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Article

Tris(dimethylamino)oxosulfonium Difluorotrimethylsilicate, $(Me_2N)_3SO^+Me_3SiF_2^-$ (TAOS Fluoride)

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In the OSF_4/Me_2NSiMe_3 system besides the long known $Me_2NS(O)F_3$ only the trisubstituted derivative is isolated as $(Me_2N)_3SO^+Me_3SiF_2^-$ (**3**). Similar to $(Me_2N)_3S^+Me_3SiF_2^-$ compound **3** is an excellent fluoride ion donor. With AsF_5 and HF the corresponding hexafluoroarsenate $(Me_2N)_3SO^+AsF_6^-$ (**4**) and the hydrogen bifluoride $(Me_2N)_3SO^+HF_2^-$ (**5**) are formed in almost quantitative yield. X-ray structure determinations of **3**–**5** surprisingly showed two different types of structures for the cation. In **3** and **5** this cation has C_3 symmetry, while in the hexafluoroarsenate **4** a $(Me_2N)_3S^+$-like structure with C_s symmetry is determined. The experimental results for $(Me_2N)_3SO^+$ and $(Me_2N)_3S^+$ are compared with theoretical calculations for these cations and their isoelectronic neutral counterparts, the phosphorus amides $(Me_2N)_3PO$ and $(Me_2N)_3P$, respectively.

Introduction

In the reaction of SF_4 with R_2NSiMe_3 the sulfur-bonded fluorine substituents are exchanged in a stepwise manner for Me_2N groups[1−11] forming R_2NSF_3 (DAST) (*di*alkyl*a*mino*s*ulfur *t*rifluoride), $(R_2N)_2SF_2$, and $(R_2N)_3S^+Me_3SiF_2^-$ (TASF) (*t*ris(di*a*lkylamino)*s*ulfonium "*f*luoride")[7,8,12] Besides SF_4[13] DAST[14] is of great importance in preparative chemistry for the introduction of fluorine into inorganic and organic molecules; the use of $(R_2N)_2SF_2$ is limited because it tends to decompose explosively at higher temperatures.[10,15] TASF is widely used as a reagent containing an almost "naked" fluoride.[16−19] In its reactivity OSF_4 is similar to SF_4; an analogous substitution pattern is expected for the reaction with silylamines. Due to its much more limited availability only a few reactions of this type have been described for OSF_4. $R_2NS(O)F_3$ (R_2N = Me_2N, Et_2N, Pip)[2,20,21] were

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isolated, and exchange reactions were reported with $R_3SiNCNSiR_3$ and $CF_3CON(SiMe_3)_2$ to give $RN{=}S(O)FNR'_2$ ($R = NC$, $CF_3C(O)$; $R' = Me$, Et).[22] The latter reactions show that further exchange of the sulfur-bonded fluorine substituents in $R_2NS(O)F_3$ is possible. In this paper we report the preparation of $(Me_2N)_3SO^+Me_3SiF_2^-$ (**3**) and the reactions of **3** with AsF_5 and HF to give $(Me_2N)_3SO^+AsF_6^-$ (**4**) and $(Me_2N)_3SO^+HF_2^-$ (**5**), respectively. In analogy to "TAS fluoride"[12] ($(Me_2N)_3S^+Me_3SiF_2^-$) we suggest for $(Me_2N)_3SO^+Me_3SiF_2^-$ the acronym "TAOS fluoride".

X-ray structure investigations for **3**−**5** surprisingly show two different types of structures for the $(Me_2N)_3SO^+$ cation (C_s and C_3). The experimental results are compared with theoretical calculations (RHF, B3LYP, MP2) for the $(Me_2N)_3SO^+$ cation and the related $(Me_2N)_3S^+$ as well as for the isoelectronic neutral phosphorus species $(Me_2N)_3PO$ (HMPA) and $(Me_2N)_3P$.

Experimental Section

The starting materials OSF_4,[23] Me_2NSiMe_3,[24] and AsF_5[25] were prepared according to the literature. IR spectra were recorded on a Biorad Digilab FTS7 FT-IR spectrometer as Nujol or Kel-F mulls. NMR spectra were recorded on a Bruker AC80 and Bruker WH 360 in CD_3CN as solvent, and mass spectra, on a Finnigan MAT 8200 spectrometer. All operations were carried out in a dry nitrogen atmosphere due to the moisture sensitivity of the products. Elemental analyses were performed by the Mikroanalytisches Labor Beller, Göttingen, Germany.

3. At −196 °C 60 mL of *n*-pentane (as solvent), 8.0 g of OSF_4 (64.5 mmol), and 26.4 g of Me_2NSiMe_3 (225.8 mmol) were condensed via a vacuum line into a 250 mL glass vessel with a Teflon valve and a magnetic stirring bar. The vessel was placed in a −100 °C cooling bath and warmed with rapid stirring to room temperature over 2 days. The monosubstituted product $Me_2NS(O)F_3$ (mp −22 °C) was formed under these conditions as a colorless clear oil. After 12 h at room temperature this oil became very viscous and then more crystalline over a period of 2 days. When the reaction mixture was quenched with liquid nitrogen, the crystalline solid was detached from the glass wall. Subsequently, the mixture was stirred for 3 days. The solvent was decanted and the residue washed several times with pentane. The remaining solvent and volatile products were removed at −40 °C to avoid loss of Me_3SiF. Yield: 16.3 g of **3** (56 mmol, 87%). Mp: 57 °C. To prevent decomposition, **3** should be stored at −20 °C. IR (cm^{-1}): 3032 (w), 3021 (w), 2969 (m), 2948 (m), 2927 (m), 2828 (w, sh), 1741 (vw), 1608 (vw), 1492 (s, sh), 1450 (m), 1419 (m), 1365 (s), 1339 (s, sh), 1302 (vs, br), 1248 (s), 1238 (s), 1186 (s, br), 1154 (m), 1123 (w), 1068 (s), 964 (vs, br), 861 (m, sh), 819 (s, sh), 765 (s), 751 (m, sh), 729 (m, sh), 684 (m). NMR (233 K): ^1H, Me_3SiF_2 −0.12 ppm (s), $(Me_2N)_3SO^+$ 3.07 ppm (s); ^{19}F, $Me_3SiF_2^-$ −62.03 ppm (s); ^{13}C, $(Me_2N)_3SO^+$ 38.92 ppm (s); ^{14}N, $(Me_2N)_3SO^+$ 314 ppm ± 3 ppm (br, s). MS (FAB, positive, in NBA) [*m*/*e* (rel intens, %; fragment): 399 (1.5; $((Me_2N)_3SO)_2HF_2^+$), 379 (10; $((Me_2N)_3SO)_2F^+$), 180 (100; $(Me_2N)_3SO^+$), 136 (1; $(Me_2N)_3SO^{+-}NMe_2$), 92 (20; $(Me_2N)_3SO^+ - 2NMe_2$). Anal. Found (calcd) for $C_9H_{27}F_2N_3OSSi$ ($M_r = 291.48$): C, 35.9 (37.11); H, 9.2 (9.28); F, 13.0 (13.16).

4. Onto 1.41 g of **3** (4.85 mmol) in a 150 mL glass vessel with Teflon valve and stirring bar were condensed 25 mL of SO_2 as solvent and 0.93 g of AsF_5 (5.5 mmol) at −196 °C. The reaction mixture was slowly warmed to −60 °C and stirred at this temperature for 2 h. After removal of all volatile compounds, 1.77 g of **4** (4.8 mmol, 99%) remained as a colorless solid, mp 252 °C (dec). IR (cm^{-1}): 2960 (m), 2922 (m, sh), 2874 (w), 2844 (vw), 2811 (vw), 1455 (w), 1414 (vw), 1365 (vw, sh), 1300 (s), 1277 (s), 1246 (s), 1157 (s), 1155 (s, sh), 1160 (s), 1110 (m), 1061 (s), 969 (vs), 816 (vw), 776 (s), 773 (s), 723 (s), 702 (vs), 665 (s,sh), 637 (w), 608 (vw), 576 (vw), 551 (vw), 514 (w), 508 (m). NMR (303 K): ^1H, $(Me_2N)_3SO^+$ 3.06 ppm (s); ^{19}F, $\delta(AsF_6)$ −64.05 ppm (q), $^1J_{As,F} = 930$ Hz. MS (FAB (positive in NBA) [*m*/*e* (rel intens, %; fragment): 180 (100; $(Me_2N)_3SO^+$), 136 (6.5; $(Me_2N)_3SO^{+-}NMe_2$), 92 (15; $(Me_2N)_3SO^+ - 2NMe_2$).

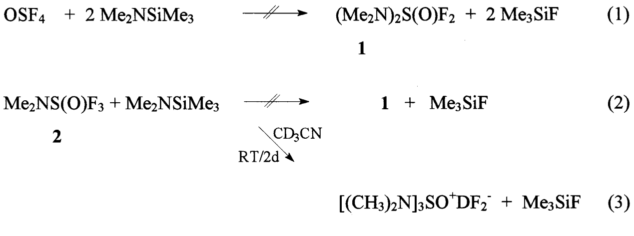
Anal. Found (calcd) for $C_6H_{18}AsF_6N_3OS$ ($M_r = 369.20$): C, 19.5 (19.51); H, 4.9 (4.88); F, 30.7 (30.89).

5. A 1.0 g amount of **3** (3.44 mmol) were placed in a Teflon vessel with a Teflon valve and stirring bar. On a metal vacuum line 5 mL of HF is added at −196 °C. The reaction mixture was stirred at −30 °C for 2 h. After removal of all volatiles at −30 °C **5** remained as a yellow, viscous oil. After recrystallization from CH_3CN/diethyl ether 0.6 g (2.74 mmol, 80%) of **5** was isolated as a colorless solid, mp 45 °C. IR (cm^{-1}): 2979 (m), 2954 (w), 2917 (vw), 2823 (w, sh), 2819 (vw), 1961 (vw), 1365 (s, sh), 1346 (m, sh), 1298 (w), 1250 (w, sh), 1237 (w), 1181 (w, sh), 1154 (m), 1069 (m), 996 (s, sh), 946 (vs, br), 771 (vs, sh), 761 (vs), 723 (m, sh), 697 (vw, sh), 667 (vw). NMR (303 K): ^1H, $(Me_2N)_3SO^+$ 3.06 ppm (s); ^{19}F, HF_2 −147.9 ppm (d), $^1J_{H,F} = 114.3$ Hz. MS (FAB positive) (rel intens, %; fragment): 399 (2; $((Me_2N)_3SO)_2HF_2^+$), 379 (9; $((Me_2N)_3SO)_2F^+$), 242 (3), 180 (100; $(Me_2N)_3SO^+$), 92 (17; $(Me_2N)_3SO^+ - 2NMe_2$). Anal. Found (calcd) for $C_6H_{19}F_2N_3OS$ ($M_r = 219.29$): C, 33.0 (32.88); H, 8.8 (8.68); F, 15.9 (17.35).

X-ray Crystallography. Single crystals were prepared by slow diffusion of diethyl ether into a solution of the TAOS salts in CH_3CN at −30 °C in a λ-shaped glass vessel fitted with a Teflon valve. The crystals were mounted on a thin glass fiber using the oil-drop technique (Kel-F-oil). The data were collected on a Siemens P4 diffractometer using Mo Kα radiation ($\lambda = 71.073$ pm) at the temperatures given in Table 1. The structures were solved by direct methods (SHELXS).[26]

Results and Discussion

When OSF_4 is reacted with Me_2NSiMe_3 in a molar ratio 1:2 or when $Me_2NS(O)F_3$ is reacted with Me_2NSiMe_3 in the ratio 1:1 the expected disubstituted product **1** (eq 1) could not be detected:



The reaction of **2** with Me_2NSiMe_3 in CD_3CN was followed by NMR spectroscopy over a period of 2 days. No changes

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Table 1. Crystal and Structure Refinement Data for **3**−**5**

param	**3**	**4**	**5**
chem formula	$C_9H_{27}F_2N_3OSSi$	$C_6H_{18}AsF_6N_3OS$	$C_6H_{19}F_2N_3OS$
fw	291.49	369.21	219.30
temp (K)	173(2)	173(2)	173(2)
wavelength (pm)	71.073	71.073	71.073
cryst system, space group	monoclinic, $P2_1$	orthorhombic, *Pbca*	monoclinic, $P2_1/n$
unit cell dimens (pm, deg)	$a = 807.3(1)$ $b = 858.3(2)$ $c = 1114.8(1)$ $\beta = 94.36(1)$	$a = 1118.4(2)$ $b = 1353.1(4)$ $c = 1869.6(3)$	$a = 602.8(1)$ $b = 1235.2(1)$ $c = 1453.2(1)$ $\beta = 101.33(1)$
V (nm^3)	0.7702(2)	2.8293(11)	1.06093(11)
Z; calcd density (Mg/m^3)	2; 1.257	8; 1.734	4; 1.373
abs coeff (mm^{-1})	0.300	2.611	0.304
absolute struct param	0.03(9)		
final R indices^a	R1 = 0.0455, wR2 = 0.1132	R1 = 0.0414, wR2 = 0.0822	R1 = 0.0341, wR2 = 0.0937
R indices (all data)^a	R1 = 0.0479, wR2 = 0.1145	R1 = 0.0753, wR2 = 0.0884	R1 = 0.0391, wR2 = 0.0971

[a] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

are detected in the ^{1}H and ^{19}F NMR spectra below 20 °C. In the ^{1}H NMR spectrum of **2** at −30 °C the triplet at $\delta = 2.84$ ppm ($^4J = 4.2$ Hz) due to coupling with the axial fluorines is split further into doublets ($^4J = 2.2$ Hz) from coupling with the equatorial fluorine. Above 0 °C this multiplet changes to a broad signal at 3.22 ppm. At 20 °C this characteristic ^{1}H signal diminishes and a singlet appears at 3.05 ppm, which we assign to the $(Me_2N)_3SO^+$ cation. In the ^{19}F NMR of **2** the eight lines of an A_2B system are observed. During the experiment the intensity of these signals decreases. Parallel to this decrease an increase of a broad signal at $\delta = -148$ ppm is observed which we assign to the DF_2^- anion.

When pentane is used as a solvent instead of CH_3CN, $(Me_2N)_3SO^+Me_3SiF_2^-$ (**3**) is isolated in high yield. This reaction cannot be followed by NMR spectroscopy because of the low solubility of **3** in this solvent.

$$\mathbf{2} + Me_2NSiMe_3 \xrightarrow[25\ °C]{n\text{-pentane}} \{\mathbf{1}\} + Me_3SiF \qquad (4)$$

$$2\{\mathbf{1}\} + Me_3SiF \rightarrow \underset{\mathbf{3}}{(Me_2N)_3SO^+Me_3SiF_2^-} + Me_2NS(O)F_3 \qquad (5)$$

$$\{\mathbf{1}\} + Me_2NSiMe_3 \rightarrow \mathbf{3} + Me_3SiF \qquad (6)$$

Whether **3** results from a dismutation of **1** or from further reaction with the silylamine is not known. **3** is a colorless crystalline solid, mp 57 °C. The compound is very moisture sensitive; at room-temperature slow decomposition occurs with the formation of a colorless oil. Storage of **3** at −20 °C is recommended. Compared to $(Me_2N)_3S^+Me_3SiF_2^-$, **3** is less soluble in acetonitrile, the most suitable solvent for reactions of these two excellent fluoride ion donors.

At −40 °C in the ^{1}H NMR spectrum of **3** in CD_3CN two resonances are observed in the intensity ratio 2:1; the signal for $(Me_2N)_3SO^+$ at 3.05 ppm and a sharp singlet for the $Me_3SiF_2^-$ anion at −0.12 ppm. In the ^{13}C NMR spectrum of **3** only one signal due to the equivalent methyl groups of the $(Me_2N)_3SO^+$ cation is observed ($\delta = 38.9$ ppm). In the ^{14}N NMR spectrum the three equivalent amino groups give rise to a broad singlet at $\delta = 314$ ppm. In the ^{19}F NMR spectrum the resonance for the $Me_3SiF_2^-$ is found at $\delta = -62.0$ ppm. Warming of these solutions above 0 °C leads to decomposition of the anion and formation of DF_2^-. Reactions with **3** should be carried out below −10 °C. According to our knowledge **3** is the first $(Me_2N)_3SO^+$ salt prepared.[27] To elucidate the influence of the counteranions on the structure of the $(Me_2N)_3SO^+$ cation, **3** was reacted with AsF_5, a strong Lewis acid, to give the corresponding hexafluoroarsenate $[(Me_2N)_3SO]^+(AsF_6)^-$ (**4**), a salt with a weakly interacting anion. The TAOS cation $(Me_2N)_3SO^+$ is isoelectronic with $(Me_2N)_3PO$ (HMPA), known as an extremely powerful ligand in coordination chemistry. The positive charge in $(Me_2N)_3SO^+$ reduces the donor properties drastically; no stable adduct such as $[(Me_2N)_3SO\cdot AsF_5]^+(AsF_6)^-$ was isolated with excess AsF_5:

$$\mathbf{3} + AsF_5 \xrightarrow{SO_2} \underset{\mathbf{4}}{[(Me_2N)_3SO]^+AsF_6^-} + Me_3SiF \qquad (7)$$

$$\mathbf{3} + HF \xrightarrow{HF} \underset{\mathbf{5}}{[(Me_2N)_3SO]^+HF_2^-} + Me_3SiF \qquad (8)$$

Reaction with HF afforded the bifluoride salt **5** in which a relatively strong anion−cation interaction is expected. Salts **4** and **5** were isolated in almost quantitative yield.

Structural Studies on $[(Me_2N)_3SO]^+Me_3SiF_2^-$ (3), $[(Me_2N)_3SO]^+AsF_6^-$ (4), and $[(Me_2N)_3SO]^+HF_2^-$ (5). Single crystals suitable for X-ray structure investigations were obtained by crystallization from CH_3CN/diethyl ether at −40 °C. The molecular structures of **3**−**5** are presented in Figures 1−3. Table 1 shows the crystal data and the structure refinement for these compounds. In Table 2 selected bond distances and angles for the cations of **3**−**5** are compared with the geometrical data for the isoelectronic neutral phosphorus derivative $OP(NMe_2)_3$ (HMPA)[28] and the cocrystallizates of $OP(NMe_2)_3$ with S_7NH[29] and $Ph_2(Me)AsS$,[30]

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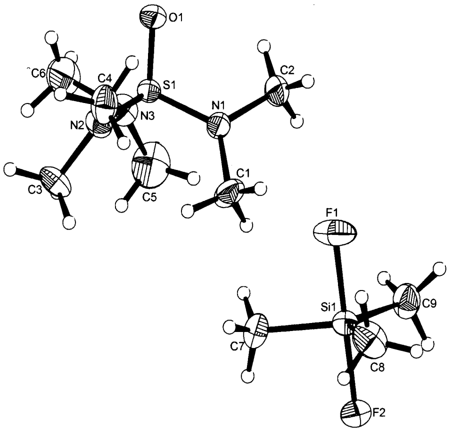

Figure 1. X-ray structure of “TAOS fluoride” $(Me_2N)_3SO^+Me_3SiF_2^-$ (**3**), showing ellipsoids at 50% probability.

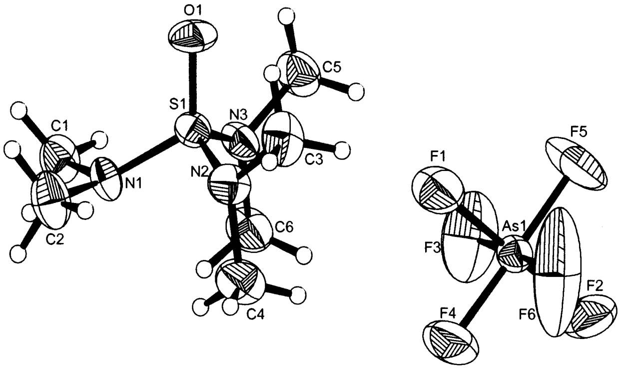

Figure 2. X-ray structure of $(Me_2N)_3SO^+AsF_6^-$ (**4**), showing ellipsoids at 50% probability.

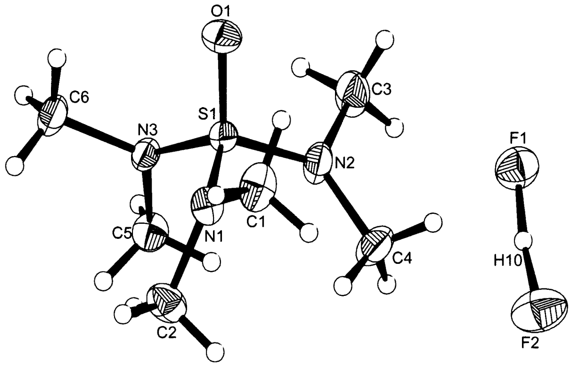

Figure 3. X-ray structure of $(Me_2N)_3SO^+HF_2^-$ (**5**), showing ellipsoids at 50% probability.

respectively. Numerous complexes of $OP(NMe_2)_3$ have been characterized by X-ray crystallography. The examples given in Table 2 were chosen because in these cocrystallizates only a small influence on the structure of the $OP(NMe_2)_3$ molecules from the second component was expected.

The SO bond distances in **3** (142.5(1) pm), **4** (143.0(3) pm), and **5** (142.9(1) pm) are not significantly different. The same can be stated for the SN bond lengths, which are found in the range 157.9(4)−159.4(2) pm. But with respect to the bond angles, the structure of the $[OS(NMe_2)_3]^+$ cation in the hexafluoroarsenate **4** differs significantly from those of the $Me_3SiF_2^-$ (**3**) and the HF_2^- salts (**5**). While the latter two show a structure with almost regular C_3 symmetry and three almost planar nitrogen centers, for the hexafluoroarsenate salt C_s symmetry is observed. Two different types of nitrogen are found: one slightly more pyramidal (sum of the angles 351.7°) than the other two (356.0−357.4°). The OSN angle to the first (119.3°) is much wider than the other two (107.8−108.8°). The NSN angle between these two nitrogen is 116.4 (2)°, while the other two NSN angles are only 102.2(2) and 102.6(2)°, respectively.

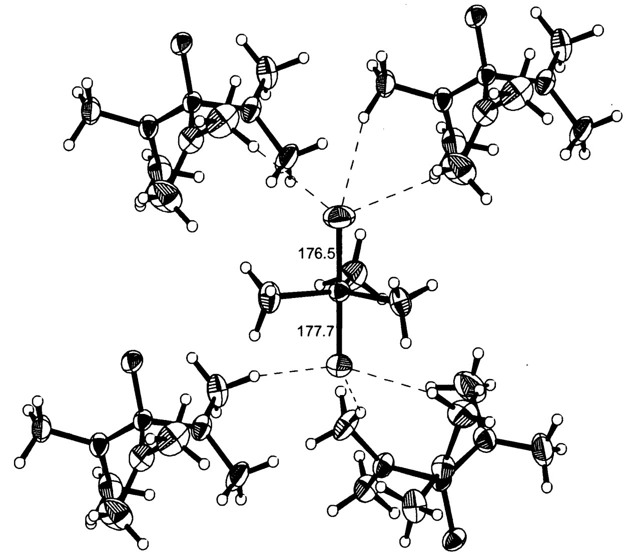

Figure 4. Anion−cation interaction in **3** in the solid state.

The difference in the structures of the $[OS(NMe_2)_3]^+$ cation in salts **3**−**5** might be due to anion−cation interactions in the solid state. For the hexafluoroarsenate, due to the large anion, the weakest anion−cation interaction is expected. For the HF_2^- salt this interaction should be strongest. For the $Me_3SiF_2^-$ salt, this anion−cation interaction leads to significantly different bond distances of the axially bonded fluorines (176.5(2) and 177.7(1) pm, respectively). The sum of the distances to the three nearest hydrogen atoms for the latter is 751.5 pm and for the other 785.2 pm, as shown by Figure 4. Stronger H···F interactions lead to an elongation of the Si−F bond.

The structural behavior of the $(Me_2N)_3SO^+$ cation parallels that of the isoelectronic neutral $OP(NMe_2)_3$ molecule. In neat $OP(NMe_2)_3$[28]—comparable with the $(Me_2N)_3SO]^+$ salt containing a “naked” $[(Me_2N)_3SO]^+$ cation because of the “noninteracting” anion AsF_6^-—the molecule adopts a C_s structure. Even small perturbations change the C_s to C_3 symmetry, as shown e.g. for $S_7NH{\cdot}OP(NMe_2)_3$[29] or $Ph_2(CH_3)AsS{\cdot}OP(NMe_2)_3$.[30]

The structure of the related phosphane $P(NMe_2)_3$ has been under discussion for a long time. Since the early work of Vilkov and co-workers, who concluded from electron diffraction experiments in favor of C_3 symmetry,[31] further

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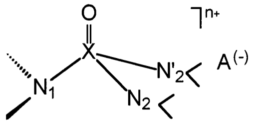
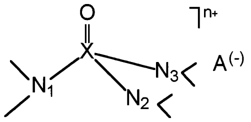
Table 2. Comparison of the $(Me_2N)_3SO^+$ Cation in **3**−**5** with $(Me_2N)_3PO$[28] and the Cocrystallizates, $OP(NMe_2)_3 \cdot S_7NH$[29] and $(Me_2N)_3PO \cdot Ph_2MeAsS$[30]





X =	S, n = 1	P	S, n = 1		P	
A =	AsF_6 (**4**)		Me_3SiF_2 (**3**)	HF_2 (**5**)	S_7NH	$Ph_2(Me)AsS$
XO	143.0(3)	147.2(3)	142.5(1)	142.9(1)	148.7(6)	146.1(7)
XN_1	158.8(3)	165.0(4)	158.3(2)	159.0(1)	162.8(11)	165.4(8)
XN_2	158.8(4)	164.4(3)	158.7(2)	158.7(1)	162.1(9)	164.1(8)
XN_2'/N_3	157.9(4)	164.4(3)	159.4(2)	158.7(1)	163.5(8)	165.2(8)
$\Sigma \measuredangle N_1$	351.7	348.0	359.8	357.5		360.0
$\Sigma \measuredangle N_2$	356.0	354.7	358.9	359.9		359.0
$\Sigma \measuredangle N_2'/N_3$	357.4	354.7	359.6	357.0		358.6
OXN_1	119.3(2)	119.1(2)	110.5(1)	109.9(1)	111.2(4)	112.7(4)
OXN_2	108.8(2)	109.9(1)	110.7(1)	111.5(1)	110.6(4)	111.6(4)
OXN_2'/N_3	107.8(2)	109.9(1)	110.7(1)	109.8(1)	110.5(4)	111.1(4)
N_1XN_2	102.2(2)	102.4(1)	109.3(1)	109.7(1)	108.2(4)	107.9(4)
N_1XN_2'/N_3	102.6(2)	102.4(1)	108.6(1)	109.7/1)	107.8(4)	105.8(4)
N_2XN_2'/N_3	116.4(2)	112.8(2)	106.9(1)	106.2(1)	108.6(4)	107.3(4)

Table 3. Comparison of Selected Bond Distances (pm) and Bond Angles (deg) of $(Me_2N)_3P$ (GED)[37] and $(Me_2N)_3P$ (X-ray)[36] with the Data for the Isoelectronic Cation $(Me_2N)_3S^{+}$ [42]

	$(Me_2N)_3P$ (GED)	$(Me_2N)_3P$ (X-ray)	$(Me_2N)_3S^+$ (X-ray)
X−N(2)/N(2′)	170.3(6)	168.4	161.5
X−N(1)	173.8(6)	173.0	168.9
N(2)−X−N(2)	108.3(6)	110.7	115.4
N(1)−X−N(2)	96.8(6)	97.6	99.2
sums of angles at N(2)/N(2′)	353	355.9	354.1
sums of angles at N(1)	337	337.3	337.0

reports favoring C_s[32,33] and also C_3 symmetry[34,35] are found in the literature. This controversy has been settled by a recent X-ray structure investigation confirming C_s symmetry.[36] Subsequently it was shown that the C_s structure is also adopted in the gas phase by the $(Me_2N)_3P$ molecule[37] and that even in coordination compounds this symmetry is maintained.[38−41] C_s symmetry is an *inherent structural property of* $(Me_2N)_3P$[36] and its heavier group 15 homologues.[37] This behavior is exactly paralleled by the isoelectronic cationic sulfur counterpart $(Me_2N)_3S^+$.

In Table 3 the average bond distances and angles of six different $(Me_2N)_3S^+$ salts, reported in a comprehensive experimental and theoretical investigation by Farnham and Dixon et al.,[42] are compared with the GED[37] and X-ray data for $(Me_2N)_3P$.[36] Since the report of Farnham and Dixon et al., X-ray structures of more than 20 $(Me_2N)_3S^+$ salts including $(Me_2N)_3S^+Me_3SiF_2^-$ [43] and $(Me_2N)_3S^+AsF_6^-$ and $(Me_2N)_3S^+PF_6^-$ [44] have been determined, in our and other groups. The structures of the cations in all of these salts almost exactly correspond to that listed in Table 3. That C_s symmetry is an inherent structural property of $(Me_2N)_3S^+$ has also been confirmed by ab initio calculations for the model cation $S(NH_2)_3^+$.[42]

In Tables 4−6 the RHF-, MP2-, and B3LYP-calculated[45] energies and geometries for $S(NMe_2)_3^+$, $OS(NMe_2)_3^+$, $P(NMe_2)_3$, and $OP(NMe_2)_3$ are reported. The calculated structural data are in excellent agreement with the experimental findings for $S(NMe_2)_3^+$ (C_s symmetry), $OS(NMe_2)_3^+$ (C_s and C_3 symmetry), $P(NMe_2)_3$ (C_s symmetry), and $OP(NMe_2)_3$ (C_s and C_3 symmetry). RHF calculations seem to reproduce the experimentally determined bond distances slightly better than the other two methods, while the best agreement in bond angles is found with the B3LYP calculations.

For all four compounds C_s symmetry is the ground-state symmetry; the energy difference to the next higher minimum

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Table 4. RHF/6-311G* Calculated Energies and Geometries of $(Me_2N)_3S^+$, $(Me_2N)_3SO^+$, and Their Isoelectronic Phosphorus Analogues $(Me_2N)_3P^+$ and $(Me_2N)_3PO$

	$(Me_2N)_3S^+$ C_s	$(Me_2N)_3S^+$ C_3	$(Me_2N)_3SO^+$ C_s	$(Me_2N)_3SO^+$ C_3	$(Me_2N)_3P$ C_s	$(Me_2N)_3P$ C_3	$(Me_2N)_3PO$ C_s	$(Me_2N)_3PO$ C_3
energy (au)	−798.3328	−798.3247	−873.1768	−873.1707	−741.8276	−741.8198	−816.7670	−816.7624
Δ*E* (kJ/mol)	0.0	21.3	0.0	16.0	0.0	20.5	0.0	12.1
XO (pm)			141.4	141.2			146.1	146.0
XN_1 (pm)	167.9	164.3	160.7	159.1	173.2	170.2	166.7	165.8
XN_2 (pm)	162.0	164.3	160.3	159.1	169.6	170.2	166.4	165.8
ΣWN_1 (deg)	336.6	347.0	344.4	359.7	339.4	359.2	346.9	359.9
ΣWN_2 (deg)	355.0	347.0	355.2	359.7	356.4	359.2	356.5	359.9
OXN_1 (deg)			115.1	110.5			118.2	112.1
OXN_2 (deg)			108.9	110.5			110.2	112.1
N_1XN_2 (deg)	101.1	108.9	103.5	108.4	98.8	104.3	102.7	106.7
N_2XN_2 (deg)	114.5	108.9	115.1	108.4	110.1	104.3	112.6	106.7
Nimag	0	0	0	0	0	0	0	0

Table 5. MP2/6-311G* Calculated Energies and Geometries of $(Me_2N)_3S^+$, $(Me_2N)_3SO^+$, and Their Isoelectronic Phosphorus Analogues $(Me_2N)_3P^+$ and $(Me_2N)_3PO$

	$(Me_2N)_3S^+$ C_s	$(Me_2N)_3S^+$ C_3	$(Me_2N)_3SO^+$ C_s	$(Me_2N)_3SO^+$ C_3	$(Me_2N)_3P$ C_s	$(Me_2N)_3P$ C_3	$(Me_2N)_3PO$ C_s	$(Me_2N)_3PO$ C_3
energy (au)	−799.8227	−799.8128	−874.8682	−874.8600	−743.3006	−743.2900	−818.4329	−818.4264
Δ*E* (kJ/mol)	0.0	26.0	0.0	21.5	0.0	27.8	0.0	17.1
XO (pm)			144.4	144.0			148.8	148.5
XN_1 (pm)	170.4	166.5	162.8	161.2	174.9	171.6	168.1	167.2
XN_2 (pm)	164.3	166.5	162.9	161.2	171.2	171.6	168.1	167.2
ΣWN_1 (deg)	331.6	341.9	341.4	358.6	334.4	357.5	343.6	358.9
ΣWN_2 (deg)	352.0	341.9	351.7	358.6	353.2	357.5	353.1	358.9
OXN_1 (deg)			120.1	110.7			120.8	112.7
OXN_2 (deg)			108.5	110.7			110.1	112.7
N_1XN_2 (deg)	98.5	108.2	101.2	108.2	96.6	103.4	100.7	106.1
N_2XN_2 (deg)	117.5	108.2	117.7	108.2	111.8	103.4	114.1	106.1
Nimag								

Table 6. B3LYP/6-311G* Calculated Energies and Geometries of $(Me_2N)_3S^+$, $(Me_2N)_3SO^+$, and Their Isoelectronic Phosphorus Analogues $(Me_2N)_3P^+$ and $(Me_2N)_3PO$

	$(Me_2N)_3S^+$ C_s	$(Me_2N)_3S^+$ C_3	$(Me_2N)_3SO^+$ C_s	$(Me_2N)_3SO^+$ C_3	$(Me_2N)_3P$ C_s	$(Me_2N)_3P$ C_3	$(Me_2N)_3PO$ C_s	$(Me_2N)_3PO$ C_3
energy (au)	−801.7235	−801.7149	−876.9295	−876.9240	−745.1865	−745.1796	−820.4790	−820.4750
Δ*E* (kJ/mol)	0.0	22.6	0.0	14.4	0.0	18.1	0.0	10.5
XO (pm)			145.0	144.7			149.0	148.8
XN_1 (pm)	173.0	168.2	164.5	162.7	176.4	172.7	169.1	168.2
XN_2 (pm)	165.8	168.2	164.7	162.7	172.2	172.7	169.0	168.2
ΣWN_1 (deg)	334.9	344.8	345.1	359.8	338.8	359.4	347.8	360.0
ΣWN_2 (deg)	354.6	344.8	354.1	359.8	356.4	359.4	356.2	360.0
OXN_1 (deg)			119.5	110.8			119.9	112.6
OXN_2 (deg)			108.5	110.8			110.1	112.6
N_1XN_2 (deg)	99.0	108.6	101.7	108.1	97.2	103.4	101.5	106.2
N_2XN_2 (deg)	116.9	108.6	117.3	108.1	111.0	103.4	113.5	106.2
Nimag	0	0	0	0	0	0	0	0

with C_3 symmetry is appreciably larger for $S(NMe_2)_3^+$ and $P(NMe_2)_3$ than for $OS(NMe_2)_3^+$ and $OP(NMe_2)_3$. These calculations nicely confirm the experimental findings: for $S(NMe_2)_3^+$ and $P(NMe_2)_3$ until now only C_s symmetry is experimentally confirmed, while for $OS(NMe_2)_3^+$ and $OP(NMe_2)_3$ structures with both symmetries are found. The smallest energy difference between the C_s and the disfavored C_3 symmetry is calculated for $OP(NMe_2)_3$. Experimentally it has been shown for this compound that even small perturbations cause the symmetry change, while for $OS(NMe_2)_3^+$ this change occurs with slightly stronger interacting counteranions. As pointed out by Seppelt[46] in his comments on the paper of Mitzel and al. on $P(NMe_2)_3$,[36] ab initio calculations predict (and confirm) even complex structures quite well but they give no real explanation.

Conclusions

As pointed out by Bartlett[47,48] in his investigations on SF_3^+ salts, the geometry of the sulfonium cation exactly agrees with that of its neutral isoelectronic counterpart PF_3.[49] Sulfur cations might be considered as structural models for the neutral phosphorus systems and vice versa. This paper nicely confirms this point of view. Even in more complex systems the influence of the substituents on the two types of structure is identical. Small differences in the geometry arise from the different bond distances. Owing to the smaller covalent radius of sulfur compared to that of phosphorus and due to the positive charge on sulfur, bonds to more electronegative substituents will be shorter for sulfur than for phosphorus. For bulkier substituents this will lead to stronger steric interactions and a slight widening of the angles in the case of sulfur. Especially intriguing and still not really understood

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are the reasons for the higher stability of the unsymmetrical C_s structures of $[S(NMe_2)_3]^+$, $[OS(NMe_2)_3]^+$, and their isoelectronic phosphorus analogues $P(NMe_2)_3$ and $OP(NMe_2)_3$. The reasons surely are electronic effects due to the mutual interactions of the amino groups,[42,46] influenced by the interactions with cosubstituents and modified by steric interactions.[42] This problem is not restricted to the examples in this paper; e.g. for $(CF_3S(NMe_2)_2]^+$ we reported a TAS-like structure with two structurally identical almost planar Me_2N groups.[50] The position of the pyramidal Me_2N group of $S(NMe_2)_3^+$ is occupied by the CF_3 group. In $[FS(NMe_2)_2]^+$ the two Me_2N groups are completely different: besides one almost planar group (sum of the angles 359°) with a short SN bond (156.5 pm) a pyramidal geometry (339.2°) with the expected long SN bond (165.0 pm) is found.[51] Further theoretical investigations are necessary to explain these phenomena.

Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.[52]

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