Inorg. Chem. **2003**, *42*, 4071–4075

Inorganic Chemistry
Article

# Structure and Conformations of *N*-(Fluoroformyl)imidosulfurous Dichloride, $FC(O)N{=}SCl_2$

**Christiane Leibold,[†] Rosa M. S. Alvarez,[‡] Edgardo H. Cutin,[‡] Carlos O. Della Vedova,[§] and Heinz Oberhammer*[,†]**

*Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 72076 Tübingen, Germany, Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, Ayacucho 491, (4000) Tucumán, Republic of Argentina, and CEQUINOR (CONICET), Laboratorio de Servicios a la Industria y al Systema Científico (UNLP-CIC-CONICET), and Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115, (1900) La Plata, Republic of Argentina*

Received February 10, 2003

The IR (gas) and Raman (liquid) spectra of $FC(O)NSCl_2$ demonstrate the presence of a conformational mixture in both phases. According to a gas electron diffraction study, the main conformer (94(8)%) possesses a syn–syn structure (C(O)F group synperiplanar with respect to the $SCl_2$ bisector and the C═O bond synperiplanar to the N═S bond). Quantum chemical calculations (HF, B3LYP and MP2 with 6-31G* basis set, and MP2/6-311(2df)) predict a syn–anti structure for the second conformer. Analysis of the IR (gas) spectrum results in a contribution of 5(1)% of the minor form, corresponding to a Gibbs free energy difference $\Delta G^\circ = G^\circ(\text{syn–anti}) - G^\circ(\text{syn–syn}) = 1.75(15)$ kcal/mol. This value is reproduced very well by quantum chemical calculations, which include electron correlation effects ($\Delta G^\circ = 1.28$–$1.56$ kcal/mol). The HF approximation overestimates this energy difference ($\Delta G^\circ = 3.24$ kcal/mol).

## Introduction

All imidosulfurous difluorides of the type $RN{=}SF_2$ with R = Cl,[1] $CF_3$,[2] NC,[3] $SF_5$,[4] FC(O),[5] $CF_3C(O)$,[6] and $SO_2F$[7] whose gas-phase structures have been determined possess syn conformation around the N═S bond (substituent R synperiplanar with respect to the $SF_2$ bisector). The only imidosulfurous dichloride, $CF_3N{=}SCl_2$,[8] whose structure was determined in the gas phase also possesses a syn structure. In this we report a structural and conformational investigation of $FC(O)N{=}SCl_2$ using vibrational spectroscopy, gas electron diffraction, and quantum chemical calculations. The main interests in this structural study are the conformational properties of this imidosulfurous dichloride in comparison with similar compounds investigated previously in our group. The first synthesis of this compound was reported by Roesky and Mews.[9] The authors characterized the compound by IR spectra of the liquid, where they observed a single band in the C═O region, and by the $^{19}F$ NMR spectrum, which shows a single signal.

## Quantum Chemical Calculations

$FC(O)N{=}SCl_2$ can adopt four different conformations (see Chart 1) with syn or anti orientation around the N═S double bond and with relative syn or anti orientation of the C═O and N═S double bonds. Geometry optimizations for these four forms were performed with four different methods (HF, B3LYP and MP2 with 6-31G* basis sets, and MP2/6-311G(2df)). The calculated relative energies

---

* To whom correspondence should be addressed. E-mail: heinz.oberhammer@uni-tuebingen.de.

[†] Universität Tübingen.

[‡] Universidad Nacional de Tucumán.

[§] Universidad Nacional de La Plata.

(1) Haase, J.; Oberhammer, H.; Zeil, W.; Glemser, O.; Mews, R. *Z. Naturforsch.* **1970**, *23A*, 153.

(2) Trautner, F.; Christen, D.; Mews, R.; Oberhammer, H. *J. Mol. Struct.* **2000**, *525*, 135.

(3) Alvarez, R. S. M.; Cutín, E. H.; Della Védova, C. O.; Mews, R.; Haist, R.; Oberhammer, H. *Inorg. Chem.* **2001**, *40*, 5188.

(4) White, R. M.; Bailey, S. R.; Graybeal, J. D.; Thrasher, J. S.; Palmer, M. H. *J. Mol. Spectrosc.* **1988**, *129*, 243.

(5) Leibold, C.; Cutín, E. H.; Della Védova, C. O.; Mack, H.-G.; Mews, R.; Oberhammer, H. *J. Mol. Struct.* **1996**, *375*, 207.

(6) Mora Valdez, M. I.; Cutín, E. H.; Della Védova, C. O.; Mews, R.; Oberhammer, H. *J. Mol. Struct.*, in press.

(7) Haist, R.; Alvarez, R. M. S.; Cutín, E. H.; Della Védova, C. O.; Oberhammer, H. *J. Mol. Struct.* **1999**, *484*, 249.

(8) Haist, R.; Cutín, E. H.; Della Védova, C. O.; Oberhammer, H. *J. Mol. Struct.* **1999**, *475*, 273.

(9) Roesky, H. W.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 217.

10.1021/ic030058p CCC: $25.00

**Chart 1**

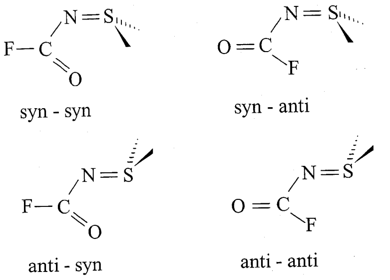

**Table 1.** Relative Energies and Gibbs Free Energies (kcal/mol) of Syn–Syn, Syn–Anti, Anti–Syn, and Anti–Anti Conformers of $FC(O)N{=}SCl_2$

| | syn–syn: | syn–anti | | anti–syn: | anti–anti: |
|---|---|---|---|---|---|
| | $\Delta E/\Delta G°$ | $\Delta E$ | $\Delta G°$ | $\Delta E$ | $\Delta E$ |
| HF/6-31G* | 0.00 | 3.51 | 3.24 | 4.79 | 8.81 |
| B3LYP/6-31G* | 0.00 | 1.49 | 1.28 | 7.85 | 8.63 |
| MP2/6-31G* | 0.00 | 1.73 | 1.42 | 7.46 | 8.82 |
| MP2/6–311(2df) | 0.00 | 1.87 | 1.56 | 7.72 | |

are summarized in Table 1. All methods predict the same sequence of stability for these four conformers, syn–syn > syn–anti > anti–syn > anti–anti. The relative energies obtained with the HF approximation, however, differ appreciably from those predicted by methods which include electron correlation effects. According to these latter methods it is expected that small amounts of the syn–anti form will be observed in the experiments, in addition to the prevailing syn–syn conformer. For these two structures the relative Gibbs free energies $\Delta G°$ were calculated which allow a direct comparison with the experiment. Structures with syn orientation around the N=S bond are predicted to possess $C_s$ symmetry, those with anti orientation possess $C_1$ symmetry due to a twist around the N=S bond of about 45° (anti–syn) or 23° (anti–anti) away from the $C_s$ structure.

Vibrational frequencies for the syn–syn and syn–anti conformers were calculated with the B3LYP and MP2 methods and 6-31G* basis sets. The Cartesian force constants obtained with the MP2 method were transformed to a symmetry force field, and vibrational amplitudes were derived with the program ASYM40.[10] All quantum chemical calculations were performed with the program suite GAUSSIAN 98.[11]

## Experimental Section

$FC(O)NSCl_2$ was synthesized by the reaction between $FC(O)NSF_2$ and $PCl_5$.[9] The product was purified at reduced pressure by repeated trap-to-trap distillations at −80 °C.

The gas IR spectrum at 5 Torr and liquid IR spectrum were recorded between 4000 and 400 $cm^{-1}$ (resolution 2 $cm^{-1}$) with a FT-IR Perkin-Elmer Paragon 500 spectrometer (Figure 1).

Raman spectra of the liquid between 3500 and 50 $cm^{-1}$ (Figure 2) were obtained using a FT Bruker IFS 66v spectrometer (spectral resolution of 4 $cm^{-1}$) equipped with a Nd:YAG laser (1064 nm). The liquid samples were handled in glass capillaries at room temperature.

Electron diffraction intensities were recorded with a KD-G2 gasdiffraktograph[12] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample was kept at −36 °C during the experiment, and inlet system and nozzle were at room temperature. The photographic plates (Kodak electron image plates 18 × 13 cm) were analyzed with the usual procedures,[13] and averaged molecular intensities in the $s$-ranges 2−18 and 8−35 $Å^{-1}$ are shown in Figure 3 ($s = (4\pi/\lambda)\sin\theta/2$; $\lambda$ is the electron wavelength, and $\theta$ is the scattering angle).

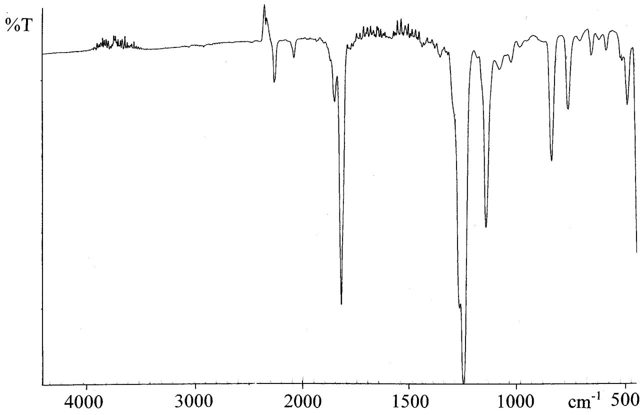

**Figure 1.** Infrared spectrum of gaseous $FC(O)NSCl_2$ at 5 Torr and room temperature (resolution 2 $cm^{-1}$).

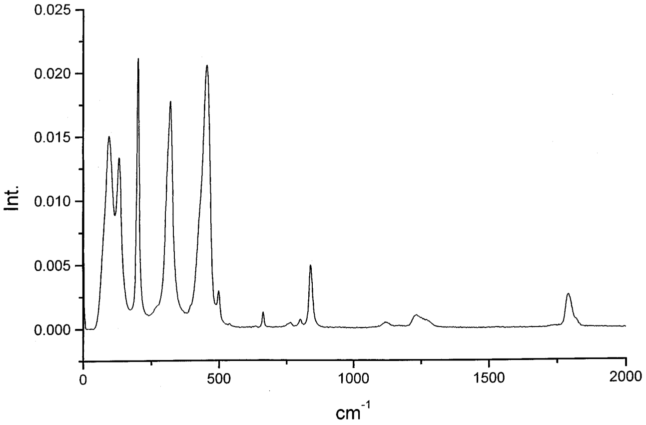

**Figure 2.** Raman spectrum of liquid $FC(O)NSCl_2$ at room temperature (resolution 4 $cm^{-1}$).

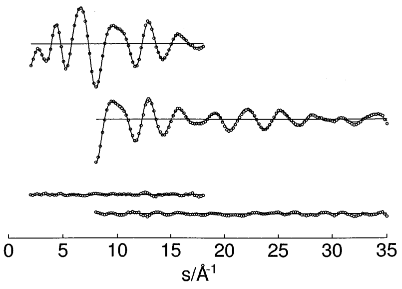

**Figure 3.** Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

---

[10] Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

[11] 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.; Stratman, 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.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

**Table 2.** Experimental and Calculated Wave Numbers of the Syn−Syn Conformer and Tentative Assignments[a]

| mode | assgnt[a] | IR | intensity | Raman | intensity | B3LYP/6-31G* | MP2/6-31G* |
|---|---|---|---|---|---|---|---|
| $\nu_1(A')$ | (C═O) stretch | 1818 | s | 1791 | m | 1880 | 1884 |
| $\nu_2(A')$ | (S═N) stretch | 1245 | vs | 1233 | w | 1280 | 1310 |
| $\nu_3(A')$ | (C−F) stretch | 1143 | s | 1116 | w | 1180 | 1197 |
| $\nu_4(A')$ | (C−N) stretch | 843 | m | 839 | m | 845 | 864 |
| $\nu_5(A'')$ | (FCO) oop def | 767 | m | 764 | w | 762 | 762 |
| $\nu_6(A')$ | (NCO) def | 663 | w | 662 | w | 658 | 664 |
| $\nu_7(A')$ | (NCF) def | 498 | m | 498 | m | 492 | 496 |
| $\nu_8(A')$ | ($SCl_2$) sym stretch | | | 455 | vs | 418 | 421 |
| $\nu_9(A'')$ | ($SCl_2$) asym stretch | | | 455 | vs | 399 | 408 |
| $\nu_{10}(A')$ | ($SCl_2$) wagging | | | 320 | vs | 304 | 313 |
| $\nu_{11}(A'')$ | ($SCl_2$) rocking | | | 320 | vs | 298 | 304 |
| $\nu_{12}(A')$ | ($SCl_2$) def | | | 201 | vs | 173 | 190 |
| $\nu_{13}(A')$ | (SNC) def | | | 131 | s | 111 | 118 |
| $\nu_{14}(A'')$ | (N═S) torsion | | | 94 | s | 75 | 84 |
| $\nu_{15}(A'')$ | (C−N) torsion | | | | | 54 | 59 |

[a] Stretch, stretching; sym, symmetric; asym, asymmetric; def, deformation; oop, out-of-plane. The assignments correspond to the largest contribution in the potential energy distribution derived from the calculated force field.

## Vibrational Spectra

Table 2 lists the experimental IR (gas) and Raman (liquid) wavenumbers together with calculated values. The assignment of the bands for $FC(O)N{=}SCl_2$ was performed on the basis of the observed features for the FC(O)N═S moiety of the analogous difluoride derivative.[14]

Furthermore, calculated vibrational frequencies and intensities were considered. As in the case of $FC(O)N{=}SF_2$ and $FC(O)N{=}S(F)CF_3$,[15] the N═S and N−C modes are strongly coupled. The strong IR signal centered at 1245 $cm^{-1}$ is assigned to the N═S stretching vibration. This vibrational frequency decreases from 1330 $cm^{-1}$ in $FC(O)N{=}SF_2$ to 1245 $cm^{-1}$ in the dichloride, parallel to the decreasing electronegativity of the substituents at sulfur. This lowering of the vibrational frequency is also in agreement with the lengthening of the N═S bond length (see below). Two stretching modes are expected for the S−Cl bonds. The symmetric mode is calculated at 418/421 $cm^{-1}$, and the asymmetric one at 399/408 $cm^{-1}$ (B3LYP and MP2, respectively). In the Raman spectrum only one very strong and broad signal is observed at 455 $cm^{-1}$, which can be assigned to these two fundamentals. The deformation modes belonging to the $NSCl_2$ group were assigned according to the calculated frequencies and the potential energy distribution. In general, the vibrations of $FC(O)NSCl_2$ occur at lower wavenumbers compared to those in the fluorinated compound, with the exception of the N−C═O deformation (663 $cm^{-1}$ vs 554 $cm^{-1}$). Also the torsion around the N−C bond is predicted to be slightly higher in the chlorine derivative (54 $cm^{-1}$) than in the fluorine compound (42 $cm^{-1}$).

The C═O vibration in the IR (gas) spectrum is split into two bands, a weak band at 1851 $cm^{-1}$ and a much stronger band at 1818 $cm^{-1}$. On the basis of the calculated frequencies, the strong band can be assigned to the syn−syn form and the weak band to the syn−anti conformer. The calculated splitting ($\Delta\nu = \nu(\text{syn−anti}) - \nu(\text{syn−syn}) = 30$ and 33 $cm^{-1}$ according to B3LYP and MP2 calculations, respectively) is in excellent agreement with the experimental splitting ($\Delta\nu = 33$ $cm^{-1}$). The absorbance ratio of the two bands $A(\text{syn−anti})/A(\text{anti−anti}) = 0.14(1)$. Taking into account the ratio of the calculated intensities (square of transition moments) of the two bands, $I(\text{syn−anti})/I(\text{syn−syn}) = 2.55$, which is the mean value of B3LYP (2.38) and MP2 (2.72) calculations, the contribution of the syn−anti form is 5(1)%. The uncertainty is estimated from the uncertainties in the absorbance ratio and in the calculated intensities. This contribution corresponds to $\Delta G° = 1.75(15)$ kcal/mol.

Furthermore, a well-defined shoulder at higher wavenumbers of the band assigned to the N═S stretching mode at 1245 $cm^{-1}$, which is the strongest band in the IR spectrum, gives evidence of the presence of a second conformer. The experimental shift (18 $cm^{-1}$) is in good agreement with the calculated (B3LYP) wavenumber difference (14 $cm^{-1}$). The peaks for the C═O and N═S stretches in the Raman spectrum also clearly indicate the existence of two conformers in the liquid phase. A quantitative conformational analysis, however, is not possible, since the Raman intensities of both vibrations are very weak (see Figure 2). Considering the good agreement between these observed and calculated wavenumber differences for the two conformers, it is reasonable to assign the weak IR band at 1083 $cm^{-1}$ to the C−F stretch of the syn−anti form ($\Delta\nu = -60$ $cm^{-1}$ from experiment and −63 $cm^{-1}$ from B3LYP calculation). Similarly, the weak peak at 801 $cm^{-1}$ in the Raman spectrum of the liquid can be assigned to the C−N stretch of the less abundant form ($\Delta\nu = -38$ $cm^{-1}$ from experiment and −34 $cm^{-1}$ from B3LYP calculation).

## Structure Analysis

The experimental radial distribution function (RDF) was derived by Fourier transformation of the molecular intensities using an artificial damping function of $\exp(-\gamma s^2)$ ($\gamma = 0.0019$ Å$^2$). Calculated RDF's for the syn−syn and syn−anti conformers are compared with the experimental curve in Figure 4. The RDF can be reproduced satisfactorily only

---

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

(13) Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.

(14) Alvarez, R. M. S.; Cutin, E. H.; Romano, R.; Della Vedova, C. O. *Spectrochim. Acta* **1996**, *A52*, 667.

(15) Trautner, F.; Cutín, E. H.; Della Védova, C. O.; Mews, R.; Oberhammer, H. *Inorg. Chem.* **2000**, *39*, 4833.

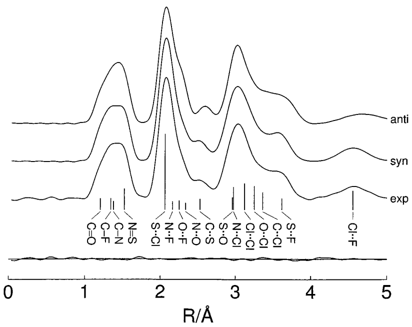

**Figure 4.** Calculated RDF's for anti and syn conformers, experimental RDF, and difference curve. Interatomic distances for the prevailing syn–syn conformer are shown by vertical bars.

**Table 3.** Experimental and Calculated Geometric Parameters for the Syn–Syn Conformer of $FC(O)N{=}SCl_2$[a]

| | GED | B3LYP/6-31G* | HF/6-31G* | MP2/6-31G* |
|---|---|---|---|---|
| N=S | 1.519(5) | 1.536 | 1.524 | 1.519 |
| S–Cl | 2.064(3) | 2.154 | 2.047 | 2.087 |
| C–N | 1.372(20) | 1.396 | 1.374 | 1.396 |
| C=O | 1.203(6) | 1.194 | 1.175 | 1.188 |
| C–F | 1.348(16) | 1.335 | 1.304 | 1.326 |
| C–N=S | 122.8(17) | 126.8 | 123.3 | 123.9 |
| N–C=O | 129.4(17) | 128.4 | 128.7 | 128.7 |
| N–C–F | 105.9(10) | 108.3 | 109.3 | 108.2 |
| N=S–Cl | 110.9(10) | 110.9 | 110.7 | 110.6 |
| Cl–S–Cl | 98.0(7) | 98.1 | 98.5 | 96.2 |
| % syn–anti | 5(1)[b] | 10 | <1 | 7 |
| $\Delta G°$ (kcal/mol) | 1.75(15)[b] | 1.28 | 3.24 | 1.56 |

[a] Values in Å and deg; uncertainties are $3\sigma$ values. [b] Value from IR (gas) spectrum.

with a syn–syn structure. The preliminary geometric parameters, which were derived from the RDF, were refined by least-squares fitting of the molecular intensities. The structure was constrained to $C_s$ symmetry in this refinement. Vibrational amplitudes, which caused high correlations for geometric parameters or which were poorly determined in the GED experiment, were set to the calculated values. Ten geometric parameters and five vibrational amplitudes were refined simultaneously, and the following correlation coefficients had values larger than $|0.6|$: N–C/C–F = –0.79; N–C/CNS = –0.66; N–C/NCO = –0.62; C–F/NCO = 0.72; CNS/NCF = –0.78; ClSCl/*l*1 = –0.67. The fit of the molecular intensities improved only slightly if small amounts of syn–anti conformer were added. The geometric parameters of this minor form were tied to those of the prevailing conformer, using the calculated (MP2) differences. All vibrational amplitudes were set to calculated values. The quality of the fit was judged by the agreement factor for the intensities of the long nozzle-to-plate distance (R50). Least-squares analyses with different but fixed contributions resulted in a minimum of R50 for 6(8)% syn–anti conformer. R50 decreased only from 4.98% to 4.95% when 6% syn–anti conformer is added. The error limit was obtained by the Hamilton test at 1% significance level.[16] The final results are listed together with calculated values in Table 2 (geometric parameters) and Table 3 (vibrational amplitudes), and a structural model of the main conformer is shown in Figure 5.

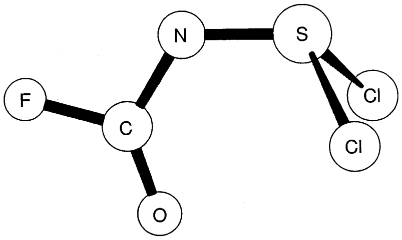

**Figure 5.** Molecular model of the syn–syn conformer of $FC(O)N{=}SCl_2$.

**Table 4.** Interatomic Distances and Experimental and Calculated Vibrational Amplitudes for $FC(O)N{=}SCl_2$[a]

| | | amplitudes | | |
|---|---|---|---|---|
| | dist | exptl (GED) | l | calcd (B3LYP) |
| C=O | 1.20 | 0.036[b] | | 0.036 |
| C–F | 1.35 | 0.044[b] | | 0.044 |
| C–N | 1.37 | 0.047[b] | | 0.047 |
| N=S | 1.52 | 0.040[b] | | 0.040 |
| S–Cl | 2.06 | 0.068(3) | *l*1 | 0.062 |
| N···F | 2.17 | 0.057[b] | | 0.57 |
| O···F | 2.26 | 0.051[b] | | 0.051 |
| N···O | 2.33 | 0.053[b] | | 0.053 |
| S···C | 2.54 | 0.061[b] | | 0.061 |
| N···Cl | 2.97 | 0.089[b] | | 0.089 |
| S···O | 2.98 | 0.108(14) | *l*2 | 0.100 |
| Cl···Cl | 3.11 | 0.108(14) | *l*2 | 0.105 |
| O···Cl | 3.27 | 0.348(66) | *l*3 | 0.254 |
| C···Cl | 3.38 | 0.160[b] | | 0.160 |
| S···F | 3.63 | 0.098(14) | *l*4 | 0.055 |
| F···Cl | 4.58 | 0.201(28) | *l*5 | 0.190 |

[a] Values in Å; uncertainties are $3\sigma$ values. [b] Not refined.

## Discussion

The prevailing conformer of $FC(O)N{=}SCl_2$ possesses a syn–syn structure in the gas and liquid phases. The vibrational spectra demonstrate a 5(1)% presence of a second form, which possesses a syn–anti structure according to quantum chemical calculations. The GED intensities are not sensitive enough to determine definitely such a small contribution of a second conformer. Due to a low barrier to internal rotation around the N–C bond, which is calculated to be 4.85 kcal/mol (MP2/6-31G*), only a single signal is observed in the $^{19}F$ NMR spectrum.[9]

The conformational properties of this compound can be rationalized on the basis of orbital interactions between the sulfur and nitrogen lone pairs and opposite $\sigma^*$ orbitals (anomeric effects). The sterically unfavorable syn orientation around the N=S bond is stabilized by $lp(N) \rightarrow \sigma^*(S{-}Cl)$ and $lp(S) \rightarrow \sigma^*(N{-}C)$ interactions for which a natural bond orbital (NBO) analysis of the B3LYP wave function results in a stabilization energy of 36.0 kcal/mol. Orbital interactions between the nitrogen lone pair and the C–F and C=O $\sigma^*$ orbitals favor the syn orientation of the N=S and C=O double bonds by 1.6 kcal/mol relative to the anti orientation. This difference in interaction energies is very close to the difference in total energies between syn–syn and syn–anti forms (1.49 kcal/mol from B3LYP).

The N=S bond in $FC(O)N{=}SCl_2$ (1.519(5) Å; Table 4) is 0.04 Å longer than that in the analogous difluoride (1.479(4) Å),[5] and within experimental uncertainties it

---

(16) Hamilton, W. *Acta Crystallogr.* **1965**, *18*, 502.

is equal to that in $CF_3N{=}SCl_2$ (1.513(6) Å).[8] Substitution of fluorine by chlorine in these imidosulfurous compounds leads to a slight decrease of the C−N═S angle (122.8(17)° vs 126.1(11)°), and the N═S−Cl angles (110.9(10)°) are equal to the N═S−F angles (110.4(8)°). The Cl−S−Cl angle (98.0(7)°) is slightly larger than the F−S−F angle (93.4(3)°). If we take into account that the vibrationally averaged experimental $r_a$ bond lengths are systematically longer than equilibrium ($r_e$) distances by a few thousands of an angstrom, all three quantum chemical methods reproduce the bond lengths to within ±0.03 Å, except for the S−Cl bond (2.064(3) Å) which is predicted too long by almost 0.1 Å by the hybrid method (2.154 Å). Bond angles are reproduced to within ±3°, except for the C−N═S angle which is calculated too large by 4° with the hybrid method.

**Acknowledgment.** R.M.S.A. and E.H.C. thank the Universidad Nacional de Tucumán and CONICET, República Argentina, and DAAD for financial support. C.O.D.V. also thanks the CONICET, ANPCYT (PICT 122) (Argentina), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), and the Universidad Nacional de La Plata, La Plata, Republic of Argentina, for financial support. Furthermore, we thank Prof. R. Mews, University of Bremen, Bremen, Germany, for providing facilities for preparation of the compound.

IC030058P