## Methanesulfonamide in Superacids: Investigations of the CH<sub>3</sub>SO<sub>2</sub>NH<sub>3</sub><sup>+</sup> Cation

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Dedicated to Prof. Dr. Wolfgang Beck on the Occasion of his 85th Birthday

Abstract. The preparation of protonated methanesulfonamide was carried out using the superacidic systems HF/AsF<sub>5</sub> and HF/SbF<sub>5</sub>. The vibrational spectroscopic characterization was supported by quantum chemical calculations performed with the PBE1PBE method using the 6-311G++(3df, 3pd) basis set. A remarkable long nitrogen-sulfur bond length of 1.804(6) Å was observed in a single-crystal X-ray structure analysis of [CH<sub>3</sub>SO<sub>2</sub>NH<sub>3</sub>]<sup>+</sup>[Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup>. It crystallizes in the orthorhombic space group  $P2_1/c$  with four formula units in the unit cell. Furthermore the crystal structure of CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> was revisited.

## Introduction

Sulfonamides are of remarkable research interest due to their high biological activity.<sup>[1,2]</sup> Despite their common applications, the acid/base properties of sulfonamides are rarely described in literature. The first study was reported by LeMaire and Lucas, who estimated the  $pK_a$  value of the conjugate acid of p-toluenesulfonamide to be ca. 3.2.<sup>[3]</sup> Laughlin investigated the basicity of aliphatic sulfonamides based on the determination of the NMR chemical shifts as a function of solvent acidity. He found that the protonation of sulfonamides takes place at the nitrogen atom.<sup>[4]</sup> Bagno et al. confirmed these findings by other NMR spectroscopic investigations.<sup>[5]</sup> Additionally, it was found that the basicity of the nitrogen as a function of the hydrogen acceptor power is 2.8 kcal·mol<sup>-1</sup> higher than that of the oxygen atom. These experimental results are supported by quantum chemical calculations comparing the total energies of the O-protonated species with the N-protonated species.<sup>[6]</sup> In the course of our investigations it was interesting for us to study methanesulfonamide as one of the simplest representatives of sulfonamides in the superacidic solutions  $HF/MF_5$ (M = As; Sb) with the aim to isolate and characterize the hitherto structural unknown CH<sub>3</sub>SO<sub>2</sub>NH<sub>3</sub><sup>+</sup> cation. Furthermore we present a reinvestigation of the crystal structure of CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>, which has been reported in a previous work.<sup>[7]</sup>

## **Results and Discussion**

The preparation of salts containing the [CH<sub>3</sub>SO<sub>2</sub>NH<sub>3</sub>]<sup>+</sup> cation was carried out by the reaction of methanesulfonamide with the superacidic solutions HF/AsF<sub>5</sub> and HF/SbF<sub>5</sub>. For a

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detailed vibrational spectroscopic investigation the corresponding D-isotopomeres were prepared [Equation (1)]. An excess of SbF<sub>5</sub> does not lead to a diprotonation of methanesulfonamide but to a formation of  $Sb_2F_{11}^{-}$  salts [Equation (2)].

$$CH_{3}SO_{2}NX_{2} + MF_{5} \xrightarrow{XF} [CH_{3}SO_{2}NX_{3}]^{+}[MF_{6}]^{-}$$
(1)  
(X = H, D; M = As, Sb)  
$$CH_{3}SO_{2}NX_{2} + 2SbF_{5} \xrightarrow{XF} [CH_{3}SO_{2}NX_{3}]^{+} [Sb_{2}F_{11}]^{-}$$
(2)

(X = H, D)

The reactions were performed at -40 °C. The solvent was removed at -78 °C in dynamic vacuum overnight. The formed salts remaining as colorless crystalline precipitates are stable under dry inert gas atmosphere up to room temperature.

#### Vibrational Spectroscopy

The low temperature infrared and Raman spectra of  $[CH_3SO_2NH_3]^+[AsF_6]^-,$  $[CH_3SO_2ND_3]^+[AsF_6]^-$ , [CH<sub>3</sub>SO<sub>2</sub>NH<sub>3</sub>]<sup>+</sup>[SbF<sub>6</sub>]<sup>-</sup>, and CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> are shown in Figure 1. In Table 1 the observed frequencies of the protonated species are summarized together with the quantum chemically calculated frequencies of [CH<sub>3</sub>SO<sub>2</sub>NH<sub>3</sub>]<sup>+</sup>·3HF and [CH<sub>3</sub>SO<sub>2</sub>ND<sub>3</sub>]+·3HF.

For the  $[CH_3SO_2NH_3]^+$  cation with  $C_s$  symmetry 27 fundamental vibrations are expected. All modes are both Raman and infrared active. The  $v_{as}(NH_2)$  are detected at 3191 cm<sup>-1</sup> (a), 3197 cm<sup>-1</sup> (f), and 3196 cm<sup>-1</sup> (e) and are about 200 cm<sup>-1</sup> redshifted compared to the amino group in the neutral compound. The corresponding  $v_{as}(ND_2)$  are observed at 2394 cm<sup>-1</sup> (c) and 2399 cm<sup>-1</sup> (d), respectively, and they are in fair agreement with the Teller-Redlich rule for an H/D isotopic effect.<sup>[8]</sup> The frequencies of the CH3 group remain approximately un-

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**Figure 1.** Low temperature vibrational spectra of  $[CH_3SO_2NH_3]^+[AsF_6]^-$ : (a) IR spectrum, (f) Raman spectrum;  $[CH_3SO_2NH_3]^+[SbF_6]^-$ : (b) IR spectrum, (e) Raman spectrum;  $[CH_3SO_2ND_3]^+[AsF_6]^-$ : (c) IR spectrum, (d) Raman spectrum;  $CH_3SO_2NH_2$ : (g) Raman spectrum.

changed in all cases and are comparable to  $CH_3SO_2NH_2$ .<sup>[9]</sup> The SO<sub>2</sub> stretching vibrations occur at 1400 cm<sup>-1</sup> and 1200 cm<sup>-1</sup> and are blue-shifted by approximately 60 cm<sup>-1</sup> compared to  $CH_3SO_2NH_2$ . The v(SN) mode at around 500 cm<sup>-1</sup> is blue-shifted by approximately 270 cm<sup>-1</sup>. This is in accordance with the significant elongation of the S–N bond in the protonated species found in the crystal structure, which is discussed later. For the anions  $AsF_6^-$  and  $SbF_6^-$  with ideal octahedral symmetry more vibrations are observed than expected. This can be explained by distortion of the anions in the solid state, which leads to a lower symmetry.

## Crystal Structure of [CH<sub>3</sub>SO<sub>2</sub>NH<sub>3</sub>]<sup>+</sup>[Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup>

 $[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$  crystallizes in the monoclinic space group  $P2_1/c$  with four formula units in the unit cell. Selected geometric parameters are summarized in Table 3. In Figure 2 an asymmetric unit of  $[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$  is illustrated.

The sulfur atom shows a distorted tetrahedral coordination. Compared to the starting material the bond angles C1–S1–N1 [101.7(3)°] and N1–S1–O1 [103.5(3)°] are decreased by  $6.6^{\circ}$  and  $3.6^{\circ}$ , respectively, and the bond angles C1–S1–O1 [112.2(3)°] and O1–S1–O2 [122.0(3)°] are increased by  $4.3^{\circ}$ 

and 3.6°, respectively. The short S-N bond observed in the starting material [1.612(2) Å] can be explained by negative hyperconjugation as previously discussed for other sulphonamide derivatives.<sup>[10]</sup> Due to the N-protonation this effect seems to be revoked, resulting in a significant S-N bond elongation to 1.804(6) Å in the protonated species. The S-C bond lengths of 1.747(7) Å as well as the S-O bond lengths [1.416(5) Å / 1.422(5) Å] are slightly shorter than in CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>. Experimental bond lengths and angles of the CH<sub>3</sub>SO<sub>2</sub>NH<sub>3</sub><sup>+</sup> cation are in good agreement with the quantum chemical calculations (Table 2). The observation, that the experimental and calculated S-N and S-C bond lengths are in good accordance to the theoretical values, can be considered as another proof for the correct assignment of the nitrogen and carbon atom in the crystal structure. Furthermore, hydrogen bonds are only observed for the NH<sub>3</sub> group. The  $Sb_2F_{11}^{-}$  anion possesses a staggered conformation. The Sb1-F6-Sb2 bond angle [145.3(2)°] is comparable to the corresponding Sb-F-Sb bond angle observed in [XeCl]<sup>+</sup>[Sb<sub>2</sub>F<sub>11</sub>]<sup>-.[11]</sup> The terminal Sb-F bond lengths in the  $Sb_2F_{11}^{-}$  anion are in the range from 1.844(4) to 1.896(4) Å, whereas the bridging Sb-F bond lenghts are 2.033(4) Å and 2.049(4) Å, respectively.

In the crystal structure of  $[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$  the ions are connected via N–(H)···F hydrogen bonds, which are marked as dashed lines in Figure 3. A three-dimensional network is formed through the connection of each cation to four anions. The medium strong<sup>[12]</sup> hydrogen bonds have donoracceptor distances ranging from 2.762(7) Å to 3.098(7) Å.

#### Crystal Structure of CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>

The crystal structure of  $CH_3SO_2NH_2$  has previously been reported by *Vorontsova* in 1963.<sup>[7]</sup> The structure was determined using an RGIK camera. The reported space group *Pnma* can be confirmed by this study. However, due to an *R* value of 0.174, the previous measurement was not suitable to determine bond lengths and bond angles accurately. In Figure 4 the asymmetric unit is shown.

Selected bond lengths and bond angles are summarized in Table 2. The S–N bond length of 1.612(3) Å is comparable to the S–N bond in sulfamide [1.620(1) Å].<sup>[13]</sup> The S–C bond length of 1.756(3) Å and the S–O bond length of 1.435(2) Å are slightly shorter than dimethyl sulfone.<sup>[14]</sup> In contrast to the calculation the S–O bond was found to be slightly longer. This can be explained by the participation of the oxygen atom in hydrogen bonds. In the crystal structure of CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> each molecule is connected to four neighboring molecules by medium strong hydrogen bonds along the *b* axis with a donor-acceptor distance of 2.459(1) Å (Figure 5). This linkage leads to 14-membered rings, which are condensed to (CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>)<sub>*n*</sub> layers in the [100] plane.

#### **Theoretical Calculations**

The quantum chemical calculations were performed with the PBE1PBE method using the 6-311G++(3df,3pd) basis set. In case of the  $[CH_3SO_2NH_3]^+$  cation it was found that the ad-

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**Table 1.** Experimental vibrational frequencies <sup>a)</sup> /cm<sup>-1</sup> of  $[CH_3SO_2NH_3]^+[AsF_6]^-$ ,  $[CH_3SO_2ND_3]^+[AsF_6]^-$  and  $[CH_3SO_2NH_3]^+[SbF_6]^-$  (see Figure 1) and calculated vibrational frequencies /cm<sup>-1</sup> of  $[CH_3SO_2NH_3]^+\cdot 3HF$  and  $[CH_3SO_2ND_3]^+\cdot 3HF$ .

[CH <sub>3</sub> SO <sub>2</sub> N (a) IR	$H_3]^+[AsF_6]^-$ (f) Raman	[CH <sub>3</sub> SO <sub>2</sub> N (c) IR	$D_3]^+[AsF_6]^-$ (d) Raman	[CH <sub>3</sub> SO <sub>2</sub> N (b) IR	H <sub>3</sub> ] <sup>+</sup> [SbF <sub>6</sub> ] (e) Raman	[CH <sub>3</sub> SO <sub>2</sub> ND <sub>3</sub> ]+•3HF calcd. <sup>b)</sup> (IR / Raman)	F [CH <sub>3</sub> SO <sub>2</sub> NH <sub>3</sub> ] <sup>+</sup> ·3HF calcd. <sup>b)</sup> (IR / Raman)	Assig	nment <sup>c)</sup>	
3191 (s)	3197(3)	2394 (s)	2399(20)		3196(3)	2441 (243/31)	3411 (506/51)		Δ"	$v_{\rm c}(NX_{\rm e})$
3161(s)	3129(16)	2371(s)	2379(6)	3174(s)	5150(5)	2399 (341/37)	3364 (549/69)	V17	A'	$v_{as}(10X_2)$
5101 (3)	512)(10)	2274 (m)	2377(0)	5174 (3)		2265 (244/31)	3269 (500/148)	V1 V2	A'	$v_{oph}(NX_2)$
3063 (m)	3063(20)	3064(s)	3063(23)		3036(5)	3118 (9/37)	3198 (8/34)	V10	A"	$v_{1pn}(CH_2)$
	3035(13)	5001 (5)	3035(19)		5050(5)	3092 (15/48)	3171 (14/43)	V18 V2	A'	$v_{as}(CH_2)$
2951 (m)	2952(58)	2952 (m)	2952(77)	2951 (m)	2952(14)	2994 (15/150)	3071 (18/133)	V4	A'	Viet (CH <sub>2</sub> )
1535 (m)	1536(14)	1122 (s)	1119(7)	1534 (w)	1535(10)	1145 (14/1)	1638 (29/2)	V5	A'	$\delta(NX_2)$
		1092 (w)	1083(11)			1140 (1/1)	1633 (8/2)	V10	A"	$\delta(NX_2)$
1418 (s)	1419(4)	1417 (s)	1418(6)	1420 (w)		1421 (111/6)	1504 (193/5)	V20	A"	$v_{\rm es}(SO_2)$
		(3)				1028 (61/3)	1449 (93/0)	V 20	A'	$\delta(NX_2)$
						1393 (8/3)	1436 (23/3)	V7	A'	$\delta(CH_2)$
1387 (m)	1388(53)	1399 (s)	1390(58)	1388 (w)	1389(20)	1386 (71/7)	1433 (37/6)	V21	A"	$\delta(CH_2)$
1332 (m)	1334(4)	1335(m)	1335 (4)	1329 (w)	1330(2)	1301 (15/1)	1357 (31/1)	V <sub>8</sub>	A'	δ(CH <sub>3</sub> )
1203 (s)	1195(100)	1199 (s)	1197(100)	1200 (w)	1193(49)	1177 (107/22)	1255 (125/18)	Vo	A'	$v_{s}(SO_{2})$
1027 (w)	1025(15)		· · · ·	1026 (w)	1027(7)	785 (41/5)	1057 (16/3)	V10	A'	$\rho(NX_3)$
1008 (w)	1006(2)			1013 (w)	1014(1)	949 (2/1)	1022 (11/1)	V22	A"	$\tau(NX_3)$
954 (m)	958(5)			956 (w)		719(1/1)	963 (0/1)	V23	A"	$\tau(NX_3)$
. ,		981 (w)	993(13)			946 (24/1)	956 (60/0)	V11	A'	$\rho(CH_3)$
757 (w)	758(43)		769(5)	752 (m)	756(28)	785 (41/5)	757 (26/11)	V12	A'	v (SC)
. ,	506(39)	496 (m)	497(4)	~ /	505(22)	510 (97/4)	585 (92/9)	V13	A'	v (SN)
495 (w)	495(5)	487 (m)	487(4)			455 (20/5)	499 (18/5)	V <sub>14</sub>	A'	$\delta$ (SO <sub>2</sub> )
		445 (w)			458(24)	389 (14/7)	454 (26/4)	V <sub>15</sub>	A'	$\rho(CH_3)$
	410(4)	417 (w)				325 (2/0)	403 (2/1)	V24	A"	$\tau(NX_3)$
			316(8)			338 (2/3)	374 (4/2)	V25	A"	δ(CSO)
						272 (2/1)	308 (4/2)	V26	A"	$\tau(SO_2)$
						263 (19/1)	289 (43/1)	v <sub>16</sub>	A'	δ(NSC)
			117(73)			198 (2/0)	208 (5/0)	V <sub>27</sub>	A"	δ(CH <sub>3</sub> )
702 (s)	697(22)	701 (w)								$[AsF_6]^-$
678 (m)			682(76)							$[AsF_6]^-$
	568(36)									$[AsF_6]^-$
379 (w)	374(34)									$[AsF_6]^-$
				660 (m)						$[SbF_6]^-$
					656(100)					$[SbF_6]^-$
					571(28)					[SbF <sub>4</sub> ] <sup>-</sup>

a) Abbrevations for IR intensities: v = very, s = strong, m = medium, w = weak. IR intensity in km·mol<sup>-1</sup> and Raman intensity in Å<sup>4</sup>· $\mu^{-1}$ ; Raman activity is stated to a scale of 1 to 100. b) Calculated at the PBE1PBE/6–311G + +(3df,3dp) level of theory. c) X = H, D.



**Figure 2.** Asymmetric unit of  $[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$  (50% probability displacement ellipsoids).

	CH <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub>	$[CH_3SO_2NH_3]^+Sb_2F_{11}^-$	[CH <sub>3</sub> SO <sub>2</sub> NH <sub>3</sub> ] <sup>+</sup> • 3HF <sup>a)</sup>
Bond length			
S1-N1	1.612(2)	1.804(6)	1.820
S1-O1	1.435(1)	1.416(5)	1.415
S1-O2	1.435(1)	1.422(5)	1.415
S1-C1	1.756(3)	1.747(7)	1.749
Donor-acceptor	distance		
N1-(H1D)•••F9		2.762(7)	
N1-(H1E)•••F3		2.942(7)	
N1-(H1E)•••F4		2.839(7)	
N1-(H1F)•••F8		2.782(7)	
N1-(H1F)•••F1		3.098(7)	
Bond angle			
C1-S1-N1	108.3(2)	101.7(3)	100.5
C1-S1-O1	107.9(1)	112.2(3)	111.7
N1-S1-O1	107.1(1)	103.5(3)	102.6
O1-S1-O2	118.3(1)	122.0(3)	123.9

a) Calculated on the PBE1PBE/6-311G++(3pd,3df)-level of theory.

dition of three HF molecules leads to the most closely match with the experimentally determined geometry in the crystal

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**Figure 3.** View of the packing along the *b* axis (50% probability displacement ellipsoids). Hydrogen bonds are drawn as dashed lines. Methyl protons are not shown in this figure. Symmetry codes: i: 1-x, 0.5 + y, 0.5 - z; ii: 2 - x, 0.5 + y, 0.5 - z; iii: 1 + x; y; z.



Figure 4. Molecular unit of CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> (50% probability displacement elipsoids).



**Figure 5.** Crystal packing of  $CH_3SO_2NH_2$ . View along the *c* axis. Hydrogen bonds are drawn as dashed lines. The protons of the methyl group are not shown (50% probability displacement ellipsoids).

structure. Therefore the calculated frequencies as well as Raman and IR intensities of  $[CH_3SO_2NX_3]^+ \cdot 3HF$  (X = D, H), which were carried out in the harmonic approximation and taken into account for the vibrational assignments. In previous studies the method of adding HF molecules to the naked cation already became apparent as a powerful tool for the simulation of hydrogen bonds in the solid state.<sup>[15,16]</sup>

## Conclusions

In the course of this study the  $CH_3SO_2NH_{3+}$  cation was isolated as  $AsF_6^-$  and  $SbF_6^-$  salt, respectively, for the first time. For a complete vibrational analysis, the isotopomeres  $[CH_3SO_2ND_3]^+[MF_6]^-$  (M = As; Sb) were synthesized. It was shown that an *N*-protonation of methanesulfonamide exclusively takes place. The vibrational assignments are supported by quantum chemical calculations. An excess of SbF<sub>5</sub> does not lead to a diprotonation of methanesulfonamide but to the formation of Sb<sub>2</sub>F<sub>11</sub><sup>-</sup> salts.  $[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$  and  $CH_3SO_2NH_2$  were characterized by single-crystal X-ray structure analysis. This study shows that the *N*-protonation causes a remarkable elongation of the S–N bond length from 1.612(2) Å in the neutral compound to 1.804(6) Å in the protonated species. This observation is in accordance with the hypothesis that the appearance of negative hyperconjugation is the reason for the short S–N bonds observed in sulfonamides.

## **Experimental Section**

**Caution!** The hydrolysis of  $AsF_5$  and  $SbF_5$  as well as the reported salts might form HF, which burns skin and causes irreparable damage. Avoid contact with any of these compounds. Safety precautions should be taken when using and handling these materials.

Apparatus and Materials: All reactions were carried out by employing standard Schlenk techniques using a stainless-steel vacuum line. Reactions in superacidic media where performed in FEP/PFA reactors, which were closed with a stainless-steel valve. All reaction vessels were dried with fluorine prior to use. Raman spectroscopic investigations were performed at -196 °C with a Bruker MultiRAM FT-Raman spectrometer with Nd:YAG laser excitation up to 1000 mW  $(\lambda = 1064 \text{ nm})$  in the range between 250 and 4000 cm<sup>-1</sup>. Low-temperature IR measurements were performed with a Bruker Vertex-80V FTIR spectrometer. For the measurements in a cooled cell small amounts of the sample were placed on a CsBr single-crystal plate. IR spectra were recorded in a range between 350 and 4000 cm<sup>-1</sup>. The single-crystal X-ray structure analysis was carried out with an Oxford Xcalibur3 diffractometer, which is equipped with a Spellman generator (50 kV, 40 mA, with Mo- $K_{\alpha}$  radiation of  $\lambda = 0.7107$  Å) and a KappaCCD detector. The measurement was performed at a temperature of 173 K. Data collection was carried out using the CrysAlis CCD software,[17] and for its reduction the program CrysAlis RED software<sup>[18]</sup>. The solution and refinement of the structure was performed with the programs SHELXS<sup>[19]</sup> and SHELXL-97<sup>[20]</sup> implemented in the WinGX software package<sup>[21]</sup> and finally checked with the PLATON software<sup>[22]</sup> The absorption correction was carried out by employing the SCALE3 AS-PACK multi scan method.<sup>[23]</sup> CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> (Alfa Aesar) was used as received. CH<sub>3</sub>SO<sub>2</sub>ND<sub>2</sub> was prepared by several recrystallizations from D<sub>2</sub>O (Euriso-Top). SbF<sub>5</sub> (Merck) was triple distilled prior to use. AsF<sub>5</sub> was synthesized from the elements and purified by several condensations. HF (Linde) was first purified by trap-to-trap condensation under vacuum and then dried with fluorine for two weeks in a stainlesssteel pressure cylinder. DF was prepared from dried CaF2 and D2SO4. Quantum-chemical calculations were carried out using the Gaussian09 package<sup>[25]</sup> using the PBE1PBE density functional approach with a 6-311GG++(3pd, 3df). Crystal data and structure refinement for  $CH_3SO_2NH_2$  and  $[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$  are listed in Table 3.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1555583 (for  $[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$ ) and CCDC-

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Table 3. Crystal data and structure refinement for  $CH_3SO_2NH_2$  and  $[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$ .

	$CH_3SO_2NH_2$	$[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$
M <sub>r</sub>	95.12	548.63
Crystal system	orthorhombic	monoclinic
Space group	Pnma	$P2_1/c$
a /Å	9.9598(5)	7.7391(3)
b /Å	7.4262(4)	9.8130(3)
c /Å	5.3555(3)	15.8449(6)
a /°	90	90
β /°	90	96.024(4)
γ /°	90	90
V/Å <sup>3</sup>	396.11(4)	1196.68(7)
Ζ	4	4
$\rho_{\rm calcd}$ , /g·cm <sup>-3</sup>	1.595	3.045
$\mu$ /mm <sup>-1</sup>	0.637	4.826
$\lambda$ (Mo-K <sub>a</sub> ) /Å	0.71073	0.71073
F(000)	200	1008
<i>T</i> /K	173(2)	173(2)
hkl range	-9:12; -9:8; -6:5	-4:9; -12:11; -19:18
Refl. measured	1518	5947
Refl. unique	439	2335
R <sub>int</sub>	0.0284	0.0252
Parameters	39	165
$R(F)/wR(F^2)^{a)}$	0.0338	0.0359
(all reflexions)		
Weighting scheme b)	0.0502/0.0727	0.0071/12.9881
S(GoF) <sup>c)</sup>	1.145	1.240
Residual density /e•Å <sup>-3</sup>	0.390/-0.336	1.151/-0.720
Device type	Oxford XCalibur	Oxford XCalibur
Solution/refinement	SHELXS-97 <sup>[21]</sup> ,	SHELXS-97 [21],
	SHELXL-97 [14]	SHELXL-97 [14]

a)  $R_1 = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$ . b)  $wR_2 = [\Sigma [w(F_0^2 - F_c^2)^2]/\Sigma [w(F_0)^2]]^{1/2}$ ;  $w = [\sigma_c^2(F_0^2) + (xP)^2 + yP]^{-1}$ ;  $P = (F_0^2 + 2F_c^2)/3$ . c) GoF =  $\{\Sigma [w(F_0^2 - F_c^2)^2]/(n-p)\}^{1/2}$  (*n* = number of reflexions; p = total number of parameters).

1555585 (for  $CH_3SO_2NH_2$ ) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

**Synthesis of [CH<sub>3</sub>SO<sub>2</sub>NX<sub>3</sub>]<sup>+</sup>[AsF<sub>6</sub>]<sup>-</sup> (X = H, D).** Anhydrous hydrogen fluoride, HF, (ca. 2 mL) or deuterium fluoride, DF, (ca. 2 mL) and arsenic pentafluoride, AsF<sub>5</sub>, (1.10 mmol, 187 mg) were condensed at –196 °C into a reactor (FEP tube). The mixture was allowed to warm up to 0 °C to mix the components and form the superacid system. Methanesulfonamide, CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>, (95 mg, 1.00 mmol) or its isotopomere, CH<sub>3</sub>SO<sub>2</sub>ND<sub>2</sub>, (98 mg, 1.00 mmol) were added in an inert nitrogen atmosphere at –196 °C. The mixture was warmed to –50 °C for 10 min. A colorless perticipate was formed. Afterwards the reactor was cooled to –78 °C. Excess anhydrous hydrogen fluoride (or deuterium fluoride) and arsenic pentafluoride were removed in dynamic vacuum. After 12 h, [CH<sub>3</sub>SO<sub>2</sub>NH<sub>3</sub>]<sup>+</sup>[AsF<sub>6</sub>]<sup>-</sup> (or [CH<sub>3</sub>SO<sub>2</sub>ND<sub>3</sub>]<sup>+</sup>[AsF<sub>6</sub>]<sup>-</sup>) was obtained as colorless solid. The moisture sensitive salts are stable up to room temperature.

Synthesis of  $[CH_3SO_2NX_3]^+[SbF_6]^-$  (X = H, D) and  $[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$ : Antimony pentafluoride, SbF<sub>5</sub>, (0.35 mmol, 76 mg), and anhydrous hydrogen fluoride (ca. 2 mL) were condensed into a reactor (FEP tube) at -196 °C. The reactor was warmed for 10 min to 0 °C to allow the mixture of the components and form the superacid system. Methanesulfonamide, CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>, (0.35 mmol, 33 mg), or its isotopomere, CH<sub>3</sub>SO<sub>2</sub>ND<sub>2</sub>, (0.35 mmol, 34 mg) were added in an inert nitrogen atmosphere at -196 °C. The mixture was warmed to -50 °C for 10 min. Afterwards the reactor was cooled to -78 °C. Excess anhydrous hydrogen fluoride was removed in dynamic

vacuum. After 12 h,  $[CH_3SO_2NX_3]^+[SbF_6]^-$  (X = H, D), was obtained as a colorless solid. The synthesis of  $[CH_3SO_2NH_3]^+[Sb_2F_{11}]^-$  was carried out by the reaction of 9 equiv. of SbF<sub>5</sub> under analogous conditions. The obtained colorless salts are stable up to room temperature.

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**Keywords:** Methanesulfonamide; Protonation; Superacid chemistry; Vibrational spectroscopy; X-ray diffraction

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CH <sub>3</sub> SO <sub>2</sub> NH <sub>3</sub> <sup>+</sup> Cation							

