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Gas Phase Structure of Methyl Trifluoromethanesulfonate, $CH_3OSO_2CF_3$, and Conformational Properties of Covalent Sulfonates

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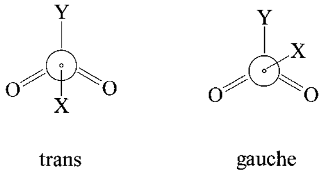
The molecular structure of methyl trifluoromethanesulfonate ($CH_3OSO_2CF_3$, methyl triflate) was investigated by gas electron diffraction (GED) and quantumchemical calculations (HF/3-21G* and B3LYP/6-31G*). The GED analysis revealed a gauche conformation (methyl group gauche with respect to CF_3 group) with a dihedral angle $\phi(C-O-S-C) = 89(7)°$. This value is reproduced correctly by the calculations. Some calculated bond lengths and bond angles, however, differ from experimental values by up to ±0.07 Å and ±6°. Additional B3LYP/6-31G* calculations have been performed for some covalent sulfonates. The potential functions for internal rotation around the S−O single bond in $FOSO_2F$ and $ClOSO_2F$ possess minima for gauche and trans orientation of the O−X (X = F or Cl) bond. The trans minima are 1.6 and 1.3 kcal mol^{-1} higher in energy. The potential functions for triflic acid, $HOSO_2CF_3$, for CH_3OSO_2Cl and CH_3OSO_2F possess minima only for gauche structures and maxima for trans orientation. These results are in partial contrast to previous experimental studies.

Introduction

A small number of gas-phase structures of covalent sulfonates of the type $XOSO_2Y$ have been reported in the literature. The most interesting structural features of these compounds are the length of the S−O single bond and the orientation of the O−X bond relative to the SO_2Y group. For steric reasons one expects staggered conformations with X either trans ($\phi(X-O-S-Y) = 180°$) or gauche ($\phi(X-O-S-Y) \approx 60°$) to Y (see Newman projection along S−O bond in Scheme 1).

Rather different conformational properties have been reported for such compounds. In gas electron diffraction (GED) and IR-matrix investigations of the two fluorosulfonates $FOSO_2F$ and $ClOSO_2F$, only the gauche conformer with a dihedral angle $\phi(X-O-S-F)$ of about 70° has been observed.[1] A GED study of methyl chlorosulfonate, CH_3OSO_2Cl, resulted in a mixture of 89(8)% gauche and 11(8)% trans conformers.[2] On the other hand, microwave spectra (MW) of methyl fluorosulfonate, CH_3OSO_2F, were interpreted in terms of a trans structure possessing C_s symmetry.[3] This result is supported by ab initio calculations at the STO-6G level.[3] However, GED data for this compound favor a mixture of gauche and trans conformers.[3] The structure of triflic acid, $HOSO_2CF_3$ (trifluormethanesulfonic acid), was also studied by GED, but the orientation of the O−H bond could not be determined in this experiment. Trans orientation was assumed.[4] An X-ray investigation of the acid hemihydrate, $2HOSO_2CF_3{\cdot}H_2O$, resulted in gauche orientation of the O−H bond.[5] Due to strong intermolecular hydrogen bonds, however, the conformation in the solid state may be different from that of the free acid. Various theoretical calculations for the isolated molecule predicted gauche orientation of the O−H bond with dihedral angles $\phi(H-O-S-C)$ between 110.4° (HF/3-21G*)[6] and 97.6° (MP2/6-31G*).[7] In the present work we report a structure determination of methyl trifluoromethanesulfonate, $CH_3OSO_2CF_3$ (methyl triflate), applying GED and quantum chemical calculations. This compound is a widely used reagent and it has been shown to be the most effective methylating agent with potassium enolates.[8] The IR and Raman spectra have been assigned on the basis of C_s symmetry, i.e., trans orientation of the methyl group ($\phi(C-O-S-C) = 180°$).[9] In addition, we perform a theoretical study of the conformational properties of the covalent sulfonates $FOSO_2F$, $ClOSO_2F$, CH_3OSO_2Cl, CH_3OSO_2F, and $HOSO_2CF_3$, whose gas phase structures have been reported previously (see above).

Scheme 1



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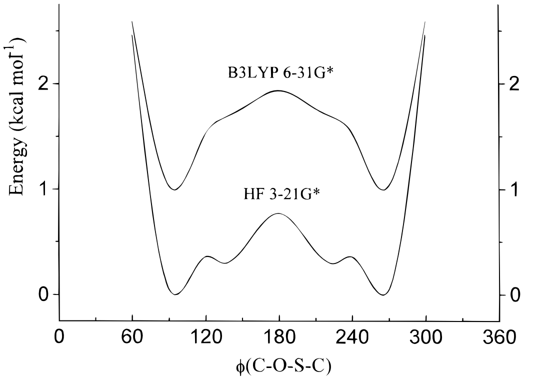

Figure 1. Calculated potential functions for rotation around the S−O bond in $CH_3OSO_2CF_3$. The B3LYP curve is shifted by 1 kcal mol^{-1}.

Quantum Chemical Calculations. The geometry of methyl triflate was optimized for various fixed dihedral angles ϕ(C−O−S−C) using the Gaussian 94 program[10] with the HF/3-21G* and B3LYP/6-31G* methods. The structures for minima in the potential curve were fully optimized. The HF approximation predicts two different minima in the potential for internal rotation at $\phi = 94.8°$ and 133.3° (Figure 1). The latter minimum is 0.3 kcal mol^{-1} above the ground-state stucture.

According to the B3LYP method, however, only a single rotational isomer exists for this compound. A weak shoulder in the potential function is predicted at the orientation where the HF approximation shows a second minimum. The potential curves derived with both methods possess maxima at ϕ(C−O−S−C) = 0° and 180°, i.e., for structures in which the methyl group eclipses the CF_3 group ($\phi = 0°$) or staggers the two S═O double bonds ($\phi = 180°$). The barriers to internal rotation at $\phi = 0°$ are calculated to be 7.0 kcal mol^{-1} (HF) and 7.7 kcal mol^{-1} (B3LYP) and those at $\phi = 180°$ are 0.8 kcal mol^{-1} (HF) and 0.9 kcal mol^{-1} (B3LYP), respectively. The optimized parameters for the ground-state structure are listed together with the experimental results in Table 1. Vibrational amplitudes were derived with the program ASYM 40.[11] Theoretical Cartesian force constants (HF/3-21G*) were scaled with the empirical factor 0.85 and transformed to a symmetry force field. The calculated amplitudes are included in Table 2.

Gas Electron Diffraction. The radial distribution function (RDF) which was obtained by Fourier transformation of the molecular intensities is shown in Figure 2. In the range $r > 3$ Å, it can be fitted satisfactorily only with a gauche structure. A preliminary structural model was refined by least-squares fitting of the molecular intensities. The intensities were multiplied with a diagonal weight matrix. The CF_3 and CH_3 groups were constrained to local C_{3v} symmetry and tilt and torsional angles for both groups were set to calculated mean values of HF and B3LYP results. Furthermore, the C−H bond length and H−C−H angle were not refined. On the basis of the calculations, the two S═O bond lengths and the C−S═O angles of the CF_3SO_2 group were set equal. Calculated differences for these parameters are less than 0.005 Å or 1°. The C−S−O angle which caused large correlations with other parameters had to be fixed to the theoretical value. For this angle an estimated uncertainty of ±1° is taken into account in the experimental uncertainties of refined parameters. Amplitudes which either caused high correlations with other parameters or which were poorly determined by the GED experiment were fixed to the calculated values. With these assumptions 10 geometric parameters (p) and six amplitudes (l) were refined simultaneously. The following correlation coefficients had values larger than |0.6|: $p_1/p_2 = 0.61$, $p_2/p_4 = -0.89$, $p_3/p_9 = 0.69$, $p_7/p_8 = -0.62$, $p_5/p_9 = 0.66$, $p_2/l_1 = 0.73$, $p_4/l_1 = -0.81$. Experimental and calculated results are shown in Table 1 (geometric paramters) and Table 2 (vibrational amplitudes), and the structure is presented in Figure 3.

Table 1. Experimental and Calculated Geometric Parameters for Methyl Triflate, $CH_3OSO_2CF_3$

	GED[a]		HF3-21G* [b]	B3LYP/6-31G* [b]
S═O	1.413(3)	p_1	1.416	1.453
S−O	1.555(4)	p_2	1.542	1.622
S−C	1.838(5)	p_3	1.769	1.871
O−C	1.451(22)	p_4	1.490	1.455
C−F	1.323(2)	p_5	1.341	1.333
C−H	1.100[c]		1.075	1.091
C−S−O	99.1 [10][d]		98.4	99.8
C−S═O	106.6 (9)	p_6	106.9	107.0
O−S═O	108.1(6)	p_7	109.7	108.6
Δ(O−S═O)	2.0[c]		0.1	3.8
O═S═O	125.3(23)		122.4	123.3
S−O−C	124.5(21)	p_8	123.4	118.4
F−C−F	109.9(9)	p_9	109.0	109.6
tilt (CF_3)	0.8[c]		1.1	0.7
H−C−H	111.5[c]		112.0	110.6
tilt (CH_3)	3.5[c]		2.9	4.2
ϕ(O1−S−C1−F1)	182.0[c]		183.9	180.4
ϕ(S−O1−C2−H)	166.2		163.5	169.5
ϕ(C2−O1−S−C1)	89(7)	p_{10}	94.8	92.7

[a] r_a values in Å and degrees. Uncertainties are 3σ values. For atom numbering see Figure 3. [b] Mean values are given for parameters which are not unique. [c] Not refined. [d] Not refined, but varied within the range given in brackets.

Discussion

The experimental electron diffraction intensities of methyl triflate are fitted very well with a single conformer which possesses gauche orientation of the methyl group with ϕ(C−O−S−C) = 89(7)°. The fit of the intensities did not improve if small amounts of a second conformer with ϕ(C−O−S−C) around 130° were added. Such a second form, which is suggested by the HF calculations, is not observed in the GED experiment. The potential functions for internal rotation derived by both computational methods possess a maximum at $\phi = 180°$, and thus, the existence of a trans conformation can be excluded. Both computational methods do not reproduce the bond lengths satisfactorily. The HF approximation calculates the S−C bond too short by 0.07 Å and the O−C bond too long by 0.04 Å. The B3LYP method predicts all bond lengths to sulfur too long by 0.03−0.07 Å. Both methods reproduce the experimental bond angles to within ±3° except for the S−O−C angle, which is calculated too small by 6° with the hybrid method. The calculated dihedral angles ϕ(C−O−S−C) agree with the experimental value within its uncertainty. The refined vibrational amplitudes (Table 2) agree closely with the calculated values.

Table 3 compares the results of the present study for $CH_3OSO_2CF_3$ with those of the covalent sulfonates of the type $XOSO_2Y$ which have been investigated in the gas phase. The conformational properties and S−O bond lengths derived from

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Table 2. Interatomic Distances and Experimental and Calculated Vibrational Amplitudes (without Distances Involving Hydrogen Atoms)[a]

		amplitude					amplitude		
	distance	GED		HF		distance	GED		HF
C−F	1.32	0.043		0.043	O3···F2	2.88	0.130(13)	l_4	0.127
S=O	1.41	0.035(3)	l_1	0.035	C2···O2	2.88	0.164(26)	l_5	0.128
C−O	1.45	0.052		0.052	O1···F2	2.90	0.130(13)	l_4	0.145
S−O	1.56	0.041		0.041	O2···F3	2.93	0.130(13)	l_4	0.131
C−S	1.84	0.038(7)	l_2	0.047	O2···F1	3.00	0.130(13)	l_4	0.138
F···F	2.17	0.052(3)	l_3	0.058	O3···F1	3.09	0.130(13)	l_4	0.134
O3···O1	2.39	0.061		0.061	C2···F3	3.12	0.219		0.219
O2···O1	2.42	0.060		0.060	C2···C1	3.43	0.164(26)	l_5	0.142
O3···O2	2.51	0.055		0.055	O3···F3	3.72	0.076 (2)	l_6	0.068
S···F	2.59	0.067		0.067	O2···F2	3.73	0.076 (2)	l_6	0.067
C1···O1	2.59	0.077		0.077	C2···O3	3.75	0.076 (2)	l_6	0.080
S1···F1	2.60	0.070		0.070	O1···F1	3.76	0.076 (2)	l_6	0.070
C1···O3	2.62	0.072		0.072	C2···F2	3.91	0.218		0.218
C2···S1	2.66	0.066		0.066	C2···F1	4.61	0.138		0.138
O1···F3	2.86	0.130(13)	l_4	0.140					

[a] Values in Å. Uncertainties are 3σ values. For atom numbering see Figure 3.

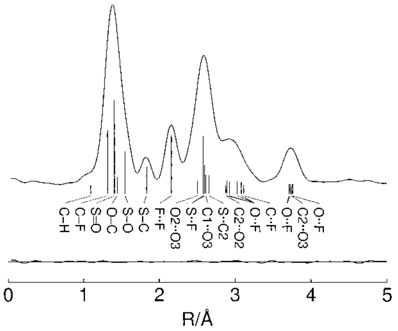

Figure 2. Experimental radial distribution function and difference curve for $CH_3OSO_2CF_3$. Important interatomic distances are shown by vertical bars.

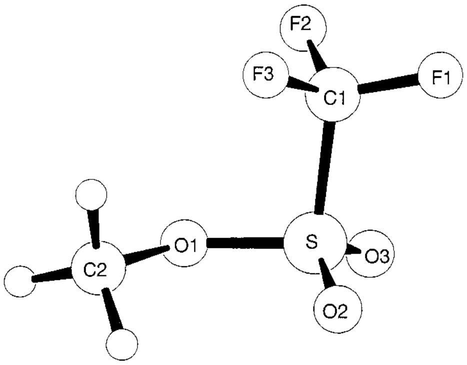

Figure 3. Molecular model with atom numbering for $CH_3OSO_2CF_3$.

the experiments and from B3LYP calculations are listed. As in the case of $CH_3OSO_2CF_3$, only gauche conformers were observed for the fluorosulfonates $FOSO_2F$ and $ClOSO_2F$.[1] From IR-matrix spectra the contribution of a trans form was estimated to be less than 5%. Theoretical calculations for these two compounds predict minima for gauche and trans conformations. The potential curve for internal rotation around the S−O bond in $FOSO_2F$ obtained with the HF/6-31G* approximation is shown in ref 1. To allow a systemtic comparison with the other sulfonates, additional B3LYP/6-31G* calculations were performed. Again, gauche and trans minima were obtained. No imaginary frequency occurred for the trans conformer. The trans form for $FOSO_2F$ is calculated to be higher in energy by 2.8 kcal mol^{-1} (HF) or 1.6 kcal mol^{-1} (B3LYP) and that of the chlorine derivative, $ClOSO_2F$, by 2.1 kcal mol^{-1} (HF) or 1.3 kcal mol^{-1} (B3LYP). The contributions of the trans conformer in Table 3 were estimated from the B3LYP energy differences. This potential function corresponds to the expectation based on simple steric interactions. Minima occur for staggered orientations of the O−F and O−Cl bond with respect to the SO_2F group. The gauche orientation, where the substituent lies between a double and a single bond, is favored relative to the trans orientation, where the substituent lies between two double bonds (see Scheme 1).

The calculated potential function for triflic acid, $HOSO_2CF_3$ (Figure 4, bottom curve), shows a minimum for gauche orientation with $\phi = 99.4°$ and a maximum for trans orientation that is 1.8 kcal mol^{-1} higher in energy. This result is in good agreement with earlier calculations that predict dihedral angles of $\phi = 110.4°$ (HF/3-21G*),[6] 98.8° (HF/6-31G*),[7] and 97.6° (MP2/6-31G**).[7] The HF/3-21G* method resulted in a barrier of 1.0 kcal mol^{-1} at $\phi = 180°$.[6] The existence of a maximum for the trans orientation contradicts chemical intuition. A possible explanation for the shape of this potential function is a superposition of steric effects such as in the two fluorosulfonates and an intramolecular O−H···O hydrogen bond. This leads to a shift of the minimum to a larger dihedral angle, i.e., close to eclipsed orientation of the O−H and S=O bonds. This explanation is supported by the B3LYP calculation which results in a small positive Mulliken overlap population for this H···O interaction. The theoretical calculations which predict gauche conformation for triflic acid agree with the crystal stucture and suggest that the assumption of trans orientation of the O−H bond that was made in the GED analysis is not correct.

The calculated potential functions for internal rotation around the S−O bond are similar for the three methyl-substituted sulfonates, CH_3OSO_2Cl, CH_3OSO_2F, and $CH_3OSO_2CF_3$ (Figures 4 and 1). These functions possess minima for gauche orientation (ϕ between 74° and 89°) and broad maxima for trans orientation. One imaginary frequency occurs in the trans conformer of these three compounds. According to our calculations, only gauche structures should be observed in the gas phase and this is in partial contrast to the reported conformational properties. For CH_3OSO_2Cl, the GED intensities were fitted with a mixture of 89(8)% gauche and 11(8)% trans conformers. This result is in close agreement with the theoretical prediction. The experimental dihedral angle of the gauche form, $\phi = 74(4)°$, agrees with the calculated value of $\phi = 77.3°$, and the contribution of the trans conformer is only slightly larger than its experimental uncertainty. The maximum in the calculated potential function at the trans orientation lies 2.5 kcal mol^{-1}

Table 3. Experimental and Calculated Conformational Properties and S−O Bond Lengths of Some Covalent Sulfonates of the Type $XOSO_2Y$

	conformational properties						S−O	
	experiment			B3LYP				
compound	% gauche	ϕ(XOSY)	% trans	% gauche	ϕ(XOSY)	% trans	exp.	B3LYP
$FOSO_2F^a$	>95	73(3)	<5	97	68.6	3	1.606(8)	1.676
$ClOSO_2F^a$	>95	69(7)	<5	95	71.0	5	1.589(10)	1.654
$HOSO_2CF_3^b$			100	100	99.4		1.558(7)	1.633
$CH_3OSO_2Cl^c$	89(8)	74(4)	11(8)	100	77.3		1.562(4)	1.611
CH_3OSO_2F			100^d	100	73.9			
	70^e	127/100	30^e	100	73.9		1.558(7)	1.600
$CH_3OSO_2CF_3^f$	100	89(7)		100	92.7		1.555(4)	1.622

[a] Reference 1. [b] Reference 4. [c] Reference 2. [d] MW result from ref 3. [e] GED result from ref 3. [f] This work.

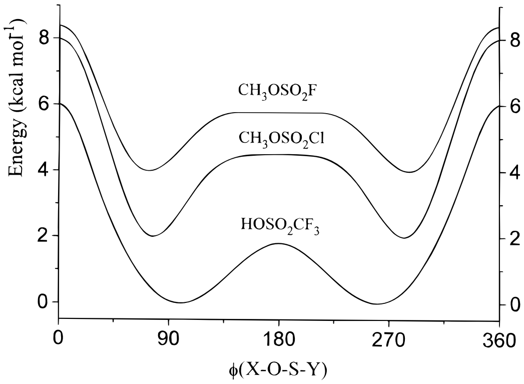

Figure 4. Calculated potential functions (B3LYP/6-31G*) for rotation around the S−O bond in $HOSO_2CF_3$ (bottom curve), CH_3OSO_2Cl (middle curve, shifted by 2 kcal mol^{-1}), and CH_3OSO_2F (top curve, shifted by 4 kcal mol^{-1}).

above the ground-state structure. The discrepancy between experimental and calculated conformational properties is more serious in the case of CH_3OSO_2F. As mentioned in the Introduction, MW spectra for methyl fluorosulfonate were interpreted in terms of trans configuration with C_s symmetry.[3] This result is based on the experimental dipole moment in the c direction. For the trans form the *c*-axis is perpendicular to the symmetry plane and μ_c is zero. From the experimental estimate ($\mu_c = 0.02 \pm 0.02$ D) it was concluded that the molecule possesses C_s symmetry. This conclusion was supported by ab initio calculations at the STO-6G level. However, the potential function for internal rotation around the S−O bond, which was derived by the B3LYP method (Figure 4), possesses a minimum for the gauche structure and a broad and flat maximum for the trans form, 1.8 kcal mol^{-1} higher in energy. The calculated μ_c component for the gauche form is small ($\mu_c = 0.2$ D). We suspect that the accuracy of the experimental dipole moment is overestimated, which led to a wrong conclusion concerning the conformation of CH_3OSO_2F. On the other hand, a GED analysis of this compound, which was performed simultaneously with the MW study, resulted in a mixture of 70% gauche and 30% trans conformers.[3] For the gauche form dihedral angles of ϕ around 127° or 100° fit the GED intensities equally well. Both values are larger than the predicted angle of 74.0°. The authors of the GED analysis point out that the molecular intensities are rather insensitive toward the conformation (gauche or trans) and therefore also toward the conformational composition of this compound. Thus, it seems likely that the GED intensities can be fitted also with a single gauche stucture, which would be in agreement with our calculations.

The S−O bond lengths in triflic acid and in the methyl-substituted sulfonates are equal within their experimental uncertainties (about 1.558 Å). The bonds are considerably longer in fluorine and chlorine fluorosulfonates, 1.606(8) and 1.598(10) Å, respectively. These trends can be rationalized by different polarities of this bond. In the case of the acid and the methyl-substituted sulfonates, the oxygen atom carries a large negative charge. This leads to high polarity of the S^+-O^- bond and to a short bond length due to electrostatic attraction. If the electronegativity of the substituent increases (F or Cl), the net charge at the oxygen atom is reduced. This causes a decrease of polarity and lengthening of the S−O bond. The B3LYP/6-31G* method predicts the S−O bonds in these compounds systematically too long by about 0.04−0.07 Å. The trends are reproduced approximately.

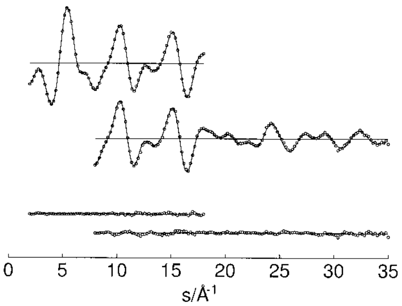

Figure 5. Experimental (dots) and calculated (full line) molecular intensities and differences for $CH_3OSO_2CF_3$.

Conclusion

A GED analysis of methyl triflate, $CH_3OSO_2CF_3$, results in a structure with gauche orientation of the methyl group relative to the CF_3 group. This is reproduced correctly by B3LYP/6-31G* calculations. This method predicts the existence of only gauche structures also for triflic acid and for the covalent sulfonates CH_3OSO_2F and CH_3OSO_2Cl. These predictions do not fully agree with previous experimental results. Gauche structures have also been predicted by theoretical calculations for fluorosulfonic acid $HOSO_2F$ ($\phi = 86.9°$, MP2/6-31G**)[12] and for the two silyl sulfonates $SiH_3OSO_2CF_3$ ($\phi = 110.3°$, B3LYP/6-31G**)[13] and $SiMe_3OSO_2CF_3$ ($\phi = 113.1°$, B3LYP/6-31G**).[14] These latter calculations were performed in the context with vibrational studies. Only in the case of fluorine and chlorine fluorosulfonates, $FOSO_2F$ and $ClOSO_2F$, the B3LYP calculations result in a second minimum at trans orientation, which, however, is considerably higher in energy than the gauche conformer and which is not observed experimentally. From these experimental and theoretical studies, we conclude that the existence of gauche structures or the preference of the gauche conformer is a general structural property of covalent sulfonates.

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Experimental Section

$CH_3OSO_2CF_3$ was prepared by the reaction of $AgCF_3SO_3$ with CH_3I.[9] The sample was purified by vacuum distillation and its purity was checked by IR gas spectra. The electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2 [15] at 25 and 50 cm nozzle-to-plate distances with an accelerating voltage of about 60 kV. The sample reservoir was kept at 0 °C and the inlet system and nozzle were at room temperature. The photographic plates were analyzed with the usual methods[16] and averaged molecular intensities in the scattering ranges 2−18 and 8−35 $Å^{-1}$ are shown in Figure 5.

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