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# PREPARATION AND CRYSTAL STRUCTURE OF $[(CF_3)_2NCF{=}NHCF_3]^+AsF_6^-$ . HF

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## SUMMARY

$(CF_3)_2NCF{=}NCF_3$(I) is formed from $CF_3N{=}CF_2$(II) by fluoride ion-catalyzed dimerisation. In excess anhydrous HF at room temperature a reverse reaction to give the monomer is possible. (II) adds HF to form the amine $(CF_3)_2NH$ (III).

Below -30 °C in superacid $HF/AsF_5$ the protonated cation of (I) is obtained and $[(CF_3)_2NCF{=}NHCF_3]^+AsF_6^-$ • HF can be crystalized. A structure of this salt has been determined at 160 K and shows a monoclinic structure $P2_1/m$, a = 861.9(9) pm, b = 777.3(9) pm, c = 942.6(9) pm, ß = 100.53(6)°, Z = 2.

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Additional information on the crystal structure determination may be obtained through the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen, by giving the number CSD-52259, the authors and the journal.

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** X-ray analysis.

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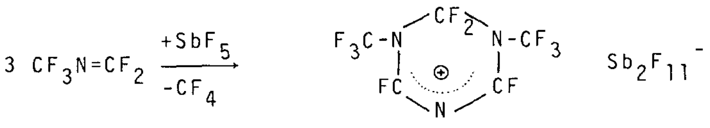
## INTRODUCTION

The reactions of N-(Trifluoromethyl)difluoromethaneimine with strong Lewis acids have been studied in detail [1 - 5]. As observed by H. Bürger, (II) reacts with excess $SbF_5$ to form a cyclotrimer according to (1),



(1)

whereas with the less acidic $AsF_5$ no reaction can be observed [2]. In HF an addition to the double bond takes place and the amine $(CF_3)_2NH$ (III) is formed [5]; according to D. Desmarteau (III) is protonated to give the corresponding ammonium salt in superacid $HF/AsF_5$ [1].

$$\text{(II)} + HF \rightarrow \underset{\text{(III)}}{(CF_3)_2NH} \qquad (2)$$

$$\text{(III)} + H_2F^+AsF_6^- \xrightarrow[-HF]{} (CF_3)_2NH_2^+AsF_6^- \qquad (3)$$

The same behaviour has been reported by D. Lentz for $CF_3N=CHF$ [7]. The dimerisation (4) of (II) to (I) in presence of fluoride ions has already been reported in the literature and occurs without problems [6]. We wish to report our investigations on the behaviour of the C=N double bond of (I) towards anhydrous HF: its reactivity is similar to that already observed for (II).

$$2\ \text{(II)} \xrightarrow{(F^-)} (CF_3)_2\ \underset{\text{(I)}}{N-CF=NCF_3} \qquad (4)$$

## RESULTS AND DISCUSSION

When (I) is reacted with an equimolar amount of $AsF_5$ in anhydrous HF a white hydrolyzable solid (IV), which is stable up to -30 °C, is formed. Its crystal structure has been determined by X-ray analysis at 160 K. At room temperature it decomposes according to (5) into the starting materials (I), $AsF_5$ and HF, as has been shown by IR-spectroscopic examination.

The $^{19}F$-NMR spectrum was recorded at -50 °C in HF acidified with $AsF_5$. Besides the $AsF_6^-$ quartet at -58.3 ppm and the HF singlet at -192.2 ppm it exhibits three signals that can be assigned to (IV).

$$(I) \xrightarrow{HF/AsF_5} [(CF_3)_2NCF{=}NHCF_3]^+AsF_6^- \qquad (5)$$

TABLE 1

Comparison of the $^{19}F$-NMR spectra of $[(CF_3)_2NCF{=}NHCF_3]^+AsF_6^-$ (IV) in HF at -50 °C and $(CF_3)_2NCF{=}NCF_3$ (I) in $SO_2$ at -25 °C

| | $[(CF_3)_2NCF{=}NHCF_3]^+$ (IV)<br>δ[ppm] | <br>(I) [Hz] | $(CF_3)_2NCF{=}NCF_3$ (I) [8]<br>δ[ppm] |
|---|---|---|---|
| $(CF_3)_2N$- | -53.3 (d) | 15.5 | -56.2 |
| =N-$CF_3$ | -54.9 (d) | 17.5 | -56.1 |
| =CF- | -31.9 (m) | 17.5 | -19.6 |

Heating the sample to -20 °C resulted in the disappearance of the signals of (IV); only the singlet due to $(CF_3)_2NH_2^+AsF_6^-$ appears at -58.1 ppm (lit. [1] -58.3 ppm). The same monomerisation can also be observed for (I) in pure HF. The cation (IV) formed as an intermediate cannot be stabilized by the $HF_2^-$ anion. Finally the $^{19}F$-NMR shows only the signal of the $(CF_3)_2NH_2^+$ cation according to (6).

$$(I) + 6\ HF \rightarrow 2\ (CF_3)_2NH_2{}^+HF_2{}^- \qquad (6)$$

This result is a confirmation of the extremely negative $H_0$-value of -15.1 reported for absolutely pure anhydrous HF [9]. Protonation of the very weak base $(CF_3)_2NH$ is possible in this medium.

Figure 1 shows the geometry of a formula unit, table 2 bond distances and bond angles. Besides the $AsF_6{}^-$ ion and the $(CF_3)_2NCF{=}NCF_3$ unit the F-syntheses shows an additional peak. A neutral F atom was attached to this position. Bond angles and distances suggest a HF-bridging between N(2) and F(4) of the $AsF_6{}^-$. For this reason H atoms were placed in geometrically calculated positions (H(1) in the plane through N(2), C(2), C(3): N(2)-H(1) 95 pm, H(1)-N(2)-C(2) = H(1)-N(2)- C(3) = 120 °; H(2) on the line connecting F(4)...F(100): F(100)- H(2) = 95 pm). The $AsF_6{}^-$ anion forms a slightly distorted octahedron. The maximum deviation from the ideal angles 90° and 180° is 2.0(3)°. The As-F bond distances have values between 168.9(8) and 171.9(7) pm.

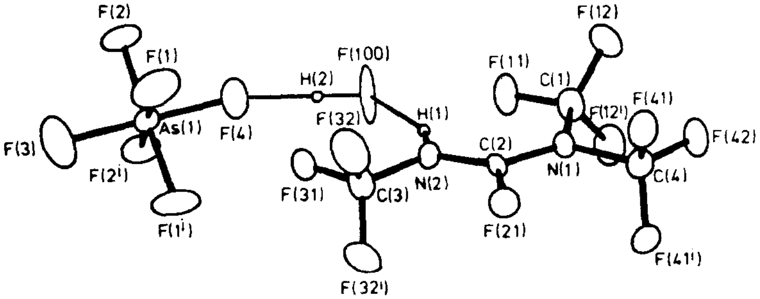


Fig. 1. General view of one formula unit of $[(CF_3)_2NCF{=}NHCF_3]^+AsF_6{}^- \cdot HF$, at 160 K showing the atom numbering. H atoms were placed in geometrically calculated positions. The group shown resides on a mirror plane ((i) corresponding to the symmetry operation x, 0.5-y, z).

TABLE 2

Bond distances and angles for
$[(CF_3)_2NCF{=}NHCF_3]^+ \text{-} AsF_6^- \cdot HF$ at 160 K

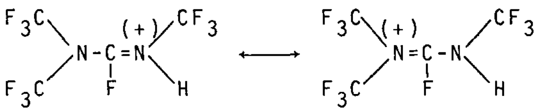
| | | | |
|---|---|---|---|
| As(1)-F(1) | 170.4(6) | N(1)-C(1) | 151(2) |
| As(1)-F(2) | 171.3(5) | N(1)-C(4) | 149(2) |
| As(1)-F(3) | 168.9(8) | N(1)-C(2) | 132(1) |
| As(1)-F(4) | 171.9(7) | N(2)-C(2) | 128(1) |
| C(1)-F(11) | 130(1) | N(2)-C(3) | 145(1) |
| C(1)-F(12) | 131.6(8) | F(100)...N(2) | 277(1) |
| C(2)-F(21) | 130(1) | F(100)...F(4) | 252(1) |
| C(3)-F(31) | 130(2) | F(100)...F(31) | 276(1) |
| C(3)-F(32) | 130(1) | F(100)...F(11) | 260(1) |
| C(4)-F(41) | 130.1(9) | | |
| C(4)-F(42) | 130(1) | | |
| F(1)-As(1)-F(1) | 89.5(3) | N(1)-C(1)-F(11) | 109.9(8) |
| F(1)-As(1)-F(2) | 90.5(3) | N(1)-C(1)-F(12) | 108.9(7) |
| F(1)-As(1)-F(2) | 178.0(3) | N(1)-C(4)-F(41) | 109.1(6) |
| F(1)-As(1)-F(4) | 89.6(3) | N(1)-C(4)-F(42) | 107.8(9) |
| F(1)-As(1)-F(3) | 90.9(4) | N(2)-C(3)-F(31) | 106(1) |
| F(2)-As(1)-F(4) | 88.4(3) | N(2)-C(3)-F(32) | 111.7(6) |
| F(2)-As(1)-F(3) | 91.1(4) | C(1)-N(1)-C(4) | 116.8(8) |
| F(3)-As(1)-F(4) | 180.0(6) | C(1)-N(1)-C(2) | 123.8(9) |
| F(11)-C(1)-F(12) | 109.8(3) | N(1)-C(2)-F(21) | 112.2(9) |
| F(41)-C(4)-F(41) | 110.3(9) | N(1)-C(2)-N(2) | 130(1) |
| F(41)-C(4)-F(42) | 110.2(6) | N(2)-C(2)-F(21) | 117.8(8) |
| F(31)-C(3)-F(32) | 109.3(7) | C(2)-N(2)-C(3) | 120(1) |
| F(32)-C(3)-F(32) | 108(1) | N(2)...F(100)...F(4) | 120.3(4) |

These values are within the expected range for As-F distances and can be compared to those for the compounds $H_3O^+AsF_6^-$ (172 pm [10]) and $CF_3SCl_2^+AsF_6^-$ (171 pm [11]).

The bond angles at N(1), N(2) and C(2) and the bond distances C(2)-N(1) and C(2)-N(2) indicate these atoms to be $sp^2$-hybridized.

The bond distances N(1)-C(1), N(1)-C(4) and N(2)-C(3) correspond to single bond lengths. Table 3 lists C-N bond distances in comparable compounds.

The C=N bond length can be explained by delocalised π-bonding in accordance with (7).



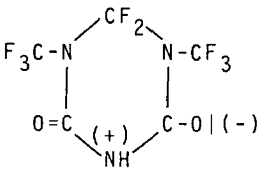
(7)

The $CF_3$ groups form distorted tetrahedra. The C-F distances lie between 130(1) and 131.6(8) pm, while the F-C-F and F-C-N bond angles vary from 106(1) to 111.7(6)°, suggesting an $sp^3$-hybridized carbon atom.

The additional fluorine atom (F(100)) lies in a plane with the $C_2NCN$ skeleton and shows short contact distances to the atoms F(4) (252(1) pm), F(11) (260(1) pm), F(31) (276(1) pm) and N(2) (277(1) pm). The distances H(1)...F(100) and H(2)...F(4) are 190(2) pm and 157(2) pm, respectively, with an H(2)-F(100)...H(1) angle of 130(1)°.

TABLE 3

C-N bond distances for selected compounds (in pm)

| | C-N | C=N | Ref. |
|---|---|---|---|
| $CF_3$-N=$CF_2$ | 141.9(5) | 126.9(10) | [12] |
| $CF_3$-N=CHF | 141.4(7) | 127.7(7) | [ 7] |
| $(CF_3)_3N$ | 143(3) | - | [13] |
| $(CF_3)_2C$=NH | - | 129.3 | [14] |
|  | 144.6(9)<br>to<br>146.5(9) | 134.9(7) | [ 2] |
| $(CF_3)_2N\overset{\cdots}{-}CF\overset{\cdots}{-}NHCF_3^+$ | 145(1)<br>to<br>151(2) | 128(2)<br><br>132(2) | |
| $(CH_3)_2NCl\cdot BCl_3$ | 152(3) | | [15] |
| $(CH_3)_2NF\cdot BCl_3$ | 148(2) | | [15] |

## EXPERIMENTAL

### Dimerisation of $CF_3N = CF_2$ (II)

500 mg (II) are condensed onto ca. 100 mg finely powdered dry CsF. After 24 h at room temperature the formation of $(CF_3)_2NCF{=}NCF_3$ (I) is complete. (I) and CsF are separated in vacuo. The purity of the product is checked by $^{19}F$-NMR spectroscopy at -25 °C in $SO_2$.

### Preparation of $[(CF_3)_2NCF{=}NHCF_3]^+AsF_6^-$

3 ml HF are condensed onto 200 mg (0.75 mmol) $(CF_3)_2NCF = NCF_3$ in a KEL-F reactor. 170 mg (1 mmol) $AsF_5$ are added in small portions. At intervals the reaction mixture is allowed to warm up from -196 °C to -40 °C and homogenized by stirring. When all $AsF_5$ is added the solution is stirred at -50 °C for ca. 3 h. At this temperature HF and unreacted starting material are removed in vacuo. The residue (IV) is a white hydrolyzable salt which is unstable at room temperature. The $^{19}F$-NMR spectra are recorded at -50 °C in HF acidified with $AsF_5$ and $CFCl_3$ as an external reference.

The single crystals for the X-ray analysis are prepared from anhydrous HF. At 0 °C 500 mg of (IV) are dissolved in 3 ml HF. The solution is cooled stepwise 0,5° at a time until crystals are formed. Diffraction data were collected at 160 K using a Nonius CAD-4 diffractometer, R = 0.085, 1089 observed reflections, 130 refined parameters. The IR spectra were recorded with a Perkin Elmer 580 B Spectrometer, the NMR spectra were recorded with either a Bruker WP 80 or a Bruker AM 300 Spectrometer. All chemical shifts are reported with reference to $CFCl_3$ as an external standard.

## ACKNOWLEDGEMENT

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