6)	[0.165]
$R^{b,c}(\text{LC})^c$	0.036		0.042	
$R^{b,c}(\text{MC})^d$	0.068		0.070	

<sup>a</sup> Distances ( $r$ ) and r.m.s. vibrational amplitudes ( $l$ ) are in Ångströms, angles ( $\angle$ ) are in degrees.

<sup>b</sup> Quality of agreement factor,  $R = [\sum_i w_i \Delta_i^2 / \sum_i w_i (s_i I_i(\text{obsd}))^2]^{1/2}$  where  $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$ .

<sup>c</sup> Long camera distance.

<sup>d</sup> Middle camera distance.

evidence — either experimental or theoretical — for preponderance of these forms we carried out the final refinements with the mole fractions of all ten conformers held at the values estimated from either the MM3 or the ab initio calculations. The refined parameters were in each case the bond distances ( $r(\text{C-H})$ ,  $r(\text{C-F})$  and  $\langle r(\text{C-C}) \rangle$ ), the bond angles ( $\angle\text{C-C-C}$ ,  $\angle\text{C-C-F}$  and  $\angle\text{H-C-H}$ ), and the seven amplitudes of vibration evident from Table 3.

The results of the final refinements are given in Table 3 and the theoretical RD curves for the corresponding models are shown in Fig. 3. The correlation matrices for the parameters of each refinement are given in Table 4.

## 5. Discussion

The main object of our study of 1,4-difluorobutane was to ascertain the relative importance of those “coiled” rotational conformers that permitted close approach of the two fluorine atoms (or C-F bonds). Having determined that there is no experimental evidence for a predominance of such species, we conclude that any effect similar to the gauche effect that operates in 1,2-difluoroethane is absent. Since 1,4-difluorobutane and 1,4-butanediol are isoelectronic and the two kinds of substituent have similar electronegativities, such an effect is also expected to be absent in 1,4-butanediol. Further, since in

Table 4  
Correlation matrices ( $\times 100$ ) for parameters of 1,4-difluorobutane<sup>a, b</sup>

	$\sigma_{LS}^c$	Correlation coefficients										$\sigma_{LS}^c$						
$r(C-F)$	0.048	100		100	42	17	28	-43	-19	7	-6	25	2	-14	4	-6	0.045	$r(C-F)$
$\langle r(C-C) \rangle$	0.062	42	100		100	18	46	-53	-40	13	4	33	16	-16	10	-5	0.058	$\langle r(C-C) \rangle$
$r(C-H)$	0.111	18	19	100		100	31	-12	-6	1	-2	7	7	-4	5	-1	0.106	$r(C-H)$
$\angle H-C-H$	106.	28	48	32	100		100	-73	-56	23	21	23	25	-37	-11	-10	101.0	$\angle H-C-H$
$\angle F-C-C$	11.3	-43	-52	-12	-68	100		100	56	-16	-11	-23	-6	29	19	13	11.05	$\angle F-C-C$
$\angle C-C-C$	15.7	-17	-38	-5	-47	50	100		100	-4	-1	17	-17	16	30	9	11.05	$\angle C-C-C$
$l(C-C)$	0.076	8	14	1	25	-17	-3	100		100	85	10	25	-1	14	4	0.072	$l(C-C)$
$l(F-C)$	0.068	-5	5	-2	23	-11	1	85	100		100	8	28	-1	15	5	0.064	$l(F-C)$
$l(C-H)$	0.096	26	34	8	24	-23	-15	11	9	100		100	8	-4	5	-1	0.091	$l(C-H)$
$l(C_2 \cdot F_5)$	0.115	3	18	7	27	-6	-14	26	28	9	100		100	-20	34	-1	0.109	$l(C_2 \cdot F_5)$
$l(C_3 \cdot F_5)$	0.585	20	-30	-10	-56	40	22	-10	-9	-13	-24	100		100	1	4	0.403	$l(C_3 \cdot F_5)$
$l(C_1 \cdot H_{10})$	0.196	6	12	5	-4	14	26	15	16	7	36	-1	100		100	2	0.183	$l(C_1 \cdot H_{10})$
$l(C_1 \cdot C_4)_{gauche}$	0.789	-3	-1	-1	-5	9	5	5	5	2	-1	-11	1	100		100	0.656	$l(C_1 \cdot C_4)_{gauche}$

<sup>a</sup> Normal type: ED/ab initio; italics: ED/MM3.

<sup>b</sup> Distances ( $r$ ) and amplitudes ( $l$ ) are in Ångströms, angles ( $\angle$ ) are in degrees.

<sup>c</sup> Standard deviations ( $\times 100$ ) from least squares refinements.



Table 5

Structures of 1,4-difluorobutane and some related compounds<sup>a</sup>

	1,4-difluorobutane	1,4-butanediol	1,3-difluoropropane	1,2-difluoroethane
$r(\text{C-H})$	1.105 (3)	1.109 (14)	1.094 (5)	1.108 (4)
$r(\text{C}_1\text{--C}_2)$	1.513 (2)	} 1.530 (2) <sup>b</sup>	1.513 (3)	1.506 (3)
$r(\text{C}_2\text{--C}_3)$	1.537 (2)		—	—
$r(\text{C-X})$	1.398 (2)	1.428 (2)	1.391 (2)	1.391 (2)
$\angle \text{X-C-C}$	110.9 (3)	111.2 (16)	110.1 (3)	110.3 (1)
$\angle \text{C-C-C}$	112.9 (3)	114.9 (20)	112.9 (8)	—
Ref.	This work	[9]	[20]	[21]

<sup>a</sup> Distances ( $r_g$ ) are in Ångströms, angles ( $\angle$ ) are in degrees.<sup>b</sup>  $r(\text{C}_1\text{--C}_2)$  and  $r(\text{C}_2\text{--C}_3)$  assumed to be equal.

1,4-butanediol there does exist a large amount of those coiled conformers that bring the OH groups close together, the reason must lie almost entirely in the formation of internal hydrogen bonds.

As is seen from Table 2, the MM3 and the ab initio calculations lead to similar values for the bond distances, valence angles and torsion angles. Table 1 shows, however, that the two calculations predict some appreciable differences between the energies for certain of the conformers. Both methods indicate that the  $\text{G}^+\text{AG}^-$  form, the one observed in the solid phase [10], has the lowest energy. The composition of gaseous 1,4-difluorobutane, however, is also determined by the enantiomorphic multiplicities of the conformers. Thus, the greater multiplicity of the AAG form, which according to MM3 has slightly higher steric energy than  $\text{G}^+\text{AG}^-$ , leads to this form having the greatest abundance. On the other hand, the ab initio results predict the form of greatest abundance to be  $\text{G}^+\text{AG}^-$ . Both methods indicate that the three forms AAG,  $\text{G}^+\text{AG}^-$  and  $\text{G}^+\text{AG}^+$  together make up about two-thirds of the molecules in the gas phase.

Use of either the MM3 or the ab initio results as constraints in the refinements of the GED data gave good agreement with experiment, but, judged both from the slightly lower “*R*-factor” (Table 3) and the slightly better fit between experimental and theoretical RD curves, the model based on the MM3 results may be a bit better. We are reluctant to conclude, however, that the better fit from the ED/MM3 refinement means that the MM3-calculated composition is the more realistic. There are many assumptions built into the models

other than adoption of the calculated compositions, and changes in these assumptions would also alter the quality of the fit. Since no attempt was made to evaluate the effect of such changes, the question of the better theoretical prediction of composition must remain an open one.

The values found for the refined geometrical parameters are generally in good agreement with those calculated theoretically, but both methods calculate  $r(\text{C-F})$  about 0.02–0.03 Å too short, and the ab initio calculations gave a smaller value (109.4°) than ED/ab initio (111.1(3°) for  $\angle \text{C-C-F}$ . In Table 5 the geometry determined for 1,4-difluorobutane (ED/MM) is listed together with results reported for 1,4-butanediol [9], 1,3-difluoropropane [20], and 1,2-difluoroethane [2]. The values for comparable parameters differ very little, but  $r(\text{C-F})$  is slightly longer and  $\angle \text{C-C-F}$  slightly larger in 1,4-difluorobutane than in the other two difluorides.

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