

Figure 5. Potential for torsion around the conjugated single bond.

chloro-1,3-butadiene, appears to reflect the C_4 rather than the C_3O moiety. In view of these considerations, it is not surprising that the bond distances in oxalyl chloride with its $O=C-C=O$ backbone are rather different from those in the other molecules.

In general, the bond length within the backbones of the molecules cited are in accord with conventional views about the relative importance of conjugation in the different backbone chains. This is most clearly seen in the value of the conjugated $C-C$ single bond in CPC. Regarded as a "hybrid" of the weakly conjugated oxalyl chloride and the strongly conjugated 2,3-dichloro-1,3-butadiene, CPC is expected and found to have a $C-C$ distance intermediate between its isoelectronic "parents". The same comparison, however, fails to predict correctly the planar or near planar conformation of CPC from the distinctly gauche forms of both parents. We suggest that the different syn conformations of these molecules are the result of different degrees of conformational stabilization ($C=C-C=C > C=C-C=O > O=C-C=O$) opposed by differing steric effects. The syn form of 2,3-dichloro-1,3-butadiene is nonplanar despite the strong conjugation because of even stronger repulsion between methylene hydrogens which that form would place in very close proximity. A coplanar syn form of oxalyl

chloride would experience weaker van der Waals repulsion than would the butadiene, but the weak $O=C-C=O$ conjugation is insufficient to overcome it. The coplanar or nearly coplanar syn form for CPC has about the same level of steric repulsion between opposite ends of the molecule as oxalyl chloride, but in this case the conjugation effect dominates.

The observed temperature dependence of the sample composition affords estimates of the energy and entropy differences between the two conformers. Figure 4 is a plot of the data in the form $R \ln K_{eq} = -\Delta E^\circ/T + \Delta S^\circ$, where $k_{eq} = N_s/N_a$, $\Delta E^\circ = E_s^\circ - E_a^\circ$, and $\Delta S^\circ = S_s^\circ - S_a^\circ$. The results are $\Delta E = 3.8(\sigma=2.2)$ $\text{kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\circ = 2.7(\sigma=5.6)$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. These values are somewhat higher than the values found for propenyl chloride² ($\Delta E^\circ = 1.0(\sigma=0.8)$ $\text{kJ}\cdot\text{mol}^{-1}$, $\Delta S^\circ = -0.6(\sigma=2.1)$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). The values observed for ΔE° in oxalyl chloride⁷ ($5.8(\sigma=1.5)$ $\text{kJ}\cdot\text{mol}^{-1}$) and in 2,3-dichloro-1,3-butadiene⁶ ($9.2(\sigma=2.3)$ $\text{kJ}\cdot\text{mol}^{-1}$) are both larger than the value determined for CPC.

With adoption of the 2S model it is possible to calculate a crude potential function of the form $2V = \sum V_i(1 - \cos i\phi)$ for internal rotation in CPC. The method has been described.^{2,7} The results in kJ/mol are $V_1 = 2.1(\sigma=1.3)$, $V_2 = 8.0(\sigma=0.5)$, and $V_3 = 1.7(\sigma=0.3)$; the function is plotted in Figure 5. It is also possible to estimate the torsional frequencies for the anti and syn forms. The estimate is based on the rough approximation that torsional motions are harmonic in the angle displacements; from the three temperatures the average values are $k_A = RT/\sigma_A^2 = 0.045$ (11) $\text{aJ}\cdot\text{rad}^{-2}$ and $k_s = 0.012$ (5) $\text{aJ}\cdot\text{rad}^{-2}$. The torsional wave numbers are $\omega_A = 44$ (6) cm^{-1} and $\omega_s = 23$ (5) cm^{-1} . No measurements of the vibrations are on record for comparison.

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Supplementary Material Available: Tables of total intensities, final backgrounds, average molecular intensities, symmetry coordinates, force constants, and figures equivalent to Figure 2 for 377 and 475 K (42 pages). Ordering information is given on any current masthead page.

Conformational Analysis. 13. 2-Fluoroethanol. An Investigation of the Molecular Structure and Conformational Composition at 20, 156, and 240 °C. Estimate of the Anti-Gauche Energy Difference

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Abstract: The gas-phase molecular structure and anti-gauche conformational composition of 2-fluoroethanol have been investigated at 20, 156, and 240 °C with use of electron-diffraction data, augmented by rotational constants and dipole moment data from microwave spectroscopy. Because of the combined influence of the gauche effect and the internal $O-H\cdots F$ hydrogen bond, both of which stabilize the gauche conformer, the amounts of the anti form at the two lower temperatures were too small to detect. At the highest temperature the mole fraction of the anti form was measured to be 0.098 ($2\sigma = 0.067$). Values of some of the important distances (r_g) and angles (\angle_a) with uncertainties estimated at the 95% confidence level are $C-O = 1.432$ (16) Å, $C-C = 1.518$ (6) Å, $C-F = 1.398$ (24) Å, $(C-H, O-H) = (4C-H + O-H)/5 = 1.091$ (18) Å, $\Delta(C-H, O-H) = C-H-O-H = 0.137$ (36) Å, $\angle CCO = 112.3$ (14)°, $\angle CCF = 108.5$ (8)°, $\angle COH = 105.8^\circ$ (assumed), $\angle HCH = 111.7$ (50)°, $\angle OCCF = 64.0$ (8)°, $\angle CCOH = -54.6$ (78)°. A crude estimate of the conformational energy difference is $\Delta E = E_s^\circ - E_g^\circ = 2.7$ (+1.8 - 1.5) kcal/mol . It was not possible to obtain a reliable measure of the energy of the internal hydrogen bond.

Some years ago a gas-phase electron-diffraction investigation of 2-fluoroethanol¹ (Figure 1; hereafter FE) was reported from

this laboratory as one of the earliest in a series of studies of internal hydrogen bonding in disubstituted ethanes. The gauche form was

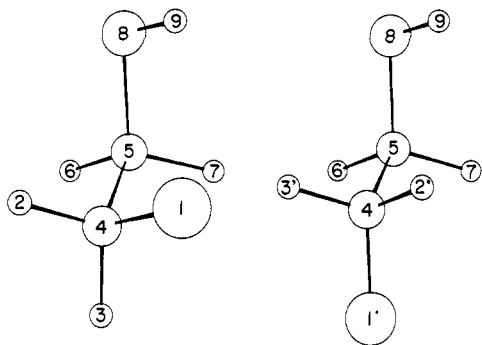


Figure 1. Atom numbering for gauche and anti forms of 2-fluoroethanol.

expected to predominate over the anti, and to increase the amount of the latter in the conformational mixture the experiment was done with the sample vapors at 156 °C, the higher end of the temperature range accessible with the nozzle in use at that time. Even so, the amount of the anti conformer was too small to be detected with certainty; statistical tests on the diffraction data led us to conclude that there exists less than 10% of the anti form in FE at this temperature. This result is quite different from the 15–25% anti found at a similar sample temperature in 2-chloroethanol^{2,3} and was attributed to a stronger gauche-stabilizing internal hydrogen bond in FE.

Other results cloud this simple picture. For example, in 1,2-difluoroethane,^{4–6} where internal hydrogen bonding cannot exist, the gauche conformer has also been found to predominate: the anti-gauche ratio is about 10% at 203 °C.⁵ This “gauche effect”⁷ operates most strongly between vicinally situated, very electronegative atoms or groups, among which are those that also tend strongly to form internal hydrogen bonds.

Our studies of the 1,2-disubstituted ethanes are intended to accumulate data about the anti-gauche ratios with the ultimate object of assessing the relative importance of internal hydrogen bonding and the gauche effect in the stabilization of gauche forms. A partial answer to this question in the case of the O–H...F bond is obviously related to the structural and compositional properties of the FE vs 1,2-difluoroethane systems. The earlier study of FE did not provide measurements of these properties, particularly the mixture composition, with sufficient precision for the purpose. Since then a new nozzle has been built that allows sample gases to be heated to much higher temperatures, affording the possibility for generation of the anti form in amounts large enough to be detected. Further, improvements in our computational techniques for structure analysis, such as the use of rotational constants and dipole moment components⁸ (both of which have been measured for FE⁹) together with the diffraction data as observables, promised to resolve other ambiguities of the early study. The ambiguities from the earlier study included some necessary assumptions: the difference between the nonresolvable C–O and C–F bond lengths, the value of $\angle\text{COH}$, and the value of the CCOH torsion angle that determines the position of the H_O atom. These considerations have led us to reinvestigate the FE system.

Experimental Section

Materials. The samples of FE were obtained from Sigma Chemical (new data) and K. & K. Laboratories (data from the early study). The purity of the samples was >95%; the likely impurity was water.

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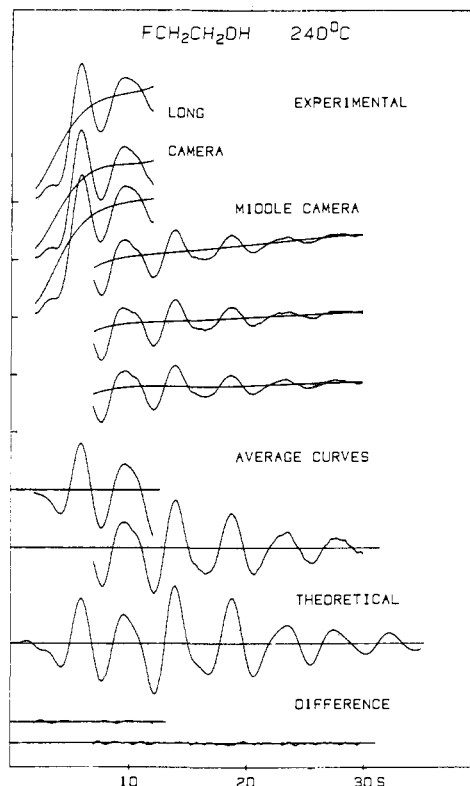


Figure 2. Intensity curves. The experimental total intensities, $s^4 I_t(s)$, multiplied by 5, are shown superimposed on the final backgrounds. The averaged curves, $s I_m(s)$, are in the form $s[s^4 I_t(s) - \text{bkgd}]$. The theoretical curve corresponds to the 240 °C model of Table II. The difference curve is experimental minus theoretical.

Apparatus and Procedure. Mass spectrometric experiments showed that the sample gas could be safely heated to 240 °C without thermal decomposition. New diffraction experiments were done with the Oregon State apparatus with the nozzle tip at 20 and 240 °C. Other experimental conditions were as follows: r^2 sector; 8×10 in Kodak projector slide plates (medium contrast) developed for 10 min in D-19 developer diluted 1:1; 0.36–0.62- μA beam currents; 90–180-s exposure times; electron wavelength, 0.05649–0.05654 Å calibrated in separate experiments against CO₂ ($r_a(\text{C–O}) = 1.1646$ Å, $r_a(\text{O–O}) = 2.3244$ Å); nozzle-to-plate distances, 747.25 and 298.08 mm for the 20 °C experiments and 747.05 and 298.05 mm for the 240 °C ones; 5×10^{-6} Torr ambient apparatus pressure during exposure. Data for the 156 °C experiments are found in the earlier article.¹

Five plates from the 20 °C experiment and six from the 240 °C one were selected for analysis. Also, five of the plates made at 156 °C in the early experiment were retrieved for reanalysis: improvements in our microphotometric equipment suggested better quality data might be obtained from these plates. The scattered intensity distributions were obtained by procedures previously described.¹⁰ Experimental backgrounds were calculated¹¹ and subtracted to yield molecular intensity data. The data range from the longer camera distance was $2.00 \leq s/\text{Å} \leq 12.00$ and from the shorter distance $7.00 \leq s/\text{Å} \leq 30.00$. The data interval was $\Delta s = 0.25 \text{ Å}^{-1}$. Curves of the total scattered intensities ($s^4 I_t(s)$), the final backgrounds, and the averaged molecular intensities ($s I_m(s)$) for the 240 °C data are shown in Figure 2. Similar curves for the 20 °C data are shown in Figure 4 in the supplementary material (see the paragraph at the end of the paper). Those for 156 °C data are virtually identical with the curves presented in the first article.¹

Radial distribution (RD) curves were calculated in the usual way¹⁰ from the function $I'(s) = s I_m Z_C Z_F (A_C A_F)^{-1} \exp(-0.0025s^2)$. Modified electron scattering amplitudes $A_i = s^2 F_i$ and phases for these and other calculations were generated from tables.¹² The final experimental RD curves are shown in Figure 3. There is a weak feature, designated 1'–8,

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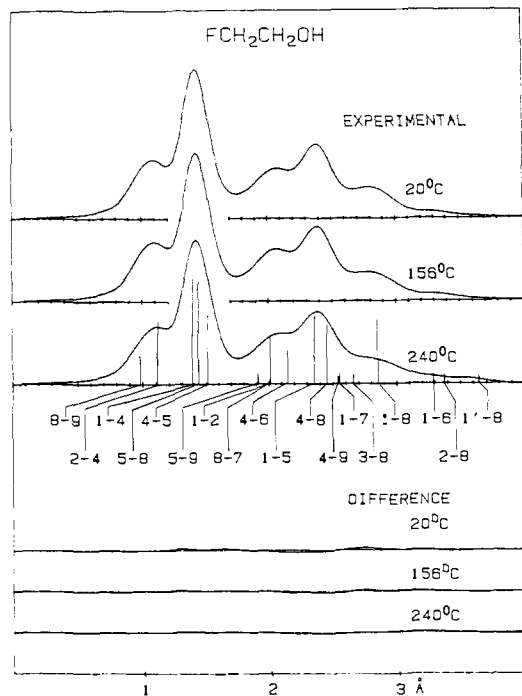


Figure 3. Radial distribution curves. The experimental curves were calculated with use of theoretical data from the final models for the unobserved region $s \leq 1.75 \text{ \AA}^{-1}$. The damping coefficient B was equal to 0.0025 \AA^{-2} .

in these curves near 3.6 \AA where the O...F distance in the anti conformer of FE is expected. The feature has the largest area in the curve from the highest temperature, but evidently the amount of the anti form even at this temperature is very small.

Structure Analysis

Vibrational Corrections. Because we were to make use of the microwave data for FE in the structure analysis, it was necessary to calculate terms for the conversions $B_0 \rightarrow B_z$ ($B_z = B_0 + \sum \alpha^{\text{har}}/2$) and $r_a \rightarrow r_a^0$ ($r_a = r_g - l^2/r = r_a^0 + 3/2a[(l^2)^T - (l^2)^0] + \delta r^T + K^0 - (l^2)^T/r$). The Morse anharmonicity constants a were given the value 2.00 \AA^{-1} for all bonds and were set to zero for nonbonds. The harmonic quantities α^{har} , amplitudes l , centrifugal distortions δr , and perpendicular amplitudes K were calculated with the program ASYM20.¹³ A set of quadratic force constants consisting of combinations of bond stretching, angle bending, and torsional constants was constructed from molecules similar to FE and adjusted to fit, with an accuracy of at least 98%, the 21 fundamental wavenumbers assigned to the gauche conformer from IR spectroscopy.¹⁴ Since no vibrational frequencies were available for the anti conformer, the same force field was used to estimate the corrections for it. The calculated differences between distance types are seen in Tables I and II, and those between types of rotational constants in Table IV. Details of the force field may be obtained from the authors.

Refinement Conditions. The parameters used to define the molecular geometry were the distances and angles listed in the first column of Table I. The structure was refined by least-squares analysis in the usual way¹⁵ to fit simultaneously the electron-diffraction intensities and, for the normal species of the gauche conformer, the three rotational constants and the three dipole moment components.⁹ The dipole vector in FE was considered to be the resultant of group moments for $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{F}$. The moment for CH_2OH was assigned the magnitude (1.70 D)¹⁶ and direction (55.6° with respect to the C-O bond)¹⁷ found for CH_3OH . This group moment was resolved into two "bond" components, one directed along the C-O bond comprising an $-\text{CH}_2\text{OH}$ fragment and the other along the H-O bond. The group moment for CH_2F was as-

Table I. Parameter Values of 2-Fluoroethanol for Experiments at Different Temperatures^a

parameter	best model			20 °C	156 °C	240 °C
	r_a^0, \angle_α	r_g^b				
$r(\text{C-O})$	1.426 (16)	1.432	1.431 (12)	1.419 (27)	1.427 (10)	
$r(\text{C-C})$	1.513 (6)	1.518	1.510 (4)	1.515 (5)	1.513 (4)	
$r(\text{C-F})$	1.393 (24)	1.398	1.389 (12)	1.403 (25)	1.386 (10)	
$\langle r(\text{C-H, O-H}) \rangle^c$	1.074 (18)	1.091	1.068 (4)	1.073 (4)	1.082 (4)	
$\Delta r(\text{C-H, O-H})^d$	0.148 (36)	0.137	0.138 (11)	0.143 (11)	0.164 (8)	
$\angle \text{CCO}$	112.3 (14)		112.0 (10)	111.9 (21)	112.9 (7)	
$\angle \text{CCF}$	108.5 (8)		108.9 (10)	108.8 (21)	108.3 (7)	
$\angle \text{COH}$	[105.8]		[105.8]	[105.8]	[105.8]	
$\angle \text{HCH}$	111.7 (50)		109.6 (20)	113.4 (23)	112.0 (19)	
$\angle \text{OCCF}$	64.0 (8)		64.2 (4)	64.1 (4)	63.6 (4)	
$\angle \text{CCOH}$	-54.6 (78)		-58.1 (54)	-53.1 (60)	-52.7 (50)	
$X(\text{anti})^e$			[0.01]	[0.05]	0.098 (67)	
R^f			0.047	0.050	0.042	

^aDistances (r) in angstroms, angles (\angle_α) in degrees. Quantities in parentheses are estimated 2σ uncertainties; quantities in brackets were assumed. ^bUncertainties estimated to be equal to those for r_a^0 . ^cEqual to $[4r(\text{C-H}) + r(\text{O-H})]/5$. ^dEqual to $r(\text{C-H}) - r(\text{O-H})$. ^eMole fraction of anti form. ^f $R = [\sum w_i \Delta_i^2 / \sum w_i (s_i I_i(\text{obsd}))^2]^{1/2}$, where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

signed the magnitude found for CH_3F (1.90 D)¹⁸ and a direction along the C-F bond; it was regarded to be the C-F "bond" component. The dipole moment components of FE in the principal axis system were calculated from these "bond" components and, in fashion similar to the rotational constants, compared to the observed values ($\mu_a = 0.38 \pm 0.02 \text{ D}$, $\mu_b = 1.47 \pm 0.01 \text{ D}$, $\mu_c = 0.0 \text{ D}$)⁹ used to aid refinement of the structure. The relative weighting of the three kinds of observables, always a problem because of differing magnitudes and uncertainties, was set for the final refinements to the approximate ratio $\sum w_i B_i^2 : \sum (s_i I_i(s))^2 : \sum w_i \mu_i^2 = 1000000:300:1$. The rotational constants were weighted equally, but the weights of the dipole moment components were set relatively to $\mu_a : \mu_b : \mu_c = 1:1:5$ because μ_c was found to be much more sensitive to $\angle \text{CCOH}$ than were the others. These weightings permitted, primarily, the diffraction data to dominate the determination of the heavy-atom positions and the rotational constants and dipole moment components to dominate the determination of the torsion angles and the hydrogen atom positions.

Besides the skeletal parameters just mentioned, there is an anti-gauche composition parameter and a large number of vibrational parameters corresponding to the many interatomic distances. The latter were refined in the usual way, some individually and some in groups as indicated in Table II. Differences between amplitudes in a group were taken from calculated values. It was found that the O-H and C-H bond amplitudes did not refine to reasonable values, and accordingly they were set at the calculated values. Because of the small amounts of anti conformation at the two lower temperatures, the composition parameter could also not be refined. The values assigned to this parameter are discussed in the following section.

In the previous study it was not possible to refine simultaneously the highly correlated distance pair $r(\text{C-O})$ and $r(\text{C-F})$ and the angles $\angle \text{COH}$ and $\angle \text{CCOH}$ under any conditions. The angles were fixed at the values assumed in the microwave work (105.8° and 55.5°), and $r(\text{C-O})$ was assigned the value 1.418 \AA . In our present study, despite the additional spectroscopic data, it was found that $\angle \text{COH}$ could still not be refined, but with the assumption $\angle \text{COH} = 105.8^\circ$ (the value reported for CH_3OH ¹⁷), all other structural parameters could be refined simultaneously.

Results and Discussion

Parameter values obtained from refinement of the structure are contained in Tables I and II. The correlation matrix for the 240 °C experiment is given in Table III. Those for the remaining experiments are similar; details may be had from the authors.

We note first that, largely because of the augmentation of the diffraction data with the spectroscopic observations, our results are much more complete than the earlier ones based on the 156 °C data.¹ The two sets of parameter values are otherwise in excellent agreement. Table IV shows the good agreement with the results of the spectroscopic measurements⁹ provided by our structures; the similarly good fits to the diffraction data are seen in the curves of Figures 2 and 3.

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Table II. Distances (r) and Vibrational Amplitudes (l) for 2-Fluoroethanol^a

	20 °C			156 °C			240 °C		
	r_g	r_a	l	r_g	r_a	l	r_g	r_a	l
	For Both Conformers								
C-O	1.436 (12)	1.434	0.054	1.424 (27)	1.422	0.055	1.434 (10)	1.431	0.060
C-C	1.514 (4)	1.512	0.056	1.519 (5)	1.517	0.057	1.520 (4)	1.517	0.062
C-F	1.393 (12)	1.391	0.052	1.407 (25)	1.405	0.053	1.392 (10)	1.390	0.058
C-H	1.110 (4)	1.105	[0.078]	1.116 (5)	1.110	[0.078]	1.129 (4)	1.123	[0.078]
O-H	0.985 (10)	0.980	[0.070]	0.986 (11)	0.981	[0.070]	0.978 (9)	0.973	[0.070]
C ₄ O	2.441 (16)	2.439	0.069	2.434 (28)	2.432	0.076	2.454 (10)	2.452	0.077
C ₅ F	2.361 (15)	2.359	0.067	2.375 (26)	2.373	0.074	2.354 (10)	2.352	0.074
C ₄ H ₉	2.567 (44)	2.557	0.164	2.523 (57)	2.510	0.178	2.543 (36)	2.530	0.183
C ₅ H ₉	1.940 (13)	1.933	0.119	1.931 (26)	1.923	0.119	1.932 (12)	1.923	0.131
C ₄ H ₆	2.141 (6)	2.135	0.112	2.138 (9)	2.132	0.112	2.147 (5)	2.140	0.123
F-H ₂	2.055 (15)	2.049	0.109	2.060 (33)	2.054	0.108	2.065 (13)	2.058	0.119
O-H ₇	2.073 (14)	2.067	0.110	2.055 (29)	2.049	0.110	2.073 (12)	2.066	0.120
	For Gauche Conformer								
F-O	2.866 (4)	2.860	0.131	2.867 (4)	2.860	0.141	2.866 (3)	2.856	0.175
O-H ₃	2.663 (19)	2.649	0.194	2.635 (25)	2.620	0.204	2.673 (15)	2.652	0.237
F-H ₇	2.581 (27)	2.572	0.148 ^b	2.568 (50)	2.557	0.161	2.565 (20)	2.554	0.164
F-H ₉	2.489 (39)	2.477	0.176	2.450 (38)	2.434	0.194	2.462 (29)	2.445	0.201
O-H ₂	3.373 (13)	3.368	0.129	3.362 (21)	3.358	0.118	3.391 (9)	3.384	0.156
F-H ₆	3.302 (15)	3.297	0.127	3.316 (26)	3.312	0.116	3.307 (9)	3.300	0.155
	For Anti Conformer								
F-O	3.635 (4)	3.633	[0.068]	3.638 (5)	3.637	[0.076]	3.634 (4)	3.632	[0.081]
F-H ₆	2.609 (22)	2.602	0.132	2.622 (41)	2.613	0.154	2.605 (14)	2.595	0.157
O-H ₂ '	2.690 (14)	2.684	0.131	2.689 (25)	2.679	0.156	2.711 (9)	2.701	0.159
F-H ₉	3.826 (28)	3.822	[0.130]	3.807 (35)	3.800	[0.163]	3.806 (22)	3.798	[0.170]

^a Values in angstroms. Quantities in parentheses are estimated 2 σ ; those in brackets were adopted from force field calculations; those in braces were refined as groups. ^b Refined in same group with C₄O, C₅F, and C₄H₉.

Table III. Correlation Matrix ($\times 100$) for 2-Fluoroethanol at 240 °C

	σ^a	r_1	r_2	r_3	r_4	r_5	\angle_6	\angle_7	\angle_8	\angle_9	\angle_{10}	\angle_{11}	l_{12}	l_{13}	l_{14}	l_{15}	X_{16}
1. $r(\text{C-O})$	0.37	100															
2. $r(\text{C-C})$	0.12	-10	100														
3. $r(\text{C-F})$	0.36	-99	10	100													
4. $\langle r(\text{C-O-H}) \rangle$	0.13	9	4	-9	100												
5. $\Delta r(\text{C-O-H})$	0.29	-10	6	10	-34	100											
6. $\angle(\text{C-C-F})$	25.8	53	-26	-54	7	-8	100										
7. $\angle(\text{C-C-O})$	26.0	-53	<1	53	-1	7	-93	100									
8. $\angle(\text{O-C-C-F})$	12.8	-15	-10	16	-9	-13	-26	6	100								
9. $\angle(\text{C-C-O-H})$	176.	-21	-16	20	-18	7	-21	14	26	100							
10. $\angle(\text{H-C-H})$	68.5	-11	60	18	56	<1	-23	11	-27	9	100						
11. $l(\text{C-O})$	0.21	-95	-1	96	-12	12	-48	51	14	24	10	100					
12. $l(\text{C-O})$	0.33	-36	3	37	<1	2	51	-52	-8	-2	6	39	100				
13. $l(\text{C-H})$	0.22	-21	15	23	10	1	15	-17	-19	6	29	24	51	100			
14. $l(\text{F-O})$	0.43	-4	-26	1	-5	-4	10	-7	17	13	-25	5	10	-13	100		
15. $l(\text{O-H})$	1.79	-1	6	1	-1	1	6	-8	-5	4	6	<1	11	3	20	100	
16. $X(\text{anti})$	2.37	2	10	-2	2	1	4	-6	-10	2	11	-3	6	2	21	61	100

^a Standard deviation ($\times 100$) from least-squares refinement. Distances (r) and amplitudes (l) in angstroms; angles (\angle) in degrees.

The r_a structure of FE is affected by temperature to the extent of the temperature dependence of centrifugal distortions δr and the anharmonicity corrections $\langle \Delta z \rangle$. These changes are predicted to be much smaller than the experimental uncertainties for the parameter values. The good agreement of the measurements at the three temperatures is consistent with this prediction and allows calculation of a "best model" comprising weighted averages of the three sets of r_a bond-distance and angle values. The model appears in Table I together with values for the corresponding r_g bond-length parameters that we judge will be of comparable reliability for molecules at 25 °C. One notes that the bond lengths and bond angles involving the heavy atoms in FE show little if any effect of the existence of an internal hydrogen bond; their values are similar to those in related molecules such as fluoroethane (MW¹⁹ C-C = 1.505 (5) Å, C-F = 1.398 (7) Å, $\angle \text{CCF} = 109.7$ (5)°; ED²⁰ C-C = 1.502 (5) Å, C-F = 1.397 (4) Å, $\angle \text{CCF} = 110.4$ (2)°), 1,2-difluoroethane⁴⁻⁶ (ED C-C = 1.503 (3) Å, C-F

Table IV. Experimental and Calculated Rotational Constants, Dipole Moment Components, and Hydroxyl Hydrogen-Atom Coordinates^a

	exptl ^b	calcd from final models		
		20 °C	156 °C	240 °C
A_z^c	15 859.97	15 860.17	15 860.17	15 860.16
B_z^c	5400.26	5401.22	5400.59	5400.87
C_z^c	4522.18	4521.35	4522.44	4521.58
μ_a	0.38	0.55	0.59	0.63
μ_b	1.47	1.40	1.42	1.41
μ_c	0.0	0.22	0.11	0.10
a_H	0.9304	0.997	0.944	0.975
b_H	1.3168	1.288	1.282	1.274
c_H	0.0 \pm 0.1	-0.074	-0.006	0.002

^a Rotational constants are in megahertz, dipole moments in debye, coordinates in angstroms. ^b Reference 9. ^c B_0 values are $A = 15 875.18$ Mhz, $B = 5409.26$ Mhz, $C = 4525.83$ Mhz. $B_0 - B_z$ differences calculated from the force field. $B_z = 505379/I_z$.

= 1.389 (2) Å, $\angle \text{CCF} = 110.3$ (1)°, and 2-chloroethanol^{21,2} (ED C-C = 1.516 (5) Å, C-O = 1.421 (5) Å, $\angle \text{CCO} = 111.5$ (6)°).

(19) See: Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, Group II; *Structure Data of Free Polyatomic Molecules*; Hellwege, K.-H., Hellwege, A. M., Eds.; Springer-Verlag: New York, 1976.

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The F...H_O distance is about equal to the van der Waals value (2.55 Å).

In other work on similar (gauche ⇌ anti) systems of conformers we have determined the internal energy and entropy differences from a van't Hoff plot of the function $-R \ln K(T) = \Delta U^\circ/T - \Delta S^\circ$ where $K = X_a/X_g$. This method cannot be applied to FE because the mole fraction of the anti form at the two lower temperatures was too small to measure. However, a rough estimate of the energy difference may be obtained as follows. There is a 2-fold skeletal degeneracy of the gauche form relative to the anti. The H_O atom may be assumed to be fixed in one position in the gauche form due to the internal hydrogen bonding, but in the anti form there are three potential minima derived from rotation about the C-O bond. Since the calculated vibrational and rotational contributions to the entropies of each conformer are very nearly equal, their entropy difference will arise only from these statistical factors. With $S_a^\circ - S_g^\circ = R(\ln 3 - \ln 2) = 0.81 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and $K(240^\circ\text{C}) = (0.098/0.902)$, $\Delta U^\circ = -RT \ln K + T\Delta S^\circ$ is found to be 2.7(+1.8, -1.5) kcal/mol, where the uncertainty includes the effect of uncertainty in the measurements of mole fraction and of uncertainty in ΔS° as implied by the assumed arbitrary range $0.0 \leq \Delta S^\circ/\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \leq 2.0$. The value agrees (rather fortuitously) with our earlier guess of $\Delta U^\circ > 2.8$ kcal/mol.¹ It also agrees with the result from spectroscopic measurements²² of band intensities in CCl₄ solution ($\Delta U^\circ = 2.07 \pm 0.53$ kcal/mol). However, the spectroscopic results also include $\Delta S^\circ = 3.6 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, which, assuming negligible temperature dependence of ΔU° over our temperature range, leads to the prediction of a substantially greater amount (28%) of the anti form at 240 °C than we observe. The discrepancy may be attributed to entropy effects in solution that are quite different from those in our gaseous mixture.

There remains the question of the energy of the O-H...F hydrogen bond. As we have pointed out, both the gauche effect and the internal hydrogen bond are expected to contribute to the

greater stability of the gauche form of FE, and the relative importance of these effects is not known. The importance of the gauche effect increases as the polarity of the two bonds in question increases, i.e., in the 1,2-disubstituted ethanes as the electronegativities of the bonded groups increases. Since the electronegativity of the fluorine atom (4.0) is slightly greater than that of the hydroxyl group (3.7), the gauche effect is expected to operate more strongly in 1,2-difluoroethane than in FE. Based on the energy difference of the two forms in 1,2-difluoroethane (1.76 (51) kcal/mol),⁵ a crude estimate of the magnitude of the gauche effect in FE is 1.0 kcal/mol. If internal hydrogen bonding and the gauche effect contribute additively to the stabilization of the gauche conformer in FE, our estimated conformational energy difference leads to an internal hydrogen-bond energy no greater than about 2.2 kcal/mol. Such a value is rather small. For example, one expects the energy of an O-H...Cl internal hydrogen bond to be smaller than O-H...F; however, we estimate the value in 2-chloroethanol to be about 2.4 (2) kcal/mol.²³ We are inclined to be skeptical of our FE result, which is dependent on a number of arbitrary assumptions. Unfortunately, sample decomposition at higher nozzle temperatures prevented us from carrying out experiments that would have given a more reliable results for the conformational energy difference.

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Supplementary Material Available: Tables of total intensities, final backgrounds, and average molecular intensities for all temperatures and figures analogous to Figure 2 for 20 and 156 °C (21 pages). Ordering information is given on any current masthead page.

(23) This value is taken to be equal to the energy difference $E_a - E_g = 2.4$ (2) kcal/mol.³ Assignment of equality to ΔE° and E_H is justified by the fact that the gauche effect between the bonds C-Cl and C-F (and by implication C-O) is apparently negligible, according to results for 1-chloro-2-fluoroethane ($E_a - E_g = -0.44$ (27) kcal/mol; Huang, J.; Hedberg, K., unpublished work).

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