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Vibrational Spectra and Gas-Phase Structure of *N*-Methyl-S,S-bis(trifluoromethyl)sulfimide, $CH_3N{=}S(CF_3)_2$

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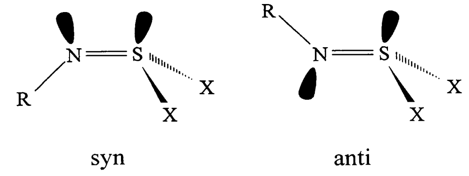
The molecular structure of *N*-methyl-S,S-bis(trifluoromethyl)sulfimide, $CH_3N{=}S(CF_3)_2$, was determined by gas electron diffraction and quantum chemical calculations [B3LYP and MP2 with 6-31+G(2df,p) basis sets]. Furthermore, vibrational spectra, IR (gas) and Raman (liquid), were recorded. These spectra were assigned by comparison with analogous molecules and with calculated frequencies and intensities (HF, B3LYP, and MP2 with 6-311G* basis sets). All experimental data and computational methods result in a single conformer with syn orientation of the CH_3 group relative to the bisector of the two CF_3 groups. The molecule possesses C_1 symmetry, slightly distorted from C_S symmetry. The N═S bond length in this compound [1.522(10) Å] is longer than that in imidosulfur difluorides $RN{=}SF_2$ [1.476(4) Å – 1.487(5) Å].

Introduction

For imidosulfur difluorides of the type $RN{=}SF_2$ with R = Cl,[1] CF_3,[2,3] SF_5,[4] CN,[5] FC(O),[6] $CF_3C(O)$,[7] and FSO_2,[8] whose gas-phase structures have been determined, only the syn configuration around the S═N double bond was observed (see Chart 1). This sterically unfavorable configuration is stabilized by orbital interactions of the sulfur and nitrogen lone pairs with the opposite N−R and S−F antibonding σ^* orbitals, respectively. Quantum chemical calculations for compounds with R = CF_3 and $CF_3C(O)$ predict the anti configuration to be higher in energy by more than 4 kcal/mol.[3,7] On the other hand, the imidosulfurous compounds $FC(O)N{=}S(F)CF_3$[9] and $CF_3C(O)N{=}S(F)CF_3$,[10] in which one fluorine atom bonded to sulfur is replaced by a CF_3 group, prefer the anti configuration, with only small contributions of the syn form. These results, derived with gas electron diffraction (GED) and vibrational spectroscopy, were reproduced correctly by quantum chemical calculations. In this context, the configuration of imidosulfurous compounds of the type $RN{=}S(CF_3)_2$ with two CF_3 groups bonded to sulfur are of great interest. It could be expected that two CF_3 groups bonded to sulfur stabilize the anti configuration even more. In the present study, we report the gas-phase structure of $CH_3N{=}S(CF_3)_2$, on the basis of GED data, vibrational

Chart 1



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spectroscopy, and quantum chemical calculations. The first synthesis of this compound by the reaction of bis(trifluoromethyl)sulfur difluoride with methylamine was reported by Morse and Shreeve.[11] Preliminary vibrational spectra and NMR data did not provide any indication about the conformation of this imidosulfurous compound. The syn configuration was assumed in analogy with the structure of $ClN{=}SF_2$, whose structure was known at that time.[1]

Quantum Chemical Calculations

The geometries of the syn and anti forms of $CH_3N{=}S(CF_3)_2$ were optimized with MP2 approximation and with the DFT method B3LYP, using 6-31G* basis functions. Both methods predict the two conformers to correspond to stable structures with the syn form lower in energy by $\Delta E = 5.19$ kcal/mol (B3LYP) and 5.34 kcal/mol (MP2). A slightly lower energy difference (3.40 kcal/mol) is obtained with the HF/6-311G* approximation and a slightly higher value (6.43 kcal/mol) with the B3LYP/6-311G* method. Thus, only the syn conformer is expected to be observed in the experiments. Additional geometry optimizations for the syn structure were performed with larger basis sets [6-31+G(2df,p)]. These geometric parameters are listed together with the experimental values (see below). All calculations predict C_1 overall symmetry for this molecule. Both CF_3 groups are rotated around the S−C bonds in the same direction by torsional angles with the same sign and slightly different values. Calculations starting with C_S symmetry (rotation of the two CF_3 groups in opposite directions and torsional angles with different signs) converged toward structures with C_1 symmetry. Vibrational frequencies were calculated with the HF and B3LYP methods using 6-311G* basis sets and at the MP2 level with 6-31+G(2df,p) basis sets. Vibrational amplitudes and corrections $\Delta r = r_a - r_{h1}$ for interatomic distances have been derived from a calculated force field (B3LYP/6-311G*) using the method of Sipachev.[12] This method takes better account of large amplitude motions than the conventional concept of perpendicular vibrations. All quantum chemical calculations were performed with the Gaussian03 program set.[13]

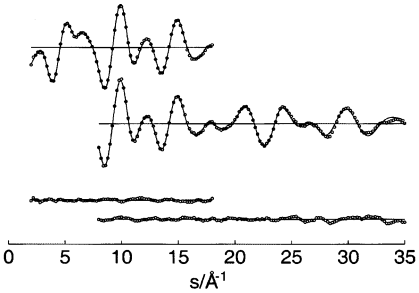

Figure 1. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

Experimental Section

$CH_3N{=}S(CF_3)_2$ was synthesized by the reaction between $(CF_3)_2SF_2$ and CH_3NH_2.[11] The product was purified at reduced pressure by several trap-to-trap distillations. $CH_3N{=}S(CF_3)_2$ reacted with moisture and had to be handled in a vacuum line and dry bag.

The gas IR spectrum at 5 Torr was recorded between 4000 and 400 cm^{-1} (resolution 2 cm^{-1}) with an FT IR Perkin-Elmer Paragon 500 spectrometer, using a gas cell equipped with KBr windows. Raman spectra of the liquid between 4000 and 50 cm^{-1} were obtained using a Jobin Yvon V1000 spectrometer equipped with an argon ion laser (Spectra Physics model 165), and radiation of 514.5 nm (Ar^+) was used for excitation. The liquid samples were handled in glass capillaries at room temperature.

Electron diffraction intensities were recorded with a KD-G2 Diffraktograph[14] 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 were obtained from the TIFF file using the program SCAN3.[15] Averaged experimental molecular intensities in the ranges $s = 2-18$ and $8-35$ Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} [$s = (4\pi/\lambda)\sin\theta/2$, where λ is the electron wavelength and θ is the scattering angle] are shown in Figure 1.

Vibrational Spectra

The vibrational analysis for $CH_3N{=}S(CF_3)_2$ was based on the evaluation of characteristic wavenumbers and on calculated vibrational frequencies and intensities, with a subsequent normal coordinate analysis. The observed features in the IR (gas phase) and Raman (liquid phase) spectra are consistent with the existence of a single conformer. A structure with C_1 symmetry, as derived by theoretical calculations and by the electron diffraction study (see below), was used in the analysis of the vibrational spectra.

Table 1 lists the experimental and calculated wavenumbers, as well as a tentative assignment for $CH_3N{=}S(CF_3)_2$. The HF values (scaled with 0.9) and the unscaled B3LYP and MP2 values agree reasonably well with the experimentally observed wavenumbers. However, many vibrations appear to be strongly coupled, making their identification difficult. Reported vibrational data of molecules such as CF_3NSCl_2,[16] CF_3NSF_2,[17] $FC(O)NSF_2$,[18] $FC(O)NSCl_2$,[19] $FC(O)NSFCF_3$,[20]

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Table 1. Experimental and Calculated Wavenumbers (cm^{-1}) for $CH_3N{=}S(CF_3)_2$ and Tentative Assignments of Fundamental Modes

mode	assignments[a]	IR[b,c]	Raman[c,d]	HF 6-311G*[e]	B3LYP 6-311G*	MP2 6-31+G (2df,p)
ν_1	CH_3 asym. stretch.	2994 w	2987 w	2957	3121	3202
ν_2	CH_3 asym. stretch.	2937 m	2934 m	2903	3064	3163
ν_3	CH_3 sym. stretch.	2890 m	2884 w	2854	3009	3076
ν_4	CH_3 asym. def. (rocking)	1473 w	1468 vw	1482	1520	1522
ν_5	CH_3 asym. def.	1458 m	1459 vw	1468	1507	1506
ν_6	CH_3 sym. def.	1420 m	1421 vw	1445	1475	1464
ν_7	CF_3 asym. stretch. i. ph.	1228 vs		1274	1224	1265
ν_8	CF_3 asym. stretch. i. ph.	1228 vs		1252	1208	1247
ν_9	CF_3 asym. stretch. o. o. ph.	1221 vs		1223	1206	1230
ν_{10}	CF_3 asym. stretch. o. o. ph.	1221 vs		1216	1173	1199
ν_{11}	N=S stretch.	1208 vs	1213 m	1211	1165	1187
ν_{12}	CF_3 sym. stretch. i. ph.	1168 s	1162 vw	1149	1158	1162
ν_{13}	CH_3 asym. def.		1150 vw	1137	1126	1153
ν_{14}	CF_3 sym. stretch. o. o. ph.	1133 s	1129 w	1129	1121	1128
ν_{15}	CH_3 asym. def.	1090 vs	1079 w	1112	1070	1115
ν_{16}	C−N stretch.	812 s	809 s	788	814	846
ν_{17}	CF_3 sym. def. i. ph.	738 m	740 vs	751	732	746
ν_{18}	CF_3 sym. def. o. o. ph.			749	727	743
ν_{19}	CF_3 def.	581 m	584 w	581	575	591
ν_{20}	CF_3 def.	554 w	555 w	559	546	558
ν_{21}	CF_3 def.	530 vw		548	539	551
ν_{22}	CF_3 def.	512 w		530	523	530
ν_{23}	C−S−C sym. stretch.	486 m	481 w	482	482	488
ν_{24}	C−S−C asym. stretch.		445 w	471	438	459
ν_{25}	CF_3 def.		382 s	404	377	390
ν_{26}	CF_3 def.		273 s	289	276	285
ν_{27}	CF_3 def.			287	265	283
ν_{28}	C−N−S def. o. o. p.		262 s	273	252	261
ν_{29}	CF_3 def.		243 w	254	238	247
ν_{30}	C−N−S def.		211 w	235	209	216
ν_{31}	torsion		167 m	168	160	172
ν_{32}	CH_3 torsion		137 sh	141	143	149
ν_{33}	CH_3NS torsion		111 m	131	125	134
ν_{34}	CF_3 torsion			90	98	95
ν_{35}	CF_3 torsion		62 m	63	54	63
ν_{36}	skeletal torsion		51 m	34	40	58

[a] stretch. = stretching; def. = deformation; i. ph. = in-phase; o. o. ph. = out-of-phase; o. o. p. = out-of-plane. [b] Gas phase. [c] Relative intensities: vw = very weak; w = weak; m = medium; s = strong; vs = very strong; sh = shoulder. [d] Liquid phase. [e] Scaled by the factor 0.9.

and $CF_3C(O)NSFCF_3$,[10] together with preliminary calculations for CH_3NSF_2, CH_3NSFCF_3, CF_3NSFCF_3, and $CF_3NS(CF_3)_2$, were considered in order to evaluate the general dependency of certain fundamental modes on the substituents at the nitrogen and sulfur atoms.

The features observed at the highest wavenumbers in the vibrational spectra (2994, 2937, and 2890 cm^{-1} in the IR) are immediately associated with two asymmetric modes and one symmetric stretching mode of the CH_3 group. Similarly, the region between 1400 and 1480 cm^{-1} shows characteristic signals belonging to the CH_3 deformation modes. Thus, the weak IR bands centered at 1473 cm^{-1} (1468 cm^{-1} in Raman), 1458 cm^{-1} (1459 cm^{-1}, Raman), and 1420 cm^{-1} (1421 cm^{-1}, Raman) are assigned to the CH_3 rocking and to asymmetric and symmetric CH_3 deformation modes. An additional band observed in the gas-phase IR spectrum at 2815 cm^{-1}, and in the Raman at 2811 cm^{-1}, is assigned to the overtone of the symmetric CH_3 deformation mode (ν_6) in Fermi resonance with the symmetric CH_3 stretching (ν_3). The CH_3 features are in very good agreement with the calculated values and with the reported behavior for $(CH_3)_2NC(O)SCH_3$[21] and $FC(O)OCH_3$.[22]

All related molecules of the type RN=SXY [R = CF_3, FC(O), $CF_3C(O)$; X, Y = F, Cl, CF_3] show the N=S stretching as a very strong IR band and as a medium-intensity band in the Raman spectra. The position of this fundamental is strongly influenced by the electronegativity of the groups attached to the N and S atoms. The N=S stretching mode for $CH_3NS(CF_3)_2$ is calculated at 1211, 1165, and 1187 cm^{-1} [HF/6-311G*, B3LYP/6-311G*, and MP2/6-31+G (2df,p), respectively], and it is assigned to the medium-intensity band centered at 1213 cm^{-1} in the Raman spectrum. The strongest band in the IR spectrum shows a complex structure with three maxima at 1228, 1221, and 1208 cm^{-1}. The last feature is considered to be the IR counterpart of the N=S stretching mode. This assignment confirms the inverse relationship between the wavenumbers of the N=S stretching mode and the corresponding bond lengths: $CF_3C(O)NSFCF_3$ [988

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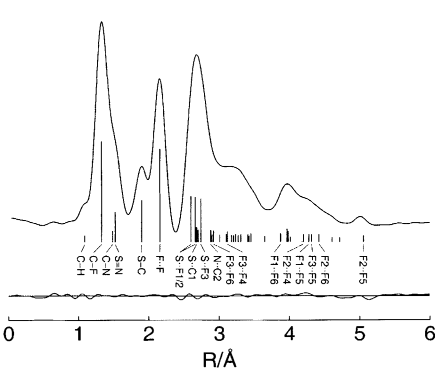

Figure 2. Experimental radial distribution function and difference curve. Important interatomic distances are indicated by vertical bars.

cm^{-1}, 1.554(8) Å]; $FC(O)NSFCF_3$[9,20] [1105 cm^{-1}, 1.549(5) Å]; $CH_3NS(CF_3)_2$ [1208 cm^{-1}, 1.522(10) Å]; $FC(O)NSCl_2$[19] [1245 cm^{-1}, 1.519(5) Å]; CF_3NSCl_2[16] [1314 cm^{-1}, 1.513(6) Å]; $FC(O)NSF_2$[18] [1330 cm^{-1}, 1.479(4) Å]; CF_3NSF_2[3,17] [1384 cm^{-1}, 1.477(6) Å].

The remaining two maxima of the strongest IR band (1228, 1221 cm^{-1}) are assigned to the four asymmetric CF_3 stretching vibrations expected for the two CF_3 groups of the title molecule, two of which overlap. The two corresponding CF_3 symmetric modes are also observed as very strong bands centered at 1168 and 1133 cm^{-1} in the IR spectrum (1162 and 1129 cm^{-1} in Raman). All calculations for $CH_3N{=}S(CF_3)_2$ predict these stretching fundamentals, as well as the deformation modes, to be coupled in-phase and out-of-phase vibrations involving both CF_3 groups. The C−N stretching mode is assigned to the medium-intensity IR and the strong and sharp Raman bands centered at 812 and 809 cm^{-1}, respectively. This is in good agreement with the values observed for this mode in CF_3NSCl_2[16] (803 cm^{-1}) and CF_3NSF_2[17] (794 cm^{-1}) and is in accordance with the calculated values for the title compound.

In $CF_3C(O)NSFCF_3$,[10] the IR and Raman spectra show bands of medium intensity centered at 472 cm^{-1}, which are assigned to the S−C stretching mode. Two S−C vibrations are expected for $CH_3N{=}S(CF_3)_2$ defined as symmetric and asymmetric stretching. They are assigned to the Raman bands at 481 cm^{-1} (486 cm^{-1} in the IR) and at 445 cm^{-1} (no counterpart is observed in IR), respectively, in agreement with the theoretically predicted wavenumbers. Preliminary calculations (HF/6-31+G*) for CH_3NSFCF_3, CF_3NSFCF_3, and $CF_3NS(CF_3)_2$ predict the S−C stretching modes at 434, 468, and 477 cm^{-1} (asymmetric) and 438 cm^{-1} (symmetric), respectively. The CF_3 deformation modes are assigned in agreement with the observed and calculated behavior for $CF_3C(O)NSFCF_3$.[10] The remaining deformation and torsional modes are assigned according to the theoretical predictions.

Structure Analysis

The radial distribution function (RDF) was calculated by Fourier transformation of the molecular intensities and is shown in Figure 2. The experimental RDF is reproduced satisfactorily only with a syn structure, as predicted by the quantum chemical calculations. A preliminary molecular model derived from the RDF was refined by a least-squares fitting of the molecular intensities. The following constraints, which are based on the quantum chemical results, were applied in the least-squares analyses. (1) The $CH_3N{=}SC_2$ moiety possesses C_S symmetry and the CH_3 group local C_{3v} symmetry. (2) All C−F bond lengths and F−C−F bond angles are equal. (3) C−H bond lengths and H−C−H bond angles were not refined, and the differences between the S−C−F bond angles were set to calculated (MP2) values. (4) Vibrational amplitudes were collected in groups according to the calculated values, and such amplitudes which are poorly determined in the GED experiment or which caused large correlations between geometric parameters are fixed to their calculated values. With these assumptions, 10 geometric parameters and seven vibrational amplitudes were refined simultaneously. Only two correlation coefficients had absolute values larger than 0.7: S = N/C−N = −0.78 and C−F/S−C−F = 0.79. The results of the least-squares refinement are listed together with calculated values in Table 2 (geometric parameters) and Table 3 (vibrational amplitudes). A molecular model with atom numbering is shown in Figure 3.

Table 2. Experimental and Calculated Geometric Parameters for $CH_3N{=}S(CF_3)_2$

	GED (r_{h1})[a]		MP2/6-31+G(2df,p)	B3LYP/6-31+G(2df,p)
S=N	1.522 (10)	*p1*	1.542	1.538
S−C	1.901 (5)	*p2*	1.906	1.951
C−N	1.487 (26)	*p3*	1.469	1.464
$(C{-}F)_{mean}$	1.329 (2)	*p4*	1.331	1.335
C−H	1.100[b]		1.092	1.095
C−N−S	125.0 (29)	*p5*	122.6	124.9
N−S−C	113.7 (11)	*p6*	112.7	112.9
C−S−C	94.8 (14)	*p7*	91.6	93.1
S−C−F1/4	110.4 (3)	*p8*	110.5	110.1
S−C−F2/5	105.7 (3)[c]	*p8*	105.8	105.6
S−C−F3/6	114.0 (3) [c]	*p8*	114.1	114.7
$(F{-}C{-}F)_{mean}$	108.7(3) [d]		108.7	108.7
H−C−H	108.5 [b]		108.5	108.2
τ (N−S−C1−F1)	170.1 (27)	*p9*	165.2	170.8
τ (N−S−C2−F4)	168.6 (45)	*p10*	161.7	163.7

[a] r_{h1} values in Å and deg. Error limits in parentheses refer to the last digit and are 3σ values. For atom numbering, see Figure 3. [b] Not refined. [c] Difference to previous parameter fixed to calculated (MP2) value. [d] Dependent parameter.

Discussion

The GED results as well as various quantum chemical calculations demonstrate unambiguously that $CH_3N{=}S(CF_3)_2$ possesses a syn configuration, in contrast to the expectation discussed in the introduction. The vibrational spectra confirm the presence of a single conformer at room temperature. A comparison of experimental gas-phase structures of compounds of the type $RN{=}SF_2$ indicates that the N=S bond length is not very sensitive toward the substituent R. For R = Cl,[1] CF_3,[2,3] CN,[5] FC(O),[6] $CF_3C(O)$,[7] and FSO_2,[8] the N=S bond varies only between 1.476(4) and 1.487(5) Å. It should be pointed out, however, that all of these substituents possess rather similar electronegativities. On the other hand, substitution of the fluorine atoms at sulfur by chlorine leads to considerable lengthening of the N=S bond. Values of 1.513(6) and 1.519(5) Å have been reported for CF_3NSCl_2[16] and

Table 3. Interatomic Distances, Experimental and Calculated Vibrational Amplitudes, and Vibrational Corrections in Å

	distance	amplitude (exp)[a]		amplitude (calc)[b]	$\Delta r = r_a - r_{h1}$
C−H	1.09	0.076[c]		0.076	0.005
C−F	1.33	0.047 (2)	*l1*	0.044	0.001
C−N	1.49	0.050[c]		0.050	0.002
S═N	1.52	0.042[c]		0.042	0.001
C−S	1.90	0.053 (6)	*l2*	0.061	0.002
F···F	2.16	0.056 (2)	*l3*	0.057	0.004
S···F	2.60−2.74	0.085 (5)	*l4*	0.078	0.006
F1···F4	2.69	0.225[c]		0.225	−0.011
C1···C2	2.80	0.085 (6)	*l4*	0.084	0.003
N···C	2.87	0.089[c]		0.089	0.004
F3···F6	2.89	0.140 (36)	*l5*	0.187	−0.029
C1···F4	2.91	0.140 (36)	*l5*	0.178	0.005
C2···F3	3.00	0.140 (36)	*l5*	0.159	−0.002
F3···F4	3.14	0.366[c]		0.366	0.041
N···F2	3.11	0.140 (36)	*l5*	0.158	0.004
C2···F1	3.16	0.140 (36)	*l5*	0.170	0.013
C3···F6	3.20	0.209[c]		0.209	−0.015
C1···F6	3.25	0.147[c]		0.147	0.004
N···F6	3.24	0.140 (36)	*l5*	0.161	0.004
N···F5	3.30	0.140 (36)	*l5*	0.178	0.014
C3···F3	3.40	0.255[c]		0.255	0.005
N···F3	3.40	0.140 (36)	*l5*	0.165	0.011
C1···C3	3.44	0.097 (48)	*l6*	0.135	0.005
C3···F2	3.66	0.266[c]		0.266	0.018
F6···F1	3.89	0.262[c]		0.262	0.036
C1···F5	3.98	0.102 (15)	*l7*	0.087	0.019
N···F1	3.97	0.102 (15)	*l7*	0.091	0.019
N···F4	3.97	0.102 (15)	*l7*	0.081	0.019
C2···F2	3.99	0.102 (15)	*l7*	0.096	0.019
C3···F5	3.99	0.266[c]		0.266	0.030
F4···F2	4.20	0.140 (36)	*l5*	0.167	0.028
F5···F1	4.27	0.140 (36)	*l5*	0.173	0.024
F5···F3	4.31	0.145[c]		0.145	0.020
F6···F2	4.41	0.140 (36)	*l5*	0.168	0.018
C3···F4	4.60	0.134[c]		0.134	0.021
C3···F1	4.70	0.133[c]		0.133	0.025
F5···F2	5.05	0.088[c]		0.088	0.031

[a] Values in Å; error limits are 3σ values. For atom numbering, see Figure 3. [b] B3LYP/6-311G*. [c] Not refined.

FC(O)NSCl$_2$,[19] respectively. A very similar N═S bond length [1.522(10) Å] occurs in CH$_3$N═S(CF$_3$)$_2$. This is not surprising, since the electronegativity of CF$_3$ groups is close to that of Cl. Although the CH$_3$ group is more electropositive than all substituents R discussed above, it does not appear to have a marked effect on the N═S bond length.

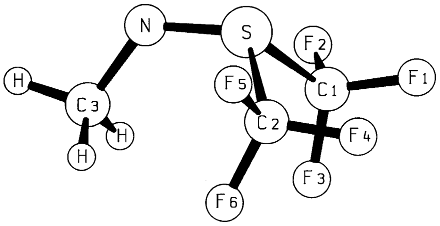

Figure 3. Molecular model and atom numbering.

The crystal structure of (CH$_3$)$_2$NS(CF$_3$)$_2$$^+AsF_6$$^-$ has been determined by X-ray diffraction.[23] The cation possesses near C_S symmetry with one methyl group oriented syn and the other one anti relative to the two CF$_3$ groups. The nitrogen sulfur bond length [1.578(5) Å] is intermediate between the N═S double bond in CH$_3$N═S(CF$_3$)$_2$ [1.522(10) Å] and N−S(IV) single bonds in (CH$_3$)$_2$NSF$_3$ [1.639(13) Å][24] or [(CH$_3$)$_2$N]$_2$SF$_2$ [1.658(2) Å].[25] All other skeletal geometric parameters of the cation are similar to those of the title compound, except for the NSC bond angle. This angle is smaller in the cation [108.0(2)°] compared to that in CH$_3$N═S(CF$_3$)$_2$ [113.7(11)°], in accordance with the N−S single bond character in the cation.

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