1844 *J. Phys. Chem. A* **2004,** *108,* 1844−1850

Fluorinated Dimethyl Ethers, CH_2FOCH_2F, CHF_2OCHF_2, and CF_3OCHF_2: Unusual Conformational Properties

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Received: September 9, 2003; In Final Form: December 1, 2003

The geometric structures and conformational properties of bis(fluoromethyl) ether, CH_2FOCH_2F, bis(difluoromethyl) ether, CHF_2OCHF_2, and pentafluoromethyl ether, CF_3OCHF_2, have been studied with gas electron diffraction and quantum chemical methods (B3LYP/6-31G* and MP2 with 6-31G*, cc-pVTZ or 6-311G(2df) basis sets). IR(matrix) spectra have been recorded for CF_3OCHF_2. The most stable [sc,sc] conformer of CH_2FOCH_2F possesses C_2 symmetry with the C−F bonds of both CH_2F groups in synclinal (sc, counterclockwise) orientation (ϕ(C−O−C−F) = 70(2)°). A small contribution (≤14%) of the [sc,−sc] form with C_s symmetry cannot be excluded (−sc = synclinal, clockwise). CHF_2OCHF_2 exists in the gas phase as a mixture of two forms. In the main [ap,sp] conformer (82(8)%) one C−H bond is oriented antiperiplanar (ap), the other one synperiplanar (sp). This latter C−H bond nearly eclipses the opposite O−C bond with ϕ(C−O−C−H) = 18(2)°. Nearly eclipsed orientation of the C−H bond is also favored in CF_3OCHF_2 with ϕ(C−O−C−H) = 19(3)°. According to IR(matrix) spectra a small (8(3)%) contribution of the [ap] conformer with the C−H bond antiperiplanar relative to the opposite O−C bond is present at room temperture. The conformational properties of these fluorinated dimethyl ethers can be rationalized by orbital interaction energies derived from a natural bond orbital (NBO) analysis.

Introduction

Because chlorofluorocarbons (CFC's) were found to play an important role in the depletion of stratospheric ozone, fluorinated ethers have gained great interest as alternative refrigerants. Furthermore, such ethers can act as inhalation anaesthetics. Determination of thermodynamic properties of these compounds require the knowledge of their structural and conformational properties. The most simple compounds in this class are fluorinated dimethyl ethers.

The geometric structures and conformations of three members of this series, CH_2FOCH_3,[1] CF_3OCH_3,[2] and CF_3OCF_3,[3] have been determined by microwave spectroscopy (MW) and/or gas electron diffraction (GED). In the present study we report gas-phase structures and conformational properties of bis(fluoromethyl) ether, CH_2FOCH_2F, bis(difluoromethyl) ether, CHF_2OCHF_2, and pentafluoromethyl ether, CF_3OCHF_2, applying GED, quantum chemical calculations, and IR matrix spectroscopy. Several quantum chemical studies with different computational methods have been reported in the literature for these compounds.[4−9] Whereas no experimental investigations about the geometric structures and/or conformational properties have been reported for CH_2FOCH_2F and CF_3OCHF_2, two independent MW investigations combined with ab initio calculations have been performed for CHF_2OCHF_2.[10,11] Both studies agree with respect to the most stable conformer of this compound, which possesses C_1 symmetry with antiperiplanar orientation of one C−H bond and synperiplanar (sp) orientation of the other C−H bond.[12] Horn et al.[11] observe a small amount of a second conformer in the IR(matrix) spectra, but no rotational transitions of this conformer could be assigned in the MW spectrum. Although Suenram et al.[10] determined rotational constants for six isotopomers (^{13}C, ^{18}O, and ^{2}H), it was not possible to derive a consistent geometric structure from these data.

Quantum Chemical Calculations

Geometric parameters of stable structures of the three fluorinated dimethyl ethers have been optimized with the B3LYP/6-31G* method and MP2 approximation using 6-31G* and cc-pVTZ basis sets. Furthermore, potential curves for internal rotation around O−C bonds and vibrational frequencies for stable conformers were derived with both methods and 6-31G* basis sets. The various conformers of these compounds are named according to the orientation of the unique C−F bond in CH_2F groups and the unique C−H bond in CHF_2 groups. All quantum chemical calculations were performed with the GAUSSIAN98 program package[13] and vibrational amplitudes were derived from the Cartesian force field with the program SHRINK.[14]

CH_2FOCH_2F. Depending on the orientation of the C−F bonds, three stable conformers, [ap,ap], [sc,sc], and [sc,−sc], occur in this ether (see Chart 1 and ref 12 for definition of ap, sc, −sc, ac, and ap). The [ap,sc] conformer does not correspond to a stable structure and a geometry optimization started with such a structure converges to the [sc,sc] form. The relative energies of the stable forms which were derived with the B3LYP/6-31G* and MP2/cc-pVTZ methods and the relative Gibbs free energies are listed in Table 1. The results of these calculations are in strong contrast to those of Orgel et al.,[6] which predict the [ap,ap] form to be most stable. The potential function for simultaneous internal rotation of both CH_2F groups (structures with C_2 symmetry), which is shown in Figure 1,

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10.1021/jp0310605 CCC: $27.50

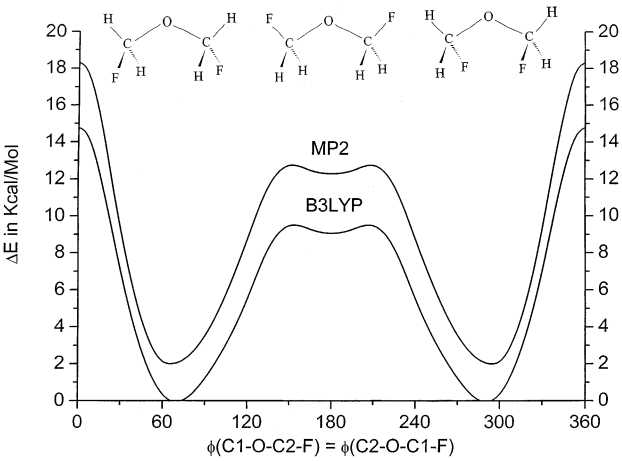


Figure 1. CH_2FOCH_2F: Potential function for simultaneous rotation around both O−C bonds (structures with C_2 symmetry), derived with B3LYP and MP2 approximation and 6-31G* basis sets. The MP2 curve is shifted by 2 kcal/mol.

CHART 1

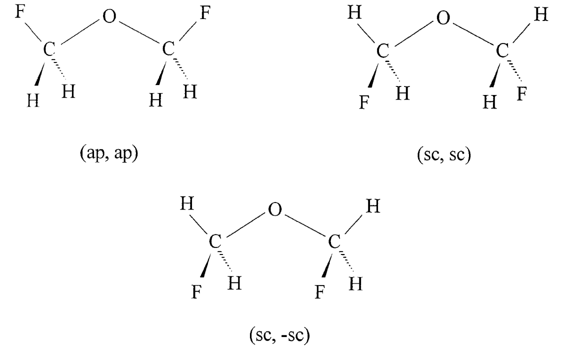

(ap, ap)
(sc, sc)
(sc, -sc)

TABLE 1: Relative Energies (kcal/mol) of Stable Conformers of CH_2FOCH_2F, CHF_2OCHF_2, and CF_3OCHF_2

	B3LYP/6-31G*			
conformer	ΔE	$\Delta G°$	MP2/cc-pVTZ ΔE	MP2/6-31G* ΔE
		CH_2FOCH_2F		
[sc,sc] (C_2)	0.00	0.00	0.00	
[sc,-sc] (C_S)	1.49	1.38	1.57	
[ap,ap] (C_{2v})	8.95	8.48	8.71	
		CHF_2OCHF_2		
[ap,sp] (C_1)	0.00	0.00	0.00	
[sc,sc] (C_2)	0.94	1.31	0.80	
[ap,ap] (C_2)	1.16	1.68	2.02	
		CF_3OCHF_2		
[sp] (C_1)	0.00	0.00	0.00	0.00
[sc] (C_1)				0.05
[ap] (C_1)	0.27	1.17	1.13	−0.22

demonstrates that a very shallow minimum occurs for the [ap,-ap] conformer, whose energy is about 9 kcal/mol higher in energy than that of the [sc,sc] form.

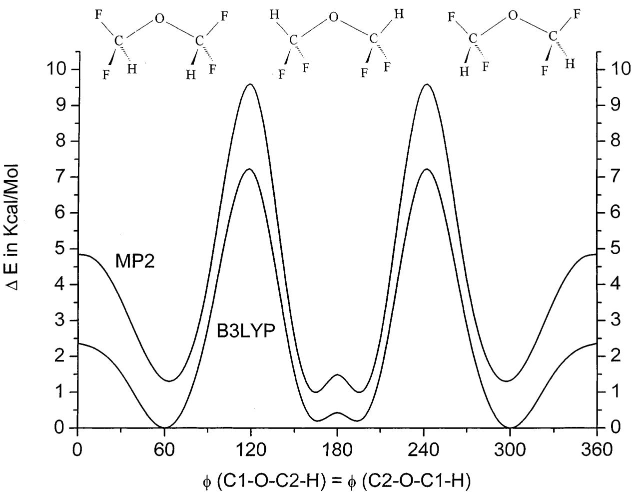
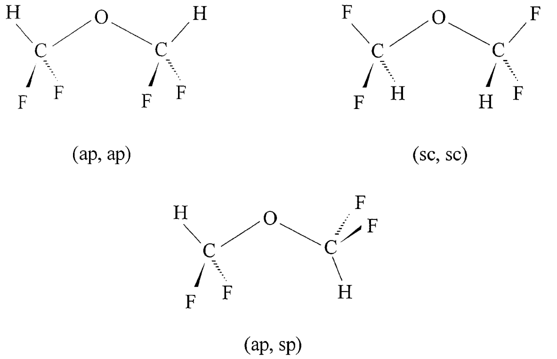


Figure 2. CHF_2OCHF_2: Potential function for simultaneous rotation around both O−C bonds (structures with C_2 symmetry), derived with B3LYP and MP2 approximation and 6-31G* basis sets. The MP2 curve is shifted by 1 kcal/mol.

CHART 2


(ap, ap)
(sc, sc)
(ap, sp)

CHF_2OCHF_2. In principle, four conformations with staggered arrangements of the two CHF_2 groups, [ap,ap], [ap,sc], [sc,sc] and [sc,−sc] are conceivable for this ether. Theoretical calculations of Suenram et al.[10] and Horn et al.,[11] as well as those performed in our group, demonstrate that the [ap,sc] form is distorted to an [ap,sp] form with one C−O−C−H dihedral angle smaller than 30°. According to all calculations, this conformer with C_1 symmetry possesses the lowest energy. This is confirmed by analysis of the MW spectra,[10,11] which result in a dihedral angle of about 24° for this CHF_2 group.[10] Orgel et al.[6] claim that the [ap,ap] conformer is lowest in energy. Although the [sc,−sc] structure has been predicted to be a stable conformer by Suenram et al. on the basis of MP2/6-31G* calculations,[10] this structure corresponds to a transition state, as pointed out by Horn et al.[11] MP2/6-31G*, MP2/6-311++G**, and B3LYP/6-31G* calculations predict one imaginary frequency for this structure. Thus, only three stable conformers shown in Chart 2 exist for this ether. The potential function for simultaneous internal rotation around both O−C bonds (structures with C_2 symmetry) is shown in Figure 2 and that for rotation of the CHF_2 group with sp-oriented C−H bond in Figure 3. The torsional motion of this group occurs in a very shallow double-minimum potential with minima near 10° (B3LYP) or 20° (MP2). The predicted barriers at the exactly eclipsed orientation (0.018 and 0.033 kcal/mol at ϕ(C1−O−C2−H) = 0°) are below the zero point vibration (18 and 26 cm^{-1}, respectively). Relative energies and Gibbs free energies of the three conformers are listed in Table 1. Gibbs free energies have to be considered with caution, because the value for the lowest torsional frequency depends on the computational method and the approximation of harmonic vibrations is applied.

CF_3OCHF_2. Potential functions for internal rotation around the O−CHF_2 bond derived with B3LYP and MP2 methods and 6-31G* basis sets (Figure 4) differ appreciably. Whereas only two minima for [sp] and [ap] conformers (ϕ(C−O−C−H) = 20.7° and 167.6°, see Chart 3) are predicted by the hybrid method, the MP2 approximation results in a third minimum for an [sc] form with ϕ(C−O−C−H) near 60°. Additional calculations with the MP2 approximation and larger basis sets (6-311G-

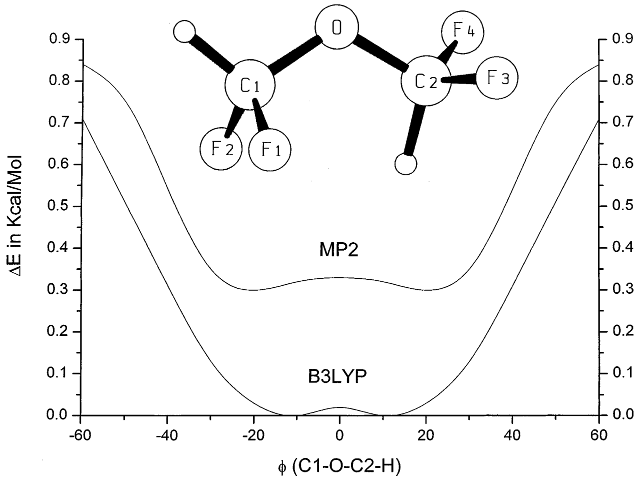


Figure 3. CHF_2OCHF_2: Potential function for rotation around both O−C2 bond in the [ap,sp] conformer derived with the B3LYP and MP2 approximation and 6-31G* basis sets. The MP2 curve is shifted by 0.3 kcal/mol.

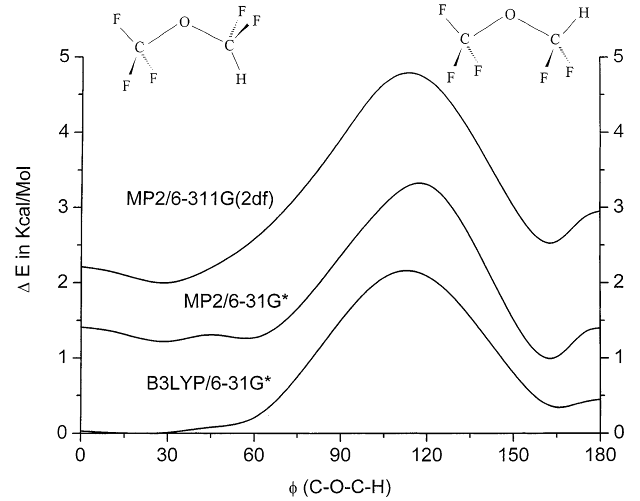


Figure 4. CF_3OCHF_2: Potential function for rotation around O−CHF_2 bond derived with different methods. The MP2 curves are shifted by 1 and 2 kcal/mol, respectively.

CHART 3

(sp) (ap)

(2df)) confirm the existence of only two minima corresponding to [sp] and [ap] forms, however. The relative energies of these conformers are listed in Table 1. Besides the potential functions, also the frequencies for the torsional vibration around the O−CHF_2 bond derived with B3LYP and MP2 methods and 6-31G* basis sets differ strongly (17 and 37 cm^{-1}, respectively). This strong dependence of vibrational frequencies on the computational method and the shape of the potential function, which deviates strongly from a harmonic potential, makes the values derived for Gibbs free energies rather uncertain. Similarly, vibrational amplitudes and vibrational corrections for torsion dependent interatomic distances derived with the two methods differ strongly and cannot be considered reliable.

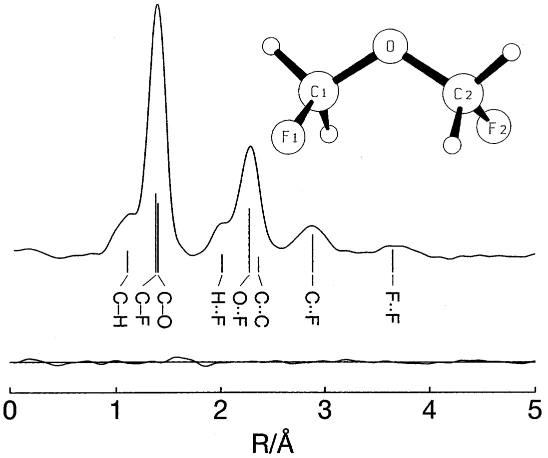


Figure 5. CH_2FOCH_2F: Experimental radial distribution function and difference curve.

Structure Analyses

Although these fluorinated ethers are small molecules with only nine atoms, the determination of their geometric structures and conformational properties by GED is difficult for three reasons: (1) All bond lengths (C−F and O−C) and all one-angle nonbonded distances (F··F and O··F) are similar and difficult or impossible to resolve. (2) The contribution of nonbonded distances, which are characteristic for a certain conformer, is small. (3) Low-frequency torsional vibrations cause large amplitude motions. The torsional frequencies predicted for CHF_2OCHF_2 and CF_3OCHF_2 (see above) suggest the use of a dynamic model in the analysis of the GED intensities. For both compounds double-minimum potentials of the type $V = V_0[1 - (\phi/\phi_e)^2]^2$ were used for the torsion of the CHF_2 groups with an sp-oriented C−H bond. V_0 corresponds to the barrier at ϕ(C−O−C−H) = 0° and ϕ_e is the dihedral angle at the potential minimum. Attempts to refine such a dynamic model demonstrated that V_0 and ϕ_e are strongly correlated and cannot be determined simultaneously. Depending on the assumption for V_0, ϕ_e varied in a range of 10°. The fit of the experimental intensities with dynamic models did not improve compared to that with rigid models. Therefore, we decided to use rigid models for these ethers. Because the calculations of vibrational corrections $\Delta r = r_a - r_\alpha$ from theoretical force fields are not reliable, as pointed out above, we determined r_a structures, in which the dihedral angles derived correspond to "effective" values. Constraints for geometric parameters, which are made in the least squares analyses, are based on MP2 results with large basis sets (cc-pVTZ). Because calculated geometric parameters are in close agreement with the final experimental values, calculated differences between such parameters are expected to be reliable.[15] Assumptions for vibrational amplitudes are based on force fields derived with the MP2/6-31G* approximation. Scattering amplitudes and phases of ref 16 were used.

CH_2FOCH_2F. The radial distribution curve derived by Fourier transformation of the molecular intensities with an artificial damping function $\exp(-\gamma s^2)$, $\gamma = 0.0019$ Å^2 (Figure 5), is reproduced best with an [sc,sc] conformation. C_2 overall symmetry was assumed in the least squares refinement. Differences between bond angles that describe the position of hydrogen atoms were set to theoretical values. Calculated F−C−H angles differ by less than 1° and were set equal. Vibrational amplitudes, which either caused high correlations with geometric parameters or were badly determined in the GED experiment, were fixed to calculated values. The amplitudes for

TABLE 2: Experimental and Calculated Geometric Parameters for the [sc,sc] Conformer of CH_2FOCH_2F[a]

	GED[b]		B3LYP/6-31G*	MP2/cc-pVTZ
O−C	1.395(6)[c]	p1	1.395	1.388
C−F	1.374(6)[c]	p2	1.383	1.378
$(C-H)_{mean}$	1.097(8)	p3	1.093	1.088
C−O−C	115.9(14)	p4	114.4	113.2
O−C−F	110.4(3)	p5	110.7	110.4
O−C−H(ap)	108.1(17)	p6	106.3	106.8
O−C−H(sc)	113.2(17)[d]		111.3	111.6
$(F-C-H)_{mean}$	109.3(17)[d]		108.3	107.8
ϕ(C−O−C−F)	70.2(21)	p7	69.3	72.8

[a] Values in Å and deg. [b] r_a values with 3σ uncertainties. [c] Uncertainty includes possible systematic error due to constraints of vibrational amplitudes (see text). [d] Difference to previous angle fixed to calculated value (MP2).

TABLE 3: Interatomic Distances and Vibrational Amplitudes (without Nonbonded Distances Involving Hydrogen Atoms) for the [sc,sc] Conformer of CH_2FOCH_2F[a]

	distance	ampl (GED)		ampl (MP2)
C−H	1.10	0.083(8)	*l*1	0.076
C−F	1.37	0.046[3][b]		0.046
O−C	1.40	0.047[3][b]		0.047
O···F	2.27	0.058(3)	*l*2	0.060
C···C	2.37	0.064[c]		0.064
C1···F2	2.88	0.137(10)	*l*3	0.137
F1···F2	3.64	0.210(35)	*l*4	0.300

[a] Values in Å with 3σ uncertainties. For atom numbering see Figure 5. [b] Not refined, but varied within the range given in brackets (see text). [c] Not refined.

the C−F and O−C distances were varied by ±0.003 Å, to estimate possible systematic errors for the refined bond lengths. This systematic error is included in the uncertainties for these bond lengths. With these assumptions seven geometric parameters (p1 to p7) and four vibrational amplitudes (*l*1 to *l*4) were refined simultaneously. Two correlation coefficients had values larger than |0.7|: p1/p2 = −0.94 and p4/p7 = −0.84. The results of the least squares refinement are listed in Table 2 (geometric parameters) and Table 3 (vibrational amplitudes) together with calculated values. Refinements for mixtures of [sc,sc] and [sc,−sc] conformers resulted in a contribution of 6(8)% of the [sc,−sc] form. Experimental uncertainties given in parentheses are in all cases 3σ values. This contribution corresponds to $\Delta G^\circ \geq 1.1$ kcal/mol, in agreement with the value of 1.38 kcal/mol, derived with the B3LYP method.

CHF_2FOCHF_2. The lowest energy conformer [sp,ap] fits the experimental radial distribution curve (Figure 6) best among the three possible forms, which are predicted by quantum chemical calculations. In the least squares refinement the two sc-oriented C1−F bond lengths and the two anticlinal (ac)-oriented C2−F bond lengths were set equal. The calculated differences are less than 0.003 Å. Angles, which differ by less than 1° according to the calculations, were set equal and the mean O−C−H and F−C−F angles were constrained to calculated angles. The differences between the two types of C−F bond lengths and between the two O−C bond lengths were fixed to calculated values. Similar assumptions as described above were applied for the vibrational amplitudes. Eight geometric parameters and five vibrational amplitudes were refined simultaneously. Two correlation coefficients had values larger than |0.7|: p1/p2 = −0.76 and p5/*l*1 = −0.95. The fit of the experimental intensities improved if 18(8)% of [sc,sc] conformer were addded. The agreement factor *R* decreased from 0.057 to 0.051. Bond lengths and angles of this conformer were tied to those of the prevailing form using the calculated differences.

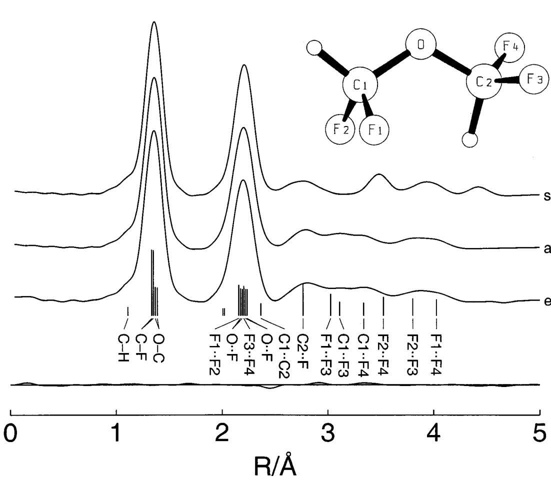


Figure 6. CHF_2OCHF_2: Experimental and calculated radial distribution functions and difference curve for mixture. Interatomic distances for [ap,sp] conformer.

TABLE 4: Experimental and Calculated Geometric Parameters for the [ap,sp] Conformer of CHF_2OCHF_2[a]

	GED[b]		B3LYP/6-31G*	MP2/cc-pVTZ
O−C1	1.366(7)[c]	p1	1.374	1.368
O−C2	1.385(7)[c,d]		1.394	1.387
C1−F	1.346(5)[c]	p2	1.359	1.350
C2−F	1.336(5)[c,d]		1.348	1.340
C−H	1.109(17)	p3	1.090	1.084
C−O−C	118.4(17)	p4	116.4	115.3
$(O-C-F)_{mean}$	108.5(15)	p5	109.6	109.7
$(O-C-H)_{mean}$	110.5[e]		110.4	110.5
$(F-C-H)_{mean}$	110.2(9)	p6	110.0	111.0
$(F-C-F)_{mean}$	107.1[e]		107.2	107.1
ϕ_1(C2−O−C1−H)	179.3(18)	p7	178.5	176.8
ϕ_2(C1−O−C2−H)	18.4(17)	p8	11.9	18.1

[a] Values in Å and deg; for atom numbering, see Figure 6. [b] r_a values with 3σ uncertainties. [c] Uncertainty includes possible systematic error due to constraints of vibrational amplitudes (see text). [d] Difference to previous parameter fixed to calculated value (MP2). [e] Not refined.

TABLE 5: Interatomic Distances and Vibrational Amplitudes (without Nonbonded Distances Involving Hydrogen Atoms) for the [sp,ap] Conformer of CHF_2OCHF_2[a]

	distance	ampl (GED)		ampl (MP2)
C−H	1.11	0.075[b]		0.075
C−F	1.33−1.35	0.045[3][c]		0.045
O−C	1.37−1.39	0.046[3][c]		0.046
F···F	2.16−2.18	0.061(6)	*l*1	0.057
O···F1,2	2.22	0.061(6)	*l*1	0.057
O···F1,2	2.20	0.066(6)[d]		0.062
C···C	2.36	0.063[b]		0.063
C2···F1,2	2.76−2.77	0.121(37)	*l*2	0.228
C1···F3,4	3.11−3.34	0.093(25)	*l*3	0.131
F···F	3.02−3.52	0.214(65)	*l*4	0.514
F···F	3.81−4.02	0.121(37)	*l*5	0.205

[a] Values in Å with 3σ uncertainties. For atom numbering, see Figure 6. [b] Not refined. [c] Not refined, but varied within the range given in brackets (see text). [d] Difference to previous amplitude fixed.

The dihedral angle and vibrational amplitudes were fixed to calculated values. The results of the least squares refinement are listed in Table 4 (geometric parameters) and Table 5 (vibrational amplitudes) together with theoretical values. The conformational composition corresponds to $\Delta G^\circ = 0.9(3)$ kcal/mol, slighly smaller than the value predicted by the B3LYP method (1.31 kcal/mol, Table 1). Because the energy difference predicted by the MP2 approximation ($\Delta E = 0.80$ kcal/mol) is slightly smaller than the B3LYP value, the corresponding ΔG°

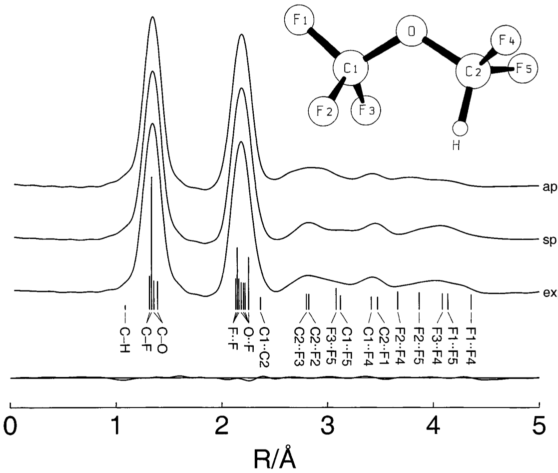


Figure 7. CF_3OCHF_2: Experimental and calculated radial distribution functions. Difference curve and interatomic distances for [sp] conformer.

TABLE 6: Experimental and Calculated Geometric Parameters for the [sp] Conformer of CF_3OCHF_2[a]

	GED[b]		B3LYP/6-31G*	MP2/cc-pVTZ
O−C1	1.356(7)[d]	p1	1.364	1.360
O−C2	1.389(7)[d,e]		1.399	1.392
C−F[c]	1.335(4)[d]	p2	1.345	1.336
C1−F1	1.315(4)[d,e]		1.326	1.316
C−H	1.100[f]		1.092	1.086
C−O−C	118.6(11)	p3	116.6	115.3
O−C−F1	108.3(5)	p4	107.8	107.7
O−C−F2,3	112.4(5)[e]		111.8	111.8
O−C−F4	109.9(5)[e]		109.1	109.3
O−C−F5	107.2(5)[e]		106.9	106.6
O−C−H	112.5[f]		112.6	112.5
H−C−F4,5	108.9(13)	p5	110.0	110.0
Φ_1(C2−O−C1−F1)	178.4(30)	p6	175.8	176.6
Φ_2(C1−O−C2−H)	18.6(28)	p7	20.7	24.7

[a] Values in Å and deg; for atom numbering, see Figure 7. [b] r_a values with 3σ uncertainties. [c] All C−F distances except C1−F1. [d] Uncertainty includes possible systematic error due to constraints of vibrational amplitudes (see text). [e] Difference to previous parameter fixed to calculated value (MP2). [f] Not refined.

TABLE 7: Interatomic Distances and Vibrational Amplitudes (without Nonbonded Distances Involving Hydrogen Atoms) for the [sp] Conformer of CF_3OCHF_2[a]

	distance	ampl (GED)		ampl (MP2)
C−H	1.10	0.075[b]		0.075
C−F	1.32−1.33	0.044[3][c]		0.044
O−C	1.36−1.39	0.047[3][c]		0.047
F···F	2.14−2.15	0.052(6)	*l*1	0.056
O···F1,2,3	2.19−2.23	0.052(6)	*l*1	0.056
O···F4,5	2.23	0.056(6)[d]		0.060
C···C	2.36	0.063[b]		0.063
C2···F3	2.79	0.100(27)	*l*2	0.131
C2···F2	2.81	0.100(27)	*l*2	0.147
C1···F5	3.12	0.110(49)	*l*3	0.171
C1···F4	3.41	0.103(31)	*l*4	0.093
C2···F1	3.48	0.063[b]		0.063
F3···F5	3.07	0.296(218)	*l*5	0.290
F2···F4	3.66	0.296(218)	*l*5	0.270
F3···F5	3.86	0.110(49)	*l*3	0.230
F3···F5	4.07	0.103(31)	*l*4	0.133
F3···F5	4.15	0.234(167)	*l*6	0.148
F3···F5	4.37	0.150(76)	*l*7	0.087

[a] Values in Å with 3σ uncertainties. For atom numbering, see Figure 7. [b] Not refined. [c] Not refined, but varied within the range given in brackets (see text). [d] Difference to previous amplitude fixed.

value is expected to agree with the experimental result within the experimental uncertainty.

CF_3OCHF_2. The experimental radial distribution curve (Figure 7) is reproduced better with the [sp] than with the [ap] conformer. All C−F bonds, except the C1−F1 bond, have very similar lengths and deviate from their mean value by less than 0.003 Å. Therefore, they were set equal in the least squares refinement. The ap-oriented C1−F1 bond is shorter and the difference to the other C−F bond lengths, as well as the difference between the O−C bond lengths were fixed to calculated values. Bond angles that differ by less than 1° were set equal, and larger differences were constrained to MP2 values. The C−H bond length and O−C−H bond angle were not refined. Asumptions for vibrational amplitudes were analogous to those described above. Seven geometric parameters and six vibrational amplitudes were refined simultaneously. Only one correlation coefficient had a value larger than |0.7|: $p1/p2 = -0.74$. The results of the least squares refinement are listed in Table 6 (geometric parameters) and Table 7 (vibrational amplitudes) together with theoretical values.

Unfortunately, the radial distribution curves for [sp] and [ap] conformers (Figure 7) are rather similar and the contribution of the [ap] form is badly determined (13(16)%). The IR(matrix) spectra, however, allow a more accurate determination of the conformational composition. The strongest band in this spectrum at 1195 cm^{-1}, which corresponds to the asymmetric CF_3 stretching vibration of the [sp] conformer, has been analyzed in detail. According to the B3LYP method, its frequency in the [ap] form is shifted by 33 cm^{-1} (from 1226 to 1259 cm^{-1}). A weak band at 1229 cm^{-1}, which is shifted by 34 cm^{-1} from the band at 1195 cm^{-1}, is readily assigned to the asymmetric CF_3 stretch of the [ap] conformer. The intensity of this weak peak increases, if the temperature of the compound/Ar mixture is increased from 21 to 165 °C before the gas is trapped in the matrix. This temperature dependence corresponds to $\Delta H^\circ = 0.8(2)$ kcal/mol. The B3LYP method predicts very similar line strengths (450 and 428 km/mol, respectively) for this vibration in both conformers. From the relative areas of the two peaks at 21 °C and the calculated ratio of the line strengths we obtain a contribution of 8(3)% of the [ap] conformer. This corresponds to $\Delta G^\circ = 1.5(3)$ kcal/mol. Error limits are estimated from uncertainties in the areas and in calculated intensities. The difference between ΔH° and ΔG° is due to different entropies of the two conformers. The above experimental values for ΔH° and ΔG° correspond to $\Delta S^\circ = -2.3$ cal/(K mol), in good agreement with the calculated (B3LYP) value of −3.2 cal/(K mol). Calculated energy differences depend strongly on the computational method and predicted values vary between −0.22 and +1.13 kcal/mol (Table 1). According to the B3LYP method ΔE and ΔG° differ by 0.9 kcal/mol. Thus, predicted ΔG° values range from about +0.7 to +2.0 kcal/mol, in agreement with the experiment.

Discussion

The most interesting feature of these fluorinated dimethyl ethers is their conformational properties. Intuitively, one expects conformations with staggered arrangements around the O−C bonds. The CH_3 groups in dimethyl ether possess staggered orientation and internal rotation is well described with a V_3 potential and a barrier of 2.6 kcal/mol.[17] Staggered orientation is observed experimentally also in the case of CH_2FOCH_2F, where the [sc,sc] conformer with dihedral angles ϕ(C−O−C−F) = 70(2)° is preferred. In the other two ethers, CHF_2OCHF_2 and CF_3OCHF_2, however, which contain one or two CHF_2 groups, one C−H bond nearly eclipses the opposite O−C bond in the preferred conformation ([ap,sp] and [sp], respectively).

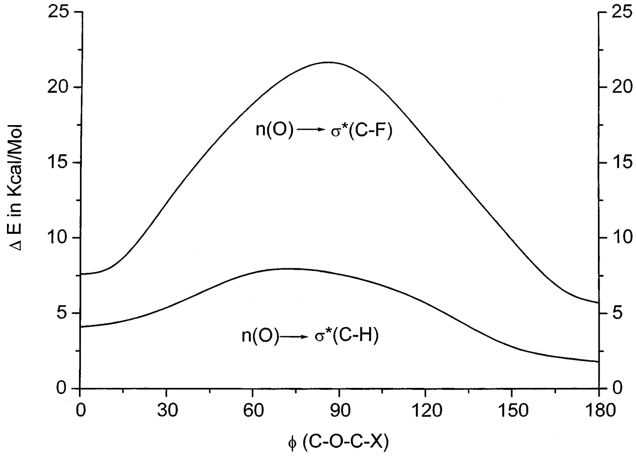


Figure 8. Stabilization energies due to orbital interactions in CH_2FOCH_3 for different dihedral angles.

The conformational properties of these ethers are mainly determined by steric repulsions between the substituents of the two methyl groups and by orbital interactions between the oxygen lone pairs ($n_\sigma(O)$ and $n_\pi(O)$) and the antibonding σ^* orbitals of the C−F and C−H bonds (anomeric effects). The stabilization energies due to these orbital interactions can be determined quantitatively by a natural bond orbital (NBO) analysis,[18] whereas steric repulsions can be estimated only qualitatively. Both effects depend strongly on the torsional angle around the O−C bonds. Stabilization energies $n(O) \rightarrow \sigma^*(C-X)$ have been derived from the B3LYP/6-31G* wave function for the compound CH_2FOCH_3 and their dependence on the dihedral angle $\phi(C-O-C-X)$, X = F or H, is shown in Figure 8. These energies possess their maxima for dihedral angles around 80°, and the $n(O) \rightarrow \sigma^*(C-F)$ stabilization is 2−3 times stronger than the $n(O) \rightarrow \sigma^*(C-H)$ stabilization. Furthermore, the interaction energies for synclinal ($\phi = 60°$) and anticlinal ($\phi = 120°$) orientation of the C−F bond are similar. Both values are considerably larger than that for antiperiplanar orientation ($\phi = 180°$). This explains, why only the [sc] conformer was observed in the MW spectra of CH_2FOCH_3.[1] The experimental dihedral angle ($\phi(C-O-C-F) = 69.2(16)°$) is a compromise between anomeric interactions, which favor an angle of ca. 80°, and steric repulsions, which favor an angle of about 60°. The [ap] form is calculated to be higher in energy by 4.24 kcal/mol.

Anomeric effects also rationalize the strong preference of the [sc,sc] conformer for CH_2FOCH_2F over the [ap,ap] form. The sum of all orbital interaction energies of the oxygen lone pairs with C−F and C−H bonds is 50.8 and 40.4 kcal/mol for these two conformers, respectively. The difference between these anomeric effects (10.4 kcal/mol) is close to the relative energies derived with the same computational method (8.95 kcal/mol, see Table 1). Anomeric effects are very similar for [sc,sc] and [sc,−sc] forms (50.8 vs 50.1 kcal/mol), but the former conformer is favored by steric interactions.

In CHF_2OCHF_2 anomeric effects are stronger in the [ap,sp] conformer (62.7 kcal/mol) than in the sterically favored [sc,sc] form (58.5 kcal/mol). Strong orbital interactions are present also in the [ap,ap] conformer (61.2 kcal/mol), but steric repulsions between the synclinal fluorine atoms apparently destabilize this structure.

An NBO analysis for CF_3OCF_2H shows that anomeric effects favor a CHF_2 group with ap-oriented C−H bond and staggered arrangement (29.5 kcal/mol) over the CHF_2 group with sp-oriented C−H bond and nearly eclipsed arrangement (27.8 kcal/mol). On the other hand, steric repulsions between fluorine atoms of the ap-oriented CHF_2 group with those of the opposite CF_3 group lead to a stronger deviation of the CF_3 group from the exact staggered arrangement. This decreases the stabilization energy for the CF_3 group form 39.5 kcal/mol in the [sp] conformer to 37.3 kcal/mol in the [ap] form. Thus, according to the B3LYP method, the sum of the stabilization energies favors slightly the [sp] conformer (67.3 kcal/mol) over the [ap] form (66.8 kcal/mol). This difference is close to the relative energy derived with this computational method (0.27 kcal/mol). The relative Gibbs free energy derived from the IR(matrix) spectra ($\Delta G° = 1.5(3)$ kcal/mol) is larger than relative energies predicted by theoretical methods or the $\Delta G°$ value obtained with the B3LYP approximation (Table 1).

SCHEME 1

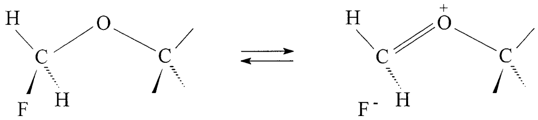


TABLE 8: Skeletal Geometric Parameters in Fluorinated Dimethyl Ethers

C1−O−C2	r(O−C1)	r(O−C2)	∠(C1−O−C2)
CH_3-O-CH_3[a]	1.415(1)	1.415(1)	111.8(2)
$CH_2F-O-CH_3$[b]	1.362(6)	1.427(7)	113.6(6)
$CH_2F-O-CH_2F$[c]	1.395(6)	1.395(6)	115.9(14)
$CHF_2-O-CHF_2$[c]	1.366(5)	1.385(5)	118.4(17)
CF_3-O-CH_3[d]	1.347(9)	1.426(9)	115.5(4)
$CF_3-O-CHF_2$[c]	1.355(5)	1.390(5)	118.6(11)
CF_3-O-CF_3[e]	1.369(4)	1.369(4)	119.1(8)

[a] Reference 20. [b] Reference 1. [c] This work. [d] Reference 2. [e] Reference 3.

The nearly eclipsed orientation of the C−H bond of CHF_2 groups with effective torsional angles $\phi(C-O-C-H) = 18(2)°$ and 19(3)° in CHF_2OCHF_2 and CF_3OCHF_2, respectively, seems to be a characteristic feature of such groups in fluorinated ethers. Such an arrangement has previously been observed also for the inhalation anaesthetic enflurane, $CHFCl-CF_2-O-CHF_2$, with $\phi(C-O-C-H) = 22(4)°$.[19]

Trends in C−F and O−C bond lengths in fluorinated ethers can be rationalized by a combination of polar effects and orbital interactions. Because the positive net charge at the carbon atom increases with increasing fluorination, polar effects, C^+-F^- and O^--C^+, increase as well and cause shortening of both bond lengths. The anomeric interaction $n(O) \rightarrow \sigma^*(C-F)$ corresponds to a no-bond−double-bond mesomeric structure (Scheme 1) and leads to lengthening of sc- or ac-oriented C−F bonds and to shortening of O−C bonds. The influence of the anomeric effect on C−F bond lengths has been determined experimentally for CF_3OCH_3, where the sc-oriented C−F bonds (1.336(5) Å) are longer than the ap-oriented C−F bond (1.318(7) Å).[2] Both polar and anomeric effects lead to a large range of C−F bond lengths in the fluorinated ethers, which vary from 1.374(6) Å in CH_2FOCH_2F to 1.315(4) Å for the ap-oriented C−F bond in CF_3OCHF_2. The effects of fluorination on O−C bond lengths and C−O−C bond angles are summarized in Table 8.

Experimental Section

Samples of the three fluorinated ethers were obtained from commercial sources: CH_2FOCH_2F from Lancaster PCR (99%), CHF_2OCHF_2 from Fluorochem Ltd. (97%), and CF_3OCHF_2 from Matrix Scientific, Columbia, SC, (90)%. The last two samples were purified by repeated trap-to-trap condensation. The purity of CF_3OCHF_2 was checked by IR[21,22] and ^{19}F NMR spectra.[23]

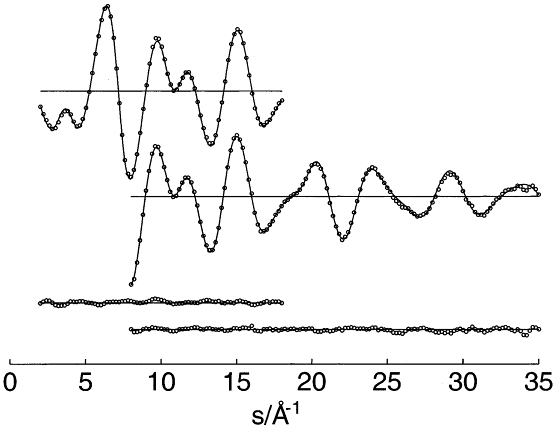


Figure 9. CHF_2OCHF_2: Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

Electron diffraction intensities for the three compounds were recorded with a Gasdiffraktograph KD-G2[24] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of ca. 60 kV. The sample reservoirs were cooled to −45, −65, and −94 °C, respectively. The inlet system with the nozzle was at room temperature. The photographic plates were analyzed with the usual procedures[25] and averaged intensities for CHF_2-$OCHF_2$ in the *s*-ranges 2−18 and 18−35 Å^{-1} in intervals $\Delta s = 0.2$ Å^{-1} ($s = (4\pi/\lambda)\sin\theta/2$, λ = electron wavelength, θ = scattering angle) are shown in Figure 9. The molecular intensities for the other two fluorinated ethers are shown in Supporting Information.

Matrix infrared spectra were recorded in the range 4000−400 cm^{-1} with a Bruker IFS 66v spectrometer and with a resolution of 1 cm^{-1}. Mixtures of CF_3OCF_2H with Ar (1:900) were deposited at 15 K on an aluminum-plated copper mirror in a He-cooled cryostat. Details of the matrix-isolation apparatus have been given elsewhere.[26] The matrix deposition was made at 21 and 165 °C.

Acknowledgment. This paper is dedicated to Professor Gerd-Volker Roeschenthaler on his 60th birthday. We are grateful for financial support by the Deutsche Forschungsgemeinschaft. S.E.U. thanks DAAD (Deutscher Akademischer Austauschdienst) and Universidad Nacional de La Plata, República Argentina, for financial support. She is indebted to Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (PIP 4695/96) and Facultad de Ciencias Exactas (UNLP) for support. We thank Prof. H. Willner, Universität Duisburg, for helpful discussions and comments.

Supporting Information Available: Molecular intensities for CH_2FOCH_2F and CF_3OCHF_2.. This material is available free of charge via the Internet at http://pubs.acs.org.

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