Solid- and Gas-Phase Structures and Spectroscopic and Chemical Properties of Tris(pentafluorosulfanyl)amine, $\text{N}(\text{SF}_5)_3$, and Bis(pentafluorosulfanyl)aminyl Radical, $\cdot\text{N}(\text{SF}_5)_2$.

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GRAPHICAL ABSTRACT

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ABSTRACT

Tris(pentafluorosulfanyl)amine, $\text{N}(\text{SF}_5)_3$, and the bis(pentafluorosulfanyl)aminyl radical, $\cdot\text{N}(\text{SF}_5)_2$, 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 $\cdot\text{N}(\text{SF}_5)_2$ and $\cdot\text{SF}_5$ radicals of 6.9 kcal mol⁻¹, and its half-life at room temperature is only 50 minutes. 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 $\text{FN}(\text{SF}_5)_2$. This radical is much more stable than the amine (half-life at room temperature is 130 minutes). Dimerization and formation of the corresponding hydrazine, $(\text{SF}_5)_2\text{NN}(\text{SF}_5)_2$, was not observed, nor was the nitrene $:\text{NSF}_5$ or its isomer $\text{FN}=\text{SF}_4$.

Introduction

Structural, spectroscopic, and chemical properties of simple nitrogen molecules such as NX_3 , N_2X_4 , and radicals $\cdot\text{NX}_2$ with e.g. $\text{X} = \text{H}, \text{F}, \text{CH}_3, \text{CF}_3$ are of general interest. The parent and perfluorinated molecules are very different in their structures and chemical behaviour. While NH_3 and $\text{N}(\text{CH}_3)_3$ are basic with an XNX bond angle of $107.2(2)^\circ$ [1] and $110.9(6)^\circ$ [2], respectively, the stable amines NF_3 and $\text{N}(\text{CF}_3)_3$ are not basic at all and their XNX angles are $102.37(3)^\circ$ [3] and $117.9(4)^\circ$ [4], respectively. All mentioned hydrazines are quite stable, but the respective radicals are very reactive. For example, $\cdot\text{N}(\text{CF}_3)_2$ is postulated to be involved in many reactions, but it is not spectroscopically characterized, and $\cdot\text{NF}_2$ 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 $\text{N}(\text{SF}_5)_3$ were raised, since the gas phase structure of $(\text{SF}_5)_2\text{NF}$ [6] possesses an S-N-S angle of $138.3(1.0)^\circ$, 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, $\text{N}(\text{SF}_5)_3$, 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 $\text{AB}_4\text{A}'\text{B}_4'\text{A}''\text{B}_4''$ spin system with $\delta_{\text{A}} = 69.6$ and $\delta_{\text{B}} = 88.5$ ppm and $J_{\text{AB}} = 145$ 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 showed a temperature dependent 11-line EPR spectrum, consistent with the $\cdot\text{N}(\text{SF}_5)_2$ radical. From this observation, a chemical ionization mass spectrum with a predominate peak at 269 m/z [$(\text{SF}_5)_2\text{NH}^+$], and from an elemental analysis. it was proposed that the new compound was the hydrazine $(\text{SF}_5)_2\text{NN}(\text{SF}_5)_2$ [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 $< -80^\circ\text{C}$. 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 S₂F₁₀ [8,9] (see below). This mixture demonstrates that the colourless, sublimeable, crystalline solid obtained in the photoreaction (1) of SF₅NCl₂ with SF₅Cl might indeed be the amine N(SF₅)₃, which thermally decomposes to a mixture of aminyl radical and S₂F₁₀ 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].

Further support for the thermal decomposition of N(SF₅)₃ according to the first step in reaction (2) came from a matrix isolation study [11]. By low-pressure flash pyrolysis of N(SF₅)₃, highly diluted in Ar with subsequent quenching of the products in an Ar matrix at 15 K, the ·SF₅ radical was obtained together with the aminyl radical ·N(SF₅)₂ as by-product. In all experiments no sign for the existence of (SF₅)₂NN(SF₅)₂ was observed. In this contribution, we report in detail about the synthesis, molecular structures of N(SF₅)₃ (both solid and gas phases) and the radical ·N(SF₅)₂, and their chemical and spectroscopic properties. The structures of the aminyl radical and the amine are shown in Figure 1.

Figure 1

Experimental Section and Computational Details

Caution! The compound SF₅NCl₂ is explosive and should be handled with appropriate safety precautions. Furthermore, S₂F₁₀ and SF₅Cl 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.

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 $\text{N}(\text{SF}_5)_3$ 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 $\text{N}(\text{SF}_5)_3$ (2.48 g, 6.3 mmol) in the $-50\text{ }^\circ\text{C}$ in 94% yield along with Cl_2 and S_2F_{10} and some noncondensables (presumably N_2). Subsequent submissions of samples of $\text{N}(\text{SF}_5)_3$ 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 $\cdot\text{N}(\text{SF}_5)_2$: For the synthesis of the $\cdot\text{N}(\text{SF}_5)_2$ radical, about one gram of the amine $\text{N}(\text{SF}_5)_3$ 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 $\text{N}(\text{SF}_5)_3$ vapour ($< 1\text{ mbar}$) was passed through three U-traps held at $+70$, -50 , and $-196\text{ }^\circ\text{C}$. In the trap at $-50\text{ }^\circ\text{C}$, the unreacted amine was recovered, and at $-196\text{ }^\circ\text{C}$, a blue solid deposited. During the evaporation of the products by slowly warming the $-196\text{ }^\circ\text{C}$ trap, the most volatile materials SF_6 , SF_4 , SOF_2 , and some S_2F_{10} were observed in the IR spectra and discarded. The less volatile blue fraction contained $\cdot\text{N}(\text{SF}_5)_2$, S_2F_{10} , and little $(\text{SF}_5)_2\text{NH}$, which are difficult to separate due to their similar vapour pressures.

Instrumentation.

(I) Single-Crystal X-ray Diffraction (XRD). Suitable crystals of $\text{N}(\text{SF}_5)_3$ were obtained and sealed under nitrogen in thin-walled glass capillaries. The X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer by the $\theta - 2\theta$ scan technique at 298 K [12]. Several crystals had to be examined before one would last long enough for a full data set to be collected. Final lattice parameters as determined by least-squares refinement of 24 reflections ($2\theta > 35^\circ$) accurately centered on the diffractometer are given in Table S1. The space group (either $\overline{\text{R}}3\text{m}$ or

$R\bar{3}c$) was shown to be the latter by successful refinement. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Calculations were carried out on an IBM-3081D computer with the SHELX system of computer programs [13]. Neutral-atom scattering for N, F, and S were taken from the compilation of Cromer and Waber [14]. The structure was solved by the straightforward application of the direct methods program MULTAN [15], which gave the location of the sulfur atom. All of the other atoms were located from a subsequent difference Fourier map. All atoms were refined with the use of anisotropic thermal parameters. The following reflections were deleted from the data set due to a large extinction problem ($h\ k\ l$): 0 3 0, -2 4 0, -2 7 0, 0 1 2, -3 7 2, -2 7 3, -1 2 0, -3 6 0, -2 3 1, and -4 4 4. Refinements using least-squares methods led to a final $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.476$, $R_w = \Sigma [w(F_o - F_c)^2 / w(F_o)^2]^{1/2} = 0.0533$. The weighting scheme was based on unit weights, and systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. A final difference Fourier showed no feature greater than $0.1\ e^{-\text{\AA}^{-3}}$. Important bond distances and angles as well as nonbonded intramolecular and intermolecular contact distances under $3.10\ \text{\AA}$ are either discussed in the text below, where appropriate, or are given in Tables S2 and S3, respectively.

(II) Gas-phase Electron Diffraction. Scattering intensities for the products of thermolysis (2) and photoreaction (1) were recorded at 25 cm and 50 cm camera distances and accelerating voltage of about 60 kV with a Balzers KD-G2 Gas Diffractograph [16]. Two Kodak Electron Image plates for each camera distance were evaluated by standard methods [17] and scattering intensities in the s ranges of $2 - 18$ and $8 - 35\ \text{\AA}^{-1}$ [$s = (4\pi/\lambda) \sin \delta/2$, where λ = electron wavelength and δ = scattering angle] were used in the structure analyses (Figures S1 and S2). For both compounds r_a structures were determined and no vibrational corrections were used.

(III) Vibrational Spectroscopy. Temperature-dependent IR spectra of gaseous samples in the range 287 to 326 K were recorded on a Bruker IFS 66v FTIR spectrometer employing a resolution of 2 cm^{-1} using a KBr beam splitter and MCT detector. A double-walled gas cell with an optical path length of 20 cm was used, equipped with silicon windows (0.5 mm thick), a pressure gauge (221 AHS-100, MKS Baratron), and a Pt-100 temperature sensor. The cell was placed inside the evacuated sample chamber of the spectrometer. The temperature was controlled by adjusting the flow of a cold stream of nitrogen gas. For each temperature, a new background was measured, and the cell was filled with a new sample (ca. 1 mbar) from the $\text{N}(\text{SF}_5)_3$ reservoir.

Raman spectra were recorded on a Bruker-Equinox 55 FRA 106/S FT-Raman spectrometer using a 1064 nm Nd:YAG laser (200 mW). Samples of $\text{N}(\text{SF}_5)_3$ or $\text{N}(\text{SF}_5)_2$ were condensed in high vacuum onto a stainless steel finger cooled with liquid nitrogen, and spectra of the solid spots were recorded at a resolution of 1 cm^{-1} and 100 added scans.

(IV) NMR Spectroscopy. ^{19}F NMR spectra (376.5 MHz) were measured on a Bruker Avance 400 spectrometer at room temperature in flame-sealed glass tubes (o.d. 4.0 mm, i.d. 3.0 mm, length 15 cm) placed in thin-walled 5-mm NMR tubes with a thin film of C_6D_6 as external lock. The chemical shifts were referenced to internal CCl_3F . The ^{19}F NMR spectrum of $\text{N}(\text{SF}_5)_3$ depicted in Figure S3 is consistent with an $\text{AB}_4\text{A}'\text{B}_4'\text{A}''\text{B}_4''$ spin system with $\delta_{\text{A}} = 87.8$ (4F), $\delta_{\text{B}} = 69.1$ (1F) ppm, and $J_{\text{FF}} = 142$ Hz as in the first report [7]. G. Hägele of the Heinrich-Heine-Universität Düsseldorf attempted to simulate the ^{19}F NMR spectrum of $\text{N}(\text{SF}_5)_3$ without success [18]; however, the spectrum was found to be more complicated than a $\text{AB}_4\text{A}'\text{B}_4'$ spin system, such as those seen in the ^{19}F NMR spectra of geminyl SF_5 -amines [6]. In the product mixture, obtained from the thermolysis of $\text{N}(\text{SF}_5)_3$, signals of S_2F_{10} and $(\text{SF}_5)_2\text{NH}$ were also observed.

(V) EPR Spectroscopy. As indicated in the initial EPR study of the $\cdot\text{N}(\text{SF}_5)_2$ radical [7], the magnitude of the hyperfine coupling constants indicated that the aminyl radical was a π -type radical. This was also confirmed then with INDO calculations as well as with the current calculations (see below). During the initial EPR experiments, the intensity of the radical signal was observed to increase with increasing temperature. A more thorough investigation revealed that this phenomenon was reversible in the temperature range of 270 to 317 K for solutions of approximately 10^{-3} M of $\text{N}(\text{SF}_5)_3$ in CCl_3F . Thus, in solution, the first part of equation (2) is reversible during this temperature range, while at temperatures below 270 K, the concentration of the aminyl radical signal is too low to be measured, and at temperatures above 317 K, the reaction becomes irreversible. It is obvious that $\cdot\text{SF}_5$ radicals should also be present; however, this radical was not detected in our EPR spectra probably due to its fast combination to give S_2F_{10} . If the concentration of $\cdot\text{SF}_5$ radicals is assumed to be in the same order of magnitude as that of the aminyl radicals, then the equilibrium equation K_c can be expressed as shown in equation (3).

$$K_c = [\cdot\text{N}(\text{SF}_5)_2][\cdot\text{SF}_5]/[\text{N}(\text{SF}_5)_3] \quad (3)$$

Thus, a variable temperature EPR study was carried out on a Varian E-12 spectrometer in hopes of obtaining an estimate of the bond dissociation energy of the N-S bond in $\text{N}(\text{SF}_5)_3$. The microwave frequency was read with a Hewlett-Packard Model 5246L frequency counter, and the magnetic field was measured by a Bruker model ER 035M NMR gaussmeter. Hyperfine coupling constants were obtained by measuring the distance between peaks, and spectral integrations were carried out by cutting out and weighing the area under each peak recorded on high-quality weighing paper. Each integration was relative to a Cr^{3+} standard [19]. The number of absolute spins, N_x , in the sample at each temperature was calculated using the methodology outlined in a monograph by Wertz and Bolton [20]. Then a plot of $\ln K_c$ versus $1/T$ (K) (see Figure S4) gave us an approach

for assessing the N-S bond dissociation energy from the slope of the linear least squares fit of the data as well as the Gibb's free energy and the entropy change.

(VI) UV/Vis Spectroscopy. UV/Vis spectra of gaseous samples in a glass cell (optical path length 10 cm) equipped with quartz windows (Suprasil, Heraeus, Hanau, Germany) were recorded on a Perkin-Elmer Lambda 900 spectrometer in the spectral range of 200 to 1100 nm. Pressures were measured with a capacitance manometer (MKS Baratron, 100 mbar absolute).

(VII) Vapour Pressure. The vapour pressure measurements of solid $\text{N}(\text{SF}_5)_3$ (m.p. 51 °C) were performed with a small sample in a container connected to a vacuum line with a total volume of 50 mL, equipped with a calibrated capacitance manometer (MKS Baratron, 10 mbar absolute). In the temperature range of -30 to 24 °C, the vapour-pressure curve of the solid is shown in Figure S5, where a plot of $\log P$ versus $1000/T$ (K) gives linear least squares fit of $\log p = -2695.5/T + 10.169$ (P in mbar, T in K). Molecular weight determination by vapour density gave a value of 389 g/mol (versus a theoretical value of 395.17 for NF_{15}S_3), which is understandably low due to the instability of $\text{N}(\text{SF}_5)_3$ in the gas phase (see below), but nevertheless much closer to the expected value for the tris-amine rather than the corresponding tetrakis-hydrazine.

(VIII) Methods for Calculations. Molecular structures and vibrational frequencies of the amine and aminyl radical were calculated with HF, MP2, and B3LYP methods and different basis sets using the Gaussian 98 program system [21]. Details of computational methods and results are given below and in Tables 1 and 2. Only unrestricted calculations were performed for the radical.

Results and Discussion

Synthesis and properties of $\text{N}(\text{SF}_5)_3$ and $\cdot\text{N}(\text{SF}_5)_2$.

Tris(pentafluorosulfanyl)amine is prepared through photolysis of 1:3 molar mixtures of the gases SF_5NCl_2 and SF_5Cl at 0 °C. According to the UV spectra depicted in Figure 2, SF_5Cl is a good absorber of the 254 nm radiation from the low-pressure mercury lamp. The reactant SF_5Cl is

Figure 2

photodissociated into $\cdot\text{SF}_5$ and $\cdot\text{Cl}$, the Cl atom abstracts chlorine from SF_5NCl_2 , and the resulting SF_5NCl radical combines with $\cdot\text{SF}_5$ to form $(\text{SF}_5)_2\text{NCl}$. The same reaction circle is repeated again, and $\text{N}(\text{SF}_5)_3$ is finally formed. In a side reaction, $\cdot\text{SF}_5$ radicals give S_2F_{10} , and therefore an excess of SF_5Cl is needed. The amine also absorbs at 254 nm but it escapes from photolysis by forming solid $\text{N}(\text{SF}_5)_3$ with low vapour pressure (2 mbar) on the cold glass walls of the photoreactor. The product is trapped in dynamic vacuum at -50 °C. As mentioned in the Experimental section, $\text{N}(\text{SF}_5)_3$ can be prepared in higher yield from the direct photolysis of the chloramine $(\text{SF}_5)_2\text{NCl}$.

$\text{N}(\text{SF}_5)_3$ is a colourless solid with a vapour pressure at room temperature of about 10 mbar. It melts at 51 °C without noticeable decomposition. In the gas phase, pure $\text{N}(\text{SF}_5)_3$ decomposes at room temperature according to a first-order rate law with a half-life of 50 min. In the IR spectrum simultaneous formation of S_2F_{10} and a little $\cdot\text{N}(\text{SF}_5)_2$, as well as formation of N_2 as non-condensable gas, was noted. In Figure S6, changes in the IR spectrum are shown over time, and in Figure S7, decay of the band at 787 cm^{-1} of $\text{N}(\text{SF}_5)_3$ is depicted. In CCl_3F solution, the amine is much more stable (20% decomposition within 3 weeks), and depletion of $\text{N}(\text{SF}_5)_3$ with simultaneous formation of S_2F_{10} was observed by ^{19}F NMR spectroscopy. The rate-determining step of the decomposition in the gas phase seems to be dissociation according to equation (2) followed by a fast recombination of $\cdot\text{SF}_5$ to S_2F_{10} . The aminyl radical $\cdot\text{N}(\text{SF}_5)_2$ was found to deplete in the gas phase slower than the amine (half-life at room temperature 130 min., nearly first

order) according to equation (4) without detectable amounts of other intermediates as shown in Figure 3.

Figure 3

Figure 4 shows the UV/Vis spectrum of the radical $\cdot\text{N}(\text{SF}_5)_2$, and the decrease of the band intensity at $\lambda_{\text{max}} = 780 \text{ nm}$ is depicted in Figure S8. The decomposition rate constants of $\text{N}(\text{SF}_5)_3$ according

Figure 4

to equation (2) were determined in the temperature range of 287 to 326 K, and from the Arrhenius plot an activation barrier of $6.9 \text{ kcal mol}^{-1}$ has been obtained (see Figure 5).

Figure 5

The free radical $\cdot\text{N}(\text{SF}_5)_2$ is formed in preparative scale by thermal decomposition of the amine $\text{N}(\text{SF}_5)_3$ at low pressures ($< 1 \text{ mbar}$) and temperatures between 70 and 100 °C. Under these conditions the radical survives because it is thermally more stable than the amine (see above), and at the same time the recombination of $\cdot\text{SF}_5$ radicals to S_2F_{10} compete with their disproportionation into $\text{SF}_6 + \text{SF}_4$. The isolation of the aminyl radical from the product mixture was found to be difficult, because the by-products S_2F_{10} and $(\text{SF}_5)_2\text{NH}$ have similar vapour pressure. Characteristic of the radical is its blue colour, which does not vanish (by dimerization) even in the liquid state at low temperatures ($< -80 \text{ °C}$). Further thermal decay of the radical into the possible nitrene $:\text{NSF}_5$

or its isomer SF_4NF has not been observed. However, during the thermal decay of the $\cdot\text{N}(\text{SF}_5)_2$ radical in the gas phase, it scavenges $\cdot\text{SF}_5$ radicals to reform the amine.

From the aforementioned EPR study, K_c was calculated to be $3 (\pm 5) \times 10^{-5}$ M at 300 K, and from the equation $\Delta G = -RT \ln K_c$, the free energy change related to the fission of the N-S bond can be calculated to be $6.2 (\pm 5)$ kcal mol $^{-1}$. The entropy change associated with the dissociation of $\text{N}(\text{SF}_5)_3$ was calculated to be $\Delta S = (\Delta H - \Delta G)/T = 84$ cal K $^{-1}$. The enthalpy change or ΔH was obtained from the slope of a plot of $\ln K_c$ versus $1/T$ (K), which gave a value of $31.7 (\pm 0.7)$ kcal mol $^{-1}$ for the bond dissociation energy of the N-S bond in $\text{N}(\text{SF}_5)_3$. The low N-S bond energy is associated with both the large steric bulk and the strong electron withdrawing power of the highly electronegative SF_5 groups. A previous correlation of S-N bond energies to bond distances and bond order (i.e., 59 kcal mol $^{-1}$ for a S-N single bond of 1.67 to 1.69 Å and 80 kcal mol $^{-1}$ for a S-N double bond of 1.58 Å) [22] would certainly be indicative of a highly elongated N-S bond in $\text{N}(\text{SF}_5)_3$, as will be seen below.

Gas Phase Structure of the $\cdot\text{N}(\text{SF}_5)_2$ Radical.

To obtain the gas phase structure of the aminyl radical $\cdot\text{N}(\text{SF}_5)_2$, the vapour of the aforementioned blue liquid product at -55 °C (vapour pressure of about 10 mbar) was studied by the gas electron diffraction (GED). The experimental radial distribution function (RDF) (Figure 6), derived from the GED intensities, possesses besides the expected peaks for the aminyl radical an additional peak around 2.7 Å, which could not be reproduced with any structure of the radical. Fortunately, at the same time, the gas phase structure of S_2F_{10} was being restudied in our laboratory [8]. The RDF of this molecule possesses a strong peak near 2.7 Å, corresponding to $\text{S}\cdots\text{F}$ distances between S and the equatorial fluorine atoms of the neighbouring SF_5 group. The RDF's of the radical and S_2F_{10} are rather similar (see Figure 6). The strongest peak around 1.6 Å corresponds to S-F bonded distances, with a smaller contribution of S-N distances in the case of the radical. The second peak

Figure 6

around 2.2 Å corresponds mainly to F··F distances within the SF₅ groups with smaller contributions of N··F distances in the radical and of the S–S bond distance [2.274 (5) Å] in the case of S₂F₁₀. The peak around 2.7 Å occurs only in the RDF of S₂F₁₀. With a mixture of aminyl radical and S₂F₁₀ the experimental scattering intensities and radial distribution curve could be fitted very well (see difference curve). In the least squares analyses, the geometric parameters and vibrational amplitudes of S₂F₁₀ were fixed to the values derived in a previous experiment [8].

The structure of the aminyl radical is assumed to possess *C*₂ symmetry with local *C*_{4v} symmetry for the SF₅ groups and five geometric parameters, namely the N–S and (S–F)_{mean} bond distances, the S–N–S and (F_{eq}–S–F_{ax})_{mean} bond angles, and the torsional angle around the N–S bonds. Furthermore, the ratio of the two compounds and seven vibrational amplitudes were refined simultaneously. The results of the least squares analysis with R = 3.8% are listed in Table 1 (geometric parameters) together with values predicted by different quantum chemical calculations, and the vibrational amplitudes are given in Table S4. The refined contribution of the aminyl radical [51(8) %] does not correspond to the stoichiometric ratio of reaction (2). The higher contribution of S₂F₁₀ is due to its slightly higher vapour pressure at -55 °C. A possible small contribution of (SF₅)₂NH in the thermolysis product could not be observed, since its structure is very similar to that of the radical (see below) and the H atom contributes very little to the scattering intensities.

The gas phase structure of the aminyl radical is similar to that of (SF₅)₂NF [N–S = 1.685(5) Å, <S–N–S = 138.3(10)°] and (SF₅)₂NH [N–S = 1.679(7) Å, <S–N–S = 134.8(10)°] [6]. Its structure is poorly reproduced by B3LYP and MP2 quantum chemical calculations with large basis sets, but

considerable better with the unrestricted HF method with small basis sets. The N-S bond length is predicted too long by 0.06 to 0.10 Å and the S-N-S angle too small by 8 to 10°. Good agreement is obtained only with the low-level HF/3-21G(d) method. An examination of the Mulliken population analysis at this level of theory also confirms that $\cdot\text{N}(\text{SF}_5)_2$ is a π -type radical, as vast majority of the lone electron density (> 98%) is in a *p*-orbital perpendicular to the molecular plane. The failure of higher-level calculations is even stronger for SF_5NF_2 . Here MP2 and B3LYP methods with cc-pVTZ basis sets predict the S-N bonds too long by 0.17 and 0.22 Å, respectively, compared to the experimental value of 1.697(4) Å [23].

Table 1

Molecular Structure of $\text{N}(\text{SF}_5)_3$.

The geometric structure of the amine was determined in the gas phase by gas electron diffraction (GED) and in the crystalline phase by X-ray diffraction. The GED intensities of the vapour were recorded at 20 °C (sublimation pressure about 10 mbar). The RDF is shown in Figure 7. In the analysis of the intensities C_3 overall symmetry and C_{4v} local symmetry for the SF_5 groups was assumed. Attempts to refine separate values for angles between axial and equatorial fluorine atoms as derived from the crystal structure and from quantum chemical calculations resulted in experimental uncertainties, which are larger than the differences between these angles. Similarly, equatorial and axial S-F bond distances could not be refined separately. Five geometric parameters and 11 vibrational amplitudes were refined simultaneously. The geometric parameters derived by the least squares refinement (agreement factor $R = 4.2\%$) are listed in Table 2, and the vibrational amplitudes are given in Table S5.

Figure 7

Table 2

The solid-phase molecular structure of $\text{N}(\text{SF}_5)_3$ is shown in Figure 8, where the planarity of the heavy atom skeleton and 120° S-N-S bond angles are imposed by the requirements of the trigonal space group. Other primary results of the X-ray study are included in Table 2 along with the

Figure 8

corresponding results of quantum chemical calculations. Meanwhile the summary of XRD crystal data and data collection conditions are shown in Table S1; the interatomic bond distances and angles are given in Table S2; the nonbonded intra- and intermolecular distances less than $3.1 \text{ \AA}$ and the torsion angles are given in Table S3; and two views of the unit cell are shown in Figure S9.

The geometric parameters in the gas phase and in the crystal agree within their experimental uncertainties. Both methods result in a planar NS_3 skeleton. The slight deviation of the gas phase structure from planarity [$\text{S-N-S} = 119.7(2)^\circ$] is due to vibrational effects (shrinkage effect). The MP2/cc-p-VTZ method reproduces the N–S bond length very well and predicts S–F bonds slightly too long. The B3LYP/6-311++G(df) method predicts all bonds too long by 0.04 to $0.05 \text{ \AA}$. All quantum chemical calculations reproduce the planarity of the NS_3 skeleton correctly. Again, examination of the Mulliken population analysis reveals that the vast majority of the lone-pair electron density remains in a p -orbital perpendicular to the molecular plane with some $p\pi$ - $p\pi$ back-bonding between nitrogen and sulfur.

The experimental structure provides an explanation for the stability of $\text{N}(\text{SF}_5)_3$, despite the high steric requirements of SF_5 groups. The N–S bonds in $\text{N}(\text{SF}_5)_3$ [$1.829(6)$ in the gas phase vs. $1.827(3)$ in the solid phase] are 0.14 to $0.15 \text{ \AA}$ longer than such bonds in $(\text{SF}_5)_2\text{NH}$ ($1.679(7) \text{ \AA}$) [6], $(\text{SF}_5)_2\text{NF}$ ($1.685(5) \text{ \AA}$) [6], and in the $\cdot\text{N}(\text{SF}_5)_2$ radical ($1.692(4) \text{ \AA}$). Due to these long N-S bonds, the S...S contacts in the amine with three SF_5 groups and S–N–S angles of 120° ($3.16 \text{ \AA}$) are

even slightly longer than those in the amines with two SF_5 groups (3.11 to 3.15 Å) and S–N–S angles between 135 and 138°. Another way to say this is to look at the nonbonded F··F contact distances of equatorial fluorine atoms on neighbouring SF_5 groups within an $\text{N}(\text{SF}_5)_3$ molecule. When compared to these contact distances in $(\text{SF}_5)_2\text{O}$ [24], S_2F_{10} [8,9], $(\text{SF}_5)_2\text{NF}$ [6], and $(\text{SF}_5)_2\text{CF}_2$ [25] that range from 2.40 to 2.55 Å, values of 2.35 and 2.40 Å are found in $\text{N}(\text{SF}_5)_3$. Thus, as much as anything, regardless of the S–N–S bond angles in these compounds, it is the nonbonded F··F contact distances of equatorial fluorine atoms on neighbouring SF_5 groups within the molecule that help control the central atom-sulfur bond distances along with perhaps polar effects to some degree. Furthermore, unlike other trigeminal amines such as $\text{N}(\text{SiH}_3)_3$ [26] and $\text{N}(\text{SCF}_3)_3$ [27] where the substituent atom-nitrogen bond distances have been shortened, the sulfur-nitrogen bond distances in $\text{N}(\text{SF}_5)_3$ have been elongated.

Vibrational Spectroscopy of $\text{N}(\text{SF}_5)_3$ and $\cdot\text{N}(\text{SF}_5)_2$.

The IR (gas phase) and Raman (solid) spectra of $\text{N}(\text{SF}_5)_3$ are depicted in Figure 9, and the IR (gas phase) spectrum of $\cdot\text{N}(\text{SF}_5)_2$ is shown in Figure 10. The observed band positions and band intensities are listed in Table 3 and 4, respectively, and are compared with the calculated harmonic frequencies and intensities at the B3LYP/6-311+G(d) level of theory.

Figure 9

Figure 10

According to the structural determination and quantum chemical calculations, the free $\text{N}(\text{SF}_5)_3$ molecule adopts D_3 symmetry with a planar NS_3 skeleton, and the three SF_5 groups rotated at the same extend out of the mirror plane. Therefore, the irreducible representation of the 34 fundamental vibrations and their activities follows equation (5):

$$\Gamma_{\text{vib}} = 8 A_1(\text{Ra}) + 9 A_2(\text{IR}) + 17 E(\text{IR}, \text{Ra}) \quad (5)$$

Of these possible 34 fundamentals, 16 have been observed. In the gas phase some IR bands overlap, but in matrix they are separated. The missing bands are either too weak for detection or outside the range of our spectrometer. As can be seen in Table 3, the agreement between experimental and calculated band positions and intensities are reasonable. The 12 bands at highest energy are assigned to the stretching modes, and their approximate descriptions, presented in Table 3, are based on the calculated displacement vectors of the 19 atoms.

According to the structural determination and quantum chemical calculations, the free $\cdot\text{N}(\text{SF}_5)_2$ radical adopts C_2 symmetry. Therefore, the irreducible representation of its 33 fundamental vibrations and their activities follows equation (6):

$$\Gamma_{\text{vib}} = 17 A(\text{IR}, \text{Ra}) + 16 B(\text{IR}, \text{Ra}) \quad (6)$$

Due to the difficulties in isolation of the pure $\cdot\text{N}(\text{SF}_5)_2$ radical, less complete data (see Table 4) exist in comparison to those of $\text{N}(\text{SF}_5)_3$. However, additional IR data for $\text{N}(\text{SF}_5)_3$ and $\cdot\text{N}(\text{SF}_5)_2$ were obtained from matrix isolation experiments. The low-pressure, flash pyrolysis of $\text{N}(\text{SF}_5)_3$, highly diluted in Ar, with subsequent quenching of the products in a matrix at 15 K resulted in an equal molar mixture of $\cdot\text{N}(\text{SF}_5)_2$ and $\cdot\text{SF}_5$ radicals. Because the band positions of $\cdot\text{SF}_5$ and $\text{N}(\text{SF}_5)_3$ are known, the bands of the new aminyl radical are easily assigned.

For both $\cdot\text{N}(\text{SF}_5)_2$ and $\text{N}(\text{SF}_5)_3$ no definitively characteristic vibrations exists, and furthermore, the vibrations are strongly mixed. For the most part, this limits the potential value in being able to compare the vibrational frequencies of the N-S stretching frequencies and corresponding force constants in $\cdot\text{N}(\text{SF}_5)_2$ and $\text{N}(\text{SF}_5)_3$ to those in other nitrogen-sulfur compounds where correlations

to bond distances, etc. have been made [28,29]. Nevertheless the IR spectra are valuable for their identification and purity check.

Table 3

Table 4

Conclusions

In the first instance it could not be decided whether the product of the photolytic reaction of $(\text{SF}_5)_2\text{NCl}$ and SF_5Cl , a white crystalline solid with high sublimation pressure, was the amine $\text{N}(\text{SF}_5)_3$ or the hydrazine $(\text{SF}_5)_2\text{N}-\text{N}(\text{SF}_5)_2$. The high steric requirements of SF_5 groups, observed in the gas phase structure of $(\text{SF}_5)_2\text{NF}$ with $\text{S}-\text{N}-\text{S} = 138.3(1.0)^\circ$, made it unlikely that three SF_5 groups would fit around a N atom. The formation of the $\cdot\text{N}(\text{SF}_5)_2$ radical, in CCl_3F solutions and upon thermolysis and the first elemental analysis, which later turned out to be wrong, initially indicated that the photolysis product was the hydrazine [7]. However, a gas electron diffraction study of the thermolysis products that resulted in a mixture of the radical and S_2F_{10} demonstrated that the white solid might be the amine. This was then confirmed by gas electron and X-ray diffraction structural determinations. The amine $\text{N}(\text{SF}_5)_3$ possesses much longer N-S bonds than $(\text{SF}_5)_2\text{NF}$ and the aminyl radical, which allow the arrangement of three SF_5 groups around N and also explain its easy thermal decomposition into aminyl and SF_5 radicals. The later radical recombines into S_2F_{10} in the liquid state. Due to the high steric requirements of the SF_5 groups, the NS_3 skeleton is perfectly planar. Planar or nearly planar NC_3 skeletons have also been observed in gas phase structures of triisopropylamine, $\text{N}[\text{CH}(\text{CH}_3)_2]_3$ $\{\text{C}-\text{N}-\text{C} = 119.2(3)^\circ$ [30]}, perfluorotriethylamine, $\text{N}(\text{CF}_2\text{CF}_3)_3$ $\{\text{C}-\text{N}-\text{C} = 119.3(4)^\circ$ [31]}, and perfluorotripropylamine, $\text{N}(\text{CF}_2\text{CF}_2\text{CF}_3)_3$ $\{\text{C}-\text{N}-\text{C} = 120.0(2)^\circ$ [32]}.

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Table 1. $\cdot\text{N}(\text{SF}_5)_2$: Molecular structure from GED and quantum chemical calculations.

Parameter	GED ^a	HF/ 3-21G(d)	B3LYP/ 6-311++G(df)	MP2/ cc-pVTZ
N-S	1.692(4)	1.700	1.795	1.747
(S-F) _{mean}	1.561(2)	1.559	1.618	1.580
S-N-S	135.1(5)	131.5	125.3	126.8
(F _{ax} -S-F _{eq}) _{mean}	88.8(3)	89.5	89.5	89.5
τ ^b	30.8(4)	25.1	24.5	24.5

^a r_a values with 3σ uncertainties (σ = standard deviation). ^b Torsional angle around S-N bonds; $\tau = 0^\circ$ corresponds to the orientation with two equatorial fluorine atoms perpendicular to the S-N-S plane.

Table 2. $\text{N}(\text{SF}_5)_3$: Molecular structure from GED, X-ray diffraction, and quantum chemical calculations.

Parameter	GED ^a	X-ray	B3LYP/ 6-311++G(2df)	MP2/ cc-pVTZ
N-S	1.829(6)	1.827(3)	1.871	1.835
S-F _{eq}	1.561(2) ^b	1.555(4)	1.608	1.573
S-F _{ax}		1.570(7)	1.624	1.588
S-N-S	119.7(2)	120.0	120.0	120.0
F _{ax} -S-F _{eq}	88.6(3) ^b	87.6(2)/89.0(2)	88.2 / 88.7	88.0 / 88.7
τ ^c	27.2(10)	26.7(8)	27.1	27.1

^a r_a values with 3σ uncertainties (σ = standard deviation). ^b mean value. ^c Torsional angle around S-N bonds; $\tau = 0^\circ$ corresponds to the orientation with two equatorial fluorine atoms perpendicular to the plane of the sulfur atoms.

Table 3. Calculated and observed vibrational band positions (cm^{-1}) and band intensities of $\text{N}(\text{SF}_5)_3$ (D_3 symmetry).

IR (gas phase) ^a	IR (Ne matrix)	Raman (solid) ^a	calculated ($I_{\text{IR}}/I_{\text{Ra}}$) ^b	Sym	Approx. descrip. of modes ^c
989 vs	985	988 w	990 (982)[6]	E	$\nu_{\text{as}}(eq\text{-SF}_4)$ o.o.p.
966 vs	958		977 (799)[0]	A_2	$\nu_{\text{as}}(eq\text{-SF}_4)$ i.p.
909 w	905	892 w	923 (18)[3]	E	$\nu_{\text{as}}(eq\text{-SF}_4)$ o.o.p.
891 m	889		897 (17)[0]	A_2	$\nu_{\text{as}}(eq\text{-SF}_4)$ o.o.p.
799 m, sh	802	873 w; 864 m	878 (0)[4]	A_1	$\nu(\text{SF}_{\text{ax}})$ i.p.
788 vs	782		800 (1094)[0.3]	E	$\nu(\text{SF}_{\text{ax}})$ o.o.p.
719 s	717	773 w	757 (10)[5]	E	$\nu_{\text{as}}(\text{NS}_3)$
		738 vs	704 (0)[42]	A_1	$\nu_{\text{sym}}(eq\text{-SF}_4)$ i.p.
618 w	617	725 w	691 (41)[0.1]	E	$\nu_{\text{sym}}(eq\text{-SF}_4)$ o.o.p.
		640 s	640 (1)[5]	E	$\nu_{\text{as}}(eq\text{-SF}_4)$ o.o.p.
		541 m	635 (0)[4]	A_1	$\nu_{\text{as}}(eq\text{-SF}_4)$ i.p.
			600 (0)[0.7]	A_1	$\nu_{\text{sym}}(\text{NS}_3)$
589 ms	590		561 (55)[0.6]	E	
			560 (25)[0]	A_2	
557 s	565	531w	541 (154)[0.8]	E	deformation
			527 (14)[0]	A_2	
			522 (118)[0.2]	E	
		451 s	488 (0)[2]	A_1	
		446 m, sh	478 (0.1)[1]	E	and rocking
			448 (7)[0]	A_2	
			414 (0.2)[3]	E	
360 w	361 w	360 m	406 (0.1)[4]	E	modes
			382 (0.1)[0]	A_2	
		274 m	330 (2)[0.8]	A_1	
			329 (0)[0.6]	E	
			314 (0.6)[0]	A_2	
			250 (0.1)[1]	E	
		248 vs	236 (0)[11]	A_1	
			214 (0.1)[0]	A_2	
		203 s	191 (11)[3]	E	
			182 (6)[3]	E	
			156 (0)[0.4]	A_1	
		85 w	85 (0.1)[0.1]	E	τ torsional modes
			75 (0.2)[0]	A_2	τ

^a Experimental band positions (cm^{-1}) and intensities: vs very strong, s strong, m medium strong, w weak, vw very weak, and sh shoulder. ^b B3LYP/6-311+G(d) level of theory; IR intensities (km mol^{-1}), Raman intensities [$\text{\AA}^4 \text{amu}^{-1}$]. ^c Tentative assignments according to the calculated vibrational displacement vectors, i.p. = in phase, o.o.p. = out of phase.

Table 4. Calculated and observed vibrational band positions (cm^{-1}) and band intensities of the $\cdot\text{N}(\text{SF}_5)_2$ radical (C_2 symmetry).

IR (gas phase) ^a	IR (Ne matrix)	Raman (solid) ^a	calculated ($I_{\text{IR}}/I_{\text{Raman}}$) ^b	Sym.	Approx. descrip. of mode ^c
	936 vs		953 (510)[2]	A	$\nu_{\text{as}}(eq\text{-SF}_4)$ i.p.
934 vs	926 vs		942 (593)[0.1]	B	$\nu_{\text{as}}(eq\text{-SF}_4)$ i.p.
910 w	909 m		906 (21)[2],	B	$\nu_{\text{as}}(eq\text{-SF}_4)$ o.o.p.
			904 (0.8)[4]	A	$\nu_{\text{as}}(eq\text{-SF}_4)$ o.o.p.
	898 m	887 w	896 (47)[6]	A	$\nu(\text{SF}_{\text{ax}})$ i.p.
887 m	877 s		875 (648)[1]	B	$\nu(ax\text{-SF})$ o.o.p.
790 m	790 m		745 (39)[4]	B	$\nu_{\text{as}}(\text{NS}_2)$
679 w	678 w	707 vs	682 (1)[25]	A	$\nu_{\text{sym}}(eq\text{-SF}_4)$ i.p.
			656 (2)[1]	B	$\nu_{\text{sym}}(eq\text{-SF}_4)$ o.o.p.
		611 m	635 (0.6)[7],	A	$\nu_{\text{sym}}(eq\text{-SF}_4)$ i.p., $\delta(\text{NS}_2)$
			634(0.6)[4],	B	$\nu_{\text{sym}}(eq\text{-SF}_4)$ o.o.p
			629 (3)[11]	A	$\nu_{\text{sym}}(\text{NS}_2)$
			583 (1)[0.4]	A	
584 m	585 s		547 (168)[0.2]	B	
	553 w		531 (17)[0.1]	B	
			526 (5)[0.8]	A	
	496 vw	510 w	517 (21)[0.1]	B	
			512 (9)[1]	A	
			457 (0.1)[2]	A	
			456 (0.2)[1]	B	
	430 vw		442 (7)[0.3]	B	
			383 (2)[1]	B	deformation and
			378 (1)[0.9]	A	
			364 (2)[0.7]	A	
			330 (0)[0]	B	
			313 (0)[0.3]	A	rocking modes
			288 (0.9)[0.1]	B	
		230 w	215 (0)[3]	A	
			203 (0)[0.5]	A	
			192 (0.4)[0.6]	B	
			147 (0)[0.1]	A	
			72 (0)[0]	A	τ torsional mode
			35 (0)[0]	B	τ

^a Experimental band positions (cm^{-1}) and intensities: vs very strong, s strong, m medium strong, w weak, vw very weak, and sh shoulder. ^b B3LYP/6-311+G(d) level of theory; IR intensities (km mol^{-1}) Raman intensities [$\text{\AA}^4 \text{amu}^{-1}$]. ^c Tentative assignments according to the calculated vibration displacement vectors, i.p. = in phase, o.o.p. = out of phase .

Figure captions

Figure 1. Structures for $\cdot\text{N}(\text{SF}_5)_2$ and $\text{N}(\text{SF}_5)_3$.

Figure 2. UV spectra of gaseous SF_5Cl (a) and $\text{N}(\text{SF}_5)_3$ (b) at room temperature (10 mbar, 10 cm optical path length).

Figure 3. IR difference spectrum of $\cdot\text{N}(\text{SF}_5)_2$ before and after thermal decomposition. The decreasing bands of $\cdot\text{N}(\text{SF}_5)_2$ are showing upwards and the appearing bands of $\text{N}(\text{SF}_5)_3$ are showing downwards.

Figure 4. UV-vis spectrum of gaseous $\cdot\text{N}(\text{SF}_5)_2$ at room temperature (10 cm optical path length). Impurities of S_2F_{10} , $\text{N}(\text{SF}_5)_3$, and $(\text{SF}_5)_2\text{NH}$ partially contribute to the absorptions below 350 nm.

Figure 5. Arrhenius plot for the thermal decomposition of $\text{N}(\text{SF}_5)_3$.

Figure 6. Experimental RDF and calculated RDF's for $\cdot\text{N}(\text{SF}_5)_2$ and S_2F_{10} and difference curve.

Figure 7. Experimental RDF and difference curve for $\text{N}(\text{SF}_5)_3$.

Figure 8. Molecular structure of $\text{N}(\text{SF}_5)_3$, obtained by single-crystal X-ray diffraction at 298 K. The thermal ellipsoids correspond to 50% probability.

Figure 9. Upper trace: IR spectrum of gaseous $\text{N}(\text{SF}_5)_3$ at 298 K in Transmission. Lower trace: Raman spectrum of solid $\text{N}(\text{SF}_5)_3$ in intensity I , resolution 2 cm^{-1} .

Figure 10. IR spectrum of gaseous $\cdot\text{N}(\text{SF}_5)_2$ at 298 K and a resolution of 2 cm^{-1} .

Figures for manuscript.

Solid- and Gas-Phase Structures and Spectroscopic and Chemical Properties of Tris(pentafluorosulfanyl)amine, $\text{N}(\text{SF}_5)_3$, and Bis(pentafluorosulfanyl)aminyl Radical, $\cdot\text{N}(\text{SF}_5)_2$.

Figure 1. Structures of $\cdot\text{N}(\text{SF}_5)_2$ and $\text{N}(\text{SF}_5)_3$

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Figure 4. UV-vis spectrum of gaseous $\text{N}(\text{SF}_5)_2$ at room temperature (10 cm optical path length). Impurities of S_2F_{10} , $\text{N}(\text{SF}_5)_3$, and $(\text{SF}_5)_2\text{NH}$ partially contribute to the absorptions below 350 nm.

Figure 5. Arrhenius plot for the thermal decomposition of $\text{N}(\text{SF}_5)_3$ in the temperature range of 14 to 53 °C

Figure 6. Experimental RDF for mixture, calculated RDF's for $\cdot\text{N}(\text{SF}_5)_2$ (r_a values from Table 1 and amplitudes from Table S4) and S_2F_{10} (r_a values and amplitudes from Ref [8]), and difference curve.

Figure 7. Experimental RDF and difference curve for $\text{N}(\text{SF}_5)_3$.

Figure 8. Molecular structure of $\text{N}(\text{SF}_5)_3$, obtained by single-crystal X-ray diffraction at 298 K. The thermal ellipsoids correspond to 50% probability.

Figure 9. Upper trace: IR spectrum of gaseous $\text{N}(\text{SF}_5)_3$ at 298 K in transmission. Lower trace: Raman spectrum of solid $\text{N}(\text{SF}_5)_3$ in intensity I , resolution 2 cm^{-1} .

Figure 10. IR spectrum of gaseous $\text{N}(\text{SF}_5)_2$ at 298 K and a resolution of 2 cm^{-1} .