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Contribution to the Chemistry of Bis(trifluoromethyl)amines: Preparation of Bis(trifluoromethyl)ammonium Hexafluorometalates $(CF_3)_2NH_2^+MF_6^-$ (M = As, Sb). Crystal Structure of $(CF_3)_2NH_2^+AsF_6^-$ and Gas-Phase Structures of $(CF_3)_2NX$ (X = H, Cl)

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$(CF_3)_2NH_2^+MF_6^-$ (M = As, Sb) were prepared by protonation of $(CF_3)_2NH$ in superacid media and characterized by infrared, Raman, and NMR spectroscopy. $(CF_3)_2NH_2^+AsF_6^-$ crystallizes in the orthorhombic space group *Pmcn*, with $a = 7.569(5)$ Å, $b = 9.031(6)$ Å, $c = 13.011(9)$ Å, and $Z = 4$. In the crystal, cation and anion reside on the mirror planes at $x = 0.25$ and $x = 0.75$ of the unit cell, with C–N bond lengths of 1.484(9) and 1.497(9) Å, respectively, and an N–H distance of 0.99(7) Å. Cation and anion have three short H···F contacts of 2.03(6), 2.26(7), and 2.31(7) Å with two anions. The geometric structures of $(CF_3)_2NX$ with X = H and Cl have been determined in the gas phase by electron diffraction and by ab initio calculations (HF/3-21G*). The N–C bonds in these two compounds (1.416(5) Å in $(CF_3)_2NH$ and 1.455(4) Å in $(CF_3)_2NCl$) are considerably shorter than those in the $(CF_3)_2NH_2^+$ cation (mean value 1.490(9) Å). These variations can be rationalized by electrostatic effects.

Introduction

Fluorocarbon–ammonium salts were first synthesized by DesMarteau by HF addition to $CF_2{=}NF$ followed by protonation with AsF_5/HF. They were identified by Raman and ^{19}F-NMR spectroscopy[1] (eqs 1 and 2). Similarly $SF_4{=}NF$, SF_5NHF, $CF_3N[OCF(CF_3)_2]H$, $CF_3N(OCF_3)H$, and $(CF_3)_2NH$ were protonated in HF/AsF_5. $(CF_3)_2NH_2^+AsF_6^-$ was identified only by its ^{19}F NMR spectra. Its vapor pressure is 20 Torr at room temperature.[1]

$$CF_2{=}NF + HF \rightarrow CF_3NHF \qquad (1)$$

$$CF_3NHF + AsF_5 + HF \rightarrow CF_3NH_2F^+AsF_6^- \qquad (2)$$

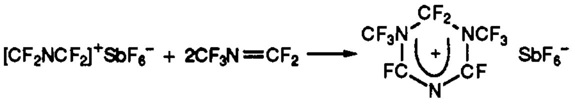
Our attempts to protonate $CF_3N{=}CF_2$ in superacid media in presence of CsF did not result in the $(CF_3)_2NH_2^+$ cation but in the protonated dimer of perfluoroazapropene $[(CF_3)_2N{-}CF{=}NHCF_3]^+AsF_6^-\cdot HF$, which was identified by X-ray analysis.[2] The reason for the formation of this unusual cation is the great tendency of $CF_3N{=}CF_2$ for dimerization in presence of fluoride ions[3] (eqs 3 and 4). The reaction of $CF_3N{=}CF_2$ with CsF leads to $CsN(CF_3)_2$[4] (eq 5). According to Bürger and Pawelke perfluoroazapropene undergoes cyclotrimerization with SbF_5 at elevated temperatures to form the cation (I) analogous to the reaction of perfluorotrimethylamine and SbF_5[5] (eqs 6 and 7).

$$2CF_3N{=}CF_2 \xrightarrow{F^-} (CF_3)_2N{-}CF{=}NCF_3 \qquad (3)$$

$$(CF_3)_2N{-}CF{=}NCF_3 + 2HF + AsF_5 \xrightarrow{HF} [(CF_3)_2N{-}CF{=}NHCF_3]^+AsF^-\cdot HF \qquad (4)$$

$$CF_3N{=}CF_2 + CsF \underset{RT}{\overset{MeCN}{\rightarrow}} CsN(CF_3)_2 \qquad (5)$$

$$CF_3N{=}CF_2 + SbF_5 \rightleftharpoons [CF_2NCF_2]^+SbF_6^- \qquad (6)$$



(7)

I

Attempts to transfer $(CF_3)_3N$ to ammonium salts failed because the bulky CF_3 groups in the nearly planar structure prevent the electrophilic attack at the nitrogen lone pair. NF_3 could not be protonated in superacid media either, because of the low basicity of the nitrogen atom.[1] In the present study we were interested in the geometric parameters of $(CF_3)_2NH$ and $(CF_3)_2NCl$, which possibly allow a correlation between the skeletal parameters and the electrophilic attack at the nitrogen lone pair.

The experimental structure determination using gas electron diffraction (GED) is supplemented by ab initio calculations which were performed with the GAUSSIAN 90 program system[6] and 3-21G* basis sets with additional d-functions at nitrogen. The primary aim of these calculations is the determination of the torsional angles of the two CF_3 groups, which are not well

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Table 1. Crystallographic Data for $(CF_3)_2NH_2^+AsF_6^-$

formula	$(CF_3)_2NH_2^+AsF_6^-$
fw	342.95
space group	*Pmcn* (No. 62)
a (Å)	7.569(5)
b (Å)	9.031(6)
c (Å)	13.011(9)
α (deg)	90.0
β (deg)	90.0
γ (deg)	90.0
V (Å^3)	889(1)
Z	4
ρ_{calcd} (g cm^{-3})	2.5612
μ(Mo Kα) (mm^{-1})	3.98
λ (Mo Kα) (Å)	0.710 73
T (K)	169
final $R(F_o)$ and $R_w(F_o)$ indices[a]	0.050, 0.054

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F_o) = [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1.0/(\sigma^2(F) + (0.0005F^2))$.

determined in the GED experiment. For this purpose HF calculations with small basis sets appear to be adequate. According to our experience, small basis sets reproduce experimental C–F and N–C bond distances about equally well as large basis sets. In addition to these gas-phase studies, we report the crystal structure of $(CF_3)_2NH_2^+AsF_6^-$.

Experimental Section

Syntheses. $CF_3N{=}CF_2$ was received from Bayer Co., Leverkusen, FRG, as a gift. Literature methods were used for the synthesis of $(CF_3)_2NH$,[7] $(CF_3)_2NCl$,[8] and $(CF_3)_2NH_2^+AsF_6^-$.[1]

Volatile substances were handled in a high vacuum line with greaseless stopcocks (Fa. Young). Solids were manipulated by Schlenk techniques. Experiments in anhydrous HF were conducted in Kel-F reactors with stainless steel valves (Fa. Hoke). AsF_5 and SbF_5 (Fa. Merck) were distilled repeatedly before use. HF was dried in a stainless steel bomb using 1.5 bar of F_2.

IR spectra of solids were recorded in a low-temperature cuvette,[9] using Si or CsBr windows between 4000 and 200 cm^{-1}; gas spectra were recorded in a gas cuvette using Si windows between 4000 and 30 cm^{-1} on a Bruker IFS 113v FT-IR, resolution 0.5 cm^{-1}.

Raman spectra were measured with a Coderg T 800, with a resolution of 0.5 cm^{-1} and excitation by a Spectra Physics Ar$^+$ laser with $\lambda = 514.5$ nm.

NMR spectra were recorded on a Bruker AM 300 FT-NMR spectrometer (^{1}H 300 MHz, ^{19}F 282.5 MHz), with a pulse number of about 1000 for ^{19}F spectra between +100 and −100 ppm relative to CCl_3F. ^{1}H spectra were recorded with about 30 pulses between 15 and −1 ppm relative to TMS. Upfield shift means negative chemical shift.

Preparation of $(CF_3)_2NH_2^+SbF_6^-$. In a typical reaction 3 mL of HF was distilled into a Kel-F reactor at −196 °C, followed by 1 mmol of SbF_5. The mixture was warmed to room temperature to form a solution of SbF_5 in HF. The reactor was then cooled to −196 °C and $(CF_3)_2NH$ (1 mmol) was added. The mixture was warmed to −60 °C and allowed to stand overnight. Pumping at this temperature resulted in a fine white solid.

Preparation of Single Crystals of $(CF_3)_2NH_2^+AsF_6^-$. A 3-mL aliquot of HF was distilled into a Kel-F reactor at −196 °C, followed by 1 mmol of AsF_5. The mixture was warmed to 20 °C to form a solution of AsF_5 in HF. The reactor was then cooled to −196 °C, and $(CF_3)_2NH$ (1 mmol) was added. The mixture was slowly warmed to −70 °C and allowed to stand overnight. On this occasion large transparent needles precipitated. The remaining solvent was pumped off. The crystals were transferred to Mark tubes at −60 °C and X-ray intensities were obtained at −104 °C.

X-ray Crystal Data of $(CF_3)_2NH_2^+AsF_6^-$. Crystallographic data are listed in Table 1. Intensity data were collected with $\omega/2\theta$ scans, variable scan speed 5.0–14.6° min^{-1} in θ, and scan width 1.2° + dispersion. A Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα radiation was used. The lattice parameters were determined from the least-squares fit of 16 reflections with $2\theta_{max} = 26.5°$. ω-Scans of low-order reflections along the three crystal axes showed acceptable mosaicity. Six standard reflections (200, 020, 002, $\bar{2}00$, $0\bar{2}0$, $00\bar{2}$) were recorded every 100 reflections, only random deviations were detected during 17.5 h of X-ray exposure, and 1890 reflections with $3.0° \leq 2\theta \leq 50.0°$, $-9 \leq h \leq 9$, $0 \leq k \leq 11$, and $0 \leq l \leq 16$ were measured. The data were corrected for Lorentz-polarization but not for absorption effects and averaged ($R_{int} = 0.040$) to 845 unique reflections, 775 of which had $F \geq 3.0\sigma(F)$. Two reflections were omitted because of suspected extinction. The systematic absences of ($h0l$), $l = 2n + 1$, and ($hk0$), $h + k = 2n + 1$, conform to space groups *Pmcn* and *P*2$_1$*cn*. The structure was solved via direct methods and $\Delta\rho$ maps. It was refined (on F) using full-matrix least-squares methods with anisotropic displacement parameters for all non-H atoms and an isotropic one for the H atoms. A total of 89 parameters were refined. Weights $w = 1.0/(\sigma^2(F) + 0.0005F^2)$ led to a featureless analysis of variance in terms of $\sin\theta$ and F_o. The refinement converged to $S = 2.29$, $R(F_o) = 0.050$, $R_w(F_o) = 0.054$, and $(\Delta/\rho)_{max} = 0.049$ (no extinction correction). The largest peak in final $\Delta\rho$ map was ±0.9(2) e Å^{-3} (near As). Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 10. The programs used are as follows: PARST,[11] SHELX76,[12] SHELXTL PLUS,[13] PLATON,[14] and SCHAKAL.[15]

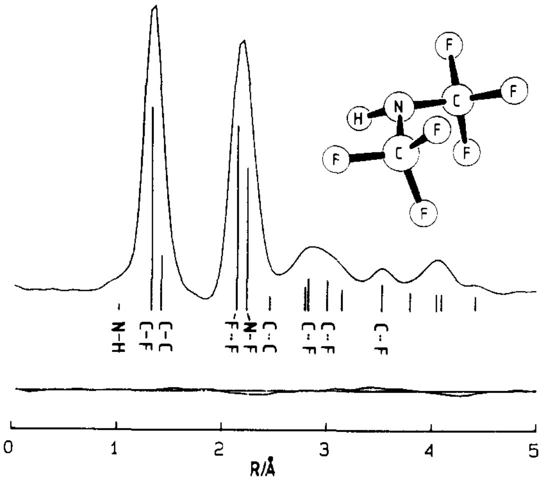

Figure 1. Experimental radial distribution function and difference curve for $(CF_3)_2NH$.

Gas Electron Diffraction of $(CF_3)_2NH$ and $(CF_3)_2NCl$. The GED intensities were recorded with a Gasdiffractograph KD-G2[16] at two camera distances (25 and 50 cm) and with an accelerating voltage of ca. 60 kV. The electron wavelength was calibrated with ZnO powder patterns (λ = 0.048 716(10) and 0.048 740(6) Å for the 25- and 50-cm camera distances, respectively). The sample reservoirs were kept at −65 °C ($(CF_3)_2NH$) and −68 °C ($(CF_3)_2NCl$) and the inlet system and nozzle were at room temperature. The pressure in the diffraction chamber was below 2 × 10^{-5} mbar. The purity of the samples were checked by gas-IR spectra after the experiment. The photographic plates were analyzed by the usual procedures,[17] and numerical values for the total scattering intensities in the s-ranges 2–18 and 8–35 Å^{-1} in steps of Δs = 0.2 Å^{-1} are available as supplementary material.

Results and Discussion

Gas-Phase Structures of $(CF_3)_2NH$ and $(CF_3)_2NCl$. The radial distribution functions for both bis(trifluoromethyl)amines are shown in Figures 1 and 2. In the least-squares analyses the molecular intensities were modified with a diagonal weight matrix

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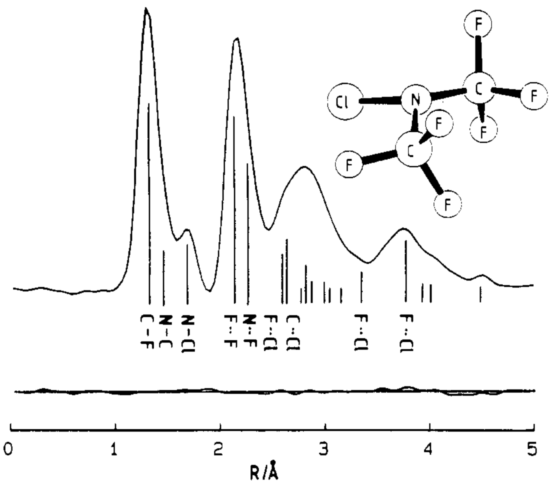

Figure 2. Experimental radial distribution function and difference curve for $(CF_3)_2NCl$.

and known scattering amplitudes and phases were used.[18] C_{3v} symmetry was assumed for the CF_3 groups with a possible tilt between the C_3 axis and the N–C bond direction. Models with different symmetries for the $(CF_3)_2N$ group were tested: (1) C_s symmetry with torsion of the CF_3 groups around the N–C bonds in opposite directions ($\tau_1 = -\tau_2$), (2) C_2 symmetry with torsion in the same directions ($\tau_1 = \tau_2$), and (3) C_1 symmetry with different torsional angles for both groups. In the case of $(CF_3)_2NCl$ the C_1 model results in the best fit of the experimental intensities and for $(CF_3)_2NH$ a C_2 model was refined, since the GED data do not allow a distinction between C_1 and C_2 symmetries. The ab initio calculations predict C_1 symmetry for the $(CF_3)_2N$ groups in both compounds but the torsional angles in $(CF_3)_2NH$ are rather similar. Vibrational amplitudes were grouped according to their distances. With these assumptions eight or nine geometric parameters and seven or eight vibrational amplitudes were refined simultaneously for $(CF_3)_2NH$ or $(CF_3)_2NCl$, respectively. The following correlation coefficients had values larger than $|0.6|$: $(CF_3)_2NH$, $p_4/p_7 = -0.75$, $p_4/p_8 = 0.64$, $p_4/a_4 = 0.70$, $p_6/a_2 = -0.62$, $p_8/a_4 = 0.77$; $(CF_3)_2NCl$: $p_4/p_7 = -0.63$, $p_6/a_3 = -0.68$, $p_6/a_4 = -0.80$, $a_3/a_4 = 0.71$. The final results and numbering of geometric parameters p_i and amplitudes a_k are given in Tables 2 and 3. The ab initio results are included in Table 2.

Considering systematic differences between the experimental r_a (thermal average) and the calculated r_e (equilibrium) structures and the low level of the ab initio calculations, the agreement between experimental and calculated geometric parameters is satisfactory. The largest discrepancy occurs for the torsional angles τ_1 and τ_2 where the experimental results are "effective" values due to large amplitude torsional vibrations.

Table 4 compares skeletal parameters of bis(trifluoromethyl)amines $(CF_3)_2NX$ with X = H, Cl, CF_3, and F. The N–C bond lengths vary from 1.416(5) Å in $(CF_3)_2NH$ to 1.455(4) Å in $(CF_3)_2NCl$. These variations do not correlate smoothly with the electronegativities of X and two effects may be important. The first of these is the electrostatic interaction between the high positive net charge of the trifluoromethyl carbon atom and the nitrogen net charge. The latter is negative in $(CF_3)_2NH$, leading to an attractive interaction ($N^{\delta-}$–$C^{\delta+}$) and thus to a short N–C bond in this amine. With increasing electronegativity of X the nitrogen atom will become less negative, leading to a lengthening of the N–C bonds. An extreme case of repulsive interaction ($N^{\delta+}$–$C^{\delta+}$) is observed for the $(CF_3)_2NH_2^+$ cation (see below) where the N–C bonds are very long (1.490(9) Å). The second of these is hybridization of the central nitrogen atom which varies from nearly sp^3 in $(CF_3)_2NF$ (the sum of the three nitrogen bond angles $\Sigma\alpha_N = 326(2)°$) to nearly sp^2 in $(CF_3)_3N$ with $\Sigma\alpha_N = 354(1)°$. The sum of the bond angles for X = H and Cl is intermediate. The trend of the N–C bond lengths between $(CF_3)_2NCl$ (1.455(4) Å) and $(CF_3)_2NF$ (1.446(4) Å), however, can not be explained by these two effects which predict a longer bond in the latter compound. The N–Cl bond in $(CF_3)_2NCl$ (1.713(6) Å) is shorter than those in CF_3NCl_2 (1.733(3) Å)[21] or NCl_3 (1.759(2) Å).[22] Since N–Cl bonds have a very low polarity, this trend reflects mainly different hybridizations of these compounds. The sum of the nitrogen bond angles $\Sigma\alpha_N$ decreases in this series from 347 to 330 and 321° with increasing chlorination. The chemical reactivity of the compounds $(CF_3)_2NX$ with X = H, Cl, and CF_3 correlates strongly with the nitrogen bond angles which in turn determine the "shape" and shielding

Table 2. Geometric Parameters for $(CF_3)_2NH$ and $(CF_3)_2NCl$ from GED and ab Initio Calculations (HF/3-21G*) and *R* Factors

	$(CF_3)_2NH$		$(CF_3)_2NCl$	
	GED[a]	ab initio[b]	GED[a]	ab initio[b]
C–F	1.332(2) (p_1)	1.342	1.322(2) (p_1)	1.337
N–C	1.416(5) (p_2)	1.398	1.455(4) (p_2)	1.418
N–X[c]	1.01(4) (p_3)	1.007	1.713(6) (p_3)	1.696
C–N–C	119.6(12) (p_4)	118.7	120.8(11) (p_4)	116.6
C–N–X[c]	111(5) (p_5)	113.9	113.3(7) (p_5)	114.8
F–C–F	107.9(3) (p_6)	107.8	108.9(3) (p_6)	108.3
tilt (CF_3)[d]	3.8(11) (p_7)	2.9	2.2(12) (p_7)	2.2
τ_1[e]	12(3) (p_8)	18.8	19.2(2) (p_8)	11.8
τ_2[e]		24.2	28(2) (p_9)	25.1
R_{50}[f]	0.036		0.042	
R_{25}[f]	0.054		0.089	

[a] r_a distances in Å and $\angle_\alpha$ angles in deg. Error limits are 3σ values. [b] Average values are given for parameters which are not unique. [c] X = H or Cl. [d] Tilt of CF_3 group toward the nitrogen lone pair. [e] Torsional angles for the two CF_3 groups. For $\tau_1 = \tau_2 = 0°$ one fluorine atom of each CF_3 group lies in the CNC plane and is trans to the opposite N–C bond. [f] Agreement factors for 50- and 25-cm camera distance, respectively. $R = [\Sigma\omega_i\Delta_i^2/\Sigma(s_iM_i(\text{exptl}))^2]^{1/2}$; $\Delta_i = s_iM_i(\text{exptl}) - s_iM_i(\text{calcd})$.

Table 3. Interatomic Distances and Vibrational Amplitudes for $(CF_3)_2NH$ and $(CF_3)_2NCl$[a]

	$(CF_3)_2NH$		$(CF_3)_2NCl$	
	dist	amplitude	dist	amplitude
C–F	1.33	0.047(2) (a_1)	1.32	0.050(2) (a_1)
N–C	1.42	0.050[b]	1.46	0.050[b]
N–X[c]	1.01	0.070[b]	1.71	0.059(7) (a_2)
F···F	2.15	0.064(3) (a_2)	2.15	0.067(5) (a_3)
N···F	2.21–2.29	0.071(7) (a_3)	2.24–2.32	0.088(9) (a_4)
C···C	2.45	0.080[b]	2.53	0.080[b]
C···X[c]	1.98	0.100[b]	2.65	0.092(15) (a_5)
C···F	2.84–3.01	0.18(4) (a_4)	2.78–3.17	0.18[b]
C···F	3.53	0.10(2) (a_5)	3.57–3.59	0.12[b]
F···X[c]	2.30–2.65	0.20[b]	2.61–3.01	0.18(5) (a_6)
F···X[c]	3.11–3.14		3.37–3.83	0.11(3) (a_7)
F···F	2.81–3.15	0.15(3) (a_6)	2.83–3.02	0.15[b]
F···F	3.80–4.10	0.12(2) (a_7)	3.96–4.06	0.18(3) (a_8)
F···F	4.41	0.10[b]	4.49	0.10[b]

[a] r_a values in Å, error limits are 3σ values and refer to the last digit. [b] Not refined. [c] X = H or Cl.

Table 4. Skeletal Parameters of $(CF_3)_2NX$ (X = H, Cl, CF_3, F) (Distances in Å; Angles in deg)

	X = H	X = Cl	X = CF_3[19]	X = F[20]
N–X	1.01(4)	1.713(6)	1.426(6)	1.376(12)
N–C	1.416(5)	1.455(4)	1.426(6)	1.446(4)
CNX	111(5)	113.3(7)	117.9(4)	104.8(7)
CNC	119.6(12)	120.8(11)	117.9(4)	116.6(6)
$\Sigma\alpha_N$[a]	342(7)	347(2)	354(1)	326(2)

[a] Sum of nitrogen bond angles.

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Table 5. Observed Infrared and Raman Frequencies (cm^{-1}) of $(CF_3)_2NH_2^+MF_6^-$ (M = As, Sb) and Infrared Frequencies of $(CF_3)_2ND_2^+MF_6^-$ (M = As, Sb)

$(CF_3)_2NH_2^+$				$(CF_3)_2ND_2^+$		
AsF_6^-		SbF_6^-				
IR	Raman	IR	Raman	AsF_6^- IR	SbF_6^- IR	approx descripns
3237 ms		3215 ms		2270 m, br	2267 m, br	ν(NH/ND)
1538 m		1538 m				δ(NH_2)/δ(CNH)
1484 m		1467 m				
				1349 vs	1351 vs	
1338 s		1334 w		1332 vs		
				1310 vs	1309 s	ν(CF_3)
1212 mw			1225 vw	1213 m	1213 s	
1188 mw		1194 ms	1188 vw	1169 m	1170 ms	
				1136 m	1130 s	δ(ND_2)
1076 s		1061 vs	1093 vw			ω(NH_2)
		1035 br				
				1090 m	1090 s	δ(CND)
884 mw	884 mw	915 ms		885 w	915 ms	ν(NC)
830 mw		831 s	868 s	830 s[a]	831 s[a]	
724 mw	718 w			732 vs/720 vs		
700 m	698 vs	697 w				ν(MX_6^-)
672 s/653 m	600 m	666 s	669 vs	661 m/624 w	663 s	ρ(CF_3)
587/574 m	562 s	574 s	594 w/556 m	562 w	574 s	
530 s	543 m	532 ms		526 m	532 m	
400 vs		408 s		399 s	406 s	
	376 s			358 s		δ(CF_3)
	326 s	324 s	337 m		324 s	δ(MF_6^-)
		296 s	287 s		296 s	
260/250 m		258 m		260 s	258 w	δ(CNC)
230 w		237 w		230 m		τ(CF_3)
185 ms	168 w					

[a] ω(ND_2) masked by ν(NC).

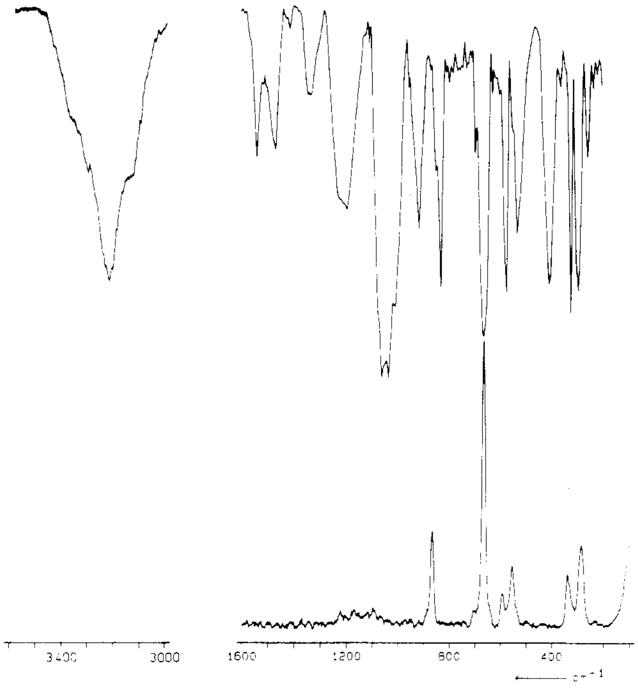

Figure 3. Infrared and Raman spectra of $(CF_3)_2NH_2^+SbF_6^-$.

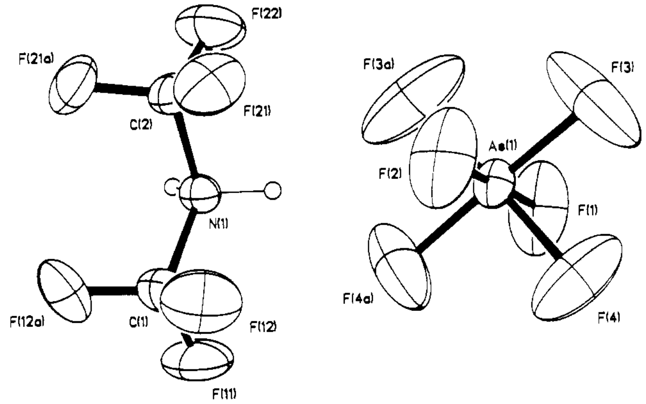

Figure 4. Structure of the asymmetric unit of $(CF_3)_2NH_2^+AsF_6^-$.

of the nitrogen lone pair. Oxidative chlorination of the most pyramidal compound $(CF_3)_2NH$ proceeds very readily, protonation of $(CF_3)_2NCl$ is possible in a superacid system, and attempts to protonate or oxidatively chlorinate the nearly planar $(CF_3)_3N$ were not successful.[23]

Bis(trifluoromethyl)ammonium Hexafluorometalates. $(CF_3)_2NH_2^+MF_6$ (M = As, Sb) was prepared by protonation of $(CF_3)_2NH$ in superacid media (HF/MF_5). The fine white solids were stable for several months at –60 °C under N_2 atmosphere, and the decomposition products at room temperature were HF, MF_5, and $(CF_3)_2NH$ (IR/MS).

Figure 3 shows the low-temperature infrared and Raman spectra of $(CF_3)_2NH_2^+SbF_6^-$; Table 5 summarizes the data of $(CF_3)_2NX_2^+MF_6^-$ (X = H, D; M = As, Sb). NH_2 vibrations could be assigned by H/D exchange and comparison with those in $NH_2F_2^+$ [24] and NH_2F.[25] Their identification is possible from the infrared spectra where these modes are expected to be more intense. In the frequency region of the NH_2 stretching modes, $(CF_3)_2NH_2^+$ exhibits one medium strong broad band at 3237 cm^{-1}. A splitting in the antisymmetric and the symmetric stretch is not observed due to H···F bridges. The δ_{NH_2} and δ_{CNH} modes were observed at 1538 and 1484 cm^{-1}. The NH_2 rocking mode is observed at 1075 cm^{-1}, and the C–N modes are observed at 884 cm^{-1} and 830 cm^{-1}, respectively. In $(CF_3)_2ND_2^+$ the ND_2 rocking mode overlapes with the lower frequency N–C stretching mode, resulting in broadening and increased intensity of this mode. As shown by X-ray diffraction the octahedron of the MF_6^- anion is distorted by anion–cation interactions. This reduction of symmetry from the point group O_h to C_s results in a splitting of the vibrational modes. Therefore an exact description of the vibrations below 700 cm^{-1} is not possible.

The ^{19}F and ^1H NMR spectra were recorded in SO_2 solution. The ^{19}F signal of the CF_3 group is observed at –55.92 ppm (AsF_6^-)

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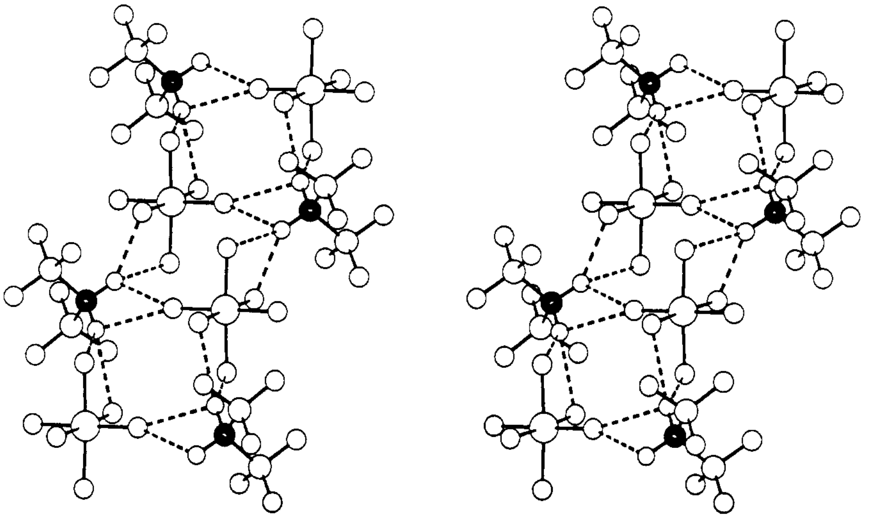

Figure 5. Stereoscopic view of a chain of cations and anions of $(CF_3)_2NH_2^+AsF_6^-$ connected via H···F contacts shorter than 2.31 Å.

Table 6. Atomic Coordinates and Equivalent Isotropic or Isotropic Displacement Parameters (Å^2 × 10^4) of $(CF_3)_2NH_2^+AsF_6^-$

	x	y	z	U_{eq}/U^a
As(1)	0.25	0.34036(7)	0.05590(6)	344
F(1)	0.25	0.4995(7)	−0.0109(6)	933
F(2)	0.25	0.1821(6)	0.1249(6)	926
F(3)	0.0827(10)	0.2699(7)	−0.0130(5)	1457
F(4)	0.0873(8)	0.4079(5)	0.1309(4)	1091
F(11)	0.75	0.4290(5)	0.2567(4)	757
F(12)	0.6100(6)	0.2290(5)	0.2855(3)	752
F(21)	0.6107(5)	0.0362(3)	0.1322(3)	646
F(22)	0.75	0.1045(6)	−0.0009(4)	737
N(1)	0.75	0.2597(6)	0.1332(4)	307
C(1)	0.75	0.2872(9)	0.2456(6)	477
C(2)	0.75	0.1018(8)	0.0981(6)	390
H(1)	0.859(9)	0.299(7)	0.100(6)	652

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

and −54.90 ppm (SbF_6^-), and the ^{1}H signal, at 10.0 ppm and 9.9 ppm, respectively.

Figure 4 shows the geometry of the asymmetric unit, and a stereoscopic view of the unit cell is shown in Figure 5. Atomic coordinates and the equivalent values of the anisotropic displacement parameters for non-H atoms are given in Table 6. Bond lengths, bond angles, torsion angles, and possible H-bonds are given in Table 7. In the crystal the cation and the anion reside on the mirror planes at $x = 0.25$ and $x = 0.75$ of the unit cell. The mirror plane bisects two F–As–F bond angles of the anion, which is a distorted octahedron with mean As–F bond distances of 1.682(5) Å and a maximum deviation of the F–As–F bond angles from the ideal angles 90° and 180° of 6.0(4)°. These values are within the expected range and can be compared to those for the compound $[(CF_3)_2N{-}CF{=}NHCF_3]^+AsF_6^-{\cdot}HF$.[2] In the cation C and N are nearly tetrahedrally coordinated. F(11), C(1), N(1), C(2), and F(22) are located on the mirror planes. The CF_3 groups with a mean C–F distance of 1.290(8) Å and F–C–F bond angles between 109.9(6) and 111.1(3)° show no irregularities and are similar to the CF_3 group of the cation $HON(CH_2)CF_3^+AsF_6^-$ [26] with the mean C–F distance of 1.302(5) Å and FCF bond angles between 110.0(3) and 111.0(3)°.

Table 7. Bond Distances (Å), Bond Angles (deg), Torsion Angles (deg) and Short H···F Contacts (Å) of $(CF_3)_2NH_2^+AsF_6^-$ [a]

As(1)–F(1)	1.679(7)	C(2)–F(22)	1.289(9)
As(1)–F(2)	1.688(6)	N(1)–C(1)	1.484(9)
As(1)–F(3)	1.677(7)	N(1)–C(2)	1.497(9)
As(1)–F(4)	1.686(6)	N(1)–H(1)	0.99(7)
C(1)–F(11)	1.289(10)	F(1)···H(11)	2.31(7)
C(1)–F(12)	1.292(6)	F(3)···H(1)	2.26(7)
C(2)–F(21)	1.288(6)	F(4)···H(1)	2.03(6)
F(2)–As(1)–F(1)	179.0(3)	F(12)–C(1)–N(1)	109.1(2)
F(3)–As(1)–F(1)	92.7(3)	F(11)–C(1)–N(1)	106.0(6)
F(3)–As(1)–F(2)	87.9(3)	F(11)–C(1)–F(12)	111.1(3)
F(4)–As(1)–F(1)	89.4(2)	F(12)–C(1)–F(12a)	110.3(6)
F(4)–As(1)–F(2)	89.9(2)	F(22)–C(2)–N(1)	106.7(6)
F(4)–As(1)–F(3)	84.0(3)	F(21)–C(2)–N(1)	109.4(4)
F(3)–As(1)–F(3a)	98.1(3)	F(21)–C(2)–F(22)	110.7(4)
F(4)–As(1)–F(4a)	93.9(3)	F(21)–C(2)–F(21a)	109.9(6)
C(2)–N(1)–H(1)	102(4)	H(1)–N(1)–H(1i)	112(6)
C(1)–N(1)–H(1)	111(4)	N(1)–H(1)···F(3)	149.0(51)
C(1)–N(1)–C(2)	117.4(5)	N(1)–H(1)···F(4)	143.0(60)
C(1)–N(1)–C(2)–F(21)	60.2(6)	H(1)–N(1)–C(1)–F(12)	−178(4)
C(1)–N(1)–C(2)–F(22)	180.0(5)	H(1)–N(1)–C(1)–F(11)	63(4)
C(2)–N(1)–C(1)–F(12)	−60.3(7)	H(1)–N(1)–C(2)–F(22)	−58(4)
C(2)–N(1)–C(1)–F(11)	180.0(5)	H(1)–N(1)–C(2)–F(21)	−178(4)

[a] Symmetry codes: (i) $1 - x, 1 - y, -z$; (a) $0.5 - x, y, z$.

The C–N bonds lengthen from 1.416(5) Å in $(CF_3)_2NH$ to 1.490(9) Å in the cation and can be compared with those in $[(CF_3)_2N{-}CF{=}NHCF_3]^+AsF_6^-$ [2] (1.45(1)–1.51(2) Å) and $HON(CH_2)CF_3^+AsF_6^-$ [26] (1.477(5) Å). This lengthening corresponds to a shift of the mean CN stretching vibration from 917 cm^{-1} in $(CF_3)_2NH$ to 857 cm^{-1} in the cation. Each H atom has three short (2.03(6), 2.26(7), and 2.31(7) Å) H···F contacts with two anions, causing distortion of the AsF_6^- octahedron. In the crystal each cation is connected to three anions with hydrogen bonds, resulting in a two dimensional ABAB chain structure.

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Supplementary Material Available: Tables of total electron diffraction intensities for $(CF_3)_2NH$ and $(CF_3)_2NCl$ and crystallographic data and thermal parameters for $(CF_3)_2NH_2^+AsF_6^-$ and a stereoscopic view of the unit cell (7 pages). Ordering information is given on any current masthead page. Further information concerning the crystal structure investigations can be obtained through the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen 2, FRG, by giving the report number, CSD-55160, the names of the authors, and the reference.

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