

THE STRUCTURE OF $TAS + CF_3C(O)NS(CF_3)NS(CF_3)NC(O)CF_3^-$; A SALT WITH A BIS(SULFINYL)AMIDE ANION

Lork, E.; Müller, M.; Mews, R

Institute of Inorganic and Physical Chemistry

University of Bremen, PO Box 330440

D-28334 Bremen, Germany

Fax: +49-421-218 4267; e-mail: mews@chemie.uni-bremen.de

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Dedicated to Professor Dr. Pedro J. Aymonino on the occasion of his 75th birthday.

Abstract

The title compound $TAS + CF_3C(O)NS(CF_3)NS(CF_3)NC(O)CF_3^-$ (**3**) was isolated as a minor product from the reaction of TAS -fluoride with $CF_3C(O)NS(CF_3)F$. The X-ray structure of **3** is reported and the bonding situation in the anion is discussed.

Resumen

Como producto secundario de la reacción entre TAS -fluoruro con $CF_3C(O)NS(CF_3)F$ se pudo aislar el compuesto $TAS + CF_3C(O)NS(CF_3)NS(CF_3)NC(O)CF_3^-$ (**3**) cuya estructura de rayos X se reporta aquí. Se discuten las características de enlace del anión.

Introduction

Acyl-sulfur(IV)imides $RN=SR'R''$ ($R = ClC(O), FC(O), CF_3C(O)$; $R' = R'' = Cl, F, CF_3$, $R' \neq R'' = F, Cl, CF_3$) are an extraordinary interesting class of compounds, not only because of spectroscopic reasons but also from a synthetic point of view. Investigations of the structures and conformations of $FC(O)NSF_2$ [1], $CF_3C(O)NSF_2$ [2], and $FC(O)NSCl_2$ [3] by gas phase electron diffraction, IR- and Raman-spectroscopy have been reported. In both the gas and in the liquid phase dominantly a *syn-syn* conformation (the acyl group *syn*-periplanar with respect to the SF_2 bisector and the oxygen directed towards the sulfur) is observed. If one of the sulfur bonded fluorines is exchanged by a CF_3 -group, as e.g. in $FC(O)N=S(CF_3)F$ [4] and $CF_3C(O)NS(CF_3)F$ [5] unexpectedly the *anti-syn* conformer (acyl group in an *anti*-position) is dominant. Besides these structural differences due to the F/CF_3 exchange also remarkable differences in the reactivity result from this exchange. While the C-N-bond in sulfur difluoride imides $RC(O)NSF_2$ ($R = F, CF_3$) is readily cleaved by fluoride ions to give salts with the sulfur difluoride imide anion (e.g. $Cs^+NSF_2^-$ [6,7] $Hg(NSF_2)_2$ [6-8] $TAS^+NSF_2^-$ [9]), with $RC(O)NS(CF_3)F$ no formation of the corresponding $NS(CF_3)F^-$ -salts is observed. Stable salts with the $RC(O)NS(CF_3)F_2^-$ anion were isolated [9].

Experimental, X-Ray Crystallography

The starting materials TASF [10] and $\text{CF}_3\text{C}(\text{O})\text{NS}(\text{CF}_3)\text{F}$ [11] were prepared according to the literature, both compounds were reacted as described in our earlier paper [9]. Onto the frozen CH_3CN solution of **3** an equal volume of diethyl ether was condensed at -196°C on a vacuum line. The reaction vessel was warmed to -30°C and kept at this temperature for several days.

By slow diffusion of the ether into the CH_3CN solution single crystals of **3** were formed. From the cold solution they were transferred to cooled KEL-F oil, single crystals were selected at the same temperature under a microscope in an atmosphere of dry nitrogen. The single crystals were mounted on a thin glass fibre.

The single-crystal X-ray structure determination (Table 1) was carried out on a Siemens P4 diffractometer using $\text{Mo}(\text{K}\alpha)$ radiation (0.71073 \AA) with a graphite monochromator. Refinement based on F^2 ; $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = \{\sum [w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)^2]]\}^{1/2}$. Programs used: SHELX-97 [12] and DIAMOND [13]

The structures were solved by direct methods (SHELXS [12]). Subsequent least-squares refinements (SHELXL-97-2 [12]) located the positions of the remaining atoms in the electron density maps. All non-H atoms were refined anisotropically.

CCDC-232900 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

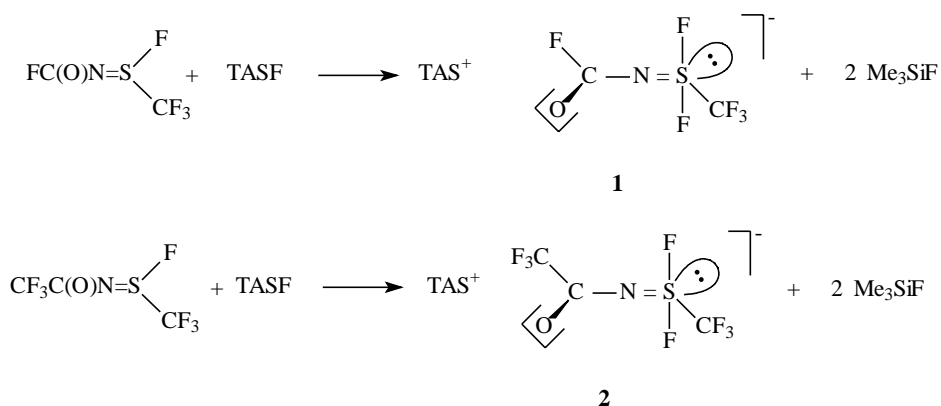
Table 1. Crystal data and structure refinement for $\text{TAS}^+\text{CF}_3\text{C}(\text{O})\text{NS}(\text{CF}_3)\text{NS}(\text{CF}_3)\text{C}(\text{O})\text{CF}_3^-$ (**3**).

Empirical Formula	$\text{C}_{12}\text{H}_{18}\text{F}_{12}\text{N}_6\text{O}_2\text{S}_3$
M	602.50
T/K	173(2)
Wave length/ pm	71.073
Crystal system	triclinic
Space group	P-1
a/pm	932.0(2)
b/pm	1095.5(2)
c/pm	1199.5(2)
$\alpha/^\circ$	92.560(10)
$\beta/^\circ$	100.600(10)
$\gamma/^\circ$	93.840(10)
U/nm^3	1.1991(4)
Z	2
$D_c/\text{Mg m}^{-3}$	1.669
$\mu (\text{MoK}\alpha) \text{ mm}^{-1}$	0.425
F(000)	608
Crystal size / mm^3	0.8 x 0.7 x 0.6

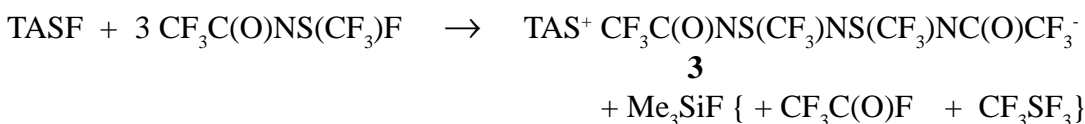
θ range/ $^{\circ}$	2.55 to 27.50
Indexrange	$-12 \leq h \leq 12, -14 \leq k \leq 14, -15 \leq l \leq 15$
Reflections collected	11078
Independent Reflections	5489 [R(int) = 0.0248]
Completeness to $\theta = 27.50^{\circ}$	99.9%
Refinement	Full-matrix least-squares on F^2
Data/Restraints/Parameter	5489/0/324
Goodness-of-fit on F^2	1.021
R1, wR_2 [$I > 2\sigma(I)$]	0.0358, 0.0933
R1, wR_2 (all Data)	0.0438, 0.0982
Extinction coefficient	0.0173(15)
Largest difference peak, hole/ $e \cdot \text{\AA}^{-3}$	0.369 / $-0.327 e \cdot \text{\AA}^{-3}$

Results And Discussion

Recently we reported the reactions of $\text{FC(O)NS}(\text{CF}_3)\text{F}$ with TAS-fluoride ($(\text{Me}_2\text{N})_3\text{S}^+\text{Me}_3\text{SiF}_2^-$ (Tris(dimethylamino)sulfonium difluorotrimethylsilicate) [9]:



1 was characterized by NMR spectroscopy and X-ray crystallography, **2** was also isolated in almost quantitative yield and unequivocally characterised by ^{19}F -NMR spectroscopy. Compound **2** seemed to be stable in solution, cleavage of the CN-bond was not observed. Therefore it was rather surprising that from our present attempt to crystallize **2** from CH_3CN /diethylether at -30°C . single crystals of **3** were isolated. The formation of **3** is rationalised by the equation.



The bridging nitrogen between the two acylsulfurimide moieties probably results from the decomposition of the primarily formed anion of salt **2**. CN bond cleavage might be the next step, followed by attack of the resulting nucleophile at $\text{CF}_3\text{C(O)NS}(\text{CF}_3)\text{F}$. In a further step SC-bond cleavage should have occurred. Until now these speculations could not be confirmed by spectroscopic investigations.

X-ray structure of $\text{TAS}^+\text{CF}_3\text{C(O)NS(CF}_3\text{)NS(CF}_3\text{)C(O)CF}_3^-$ (**3**)

3 crystallizes in the triclinic space group P-1 with 2 molecules in the asymmetric unit. The structure of the anion of **3** is presented in Figure 1, details of the structure determination of **3** are given in Table 1, Table 2 lists selected bond lengths and bond angles.

The unique anion of **3** is an imino derivative of a hitherto unknown class of compounds, of the bis(sulfinyl)amides $(\text{RS(O)})_2\text{N}^-$. The corresponding bis(sulfonyl)amides $(\text{RS(O)}_2)_2\text{N}^-$ with various counterions ($\text{R}=\text{F}$, perfluoroalkyl) have been previously reported and are presently investigated in many laboratories for their application as electrolytes in batteries and fuel cells [14]. A mixed fluorosulfinyl – fluorosulfonyl-amide, $\text{TAS}^+\text{FS(O)}_2\text{NS(O)F}^-$ was prepared in our laboratory from $\text{FS(O)}_2\text{NSO}$ and TASF [15]. In a similar way bis(sulfinyl)amides should be available from N-sulfinyl sulfinamides, e. g. $\text{CF}_3\text{S(O)NSO}$ [16], and TASF .

According to the bond distances determined the amide is best described as superposition of the two resonance structures **B** and **B'**, by **C**, because all SN distances are almost of equal length (163.2 (2)–164.0(2) pm). Compared to $\text{CF}_3\text{-C(=O)-N=S(CF}_3\text{)F}$ ($\text{SN} = 155.4(8)$ pm) the SN-bonds are significantly lengthened, while the CN bonds in **3** are shortened by approximately 5 pm, the CO distances are stretched by 2.5–2.9 pm. The negative charge is delocalised over 9 bonds.

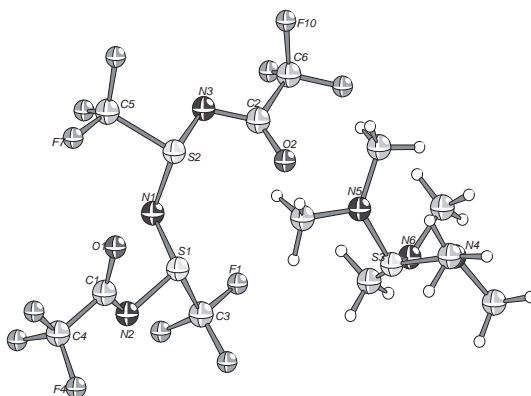
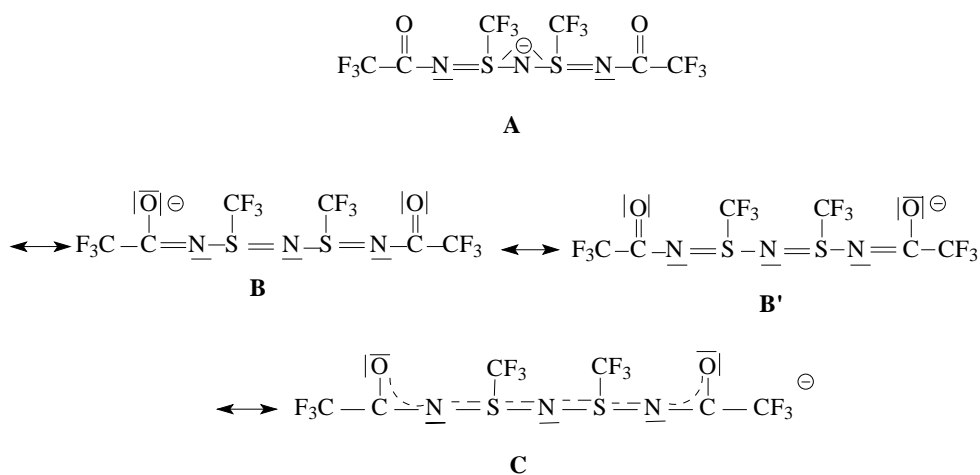


Figure 1. X-ray Structure of $\text{TAS}^+\text{CF}_3\text{C(O)NS(CF}_3\text{)NS(CF}_3\text{)NC(O)CF}_3^-$ (**3**)

Table 2 Selected bond distances and bond angles in **3**

N(1)-S(1)	163.29(15)
N(1)-S(2)	164.01(15)
S(1)-N(2)	163.64(15)
S(1)-C(3)	183.7(2)
N(2)-C(1)	134.5(2)
C(1)-O(1)	122.9(2)
C(1)-C(4)	153.2(3)
S(2)-N(3)	163.18(16)
S(2)-C(5)	183.8(2)
N(3)-C(2)	133.7(2)
C(2)-O(2)	122.6(2)
C(2)-C(6)	153.7(3)
S(3)-N(5)	160.42(16)
S(3)-N(6)	161.70(16)
S(3)-N(4)	168.37(15)
S(1)-N(1)-S(2)	108.05(9)
N(1)-S(1)-N(2)	109.58(8)
N(1)-S(1)-C(3)	98.29(9)
N(2)-S(1)-C(3)	94.68(8)
C(1)-N(2)-S(1)	107.82(13)
O(1)-C(1)-N(2)	128.58(19)
O(1)-C(1)-C(4)	119.44(17)
N(2)-C(1)-C(4)	111.97(16)
N(3)-S(2)-N(1)	110.38(9)
N(3)-S(2)-C(5)	94.82(8)
N(1)-S(2)-C(5)	98.04(9)
C(2)-N(3)-S(2)	109.62(13)
O(2)-C(2)-N(3)	130.00(18)
O(2)-C(2)-C(6)	118.81(17)
N(3)-C(2)-C(6)	111.19(16)
N(5)-S(3)-N(6)	115.26(9)
N(5)-S(3)-N(4)	100.64(8)
N(6)-S(3)-N(4)	98.83(8)

As mentioned in the introduction, of special interest is the conformation of the RC(O)-groups with respect to the $-\text{N}=\text{SRR}'$ -group. The structure of the anion of **3** corresponds to the structure of $\text{CF}_3\text{C}(\text{O})\text{N}=\text{S}(\text{CF}_3)\text{F}$ [5], two $\text{CF}_3\text{C}(\text{O})\text{NSCF}_3$ -units are connected by N1. As observed for $\text{CF}_3\text{C}(\text{O})\text{NS}(\text{CF}_3)\text{F}$ both $\text{CF}_3\text{C}(\text{O})$ -units adopt the *anti-syn* conformation: the CO-group is in an *anti*-position to the NSC bisector, the oxygen points towards the sulfur (Figure 2). The atoms CSNCO are coplanar (Figure 3), the distances S1O1 (268.1 pm) and S2O2 (274.5 pm) are considerably shorter than the sum of the v.d. Waals radii of sulfur and oxygen (330 pm) [17]. These distances are slightly shorter than in the neutral $\text{CF}_3\text{C}(\text{O})\text{NS}(\text{CF}_3)\text{F}$, probably due to increased electrostatic interaction between O and S in the anion. This electrostatic interaction might be the reason for the unexpected conformation in acyl-S-trifluoromethyl sulphurimides. In

both structures sulphur adopts nearly a \tilde{E} -trigonal bipyramidal coordination with the O-S-C atoms in axial positions. The angles O1-S1-C3 and O2-S2-C5 in **3** are 151.6° and 153.8°, respectively.

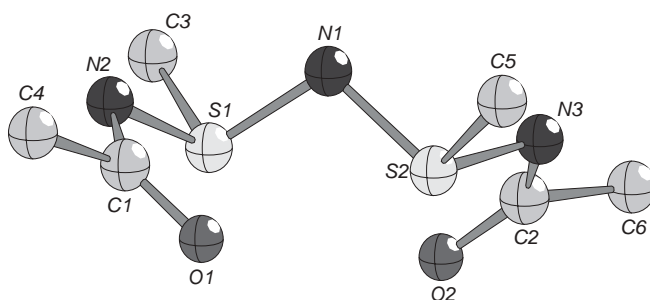


Figure 2. Conformation of the $\text{CF}_3\text{C}(\text{O})\text{NS}(\text{CF}_3)\text{NS}(\text{CF}_3)\text{NC}(\text{O})\text{CF}_3^-$ anion (for clarity the F-atoms of the CF_3 -groups are omitted)

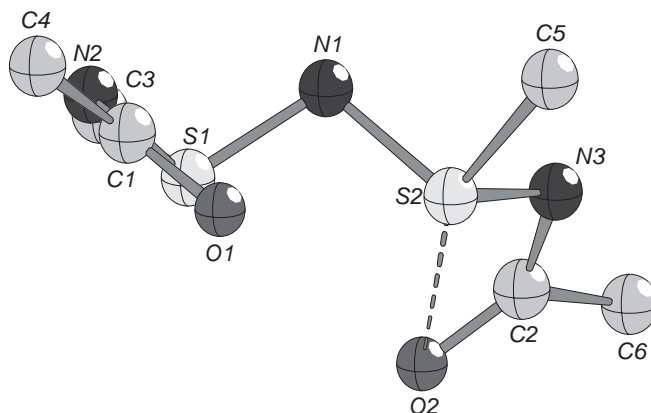


Figure 3. View showing the coplanarity of the atoms CSNCO and C and the \tilde{E} -trigonal bipyramidal environment of the sulphur atoms

Conclusions

From the reaction of TASF with $\text{CF}_3\text{C}(\text{O})\text{NS}(\text{CF}_3)\text{F}$, unexpectedly $\text{TAS}^+\text{CF}_3\text{C}(\text{O})\text{NS}(\text{CF}_3)\text{NS}$

$(\text{CF}_3)\text{NC}(\text{O})\text{CF}_3^-$ (**3**) was isolated and characterized by X-ray crystallography. The anion of **3** is the first member of a hitherto unknown class of compounds, of the bis(sulfinyl)amides $[\text{RS}(\text{NR}')_2\text{N}^-$ and $[\text{RS}(\text{O})_2\text{N}^-$, respectively. Possible direct pathways to these compounds, the reactions of $\text{RS}(\text{NR}')\text{F}$ or $\text{RS}(\text{O})\text{F}$ with $\text{LiN}(\text{SiMe}_3)_2$ or related amides or the addition of “naked” anions (nucleophiles) [18] to $\text{RS}(\text{O})\text{NSO}$ will be followed in the future.

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