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Chlorocarbonyl Trifluoromethanesulfonate, $ClC(O)OSO_2CF_3$: Structure and Conformational Properties in the Gaseous and Condensed Phases

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Pure chlorocarbonyl trifluoromethanesulfonate, $ClC(O)OSO_2CF_3$, has been prepared in about 58% yield by the ambient-temperature reaction between ClC(O)SCl and $AgCF_3SO_3$. The conformational properties of the gaseous molecule have been studied by vibrational spectroscopy [IR(gas), IR(matrix), and Raman(liquid)] and quantum chemical calculations (HF and B3LYP with 6-31+G* basis sets); in addition, the solid-state structure has been determined by X-ray crystallography. $ClC(O)OSO_2CF_3$ exists in the gas phase as a mixture of trans [ClC(O) group trans with respect to the CF_3 group] and gauche conformers, with the trans form being the more abundant [66(8)% from IR(matrix) measurements]. In both conformers, the C=O bond of the ClC(O) group is oriented synperiplanar with respect to the S–O single bond. The experimental free energy difference between the two forms, $\Delta G° = 0.8(2)$ kcal mol^{-1} (IR), is slightly smaller than the calculated value (1.0–1.5 kcal mol^{-1}). The crystalline solid at 150 K [monoclinic, $P2_1/n$, $a = 7.3951(9)$ Å, $b = 24.897(3)$ Å, $c = 7.4812(9)$ Å, $\beta = 99.448(2)°$, $Z = 8$] consists surprisingly of both trans and gauche forms. Whereas the more stable conformer for the more or less discrete molecules and the polarization effects would tend to favor the trans form, the packing effects would stabilize the gauche rotamer in the solid state.

Introduction

To sulfonates of the type $XO-SO_2Y$, we have recently added fluorocarbonyl trifluoromethanesulfonate, $FC(O)OSO_2CF_3$, the preparation, structural, spectroscopic, and other properties of which have been described elsewhere.[1] An obvious candidate to follow this compound is its chlorinated homologue, chlorocarbonyl trifluoromethanesulfonate, $ClC(O)OSO_2CF_3$.

Several antecedents reported in the literature show that $XO-SO_2Y$ molecules can adopt different conformations through internal rotation around the S−O single bond. For steric reasons, staggered structures are expected with X either trans [$\phi(X-O-S-Y) = 180°$] or gauche [$\phi(X-O-S-Y) \approx 60°$] with respect to the substituent Y. Different conformational properties have been reported in the literature, depending on the substituents X and Y. Experimental and/or quantum chemical studies involving the gaseous sulfonates $FOSO_2Y$ (Y = F or Cl),[2−4] CH_3OSO_2Y (Y = CF_3,[3,4] F,[3−5] or Cl[3,4]), CF_3OSO_2Cl,[6] and $HOSO_2CF_3$ [3,4,7] indicate a marked preference for the gauche conformation, with the possibility of a very small (≤1%) contribution from the trans form in

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the case of the two fluorosulfonates $FOSO_2Y$. This makes it all the more remarkable that the fluorocarbonyl derivative $FC(O)OSO_2CF_3$ should exist in the gas phase as a mixture of trans [FC(O) trans with respect to the CF_3 group] and gauche conformers, with the trans form being the more abundant [67(8)% from gas electron diffraction (GED) and 59(5)% from IR(matrix) experiments].[1] In both conformers, the C═O bond of the FC(O) function is oriented synperiplanar with respect to the S−O single bond. Moreover, small amounts of a trans-anti form (the C═O bond anti with respect to the S−O single bond) have been detected by IR measurements.[1]

The relative instability of sulfenic esters has again been exploited, as in the case of $FC(O)OSO_2CF_3$, to prepare chlorocarbonyl trifluoromethanesulfonate by the reaction between ClC(O)SCl and $AgCF_3SO_3$, which results, as expected, in sulfur extrusion. The product is a colorless liquid that melts at −53(2) °C and has an extrapolated normal boiling point of 73 °C as determined from the vapor pressure curve $\log p = -2423/T + 9.876$ (p/Torr, T/K). As far as we are aware, the only previous reference to such a compound is to a product with the same formula[8] produced by the oxidative addition reaction of CF_3SO_2OCl to CO that was characterized by its ^{19}F NMR and IR spectra. Most significantly, we report here a structural and conformational study of the compound $ClC(O)OSO_2CF_3$, drawing on its vibrational spectra, single-crystal structure at 150 K, and quantum chemical calculations.

Quantum Chemical Calculations

Various conformations of the sulfonate $ClC(O)OSO_2CF_3$ are feasible, depending on the torsional position of the ClC(O) group around the S−O single bond and on the orientation of the C═O double bond relative to the S−O single bond. The latter orientation can be syn or anti [$\phi(S-O-C=O) = 0$ or 180°]. Geometry optimizations for syn orientation were performed with the program suite Gaussian 98 [9] for various fixed torsional angles $\phi(C-O-S-C)$ around the S−O bond using the HF approximation and the hybrid method B3LYP with 6-31+G* basis sets. The resulting potential function for internal rotation exhibits minima for the trans [$\phi(C-O-S-C) = 180°$] and gauche [$\phi(C-O-S-C) \approx 60°$] positions. No similar potential functions could be obtained for anti orientation of the C═O bond. Whereas the trans-anti form leads to a structure with an imaginary vibrational frequency, the gauche-anti form is transformed to the gauche-syn one during the optimization process.

Table 1. Calculated Relative Energies (kcal mol^{-1}) and Wavenumbers (cm^{-1}) of the $\nu(C=O)$ Mode of the Stable Conformers of $ClC(O)OSO_2CF_3$

	HF/6-31+G*			B3LYP/6-31+G*		
conformer	ΔE	$\Delta G^{\circ a}$	$\nu(C=O)$	ΔE	$\Delta G^{\circ a}$	$\nu(C=O)$
trans-syn (**I**)	0.00	0.00	2075	0.00	0.00	1872
gauche-syn (**II**)	1.55	1.52	2087	1.09	1.00	1880

[a] Takes into account the different multiplicities of the trans ($m = 1$) and gauche ($m = 2$) conformers.

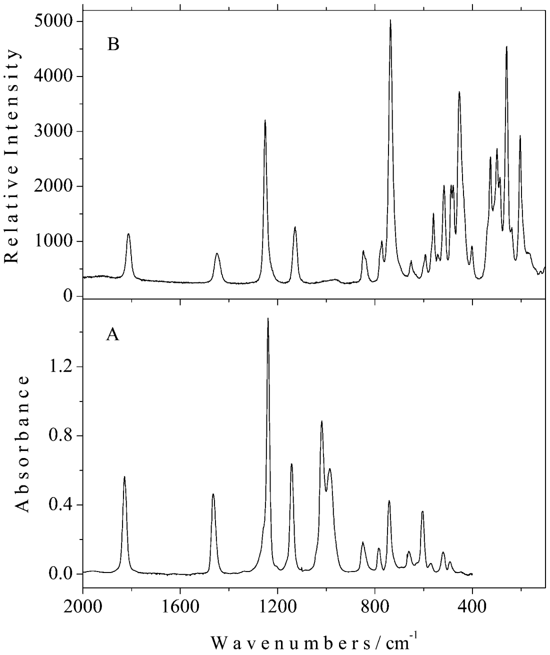

Figure 1. Vibrational spectra of $ClC(O)OSO_2CF_3$: (A) IR spectrum of the vapor, (B) Raman spectrum of the liquid.

Thus, two stable conformers appear to exist for this sulfonate, with the relative energies and Gibbs free energies listed in Table 1. Both computational methods predict the trans structure **I** to be more stable than the gauche structure **II**. With differences in $\Delta G°$ of only 1.0−1.5 kcal mol^{-1}, both methods are also agreed that the two conformers should be present together in detectable quantities in the gas phase at ambient temperatures.

Vibrational Spectra

The IR spectrum of gaseous $ClC(O)OSO_2CF_3$ and the Raman spectrum of the liquid are shown in Figure 1. The C═O stretching regions of the IR spectra recorded for the vapor isolated in solid Ar and N_2 (1:1000) at ca. 15 K are shown in Figure 2. Details of the spectra are itemized in Table 2, together with the unscaled wavenumbers calculated using the B3LYP/6-31+G* approximation. A comparison with data already reported is also include in Table 2.[8] Therefore and in consonance with the comparison of NMR data (see below), we conclude that the title compound is the same as the one reported elsewhere.[8]

Information about the conformational properties is most easily derived from the IR spectra of the matrixes with the

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Table 2. Vibrational Data for $ClC(O)OSO_2CF_3$[a]

trans-syn (B3LYP/6-31+G*)	gauche-syn (B3LYP/6-31+G*)	Ar matrix (1:1000)	N_2 matrix (1:1000)	IR (gas) 1 Torr[b]	Raman (liq) 514.5 nm	assignment[c]
	1880	1825.5	1826.6			ν C=O *g-s*
1872		1817.4	1815.8	1829 (1835)	1812	ν C=O *t-s*
		1815.4	1814.4			
			1813.3			
	1401	1463.8	1459.9			ν as SO_2 *g-s*
		1450.0	1447.3			
1391		1438.4	1436.9	1464 (1460)	1449	ν as SO_2 *t-s*
1247		1254.7	1254.6		1252	ν as CF_3 *t-s*
		1239.9				
	1246	1232.8	1240.5			ν as CF_3 *g-s*
		1228.3	1235.7			
1234	1234			1239 (1241)		ν as CF_3 *t-s, g-s*
1206				(1210)		ν s SO_2 *t-s*
	1204					ν s SO_2 *g-s*
1093	1093	1149.5	1139.5		1130	ν s CF_3 *t-s, g-s*
			1136.8			
		1140.1	1124.7	1142 (1140)		
		1138.3				
1042		1020.6	1019.9	1018 (1020)		ν C−O *t-s*
		1015.5	1018.2			
		994.1	997.5			
		975.0	986.8			
	1014	972.0	977.6	985 (990)		ν C−O *g-s*
845		854.0	855.4	850 (850)	848	ν C−Cl *t-s*
	832	843.5	843.4		838	ν C−Cl *g-s*
		786.9	786.7			
	762	778.4	777.2	785 (785)	772	δ s CF_3 *g-s*
758		742.6	743.0	742 (743)	737	δ s CF_3 *t-s*
		739.6	738.6			
		737.4				
	678					ν S−O *g-s*
665		658.1	658.1	661 (660)	652	ν S−O *t-s*
661						ρ C=O oop *t-s*
	654					ρ C=O oop *g-s*
				(630)		
571		602.7	604.8	603 (605)	593	ω SO_2 *t-s*
	567	597.1	597.3			ω SO_2 *g-s*
	551	574.6	573.3			δ_{as} CF_2 *g-s*
546		563.5	552.3	569 (570)	560	δ_{as} CF_2 *t-s*
	543				541	δ_s CF_2 *g-s*
542		519.8	516.6	520 (520)	517	δ_s CF_2 *t-s*
	496	491.6	492.8		487	δ SO_2 *g-s*
492		481.3	482.9	492 (490)	480	δ SO_2 *t-s*
				(482)		
	470					δ ClCO *g-s*
463		448.8	448.2		454	δ ClCO *t-s*
410					401	ρ SO_2 *t-s*
	381					ρ SO_2 *g-s*
	318					δ CSO *g-s*
309					326	δ CSO *t-s*
303					298	τ CF_2, τ SO_2 *t-s*
	285				287	τ CF_2, τ SO_2 *g-s*
	274					ν C−S *g-s*
264					260	ν C−S *t-s*
241					238	ρ CO_2 *t-s*
	240					ρ CO_2 *g-s*
183						ω CF_2, ρ SO_2 *t-s*
	180					ω CF_2, ρ SO_2 *g-s*
179						δ COS *t-s*
	166					δ COS *g-s*
	150					ρ ClCO *g-s*
80						ρ ClCO *t-s*
	73					torsion S−O *g-s*
66						torsion S−O *t-s*
52						torsion C−O *t-s*
	40					torsion C−O *g-s*
36						torsion C−S *t-s*
	22					torsion C−S *g-s*

[a] Wavenumbers in cm^{-1}. [b] Data from ref 8 given in parentheses. [c] B3LYP/6-31+G* results. ν = stretching, δ = deformation, τ = twisting, ρ = rocking, ω = wagging, γ = out-of-plane deformation, s = symmetric, as = antisymmetric, *t-s* = trans-syn conformer, *g-s* = gauche-syn conformer.

enhanced definition of vibrational features that they afford. The assumption is almost always made that the energy levels of the trapped conformers (nuclear, electronic, vibrational) are so little perturbed from the values in the gas phase that

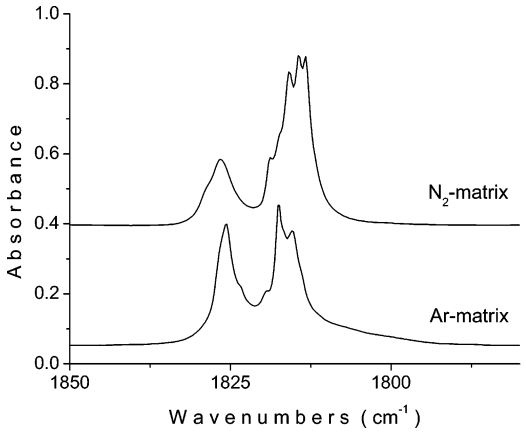

Figure 2. ν(C=O) regions of the IR spectra of $ClC(O)OSO_2CF_3$ isolated in Ar and N_2 matrixes (1:1000) at ~15 K.

conclusions about the rotational isomerism based on such observations are relevant. It is well-known that the ν(C=O) mode in XC(O)OR compounds shifts by about 30−50 cm^{-1} when the C=O bond is rotated from the synperiplanar to the antiperiplanar orientation relative to the O−R bond. The synperiplanar orientation gives the lower wavenumber, with the weakening of the C=O bond thus implied reflecting the orbital interaction between the n_σ lone pair orbital of the singly bonded oxygen with the σ*(C=O) antibonding orbital (the anomeric effect).

The assignment of the two strong bands at 1825.5 and 1817.4 cm^{-1} in the Ar matrix spectrum (Figure 2) is straightforward. According to the calculations, the ν(C=O) mode shows a small shift with the switch from trans to gauche orientation of ClC(O) relative to the CF_3 group. This shift was calculated to be 8 cm^{-1} by the two computational methods used. The calculated IR absorption coefficients are also much the same in the two conformers. On the basis of the calculated free energies, the stronger band at 1817.4 cm^{-1} is plausibly assigned to the trans conformer **I** and the band centered at 1825.5 cm^{-1} to the gauche conformer **II**. From the integrated areas of the two band regions and from the calculated IR absorption coefficients, we derive a contribution of 34(8)% for conformer **II**, with an error limit based on the estimated uncertainties in the band areas, calculated IR absorption coefficients, and the result obtained using the same procedure to analyze the corresponding region of the N_2 matrix spectrum. Broad-band irradiation ($200 \leq \lambda \leq 800$ nm) of the matrixes did not result in any appreciable change in the intensities of the measured IR absorptions. The apparent stability of the matrix-isolated $ClC(O)OSO_2CF_3$ molecule toward UV light is probably associated with the relatively large sizes of the parent molecule and its decomposition fragments, photodissociation then being inhibited by the matrix cage.

Crystal Structure

Table 3 lists the crystal data for the title compound at 150 K. Chlorocarbonyl trifluoromethanesulfonate crystallizes in the monoclinic space group $P2_1/n$, with eight $ClC(O)OSO_2CF_3$ molecules per unit cell. Of particular interest is the finding that the more or less discrete molecules adopt both the trans and *gauche* conformations, i.e., *both* the more stable and slightly less stable forms of the isolated molecule on the evidence of the calculations and the preferred form in the vapor phase. The trans form presents a larger dipole moment than the gauche form according to our theoretical calculations (Table 4). It is known that a rotamer with a larger dipole moment is always likely to be stabilized in the solid state. Consequently, packing effects would appear to stabilize the gauche form (Figure 3) in the solid, building infinite chains as depicted in Figure 4. Thus, whereas the more stable conformer for the more or less discrete molecules and the

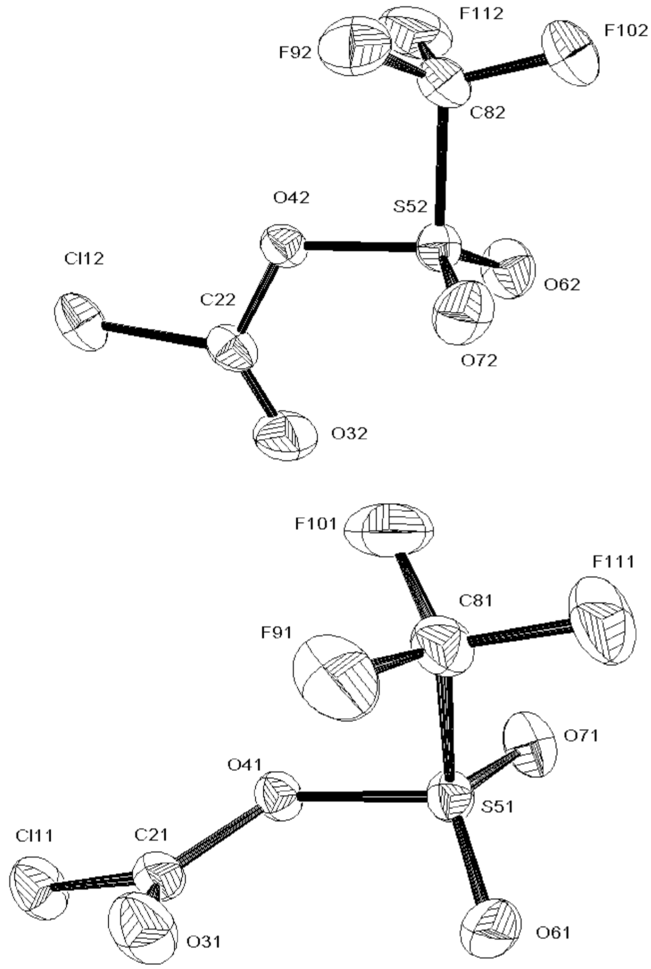

Figure 3. Molecular structures with atom numbering for trans-syn (above) and gauche-syn (below) conformers of $ClC(O)OSO_2CF_3$. Ellipsoids enclose 30% probability surfaces.

Table 3. Crystal Data for $ClC(O)OSO_2CF_3$

empirical formula	$C_2ClF_3O_4S$
fw	212.53
wavelength	0.710 73 Å
temp	150(2) K
cryst system	monoclinic
space group	$P2_1/n$
unit cell dimens	$a = 7.3951(9)$ Å
	$b = 24.897(3)$ Å
	$c = 7.4812(9)$ Å
	$\beta = 99.448(2)°$
V	1358.7(3) Å^3
no. of reflns for cell	6348 ($3 \leq \theta \leq 27°$)
Z	8
δ(calcd)	2.078 Mg m^{-3}
abs coeff	0.893 mm^{-1}
F(000)	835

Table 4. Experimental and Calculated Geometric Parameters of the Trans-Syn and Gauche-Syn Conformers of ClC(O)OSO$_2$CF$_3$ (Å, deg)

	X-ray		HF[a]		B3LYP[a]	
parameter	trans-syn	gauche-syn	trans-syn	gauche-syn	trans-syn	gauche-syn
C−Cl	1.7150(13)	1.7166(11)	1.7171	1.7191	1.7542	1.7552
C═O	1.1685(18)	1.1659(15)	1.1625	1.1605	1.1884	1.1866
C−O	1.3767(14)	1.3943(14)	1.3529	1.3596	1.3674	1.3749
O−S	1.6267(8)	1.6158(7)	1.6196	1.6137	1.7179	1.7105
S═O	1.409(1)	1.4123(9)	1.4085	1.4069	1.4479	1.4457
S═O′	1.416(1)	1.4142(9)	1.4085	1.4070	1.4479	1.4469
S−C	1.8470(14)	1.8448(12)	1.8319	1.8334	1.8976	1.9005
C−F	1.3106(17)	1.3112(16)	1.3055	1.3044	1.3334	1.3321
C−F′	1.3169(16)	1.3144(16)	1.3032	1.3047	1.3288	1.3307
C−F″	1.3149(18)	1.3190(15)	1.3032	1.3020	1.3288	1.3272
C1−C═O	126.4(1)	126.61(9)	125.54	125.19	125.35	125.08
C1−C−O	108.41(9)	107.15(7)	109.18	108.53	107.82	107.17
C−O−S	117.35(8)	121.73(7)	121.02	125.42	117.89	122.25
O−S═O	110.35(5)	111.50(5)	109.41	104.53	109.29	102.70
O−S═O′	109.71(5)	104.16(5)	109.41	110.21	109.29	110.60
O═S═O	122.84(7)	123.26(6)	123.61	123.67	124.50	124.58
O−S−C	93.33(5)	100.71(5)	93.79	99.90	91.90	99.56
O═S−C	108.65(6)	108.38(6)	108.25	106.98	108.48	107.26
O′═S−C	107.90(7)	106.45(6)	108.25	108.93	108.48	109.20
S−C−F	110.00(9)	110.67(8)	107.12	107.43	106.48	106.92
S−C−F′	106.9(1)	109.86(9)	110.09	109.39	109.99	109.23
S−C−F″	110.36(9)	107.14(9)	110.09	110.56	109.99	110.40
F−C−F	109.93(12)	109.27(11)	109.81	109.91	109.98	110.05
F−C−F	109.67(12)	110.26(11)	109.81	109.93	109.98	110.13
F−C−F	110.00(12)	109.62(11)	109.88	109.58	110.35	110.05
φ(C−S−O−C)$_{gauche}$	178.24(9)	87.53(9)	180.00	86.95	180.00	82.66
%(trans-syn)[b]	50	50	87	13	73	27
$\Delta G°$ (kcal mol^{-1})			0.0	+1.52	0.0	+1.00
μ[c]			3.16	2.12	2.63	1.59

[a] Using a 6-31+G* basis set. [b] Multiplicities of 2 and 1 were used for the gauche and trans forms, respectively. [c] Dipole moment in debyes.

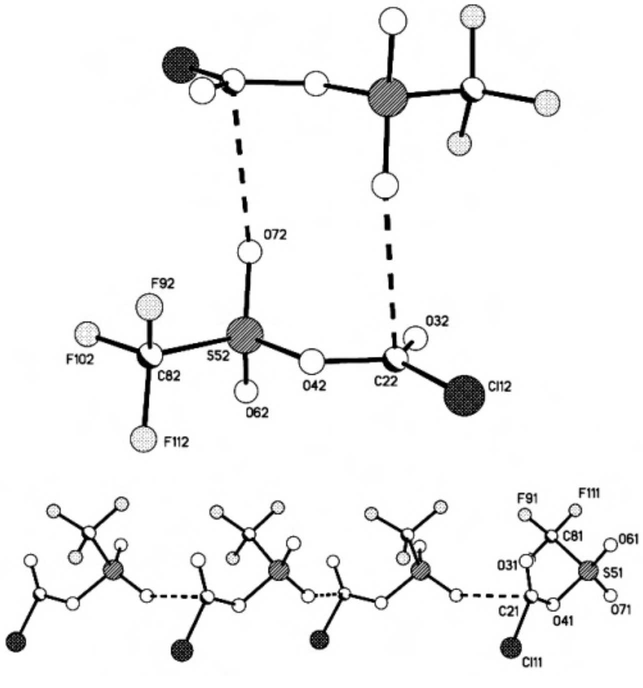

Figure 4. Packing of molecules in crystalline ClC(O)OSO$_2$CF$_3$ for rings of the trans-syn (above) and chains for gauche-syn (below) conformers.

polarization effects would tend to favor the trans form, packing effects would stabilize the gauche rotamer in the solid state.

Table 4 lists the experimental and theoretical dimensions of the two forms of ClC(O)OSO$_2$CF$_3$ illustrated in Figure 3.

How the molecules are packed in the crystal is illustrated in Figure 4. The most significant intermolecular interactions are through S═O···C═O contacts made approximately perpendicular to the plane of the C(O)Cl moiety. Such interactions are reminiscent of those observed between carbonyl groups, for example, in crystalline acetone.[10] The gauche molecules interact via O71···C21 contacts measuring 2.9711(15) Å to build chains that run along the crystallographic [1 0 1] directions. The trans molecules interact via pairs of centrosymmetrically related O72···C22 contacts [2.9618(16) Å] to form rings. For comparison, the sum of the van der Waals radii of O and C is 3.22 Å.[11] The chains are linked by long-range Cl11···O61 interactions [3.1286(10) Å]; layers of chains and rings alternate along [0 1 0].

Discussion

As mentioned in the Introduction, all sulfonates of the type XOSO$_2$Y, with X = H, CH$_3$, CF$_3$, or F and Y = F, Cl, or CF$_3$, whose molecular structures have been determined exist predominantly or exclusively as the gauche conformers in the gas phase. In the case of the fluorocarbonyl derivative FC(O)OSO$_2$CF$_3$, with X = FC(O) and Y = CF$_3$, however, the GED pattern of the vapor and the IR spectrum of the matrix-isolated vapor species imply that the vapor at ambient temperatures is made up mostly of the trans conformer (ca. 60% according to the experiments) but with an appreciable fraction of the gauche form (ca. 40%). A similar situation is now reported for the related compound ClC(O)OSO$_2$CF$_3$.

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Thus, both $FC(O)OSO_2CF_3$ and $ClC(O)OSO_2CF_3$ emerge as the first sulfonates in which the trans form is preferred to the gauche form. The conformational composition of $ClC(O)OSO_2CF_3$ vapor corresponds to $\Delta G° = G°(\text{gauche}) - G°(\text{trans}) = +0.8(2)$ kcal mol^{-1} on the evidence of the present IR data. This value is only slightly smaller than the estimates given by the computational methods (1.0−1.5 kcal mol^{-1}).

As noted previously,[1] the conformational properties of sulfonates depend primarily (i) on steric effects and (ii) on orbital interactions between the two oxygen lone pairs, n_σ and n_π, and the S−Y and S═O bonds (i.e., anomeric effects). Bond lengths and angles of the SO_2CF_3 moiety in trans-syn $ClC(O)OSO_2CF_3$ and trans-syn $FC(O)OSO_2CF_3$[1] are, as expected, quite similar. The shortening of the S−O bond with decreasing electronegativity of the substituent X in these $XOSO_2CF_3$ molecules is observed for trans-syn $ClC(O)OSO_2CF_3$ and trans-syn $FC(O)OSO_2CF_3$, with S−O distances of 1.616(1) and 1.628(1) Å, respectively, in the crystalline compounds at 150 K. This appears likewise to be a general feature of fluorosulfonates of the type $XOSO_2F$, cf. 1.606(8) Å in $FOSO_2F$,[2] 1.589(10) Å in $ClOSO_2F$,[2] and 1.558(7) Å in CH_3OSO_2F.[5]

The gaseous molecules $FC(O)OSO_2CF_3$ and $ClC(O)OSO_2CF_3$ thus show very similar conformational preferences, with the trans form being the more abundant and making up 60−90% of the molecules at ambient temperatures. It is condensation that differentiates between the two compounds. Whereas the fluorocarbonyl derivative consists exclusively of the trans conformer, the chlorocarbonyl derivative is made up of an equimolar mixture of the trans and gauche conformers. Both quantum chemical methods we have used reproduce the experimental molecular dimensions moderately well in general terms, the main exceptions being the lengths of some of the bonds around sulfur (see Table 4). Generally speaking, the calculations tend to overestimate the bond lengths (by up to 0.1 Å for the B3LYP method in the case of the S−O bond). The calculations reproduce the relative lengths of corresponding bonds in the trans and gauche conformers reasonably well. Intermolecular interactions have a significant impact on the dimensions and relative stabilities of the two conformers. Although polarization resulting in small changes in electron charge distribution favored by the permittivity of the crystal as a whole must play a part, crystal packing is probably the principal agent. Thus, while the syn orientation of the C═O bond is preserved, crystallization of chlorocarbonyl trifluoromethanesulfonate shifts the conformational balance of the free molecule away from the trans (**I**) and toward the gauche (**II**) conformer.

Experimental Section

Synthesis and Physical Properties. The preparation and manipulation of chlorocarbonyl trifluoromethanesulfonate were carried out in an evacuated Pyrex apparatus. In a Carius tube closed by a Young's valve, 0.56 g (4.3 mmol) of $ClC(O)SCl$, prepared as described previously,[12] was condensed on 1.22 g (4.7 mmol) of $AgCF_3SO_3$ (Aldrich) that had been dried previously for 3 h in vacuo (10^{-4} Torr) (1 Torr = 0.1333 kPa) at 70−80 °C. After the reaction mixture had been stirred at room temperature for 1 day, the volatile components were fractionated under dynamic vacuum through traps held at −30, −60, −90, and −196 °C. A 0.60-g (2-5 mmol) amount of $ClC(O)OSO_2CF_3$ collected in the −70 °C trap, representing a yield of 58% based on eq 1 and the quantity of ClC(O)SCl taken.

$$AgCF_3SO_3 + ClC(O)SCl \rightarrow ClC(O)OSO_2CF_3 + S + AgCl \quad (1)$$

A melting point of −53(2) °C was determined for a small, tensimetrically pure sample of the compound contained in a 6-mm-o.d. glass tube itself immersed in cold ethanol in a transparent Dewar vessel; the temperature was measured with a small (5 × 1 mm) Pt-100 resistance sensor (Hereaus) attached to the sample tube. Vapor pressures, measured in a small section of the vacuum line (total volume ca. 15 mL) using a capacitance manometer, conformed to the equation $\log p\ (\text{Torr}) = -2423/T + 9.876$ over the temperature range $T = 224-293$ K, giving an extrapolated normal boiling point of 346 K (73 °C). The measured density of the liquid at 20 °C was 2.00 g mL^{-1}. The molecular weight, found by Regnault's method, was 210.5 [$ClC(O)OSO_2CF_3$ requires 212.5]. As handled in glass apparatus, the compound is stable at room temperature for several months.

Spectroscopic Characterization. Details of the vibrational spectra of the compound are presented above (see Table 2 and Figures 1 and 2). Raman spectra were excited at $\lambda = 632.8$ nm with a He−Ne laser and measured with a Dilor Labram 300 spectrometer having a CCD detector, typically at a resolution of 2 cm^{-1}. Gas mixtures of $ClC(O)OSO_2CF_3$ with argon or nitrogen (BOC, research grade) in the proportions ca. 1:1000, prepared by standard manometric methods, were deposited on a CsI window cooled to ca. 15 K by means of a Displex closed-cycle refrigerator (Air Products model CS 202) using the pulsed deposition technique.[13,14] IR spectra of the matrix samples were recorded in the range 4000−400 cm^{-1} at a resolution of 0.5 cm^{-1}, with 256 scans and a wavenumber accuracy of ±0.1 cm^{-1}, using a Nicolet Magna 560 FTIR instrument equipped with an MCTB detector. Following deposition and IR analysis of the resulting matrix, the IR spectrum was also used to explore the effect of exposing the sample to broad-band UV−visible radiation ($200 \leq \lambda \leq 800$ nm) supplied by a Spectral Energy Hg−Xe arc lamp operating at 800 W. The same IR spectrometer was used to record the IR spectrum of the vapor contained at a pressure of ca. 1 Torr in a Pyrex-bodied cell fitted with CsI windows and having a path length of ca. 100 mm.

^{13}C and ^{19}F NMR spectra were recorded for a $CDCl_3$ solution at room temperature using a Varian UNITY-plus 500 instrument. The ^{13}C spectrum consisted of a singlet at δ_C 140.8 ppm [Cl*C*(O)O] and a quartet of equal intensity at δ_C 118.2 [$\mathit{C}F_3$, q, $^1J(CF) = 321.5$ Hz]. The ^{19}F spectrum, consisting simply of a singlet at δ_F −77.4 ppm ($C\mathit{F}_3$), tallied reasonably with that reported previously for a product with the same formula ($\delta_F = -73.4$ ppm),[8] although δ_F for CF_3SO_2OX compounds does not vary widely as a function of X.

The UV−vis spectrum of the vapor of the compound (contained in a Pyrex cell fitted with quartz windows and with a path length of 100 mm) was recorded with a Perkin-Elmer Lambda 900 spectrophotometer. Absorptions were observed with maxima cen-

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tered at 210, 257, and 298 nm and extinction coefficients of 323, 596, and 79 L/(mol·cm), respectively.

Crystal Structure. A sample of $ClC(O)OSO_2CF_3$ was held in a Pyrex capillary and mounted on a Bruker SMART APEX diffractometer equipped with an Oxford Cryosystems low-temperature device[15] and an OHCD laser-assisted crystallizer. A single crystal was grown at 200 K by Boese's laser-assisted zone-refinement method.[16] Diffraction measurements were then made on the crystal cooled to 150 K, essential data being listed in Table 3. Following integration, data reduction, and application of an absorption correction (SADABS),[17] the structure was solved by direct methods (SIR92)[18] and refined by full-matrix least-squares against F using 2488 data with $F > 4\sigma(F)$ (CRYSTALS).[19] Other calculations were carried out using PLATON.[20] All atoms were modeled with anisotropic displacement parameters. Of 8959 data collected, 2757 were unique ($R_{int} = 0.027$). The final R and R_w values were 0.0291 and 0.0311, respectively. The final difference map extremes were $+0.41$ and -0.49 e Å^{-3}.

Theoretical Calculations. All quantum chemical calculations were performed using the Gaussian 98 program package[9] under the Linda parallel execution environment using two coupled PC's. Geometry optimizations were sought (i) with the HF approximation and (ii) with the B3LYP methods; in all cases, the calculations employed 6-31+G* basis sets and standard gradient techniques with simultaneous relaxation of all geometric parameters.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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