Effect of Fluorination on the Conformational Properties of Methyl Vinyl Ether

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The geometric structures of methyl trifluorovinyl ether, $CH_3OC(F){=}CF_2$ (MTVE), and perfluoromethyl vinyl ether, $CF_3OC(F){=}CF_2$ (PMVE), were determined by gas electron diffraction and ab initio calculations (HF/3-21G and MP2/6-31G*). The orientation of the O−C(sp^3) bond changes upon fluorination of the vinyl group from synperiplanar (ϕ(C=C−O−C) = 0°) in methyl vinyl ether to anticlinal (ϕ(C=C−O−C) = 111(4)° in MTVE and 104(2)° in PMVE). The effects of partial and perfluorination on the structure and conformational properties of methyl vinyl ether are discussed.

Introduction

It was shown by microwave spectroscopy (MW) that the smallest enol, the unstable vinyl alcohol, $H_2C{=}C{-}(H)OH$, possesses a synperiplanar structure, i.e., the O−H bond eclipses the C=C double bond.[1,2] This experimental result is reproduced by theoretical calculations,[3−5] which predict in addition to this structure the existence of a second conformer with trans orientation of the O−H bond, 1.6−3.0 kcal mol^{-1} higher in energy. The barrier to internal rotation around the O−C(sp^2) bond is calculated to be ca. 4 kcal mol^{-1} for nearly perpendicular orientation of the O−H bond. Similarly, a synperiplanar structure (dihedral angle ϕ(C=C−O−C) = 0°) was determined for methyl vinyl ether (MVE), $CH_3OC(H){=}CH_2$ (methoxyethene), by MW[6,7] and gas electron diffraction (GED).[3,8−10] Various experimental techniques (see ref 5 for a review) have led to different results for the high-energy conformer with ϕ(C=C−O−C) between 80° and 180°. In a GED analysis with a sample temperature of 200 °C a contribution of ca. 30% of a conformer with ϕ(C=C−O−C) > 150° was observed.[3] From far-infrared vibrational data a potential function for internal rotation around the O−C(sp^2) bond is derived, which possesses a second minimum for an anticlinal form and ϕ(C=C−O−C) = 144°.[11] Ab initio calculations at various levels (from HF/3-21G to MP3/6-31G*) predict for the high-energy conformer a pseudoplanar anti structure with a very flat double-minimum potential, 2.0−3.5 kcal mol^{-1} above the synperiplanar conformer.[5,12] This prediction agrees with the GED analysis[3] and has been confirmed by the analysis of high-resolution mid-infrared spectra.[12]

The presence of planar or pseudoplanar structures in these $ROC(H){=}CH_2$ compounds (R = H or CH_3) has been rationalized by conjugation between the oxygen lone pair and the π system of the C=C double bond, i.e., by electron delocalization from the lone pair n_π(O) into the π^*(C=C) orbital. The preference of the syn form relative to the anti structure can be rationalized either by nonbonded attractive interactions between the hydrogen orbitals and the π system[13] or by orbital interaction between the n_σ(O) lone pair and the σ^*(C=C) orbital (generalized anomeric effect). Both explanations are in accordance with the observation that single bonds would rather eclipse a vicinal double bond (C=C) than a vicinal single bond (C−H). In the present paper we report GED investigations of the geometric structures of methyl trifluorovinyl ether (MTVE), $CH_3OC(F){=}CF_2$ (trifluoromethoxyethene), and perfluoromethyl vinyl ether (PMVE), $CF_3OC(F){=}CF_2$ (trifluoro(trifluoromethoxy)ethene). The main interest lies in the effect of fluorination on the conformational properties of the parent compound MVE. The experimental analyses are supplemented by ab initio calculations.

Fluorinated methyl vinyl ethers have attracted considerable interest as monomers in the formation of polymers with various fluorinated compounds. MTVE, however, has not reached industrial application, because of its explosive nature.[14] PMVE was first prepared in 1960 by DuPont as an outgrowth of work on perfluorinated epoxides.[15] At present it is a commercially produced monomer used for the preparation of high-performance elastomers with excellent thermal, oxidative, and chemical stability. PMVE polymerizes readily with tetrafluoroethylene to give polymers whose chemical, thermal, and oxidative stability are approximately the same as those of perfluoropolymers.[16] Subsequent work at DuPont led to a number of curing systems and commercialization of these polymers as “Kalrez” perfluoroelastomer parts.[17] Terpolymers of PMVE with tetrafluoroethylene and vinylidene fluoride are the basis of

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Table 1. Results of GED Analysis and ab Initio Calculations for MTVE

	GED[a]	HF/3-21G	MP2/6-31G*
C—H	1.10[b]	1.078	1.090
C=C	1.310 [10]	1.297	1.331
(C—F)$_{\text{mean}}$	1.335 (6) p_1	1.339	1.336
ΔCF = (C1—F) − (C2—F)	0.020 [10]	0.016	0.023
C1—F	1.348 (9)	1.351	1.352
C2—F2	1.328 (7)	1.334	1.329
C2—F2′		1.333	1.328
(O—C)$_{\text{mean}}$	1.381 (7) p_2	1.403	1.391
Δ(OC) = (O—C3) − (O—C1)	0.110 [20]	0.125	0.104
O—C1	1.326 (13)	1.341	1.339
O—C3	1.436 (13)	1.466	1.443
C2=C1—O	118.2 (5) p_3	124.3	123.9
(C=C—F)$_{\text{mean}}$	123.3 (6) p_4	122.6	122.1
ΔCCF = (C1C2F) − (C2C1F1)	4.0 [10]	3.8	4.2
C2=C1—F	120.6 (9)	120.1	119.4
C1=C2—F2	124.6 (7)	124.0	123.7
C2=C1—F2′		123.7	123.3
C—O—C	109.3 (18) p_5	116.6	112.6
H—C—H	110.5[b]	110.7	110.3
tilt(CH$_3$)	3.0[b]	3.1	3.0
ϕ(C=C—O—C)	111.1 (35) p_6	113.3	113.7

[a] r_a distances (Å) and angles (deg). Error limits in parentheses are 3σ values and include possible systematic errors (see text). They refer to the last digit. Estimated uncertainties for fixed parameters are given in brackets. For atom numbering, see Figure 1. [b] Not refined.

Table 2. Results of GED Analysis and ab Initio Calculations for PMVE

	GED[a]	HF/3-21G	MP2/6-31G*
C=C	1.310 [10]	1.296	1.332
(C—F)$_{\text{mean}}$	1.322(3) p_1	1.331	1.333
Δ1(CF) = (C3—F) − (C1—F)	−0.005 [5]	−0.006	−0.003
Δ2(CF) = (C3—F) − (C2—F)	0.010 [5]	0.006	0.012
C3—F	1.326(4)	1.332	1.336
C1—F	1.331(7)	1.338	1.339
C2—F2	1.316(7)	1.327	1.324
C2—F		1.325	1.323
O—Cl	1.373(14) p_2	1.369	1.366
O—C3		1.371	1.380
C2=C1—O	117.5(18) p_3	121.9	122.5
(C=C—F)$_{\text{mean}}$	123.9(12) p_4	123.3	122.7
ΔCCF = (C1C2F) − (C2C1F1)	1.2 [5]	0.8	1.6
C2=C1—F1	123.1(13)	122.8	121.6
C1=C2—F2	124.3(13)	123.5	123.2
C1=C2—F2′		122.7	123.2
C—O—C	118.9(19) p_5	120.1	114.3
F—C3—F	108.9(3) p_6	109.1	109.0
tilt(CF$_3$)[b]	4.2(28) p_7	1.8	2.9
ϕ(C=C—O—C)	103.7(19) p_8	93.1	90.5

[a] See footnote of Table 1. For atom numbering, see Figure 2. [b] Tilt angle away from O—C1 bond.

elastomers possessing improved properties. PMVE has been characterized by ^{19}F-NMR and by infrared spectra.[18]

Ab Initio Calculations

The potential curves for internal rotation around the O—C(sp^2) bonds in MTVE and PMVE were calculated at the HF/3-21G level by optimizing the geometric structures for various dihedral angles ϕ(C=C—O—C). The structures which correspond to minima of the potential curves were fully optimized with the HF/3-21G and MP2/6-31G* method and these results are included in Tables 1 and 2. The calculations were performed with the GAUSSIAN 92 program system.[19]

GED Analysis

The radial distribution functions (RDF) were calculated by Fourier transformation of the molecular scattering intensities using an artificial damping function exp($-\gamma s^2$) with $\gamma = 0.0019$ Å^2. The experimental RDF's are shown in Figures 1 and 2. The range $r > 2.5$ Å can be reproduced only with structural models with ϕ(C=C—O—C) near 110° and 100°, respectively. In the least-squares analyses diagonal weight matrices were applied to the intensities and known scattering amplitudes and phases were used.[20] Both compounds are not well suited for GED analyses, because bonded distances as well as first non-bonded distances are closely spaced. Therefore, mean values for some bond lengths and bond angles were determined and differences between individual parameters were constrained to the respective theoretical values. Since calculated differences depend on the computational method (HF/3-21G or MP2/6-31G*), intermediate values with estimated uncertainties were used as constraints. These estimated uncertainties (brackets in Tables 1 and 2) were included as possible systematic errors in the experimental error limits for refined parameters. If a calculated difference between two parameters is smaller than the experimental error limit for the mean value of these parameters, the two parameters were set equal in the least-squares analyses. Thus, the C—F bond lengths and C=C—F bond angles of

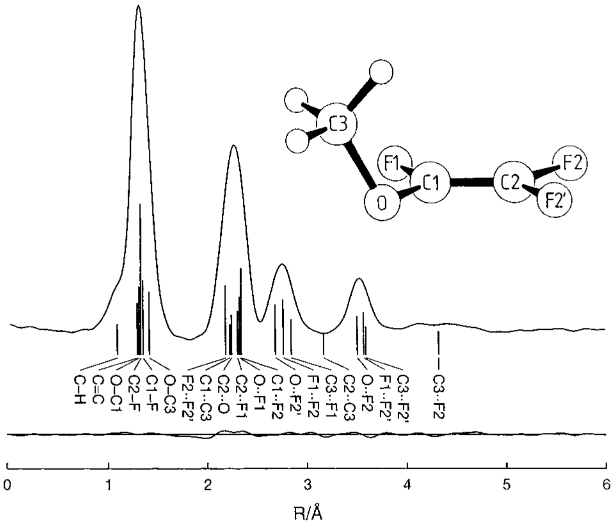

Figure 1. Experimental radial distribution function and difference curve for MTVE. The positions of important interatomic distances are shown by vertical bars.

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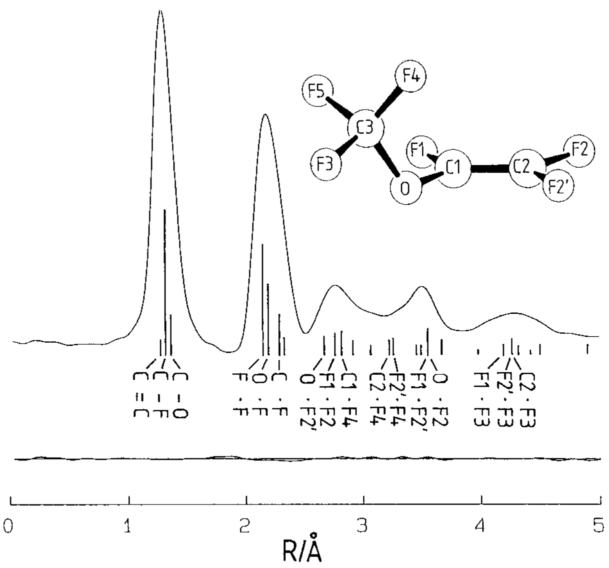

Figure 2. Experimental radial distribution function and difference curve for PMVE. The positions of important interatomic distances are shown by vertical bars.

Table 3. Interatomic Distances and Vibrational Amplitudes for MTVE (without Distances Involving Hydrogen Atoms)[a]

	distance	amplitude		distance	amplitude
C=C	1.31	0.040[b]	O···F2′	2.70	0.084(13) l_2
C−F	1.33−1.35	0.045 [3][c]	F1···F2	2.75	
O−C	1.33−1.44		C3···F1	2.83	0.080[b]
F2···F2′	2.19	0.055[b]	C2···C3	3.14	0.240[b]
C1···C3	2.25	0.062(4) l_1	O···F2	3.52	0.075(7) l_3
C2···O	2.27		F1···F2′	3.56	
O···F1	2.33		C3···F2′	3.55	0.250[b]
C···F	2.31−2.34		C3···F2	4.28	0.200[b]

[a] Values in Å. Error limits are 3σ values. [b] Not refined. [c] Not refined, but varied within the given range.

the CF_2 group were set equal in both compounds. Furthermore, the O−C(sp^3) and O−C(sp^2) bond lengths in PVME which differ by 0.002 Å (HF(3-21G) or 0.014 Å (MP2/6-31G*) according to the ab initio calculations were set equal. C_{3v} symmetry was assumed for the CH_3 and CF_3 groups, and a tilt angle between the C_3 axis and O−C bond direction was introduced. Vibrational amplitudes were collected in groups according to the type (dependent or independent on torsional motions) and to the length of the interatomic distances. Further constraints are evident from Tables 3 and 4. With these assumptions six (MTVE) and eight (PMVE) geometric parameters p_i and three (MTVE) and five (PMVE) vibrational amplitudes l_k were refined simultaneously. The following correlation coefficients had values larger than $|0.6|$. MTVE: $p_1/p_2 = -0.74$, $p_5/p_6 = 0.61$; PVME: $p_1/p_2 = -0.69$, $p_4/p_6 = -0.67$, $p_6/p_7 = -0.69$, $p_7/l_2 = -0.91$. The results of the least-squares analyses are given in Tables 1 and 2 (geometric parameters p_i) and Tables 3 and 4 (vibrational amplitudes l_k).

Discussion

Skeletal parameters of MVE, MTVE, and PMVE are collected in Table 5. The C=C bond lengths in the fluorinated derivatives were constrained to 1.31 Å, based on the experimental value for $F_2C=CF_2$ (1.311(7) Å[21]).

Table 4. Interatomic Distances and Vibrational Amplitudes for PMVE[a]

	distance	amplitude		distance	amplitude
C=C	1.30	0.040[b]	C1···F4	2.82	0.12(3) l_3
C−F	1.32−1.33	0.045 [3][c]	F1···F5	2.92	
O−C	1.37		C···F	3.05−3.24	0.18(3) l_4
F···F	2.15−2.18	0.058(6) l_1	C2···C3	3.22	
O···F	2.15−2.24		F2′···F4	3.24	
C2···O	2.28	0.064(7) l_2	C···F	3.44−3.48	0.16[b]
C···F	2.30−2.31		F1···F4	3.66	
O···F1	2.33		O···F2	3.52	0.08[b]
C1···C3	2.37		F1···F2′	3.53	
O···F2′	2.67	0.075[b]	C···F	3.90−4.40	0.20(4) l_5
F1···F2	2.76		F···F	4.17−4.89	
			F2···F3	5.51	0.10[b]

[a−c] For footnotes, see Table 3.

Table 5. Skeletal Geometric Parameters of $CH_3OC(H)=CH_2$, $CH_3OC(F)=CF_2$, and $CF_3OC(F)=CF_2$

	$CH_3OC(H)=CH_2$[a] MVE	$CH_3OC(F)=CF_2$ MTVE	$CF_3OC(F)=CF_2$ PMVE
C=C	1.339(1)	1.310[b]	1.310[b]
O−C(sp^2)	1.350(1)	1.326(13)	1.373(14)
O−C(sp^3)	1.420(1)	1.436(13)	1.373(14)
C=C−O	128.0(1)	118.2(5)	117.5(18)
C−O−C	116.1(1)	109.3(18)	118.9(19)
ϕ(C=C−O−C)	0.0	111(4)	104(2)

[a] Reference 7. [b] Not refined.

The O−C(sp^2) bond shortens upon fluorination of the vinyl group from 1.350(1) Å in MVE to 1.326(13) Å in MTVE and lengthens to 1.373(14) Å in PVME upon additional fluorination of the methyl group. Fluorination of the vinyl group has a small effect on the O−C(sp^3) bond length, but fluorination of the methyl group leads to shortening of this bond from 1.436(13) Å in MTVE to 1.373(14) Å in PMVE. A similar trend for C(sp^3)−O bonds has been observed between dimethyl ether (1.415(1) Å[22]) and perfluorodimethyl ether (1.369(4) Å[23]) which can be rationalized by electrostatic and stereoelectronic effects.[24] The C=C−O angle decreases by about 10° upon fluorination of the vinyl group from 128.0(1)° in MVE to 118.2(5)° in MTVE and 117.5(18)° in PMVE. This is primarily a consequence of the conformational change from synperiplanar to anticlinal. This conformational change leads to a similar decrease of the C−O−C angle between MVE (116.1(1)°) and MTVE (109.3(18)°). The increase of the C−O−C angle upon fluorination of the methyl group (118.9(19)° in PMVE) corresponds to the trend for this angle between dimethyl ether (111.8(2)° [22]) and perfluorodimethyl ether (119.1(8)° [23]).

The main interest in these structure analyses concerns the orientation of the OCH_3 and OCF_3 groups relative to the C=C bond of the vinyl group. Considering the conformational properties of MVE where synperiplanar or nearly planar anti forms occur, the structures of MTVE and PMVE with nearly perpendicular orientation of OCH_3 (ϕ(C=C−O−C) = 111(4)°) and OCF_3 (ϕ(C=C−O−C) = 104(2)°) are surprising. Model calculations show that synperiplanar conformations would possess H···F or F···F contacts between the CH_3 or CF_3 group and the vinyl F2′ atom of ca. 2.54 and 2.65 Å, respectively, i.e., only slightly shorter than the respective van der Waals

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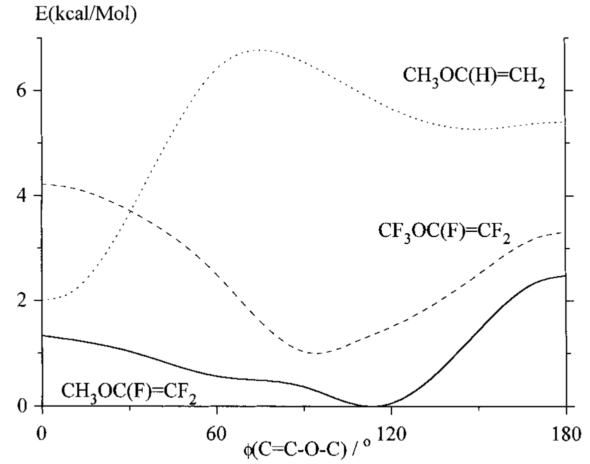

Figure 3. Calculated (HF/3-21G) potential curves for internal rotation around the O−C(sp^2) bonds for MTVE and PMVE and MVE. The curves for PMVE and MVE are shifted by 1 and 2 kcal mol^{-1}, respectively. The values for MVE are taken from ref 5.

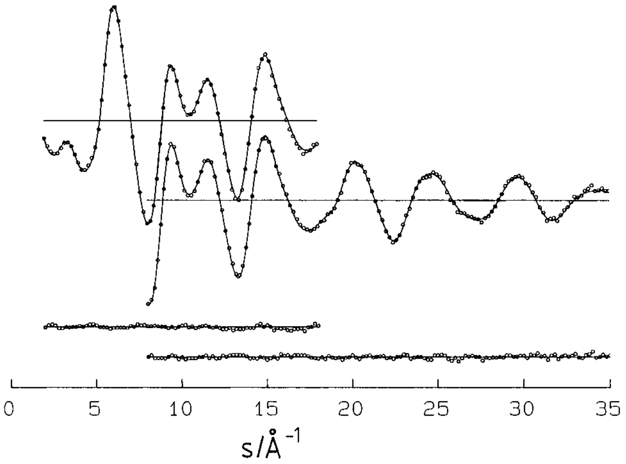

Figure 4. Averaged experimental (dots) and calculated (full line) molecular intensities for MTVE from long (above) and short (below) nozzle-to-plate distances and differences between experimental and calculated values.

distances of 2.55 and 2.70 Å. No H···F or F···F contacts which are shorter than the respective van der Waals distances would occur in the planar or nearly planar anti forms. Thus, steric interactions are not responsible for the drastic change of the conformational properties of methyl vinyl ether upon fluorination. Figure 3 shows the potenial functions for internal rotation around the O−C(sp^2) bonds in MVE, MTVE, and PMVE which were derived by single-point HF/3-21G calculations. Higher level calculations have been reported for the parent compound,[5,12] but the overall shape of the potential function does not depend on the calculational procedure. This potential curve possesses two minima for syn-periplanar and nearly planar anti structures and a maximum for perpendicular orientation of the OCH_3 group. On the other hand, the potential curves for the two fluorinated species possess maxima for the syn- and antiperiplanar conformations and the minimum occurs for anticlinal structures with nearly perpendicular orientation of the OCH_3 and OCF_3 groups. As pointed out above, this qualitative change of the torsional potentials upon fluorination cannot be explained by steric interactions alone. We have to assume that conjugative $n_\pi(O) \rightarrow \pi^*(C{=}C)$ interaction which stabilizes planar structures of $CH_3OC(H){=}CH_2$ is no longer present in the fluorinated species. This is plausible, since strong $n(F) \rightarrow \pi^*(C{=}C)$ interactions in the fluorinated vinyl group reduce or prevent the $n_\pi(O) \rightarrow \pi^*(C{=}C)$ interaction. Furthermore, fluorination of the vinyl group increases the possibility of hyperconjugative interaction between the oxygen lone pair $n_\pi(O)$ and the σ^* (C−F1) orbital which stabilizes the perpendicular orientation of the $O{-}CH_3$ and $O{-}CF_3$ groups. The experimental structures demonstrate that the latter effect dominates. A similar change of conformational properties upon fluorination has recently been observed for the analogous thio ethers $CH_3SC(H){=}CH_2$ and $CF_3SC(F){=}CF_2$.[25]

Experimental Details

MTVE was synthesized according to eq 1[26] followed by distillation. Its purity (>99%) was checked by ^1H and ^{19}F NMR spectroscopy.[27] PMVE used in this work was prepared by

$$NaOCH_3 + C_2F_4 \rightarrow CH_3OC(F){=}CF_2 \qquad (1)$$

condensation of carbonyl fluoride and hexafluoropropylene epoxide to perfluoro-2-methoxypropionyl fluoride followed by decarboxylation of the corresponding sodium salt as shown in eq 2, followed by distillation. Its purity was greater than 99%.

$$COF_2 + \overline{CF_2OC}FCF_3 \rightarrow CF_3OC(F)CF_3C(O)F \rightarrow CF_3OC(F){=}CF_2 \qquad (2)$$

An alternative synthesis of this ether involves the preaparation of trifluoromethyl hypofluorite followed by addition to 1,2-dichloro-1,2-difluoroethylene and dechlorination as shown in eq 3.[28]

$$COF_2 + F_2 \rightarrow CF_3OF \xrightarrow{CClF{=}CClF} CF_3OCClF{-}CClF_2 \rightarrow CF_3OC(F){=}CF_2 \qquad (3)$$

The GED intensities were recorded with a Gasdiffractograph[29] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of ca. 60 kV. The electron wavelength was calibrated with ZnO powder. The sample reservoirs were cooled to −43 °C (TMVE) and −85 °C (PMVE), and the inlet nozzle was at room temperature. The photographic plates (Kodak Electron Image, 18 × 13 cm) were analyzed with standard methods,[30] and averaged molecular intensities in the s-ranges 2−18 and 8−35 $Å^{-1}$ in intervalls of $\Delta s = 0.2$ $Å^{-1}$ were used in the analyses. Intensities for MTVE are shown in Figure 4.

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