

Conformational Analysis. 14. The Dihaloethanes $\text{ClCH}_2\text{CH}_2\text{F}$, $\text{BrCH}_2\text{CH}_2\text{F}$, and $\text{BrCH}_2\text{CH}_2\text{Cl}$. Investigations of the Molecular Structures, Rotameric Compositions, Anti and Gauche Energy and Entropy Differences, and Barriers Hindering Internal Rotation by Gas-Phase Electron Diffraction Augmented by Rotational Constants and *ab Initio* Calculation

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Abstract: The structures and conformational compositions of 1-chloro-2-fluoroethane (CFE), 1-bromo-2-fluoroethane (BFE), and 1-bromo-2-chloroethane (BCE) have been investigated in the gas phase by electron diffraction, each at three nozzle-tip temperatures: CFE, -25, 95, 360 °C; BFE, 20, 150, 350 °C; and BCE, 17, 125, and 302 °C. The structure analyses were aided by inclusion of experimental values of rotational constants for CFE and BFE taken from the literature and by *ab initio* geometry optimizations at the HF/3-21G* level (CFE) and HF/STO-3G* level (BFE and BCE). Each molecule exists as a mixture of anti and gauche rotamers with the former the more stable; the standard internal energy difference is least for CFE and greatest for BCE. Three types of model that take account of torsional motion in different ways gave essentially the same values for bond distances and bond angles. One of these yielded refined values, with estimated 2σ uncertainties, of potential constants for the three-term function $2V = \sum_i V_i(1 - \cos i\phi)$ for CFE, BFE, and BCE, respectively: $V_1 = 1.66$ (108), 1.68 (116), and 4.00 (190) kcal/mol; $V_2 = -0.96$ (90), -0.57 (114), and -1.85 (150) kcal/mol; $V_3 = 3.55$ (64), 3.08 (134), and 3.56 (106) kcal/mol. Distances ($r_b/\text{\AA}$) and angles (\angle_a/deg) averaged over the three temperatures, with estimated 2σ uncertainties, are as follows: CFE, $r(\text{C-H}) = 1.107$ (7), $r(\text{C-C}) = 1.504$ (6), $r(\text{C-F}) = 1.391$ (3), $r(\text{C-Cl}) = 1.784$ (3), $\angle\text{CCH} = 110.6$ (19), $\angle\text{CCF}_A = 108.5$ (11), $\angle\text{CCF}_G = 111.1$ (4), $\angle\text{CCCl}_A = 109.3$ (11), $\angle\text{CCCl}_G = 111.5$ (4), $\angle\text{FCCCl}_G = 111.9$ (16), ($\angle\text{FCCCl}_A = 0$); BFE, $r(\text{C-H}) = 1.084$ (8), $r(\text{C-C}) = 1.509$ (7), $r(\text{C-F}) = 1.393$ (4), $r(\text{C-Br}) = 1.937$ (4), $\angle\text{CCH} = 110.0$ (19), $\angle\text{CCF}_A = 107.6$ (8), $\angle\text{CCF}_G = 110.1$ (6), $\angle\text{CCBr}_A = 109.9$ (7), $\angle\text{CCBr}_G = 112.0$ (5), $\angle\text{FCCBr}_G = 112.2$ (53); BCE, $r(\text{C-H}) = 1.090$ (8), $r(\text{C-C}) = 1.515$ (5), $r(\text{C-Cl}) = 1.789$ (5), $r(\text{C-Br}) = 1.947$ (6), $\angle\text{CCH} = 111.2$ (16), $\angle\text{CCCl}_A = 109.4$ (5), $\angle\text{CCCl}_G = 111.9$ (24), $\angle\text{CCBr}_A = 109.9$ (5), $\angle\text{CCBr}_G = 112.6$ (24), $\angle\text{ClCCBr}_G = 108.6$ (30). The structures and thermodynamic properties are discussed.

It is an interesting fact that the gauche form of 1,2-difluoroethane is more stable than the anti,¹ whereas in the corresponding chloro and bromo compounds the reverse is found.² This result, which violates intuition drawn from the electrostatics of the polar C-F bonds, arises from a phenomenon known as the "gauche effect".³ The gauche effect finds explanation for the most part in a subtle interplay of several components of the torsional potential that individually reflect repulsion between nuclei, repulsion between electron charge distributions, and attraction between nuclei and the charge distributions. A description of the operation of the gauche effect is contained in the statement that there is "a tendency to adopt that structure which has the maximum number of gauche interactions between the adjacent electron pairs and/or polar bonds".³ This description, however, seems better suited to interpretation than prediction: both 1,2-difluoroethane and 1,2-dichloroethane have polar C-X bonds but different conformations as their more stable forms, and a prediction for their hybrid 1-chloro-2-fluoroethane could hardly be reliable.

In this laboratory, interest in the substituted ethanes has centered on the roles played by internal hydrogen bonding and the gauche effect in establishing the conformational and thermodynamic properties of the molecules. Many of these systems, such as 2-fluoroethanol⁴ and ethylene glycol,⁵ are characterized by geminally situated polar groups in which each effect may operate; in others (1,2-difluoroethane is an example) only the gauche effect is present. In order to evaluate the relative contributions of these

effects, a knowledge of the structures and conformational equilibria of the polar molecules 1-chloro-2-fluoroethane (CFE), 1-bromo-2-fluoroethane (BFE), and 1-bromo-2-chloroethane (BCE) (Figure 1) would seem to be important. There has been a substantial amount of work on some of these compounds: for CFE there are results from dipole-moment measurements,^{6,7} IR⁸⁻¹⁰ and Raman^{8,9} spectroscopy, molecular mechanics,¹¹ and microwave spectroscopy;¹² for BFE from IR,^{8,10} Raman,⁸ and microwave spectroscopy;¹³ and for BCE from IR,¹⁴⁻¹⁸ Raman,¹⁹ and photoelectron²⁰⁻²² spectroscopy. It is found that in the gas phase the

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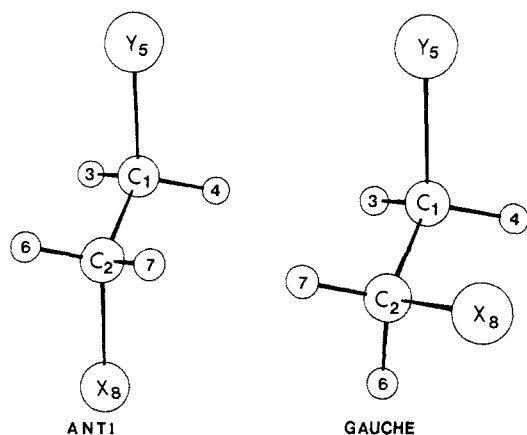


Figure 1. Atom numbering for conformers of 1,2-dihaloethanes. X is the atom of lower atomic number.

anti form of each substance is more stable than the gauche, and that the energy difference of the two forms is least for CFE and greatest for BCE. Bond length and bond angle values (derived with some assumptions about the hydrogen atom parameters) are available from the microwave work for the gauche form of CFE,^{12c} and for BFE a rough value for the gauche torsion angle has been obtained.¹³ There remain structural and conformational questions about the group, and we decided to carry out electron-diffraction investigations of each member. The work reported here was intended to permit reliable comparisons among members by using similar models for each of the interesting properties.

Experimental Section

The sample of CFE was prepared from thionyl chloride and 2-fluoroethanol by a literature method.²³ Examination by GC mass spectrometry indicated the purity to be greater than 98%. The BFE (Fairfield Chemical) had a 4% impurity determined by GC to be acetone; the low scattering of acetone relative to BFE was judged to be insignificant at this level and the sample was used as received. The BCE (Aldrich Chemical; 98%) was distilled under reduced pressure (40 Torr) through a 30-cm column packed with glass helices and a middle fraction collected for the diffraction experiments.

All diffraction experiments were carried out in the Oregon State apparatus fitted with an r^3 sector. Nominal nozzle-to-plate distances were 700 mm (long camera) and 300 mm (intermediate camera). The diffraction patterns on 8×10 in. Kodak projector slide plates, medium contrast, were developed with N_2 burst stirring for 10 min in D-19 developer diluted 2:1. Conditions set for each substance in the order CFE, BFE, and BCE were as follows. Nominal accelerating potential (calibrated in separate experiments against CO_2 with $r_a(CO) = 1.1646 \text{ \AA}$ and $r_a(O \cdots O) = 2.3244 \text{ \AA}$): 60, 44, 44 kV. Sample temperatures: -25, 95, 360 °C; 20, 150, 350 °C; 17, 125, and 302 °C. Exposure times: 100–210 s; 75–180 s; 75–210 s. Apparatus pressure during exposure: 1×10^{-6} – 3×10^{-5} Torr; 2 – 8×10^{-6} Torr; 2 – 8×10^{-6} Torr. Number of plates used in analyses from long and intermediate distances: 10 and 10; 11 and 9; 9 and 8. Ranges of data in $s/\text{\AA}^{-1}$ from long and intermediate distances: 3.00–15.00 and 11.00–37.00; 2.00–12.00 and 7.00–30.00; 2.00–12.00 and 7.00–30.00. Data interval, $\Delta s = 0.25 \text{ \AA}^{-1}$. Our usual procedures^{24,25} for obtaining the total intensities ($s^4I_t(s)$) and the molecular intensities ($sI_m(s)$) were followed. Electron-scattering amplitudes for all calculations were taken from tables.²⁶

Figures 2–4 show the s^4I_t curves obtained at one of the experimental temperatures superimposed on the backgrounds calculated from the CP cosine potential models. Similar figures for experiments at the other temperatures are available in the supplementary material. Radial distribution (RD) curves are shown in Figures 5–7. These were calculated²⁷

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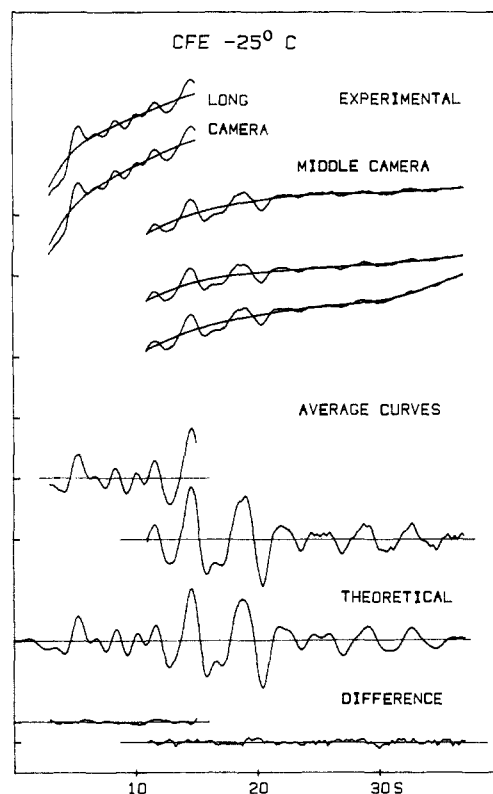


Figure 2. Intensity curves for 1-chloro-2-fluoroethane at -25 °C. The s^4I_t experimental curves are shown magnified 5 times with respect to the backgrounds on which they are superimposed. The average curves are $s[s^4I_t - \text{bkgd}]$. The theoretical curve is for the final CP model.

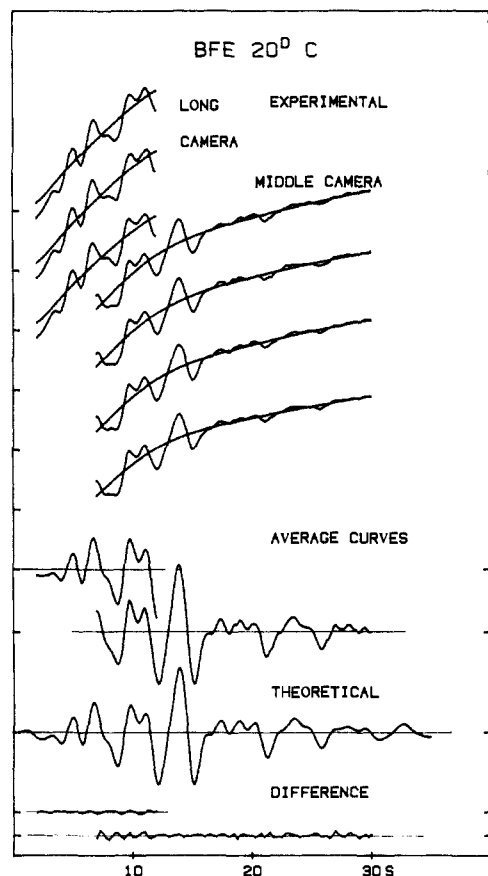


Figure 3. Intensity curves for 1-bromo-2-fluoroethane at 20 °C. See the legend to Figure 2.

from composites of the $sI_m(s)$ curves after multiplication by factors $Z_X Z_Y (s^4 F_X F_Y)^{-1} \exp(-0.0025s^2)$ where X and Y are the relevant halo-

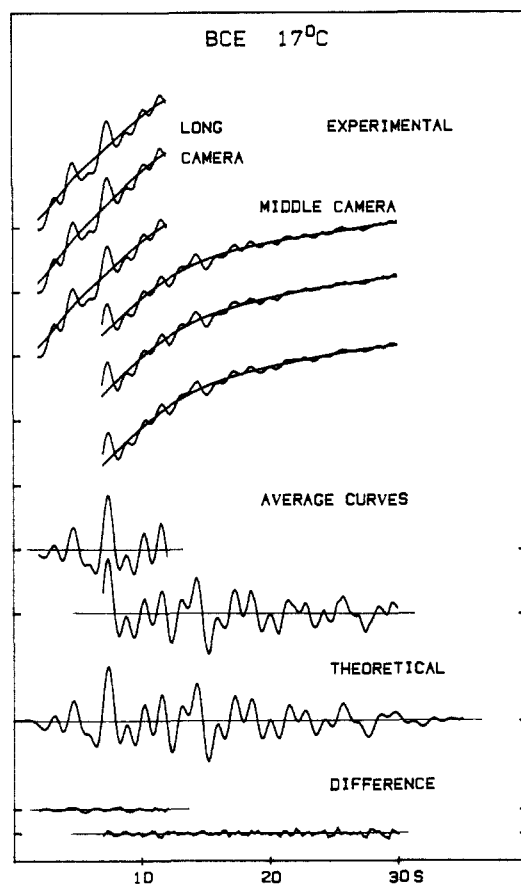


Figure 4. Intensity curves for 1-bromo-2-chloroethane at 17 °C. See the legend to Figure 2.

gen atoms and the F^* 's are electron-scattering amplitudes; missing data in the low-angle region were taken from theoretical curves. Each of the curves shows a moderately strong peak at $r \approx 4.0$ Å that corresponds to the interhalogen distances in the anti forms of the molecules. The peaks decrease in area as the temperature is increased, clear proof that the anti forms are more stable than the gauche.

Structure Analysis. Force Field Calculations. Because it was desirable to include the ground-state rotational constants that have been measured for CFE^{12a,b} and BFE¹³ as data auxiliary to the diffraction data, we set up the structure refinements for these molecules in r_a^0 space. Rotational constants are not available for BCE so the refinements were designed for in r_a space. For each of these spaces the appropriate corrections (on the diffraction side distances to r_a values and on the spectroscopic side B_0 to B_2 for CFE and BFE) were calculated with use of the program ASYM20²⁸ from quadratic force fields. Where anharmonicity corrections were needed we assumed the Morse constant a_3 to be 2.0 Å^{-1} for all bond distances and 0 for nonbond ones. The internal force constants were taken from similar molecules and adjusted to fit the observed fundamental wave numbers (15 for the anti and 18 for gauche forms of CFE⁸ and BCE;¹⁶ 18 for each form of BFE⁸) to within about 1–2%.

Ab Initio Calculations. Optimization of the structures of both conformers of CFE was carried out at the HF/3-21G* level and of BFE and BCE at the HF/STO-3G* level with the program Gaussian 86.²⁹ Although in other torsional problems we have usually made the assumption that the structures of the conformers differ only in the value of the torsion angle, we decided to incorporate certain of the ab initio results in the model descriptions. These structural assumptions are given in the next section.

Model Specification. For structural problems of the type represented by these systems, we have used models designated as 2C, 2S, and CP (see, for example, ref 1). These differ in the way the effect of large-amplitude motion is treated. The 2C (two conformer) model contains conformers

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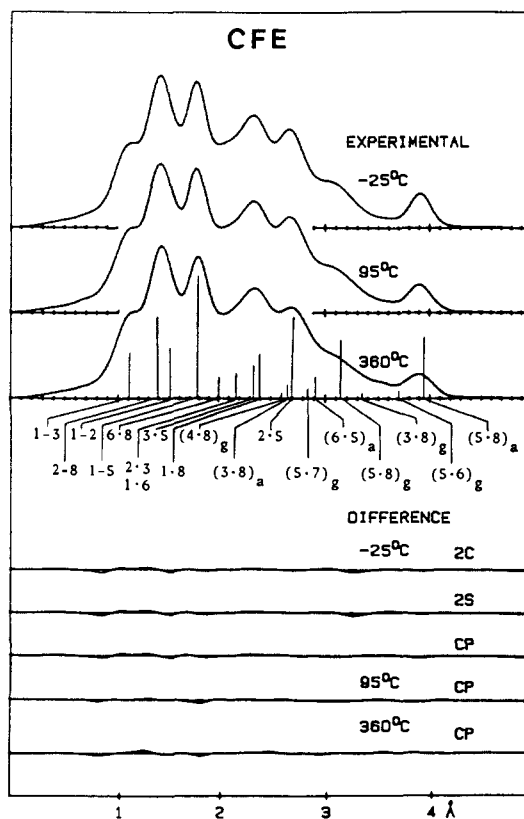


Figure 5. Radial distribution curves for 1-chloro-2-fluoroethane. The experimental curve was calculated from a composite of the average intensities with use of theoretical data for the region $0 \leq s/\text{Å} \leq 3.00$ and $B/\text{Å}^2 = 0.0025$. The vertical lines have lengths proportional to weights of the indicated distances.

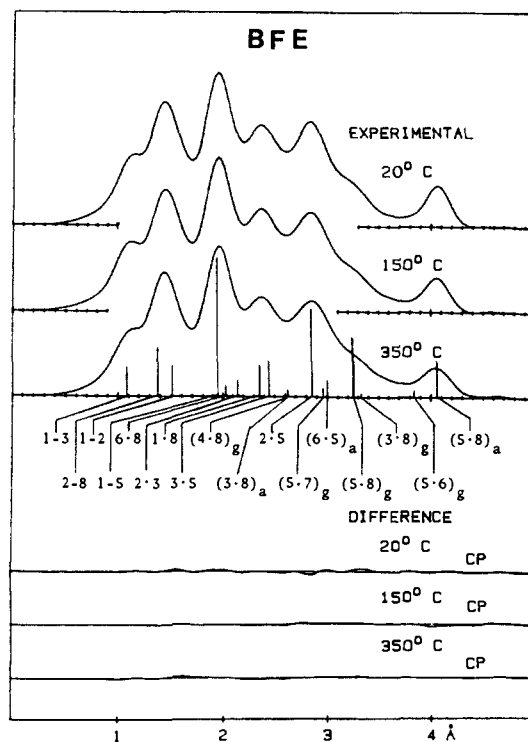


Figure 6. Radial distribution curves for 1-bromo-2-fluoroethane. See the legend to Figure 5. Theoretical data were used for the intensity region $0 \leq s/\text{Å} \leq 2.00$.

in which the vibrations are regarded as simple "frame" types. The 2S (two sigma) model represents the effect of torsional motion of the conformers by a distribution of distances both determined and weighted by Gaussian functions of the torsional potential centered on the equilibrium torsion angles. The CP model does not contain the two conformers

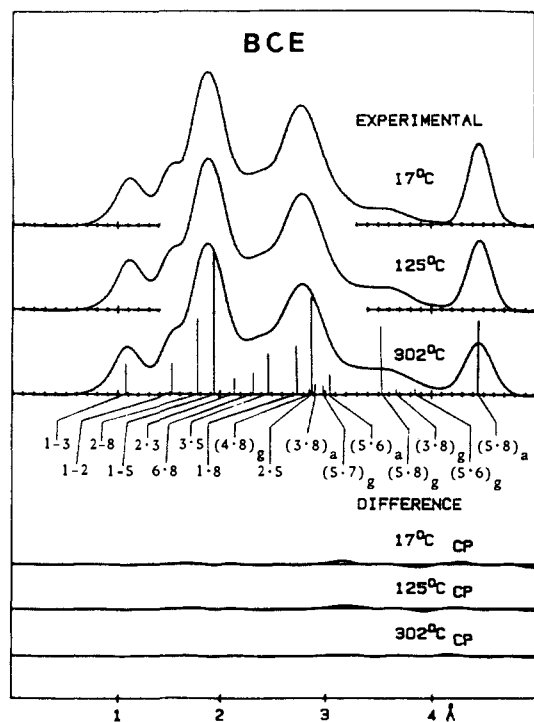


Figure 7. Radial distribution curves for 1-bromo-2-chloroethane. See the legend to Figure 5. Theoretical data were used for the intensity region $0 \leq s/\text{\AA} \leq 2.00$.

explicitly; the torsional potential is represented by a sum of terms, usually three of the form $V_i(1 - \cos i\phi)$, that determines the relative weights of distances calculated from the torsion angles selected at appropriate intervals over the range of ϕ . We tested all of these models for each of our molecules. For the 2S models the spacing was $1/2\sigma_A(1/2\sigma_G)$ for the anti (gauche) conformers over the range $-2\sigma_\phi \leq \Delta\phi \leq 2\sigma_\phi$. For the CP models the angle interval was 5.5° and 11 (34) pseudoconformers near the anti (gauche) equilibrium angles were included.

The low symmetry of our molecules leads in principle to numbers of structural parameters too large to be refined independently. Tests indicated which of these parameters were amenable to refinement; the others were given suitable assumed values. The refinable parameters for CFE and BFE were similar. They were (X is the halogen of lower atomic number) the bond lengths, bond length averages, and differences $r(C-Y)$, $r(C-H)$, $\langle r(C-C, X) \rangle = [r(C-C) + r(C-X)]/2$, $\Delta r(C-C, X) = r(C-C) - r(C-X)$; the bond angles, angle averages, and differences $\langle \angle CCH \rangle_G = [\angle CCH_{3,G} + \angle CCH_{6,G}]/2$, $\langle \angle CCY, X \rangle_G = [\angle CCY_G + \angle CCX_G]/2$, $\Delta \langle \angle CCY, X \rangle_{A-G} = \langle \angle CCY, X \rangle_A - \langle \angle CCY, X \rangle_G$; and the torsion angle $\angle XCCY_G$. For the 2C and 2S models the percentage of the anti form was also refined, and for the CP model the three potential coefficients $V_{1,2,3}$. We were also able to refine $\Delta \langle \angle CCY, X \rangle_{A-G} = \Delta \angle CCY, X_A - \Delta \angle CCY, X_G$ for CFE and $\Delta \angle CCY, X_G = \angle CCY_G - \angle CCX_G$ for BFE. For BCE the parameters $\langle r(C-C, X) \rangle$ and $\Delta r(C-C, X)$ were replaced by $\langle r(C-Y, X) \rangle$ and $\Delta r(C-Y, X)$ defined in a similar way; again, $\Delta \langle \angle CCX \rangle_{A-G}$ could be refined. The results of the test refinements led us to restrict the hydrogen angle parameters by the assumption $\langle \angle HCH \rangle_G = [\angle HC_1H_G + \angle HC_2H_G]/2 = 110.0^\circ$ (CFE), 108.3° (BFE), and 108.7° (BCE), values taken from other haloethanes. The ab initio results mentioned above show slight differences between values for parameters that, lacking these results, would have been set equal in the refinements. Although the ab initio values themselves are less reliable than the corresponding averaged experimental ones, the ab initio differences, particularly for similar types of bond angles, are arguably better assumptions than those implied by setting such differences to zero. In any case the calculated differences are very small and their inclusion or neglect could hardly lead to different structural results; we decided to include them. Our assumptions based on the ab initio results are the following: $\Delta \angle CCH_G = \angle CCH_{3,G} - \angle CCH_{6,G} = 0.5^\circ$ (CFE), 0.9° (BFE), 0.7° (BCE); $\Delta \angle HCH_G = \angle HC_1H_G - \angle HC_2H_G = 0.3^\circ$ (CFE), 0.5° (BFE), -0.2° (BCE); $\Delta \angle CCY, X_G = \angle CCY_G - \angle CCX_G = 0.3^\circ$ (CFE), 0.4° (BCE); $\Delta \langle \angle CCH \rangle_{A-G} = \langle \angle CCH_A \rangle - \langle \angle CCH_G \rangle = 0.0^\circ$ (CFE), 0.4° (BFE), 0.7° (BCE); $\Delta \langle \angle HCH \rangle_{A-G} = \langle \angle HCH_A \rangle - \langle \angle HCH_G \rangle = 0.0^\circ$ (CFE), -0.1° (BFE), 0.3° (BCE); $\Delta \langle \Delta \angle CCH \rangle_{A-G} = \Delta \angle CCH_A - \Delta \angle CCH_G = -0.3$ (CFE), 0.2 (BFE), 0.0 (BCE); $\Delta \langle \Delta \angle CCY, X \rangle_{A-G} = \Delta \angle CCY, X_A - \Delta \angle CCY, X_G = 0.3$ (BFE), -0.1 (BCE); $\Delta \langle \Delta \angle HCH \rangle_{A-G} = \Delta \angle HCH_A - \Delta \angle HCH_G = -0.3$ (CFE), -0.1 (BFE), 0.0 (BCE).

The many amplitude-of-vibration parameters were handled in the usual way. Members of the amplitude groups formed and handled as single parameters were given values consistent with results from the force-field calculations.

Refinement Conditions. The refinements were done by least-squares fitting the electron-diffraction (ED) intensity data in the usual way³⁰ and, in the cases of CFE and BFE, simultaneously these data and B_z rotational constants for the gauche conformers obtained³¹ from the microwave (MW) work. A unit weight matrix was used for the ED data, and for the rotational constants relative weights $A_z:B_z:C_z = 0.15:1.0:1.0$ (CFE) and 1:1:1 (BFE). The effect of different weighting of the MW data relative to the ED was studied and the results found to be quite insensitive to it. For our final refinement of CFE the ratio of the weights MW/ED was 500/1 and for BFE 400/1.

Results. Although the parameters used to describe the models were convenient in view of the complexity of the models, these parameters are less satisfactory for conveyance of the sense of the structures. We have chosen instead to report refined values for the more easily visualized set of parameters listed in Table I. It is evident from the CFE results that the parameter values for the molecular frame are essentially independent of model. Further, though not shown, the frame results at the higher temperatures are similar: they are essentially independent of both model type and temperature. It is also evident from the R factors for CFE that each model type gives about the same quality of fit to experiment, and it may be inferred from comparison of the difference curves of Figures 6 and 7 with those of Figure 5 that this is also true for the other molecules. Because of these similarities there is little point in listing structural details from all the models. We have selected the CP model for this purpose. Both it and the 2S model have the advantage of an explicit representation of the amplitude of the torsional motion for both conformers, but unfortunately in the latter case it was not always possible to refine σ_A . There is a disadvantage to the CP model also in that it is difficult to incorporate the rotational constant data. That is, it is difficult to refine the V 's subject to a constraint that they lead to a gauche potential minimum at a torsion angle consistent with both the MW (for CFE and BFE) and the ED data. In the end this constraint was relaxed; the result is that the gauche minima calculated from the potential functions for CFE and BFE are respectively about 3° larger and 3° smaller than those obtained in the refinement of the torsion angle. Parameter values at the lowest temperatures for all models of CFE and for the CP models of BFE and BCE are found in Table I. Detailed distance and amplitude data for the CP models are found in Table II. More complete tables that include results for the higher temperatures are available in the supplementary material. Correlation matrices for the lowest temperature results are available in the supplementary material; those for the other temperatures are similar.

Discussion

Structures. As Table I shows, the agreement between parameter values for CFE obtained from the MW work and those from the present study is generally quite good. There are significant differences, however, in the values for $r(C-C)$ and $r(C-F)$ from the two investigations: the difference between these distances is substantially greater from the MW work. The reason for the difference is not obvious, but it is likely due to slightly different assumptions about hydrogen parameters. For instance, in the MW work the projections of the bonds to carbon on a plane perpendicular to C-C were assumed to lie at angles of 120° , whereas our model leads to an average projected HCF angle of 121.6° . We believe our values for $r(C-C)$ and $r(C-F)$ to be the more accurate. Our structure provides a fit to within about 4 MHz of the B_z^{obsd} values³¹ at all temperatures, and although we used only the ^{79}Br data in the refinements, our BFE structure agrees with the ^{81}Br constants to within less than 1 MHz. The MW structure, which was adjusted to B_0 values, fits somewhat more poorly: the differences $B_0^{\text{obsd}} - B_0^{\text{calc}}$ for A, B, C are respectively 72, 5, and 7 MHz for the ^{35}Cl isotope and -132, -74, and -70 MHz for the ^{37}Cl one. For BFE the MW estimate of the FCCBr angle is too small (Table I), presumably because some of the numerous assumptions were a bit wide of the mark.

Most of the bond lengths (Tables I and II) of the same type are nearly the same from molecule to molecule. Notable among

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(31) $B_z = B_0 + 1/2 \sum \alpha_i^{\text{br}}$. For CFE (^{35}Cl) in MHz: $A_z = 13606.45 - 18.68$, $B_z = 3289.9 - 4.22$, $C_z = 2876.75 - 1.89$; for BFE (^{79}Br) $A_z = 12547.013 - 16.550$, $B_z = 2218.112(7) - 3.020$, $C_z = 1998.444(7) - 1.250$. Our conversion factor was $1/B_z = 505379 \text{ MHz}\cdot\text{u}\cdot\text{\AA}^2$.

Table I. Results for 1-Chloro-2-fluoroethane (CFE), 1-Bromo-2-fluoroethane (BFE), and 1-Bromo-2-chloroethane (BCE) from Lowest Experimental Temperatures^a

parameters ^b	CFE, -25 °C					BFE, 20 °C		BCE, 17 °C
	2C	2S	CP	MW ^c	theor ^d	CP	MW ^c	CP
$r(\text{C-H})$	1.091 (7)	1.092 (7)	1.092 (7)	[1.095]	1.078	1.093 (7)	[1.087]	1.104 (10)
$\langle r(\text{C-C,F}) \rangle^e$	1.447 (4)	1.447 (4)	1.447 (4)	[1.448] ^f	[1.461] ^f	1.449 (4)	[1.464]	
$\Delta r(\text{C-C,F})^g$	0.116 (5)	0.112 (5)	0.112 (5)	[0.165] ^f	[0.104] ^f	0.114 (10)	[0.141]	
$\langle r(\text{C-Cl,Br}) \rangle$								1.873 (5)
$\Delta r(\text{C-Cl,Br})$								0.160 (5)
$r(\text{C-C})$	1.505 (5)	1.503 (5)	1.503 (5)	1.530 (3)	1.518	1.506 (6)	[1.535]	1.514 (6)
$r(\text{C-X})$	1.389 (3)	1.391 (3)	1.390 (3)	1.365 (2)	1.404	1.392 (4)	[1.394]	1.793 (5)
$r(\text{C-Y})$	1.783 (3)	1.783 (3)	1.783 (3)	1.787 (3)	1.803	1.936 (4)	[1.950]	1.952 (6)
$\langle \angle \text{CCH} \rangle^h$	110.0 (19)	110.2 (19)	109.7 (20)	[111.4]	110.5	110.0 (17)	[108.3]	111.7 (19)
$\angle \text{CCX}_A$	107.6 (10)	108.0 (10)	107.8 (10)		107.0	107.9 (6)		109.1 (5)
$\angle \text{CCX}_G$	111.2 (5)	111.1 (5)	111.0 (5)	109.7 (4)	109.3	110.4 (5)	[107.8]	111.7 (36)
$\angle \text{CCY}_A$	109.0 (8)	109.3 (8)	109.4 (8)		109.3	110.0 (5)		109.6 (5)
$\angle \text{CCY}_G$	111.7 (5)	111.6 (5)	111.5 (5)	111.1 (3)	111.0	112.0 (4)	[110.0]	112.4 (36)
$\Delta \langle \angle \text{CCX} \rangle_{A-G}^i$	-3.1 (5)	-2.8 (5)	-2.7 (5)		-2.4	-2.3 (4)		-2.7 (37)
$\angle \text{XCCY}_G$	112.6 (16)	112.3 (16)	112.0 (16)	111.7 (4)	114.4	112.2 (32)	106.6	[107.0]
% anti	57.7 (61)	58.0 (79)	57.8 (70)			63.8 (62)		82.0 (70)
V_1			1.67 (82)	2.09 (19) ^j		1.5 (8)		5.1 (16)
V_2			-0.94 (67)	-1.75 (16) ^j		-0.5 (7)		-2.6 (12)
V_3			3.85 (140)	3.43 (29) ^j		3.3 (13)		3.8 (8)
R^k	0.113	0.111	0.108			0.104		0.106

^aDistances (r_a^0) in angstroms, angles (\angle_a) in degrees, potential constants (V) in kcal/mol. Quantities in parentheses are estimated 2σ . 2C, 2S, and CP refer to "two-conformer", "two-sigma", and "cosine potential" models; see ref 1. ^bLetter subscripts refer to anti and gauche conformers and X and Y respectively to halogens of lower and higher atomic numbers. ^cGauche form from microwave spectroscopy, ref 11. Quantities in square brackets were assumed. ^dAb initio HF/3-21* level, Gaussian 86. ^eEqual to $[r(\text{C-C}) + r(\text{C-F})]/2$. ^fCalculated from the distances. ^gEqual to $r(\text{C-C}) - r(\text{C-F})$. ^hAverage $\angle \text{CCH}$. ⁱEqual to $\langle \text{CCX} \rangle_A - \langle \text{CCX} \rangle_G$. ^jRecalculated to fit our form of the potential function for internal rotation. ^k $R = [\sum_i w_i \Delta_i^2 / \sum_i w_i (s_i I_i(\text{obsd})^2)]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

Table II. Interatomic Distances ($r/\text{\AA}$) and Vibrational Amplitudes ($l/\text{\AA}$) for CP Models of 1-Chloro-2-fluoroethane (CFE), 1-Bromo-2-fluoroethane (BFE), and 1-Bromo-2-chloroethane (BCE) at Lowest Experimental Temperatures

distance ^a	CFE, -25 °C			BFE, 20 °C			BCE, 17 °C		
	r_g	l_{obs}	l_{calc}	r_g	l_{obs}	l_{calc}	r_g	l_{obs}	l_{calc}
C-H	1.106 (7)	[0.079]	0.079	1.108 (7)	0.069 (8)	0.079	1.120 (9)	0.068 (9)	0.078
C-C	1.506 (5)	0.056	0.049	1.511 (7)	0.064	0.051	1.517 (7)	0.048 (7)	0.050
C-X	1.392 (3)	0.055	0.047	1.396 (5)	0.061	0.047	1.796 (5)	0.058	0.052
C-Y	1.785 (3)	0.057 (4)	0.048	1.941 (4)	0.056	0.051	1.955 (8)	0.056	0.051
$(\text{C}_2\text{-H}_3)_G$	2.146 (28)	0.111	0.107	2.154 (22)	0.113	0.108	2.177 (27)	0.111	0.106
$(\text{C}_2\text{-H}_3)_A$	2.142 (28)	0.112	0.108	2.155 (22)	0.112	0.107	2.184 (26)	0.112	0.106
$(\text{C}_1\text{-H}_6)_G$	2.140 (28)	0.111	0.107	2.143 (22)	0.114	0.109	2.187 (26)	0.112	0.107
$(\text{C}_1\text{-H}_6)_A$	2.142 (28)	0.112	0.108	2.148 (22)	0.112	0.107	2.192 (26)	0.112	0.107
$(\text{H}_6\text{-X})_G$	2.031 (27)	0.109	0.105	2.049 (23)	0.106	0.101	2.363 (25)	0.105	0.110
$(\text{H}_6\text{-X})_A$	2.045 (29)	0.109	0.105	2.056 (22)	0.106	0.101	2.369 (28)	0.104	0.110
$(\text{H}_3\text{-Y})_G$	2.361 (32)	0.116	0.112	2.504 (22)	0.098	0.110	2.515 (22)	0.110	0.116
$(\text{H}_3\text{-Y})_A$	2.380 (26)	0.115	0.111	2.515 (21)	0.096	0.108	2.523 (26)	0.109	0.115
$(\text{C}_1\text{-X})_A$	2.340 (16)	0.073	0.069	2.346 (8)	0.060	0.071	2.700 (6)	0.070	0.073
$(\text{C}_1\text{-X})_G$	2.388 (6)	0.070	0.066	2.383 (6)	0.057	0.069	2.743 (58)	0.070	0.073
$(\text{C}_2\text{-Y})_A$	2.689 (13)	0.078	0.071	2.831 (8)	0.071	0.073	2.844 (7)	0.073	0.076
$(\text{C}_2\text{-Y})_G$	2.723 (6)	0.075	0.068	2.865 (7)	0.072	0.074	2.893 (58)	0.073	0.073
$(\text{H}_6\text{-Y})_G$	3.687 (21)	0.106	0.103	3.836 (16)	0.109	0.107	3.883 (39)	0.105	0.104
$(\text{H}_7\text{-Y})_G$	2.845 (37)	0.159	0.156	2.971 (20)	0.169	0.167	2.978 (75)	0.173	0.172
$(\text{H}_3\text{-X})_G$	3.325 (23)	0.106	0.102	3.325 (18)	0.106	0.103	3.720 (38)	0.106	0.105
$(\text{H}_4\text{-X})_G$	2.596 (37)	0.149	0.145	2.601 (25)	0.153	0.151	2.851 (71)	0.167	0.166
$(\text{X}_8\text{-Y}_3)_G$	3.146 (6)	0.054	0.050	3.247 (5)	0.055	0.053	3.580 (97)	0.046	0.045
$(\text{H}_6\text{-Y})_A$	2.878 (35)	0.143	0.139	2.990 (33)	0.148	0.146	3.059 (42)	0.149	0.148
$(\text{H}_3\text{-X})_A$	2.601 (58)	0.138	0.134	2.616 (38)	0.142	0.140	2.923 (40)	0.145	0.144
$(\text{X}\cdot\text{Y})_A$	3.924 (8)	0.067	0.063	4.078 (8)	0.067	0.065	4.482 (7)	0.071	0.070

^aIn Angstroms. Letter subscripts refer to anti and gauche conformers and X and Y respectively to halogens of lower and higher atomic number.

these is the value of $r(\text{C-C})$, which at 1.51 Å in all the compounds is considerably shorter than the value 1.54 Å taken to be representative of $\text{sp}^3\text{-sp}^3$ C-C bonds. Although a "fluorine effect" (an increased shortening of adjacent bonds that accompanies progressive substitution of hydrogens by fluorine) has long been known and rationalized in terms of rehybridization and electronegativity effects,³² such shortenings are less well documented for the other halogens. The following accounts qualitatively for the observations.

The C-C bond length in CFE is nearly the same as in 1,2-difluoroethane¹ and in BFE and BCE it is slightly longer. In terms of the effects mentioned, this bond in 1,2-difluoroethane is shorter than that in ethane (1.533 (2) Å³³) because electron flow to the electronegative fluorine atoms confers more s character to the bonds formed by carbon; hybrid sp^2 bonds, for example, are shorter than sp^3 bonds. Repulsion of the positively charged carbon atoms arising from the polar C-X bonds³⁴ tends to elongate the bond,

(32) Excellent reviews are the following: Yokozeki, A.; Bauer, S. H. *Top. Cur. Chem.* 1975, 53, 71. Oberhammer, H. In *Stereochemical Applications of Gas-Phase Electron Diffraction*, Part B.; Hargittai, I., Hargittai, M., Eds.; VCH Publishers: New York, NY, 1988; Chapter 4.

(33) (a) Kuchitsu, K. *J. Chem. Phys.* 1968, 49, 4456. (b) Bartell, L. S.; Higgenbotham, H. K. *J. Chem. Phys.* 1965, 42, 851.

(34) Crude estimates of the carbon electronic charges calculated from bond moments are -0.18 (CH₃), +0.12 (CH₂F), +0.06 (CH₂Cl), and +0.04 (C-H₂Br).

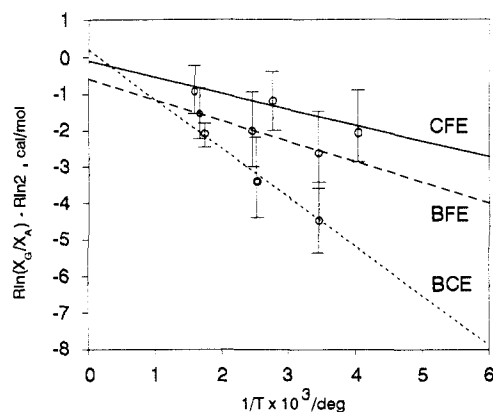


Figure 8. Temperature dependence of the conformational composition of 1-chloro-2-fluoroethane (CFE), 1-bromo-2-fluoroethane (BFE), and 1-bromo-2-chloroethane (BCE). The error bars are estimated 2σ .

but the effect is overwhelmed by the effect of rehybridization. In CFE both effects are smaller than in 1,2-difluoroethane and the distance is unchanged. From CFE through BFE to BCE the rehybridization becomes progressively less while the carbon atom charges remain similar and the distance increases.

The bond angles in our molecules are also similar when compared for the same conformations; however, the CCX angles for each molecule are appreciably larger in the gauche than in the anti forms. It is likely that the larger gauche CCX angles are a consequence of steric repulsion that operates more strongly in this form than in the anti. Molecular mechanics results are in agreement with this idea: in the gauche forms of CFE and BFE the CCF angles are calculated to be the larger by 1.0° and 1.2° , in CFE and BCE the CCCl by 0.8° and 2.1° , and in BFE and BCE the CCBBr by 0.7° and 1.8° . Our *ab initio* results (reasonably reliable only for CFE) also predict larger angles for the gauche form. Although steric interactions of the type X \cdots Y and X \cdots H are in balance in each of the gauche forms, the balance is expected to be obtained at different gauche torsion angles in the different molecules. A qualitative indication of the relative values of these angles may be had from a comparison of the X \cdots Y and X \cdots H gauche distances with the van der Waals contacts. In CFE and BFE the measured and vdW distances for X \cdots Y are about equal, but in BCE the measured Br \cdots Cl is smaller than the vdW value by about 0.2 Å. Although the data of Table I do not contain a refined value for $\angle\text{ClCCBr}_G$ for BCE, refinements of our 2C and 2S models of the three molecules lead to a slightly smaller torsion angle for BCE.

Thermodynamic Properties of the Systems. The gauche form of each molecule is found to be present in smaller amount than the anti, and the gauche amounts are increased at the expense of the anti with increased temperature. Familiar methods were used to interpret the rotameric compositions of the systems as functions of temperature. Figure 8 shows plots of the function $R \ln K - R \ln 2 = -\Delta E^\circ/T + \Delta S^\circ$ that were fitted by least squares to the observations weighted by their uncertainties. The values of $\Delta E^\circ = E_G^\circ - E_A^\circ$ and $S_G^\circ - S_A^\circ$ (note that the statistical degeneracy of the gauche form has been removed from the latter) are given in Table III. The internal energy difference of the two forms is seen to be greatest for BCE and least for CFE. These results have interest in connection with the gauche effect which, as described in the introduction, is an all-or-nothing affair (gauche forms have greater stability when geminally situated bonds of sufficient polarity are present). If the product of the atom electronegativities is taken as a measure of the tendency for stabilization of gauche forms at the expense of anti, the increase in the value of these products is found to be nicely correlated with a decrease in ΔE° throughout the following series of 1,2-dihaloethanes: 1,2-dibromoethane^{2b} (7.8, 2.20 (14) kcal/mol), BCE (8.4, 1.34 (28) kcal/mol), 1,2-dichloroethane^{2a} (9.0, 1.05 (10) kcal/mol), BFE (11.2, 0.57 (26) kcal/mol), CFE (12.0, 0.44 (27) kcal/mol), 1,2-difluoroethane¹ (16.0, -1.76 kcal/mol).

Table III. Energy and Entropy Differences, Torsional Potential Constants, Force Constants and Frequencies, and Rotational Barriers for Conformers of 1-Chloro-2-fluoroethane, 1-Bromo-2-fluoroethane, and 1-Bromo-2-chloroethane^a

parameter ^b	CFE	BFE	BCE
$\Delta E^\circ = E_G^\circ - E_A^\circ$	0.44 (27)	0.57 (36)	1.34 (28)
$\Delta S^\circ = S_G^\circ - S_A^\circ - R \ln 2$	-0.10 (70)	-0.58 (83)	0.20 (58)
V_1	1.66 (108)	1.68 (116)	4.00 (190)
V_2	-0.96 (90)	-0.57 (114)	-1.85 (150)
V_3	3.55 (64)	3.08 (134)	3.56 (106)
ω_A^{calc}	123 (19)	112 (17)	94 (17)
ω_A^{obsd}		126 ^c	123 ^d
ω_G^{calc}	128 (36)	109 (31)	86 (27)
ω_G^{obsd}	142 ^c	126 ^c	107 ^d
barrier (A \rightarrow A)	5.21 (232)	4.76 (238)	7.56 (272)

^aQuantities in parentheses are estimated 2σ . Values for V_i and ω^{obsd} are averages from three temperatures. ^bUnits: kcal/mol for ΔE° , V_i , and the barriers; cal \cdot mol⁻¹ \cdot K⁻¹ for ΔS° ; cm⁻¹ for ω . ^cReference 8. ^dReference 17.

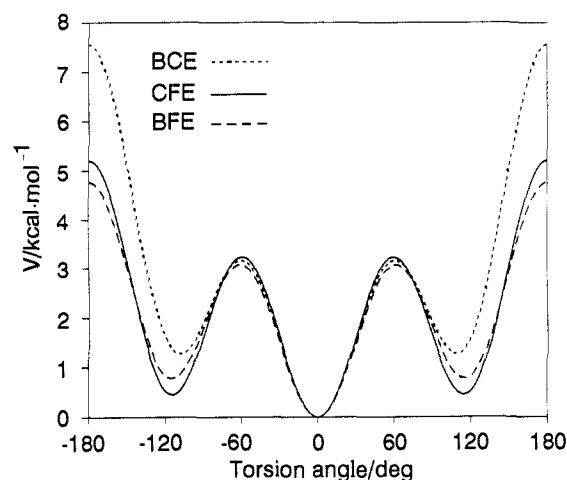


Figure 9. Torsional potentials $V = \frac{1}{2}\sum V_i(1 - \cos i\phi)$ for 1-chloro-2-fluoroethane (CFE), 1-bromo-2-fluoroethane (BFE), and 1-bromo-2-chloroethane (BCE).

Potential Functions. Figure 9 shows curves of the three-term potential functions $V = \frac{1}{2}\sum V_i(1 - \cos i\phi)$. The interhalogen distances at the cis position for the three molecules are smaller than the van der Waals contacts by 0.83 Å (BCE), 0.70 Å (BFE), and 0.62 Å (CFE), which suggests that the cis barriers should have relative values in the order BCE > BFE > CFE. The barrier heights calculated from the potential functions are given in Table III and are seen to be in fair agreement with prediction.

Torsional wave numbers for each of the conformers were estimated from the usual expression $\omega = (2\pi c)^{-1}(k_\phi/G_\phi^{-1})^{1/2}$ where the force constants were evaluated from $\partial^2 V/\partial\phi^2$ at the minima and G_ϕ^{-1} for the anti (gauche) forms was equal (in g \cdot Å² \cdot mol⁻¹ \cdot rad⁻²) to 11.6 (11.6) for CFE, 12.7 (13.7) for BFE, and 19.2 (24.9) for BCE. The results, given in Table III, are in good agreement with observation.

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Registry No. CFE, 762-50-5; BFE, 762-49-2; BCE, 107-04-0.

Supplementary Material Available: Parameter values, distances, and amplitudes of vibration for each model of the molecules at each temperature (Tables IV–VIII), symmetry coordinates (Table IX), force constants for each molecule (Tables X–XII), correlation matrices for the CP model of each molecule at the lowest temperature (Tables XIII and XV), and Figures 10–15 (similar to Figures 2–4) of intensity curves for each molecule at the two higher temperatures (19 pages). Ordering information is given on any current masthead page. Intensity data may be obtained from the authors.