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Article

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

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Pure fluorocarbonyl trifluoromethanesulfonate, $FC(O)OSO_2CF_3$, is prepared in about 70% yield by the ambient-temperature reaction between FC(O)SCl and $AgCF_3SO_3$. The geometric structure and conformational properties of the gaseous molecule have been studied by gas electron diffraction (GED), vibrational spectroscopy [IR(gas), IR(matrix), and Raman(liquid)] and quantum chemical calculations (HF, MP2, and B3LYP with 6-311G* basis sets); in addition, the solid-state structure has been determined by X-ray crystallography. $FC(O)OSO_2CF_3$ exists in the gas phase as a mixture of trans [FC(O) group trans with respect to the CF_3 group] and gauche conformers with the trans form prevailing [67(8)% from GED and 59(5)% from IR(matrix) measurements]. In both conformers the C=O bond of the FC(O) group is oriented synperiplanar with respect to the S–O single bond. The experimental free energy difference between the two forms, $\Delta G^\circ = 0.49(13)$ kcal mol^{-1} (GED) and 0.22(12) kcal mol^{-1} (IR), is slightly smaller than the calculated value (0.74–0.94 kcal mol^{-1}). The crystalline solid at 150 K [monoclinic, $P2_1/c$, $a = 10.983(1)$ Å, $b = 6.4613(6)$ Å, $c = 8.8508(8)$ Å, $\beta = 104.786(2)°$] consists exclusively of the trans conformer.

Introduction

The title molecule can be seen both as a trifluoromethanesulfonate (commonly known as triflate ion) and as a fluorocarbonyl-containing compound. Triflate ion is very frequently used as a good leaving group in organic chemistry because of its electron-withdrawing property.[1] One remarkable industrial application is the metallocene process of producing stereoregular polymerization of alkenes using zirconocene triflate as catalyst.[2] On the other hand, the importance for practical applications is only one of the reasons for the growing interest in fluorine-containing compounds. They invite comparisons with their related nonfluorinated analogues and serve as a challenge for experimental and computational chemistry. Compounds containing the fluorocarbonyl group have been systematically studied by us and other groups.[3]

From the structural point of view sulfonates of the type $XO-SO_2Y$ 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 (Chart 1). Different conformational properties have been reported in the literature,

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(1) Lawrence, G. A. *Chem. Rev.* **1986**, *86*, 17.

(2) Wulfsberg, G.; Cochran M.; Wilcox J.; Koritsanszky T.; Jackson D. J.; Howard J. C. *Inorg. Chem.* **2004**, *43*, 2031.

(3) Burgos Paci M. A.; García P.; Malanca F. E.; Argüello G. A.; Willner H. *Inorg. Chem.* **2003**, *42*, 2131.

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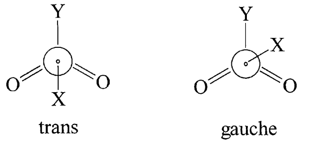
Chart 1



depending on the substituents X and Y. For the fluorosulfonates $FOSO_2F$ and $FOSO_2Cl$ (X = F and Y = F or Cl), only the gauche conformer with ϕ near 70° was observed in a gas electron diffraction (GED) investigation.[4] Potential functions for internal rotation around the S−O bond, which have been derived by different quantum chemical methods (HF, MP2, and B3LYP), possess a second minimum corresponding to the trans orientation but at an energy 2.5−3.0 kcal mol^{-1} higher than that of the gauche form. Thus, only the gauche form is observed in the GED and IR(matrix) experiments. Similarly, only a single conformer with the gauche orientation and dihedral angles near 90° was found for $CH_3OSO_2CF_3$[5] and CF_3OSO_2Cl.[6] Microwave spectra of CH_3OSO_2F were interpreted in terms of a trans structure, and electron diffraction intensities of this compound could be reproduced by a model consisting of a mixture of trans and gauche forms.[7] A mixture of both conformers has also been reported for CH_3OSO_2Cl.[8] The orientation of the O−H bond in triflic acid, $HOSO_2CF_3$, could not be determined in a GED study and was assumed to be trans to the CF_3 group.[9] On the other hand, quantum chemical calculations with the B3LYP/6-31G* method for the five sulfonates $CH_3OSO_2CF_3$,[5] CF_3OSO_2Cl,[6] CH_3OSO_2F,[5] CH_3OSO_2Cl,[5] and $HOSO_2CF_3$[5] give potential functions for internal rotation around the S−O bond each possessing minima only for the gauche and maxima for the trans orientation;[5] very similar potential functions with maxima at $\phi = 180°$ have recently been derived in one of our laboratories with the MP2/6-31G* approximation.[10] All the sulfonates studied so far in the gas phase appear therefore to exist only in the gauche conformation with the possibility of a very small (<1%) contribution from the trans form in the case of the two fluorosulfonates.

Here we report a structural and conformational study of the compound fluorocarbonyl trifluoromethanesulfonate, $FC(O)OSO_2CF_3$, using GED, X-ray crystallography, vibrational spectroscopy, and quantum chemical calculations. The relative instability of sulfenic esters has been exploited to prepare the compound by the reaction between FC(O)SCl and $AgCF_3SO_3$, which leads, as expected, to sulfur extrusion. The product is a colorless liquid which melts at −51 °C and has an extrapolated normal boiling point of 55.7 °C as determined from the vapor pressure curve $\log p = -2120/T + 9.331$ (p/Torr, T/K). As far as we know, the only previous reference to such a compound relates to an impure product produced by the reaction of CF_3SO_2OCl with FCX_3 (X = Cl or Br).[11] In this paper we report properties of the pure compound correcting therefore spectral data cited on the ref 11 and measuring the melting point more accurately.

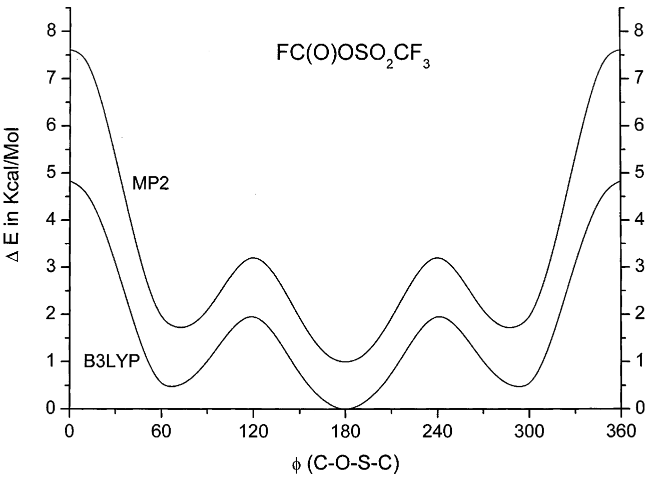


Figure 1. Calculated potential functions for internal rotation around the S−O bond with syn orientation of the C=O relative to the S−O bond. The MP2 curve is shifted by 1 kcal mol^{-1} with respect to the B3LYP one.

Quantum Chemical Calculations

Various conformations of the sulfonate $FC(O)OSO_2CF_3$ are feasible, depending on the torsional position of the FC(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 [ϕ(S−O−C=O) = 0 or 180°]. Geometry optimizations for syn orientation have been performed with the program suite GAUSSIAN 98[12] for various fixed torsional angles ϕ(C−O−S−C) around the S−O bond using the HF and MP2 approximations and the hybrid method B3LYP with 6-311G* basis sets. The resulting potential function for internal rotation (Figure 1) possesses minima for the trans [ϕ(C−O−S−C) = 180°] and gauche [ϕ(C−O−S−C) ≈ 60°] positions. Similar potential functions, about 1−2 kcal mol^{-1} higher in energy, are obtained for anti orientation of the C=O bond. Thus, four stable conformers exist for this sulfonate (Chart 2) with the relative energies and Gibbs free energies listed in Table 1. All three computational methods predict structure **I** to be the most stable and structure **IV** to be the least stable conformer of $FC(O)OSO_2CF_3$ (by $\Delta G° = 2.24−3.30$ kcal mol^{-1}; see Table

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

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

(6) Erben, M. F.; Della Védova, C. O.; Boese, R.; Willner, H.; Leibold, C.; Oberhammer, H. *Inorg. Chem.* **2003**, *42*, 7297.

(7) Hargittai, I.; Seip, R.; Nair, K. P. R.; Britt, C. O.; Boggs, J. E.; Cyvin, B. N. *J. Mol. Struct.* **1977**, *39*, 1.

(8) Schultz, G.; Hargittai, I.; Kolonits, M. *J. Chem Soc., Dalton Trans.* **1977**, 1299.

(9) Schultz, G.; Hargittai, I.; Seip, R. *Z. Naturforsch., A* **1981**, *36*, 917.

(10) Oberhammer, H. Unpublished results.

(11) Katsuhara Y., DesMarteau D. D. *J. Am. Chem. Soc.* **1980**, *102*, 2681.

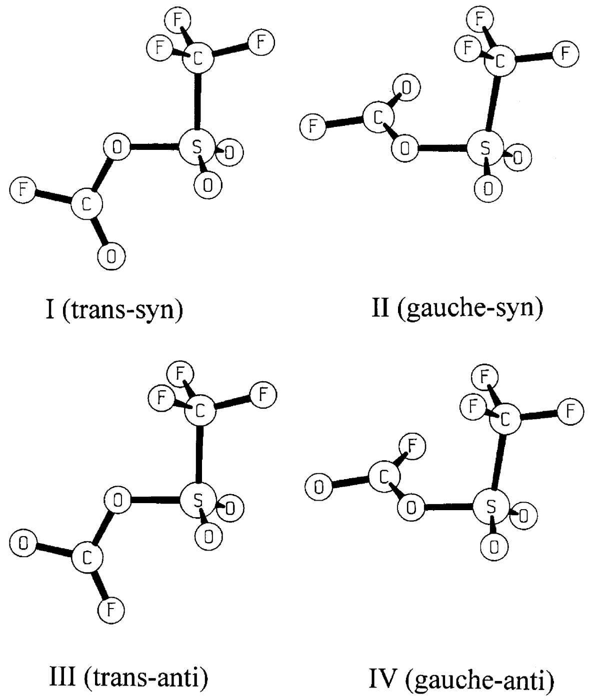
(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, 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.; Baboul, A. G.; 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.; Nayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; 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.

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

	HF/6-311G *			MP2/6-311G*			B3LYP/6-311G*		
conformer	ΔE	$\Delta G^{\circ a}$	ν(C=O)	ΔE	$\Delta G^{\circ a}$	ν(C=O)	ΔE	$\Delta G^{\circ a}$	ν(C=O)
trans-syn (**I**)	0.00	0.00	2146	0.00	0.00	1939	0.00	0.00	1937
gauche-syn (**II**)	1.38	0.94	2154	0.54	0.74	1938	0.47	0.74	1929
trans-anti (**III**)	2.04	1.29	2175	1.87	1.59	1970	0.93	0.26	1968
gauche-anti (**IV**)	3.62	3.30	2172	2.98	2.89	1968	2.13	2.24	1967

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

Chart 2



I (trans-syn)

II (gauche-syn)

III (trans-anti)

IV (gauche-anti)

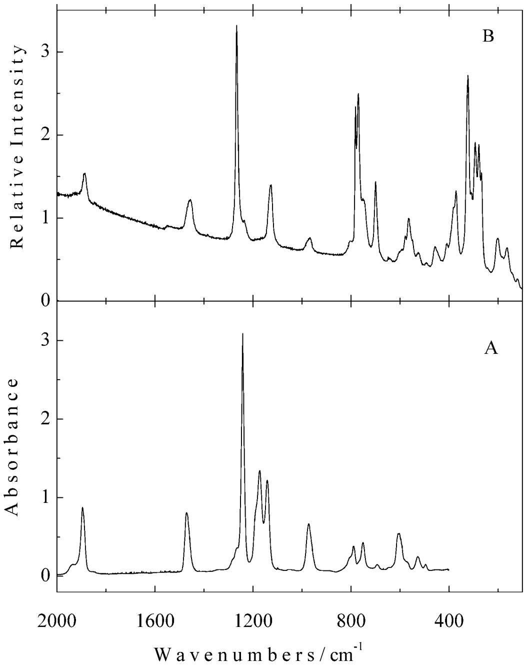


Figure 2. Vibrational spectra of $FC(O)OSO_2CF_3$: (A) IR spectrum of the vapor; (B) Raman spectrum of the liquid.

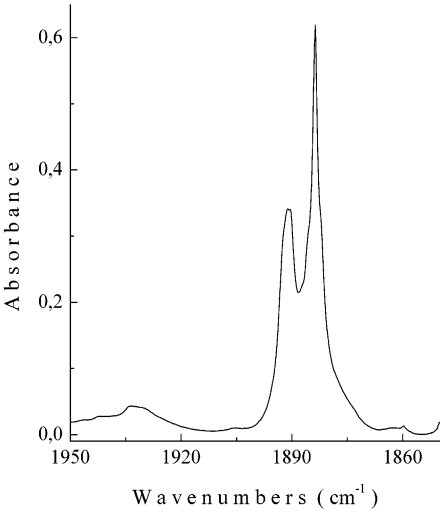


Figure 3. ν(C=O) Region of the IR spectrum of $FC(O)OSO_2CF_3$ isolated in an Ar matrix (1:1000) at ~15 K.

1). The calculations do not agree, however, on the relative stabilities of conformers **II** and **III**. According to MP2 and HF approximations, conformer **II** is more stable than conformer **III**, whereas the B3LYP method predicts the reverse order. All the methods are agreed, though, that there should be three conformers in detectable quantities in the gas phase at ambient temperatures.

Vibrational amplitudes for the optimum geometries were derived from the theoretical Cartesian force constants by Sipachev's method using the program SHRINK;[13] these were used subsequently as part of the analysis of the GED pattern (q.v.).

Vibrational Spectra

The IR spectrum of gaseous $FC(O)OSO_2CF_3$ and the Raman spectrum of the liquid are shown in Figure 2; the C=O stretching region of the IR spectrum of the compound isolated in solid Ar (1:1000) at ca. 15 K is shown in Figure 3. The details of the spectra are itemized in Table 2, together with the nonscaled wavenumbers calculated using the B3LYP/6-311G* approximation.

Information about the conformational properties can be derived from the IR spectrum of the matrix. 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 lower wavenumber occurs for the synperiplanar orientation, a finding that reflects 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), which leads to weakening of the C=O

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(13) Sipachev, V. A. *J. Mol. Struct.* **2001**, *567/568*, 67.

Table 2. Vibrational Data for $FC(O)OSO_2CF_3$ (Wavenumbers in cm^{-1})

trans-syn (B3LYP/ 6-311G*)	gauche-syn (B3LYP/ 6-311G*)	Ar (matrix)	IR(gas), 3 Torr	Raman (liquid)	assignment[a]
		1932	1935		
1937		1892			ν(C=O)
	1929	1884	1895	1887	ν(C=O)
	1416	1476			$\nu_{as}(SO_2)$
1405		1457	1469	1457	$\nu_{as}(SO_2)$
	1265	1268		1264	$\nu_{as}(CF_3)$
1255		1249			$\nu_{as}(CF_3)$
1241		1243	1240	1234	$\nu_{as}(CF_3)$
	1239	1241			$\nu_{as}(CF_3)$
	1232	1235			$\nu_s(SO_2)$
1229		1228			$\nu_s(SO_2)$
1168		1166	1172		ν(CF)
	1167	1164			ν(CF)
1094		1140		1129	$\nu_s(CF_3)$
	1086	1138	1141		$\nu_s(CF_3)$
	985	977			ν(C−O)
983		967	970	972	ν(C−O)
	780	804		802	$\delta_s(CF_3)$, ν(S-O)
772		787	791	783	$\delta_s(CF_3)$, ν(S−O)
	772	777			γ(C=O)
764		746	750	771	γ(C=O)
726		707		750	ν(S−O)
	723	703			ν(S−O)
680		691		699	δ(OCO)
	672		692		δ(OCO)
581		610	604	603	τ(SO_2)
	579	593		593	τ (SO_2)
	567	580		578	ρ(OCO)
555		567	571	564	ρ(OCO)
	553			550	$\delta(CF_2)$
552		524	528	524	$\delta(CF_2)$
	509			492	$\delta_s(SO_2)$, $\delta(CF_2)$
508		496	494	488	$\delta_s(SO_2)$, $\delta(CF_2)$
				458	
420				408	$\rho(SO_2)$, $\tau(CF_2)$
	395				$\rho(SO_2$, $\tau(CF_2)$
	343			371	δ(CSO)
333				324	δ(CSO)
310				310	ν(C−S), $\rho(CF_2)$
	305				ν(C−S), $\rho(CF_2)$
300				294	$\tau(CF_2)$, $\tau(SO_2)$
	294			279	$\tau(CF_2$, $\tau(SO_2)$
	274				ν(C−S)
260				268	ν(C−S)
	202				$\omega(CF_2)$, $\rho(SO_2)$
184				204	$\omega(CF_2)$, $\rho(SO_2)$
	199				$\tau(CF_2)$, $\tau(SO_2)$
182				164	$\tau(CF_2)$, $\tau(SO_2)$
	147				δ(COS)
93				120	δ(COS)
	83				torsion S−O
80					torsion S−O
	62				torsion C−O
51					torsion C−O
	41				torsion C−S
35					torsion C−S

[a] B3LYP/6-311G* results. ν = stretching, δ = deformation, τ = twisting, ρ = rocking, ω = wagging, γ = out-of-plane deformation, s = symmetric, and as = antisymmetric.

bond. This observation is confirmed by our quantum chemical calculations (Table 1), which predict the ν(C=O) mode to have a lower wavenumber (by about 30 cm^{-1}) in the two conformers with syn orientation of the C=O bonds (conformers **I** and **II**) than in the two corresponding anti forms **III** and **IV**. If the strongest band in the experimental spectrum, at 1884 cm^{-1}, is assigned to a syn conformer **I** or **II**, as suggested by the quantum chemical calculations, the weak feature at 1932 cm^{-1}, i.e., blue-shifted from the first by 48 cm^{-1}, can reasonably be assigned to one of the two anti conformers **III** or **IV**. From the relative areas of the two bands and the calculated IR absorption coefficients, the contribution of the anti form is estimated to be about 2%.

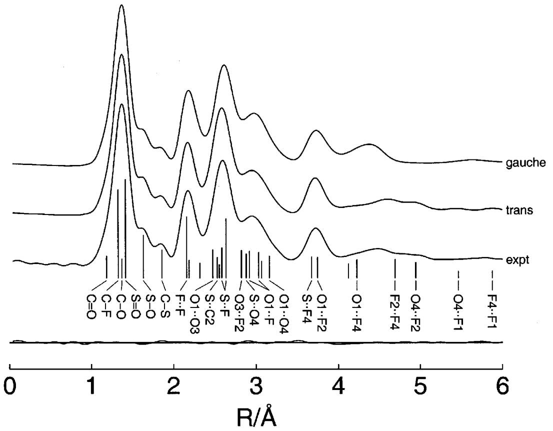

Figure 4. Experimental and calculated radial distribution functions and difference curve for the conformational mixture of gaseous $FC(O)OSO_2CF_3$. Interatomic distances correspond to the trans-syn conformer.

The assignment of the two strong bands at 1884 and 1892 cm^{-1} is not straightforward. According to all three calculations, the ν(C=O) mode shows a small shift with the switch from trans to gauche orientation of the FC(O) relative to the CF_3 group. However, estimates of the shift depend strongly on the computational method used, varying from +8 cm^{-1} (HF/6-311G*), through −1 cm^{-1} (MP2/6-311G*), and to −8 cm^{-1} (B3LYP/6-311G*). The calculated IR absorption coefficients of the mode are predicted, however, by all three methods to be much the same in the two conformers. On the basis of the calculated free energies, the strongest band at 1884 cm^{-1} is most plausibly assigned to the trans conformer **I** and the band at 1892 cm^{-1} to the gauche conformer **II**. Such an assignment is in agreement with the frequency shift predicted by the HF method, if not with that predicted by the B3LYP method. From the areas of the two bands and from the calculated IR absorption coefficients we derive a contribution of 41(5)% for conformer **II**, with an error limit based on the estimated uncertainties in the band areas and calculated IR absorption coefficients. On the other hand, there is some ambiguity about this conclusion, underlined by the observation that the intensity of the weaker band at 1892 cm^{-1} decreases slightly upon broad-band UV irradiation of the matrix, suggesting that it may belong not to the secondary but to the main conformer.

Gas-Phase Structure

It was hoped to gain more definitive information about the conformational composition of the vapor of the compound from the GED data. The experimental radial distribution function (RDF), derived by Fourier transformation of the molecular scattering intensities, is shown in Figure 4, together with the RDF's calculated for conformers **I** (trans) and **II** (gauche). Only the rather weak scattering corresponding to $r > 3.5$ Å contains information about the conformational properties. In the first step, least-squares fittings of the molecular intensities were performed for the four individual conformers. The following assumptions were made in these analyses: (i) The CF_3 group has C_{3v} symmetry with a possible tilt angle between the C_3 axis and the S−C bond direction. (ii) The FC(O)O entity is planar. (iii) For gauche conformers (with C_1 symmetry), calculated values were used for differences between O−S=O and C−S=O angles and for deviations of the $\mathrm{CF_3}$ group from an exactly staggered orientation and of the FC(O) group from an exactly eclipsed orientation (i.e. C=O or C−F eclipsed with respect to S−O). Only important amplitudes of vibration for distances which do not depend on the dihedral angle ϕ(C−S−O−C) were refined; all the other amplitudes were fixed to calculated values. (iv) The O−C bond length was fixed to the calculated value in all refinements. The quality of the fit was judged by the agreement factor for the intensities of the long nozzle-to-plate distance, R_{50}, which is more sensitive to the conformational properties of the molecule. R_{50} increased in the order **I** (5.4%) < **II** (7.3%) < **III** (10.8%) < **IV** (11.9%). From these analyses we conclude that conformers with anti orientation of the C=O bond relative to the S−O bond (**III** and **IV**) occur only in very small amounts, in agreement with the interpretation of the IR spectrum of the matrix-isolated molecule.

If some additional vibrational amplitudes were included in the refinement of conformer **I**, R_{50} decreased to 5.2%. Further improvement of the fit was obtained for a mixture of conformers **I** and **II**. The geometric parameters of the latter form were tied to those of the trans conformer **I** using the calculated differences. Vibrational amplitudes were also fixed to calculated values. The dihedral angle ϕ(C−S−O−C) of the gauche conformer **II** and its proportion were included in the list of refined parameters. In the final analysis, 13 geometric parameters, the conformational ratio and six vibrational amplitudes were amenable to simultaneous refinement. Only two correlation coefficients had values larger than |0.6|: $p3/p10 = -0.66$ and $p4/l1 = 0.70$. The best fit of the experimental molecular intensities, with $R_{50} = 4.2\%$, was obtained for a contribution of 33(8)% of the gauche form. The final results are listed in Table 3 (geometric parameters) and Table 4 (vibrational amplitudes); molecular models of both conformers are shown in Figure 5.

Crystal Structure

Table 5 lists the crystal data for the title compound at 150 K; mean values for geometric parameters have been included in Table 3. Fluorocarbonyl trifluoromethanesulfonate crystallizes in the monoclinic space group $P2_1/c$, with four $\mathrm{FC(O)OSO_2CF_3}$ molecules/unit cell. The more or less discrete molecules adopt exclusively the trans conformation **I**, i.e., the most stable form on the evidence of the calculations and the preferred form in the vapor phase. All the bond distances in the crystal are slightly but systematically shorter than those determined for the gaseous molecule; within the experimental uncertainties, the bond angles except S−O−C and O−C=O are the same. In no case, however, do the dimensions differ by more than three times the estimated uncertainty, and comparisons are necessarily clouded in any case by the differences of temperature and technique.

Table 3. Experimental and Calculated Geometric Parameters of the Trans-Syn Conformer **I** of $\mathrm{FC(O)OSO_2CF_3}$[a]

	GED[b]		X-ray[c]	MP2[d]	B3LYP[d]
S=O	1.413(3)	*p*1	1.407(2)	1.433	1.439
S−O	1.632(5)	*p*2	1.628(1)	1.694	1.713
S−C1	1.859(7)	*p*3	1.836(2)	1.858	1.895
C1−F	1.325(3)	*p*4	1.312(2)	1.322	1.323
C2−F4	1.322(3)[e]		1.307(2)	1.319	1.324
O3−C2	1.361[f]		1.357(2)	1.361	1.360
C=O	1.183(8)	*p*5	1.163(2)	1.183	1.177
C1−S−O3	92.7(16)	*p*6	92.8(1)	91.4	91.9
C1−S=O	107.5(11)	*p*7	108.8(1)	108.5	108.8
O=S−O	108.6 (11)	*p*8	109.7(1)	108.9	108.9
S−O3−C2	114.6(13)	*p*9	117.8(1)	116.4	118.1
F−C1−F	109.4(5)	*p*10	110.0(2)	109.9	110.3
O3−C2=O4	130.4(12)	*p*11	128.0(2)	128.2	128.4
O3−C2−F4	107.5(17)	*p*12	106.3(2)	106.2	106.3
tilt($\mathrm{CF_3}$)[g]	2.2[f]		2.2(2)	2.2	2.1
$\varphi(\mathrm{C1{-}S{-}O{-}C2})_{\mathrm{gauche}}$	72(6)	*p*13		66.3	66.2
% gauche	33(8)	*p*14	100	23	23
$\Delta G°$ (kcal mol^{-1})	0.49(13)			0.74	0.74

[a] Values in Å and deg. For atom numbering, see Figure 5. [b] r_a values with 3σ uncertainties. [c] Mean values for parameters that are not unique, with σ uncertainties. [d] 6-311G* basis sets. [e] Difference from r(C1−F) fixed to calculated value (MP2). [f] Fixed. [g] Tilt between C_3 axis of $\mathrm{CF_3}$ group and S−C bond direction, toward the O3 atom.

Table 4. Interatomic Distances, Experimental and Calculated Vibrational Amplitudes, and Vibrational Corrections for the Trans-Syn Conformer **I**[a]

	dist	ampl(GED)		ampl (MP2)	$\Delta r = r_\alpha - r_a$
C=O	1.18	0.039(3)	*l*1	0.036	0.0004
C−F	1.32	0.043[b]		0.043	0.0005
O3−C2	1.37	0.046[b]		0.046	0.0010
S=O	1.41	0.038(3)	*l*1	0.035	0.0003
S−O	1.63	0.048(5)	*l*2	0.052	−0.0012
S−C	1.86	0.046(5)	*l*2	0.050	0.0001
F1···F2	2.16	0.058(4)	*l*3	0.056	0.0020
O3···F4	2.17	0.057(4)	*l*3	0.055	0.0023
O4···F4	2.19	0.050[b]		0.050	0.0042
O3···O4	2.32	0.052[b]		0.052	0.0018
O1···O3	2.48	0.073[b]		0.073	0.0015
S···C2	2.53	0.066(7)	*l*4	0.067	0.0049
C1···O3	2.53	0.083[b]		0.083	0.0040
O1···O2	2.56	0.057(4)	*l*3	0.055	0.0014
S···F	2.59−2.64	0.069(7)	*l*4	0.070	0.0028
C1···O1	2.62	0.079[b]		0.079	0.0030
O3···F2	2.83	0.189(56)	*l*5	0.170	0.0091
S···O4	2.88	0.110[b]		0.110	−0.0042
O1···F3	2.92	0.122(15)	*l*6	0.147	0.0036
O1···F1	3.03	0.134(15)	*l*6	0.159	0.0076
O1···C2	3.06	0.139(15)	*l*6	0.164	0.0089
O1···O4	3.16	0.246[b]		0.246	0.0053
S···F4	3.67	0.064[b]		0.064	0.0056
O1···F2	3.75	0.071[b]		0.071	0.0149
C1···C2	3.86	0.086[b]		0.086	0.0039
C2···F3	4.13	0.189(56)	*l*5	0.186	0.0383
O1···F4	4.22	0.189(56)	*l*5	0.180	0.0242
C1···O4	4.55	0.102[b]		0.102	0.0265
C1···F4	4.65	0.119[b]		0.119	0.0461
F2···F4	4.70	0.253[b]		0.253	0.0561
F2···O4	4.95	0.189(56)	*l*5	0.181	0.0401
C2···F1	4.96	0.081[b]		0.081	0.0397
O4···F1	5.46	0.125[b]		0.125	0.0309
F4···F1	5.88	0.103[b]		0.103	0.0648

[a] Values in Å with 3σ uncertainties. For atom numbering see Figure 5. [b] Fixed.

How the molecules are packed in the crystal is illustrated in Figure 6. The main intermolecular interactions are such as to produce chains of molecules linked by C=O···C=O contacts. The chains are further linked via additional S=O···C=O contacts. The O···C distances—3.014(2) Å in

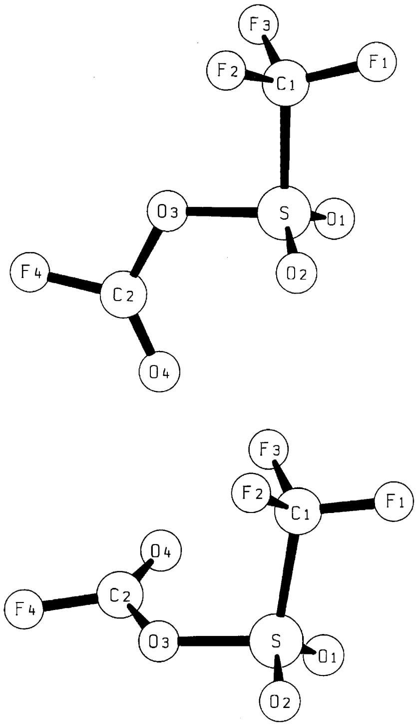

Figure 5. Molecular models with atom numbering for trans-syn (above) and gauche-syn (below) conformers of $FC(O)OSO_2CF_3$.

Table 5. Crystal Data for $FC(O)OSO_2CF_3$

empirical formula	$C_2F_4O_4S$
fw	196.08
wavelength	0.710 73 Å
temp	150(2) K
cryst system	monoclinic
space group	$P2_1/c$
unit cell dimens	$a = 10.9825(10)$ Å
	$b = 6.4613(6)$ Å
	$c = 8.8508(8)$ Å
	$\beta = 104.786(2)°$
V	607.3(1) $Å^3$
N° of reflns for cell	2591 ($3 \le \theta \le 28°$)
Z	4
δ(calcd)	2.145 Mg m^{-3}
abs coeff	0.587 mm^{-1}
F(000)	384

the former and 3.010(2) Å in the latter case—are somewhat less than the sum of the relevant van der Waals radii (3.20 Å).[14] The intermolecular forces thus implied contribute, no doubt, to the slight differences in the dimensions of the S−O−C and O−C═O units that appear, as noted above, to be produced by crystallization. It is clear, however, that the individual molecules suffer minimal perturbation as a result of such interactions, and none of the other distances betray evidence of significant intermolecular forces, in general keeping with the volatility of the compound.

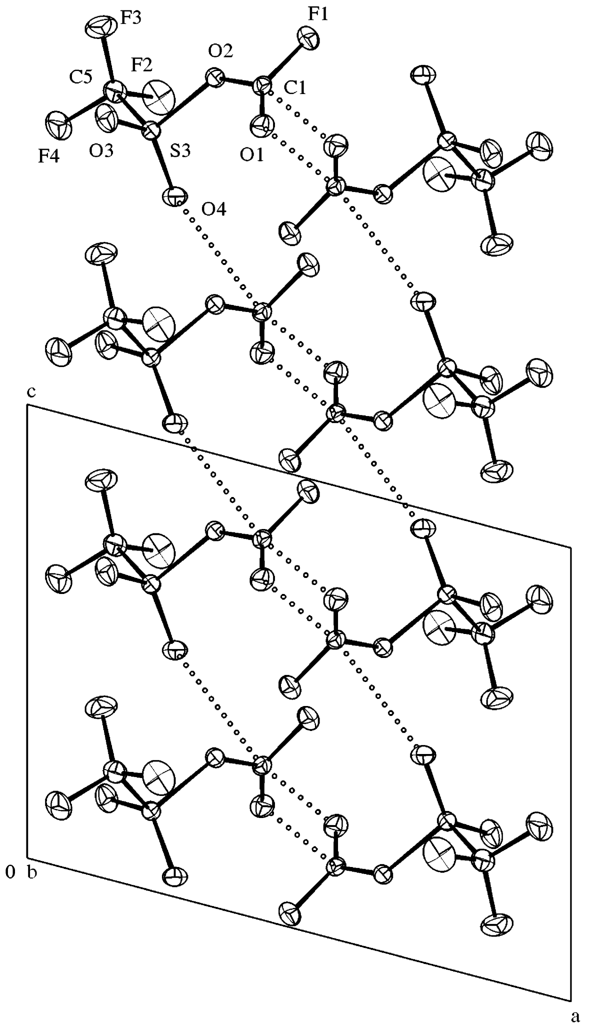

Figure 6. Packing of molecules in crystalline $FC(O)OSO_2CF_3$ at 150 K.

Discussion

As mentioned in the Introduction, all sulfonates of the type $XOSO_2Y$, with X = H, CH_3, CF_3, or F and Y = F, Cl, or CF_3, whose molecular structures have been determined, exist only as gauche conformers in the gas phase. In the case of $FC(O)OSO_2CF_3$, with X = FC(O) and Y = CF_3, the best account of the GED pattern is afforded by a model that consists of a mixture of 67(8)% of the trans conformer (**I**) and 33(8)% of the gauche conformer (**II**). This result is consistent with the proposed assignment of the IR spectrum of the matrix-isolated vapor species implying that the vapor at ambient temperatures is made up of 59(5)% of the trans and 41(5)% of the gauche form. Thus, $FC(O)OSO_2CF_3$ emerges as the first sulfonate in which the trans form is preferred to the gauche form. The conformational composition corresponds to $\Delta G° = G°(\text{gauche}) - G°(\text{trans}) = +0.49(13)$ and +0.22(12) kcal mol^{-1} on the basis of the GED and IR data, respectively. These values are only slightly smaller than the estimates given by the computational methods (0.74−0.94 kcal mol^{-1}). According to the IR spectrum of the matrix, no more than about 2% of conformers **III** or **IV**, with the C═O bond antiperiplanar to the S−O single bond, are present in the vapor at ambient temperatures. This finding runs counter to the very low $\Delta G°$ value predicted by the B3LYP method for conformer **III** (+0.26 kcal mol^{-1} relative to **I**).

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). Natural bond orbital

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(14) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(NBO) analyses have been performed for $FC(O)OSO_2CF_3$ and $CH_3OSO_2CF_3$. The two sulfonates possess rather different potential functions for internal rotation around the S−O bond. The FC(O) derivative displays minima corresponding to both trans and gauche structures, with the trans lower in energy than the gauche (see Figure 1), whereas the CH_3 derivative displays minima only for gauche forms and a maximum for the trans form. According to the NBO analysis of the MP2 wave function, the sum of these orbital interaction energies is smaller for the FC(O) than for the CH_3 compound (ca. 15 vs ca. 23 kcal mol^{-1}). In both compounds, however, the orbital interaction energies are slightly higher (by 0.4 and 0.6 kcal mol^{-1}, respectively) in the trans than in the gauche form. Thus, there is no straightforward rationalization of the different conformational properties to be found in the NBO analyses. It may be that steric effects tip the balance in these circumstances, but no quantitative estimate of such effects can be made.

Bond lengths and angles of the SO_2CF_3 moiety in the gaseous molecules $FC(O)OSO_2CF_3$ and $CH_3OSO_2CF_3$[2] are very similar, with but one exception: the S−O single bond is much shorter in the latter [1.555(4) Å] than in the former [1.632(5) Å]. A similarly short S−O bond occurs in $HOSO_2CF_3$ [1.558(3) Å].[9] This shortening of the S−O bond with decreasing electronegativity of the substituent X appears to be a general feature of fluorosulfonates of the type $XOSO_2F$; cf. 1.606(8) Å in $FOSO_2F$,[4] 1.589(10) Å in $ClOSO_2F$,[4] and 1.558(7) Å in CH_3OSO_2F.[7]

Both quantum chemical methods which allow for electron correlation reproduce the experimental bond lengths reasonably well, the main exceptions being some bond lengths around sulfur (see Table 3). In particular, the S−O bond is predicted to be too long by 0.06 and 0.08 Å. All experimental bond angles are reproduced very well, when due account of experimental uncertainties (3σ values) is taken.

Crystallization of fluorocarbonyl trifluoromethanesulfonate does not alter the conformational preference of the free molecule, for the crystal at 150 K is made up solely of the trans conformer **I** with syn orientation of the C═O bond. Whatever influence intermolecular contacts may exercise in the crystal clearly does not result in significant perturbation of either the conformational balance or the dimensions of the molecules.

Experimental Section

Synthesis and Physical Properties. The preparation and manipulation of fluorocarbonyl trifluoromethanesulfonate were carried out in evacuated Pyrex apparatus. In a Carius tube closed by a Young's valve, 0.6 g (5.2 mmol) of FC(O)SCl, prepared as described previously,[15] was condensed on 1.43 g (5.6 mmol) of $AgCF_3SO_3$ (Aldrich), which had been dried previously for 3 h in vacuo (10^{-4} Torr) (1 Torr = 0.1333 kPa) at 60−80 °C. After stirring of the reaction mixture at room temperature for 1 day, the volatile components were fractionated under dynamic vacuum through traps held at −40, −70, −95, and −196 °C. A 0.7 g (3.6 mmol) amount of $FC(O)OSO_2CF_3$ collected in the −70 °C trap, representing a yield of ca. 70% based on eq 1 and the quantity of FC(O)SCl taken.

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

A melting point of −51 °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 $\log p$ (Torr) = $-2120/T + 9.331$ over the temperature range $T = 222-293$ K, giving an extrapolated normal boiling point of 328.7 K (55.5 °C). The measured density of the liquid at 20 °C was 1.67 g mL^{-1}. The molecular weight, found by Regnault's method, was 200 [$FC(O)OSO_2CF_3$ requires 196]. The compound handled in a glass vessel is stable at room temperature by several months.

Spectroscopic Characterization. Details of the vibrational spectra of the compound have already been presented (see Table 2 and Figures 2 and 3). 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 $FC(O)OSO_2CF_3$ with argon (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.[16,17] 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 monitor 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. 3 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 doublet at δ_C 134.4 [F**C**(O)O, d, ^1J(CF) = 310.6 Hz] and a quartet of equal intensity at δ_C 118.4 [**C**F_3, q, ^1J(CF) = 322.4 Hz]. The ^{19}F spectrum displayed signals with appropriate relative intensities at δ_F −77.9 [C*F*$_3$] and −13.6 [*F*C(O)O]. Given the method of preparation and the differences from the properties of a compound formulated previously as $FC(O)SO_3CF_3$, any doubt about the authenticity of the present compound is removed by the ^{19}F resonance associated with the FC(O) moiety which is very sensitive to the environment of the C atom. The chemical shift δ_F −13.6 doesn't compare with values in the range δ_F 30−45, for example, for FC(O)S-containing molecules.[18] The possibility that the compound is in fact the sulfenic ester $FC(O)SOSO_2CF_3$ can thus be dismissed.

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. A single absorption was observed with a maximum centered at 257 nm with an extinction coefficient of 440 L/(mol·cm).

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(15) Haas, A.; Reinke, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 705.

(16) See for example: Romano, R. M.; Della Védova, C. O.; Downs, A. J.; Greene, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 5794 and references therein.

(17) Perutz, R. N.; Turner, J. J. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 452.

(18) Della Védova, C. O.; Haas, A. *Z. Anorg. Allg. Chem.* **1991**, *600*, 145.

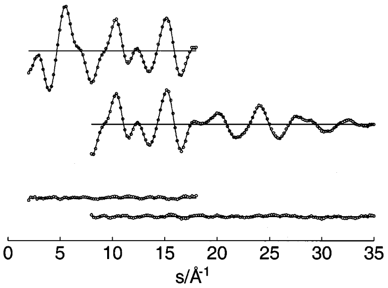

Figure 7. Experimental (dots) and calculated (full line) molecular scattering intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

GED Measurements. Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[19] at nozzle-to-plate distances of 25 and 50 cm and with an accelerating voltage of about 60 kV. The sample was cooled to -23 °C, giving a vapor pressure of about 7 Torr; the inlet system, including the nozzle, was at room temperature. The photographic plates were analyzed with an Agfa Duoscan HiD scanner, and total scattering intensity curves were obtained from the TIFF-file using the program SCAN3.[20] Experimental molecular intensities were obtained in the range $s = 2-18$ and $8-35$ Å^{-1} in steps Δs of 0.2 Å^{-1} for the long and short camera distances, respectively [$s = (4\pi/\lambda) \sin \theta/2$, where λ is the electron wavelength and θ the scattering angle]; the averaged intensities are shown in Figure 7.

Crystal Structure. A sample of $FC(O)OSO_2CF_3$ was held in a Pyrex capillary and mounted on a Bruker SMART APEX diffractometer equipped with an Oxford Cryosystems low-temperature device[21] and an OHCD laser-assisted crystallizer. A single crystal was grown at 198.2 K by Boese's laser-assisted zone-refinement method.[22] Diffraction data were then collected at 150 K, essential crystal data being listed in Table 5. Following integration, data reduction and application of an absorption correction (SADABS),[23] the structure was solved by direct methods (SIR92)[24] and refined by full-matrix least-squares against F^2 (CRYSTALS).[25] Other calculations were carried out using PLATON.[26] All atoms were modeled with anisotropic displacement parameters. Of 4390 data collected, 1433 were unique ($R_{int} = 0.030$). The final conventional R factor [based on F and 1307 data with $F > 4\sigma(F)$] was 0.0369, and wR_2 (based on F^2 and all 1433 data used for refinement) was 0.0795. The final difference map extremes were $+0.38$ and -0.31 e Å^{-3}.

Theoretical Calculations. All the quantum chemical calculations were performed using the GAUSSIAN 98 program package[12] under the Linda parallel execution environment using two coupled PC's. Geometry optimizations were sought (i) with the HF approximation and (ii) with the MP2 and B3LYP methods; in all cases, the calculations employed 6-311G* basis sets and standard gradient techniques with simultaneous relaxation of all the 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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(19) Oberhammer, H. *Molecular Structure by Diffraction Methods*; The Chemical Society: London, 1976; Vol. 4, p 24.

(20) Atavin, E. G.; Vilkov, L. V. *Prib. Tekh. Eksp.* **2002**, in press (in Russian).

(21) Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105.

(22) Boese, R.; Nussbaumer, M. In *Correlations, Transformations, and Interactions in Organic Crystal Chemistry*; Jones, D. W., Katrusiak, A., Eds.; IUCr Crystallographic Symposia, Vol. 7; Oxford University Press: Oxford, U.K., 1994; p 20.

(23) Sheldrick, G. M. *SADABS*; University of Göttingen: Göttingen, Germany, 2002.

(24) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(25) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W.; Cooper, R. I. *CRYSTALS*, issue 12; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 2003.

(26) Spek, A. L. *PLATON-A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2003. PC version in WINGX: Farrugia, L. J. *J. Appl. Crystallogr.* **1999,** *32*, 837.