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Molecular and Crystal Structure of *N,N'*-Bis(trifluoromethanesulfonyl)-*N*-(trimethylstannyl)methanesulfinamidine

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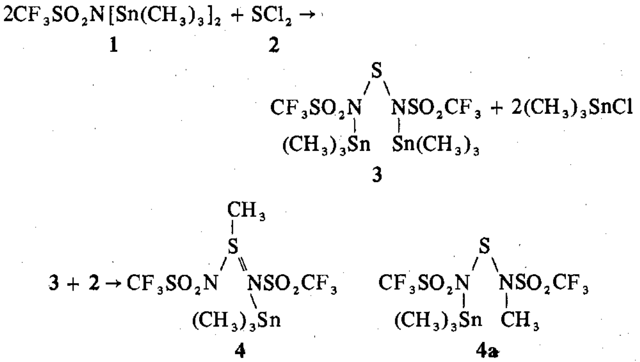
N,N'-Bis(trifluoromethanesulfonyl)-*N*-(trimethylstannyl)methanesulfinamidine ($CF_3SO_2NSn(CH_3)_3SCH_3NSO_2CF_3$) was synthesized by the reaction of *N,N*-bis(trimethylstannyl)trifluoromethanesulfonamide with sulfur dichloride. Intensities of 2286 unique reflections were measured on a four-circle computer-controlled diffractometer with Mo Kα radiation until $(\sin\theta)/\lambda = 0.70$ Å^{-1} yielding orthorhombic space group $Pn2_1a$, $a = 22.993$ (4) Å, $b = 6.764$ (1) Å, $c = 11.008$ (2) Å, and $Z = 4$. The structure was solved by Patterson and Fourier syntheses and refined by least-squares methods to a final $R_F = 0.056$ (weighted $R_{wF} = 0.033$). The absolute configuration of the polar space group has been established from an analysis of the anomalous dispersion of the tin atom. The tin atom has a distorted trigonal-bipyramidal configuration with a Sn–N contact of 2.345 (5) Å and a Sn–O contact of 2.591 (6) Å. The S–N bond lengths range between 1.553 (6) and 1.688 (5) Å.

Introduction

Sulfur dichloride is a well-known reagent to obtain sulfur diamides and sulfur diimides from organometallic compounds containing nitrogen.[2] The reaction of *N,N*-bis(trimethylstannyl)trifluoromethanesulfonamide (**1**) with sulfur dichloride (**2**) in a suspension of CH_2Cl_2 has been studied. Two different products were found according to the amount of the reagents. A sulfur diamide (**3**) is obtained[3] for two molecules of **1** and one molecule of **2**. An excess of sulfur dichloride, however, leads to the title compound (**4**). Details on the reaction procedure and spectroscopic data have been published elsewhere.[4] These data are composed of a list of IR peaks, mass spectral values, and isomer shifts from ^{19}F and ^{1}H NMR. The reaction is characterized by a methylation of the central sulfur atom which results in an imide–amide configuration of this sulfur atom. As the chemical analysis and the spectroscopic methods did not discriminate between the two possible structures **4** and **4a**, an X-ray structure determination was carried out. The different oxidation states and coordination numbers of S and N atoms in the title compound made a precise knowledge of the S–N bond distances desirable.



Crystal structure investigations of compounds with S–N bonds have given bond lengths ranging from about 1.50 Å[5] to 1.775 (2) Å for H_3NSO_3.[6] Several concepts have been developed to describe S–N bonds in a unique way. Glemser[7] gave a relation between bond length and bond order; Kálmán et al.[8] explained observed S–N distances in *N*-acylsulfilimines in terms of the hybridization state of N and the oxidation state of the sulfur atom. Truter[9] observed a relation between S–N bond lengths and valence angles around the sulfur. None of these models, however, has provided a complete picture of the observed variety of bond lengths and angles between the two atoms.

Experimental Section and Structure Refinement

Colorless needles of the title compound were obtained by recrystallization from dichloromethane. A crystal with dimensions 0.135, 0.135, 0.25, and 0.80 mm in, respectively, the 101, 10$\bar{1}$, 100, and 010 directions was selected for the experiments and sealed in a capillary, as the compound appeared very unstable in the air.

Precession photographs showed an orthorhombic unit cell. The space group extinctions corresponded to either *Pnma* or $Pn2_1a$.

The lattice constants were refined from 15 reflections with $22° < 2\theta < 37°$, carefully centered on a Syntex $P2_1$ diffractometer. They are $a = 22.993$ (4), $b = 6.764$ (1), and $c = 11.008$ (2) Å. The unit cell volume $V = 1712.2$ (5) Å^3 corresponds to four formula units per cell. The calculated density is $\rho_{calcd} = 1.92$ g cm^{-3}.

Data were collected on a Syntex $P2_1$ diffractometer with Nb-filtered Mo Kα radiation in a step-scanning mode (λ 0.71069 Å) Reflections were collected in the *hkl* and $hk\bar{l}$ octants up to $2\theta = 45°$ ($(\sin\theta)/\lambda = 0.54$ Å^{-1}) and $2\theta = 60°$ ($(\sin\theta)/\lambda = 0.70$ Å^{-1}), respectively, resulting in 4070 observations of which 2268 were unique. During the measurement the crystal rotated about an arbitrary axis, 1.5° away from the *b* axis. Background corrections were applied as calculated with the profile analysis method of Blessing et al.[10]

Three standard reflections observed after every 45 reflections showed a gradual decrease of about 4.5% in the course of the data collection, possibly due to radiation damage of the crystal. This effect was corrected for by applying a linear scale factor, depending on the reflection serial number. The decay correction factor had the form scale $= [1.0 - 0.045(Nr/4070)]^{-1}$.

The data were corrected for absorption, using a numerical integration in which the crystal volume was divided over $6 \times 6 \times 6$ Gaussian grid points.[11] The linear absorption coefficient was calculated as $\mu = 18.98$ cm^{-1}. The transmission factor ranged from 0.680 to 0.828. The equivalent reflections were weight averaged. The weight of an individual reflection was taken as $w(I) = 1/[\sigma^2(I)_{counting} + (0.02I)^2]$. The weight of an averaged intensity was taken as the sum of the weights of the individual reflections.

After averaging, 170 reflections had negative intensities and were considered as "less than" and excluded from the structure refinement. The remaining 2098 intensities were corrected for Lorentz and polarization effects and used for the structure determination and refinement.

A Wilson plot resulted in an estimate of the overall temperature and scale factor. A statistical investigation of the normalized structure factors clearly indicated the space group to be noncentrosymmetric; therefore $Pn2_1a$ was considered as the correct one. This setting corresponds to the standard group symbol $Pna2_1$ (space group No. 33).

The general position in this space group is (x, y, z; $\bar{x}, {}^1/_2 + y, \bar{z}$; ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 + z$; ${}^1/_2 + x, y, {}^1/_2 - z$). The position of the tin atom was determined from a Patterson synthesis. From a Fourier synthesis based on the tin position, one possible sulfur atom was selected to define the enantiomorph. Subsequent Fourier maps resulted in the determination of the positions of the remaining two sulfur atoms and all first row atoms.

Scattering factors for all of the atoms were taken from ref 12. Anomalous scattering factors for the tin atom ($f' = -0.873$, $f'' = 1.424$) and for the sulfur atoms ($f' = 0.110, f'' = 0.124$) were taken from Cromer and Liberman.[13] In the final cycles of refinement anisotropic thermal parameters were assigned to all atoms. Extinction effects were found to be negligible. Refinement was repeated until

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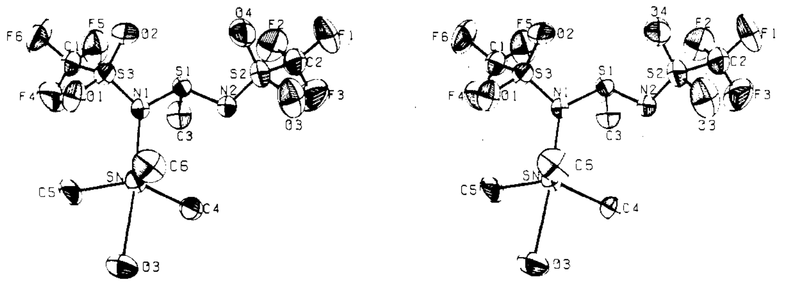

Figure 1. Stereoscopic view and numbering scheme of the structure. The thermal ellipsoids are the 50% probability surfaces.

Table I. Positional Parameters

	x	*y*	*z*
Sn	0.20617 (2)	0.0	0.22965 (3)
S(1)	0.0850 (1)	0.1524 (3)	0.0405 (2)
S(2)	0.1408 (1)	0.3275 (3)	0.8539 (1)
S(3)	0.0985 (1)	0.3366 (3)	0.2618 (2)
O(1)	0.1397 (2)	0.3517 (9)	0.3584 (4)
O(2)	0.4198 (2)	0.0014 (11)	0.6956 (4)
O(3)	0.1996 (2)	0.3338 (11)	0.8087 (5)
O(4)	0.3875 (3)	0.0014 (11)	0.3932 (4)
N(1)	0.1188 (2)	0.1567 (9)	0.1765 (4)
N(2)	0.1370 (2)	0.1468 (10)	0.9405 (4)
C(1)	0.0328 (4)	0.2463 (16)	0.3354 (8)
C(2)	0.0999 (4)	0.2512 (15)	0.7206 (7)
C(3)	0.4395 (4)	0.3990 (13)	0.5348 (8)
C(4)	0.2170 (4)	0.7984 (12)	0.0815 (6)
C(5)	0.3263 (3)	0.3843 (13)	0.8965 (6)
C(6)	0.2574 (3)	0.2601 (13)	0.2157 (7)
F(1)	0.1030 (3)	0.3957 (10)	0.6379 (4)
F(2)	0.0459 (2)	0.2237 (12)	0.7493 (4)
F(3)	0.1210 (3)	0.0877 (9)	0.6738 (5)
F(4)	0.0417 (2)	0.0855 (10)	0.3951 (5)
F(5)	0.4912 (2)	0.2160 (11)	0.2472 (4)
F(6)	0.0135 (2)	0.3814 (11)	0.4112 (5)

no parameter shifts larger than 0.1σ occurred. The final values of the reliability factors are

$$R_F = \sum\{|F_o| - |F_c|\}/\sum|F_o| = 0.056$$

$$R_{wF} = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2} = 0.033$$

$$S = \{w[|F_o| - |F_c|]^2/(\mathrm{no} - \mathrm{nv})\}^{1/2} = 2.58$$

A difference Fourier synthesis following the final cycle of refinement did not show any peaks higher than 0.3 e Å^{-3}. No hydrogen atoms could be located possibly due to the large thermal motion of the methyl groups.

As pointed out by Ibers and Hamilton,[14] the absolute configuration of the present compound may be determined from the anomalous scattering effect even though no Bijvoet pairs of reflections (*hkl* and *h$\bar{k}$l*) have been measured. Consequently the refinement was repeated with the direction of the *b* axis reversed. The resulting values of the reliability factors then were $R_F = 0.057$, $R_{wF} = 0.034$, and $S = 2.66$. Application of Hamilton's *R* ratio test[15] gives $R = R_{wF_2}/R_{wF_1} = 1.032$. Comparison with the theoretical value for acceptance of the second configuration with a 99.5% probability ($R_{1,1900,0.005} = 1.002$) indicates the configuration presented in this study to be the correct one. The effect of a wrong choice of the polarity of the structure was found to be a shift of 0.02–0.04 Å in the *y* values of the atoms with respect to the tin atom. The larger variation in Sn–C bond lengths (2.092 (9)–2.163 (8) Å for reversal of the *b* axis vs. 2.124 (9)–2.140 (8) Å for the enantiomorph presented in this work) supports the present choice of the polarity. The effect of the anomalous dispersion on the bond lengths between the light atoms was found to be negligible. The positional and anisotropic thermal parameters of the atoms are reported in Tables I and II.

Discussion

A stereoscopic view of the molecular structure and the thermal ellipsoids is shown in Figure 1 together with the numbering scheme. Bond lengths and angles are reported in Tables III and IV. The structure can be classified as an iminosulfinylamide, i.e., the coordination numbers of the nitrogen atoms N(1) and N(2) are respectively 3 and 2. The bond lengths in the sulfur–nitrogen chain are not consistent with the located double bond of formula **4**. The four S–N bonds have all lengths between the values of 1.508 (5) Å corresponding to a double bond and 1.775 (2) Å which is the single-bond length.[6] The longest bonds involve N(1) which is bonded to Sn.

Table II. Anisotropic Thermal Parameters[a]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	0.0594 (3)	0.0500 (2)	0.0381 (2)	0.0039 (4)	−0.0023 (2)	0.0031 (5)
S(1)	0.046 (1)	0.054 (1)	0.038 (1)	0.004 (1)	0.000 (1)	0.006 (1)
S(2)	0.066 (1)	0.061 (1)	0.039 (1)	−0.014 (1)	0.004 (1)	0.005 (1)
S(3)	0.076 (1)	0.048 (1)	0.048 (1)	0.010 (1)	0.008 (1)	−0.002 (1)
O(1)	0.093 (4)	0.080 (4)	0.052 (3)	0.000 (3)	−0.006 (3)	−0.022 (3)
O(2)	0.131 (4)	0.052 (3)	0.068 (3)	−0.034 (5)	−0.017 (3)	0.012 (4)
O(3)	0.066 (3)	0.142 (6)	0.079 (4)	−0.042 (4)	0.009 (3)	0.024 (4)
O(4)	0.140 (4)	0.051 (3)	0.063 (3)	−0.006 (5)	−0.009 (3)	0.002 (5)
N(1)	0.052 (3)	0.050 (3)	0.031 (2)	0.010 (3)	−0.002 (2)	−0.002 (3)
N(2)	0.054 (3)	0.061 (4)	0.041 (3)	0.011 (3)	0.010 (2)	0.008 (3)
C(1)	0.076 (6)	0.099 (7)	0.050 (5)	0.024 (5)	0.026 (4)	0.012 (5)
C(2)	0.086 (7)	0.094 (7)	0.044 (4)	0.012 (5)	−0.005 (4)	−0.005 (5)
C(3)	0.072 (5)	0.063 (5)	0.067 (5)	0.030 (4)	0.001 (5)	−0.005 (4)
C(4)	0.101 (6)	0.071 (6)	0.046 (4)	0.036 (5)	−0.008 (4)	−0.011 (4)
C(5)	0.081 (5)	0.077 (5)	0.047 (4)	−0.004 (5)	−0.005 (4)	0.032 (4)
C(6)	0.062 (5)	0.082 (6)	0.089 (6)	−0.020 (5)	0.000 (4)	0.015 (5)
F(1)	0.185 (6)	0.160 (6)	0.047 (3)	0.022 (5)	−0.011 (3)	0.035 (3)
F(2)	0.056 (3)	0.157 (6)	0.097 (4)	−0.003 (3)	−0.014 (3)	−0.021 (4)
F(3)	0.132 (4)	0.140 (6)	0.079 (3)	0.029 (4)	−0.012 (3)	−0.055 (4)
F(4)	0.101 (4)	0.133 (6)	0.103 (4)	0.013 (3)	0.038 (3)	0.061 (4)
F(5)	0.060 (3)	0.183 (7)	0.076 (4)	−0.003 (4)	−0.008 (2)	−0.002 (4)
F(6)	0.123 (4)	0.194 (7)	0.076 (3)	0.058 (5)	0.036 (3)	−0.032 (4)

[a] The temperature factor is defined as: $\exp[-2\pi^2(h^2a^{*2}U_{11} + 2hka^*b^*U_{12} + \ldots)]$.

Table III. Bond Lengths (Å)

S(1)–N(1)	1.688 (5)	C(1)–F(4)	1.288 (12)
S(1)–N(2)	1.625 (5)	C(1)–F(5)	1.335 (10)
S(2)–N(2)	1.553 (6)	C(1)–F(6)	1.314 (11)
S(3)–N(1)	1.607 (6)	C(2)–F(1)	1.337 (11)
S(1)–C(3)	1.805 (9)	C(2)–F(2)	1.297 (11)
S(2)–C(2)	1.818 (9)	C(2)–F(3)	1.312 (11)
S(3)–C(1)	1.821 (9)	Sn–C(4)	2.140 (8)
S(2)–O(3)	1.441 (5)	Sn–C(5)	2.132 (7)
S(2)–O(4)	1.413 (7)	Sn–C(6)	2.124 (9)
S(3)–O(1)	1.428 (5)	Sn–N(1)	2.345 (5)
S(3)–O(2)	1.397 (7)	Sn–O(3′)	2.591 (6)

Table IV. Bond Angles (deg)

N(1)–S(1)–C(3)	101.0 (3)	S(3)–C(1)–F(6)	109.2 (7)
N(2)–S(1)–C(3)	100.6 (4)	F(4)–C(1)–F(5)	109.4 (8)
N(1)–S(1)–N(2)	105.2 (2)	F(4)–C(1)–F(6)	108.5 (7)
N(2)–S(2)–C(2)	104.0 (4)	F(5)–C(1)–F(6)	107.3 (7)
N(2)–S(2)–O(3)	106.8 (4)	S(2)–C(2)–F(1)	108.3 (6)
N(2)–S(2)–O(4)	116.2 (3)	S(2)–C(2)–F(2)	109.9 (5)
C(2)–S(2)–O(3)	102.4 (4)	S(2)–C(2)–F(3)	111.5 (6)
C(2)–S(2)–O(4)	104.1 (4)	F(1)–C(2)–F(2)	108.7 (8)
O(3)–S(2)–O(4)	120.9 (4)	F(1)–C(2)–F(3)	109.2 (7)
N(1)–S(3)–C(1)	104.3 (4)	F(2)–C(2)–F(3)	109.2 (8)
N(1)–S(3)–O(1)	107.3 (3)	N(1)–Sn–C(4)	101.4 (2)
N(1)–S(3)–O(2)	112.8 (3)	N(1)–Sn–C(5)	94.7 (2)
C(1)–S(3)–O(1)	104.1 (3)	N(1)–Sn–C(6)	94.8 (3)
C(1)–S(3)–O(2)	104.5 (4)	N(1)–Sn–O(3′)	174.8 (2)
O(1)–S(3)–O(2)	122.1 (4)	O(3′)–Sn–C(4)	83.2 (3)
S(1)–N(1)–S(3)	113.4 (3)	O(3′)–Sn–C(5)	81.0 (2)
S(1)–N(1)–Sn	127.5 (3)	O(3′)–Sn–C(6)	85.4 (3)
S(3)–N(1)–Sn	116.5 (3)	C(4)–Sn–C(5)	117.6 (3)
S(1)–N(2)–S(2)	116.1 (4)	C(4)–Sn–C(6)	114.1 (3)
S(3)–C(1)–F(4)	112.2 (6)	C(5)–Sn–C(6)	124.1 (3)
S(3)–C(1)–F(5)	110.0 (6)		

S(3)–N(1) is 9σ longer than S(2)–N(2), and S(1)–N(1) is about 12σ longer than S(1)–N(2). The formation of the Sn–N bond reduced the ability of atom N(1) to form π bonds reflected in the longer S–N bonds involving N(1).

The shortest S–N bond is the one between S(2) and N(2) involving a four-coordinated sulfur and a two-coordinated nitrogen. The bond shortening for S–N bonds of these coordination numbers was observed for many compounds (Table VI in ref 16). This observation is in agreement with the remark reported by Kālmān et al.[8] that bonds to S(VI) are shorter than bonds to S(IV) for sulfimines. The angle N(1)–S(1)–N(2) is 105.2 (2)° similar to values found in five-membered heterocyclic rings of S and N.[17] We can, however, find no relation between bond lengths and bond angles in this particular compound.

The various sources of influence on the length of a S–N bond are the formal hybridization and oxidation states, the valence angles around the sulfur, and the coordination numbers, though we are at present unable to understand the factors at work for an individual bond.

The trimethylstannyl group forms a bond between two ligand molecules thus leading to a three-dimensional network in the crystal. The tin atom has a distorted trigonal-bipyramidal configuration and is bonded to a nitrogen atom N(1) and an oxygen atom O(3), while the three methyl groups are found in the equatorial plane. The Sn–N(1) bond length of 2.345 (5) Å is comparable to bonds found in similar structures;[18] the Sn–O(3) bond of 2.591 (6) Å is relatively long, possibly as a result of the electronegative character of the sulfate oxygen atom. However, the Sn–O distances in similar compounds have been found to be very sensitive to the environment of the oxygen atom in the crystal, and distances of 2.14–2.68 Å have been reported.[18-22] The trimethylstannyl group shows a slight deviation from planarity, the average N(1)–Sn–C angle being 96.9° vs. 83.2° for the average O(3′)–Sn–C angle.

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Supplementary Material Available: A listing of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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