

Gas phase structure of ((fluoroformyl)imido)sulfonyl difluoride, FC(O)N=S(O)F_2

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Abstract

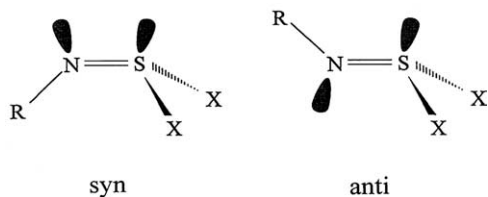
The geometric structure and conformational properties of gaseous ((fluoroformyl)imido) sulfonyl difluoride, FC(O)N=S(O)F_2 , was investigated by gas electron diffraction (GED) and quantum chemical methods (MP2 and B3LYP with 6-31G(d) and 6-311 + G(2df) basis sets). In combination with earlier reported infrared spectra, the GED study results in a mixture of at least three conformers, 71(10)% *syn(N=S)–syn(N–C)*, 14(8)% *anti(N=S)–syn(N–C)* and 15(5)% *syn(N=S)–anti(N–C)*. *Syn(N=S)* or *anti(N=S)* implies *synperiplanar* or *anticlinal* orientation of the FC(O) group with respect to the SF_2 bisector and *syn(N–C)* or *anti(N–C)* implies *synperiplanar* or *antiperiplanar* orientation of the C=O bond with respect to the N=S bond. The *anti(N=S)–anti(N–C)* conformer has not been observed, but a small amount (<5%) cannot be excluded. These conformational properties are well reproduced by quantum chemical calculations with small basis sets and the geometric parameters are reproduced satisfactorily with large basis sets.

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1. Introduction

All imidosulfur difluorides of the type RN=SF_2 with R=Cl [1], CF_3 [2,3], SF_5 [4], CN [5], FC(O) [6], $\text{CF}_3\text{C(O)}$ [7] and FSO_2 [8], whose structures have been determined in the gas phase, possess *syn(N=S)* configuration with the substituent R *synperiplanar* with respect to the bisector of the SF_2 group (see Chart 1).



Similarly, the two imidosulfonyl difluorides of the type RN=S(O)F_2 with R=CN [9] and FSO_2 [8], whose gas phase structures are known, possess structures with R *synperiplanar*

with respect to the bisector of the SF_2 group. In analogy to the imidosulfur compounds we call this configuration also *syn(N=S)*, although it implies *trans* orientation of the S=O bond relative to the substituent R. Also in carbonylbisimidosulfonyl difluoride, $\text{O=C(N=S(O)F}_2)_2$ [10], both C–N bonds are oriented *syn* with respect to the bisector of the SF_2 group. In the present study, we report the gas phase structure of ((fluoroformyl)imido) sulfonyl difluoride, FC(O)N=S(O)F_2 , which is of interest in comparison with the analogous imidosulfur difluoride FC(O)N=SF_2 [6]. Four different conformations are feasible for this sulfonyl difluoride (see Chart 2), depending on the orientation of the substituents around the N=S bond (*syn(N=S)* or *anti(N=S)*) and around the N–C bond (*syn(N–C)* or *anti(N–C)*). *Syn* implies *synperiplanar* or *synclinal* and *anti* implies *antiperiplanar* or *anticlinal*. The crystal structure, a vibrational analysis and quantum chemical calculation of FC(O)N=S(O)F_2 have been reported recently [11]. According to these calculations all four conformers correspond to stable structures with the *syn–syn* form being lowest in energy (in Ref. [11] this conformer is called *antiperiplanar–synperiplanar*). For the three other conformers relative free energies ΔG^0 between 0.67 and 2.98 kcal/mol were reported [11]. In the solid state only a single conformer was observed with the FC(O) group *syn* with respect to the SF_2

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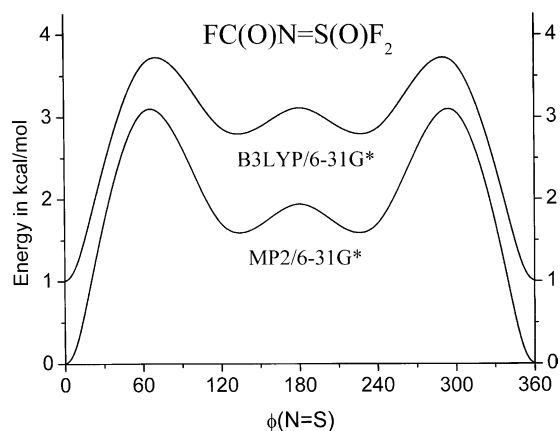
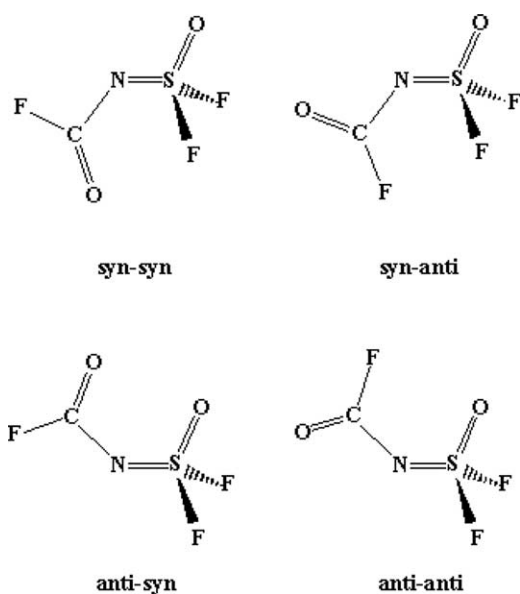


Fig. 1. Calculated potential functions for rotation around the N=S bond. The B3LYP curve is shifted by 1 kcal/mol.

bisector and with the C=O bond *syn* relative to the N=S bond (*syn-syn* conformer). Two bands in the C=O stretching region of the IR(gas) spectrum with an intensity ratio of 85(5):15(5) were interpreted in terms of a mixture of *syn*(N=C) and *anti*(N=C) conformers. An assignment to *syn*(N=S) and *anti*(N=S) forms, however, was not possible. It is hoped that additional information about the conformational properties of this compound is provided by gas electron diffraction (GED).



2. Quantum chemical calculations

The potential curve for internal rotation around N=S bond derived by structure optimizations at fixed torsional angles using MP2 and B3LYP methods with 6-31G(d) basis sets (Fig. 1). This curve was calculated for *syn* orientation of the C=O bond. Besides the global minimum for the *syn*(N=S) configuration ($\phi(\text{N}=\text{S})=0^\circ$) a second minimum exists for *anticlinal* orientation of the FC(O) group relative to the SF₂ bisector ($\phi(\text{N}=\text{S})=130.4$ and 129.5° from MP2 and B3LYP methods, respectively). A similar potential curve is derived also for *anti* orientation of the C=O bond. The predicted relative free energies and C=O vibrations for the four possible conformers (see Chart 2) are summarized in Table 1. The *syn*(N=S)–*syn*(N=C) as well as the *syn*(N=S)–*anti*(N=C) conformer possesses C_s symmetry and the *anti*(N=S)–*syn*(N=C) and *anti*(N=S)–*anti*(N=C) forms C₁ symmetry. The calculations predict a shift of $\nu(\text{C}=\text{O})$ of about 50 cm⁻¹ upon rotation around the N–C bond from *syn*(N=C) to *anti*(N=C). On the other hand, a very small shift of 1–5 cm⁻¹ is predicted upon rotation around the N=S bond from *syn*(N=S) to *anti*(N=S). Thus, vibrational spectra can discriminate very well between conformers with *syn*- or *anti*-orientation around the N–C bond, but not between conformers with *syn*- or *anti*-orientation around the N=S bond.

Since calculations with small basis sets (6-31G(d)) predict S–F, N=S and S=O bonds too long by up to 0.08 Å, the geometries of the relevant conformers were optimized with the MP2 approximation and 6-311+G(2df) basis sets. Vibrational amplitudes were derived from calculated force fields using the method of Sipachev [12]. All quantum chemical calculations were performed with the GAUSSIAN03 program system [13].

3. Experimental

FC(O)NS(O)F₂ was synthesized by reaction between Si(NCO)₄ and SOF₄ in the presence of BF₃ [14]. The compound was purified by repeated vacuum distillation. Since decomposition occurs at room temperature, the sample was stored and transported in liquid nitrogen.

Electron diffraction intensities were recorded with a KD-G2 Diffraktograph [15] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample was cooled to –26 °C and the inlet system and nozzle were at room temperature. The photographic plates (Kodak Electron Image Plates, 18×13 cm) were analyzed with an Agfa Duoscan HiD scanner and total scattering intensity curves

Table 1
Calculated relative free energies (ΔG^0) in kcal/mol, relative contributions and $\nu(\text{C}=\text{O})$ stretching frequencies of the four stable conformers

$\phi(\text{N}=\text{S})-\phi(\text{N}-\text{C})$	MP2/6-31G(d)			B3LYP/6-31G(d)		
	ΔG^0	%	$\nu(\text{C}=\text{O}), \text{cm}^{-1}$	ΔG^0	%	$\nu(\text{C}=\text{O}), \text{cm}^{-1}$
<i>syn-syn</i>	0.00	63	1887	0.00	68	1885
<i>syn-anti</i>	1.14	10	1934	0.97	13	1938
<i>anti-syn</i>	0.64	22	1882	0.96	14	1883
<i>anti-anti</i>	1.50	5	1937	1.56	5	1939

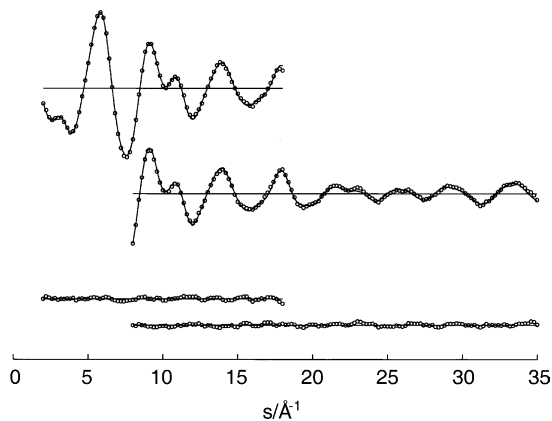


Fig. 2. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

were obtained from the TIFF-file using the program SCAN3 [16]. Averaged experimental molecular intensities in the ranges $s = 2$ – 18 and 8 – 35 \AA^{-1} in steps of $\Delta s = 0.2 \text{ \AA}^{-1}$ ($s = (4\pi/\lambda)\sin \theta/2$, where λ is the electron wavelength and θ is the scattering angle) are shown in Fig. 2.

4. Electron diffraction analysis

The experimental radial distribution function (RDF) which was derived by Fourier transformation of the molecular intensities and is shown in Fig. 3 together with calculated curves for the *syn-syn* and *anti-syn* conformers. The calculated curve for the *syn-anti* conformer is very similar to that for the *syn-syn* form and is not shown. The calculated RDF for the *syn-syn* form agrees quite well with the experimental curve, demonstrating that it is the prevailing conformer in this mixture. The structure of this conformer was refined by least squares fitting of the experimental intensities. In this analysis C_s overall symmetry was assumed. The C–F bond distance is poorly determined in this analysis due to high correlations with other parameters. It was therefore constrained to a value typical for FC(O) groups. Vibrational amplitudes were collected in

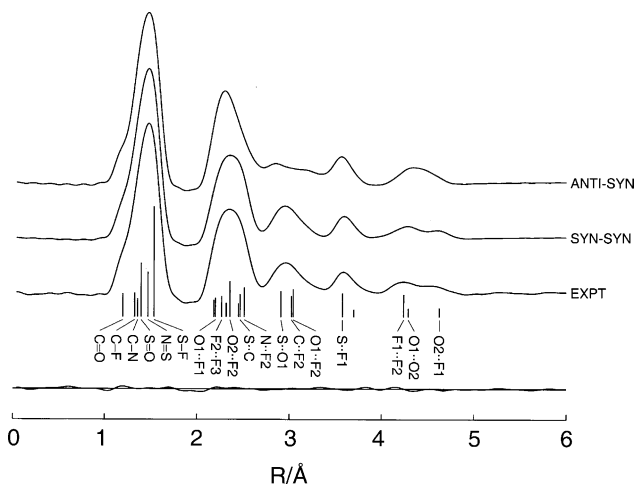


Fig. 3. Experimental and calculated radial distribution functions and difference curve. Interatomic distances for the main *syn-syn* conformer are indicated by vertical bars.

Table 2

Experimental and calculated geometric parameters for the *syn-syn* conformer and conformational composition derived by GED and quantum chemical calculations

	GED ^a	x-ray ^b	MP2/ 6-311+G(2df)	B3LYP/ 6-311+G(2df)
N=S	1.469(10)	1.492(5)	1.499	1.501
S=O	1.395(5)	1.378(6)	1.409	1.411
S–F	1.534(3)	1.518(12)	1.548	1.563
N–C	1.358(14)	1.378(6)	1.391	1.389
C=O	1.197(6)	1.172(5)	1.191	1.186
C–F	1.325 ^c	1.332(5)	1.328	1.335
C–N=S	121.5(17)	121.0(1)	120.0	122.6
N=S=O	117.5(17)	118.0(8)	118.8	118.7
N=S–F	113.6(8)	111.3(5)	111.1	111.4
F–S–F	95.3(19)	95.3(4)	94.9	95.1
N–C=O	129.7(18)	131.0(3)	129.8	130.0
N–C–F	109.0(17)	107.5(3)	107.7	107.8
% <i>syn-anti</i>	8(12)	0.0	10	13
% <i>anti-syn</i>	14(8)	0.0	22	14

^a r_{hi} values in \AA and $^\circ$. Error limits in parentheses refer to the last digit and are 3σ values.

^b Mean values of three molecules in the unit cell.

^c Not refined.

groups and amplitudes, which are badly determined in the GED experiment or which cause large correlations between geometric parameters, were set to calculated values. With these assumptions eleven geometric parameters and seven vibrational amplitudes (11–17) were refined simultaneously. The following correlation coefficients had absolute values larger than 0.7: $N=S/S=O = -0.72$, $N=S/S-F = -0.74$, $S=O/N-C = -0.76$, $N=S/l1 = 0.87$ and $F-S-F/l4 = 0.86$.

In the next step least squares refinements for mixtures with different amounts of the *syn-anti* conformer added to the *syn-syn* form were performed. The geometric parameters of this conformer were tied to those of the prevailing *syn-syn* form using the calculated differences. Vibrational amplitudes of the minor conformer were not refined. The agreement factor decreased very slightly for 8(12)% contribution of this conformer. The error limit was derived by the Hamilton method for a significance level of 0.05 [17]. Thus, the GED experiment is not sensitive towards the presence of the *syn-anti* conformer. Similar least squares analyses were performed for mixtures of *syn-syn* and *anti-syn* conformers. The lowest agreement factor was obtained for 14(8)% contribution of this form. The final results of the least squares analyses are listed in Table 2 (geometric parameters) and Table 3 (vibrational amplitudes). Molecular models of the two conformers observed in the GED experiment, *syn-syn* and *anti-syn*, are shown in Fig. 4.

5. Discussion

The combination of experimental data from IR(gas) spectra and GED results in a mixture of at least three conformers of FC(O)N=S(O)F_2 . The IR(gas) spectra are sensitive towards the orientation around the N–C bond. Two bands in the C=O stretching region demonstrate the presence of two groups of conformers, 85(5)% with *syn(N–C)* orientation (*syn-syn* and

Table 3
Interatomic distances, experimental and calculated vibrational amplitudes for *syn-syn* conformer

	Distance	Ampl. (exp) ^a		Ampl. (calc) ^b
C=O	1.20	0.037		0.037
C–F	1.33	0.045 ^c		0.045
N–C	1.36	0.047 ^c		0.047
S=O	1.40	0.034 ^c		0.034
N=S	1.47	0.040 ^c		0.040
S–F	1.53	0.045(4)	11	0.043
N⋯F1	2.18	0.060(12)	12	0.056
O⋯F1	2.20	0.051 ^c		0.051
F2⋯F3	2.27	0.063(19)	13	0.068
N⋯O1	2.32	0.053 ^c		0.053
O2⋯F2	2.36	0.059(23)	14	0.063
N⋯O2	2.45	0.060(12)	12	0.056
S⋯C	2.47	0.059(23)	14	0.062
N⋯F2	2.51	0.063(19)	13	0.069
S⋯O1	2.91	0.092(16)	15	0.104
C⋯F2	3.03	0.135 ^c		0.135
O1⋯F2	3.03	0.227(53)	16	0.231
S⋯F1	3.58	0.060(12)	12	0.056
C⋯O2	3.70	0.059(23)	14	0.064
F1⋯F2	4.24	0.229(61)	17	0.151
O1⋯O2	4.29	0.092(16)	15	0.102
F1⋯O2	4.63	0.078 ^c		0.078

^a Values in Å, error limits are 3σ values. For atom numbering see Fig. 4.

^b MP2/6-31G(d) method.

^c Not refined.

anti-syn conformers) and 15(5)% with *anti*(N–C) orientation (*syn-anti* and *anti-anti*). The GED method, however, is more sensitive towards the orientation around the N=S bond. This method results in a contribution of 14(8)% *anti-syn* conformer among the 85(5)% of the *syn*(N–C) group. Thus, the combined data result in a mixture of 71(10)% *syn-syn*, 14(8)% *anti-syn* conformers and the remaining 15(5)% consist of *syn-anti* and *anti-anti* conformers. The *anti-anti* conformer was not observed, but quantum chemical calculations predict its contribution to be small ($\approx 5\%$, see Table 1). This conformational mixture is reproduced by both quantum chemical methods within the experimental uncertainties.

The existence of a stable conformer with *anti* orientation around the N=S bond (*anti-syn* form) is surprising. Such a structure has not been observed in imidosulfonyl difluorides $\text{NCN}=\text{S}(\text{O})\text{F}_2$ [9], $\text{FO}_2\text{SN}=\text{S}(\text{O})\text{F}_2$ [8], and $\text{O}=\text{C}(\text{N}=\text{S}(\text{O})\text{F}_2)_2$ [10], which were studied previously. Similarly, all imidosulfur difluorides of the type $\text{RN}=\text{SF}_2$, mentioned in the Introduction, possess *syn* structures around the N=S bond. The only exception among imidosulfur compounds that were observed so far exists for $\text{FC}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$ [18] and $\text{CF}_3\text{C}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$ [19]. In both compounds the *anti*(N=S) conformation is preferred. These results together with that for $\text{FC}(\text{O})\text{N}=\text{S}(\text{O})\text{F}_2$ suggest, that substituents $\text{FC}(\text{O})$ or $\text{CF}_3\text{C}(\text{O})$ at nitrogen lead to stabilization of the *anti* structure.

Table 2 compares experimental geometric parameters for the title compound in the gaseous and solid state and calculated values. When comparing results of GED and X-ray diffraction, systematic differences between the two methods have to be

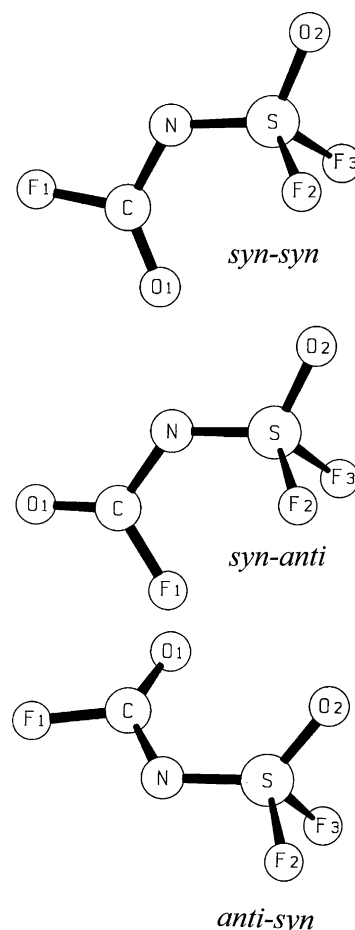


Fig. 4. Molecular models for *syn-syn*, *syn-anti* and *anti-syn* conformers with atom numbering.

taken into account. Whereas vibrationally averaged distances are derived for gaseous molecules, distances between vibrationally averaged atomic positions are obtained for the crystal. In the gaseous state only molecular vibrations affect the experimental distances. In the crystal, however, low frequency

Table 4

Comparison of N=S, S=O and S–F bond lengths (Å) in some S(VI) and S(IV) compounds (imidosulfonyl difluorides and imidosulfur difluorides)

	N=S	S=O ^a	S–F
S ^{VI}			
$\text{FC}(\text{O})\text{N}=\text{S}(\text{O})\text{F}_2$ ^b	1.466 (9)	1.395 (5)	1.535 (3)
$\text{FSO}_2\text{N}=\text{S}(\text{O})\text{F}_2$ ^c	1.475 (5)	1.392 (5)	1.529 (3)
$\text{NCN}=\text{S}(\text{O})\text{F}_2$ ^d	1.498 (12)	1.424 (5)	1.543 (6)
$\text{O}=\text{C}(\text{N}=\text{S}(\text{O})\text{F}_2)_2$ ^c	1.466 (5)	1.413 (4)	1.540 (2)
S ^{IV}			
$\text{FC}(\text{O})\text{N}=\text{SF}_2$ ^f	1.479 (4)	-	1.586 (2)
$\text{FSO}_2\text{N}=\text{SF}_2$ ^c	1.487 (5)	-	1.575 (3)
$\text{NCN}=\text{SF}_2$ ^g	1.484 (3)	-	1.593 (2)

^a In S(O)F₂ group.

^b This work.

^c Ref. [8].

^d Ref. [9].

^e Ref. [10].

^f Ref. [6].

^g Ref. [5].

lattice vibrations in addition to the molecular vibrations affect the atomic positions. A further systematic difference is due to the different methods, electron diffraction or X-ray diffraction. Whereas GED measures to a good approximation distances between nuclei, X-ray diffraction measures distances between maxima of electron densities, which may be shifted relative to the position of the nuclei. These two systematic differences may amount to up to 0.03 Å. Considering these systematic differences and the large errors of the GED study (3σ values), the structures of gaseous and solid FC(O)N=S(O)F_2 are equal. The experimental structures are reproduced reasonably well with the MP2 approximation and large basis set.

Table 4 compares N=S, S=O, and S–F bond lengths of four imidosulfuryl difluorides. The mean N=S bond length of 1.48 Å is very similar to the mean N=S bond length in the analogous imidosulfur difluorides (1.48 Å). Thus, increase of the oxidation number from S(IV) to S(VI) has no marked effect on this bond length. On the other hand, the S–F single bond shortens considerably from 1.58 to 1.54 Å upon increase of the sulphur oxidation number.

Acknowledgements

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