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# Solid- and gas-phase structures and spectroscopic and chemical properties of tris(pentafluorosulfanyl)amine, $N(SF_5)_3$, and bis(pentafluorosufanyl)aminyl radical, $\bullet N(SF_5)_2$

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ABSTRACT

Tris(pentafluorosulfanyl)amine, $N(SF_5)_3$, and the bis(pentafluorosulfanyl)aminyl radical, $\bullet N(SF_5)_2$, have been synthesized and characterized by gas electron diffraction, single crystal XRD, NMR, EPR, FT-IR, Raman, and UV–vis spectroscopy, and by their thermal decompositions. The amine possesses a planar molecular structure of $D_3$ symmetry with an unusually long N–S bond of 1.829(6) Å. The long N–S bonds are in accordance with the small Arrhenius activation barrier for the decay into $\bullet N(SF_5)_2$ and $\bullet SF_5$ radicals of 6.9 kcal $mol^{-1}$, and its half-life at room temperature is only 50 min. The aminyl radical possesses $C_2$ symmetry with N–S = 1.692(4) Å and S–N–S = 135.1(5)°, and its structure is similar to that of $FN(SF_5)_2$. This radical is much more stable than the amine (half-life at room temperature is 130 min). Dimerization and formation of the corresponding hydrazine, $(SF_5)_2NN(SF_5)_2$, was not observed, nor was the nitrene:$NSF_5$ or its isomer $FN{=}SF_4$.



## 1. Introduction

Structural, spectroscopic, and chemical properties of simple nitrogen molecules such as $NX_3$, $N_2X_4$, and radicals $\bullet NX_2$ with e.g. X = H, F, $CH_3$, $CF_3$ are of general interest. The parent and perfluorinated molecules are very different in their structures and chemical behaviour. While $NH_3$ and $N(CH_3)_3$ are basic with an XNX bond angle of 107.2(2)° [1] and 110.9(6)° [2], respectively, the stable amines $NF_3$ and $N(CF_3)_3$ are not basic at all and their XNX angles are 102.37(3)° [3] and 117.9(4)° [4], respectively. All mentioned hydrazines are quite stable, but the respective radicals are very reactive. For example, $\bullet N(CF_3)_2$ is postulated to be involved in many reactions, but it is not spectroscopically characterized, and $\bullet NF_2$ exists in equilibrium with its hydrazine $N_2F_4$ [5].

A great challenge since many years was the synthesis of an amine, hydrazine, and the aminyl radical containing the bulky $SF_5$ substituent. Doubts about the stability and existence of $N(SF_5)_3$ were raised, since the gas phase structure of $(SF_5)_2NF$ [6] possesses an S–N–S angle of 138.3(1.0)°, demonstrating large steric requirements of $SF_5$ groups, which make it unlikely to fit three such groups around nitrogen. In an attempt to synthesise tris(pentafluorosulfanyl)amine, $N(SF_5)_3$, by a photoreaction of $SF_5NCl_2$ with $SF_5Cl$, a colourless, sublimeable, crystalline solid was obtained [7]. Its $^{19}F$ NMR spectrum in $CCl_3F$ solution was difficult to simulate due to the possible $AB_4A'B_4'A''B_4''$ spin system with $\delta_A$ = 69.6 and $\delta_B$ = 88.5 ppm and $J_{AB}$ = 145 Hz for the new $SF_5$-compound. Unfortunately, from the $^{19}F$ NMR spectrum the number of $SF_5$ groups in the compound could not be determined. A similar $CCl_3F$ solution

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showed a temperature dependent 11-line EPR spectrum, consistent with the $\cdot N(SF_5)_2$ radical. From this observation, a chemical ionization mass spectrum with a predominate peak at 269 m/z $[(SF_5)_2NH^+]$, and from an elemental analysis, it was proposed that the new compound was the hydrazine $(SF_5)_2NN(SF_5)_2$ [7]. Its thermolysis product obtained at 0.1 mbar vapour pressure and 70 °C, trapped at liquid nitrogen, melts quickly on warming to a deep blue liquid at <−80 °C. This product was expected to contain the aminyl radical and possibly some undecomposed hydrazine. However, gas electron diffraction data of the vapour of this blue liquid at −55 °C could only be fit to a mixture of the aminyl radical and $S_2F_{10}$ [8,9] (see below). This mixture demonstrates that the colourless, sublimeable, crystalline solid obtained in the photoreaction (1) of $SF_5NCl_2$ with $SF_5Cl$ might indeed be the amine $N(SF_5)_3$, which thermally decomposes to a mixture of aminyl radical and $S_2F_{10}$ according to reaction (2). This was later confirmed by X-ray and gas electron diffraction (see below) of the product of the photoreaction (1) [10].

$$(SF_5)NCl_2 + 2\ SF_5Cl \xrightarrow{h\nu} N(SF_5)_3 + 2\ Cl_2 \qquad (1)$$

$$N(SF_5)_3 \xrightarrow{0.1 torr, 70^\circ C} \cdot N(SF_5)_2 + \cdot SF_5 \rightarrow \cdot N(SF_5)_2 + {}^1\!/\!_2\ S_2F_{10} \qquad (2)$$

Further support for the thermal decomposition of $N(SF_5)_3$ according to the first step in reaction (2) came from a matrix isolation study [11]. By low-pressure flash pyrolysis of $N(SF_5)_3$, highly diluted in Ar with subsequent quenching of the products in an Ar matrix at 15 K, the $\cdot SF_5$ radical was obtained together with the aminyl radical $\cdot N(SF_5)_2$ as by-product. In all experiments no sign for the existence of $(SF_5)_2NN(SF_5)_2$ was observed. In this contribution, we report in detail about the synthesis, molecular structures of $N(SF_5)_3$ (both solid and gas phases) and the radical $\cdot N(SF_5)_2$, and their chemical and spectroscopic properties. The structures of the aminyl radical and the amine are shown in Fig. 1.

## 2. Experimental section

*Caution! The compound $SF_5NCl_2$ is explosive and should be handled with appropriate safety precautions. Furthermore, $S_2F_{10}$ and $SF_5Cl$ are highly toxic, so one should only work with these compounds and their derivatives in a well-ventilated area or a leak-free environment such as a fume hood or vacuum system, respectively.*

### 2.1. General procedure and reagents

Volatile materials were manipulated in a glass vacuum line equipped with a capacitance pressure gauge (221 AHS-1000, MKS Baratron, Burlington, Massachusetts, USA) and three U-traps with PTFE valves (Young, London, U.K.). The vacuum line was connected to an IR cell (optical path length 20 cm, Si windows 0.5 mm thick), contained in the sample compartment of a Bruker Vector 25 FTIR spectrometer. The samples were purified by trap-to-trap condensation and stored in flame-sealed glass ampoules under liquid nitrogen in a long-term Dewar vessel. An ampoule was opened at the vacuum line, an appropriate amount was taken out, and then the ampoule was flame sealed again.

*Synthesis of $N(SF_5)_3$*: A 2-L glass bulb equipped with a water-cooled, low-pressure mercury lamp (TNN 15/32 Hanau Heraeus) was evacuated and filled with 25 mmol of $SF_5NCl_2$ and 70 mmol of $SF_5Cl$. The bulb was cooled with ice water and the photolysis started. At the beginning and after each hour a small sample of the gaseous reaction mixture was transferred into the IR cell (2 mbar). In this manner the decrease of the $SF_5Cl$ concentration could be followed. After about six hours, the photolysis was stopped, and the products were slowly directed through the three U-traps held at −50, −100, and −196 °C. The trap at −50 °C contained 2.6 g of pure $N(SF_5)_3$, and the other traps $SF_5NCl_2$, $S_2F_{10}$, $Cl_2$, and $SOF_4$. Yield ca. 30%. Single crystals of $N(SF_5)_3$ were grown by low-temperature sublimation.

The direct UV photolysis of the chloramine $(SF_5)_2NCl$ [6] led to an improved yield of $N(SF_5)_3$. A 1-L photolysis vessel fitted with a quartz, water-cooled immersion well was evacuated and flame dried with a torch. After the vessel had cooled to room temperature and subsequently to −196 °C, $(SF_5)_2NCl$ (4.07 g, 13.4 mmol) was condensed in. The vessel was closed and allowed to warm to room temperature, and then the cooling jacket of the immersion well was connected to a cold-water source. The low-pressure mercury lamp was then placed in the well and turned on. The chloramine was then irradiated for 3.5 h during which time crystals of $N(SF_5)_3$ were observed to have formed on the cold inner surface of the immersion well. The volatile materials were passed through a series of cold traps as described above giving $N(SF_5)_3$ (2.48 g, 6.3 mmol) in the −50 °C in 94% yield along with $Cl_2$ and $S_2F_{10}$ and some non-condensables (presumably $N_2$). Subsequent submissions of samples of $N(SF_5)_3$ sealed in fluorinated ethylene-propylene (FEP) tubes to Galibraith Laboratories, Inc. in Knoxville, Tennessee, USA gave satisfactory nitrogen and sulfur analyses for duplicate runs: Anal. calcd for $NS_3F_{15}$: N, 3.54; S, 24.34. Found: N, 3.57; S, 24.11.

*Synthesis of $\cdot N(SF_5)_2$:* For the synthesis of the $\cdot N(SF_5)_2$ radical, about one gram of the amine $N(SF_5)_3$ was condensed into a 100-mL glass bulb equipped with a Young valve. At the vacuum line, the bulb was slowly warmed up, and the $N(SF_5)_3$ vapour (<1 mbar) was passed through three U-traps held at +70, −50, and −196 °C. In the trap at −50 °C, the unreacted amine was recovered, and at −196 °C, a blue solid deposited. During the evaporation of the products by

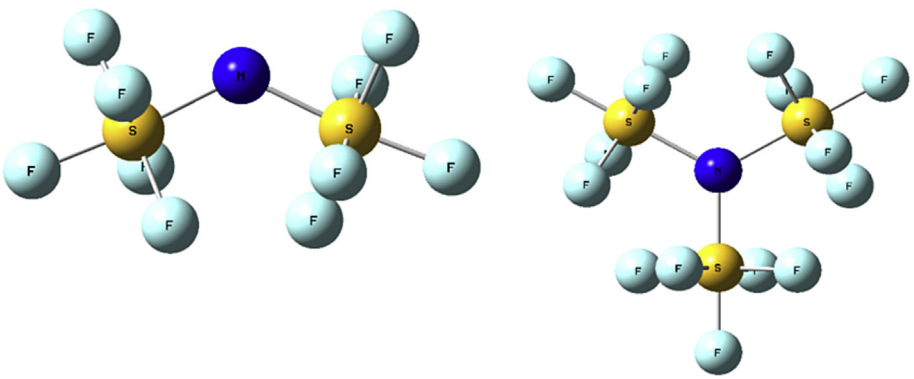


**Fig. 1.** Structures of $N(SF_5)_2$ and $N(SF_5)_3$.

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