Inorg. Chem. **2003**, *42*, 7297–7303

Inorganic Chemistry
Article

Trifluoromethyl Chlorosulfonate, CF_3OSO_2Cl: Gas Phase and Crystal Structure, Conformation and Vibrational Analysis Studied by Experimental and Theoretical Methods[†]

**Mauricio F. Erben,[‡] Carlos O. Della Védova,[*,‡,§] Roland Boese,[||] Helge Willner,[*,⊥]
Christiane Leibold,[#] and Heinz Oberhammer[*,#]**

CEQUINOR (CONICET-UNLP) and Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP-CIC-CONICET), Departamento de Quimica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115 (1900) La Plata, República Argentina, Institut für Anorganische Chemie, Universität GH Essen, Universitätsstrasse 5-7, D-45117 Essen, Germany, FB 6, Anorganische Chemie, Universität GH Duisburg, D-47048 Duisburg, Germany, and Institut für Physikalische und Theoretische Chemie, Universität Tübingen, D-72076 Tübingen, Germany

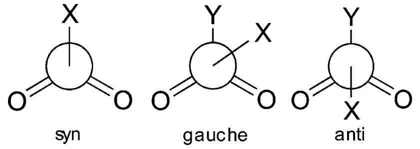
Received May 17, 2003

The geometric structure and conformational properties of trifluoromethyl chlorosulfonate (chlorosulfuric acid trifluoromethyl ester), CF_3OSO_2Cl, have been determined by X-ray crystallography, gas electron diffraction (GED), and vibrational spectroscopy (IR(gas), IR(matrix), and Raman(liquid)). These experimental investigations were supplemented by quantum chemical calculations (B3LYP with 6-311G* and 6-311+G(3df) basis sets). All experimental methods result in a single conformer with gauche orientation of the CF_3 group relative to the S–Cl bond. The dihedral angle δ(COSCl) is determined to be 91.7(3)° in the crystal and 94(3)° in the gas phase. This dihedral angle corresponds to a near-eclipsed orientation of the O—C bond relative to one of the S=O double bonds (δ(CO—SO) = –23.0(3)° and –21(3)° in the crystal and gas phase, respectively).

Introduction

The study of structural and conformational properties of covalent sulfonates ($XOSO_2Y$) is a relevant task, since only a small number of gas-phase structures have been reported and the elucidation of the factors influencing the preferred geometry is far from being understood. In principle, for steric reasons, one would expect staggered conformations with X either anti (δ(XOSY) = 180°) or gauche (δ(XOSY) = 60°) to Y. However, an eclipsed syn (δ(XOSY) = 0°) orientation cannot be excluded (see Newman projections along S−O bond in Chart 1).

Chart 1



All these possibilities have been reported in the literature for the conformation of $XOSO_2Y$ compounds. Thus, a GED study of methyl chlorosulfonate, CH_3OSO_2Cl, resulted in a mixture of 89(8)% gauche and 11(8)% anti conformers.[1] On the other hand, microwave spectra of methyl fluorosulfonate, CH_3OSO_2F, were interpreted in terms of an anti structure possessing C_s symmetry.[2] Raman and IR spectra of gaseous, liquid, and solid $HOSO_2F$ were assigned by several authors to C_s symmetry assuming either an anti[3,4] or syn structure.[5] The structure of triflic acid, $HOSO_2CF_3$ (trifluoromethansul-

---

[*] To whom correspondence should be addressed. E-mail: carlosdv@quimica.unlp.edu.ar (C.O.D.V.); heinz.oberhammer@uni-tuebingen.de (H.O.); willner@uni-duisburg.de (H.W.). Present address for H.W.: FB9, Anorganische Chemie, Universität Wuppertal, Gaussstrasse 20, D-42097 Wuppertal, Germany.

[†] This work is part of the Ph.D. thesis of M.F.E. M.F.E. is a fellow of CONICET. C.O.D.V. is a member of the Carrera del Investigador of CONICET, República Argentina.

[‡] CEQUINOR (CONICET-UNLP), Universidad Nacional de la Plata.

[§] Laboratorio de Servicios a la Industria y al Sistema Científico (UNLP-CIC-CONICET), Universidad Nacional de la Plata.

[||] Universität GH Essen.

[⊥] Universität GH Duisburg.

[#] Universität Tübingen.

(1) Schultz, G.; Hargittai, I.; Kolonits, M. *J. Chem. Soc., Dalton Trans.* **1977**, 1299.
(2) Hargittai, I.; Seip, R.; Nair, K. P. R.; Britt, C. O.; Boggs, J. E.; Cyvin, B. N. *J. Mol. Struct.* **1977**, *39*, 1.
(3) Gillespie, R. J.; Robinson, E. A. *Can. J. Chem.* **1962**, *40*, 644.
(4) Chackalackal, S. M.; Stafford, F. E. *J. Am. Chem. Soc.* **1966**, *88*, 4815.
(5) Savoie, R.; Giguere, P. A. *Can. J. Chem.* **1964**, *42*, 277.

10.1021/ic034531a CCC: $25.00

furic acid), was also studied by GED, and an anti orientation was assumed in the analysis of the diffraction pattern.[6] In contrast, an X-ray investigation of $2HOSO_2CF_3{\cdot}H_2O$ resulted in gauche orientation of the O−H bond,[7] in accordance with theoretical calculations.[8,9]

In continuation of experimental gas-phase studies and quantum chemical calculations, the structure of methyl trifluoromethanesulfonate, $CH_3OSO_2CF_3$,[10] was recently investigated ,and the GED analysis revealed the presence of a gauche conformation (δ(COSC) = 89(7)°) as the unique conformer present at room temperature. Furthermore, no other conformer was expected from the potential curve calculated for rotation around the S−O bond. Similarly, only gauche conformers with dihedral angles $\delta(XOSF) \approx 70°$ have been observed in a GED study of fluorine and chlorine fluorosulfonate ($XOSO_2F$, X = F and Cl, respectively). According to quantum chemical calculations at the HF/6-31G* level, the anti forms with $\delta(XOSF) \approx 180°$ correspond to stable structures, which are higher in energy by about 2.4 kcal/mol for X = F and by about 1.9 kcal/mol for X = Cl. However, the absence of any band splitting in the matrix IR spectra demonstrates the presence of a single conformer for both compounds at room temperature.[11]

Hence, the combination of gas-phase experimental techniques (GED and matrix IR spectroscopy) and quantum chemical calculations seems to be necessary for the complete study of the conformational behavior in sulfonates. In order to gain additional evidence about the structure of this important family of compounds, we report in the present work a structure determination of CF_3OSO_2Cl in both the gas and solid phase, applying GED and X-ray diffraction at low temperature, respectively. Matrix IR spectra were recorded using different temperatures of the spray-on nozzle to decide whether more than one conformer exist in the gas phase. Furthermore, the gas IR and liquid Raman spectra of CF_3OSO_2Cl have been measured, and the normal modes were assigned. These experimental studies were supplemented by quantum chemical calculations.

Experimental Section

Synthesis. CF_3OSO_2Cl was synthesized by reaction of CF_3OCl with SO_2 according to the method reported by Young et al.[12] Conventional vacuum techniques were used to condense CF_3OCl into a 60 mL stainless steel cylinder. This was followed by the addition of excess sulfur dioxide at −196 °C. The mixture was then allowed to warm to −20 °C and remain at that temperature for about 10 h. After this time, the products were separated by vacuum fractionation through traps held at −100, −140, and −196 °C. The −100 °C fraction was redistilled several times, and finally, pure CF_3OSO_2Cl was obtained in a yield of about 60%. CF_3OCl was synthesized by reaction of carbonyl fluoride and chlorine monofluoride in the presence of cesium fluoride (p.a. Fluka) catalyst at −20 °C. Fractionation of the reaction products through traps at −100, −140, and −196 °C yields pure CF_3OCl which is retained as a pale yellow liquid in the −140 °C trap.[13] The final purity (>98%) of the compounds was checked by IR and ^{19}F NMR spectroscopy.

SO_2 (95.5%, Linde, Munich, Germany) and F_2CO (Messer Griesheim) were obtained from commercial sources and used without further purification.

General Procedure. Volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (221 AHS-1000 and 221 AHS-10, MKS Baratron, Burlington, MA) and three U-traps and valves with PTFE stems (Young, London, U.K.). The vacuum line was connected to an IR cell (optical path length 200 mm, Si windows 0.5 mm thick) contained in the sample compartment of the FTIR instrument (Impact 400D, Nicolet, Madison, WI). This allowed us to observe the purification processes and to follow the course of the reactions. The pure compound was stored in flame-sealed glass ampules under liquid nitrogen in a long-term Dewar vessel. The ampules were opened with an ampule key[14] on the vacuum line, an appropriate amount was taken out for the experiments, and then, they were flame-sealed again.

Preparation of Matrices. In a stainless steel vacuum line (1.1 L volume), a small amount of CF_3OSO_2Cl (ca. 0.05 mmol) was mixed with an 1:1000 excess of Ar. For each experiment, ca. 0.6 mmol of this mixture was passed via a stainless steel capillary through a heated quartz nozzle, which was placed directly in front of the matrix support. The temperature of the matrix support was held at 14 K, and the nozzle temperature was adjusted at 20, 66, 142, 199, 248, and 300 °C. Photolysis experiments on the matrices were undertaken in the UV region by using a high-pressure mercury lamp (TQ 150, Hereaus, Hanau, Germany) in combination with a water filter to eliminate heat radiation. Details of the matrix apparatus have been given elsewhere.[15] Matrix IR spectra were recorded on a IFS66v/S FT spectrometer (Bruker, Karlsruhe, Germany) in the reflectance mode with a transfer optic. A DTGS detector with a KBr/Ge beam splitter in the region $\nu = 4000-400$ cm^{-1} was used. In this region, 64 scans were coadded for each spectrum by means of apodized resolution of 1 cm^{-1}.

Instrumentation. (A) Gas Electron Diffraction. Electron diffraction intensities for CF_3OSO_2Cl were recorded with a Gasdiffraktograph KD-G2[16] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of ca. 60 kV. The sample reservoir was cooled to −40 °C, and the inlet system with the nozzle was at room temperature. The photographic plates were analyzed with an Agfa Duoscan HiD scanner, and molecular intensities were derived with a slightly modified program SCAN3.[17] Averaged intensities in the ranges 2−18 and 18−35 $Å^{-1}$ in intervals of $\Delta s = 0.2$ $Å^{-1}$ are shown in Figure 1 ($s = 4\pi/\lambda \sin \phi/2$, λ electron wavelength, ϕ scattering angle).

(B) X-ray Diffraction at Low Temperature. An appropriate crystal of ca. 0.3 mm diameter of CF_3OSO_2Cl was obtained on the diffractometer at a temperature of 143 K with a miniature zone

---

(6) Schultz, G.; Hargittai, I.; Seip, R. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1981**, *36*, 917.

(7) Delaplane, G.; Lundgren, J. O.; Olovson, J. *Acta Crystallogr.* **1975**, *B31*, 2208.

(8) Otto, A. H.; Steiger, T.; Schrader, S. *J. Mol. Struct.* **1998**, *471*, 105.

(9) Gejji, S. P.; Hemansson, K.; Lindgren, J. *J. Phys. Chem.* **1993**, *97*, 6986.

(10) Trautner, F.; Ben Altabef, A.; Fernández, L. E.; Varetti, E. L.; Oberhammer, H. *Inorg. Chem.* **1999**, *38*, 3051.

(11) Aubke, F.; Casper, B.; Müller, H.; Oberhammer, H.; Willner, H. *J. Mol. Struct.* **1995**, *346*, 111.

(12) Young, D. E.; Anderson, L. R.; Gould, D. E.; Fox, W. B. *Tetrahedron Lett.* **1969**, *9*, 723.

(13) Gould, D. E.; Anderson, L. R.; Young, D. E.; Fox. W. B. *Chem. Commun*. **1968**, 1564.

(14) Gombler, W.; Willner, H. *J. Phys. E: Sci. Instrum.* **1987**, *20*, 1286.

(15) Argüello, G. A.; Grothe, H.; Kronberg, M.; Willner, H.; Mack, H.-G. *J. Phys. Chem*. **1995**, *99*, 17525.

(16) Oberhammer, H. *Molecular Structure by Diffraction Methods*; The Chemical Society: London, 1976; Vol. 4, p 24.

(17) Atavin, E. G.; Vilkov, L. V. *Instrum. Exp. Tech.* **2002**, *45*, 754.

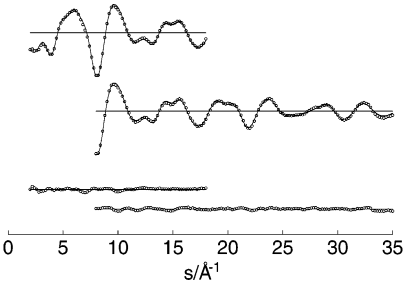


Figure 1. Experimental (○) and calculated (—) molecular scattering intensities and differences for long (upper curves) and short (lower curves) nozzle-to-plate distances for CF_3OSO_2Cl.

melting procedure using focused infrared laser radiation.[18,19] The diffraction intensities were measured at low temperature on a Nicolet R3m/V four circle diffractometer. Intensities were collected using radiation of graphite monochromated Mo Kα (λ(Mo Kα) = 0.71073 Å) and the ω-scan technique. The crystallographic data, conditions, and some features of the structure are listed in Table 1. The structure was solved by Patterson syntheses and refined by full-matrix least-squares method on F, with the SHELXTL-Plus program.[20] Absorption correction details are given elsewhere.[21] All atoms were assigned anisotropic thermal parameters. Atomic coordinates and equivalent isotropic displacement coefficients and anisotropic displacement parameters (Å^2 × 10^3) for CF_3OSO_2Cl are given as Supporting Information. Crystal structure data have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Enquiries for data can be directed to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K., CB2 1EZ or (e-mail) deposit@ccdc.cam.ac.uk or (fax) +44 (0) 1223 336033. Any requests sent to the Cambridge Crystallographic Data Centre for this material should quote the full literature citation and the reference number CCDC 206367.

(C) Vibrational Spectroscopy. Gas-phase infrared spectra were recorded with a resolution of 1 cm^{-1} in the range 4000−400 cm^{-1} on the FTIR instrument Bruker IFS 66v and FT-Raman spectra of liquid CF_3OSO_2Cl with a Bruker RFS 100/S FT Raman spectrometer. The sample in a 4 mm glass capillary was excited with 500 mW of a 1064 nm Nd:YAG laser (ADLAS, DPY 301, Lübeck, Germany).

(D) NMR Spectroscopy. The ^{19}F and ^{13}C NMR spectra of the neat liquid sample were recorded on a Bruker Advance DRX-300 spectrometer with a multinuclear probe head, operating at 282.41 and 75.74 MHz for ^{19}F and ^{13}C, respectively. The neat sample in a capillary was placed in a mixture of CD_3CN and $CFCl_3$ as an external lock and reference, respectively, and measured at 253 K.

Quantum Chemical Calculations

The potential function for internal rotation around the CO−SCl bond was derived with the B3LYP method and 6-311G* basis sets, performing geometry optimizations for fixed δ(COSCl) dihedral angles in steps of 20° (Figure 2). According to these calculations, only a single rotational isomer exists for this compound. Weak shoulders in the potential function are predicted at 160° and 220°. The potential curve possesses maxima at δ(COSCl) = 0° and 180°, i.e., for structures in which the CF_3 group eclipses the Cl atom (δ(COSCl) = 0°) or staggers the two S=O bonds (δ(COSCl) = 180°). The barriers to internal rotations were calculated to be 4.52 kcal/mol at δ(COSCl) = 0° (NImag = 1) and 2.00 kcal/mol at δ(COSCl) = 180°. The structure for the minimum in the potential curve was fully optimized, and vibrational wavenumbers and IR intensities were calculated using the B3LYP hybrid method and 6-311+G(3df) basis sets. The computed geometrical parameters and vibrational wavenumbers are listed in Tables 2 and 3, respectively. All quantum chemical calculations were performed with the Gaussian 98 software package.[22] Vibrational amplitudes and vibrational corrections $\Delta r = r_a - r_\alpha$ were derived from calculated (B3LYP/6-311G*) Cartesian force constants using the program SHRINK.[23]

NMR Spectra

The ^{19}F NMR signal of the CF_3OSO_2Cl neat sample at −70 °C was observed at −56.0 ppm. A value of −60.4 ppm has been reported for this signal in the literature.[12] The ^{13}C NMR spectrum of the same sample at −70 °C has been measured for the first time and shows one quartet at 118.5 ppm with a coupling constant $^1J_{CF}$ of 272.5 Hz which is identical to the determined value from the ^{13}C satellite positions in the ^{19}F NMR spectrum. These NMR data are in agreement with values reported for other trifluoromethoxy compounds.[24]

Vibrational Analysis and Matrix Infrared Spectra

To our knowledge, no detailed vibrational study of CF_3OSO_2Cl has been performed so far. Although the IR spectrum was reported,[12] it has been used only as a purity check, without any assignments of the bands.

The observed band positions in the IR (gas phase and matrix) and Raman spectra together with calculated wavenumbers (B3LYP/6-311+G(3df)) are collected in Table 3. Figure 3 shows the gas-phase infrared and liquid Raman spectrum of CF_3OSO_2Cl. The 21 normal modes of CF_3OSO_2Cl with C_1 symmetry are active both in the IR and Raman spectra. The agreement between calculated and observed wavenumbers and IR intensities is satisfying and is illustrated in Figure 4 by comparison of the simulated with the experimental spectrum.

---

(18) Brodalla, D.; Mootz, D.; Boese, R.; Osswald, W. *J. Appl. Crystallogr.* **1985**, *18*, 316.

(19) Boese, R.; Nussbaumer, M. In Situ crystallisation Techniques. In *Organic Crystal Chemistry*; Jones, D. W., Ed.; Oxford University Press: Oxford, England, 1994; pp 20−37.

(20) *SHELTX-Plus Version SGI IRIS Indigo, a Complex Software Package for Solving, Refining and Displaying Crystal Structures*; Siemens: Germany, 1991.

(21) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(23) Sipachev, V. A. *J. Mol. Struct.* **2001**, *67*, 567.

(24) Argüello, G. A.; Willner, H.; Malanca, F. E. *Inorg. Chem.* **2000**, *39*, 1195.

Table 1. Crystal and Structure Refinement Data for $CF_3OSO_2Cl^a$

fw	184.52 Da	reflns collected	2069
d_{calcd}	2.197 g cm^{-3}	indep reflns	958 [R(int) = 0.0317]
F(000)	360	cell measurement reflns used	1218
temp	143(2) K	cell measurement θ min/max	3.55−28.31°
cryst size	0.3 mm diameter	θ range for data collection	1.78−28.31°
cryst color	colorless	completeness to $\theta = 28.31°$	68.9%
cryst description	cylindric	index ranges	$-6 \leq h \leq 6$ $-30 \leq k \leq 17$ $-4 \leq l \leq 4$
wavelength	0.71073 Å	max/min transm	1.00/0.79
cryst syst	monoclinic	R_{merg} before/after correction	0.136/0.077
space group	$P2_1/c$	final R indices [$I > 2\sigma(I)$]	R1 = 0.0444 wR2 = 0.1081
unit cell dimensions	a =5.079(2) Å b = 22.922(9) Å c = 5.192(2) Å β = 112.651(6)°	R indices (all data)	R1 = 0.0549 wR2 = 0.1192
V	557.8(4) $Å^3$	largest diff. peak and hole	0.543 and −0.326 e $Å^{-3}$
Z	4	data/restraints/params	777/0/82
abs coeff	1.057 mm^{-1}	GOF on F^2	1.118

[a] Absorption correction details from ref 21. Computing structure solution and refinement: Bruker AXS SHELXTL Vers. 5.10 DOS/WIN95/NT. Diffractometer control software: Bruker AXS SMART Vers. 5.054 1997/98. Diffractometer measurement device: Siemens SMART CCD area detector system. Computing data reduction: Bruker AXS SAINT program Vers. 6.02×bb. Computing absorption correction: Bruker AXS SADABS program multiscan V2.03. Refinement method: full-matrix least-squares on F^2. Diffractometer measurement method: data collection in ω at 0.3° scan width, one run with 740 frames, $\varphi = 0°$, $\chi = 0°$. Weighting details: $w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.4756P]$ where $P = (F_o^2 + 2F_c^2)/3$.

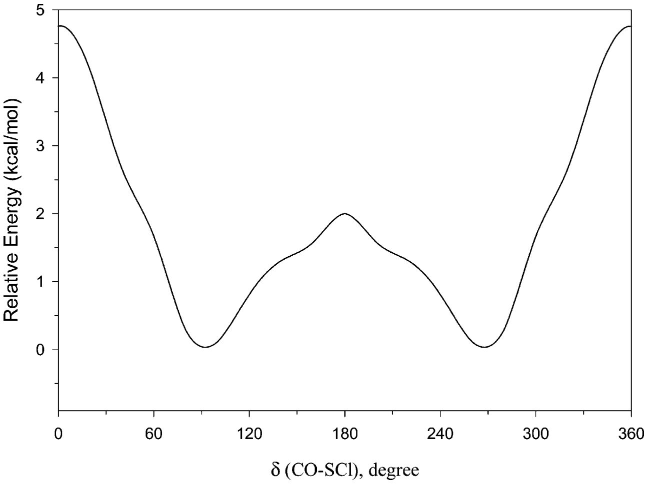


Figure 2. Potential energy curve for CF_3OSO_2Cl as a function of the CO−SCl dihedral angle calculated with the B3LYP/6-311G* approximation.

The tentative assignment of the observed bands was performed by comparison with the calculated spectrum, and the approximate description of modes is based on the calculated displacement vectors of the fundamentals, as well as on comparison with spectra of related molecules.

In the related trifluoromethyl fluorosulfonate, CF_3OSO_2F,[25] the antisymmetric and symmetric SO_2 stretching modes appear at 1493 and 1269 cm^{-1}, respectively. Therefore, the 1467 cm^{-1} band in the gas-phase spectrum of CF_3OSO_2Cl is assigned to ν_{as} SO_2. The ν_s SO_2 band cannot be assigned so easily because of the strong absorptions of the trifluoromethoxy group, which are clearly resolved in the IR matrix spectrum (1300−1200 cm^{-1}). An inspection of the Raman spectrum shows a strong band at 1223 cm^{-1} which is assigned to ν_s SO_2. Accordingly, the two other intense IR matrix bands located at 1280 and 1254 cm^{-1} are assigned as stretching modes of the CF_3 group.

Table 2. Comparison of the Geometrical Parameters of CF_3OSO_2Cl (Distances in Å, Angles in deg) Determined by Experiment and by Calculation

param[a]	X-ray[b]	GED[c]		B3LYP 6-311G*	B3LYP 6-311+G(3df)
S1=O3	1.404(3)	1.406(3)	p1	1.436	1.414
S1=O2	1.404(3)	1.406(3)	p1	1.431	1.418
S1−O1	1.595(3)	1.606(6)	p2	1.667	1.628
S1−Cl1	1.9724(14)	1.999(3)	p3	2.082	2.032
O1−C1	1.406(4)	1.420(12)	p4	1.396	1.393
C1−F2	1.290(6)	1.318(3)	p5	1.328	1.322
C1−F1	1.308(4)	1.318(3)	p5	1.333	1.324
C1−F3	1.317(5)	1.318(3)	p5	1.323	1.328
O3−S1−O2	122.94(19)	120.2(28)		124.7	124.1
O3−S1−O1	103.72(19)	105.8(21)	p6	103.8	104.1
O2−S1−O1	109.84(16)	111.3(21)	p6	109.9	109.6
O3−S1−Cl1	108.48(13)	110.1(5)	p7	108.0	107.9
O2−S1−Cl1	108.81(15)	110.1(5)	p7	108.1	108.3
O1−S1−Cl1	100.75(12)	97.3(19)	p8	99.4	100.2
C1−O1−S1	121.3(3)	122.2(12)	p9	122.3	122.9
F2−C1−F1	110.8(4)	109.9(5)		109.6	109.4
F2−C1−F3	110.5(3)	109.9(5)		109.5	109.3
F1−C1−F3	108.9(4)	109.9(5)		108.9	109.0
F2−C1−O1	111.9(3)	110.9	p10	111.6	111.9
F1−C1−O1	109.8(3)	110.9	p10	111.3	111.3
F3−C1−O1	104.7(3)	105.2	p10	105.9	105.9
C1−O1−S1−Cl1	91.7(3)	94(3)	p11	91.5	90.1
C1−O1−S1−O2	−23.0(3)	−21(3)	p11	−21.8	−23.7
S1−O1−C1−F3	−169.3(2)	177(6)	p12	−172.4	−170.0

[a] For atom numbering see Figure 6. [b] Uncertainties are σ values. [c] r_α parameters with 3σ uncertainties.

Although the CF_3 symmetric deformation is reported in the 750 cm^{-1} region for several molecules,[26] our theoretical calculations predict a S−O stretching mode for the medium intensity band centered at 785 cm^{-1} in the IR gas-phase spectrum. The infrared spectrum of the related CF_3OCl (sulfur and chlorine atom masses are similar) shows no band in the 750 cm^{-1} region, and hence, the CF_3 symmetric deformation mode for the title molecule is attributed to the band at 519 cm^{-1}.[13] The characteristic S−Cl stretching mode appears at 603 cm^{-1}. The ν_{S-O} and ν_{S-Cl} modes appear in

---

(25) Van Meter, W. P.; Cady, G. H. *J. Am. Chem. Soc.* **1960**, *82*, 6005.

(26) Bielefeldt, D.; Willner, H. *Spectrochim. Acta, Part A* **1980**, *36*, 989.

Table 3. Observed and Calculated Vibrational for CF_3OSO_2Cl (cm^{-1})

experimental				
IR gas[a]	Raman[b]	Ar matrix[a,c]	calculated[d]	mode assignment/ approximate description of mode
2095 (0.6)				$\nu_5 + \nu_6$
1741 (0.3)				$\nu_5 + \nu_9$
1467 (38)	1455 w	1460 (79)	1465 (39)	ν_1/ν_{as} (SO_2)
1281 (46)		1280 (49)	1251 (62)	ν_2/ν_{as} (CF_3)
		1268 (11)		$\nu_7+\nu_{12}$
1263 (74)	1250 m	1254 (75)	1234 (57)	ν_3/ν_{as} (CF_3)
1231 (9) sh	1223 m	1224 (8)	1218 (15)	ν_4/ν_s (SO_2)
1145 (100)	1123 vw	1138 (100)	1119 (100)	ν_5/ν_s (CF_3)
959 (26)	960 vw	957 (28)	944 (29)	ν_6/ν (O−CF_3)
785 (16)	784 s	787 (27)	763 (18)	ν_7/ν (O−S)
	727 w		690 (0.1)	ν_8/δ_s (C−O−S)
634 (18)	631 w	634 (37)	624 (19)	ν_9/δ_{as} (O−CF_3)
603 (20)	601 m	601 (36)	590 (26)	ν_{10}/ν (S−Cl)
573 (13)	571 m	571 (25)	563 (14)	ν_{11}/δ_s (SO_2)
519 (4)	517 w	517 (6)	509 (3)	ν_{12}/δ_s (CF_3)
453 (0.8)	454 m	454 (2)	441 (2)	ν_{13}/δ (O−CF_3)
			386 (0.3)	ν_{14}/δ_s (SO_2Cl)
	408 vs		368 (0.5)	ν_{15} /δ_{as} (SO_2Cl)
	346 m		338 (0.2)	ν_{16} /ρ_s (CF_3)
	296 m		284 (0.02)	ν_{17} /ρ_{as} (SO_2)
	241 m		228 (0.005)	ν_{18} /δ (O−S−Cl)
	168 w		156 (0.07)	ν_{19} /ρ (C−O−S)
			73 (0.07)	ν_{20} /τ (O−C)
	84.3		50 (0.04)	ν_{21} /τ (C−S)

[a] In parentheses, relative absorbance at band maximum. [b] Liquid, room temperature, band intensities: vs = very strong; s = strong; m = medium; w = weak; vw = very weak. [c] Band position at the most intensive matrix site. [d] B3LYP/6-311+G(3df). In parentheses, relative band strength; 100 ≡ 570.3 Km mol^{-1}.

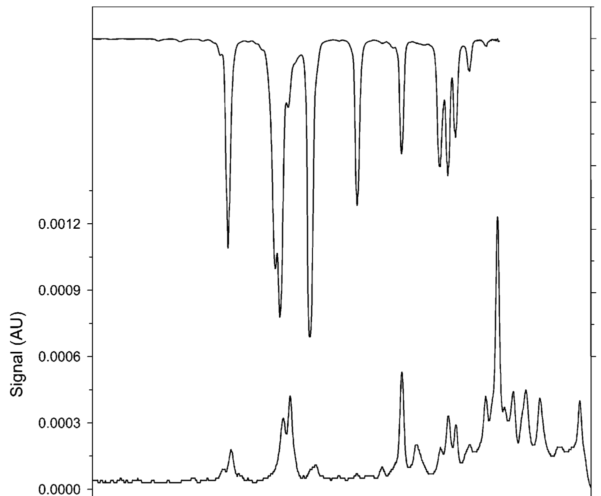


Figure 3. Gaseous IR (P = 1.3 mbar) and liquid Raman spectra for CF_3OSO_2Cl.

the Raman spectrum as intense bands at 784 and 601 cm^{-1}, respectively.

When the Ar/CF_3OSO_2Cl mixture is passed through the heated spray-on nozzle and the heated mixture is subsequently deposited onto the matrix support, no change in the spectrum is observed. The absence of any band splitting in the IR matrix spectra, even at a nozzle temperature of 300 °C, excludes at this temperature the presence of a further conformer. A high chemical stability for the compound can be deduced from this experiment because no decomposition products appear in the IR spectrum of the matrix. A high photochemical stability was also observed upon UV−vis broad-band irradiation. After 90 min irradiation, no decomposition products could be detected in the IR matrix spectrum.

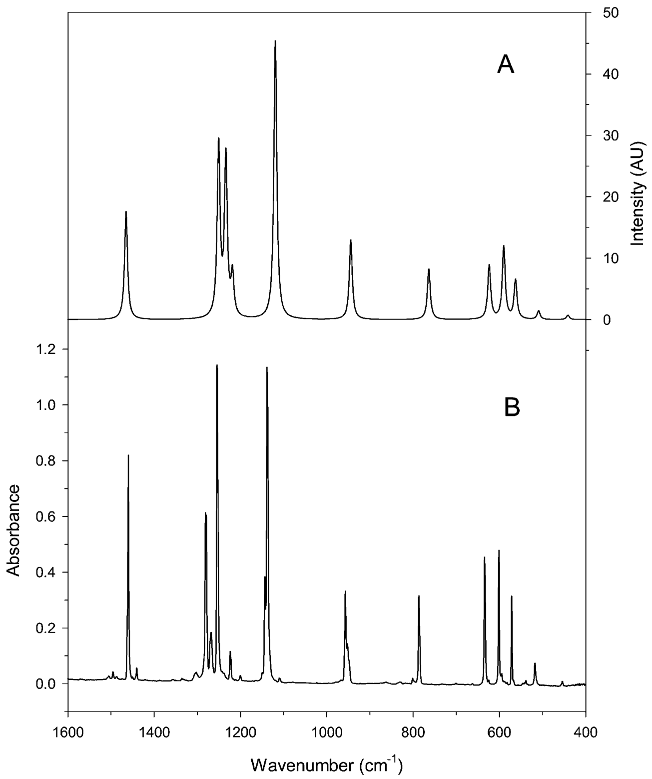


Figure 4. Ar matrix IR spectrum at 300 K (A) and simulated IR spectrum from B3LYP/6-311+G(3df) calculation (B) for CF_3OSO_2Cl.

Structure Analyses. (a) Crystal Structure. CF_3OSO_2Cl crystallizes in the monoclinic system ($P2_1/c$ spatial group) with unit cell dimensions a = 5.079(2) Å, b = 22.922(9) Å, c = 5.192(2) Å, β = 112.651(6)°, and $\alpha = \gamma = 90°$ (for all the crystallographic information, see Table 1). The overall crystal structure of CF_3OSO_2Cl is shown in Figure 5. Table 2 includes the bond lengths and bond angles measured for crystalline CF_3OSO_2Cl. The structure of the molecule in a single crystal is shown in Figure 6. The structure depicted in Figure 5 contains layers of both $ClSO_2$ and CF_3 groups alternately separated and parallel to the ac plane. The shortest nonbonded contacts across these layers are 3.138 Å for the separation O3···O3′ and 3.196 Å for the separation F2′···F1″ between $ClSO_2$ and CF_3 groups, respectively.

(b) Gas-Phase Structure. The experimental radial distribution curve (Figure 7), which was derived by Fourier transformation of the molecular intensities, is reproduced satisfactorily with gauche orientation of the CF_3 group. A preliminary molecular model was refined by least-squares fitting of the molecular intensities. The following constraints, which are based on the results of the quantum chemical calculations, were applied in the least-squares analysis: (1) S═O bond lengths and O═S−Cl bond angles were set equal. (2) C_{3v} symmetry was assumed for the CF_3 group,

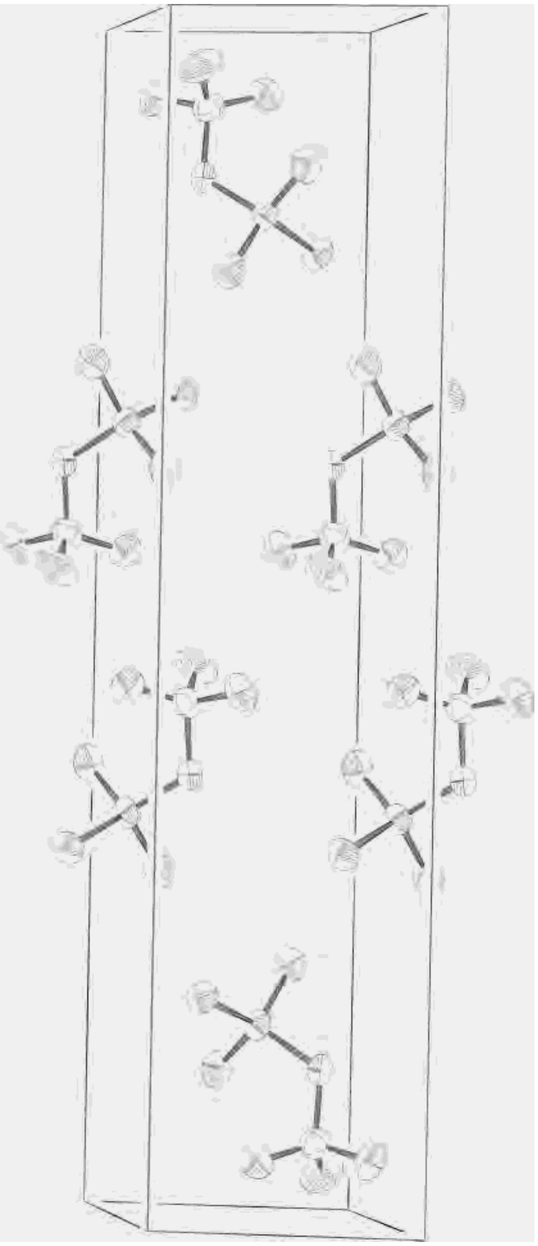


Figure 5. Stereoscopic illustration of the crystal structure of CF_3OSO_2Cl at 140 K.

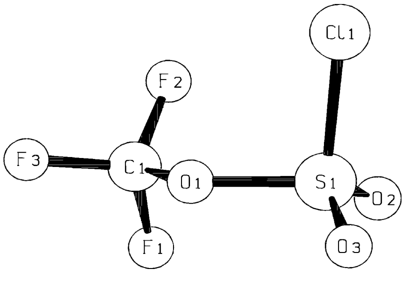


Figure 6. Structure of CF_3OSO_2Cl.

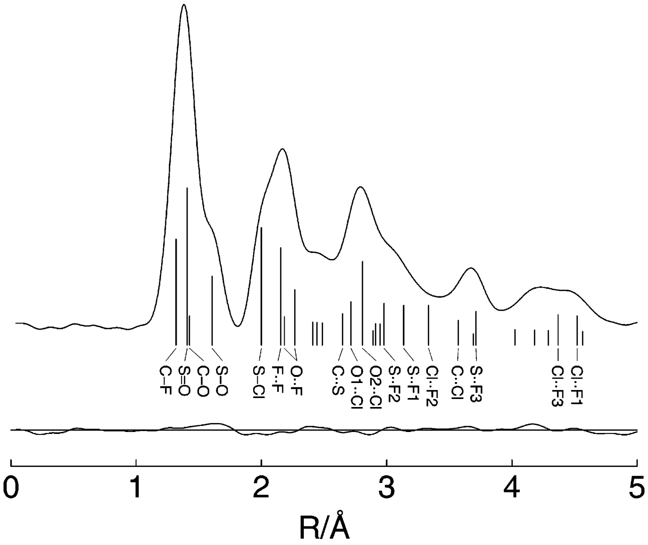


Figure 7. Experimental radial distribution function and difference curve for CF_3OSO_2Cl. Important interatomic distances of the syn structure are indicated by vertical bars.

Table 4. Interatomic Distances and Vibrational Amplitudes for $CF_3OSO_2Cl^a$

	distance	amplitude (GED)	amplitude (B3LYP)	$\Delta r = r_a - r_\alpha$
C—F	1.32	0.045^b	0.045	0.000
S=O	1.41	0.037(6) *l*1	0.035	0.000
O—C	1.42	0.050^b	0.050	0.000
S—O1	1.61	0.051^b	0.051	0.000
S—Cl	1.10	0.056(4) *l*2	0.054	0.000
F···F	2.15	0.055^b	0.055	−0.002
O1···F	2.18−2.26	0.059^b	0.059	−0.002
O1···O2	2.40	0.068^b	0.068	−0.002
O2···O3	2.44	0.056^b	0.056	−0.002
O1···O3	2.49	0.069^b	0.069	−0.001
S···C	2.64	0.082(17) *l*3	0.063	−0.005
Cl···O1	2.71	0.089^b	0.089	−0.004
Cl···O2	2.80	0.067(9) *l*4	0.075	−0.002
O2···F1	2.81	0.248^b	0.248	−0.013
O2···C	2.91	0.117^b	0.117	0.001
O2···F2	3.08	0.210^b	0.210	0.006
S···F2	3.07	0.128^b	0.128	−0.007
S···F1	3.06	0.131^b	0.131	−0.005
Cl···F2	3.28	0.191(50) *l*5	0.183	−0.030
Cl···C	3.53	0.149^b	0.149	−0.001
O3···C	3.70	0.067(9) *l*4	0.077	−0.016
S···F3	3.70	0.082(17) *l*3	0.064	−0.015
O3···F1	4.01	0.112^b	0.112	−0.022
O2···F3	4.18	0.110^b	0.110	−0.016
O3···F2	4.30	0.171^b	0.171	−0.021
Cl···F3	4.41	0.191(50) *l*5	0.188	−0.023
Cl···F1	4.40	0.232(54) *l*6	0.269	−0.004
O3···F3	4.52	0.094^b	0.094	−0.024

[a] For atom numbering, see Figure 6, values in Å, uncertainties are 3σ values. [b] Not refined.

and the calculated tilt angle between the C3 axis and the O—C bond direction was used. (3) The difference between the O—S=O angles, (O1−S−O2) − (O1−S−O3), was constrained to the calculated difference. (4) Vibrational amplitudes which either caused high correlations with geometric parameters or which are badly determined in the GED experiment were set to the values derived from the calculated force field. With these assumptions, 12 geometric parameters (p1−p12) and six vibrational amplitudes (*l*1−*l*6) have been refined simultaneously. The geometric parameters are listed in Table 2 together with the crystal data and calculated values, and the vibrational amplitudes are given in Table 4 together with the calculated values and the vibrational corrections.

Discussion

According to X-ray crystallography and the GED experiment, CF_3OSO_2Cl exists in the solid and gaseous state as a single conformer with gauche orientation of the trifluoromethyl group relative to the Cl atom and with a dihedral angle $\delta(COSCl) = 91.7(3)°$ and $94(3)°$, respectively. From the IR-(gas), IR(matrix), and Raman spectra, the presence of only the gauche form was confirmed, and no other conformer could be detected in the IR matrix spectra even at high temperatures of the deposited gas mixture. This experimental result is reproduced by B3LYP calculations which predict a single minimum in the energy curve at $\delta(COSCl) = 91.5°$ (6-311G* basis sets) or 90.1° (6-311+G(3df) basis sets). The conformational properties of CF_3OSO_2Cl are unexpected. According to chemical intuition, two stable conformers are expected for staggered orientations of the CF_3 group with respect to the SO_2Cl group and dihedral angles $\delta(COSCl)$ of 180° and near 60°. Instead, only a single conformer exists with $\delta(COSCl)$ near 90°. Thus, the CF_3 group nearly eclipses the S=O double bond ($\delta(COSO_2) \approx -20°$).

Bond lengths and bond angles in the sulfonate moiety are close to those in similar compounds, such as CH_3OSO_2Cl,[1] $CH_3OSO_2CF_3$,[10] $FOSO_2F$,[11] or $ClOSO_2F$.[11] The geometric parameters derived for the solid and for the gaseous state are in very close agreement, if systematic differences between crystal and gas phase data and the large uncertainties for some gas phase values are taken into account. The B3LYP method predicts all bond lengths around the sulfur atom to be too long, especially in the case of small basis sets (6-311G*). This method results in S−O and S−Cl bond lengths which are predicted to be too long by about 0.06 Å and 0.08 Å, respectively.

Acknowledgment. The Argentinean authors thank ANPCYT-DAAD for the German-Argentinean cooperation awards. They also thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), República Argentina. They are indebted to the Facultad de Ciencias Exactas, Universidad Nacional de La Plata, República Argentina for financial support. M.F.E. and C.O.D.V. would like to express their gratitude to Plácido García, Holger Pernice, Mike Finze, Stefan Balters, and Stefan von Ahsen for their friendship and valuable help in the laboratory work during their stay in Duisburg.

Supporting Information Available: Listing of atomic coordinates and equivalent isotropic displacement coefficients and anisotropic displacement parameters ($Å^2 \times 10^3$) for CF_3OSO_2Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034531A