Reactions of Pentafluorobenzenesulfanylamines $(C_6F_5S)_nNH_{3-n}$, n = 1, 2, 3 and the Structure of $(C_6F_5S)_3N$

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Dedicated to Professor Peter Satorius on the Occasion of his 65th Birthday

Abstract. The crystal structure of $(C_6F_5S)_3N$ has been examined. The compounds $(C_6F_5S)_2NX$, $X = SiMe_3$ and $1/_2Hg$ have been prepared from $(C_6F_5S)_2NH$ and characterised. In a number of other reactions, such as oxidation and irradiation, the S—N bond in $(C_6F_5S)_2NH$ was readily fractured, forming

the disulfide, $(C_6F_5S)_2$. The compound $(C_6F_5S)_3N$ has been found to be unreactive. Details of the mass and ¹³C NMR spectra of $(C_6F_5S)_nNH_{3-n}$, n = 1, 2, 3 are reported.

Keywords: Pentafluorobenzenesulfanylamines; crystal structure

Reaktionen der Pentafluorobenzolsulfanylamine $(C_6F_5S)_nNH_{3-n}$, n = 1, 2, 3 und Struktur des $(C_6F_5S)_3N$

Inhaltsübersicht. Ausgehend von $(C_6F_5S)_2NH$ konnten die Verbindungen $(C_6F_5S)_2NX$ (X = SiMe₃ und $\frac{1}{2}$ Hg) hergestellt und charakterisiert werden. In einer Vielzahl von Versuchen, wie z. B. Oxydation bzw. Photolyse ließ sich zeigen, daß die SN-Bindung in $(C_6F_5S)_2NH$ unter Bildung von $C_6F_5SSc_6F_5$ gespalten

Introduction

The pentafluorobenzenesulfanylamines, $C_6F_5SNH_2$, (C_6F_5S)₂NH and (C_6F_5S)₃N are well known, and can readily be prepared [1-3]. Some reactions of $C_6F_5SNH_2$ have been reported [4-6], but few reactions of (C_6F_5S)₂NH or (C_6F_5S)₃N have been described. This paper reports the preparation of compounds of the type (C_6F_5S)₂NX, some attempted reactions of (C_6F_5S)₂NH and (C_6F_5S)₃N as well as oxidation and irradiation of (C_6F_5S)₂NH.

Planar structures with three-coordinated nitrogen are known, e.g. for $(i-Pr_3)_3N$ [7]. In the gas phase $(CF_3S)_3N$ and in the solid state $(C_6H_5S)_3N$ [8, 9] have an almost planar arrangement of the three sulfur atoms around the central nitrogen atom which is discussed in terms of $(p-d)-\pi$ bonding and steric interactions.

Results and Discussion

The structure of $(C_6F_5S)_3N$ shows that the NS₃ moiety is nearly planar. The C_6F_5 rings are almost perpendicular to the NS₃ plane. The N—S—C angles are somewhat wird. Es konnte nachgewiesen werden, daß (C_6F_5S)₃N chemisch wenig reaktiv ist; in der Kristallstrukturanalyse besitzen die Moleküle annähernd C_s-Symmetrie. Massen- und ¹³C-NMR-Spektren für (C_6F_5S)₉NH_{3-n} werden erstmals aufgeführt.

greater than 90° and in the same range as for $(CF_3S)_3N$ [100(1)°] [8]. Two C_6F_5 groups are above the plane and one below, which is very similar to that found in $(CF_3S)_3N$ [8] but in contrast to $(C_6H_5S)_3N$ which has a distorted C_3 symmetry [9]. The two C_6F_5 groups on the same side of the NS₃ plane are almost cofacial. The molecular structure has almost C_s symmetry, the crystal structure is pseudo centrosymmetric.

The reactions of bis(pentafluorobenzenesulfanyl)amine are dominated by the relative instability of the S—N bond, as has been noted previously [5] and which is in marked contrast to the aliphatic analogue bis(trifluorometanesulfanyl)amine, $(F_3CS)_2NH$. Large numbers of derivatives of the type $(F_3CS)_2NX$ are stable and readily prepared, e.g. the boron compounds [10], sulfur derivatives [11] and the mercury compounds Hg[N(SCF_3)_2]_2 and PhHgN(SCF_3)_2 [12].

Rearrangement occurred when pentafluorobenzenesulfanylamine lost ammonia forming the bisamine.

 $2C_6F_5SNH_2 \rightarrow (C_6F_5S)_2NH + NH_3$

The favoured decomposition of the bisamine involved the formation of the disulfide, $(C_6F_5S)_2$, which was readily

detected in solution by its ¹⁹F NMR spectrum [13]. The trisamine decomposed above 140 °C also forming $(C_6F_5S)_2$. Small amounts of ammonium chloride were isolated in the reaction of $(C_6F_5S)_2NH$ with $C_6F_5SO_2Cl$ and pyridine. Traces of NH₃ may have been formed in the decomposition of $(C_6F_5S)_2NH$, giving $(C_6F_5S)_3N$ and NH₃, which subsequently reacted with $C_6F_5SO_2Cl$ forming traces of both $C_6F_5SO_2NH_2$ and NH₄Cl [14]. In contrast to the sulfanylamines the sulfonylamines, $C_6F_5SO_2NH_2$ and $(C_6F_5SO_2)NH_2$ with sulfur in the +VI oxidation state are very thermally stable [14].

The only compounds known to have the formula $(C_6F_5S)_2NX$ are X = H, SC_6F_5 , $SiMe_3$ and 1/2Hg, the latter two being described here. The trisamine $(C_6F_5S)_3N$ was obtained by the reaction of the bisamine with the sulfenyl chloride in the presence of Et_3N [3].

$(C_6F_5S)_2NH + C_6F_5SCl + Et_3N \rightarrow (C_6F_5S)_3N + Et_3NHCl$

Our experiments indicated that triethylamine is not a good HCl catcher for reactions involving C₆F₅SCl, with which it reacts slowly to form $Et_2NCH = C(SC_6F_5)$, [15]. The results presented here indicate that the N-H group in $(C_6F_5S)_2$ NH is considerably less acidic than that in $(C_6F_5SO_2)_2NH$, which was formed as $[(C_6F_5SO_2)_2N]NH_4$ in its preparation from $C_6F_5SO_2Cl$ and aqueous NH_3 [14]. This weak acidity is demonstrated as no reactions were observed between (C₆F₅S)₂NH and Ag₂CO₃ or $C_6F_5SO_2Cl$, Bu_3SnCl , and CF_3SCl , even in the presence of pyridine to remove with any HCl formed. The compound PhHgN(SC₆ F_5)₂ may initially have been formed in the reaction of Ph₂Hg with (C₆F₅S)₂NH and subsequently decomposed to $PhHgSC_6F_5$. In an analogous reaction using (CF₃S)₂NH it was possible to isolate PhHgN(SCF₃)₂ [12]. Similarly in the reaction of $(C_6F_5S)_2NH$ with AgO_2CCH_3 , $AgN(SC_6F_5)_2$ may have been formed initially and decomposed to $AgSC_6F_5$.

The reaction of $(CF_3S)_2NH$ and CF_3SNCO gave the trisamine $(CF_3S)_3N$ [16], but $(C_6F_5S)_3N$ could not be prepared from $(C_6F_5S)_2NH$ and C_6F_5SNCO .

The compound $C_6H_5SN=C_5Cl_2$ has been prepared in 5-6% yields from C_5Cl_6 , CF_3SCl and Me_3SiN_3 and or by oxidation of CF_3SNH_2 with PbO₂ in the presence of C_5Cl_6 [17]. The compound FC(O)SN= C_5Cl_6 has been detected in the reaction of FC(O)SCl, Me_3SiN_3 and C_5Cl_6 in yields of about 1% and is probably formed via the unstable intermediate FC(O)SN. It was characterised spectroscopically [18]. Attempts to prepare the analogous compound $C_6H_5SN=C_5Cl_2$ from C_5Cl_6 and $(C_6F_5S)_3N$ or C_6F_5SCl/Me_3SiN_3 failed. It could not be detected even in trace amounts in the mass spectrum or ¹⁹F NMR spectrum of the various impure products.

Attempts to prepare $[(C_6F_5S)_2N]_2SO$ from $(C_6F_5S)_2NH$ and SOCl₂ resulted in the formation of C_6F_5SNSO and $(C_6F_5S)_3N$ [5]. The observed reaction may be explained if the intermediate $(C_6F_5S)_2NSOCl$ decomposed to C_6F_5SNSO and C_6F_5SCl which subsequently reacted with $(C_6F_5S)_2NH$ forming $(C_6F_5S)_3N$. The attempted preparation of $(C_6F_5S)_2NSOC_6F_5$ from $(C_6F_5S)_2NH$ and C_6F_5SOcl resulted in the formation of the disulfide, $(C_6F_5S)_2$, and $C_6F_5SO_2NH_2$ [5]. The reaction of $N_3S_3Cl_3$ with $(C_6F_5S)_2NH$ yielded $C_6F_5SN=S=NSC_6F_5$ [6]. In these reactions the compounds with only one C_6F_5S group bonded to the nitrogen, such as C_6F_5SNXY , are more stable than those with two C_6F_5S groups bonded to nitrogen, such as $(C_6F_5S)_2NX$.

The reaction of pentafluorobenzenesulfanylamine with manganese dioxide caused oxidation of the sulfur yielding $C_6F_5SONH_2$ and $C_6F_5SO_2NH_2$ [4]. No oxidation of the sulfur in $(C_6F_5S)_2NH$ was observed when it was treated with manganese dioxide, rather fracture of the S—N bond occurred and the disulfide, $(C_6F_5S)_2$, was obtained. Various N-chloro compounds are known, such as 1-chloro-2,3,4,5-tetrakis(trifluoromethylsulfanyl)pyrrole [19], but it was not possible to prepare and isolate $(C_6F_5S)_2NCl$.

Irradiation of $(F_3CS)_3N$ at $-73 \,^{\circ}C$ in CFCl₃ yielded $[(F_3CS)_2N]_2$ [20] and in the presence of alkenes products corresponding to the addition of two F₃CS groups were formed [11]: similar irradiation allowed the introduction of the F₃CS group into metal carbonyls [21]. No products other than $[(F_3CS)_2N]_2$ were reported corresponding to the formation and subsequent reaction of the $(F_3CS)_2N$ radical. It is therefore probable that C_6F_5S radicals were formed in the irradiation of $(C_6F_5S)_2NH$, which recombined to form the disulfide $(C_6F_5S)_2$, while the nitrogen fragments formed an ammonium salt.

Other reactions reported for $(F_3CS)_3N$ resulted in the loss of the CF₃S group and retention of the $(F_3CS)N$ or $(F_3CS)_2N$ units. $(F_3CS)_3N$ reacted with Ph₃M, M = P, As, forming CF₃SN=MPh₃ [11, 22] and with Me₂BBr forming Me₂BN(SCF₃)₂ [10]. With SCl₂ it formed CF₃SCl, S₂Cl₂ and S₄N₃Cl [11]. Under similar conditions no reaction was observed between $(C_6F_5S)_3N$ and Ph₃P or SCl₂.

The E. I. mass spectra of $C_6F_5SNH_2$, $(C_6F_5S)_2NH$ and $(C_6F_5S)_3N$ all show the formation of the molecular ion. A predominant feature of the spectra is the formation of the $C_6F_5S^+$ ion and its decomposition products, as has been observed previously in the spectra of various compounds containing the C_6F_5S group [23].

Experimental

Reagents were available commercially, except pentafluorobenzenesulfenyl chloride, which was prepared by chlorination of pentafluorobenzenethiol [24].

NMR measurements were performed on a Bruker HX WP 80 spectrometer using CDCl₃ solutions with Me₄Si ('H and ¹³C) and CFCl₃ ('⁹F) as internal standards. Electron impact mass spectra (100 eV) were measured on a Varian MAT CH-5 mass spectrometer. Chemical analyses were performed by the analytical laboratory of the Lehrstuhl.

Bis(pentafluorobenzenesulfanyl)amine was prepared from pentafluorobenzenesulfenyl chloride and ammonia in ether [3]: this reaction yielded both $C_6F_5SNH_2$ and $(C_6F_5S)_2NH$, which were separated by distillation and $(C_6F_5S)_2NH$ was further purified by vacuum sublimation. On standing at room temperature $C_6F_5SNH_2$ slowly lost ammonia, forming $(C_6F_5S)_2NH$. Tris(pentafluorobenzenesulfenyl)amine was prepared from $(C_6F_5S)_2NH$ and C_6F_5SCl in Et₂O. The compounds were identified by their m.p./b.p., IR and ¹⁹F NMR spectra [1-3].

¹³C NMR

 $C_{6}F_{5}SNH_{2}: \quad \delta(C-1) = 112.0(t) \text{ ppm}, \quad {}^{2}J(C-F) = 21.0 \text{ Hz}; \\ (C-2,6) = 145.9(m) \text{ ppm}, \quad {}^{1}J(C-F) = 248.0 \text{ Hz}; \quad \delta(C-3,5) = 137.4(m) \text{ ppm}, \quad {}^{1}J(C-F) = 255.3 \text{ Hz}; \quad \delta(C-4) = 142.5.4(m) \text{ ppm}, \quad {}^{1}J(C-F) = 259.4 \text{ Hz}.$

 $(C_6F_5S)_2$ NH: $\delta(C-1) = 110.8(t)$ ppm, ${}^2J(C-F) = 20.0$ Hz; $\delta(C-2,6) = 145.8(m)$ ppm, ${}^1J(C-F) = 251.1$ Hz; $\delta(C-3,5) = 137.7(m)$ ppm, ${}^1J(C-F) = 254.3$ Hz; $\delta(C-4) = 143.5(m)$ ppm, ${}^1J(C-F) = 261.3$ Hz.

 $(C_6F_5S)_3N: \delta(C-1) = 110.8(t) \text{ ppm}, {}^2J(C-F) = 21.0 \text{ Hz}; \delta(C-2,6) = 145.8(m) \text{ ppm}, {}^1J(C-F) = 251.8 \text{ Hz}; \delta(C-3,5) = 137.6(m) \text{ ppm}, {}^1J(C-F) = 257.5 \text{ Hz}; \delta(C-4) = 143.4(m) \text{ ppm}, {}^1J(C-F) = 261.3 \text{ Hz}.$

Mass spectra (m/z relative intensity >5%): $C_6F_5SNH_2$ (100 °C): m/z = 215(100 M⁺), 199(65), 183(37), 168(9), 155(42), 149(21), 117(13), 111(9), 93(9), 87(7), 69(8), 63(9), 48(6).

 $(C_6F_5S)_2NH$ (50 °C): m/z = 413(100 M⁺), 398(7), 216(350), 215(47), 214(97), 213(24), 200(29), 199(80), 195(15), 194(24), 187(51), 182(36), 181(7), 180(9), 170(11), 169(5), 168(35), 164(11), 156(15), 155(71), 150(17), 149(43), 148(5), 143(25), 137(13), 131(13), 130(9), 125(12), 118(12), 117(42), 111(28), 105(12), 99(14), 98(16), 93(28), 87(27), 86(7), 79(8), 74(5), 69(28), 63(23), 47(40), 46(42), 31(11).

 $(C_6F_5S)_3N$ (80 °C): m/z = 611(3 M⁺), 414(40), 413(57), 412(100), 400(18), 399(25), 398(84), 245(7), 231(10), 226(11), 215(7), 214(14), 213(64), 201(28), 200(39), 199(90), 180(13), 169(10), 167(6), 156(15), 155(72), 150(6), 149(53), 131(12), 130(14), 125(11), 124(8), 118(8), 117(43), 111(28), 105(18), 99(8), 98(13), 93(29), 87(29), 86(8), 79(7), 74(7), 69(25), 63(19), 46(44), 31(13).

X-Ray Structure Determination: A crystal of (C₆F₅S)₃N with the approximate dimensions of $0.32 \times 0.24 \times 0.13 \text{ mm}^3$ was measured on a Siemens P4 diffractometer with Mo-K_a-radiation at room temperature. Cell dimensions, refined from the diffractometer angles of 20 centered reflections, are $a = 8.094(3), b = 12.448(3), c = 10.234(3) \text{ Å}, \beta = 100.32(2),$ V = 1014.4(8) Å³; monoclinic crystal system, Z = 2, $d_{cal.} = 2.017 \text{ gm}^{-3}, \mu = 0.51 \text{ mm}^{-1}$, space group $P2_1$, data collection of 1369 unique intensities ($R_{merg} = 0.0174$, $2\Theta_{max} =$ 45°), 990 observed ($F_o \ge 4\sigma(F)$), structure solution with direct methods and refinement with full matrix least squares (298 parameters) (rigid groups for phenyl rings, C-C distance 1.396 Å and C-C-C 120° because of the weak scattering power of the crystal), a pseudo centrosymmetry is documented by weak intensities for h0l reflections, however 36 reflections have intensities $\geq 2.5 \sigma$, the strongest [3/0/-1], [3/0/-3] and [6/0/5] have intensities of 21σ , 17σ and 10σ , respectively. These suggest a preference for the non-centrosymmetric space group leading to a reasonable model but a non-satisfying result in the refinement with severe correlation as it was found for $(C_6H_5S)_3N$, however with two independent molecules in $P2_1$



Fig. 1 Structure of $(C_6F_5S)_3N$

Table 1 Atomic coordinates $(\times 10^4)$ and equivalent isotropic displacement coefficients $(\mathring{A}^2 \times 10^3)$ of $(C_6F_5S)_3N$

	x	у	Z	U(eq)
N	2389(19)	2500	4609(15)	51(2)*
S(1)	2475(11)	3918(11)	4255(10)	103(1)*
S(2)	1506(13)	1428(13)	3103(13)	152(1)*
S(3)	3000(11)	2133(11)	6324(10)	90(1)*
C(1)	4177(13)	4036(12)	3685(11)	61(2)*
C(2)	4100	4124	2316	71(2)*+
C(3)	5574	4113	1 789	65(2)*+
C(4)	7126	4014	2631	72(2)*+
C(5)	7203	3926	3999	47(2)*+
C(6)	5729	3937	4526	60(2)*+
F(2)	2652(19)	4083(15)	1442(15)	117(2)*
F(3)	5645(20)	4130(15)	455(14)	110(2)*
F(4)	8339(10)	3836(10)	1612(9)	19(2)*
F(5)	8639(15)	3821(15)	4731(15)	81(2)*
F(6)	5944(14)	3862(14)	5825(12)	52(1)*
C(11)	3278(14)	1348(12)	2593(11)	58(2)*
C(12)	2981	1426	1211	73(2)*+
C(13)	4326	1448	529	46(2)*+
C(14)	5970	1394	1229	64(2)*+
C(15)	6267	1317	2612	82(2)*+
C(16)	4922	1 294	3293	86(2)*+
F(12)	1404(18)	1540(15)	416(15)	91(2)*
F(13)	4145(16)	1518(15)	-787(13)	72(2)*
F(14)	7527(11)	1514(11)	741(10)	21(2)*
F(15)	7743(20)	1137(16)	3301(17)	136(2)*
F(16)	5346(18)	1195(14)	4556(13)	93(2)*
C(21)	1287(14)	2414(13)	6940(13)	43(2)*
C(22)	-121	1748	6753	55(2)*+
C(23)	- 1505	2013	7328	58(2)*+
C(24)	- 1480	2944	8090	42(2)*+
C(25)	-72	3610	8277	41(2)*+
C(26)	1312	3345	7702	37(2)*+
F(22)	- 80(18)	864(15)	6007(16)	91(2)*
F(23)	-2738(16)	1388(15)	7039(14)	75(2)*
F(24)	-3015(11)	3252(11)	8774(10)	20(1)*
F(25)	-35(17)	4465(14)	9001(15)	78(2)*
F(26)	2652(18)	4046(15)	7878(16)	89(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ii} tensor

⁺ Atoms in rigid groups without standard deviations

[9]. The space group $P2_1/m$ with disordered phenyl groups lead to an even more unsatisfying model. Consequently details of the structure cannot be discussed, instead it will be taken only as evidence for the conformation which has two almost parallel phenyl rings (interplanar angle 2°) at an approximate distance of 3.6 Å (centroid to centroid). R = 0.115, R_w = 0.125, w⁻¹ = $\sigma^2(F_o) + 0.0005 \cdot F_o^2$, residual electron density 0.96 c/Å³.

The structure is shown in Figure 1. Atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, and anisotropic displacement coefficients are listed in Tables 1, 2, 3, and 4, respectively.

Chemical Reactions

All the following reactions were studied on the one to five mmol scale. Known products were identified by m.p. and/or ¹⁹F NMR spectroscopy.

Reactions of (C₆F₅S)₂NH

Preparation of $Hg[N(SC_6F_5)_2]_2$. $Hg[N(SC_6F_5)_2]_2$, white, m. p. 93-95 °C, was prepared by shaking a solution of $HgCl_2$ (0.139 g, 0.51 mmol) in 25 ml H₂O with 25 ml of an ether solu-

Table 2 Bond lengths (Å) of $(C_6F_5S)_3N$

N—S(1)	1.806(14)	N—S(2)	2.067(18)
N—S(3)	1.795(18)	S(1) - C(1)	1.596(15)
S(2)—C(11)	1.616(17)	S(3)—C(21)	1.660(16)
C(2)—F(2)	1.342(17)	C(3) - F(3)	1.377(18)
C(4)—F(4)	1.571(15)	C(5)—F(5)	1.272(15)
C(6)—F(6)	1.312(16)	C(12) - F(12)	1.392(17)
C(13)—F(13)	1.331(17)	C(14)—F(14)	1.445(15)
C(15)—F(15)	1.293(18)	C(16)—F(16)	1.282(16)
C(22)—F(22)	1.343(23)	C(23)—F(23)	1.258(20)
C(24)—F(24)	1.579(16)	C(25)—F(25)	1.294(23)
C(26)—F(26)	1.378(21)		

Table 3 Bond angles (°) of (C	$_{6}F_{5}S)_{3}N$
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tion of $(C_6F_5S)_2$ NH (0.415 g, 1.00 mmol): the product was soluble in ether and obtained after separation of the layers followed by evaporation of the solvent. Yield 80%. $C_{24}F_{20}S_4N_2$ Hg: found C, 27.5; H, 0.1; N, 2.8: calc. C, 28.1; H, 0; N, 2.7%. No molecular ion was observed in the mass spectrum, but various species containing Hg and $(C_6F_5S)_2$ and its decomposition products [21] were detected. ¹⁹F NMR: $\delta(F_{ortho}) = -133.1(m)$, $\delta(F_{para}) = -150.0(\text{tt})$ and $\delta(F_{meta}) = -160.8(\text{m})$ ppm.

Preparation of $(C_6F_5S)_2NSiMe_3$. $(C_6F_5S)_2NSiMe_3$, white, m. p. 80-2 °C, was obtained by adding 25 ml of an ether solution of Me₃SiCl (0.13 ml, 1.0 mmol) to 50 ml of an ether solution of $(C_6F_5S)_2NH$ (0.417 g, 1.00 mmol) and Et₃N (0.14 ml, 1.0 mmol) at room temperature. A white precipitate formed immediately. The solution was refluxed for 1.5 h and then filtered. The product was isolated after evaporation of the Et₂O from the filtrate. Yield of recrystallised (hexane) product 33%. C₁₅H₉F₁₀NS₂Si: found, C, 37.0; H, 1.1; N, 3.1: calc. C, 37.1; H, 1.9; N, 2.9%. NMR: ¹H, δ (CH₃) 2.17(s): ¹⁹F, δ (F_{ortho}) = -133.1(m), $\delta(\mathbf{F}_{para}) = -149.5(\text{tt})$ and $\delta(\mathbf{F}_{meta}) =$ -160.5(m) ppm. The mass spectrum did not have a peak at m/z = 495 corresponding to the molecular ion, but strong peaks at m/z = 440 ((C₆F₅S)₂NSi - R.I. 5%), 413 $((C_6F_5S)_2NH - 35), 398 ((C_6F_5S)_2 - 20), 87 ((H_3C)_3SiN - 18)$ and 214 ($C_6F_5SNH - 100$) were observed.

Reactions with silver salts. $(C_6F_5S)_2NH$ (0.415 g, 1.00 mmol) in 25 ml Et₂O was stirred with 30 ml of an aqueous solution of AgNO₃ (0.171 g, 1.00 mmol) overnight. No precipitate formed. The layers were separated and $(C_6F_5S)_2NH$ recovered from the Et₂O phase.

On stirring 25 ml of an aqueous solution of AgO_2CCH_3 (0.167 g, 1.00 mmol) with an 25 ml of an Et₂O solution of (C₆F₅S)₂NH (0.415 g, 1.00 mmol) overnight, a white precipitate formed. This was filtered off and chemical analysis showed it to be impure $AgSC_6F_5$ [13]. (C₆F₅S)₂NH was recovered from the ether layer, after separation and removal of the solvent.

50 ml of an Et_2O solution of $(C_6F_5S)_2NH$ (0.415 g, 1.00 mmol) was stirred with a suspension of Ag_2CO_3 (0.137 g, 0.50 mmol) for 5 days at room temperature. The Ag_2CO_3 was

Table 5 Done angles () 01 (061 50)311			
S(1)—N—S(2)	120.1(9)	S(1)—N—S(3)	115.6(8)	
S(2)—N—S(3)	124.2(6)	N-S(1)-C(1)	103.3(10)	
N-S(2)-C(11)	94.2(8)	N—S(3)—C(21)	102.4(8)	
S(1) - C(1) - C(2)	119.2(5)	S(1)—C(1)—C(6)	120.5(5)	
C(1)-C(2)-F(2)	122.9(9)	C(3)—C(2)—F(2)	116.5(9)	
C(2)—C(3)—F(3)	125.0(8)	C(4) - C(3) - F(3)	114.9(8)	
C(3)-C(4)-F(4)	101.7(5)	C(5)-C(4)-F(4)	137.3(5)	
C(4) - C(5) - F(5)	118.1(9)	C(6)—C(5)—F(5)	121.9(9)	
C(1)-C(6)-F(6)	124.9(7)	C(5)—C(6)—F(6)	115.1(7)	
S(2)—C(11)—C(12)	108.8(6)	S(2)—C(11)—C(16)	131.1(6)	
C(11)—C(12)—F(12)	125.0(8)	C(13)-C(12)-F(12)	114.9(8)	
C(12)—C(13)—F(13)	123.5(7)	C(14)-C(13)-F(13)	116.5(7)	
C(13)—C(14)—F(14)	128.9(5)	C(15)-C(14)-F(14)	110.8(5)	
C(14)—C(15)—F(15)	122.7(9)	C(16)—C(15)—F(15)	116.8(9)	
C(11)C(16)F(16)	125.5(8)	C(15)—C(16)—F(16)	114.5(8)	
S(3)—C(21)—C(22)	122.7(7)	S(3)—C(21)—C(26)	117.3(7)	
C(21)—C(22)—F(22)	117.5(9)	C(23)—C(22)—F(22)	122.5(9)	
C(22)—C(23)—F(23)	114.7(10)	C(24)—C(23)—F(23)	125.2(10)	
C(23)C(24)F(24)	121.0(7)	C(25)C(24)F(24)	119.0(7)	
C(24)—C(25)—F(25)	120.1(8)	C(26)—C(25)—F(25)	119.9(8)	
C(21)—C(26)—F(26)	122.1(9)	C(25)—C(26)—F(26)	117	

Table 4 Anisotropic displacement coefficients $(Å^2 \times 10^3)$ of $(C_6F_5S)_3H$

	U_{11}	U ₂₂	U ₃₃	U_{12}	U ₁₃	U_{23}
N	77(3)	. 39(3)	41(3)	-1(3)	23(2)	-2(3)
S(1)	84(2)	134(2)	107(2)	52(2)	55(2)	60(2)
S(2)	130(2)	144(3)	214(2)	27(2)	122(2)	62(2)
S(3)	81(2)	102(2)	86(2)	3(2)	13(2)	19(2)
C(1)	70(3)	38(3)	70(3)	-11(3)	2(3)	30(3)
C(3)	1 39(3)	28(3)	26(3)	-19(3)	10(3)	-9(3)
C(4)	126(3)	51(3)	49(3)	25(3)	43(3)	21(3)
C(5)	71(3)	29(3)	55(3)	3(3)	51(2)	14(3)
C(6)	104(3)	34(3)	39(3)	-16(3)	5(3)	17(3)
F(2)	175(3)	78(3)	71(3)	- 30(3)	-49(3)	30(3)
F(3)	213(3)	72(3)	51(2)	-11(3)	36(3)	2(2)
F(5)	50(2)	111(3)	89(3)	24(2)	32(2)	39(3)
F(6)	61(2)	69(3)	28(2)	-11(2)	13(2)	-2(2)
C(11)	107(3)	29(3)	46(3)	13(3)	35(3)	-11(3)
C(12)	101(3)	33(3)	69(3)	19(3)	-29(3)	4(3)
C(13)	77(3)	27(3)	43(3)	8(3)	33(3)	-4(3)
C(14)	92(3)	26(3)	58(3)	-10(3)	-27(3)	1(3)
C(15)	106(3)	25(3)	112(3)	-1(3)	10(3)	13(3)
C(16)	98(3)	32(3)	96(3)	16(3)	-68(3)	-15(3)
F(12)	105(3)	90(3)	87(3)	0(3)	42(2)	33(3)
F(13)	80(3)	87(3)	45(2)	7(3)	1(2)	29(2)
F(15)	167(3)	98(3)	103(3)	- 10(3)	-87(3)	7(3)
F(16)	154(3)	86(3)	32(2)	43(3)	2(2)	-8(2)
C(21)	60(3)	41(3)	34(3)	24(3)	21(3)	30(3)
C(22)	90(3)	38(3)	39(3)	-18(3)	21(3)	9(3)
C(23)	66(3)	58(3)	48(3)	-5(3)	2(3)	15(3)
C(24)	55(3)	35(3)	41(3)	4(3)	21(3)	6(3)
C(25)	64(3)	28(3)	39(3)	2(3)	30(2)	-8(3)
C(26)	45(3)	36(3)	41(3)	-14(3)	36(2)	-5(3)
F(22)	142(3)	47(3)	99(3)	-18(3)	60(2)	-28(3)
F(23)	87(2)	78(3)	68(2)	- 39(2)	38(2)	-17(2)
F(24)	15(2)	28(2)	21(2)	1(2)	8(2)	17(2)
F(25)	100(3)	62(3)	82(3)	-7(3)	44(2)	-33(2)
F(26)	108(3)	72(3)	94(3)	-30(3)	36(2)	-34(3)

The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11}\& + \ldots + 2hka^{*}b^{*}U_{12})$

recovered on filtration and $(C_6F_5S_2)NH$ on evaporation of the Et_2O .

*Reaction with Bu*₃*SnCl*. The reactants were recovered when 75 ml of an Et₂O solution of Bu₃*SnCl* ((0.27 ml), $(C_6F_5S)_2NH$ (0.418 g) and Et₃N (0.14 ml) (all 1.0 mmol) was refluxed for 6 h.

Reaction with $C_6F_3SO_2Cl$. A solution of $(C_6F_5S)_2NH$ (0.417 g, 1.00 mmol) pyridine (0.10 ml, 1.2 mmol) and $C_6F_3SO_2Cl$ (0.15 ml, 1.0 mmol) in 50 ml hexane was refluxed for 1 week. A similar solution in 50 ml toluene was refluxed for 20 h. There was no visible reaction in the hexane solution. A trace of a white precipitate was isolated from the toluene solution, which analysed as impure NH₄Cl. The ¹⁹F NMR spectrum of the liquid product isolated after evaporation of the solvent showed the presence of $(C_6F_5S)_2$, $C_6F_5SO_2Cl$ and somewhat less of a third unidentified product containing a C_6F_5 group, possibly $C_6F_5SO_2NH_2$.

Reaction with C_6F_5SNCO . C_6F_5SNCO (1.03 g, 4.3 mmol) in 80 ml C_6H_6 was added slowly to a refluxing solution of

 $(C_6F_5S)_2$ NH (1.77 g, 4.3 mmol) in 80 ml C_6H_6 . After 3 days the C_6H_6 was removed *in vacuo*, leaving a yellow residue, containing only the starting materials. Similar results were obtained when the reaction was studied at room temperature.

Reaction with Ph_2Hg . A solution of Ph_2Hg (0.356 g, 1.00 mmol) and $(C_6F_5S)_2NH$ (0.415 g, 1.00 mmol) in 30 ml toluene was refluxed for 90 h. After removal of the solvent by rotatory evaporation a tar formed from which $PhHgSC_6F_5$, (yield 57%) m.p. 147-9 °C (lit. m.p. 148-9 °C [13]), was isolated by extraction with hexane.

Reaction with CF_3SCl . The disulfide, $(C_6F_5S)_2$, identified from its ¹⁹F NMR spectrum or m. p., was the major product isolated from the reaction of $(C_6F_5S)_2NH$ (0.443 g, 1.0 mmol) and an excess of CF_3SCl (1.9 g, 14 mmol) in the presence of pyridine (0.2 ml, 1.0 mmol) at room temperature (1 day., no solvent) or -20 °C (12 h, Et₂O solution).

Attempted oxidation. Oxidation of $(C_6F_5S)_2NH$ (0.41 g, 1.0 mmol) or $(C_6F_5S)_3N$ (0.611 g, 1.0 mmol) in 50 ml pentane was attempted by stirring with a suspension of a large excess of MnO₂ and after 18 h the disulfide $(C_6F_5S)_2$, was isolated rather than $(C_6F_5SO)_2NH$ or $(C_6F_5SO_2)_3N$.

Reactions with Cl_2 . The preparation of $(C_6F_5S)_2NCl$ was attempted by the reaction of $(C_6F_5S)_2NH$ (0.410 g, 1.0 mmol) with 50 ml of fresh 14% aqueous NaOCl for 20 h, or by bubbling Cl_2 into 50 ml of pentane solutions of $(C_6F_5S)_2NH$ (0.414 g, 1.00 mmol) at -20 °C with 1 ml of aq. NaOH containing 250 mg NaOH (20 min.), or with $(C_6F_5S)_2NH$ (0.414 g, 1.0 mmol) in the presence of pyridine (0.10 ml, 1.2 mmol) in 50 ml of pentane at -20 °C (20 min.) or with $(C_6F_5S)_2NH$ (0.414 g, 1.0 mmol) at -5 °C in 50 ml pentane with no HCl catcher (NH₄Cl was isolated from this reaction due to the fracture of the S—N bond by HCl). The mass spectrum of the yellow liquid from the NaOH reaction showed traces of $(C_6F_5SO_2)NCl$ along with oxidation products such as $(C_6F_5SO_2)NH$ and $C_6F_5SO_2SC_6F_5$ as well as $(C_6F_5S)_2$ and starting material. The pyridine reaction charred.

A green colour was observed when Cl_2 was bubbled through 50 ml of an Et₂O solution of $[(C_6F_5S)_2N]_2Hg$ (0.450 g, 0.74 mmol)at -30 °C for 0.5 h, which changed to yellow on warming to room temperature overnight and formed a white precipitate. The ¹⁹F NMR of the Et₂O solution showed there to be 3 different C_6F_5 groups present, one of which was $(C_6F_5S)_2$.

Irradiation. Solutions of $(C_6F_5S)_2NH$ (0.418 g, 1.00 mmol) in 50 ml CCl₄ were irradiated with an Hg lamp for varying periods. Monitoring the solution by ¹⁹F NMR showed the disappearance of peaks due to $(C_6F_5S)_2NH$ and generation of peaks corresponding to $(C_6F_5S)_2$. Evaporation of the solvent left a white solid, which analysed as an impure ammonium salt, and an oil from which the disulfide, $(C_6F_5S)_2$, m. p. 53 – 4 °C, lit. 51 °C [25] was recovered.

Attempted preparations of $C_6F_5SN=C_5Cl_6$. C_6F_5SCl (4.3 ml, 31 mmol) was slowly added to a well stirred solution of freshly distilled C_5Cl_6 (4.3 g, 15.8 mmol) and Me_3SiN_3 (4.9 ml, 37 mmol) in 20 ml toluene at -30 °C. The mixture was allowed to warm slowly to room temperature and then refluxed for 3 h. The solvent was removed *in vacuo* and the liquid product fractionated. Fractions included (C_6F_5S)₂. There was no trace of any other C_6F_5 group in the ¹⁹F NMR of the various fractions. A brown tar remained, the mass spectrum of which showed no trace of $C_6F_5SN=C_5Cl_6$.

A mixture of $(C_6F_5S)_3N$ (0.7 g, 1.2 mmol), freshly distilled C_5Cl_6 (1.6 g, 5.9 mmol) in 30 ml Et₂O was heated in a Carius

tube for 4 days at 110 °C. After removal of the Et_2O , spectroscopic analysis of the brown residue showed it to be solely starting materials.

Reactions of $(C_6F_3S)_3N$. $(C_6F_3S)_3N$ (0.9 g, 1.5 mmol) and a large excess of freshly distilled SCl₂ (4 g, 38 mmol) was stirred in a Carius tube for 24 h at room temperature. After removal of the excess SCl₂, the solid residue was found to be unreacted $(C_6F_5S)_3N$.

A solution of $(C_6F_3S)_3N$ (0.4 g, 0.7 mmol) in 100 ml hexane was added to a solution of Ph₃P (0.16 g, 0.6 mmol) in 40 ml hexane. After stirring at room temperature for 6 days, a unidentified brown solid was filtered off.

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Further details of the crystal structure are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405198, the names of the authors, and the journal citation.

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