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Preparation of the first *ortho*-substituted pentafluorosulfanylbenzenes

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Abstract

The preparation of the first *ortho*-substituted pentafluorosulfanylbenzenes was achieved. Oxidative fluorination (AgF_2) of a series of aromatic disulfides containing different substituents *ortho* to the disulfide moiety gave only one *ortho*-substituted SF_5-benzene, namely 1-fluoro-4-nitro-2-pentafluorosulfanylbenzene. This compound has been transformed into a variety of other *ortho*-substituted SF_5-benzenes by nucleophilic substitution reactions. © 2001 Published by Elsevier Science B.V.

Keywords: Pentafluorosulfanylbenzene; Sulfur halogen compounds; Fluorine and compounds; Coupling reactions

1. Introduction

Recent years have been marked by a considerable increase in the interest of pentafluorosulfanylbenzene derivatives as evidenced by their inclusion in articles on the fine chemicals industry [1,2]. This interest has largely been spawned by significant improvements in the methods for preparing these compounds as well as the existence of a more diverse set of applications. Both *meta*-nitro- and *para*-nitro-SF_5-benzene have been commercially available for several years.

Sheppard prepared the first pentafluorosulfanylbenzenes in the early 1960s via the reaction of an aromatic disulfide with silver difluoride in a suspension of a chlorofluorocarbon solvent [3,4]. Raasch, a colleague of Sheppard's at DuPont, patented several ureido-substituted SF_5-benzenes based on their biological activity as plant regulants, herbicides, and bactericides [5]. Although Sheppard and Raasch carried out their reactions in copper autoclaves, it does not appear that they knew the significance of this choice. For a number of years we have been utilizing Sheppard's method to prepare more highly functionalized SF_5-benzenes for applications in the areas of polymer chemistry as well as biological activity [6–8]. We have come to learn that copper, as well as other noble metals, facilitate this reaction via the intermediacy of metal aryl thiolates [9].

At the same time, others have either improved upon Sheppard's method or developed alternate routes to these materials. For example, Williams and Foster at Zeneca were able to improve upon Sheppard's method primarily by switching to alternate solvents such as alkanes, perfluoroalkanes, and perfluoroalkylethers [10]. In the mid-1990s, BNFL fluorochemicals, which has now become F_2 chemicals, developed and patented a vastly improved procedure for preparing certain SF_5-benzenes via the direct fluorination of either aromatic thiols or disulfides in a suitable solvent such as anhydrous acetonitrile [11–13]. More recently, Philp and co-workers have collaborated with F_2 chemicals to expand upon this chemistry [14], while Chambers and co-workers have collaborated with BNFL in the development of microreactors for use with elemental fluorine [15,16]. Pentafluorosulfanylbenzenes were prepared in these microreactors.

As SF_5-benzenes became easier to prepare, an ever-increasing number of publications (primarily patents) appeared describing a variety of applications for these materials. These applications have ranged from liquid crystals [17–24] to pesticides [25–30], with the latter application sometimes being more specifically defined as herbicides [31–34], fungicides [35–37], parasiticides [38–41], and insecticides/acaricides/arthropodicides [36,42–46]. Interestingly, two of the most recent examples cover the use of SF_5-arylpyrazoles to fight flea and tick infestation in animals [47,48].

Even with these advances, no general procedure exists for preparing SF_5-benzene derivatives with a substituent other than hydrogen *ortho* to the SF_5 group. In fact, to the best of our knowledge, only one such compound actually existed prior to this work, namely 1,2,4-tris-pentafluorosulfanylbenzene. Seppelt and co-workers prepared this SF_5-benzene

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derivative via the dicobalt octacarbonyl catalyzed trimerization of SF_5–C≡C–H [49]. Furthermore, neither direct fluorination nor oxidative fluorination (with AgF_2) of bis-2-nitrophenyl disulfide gave *ortho*-nitro-SF_5-benzene [4,11–14]. Only *ortho*-nitro-SF_3-bezene resulted from these attempts, and its decomposition occurred when more forcing reaction conditions were used. Presumably, steric hindrance from the *ortho*-nitro group prevents further fluorination of the SF_3 moiety. Almost 40 years ago Sheppard suggested ''that steric interactions would occur between the fluorines (of a SF_5 group) and an *ortho*-substituent of atomic radius greater than hydrogen or fluorine [4]''. The goal of the study reported herein is the preparation of SF_5-benzenes containing an *ortho*-substituent other than a hydrogen atom.

2. Results and discussion

In an effort to investigate the possibility of having a substituent other than hydrogen *ortho* to the eventual SF_5 group in a benzene derivative, a series of symmetrical 4,4′-dinitrophenyl disulfides **1a–e** was prepared (see Tables 1 and 2). These disulfides possessed substituents of gradually increasing size adjacent to the disulfide linkage: F, Cl, Br and 4-nitrophenyl. In all cases, except compound **1b**, deactivating nitro groups were used to protect the aromatic ring.

All fluorination reactions were carried out under standard conditions in a passivated (with F_2) stainless steel reactor with intermittent shaking and within a temperature range of 60 °C (2 h) to 125–130 °C (3 h). The ratio of reagents was 0.037 mol of disulfide to 1.0 mol of AgF_2. After the fluorination was completed, the reaction mixture was extracted with chloroform and washed with an aqueous solution of $NaHCO_3$. The product mixture was analyzed by TLC and gas chromatograph–mass spectrometer (GC–MS), and the mixture was separated on a silica gel column. The presence of the SF_5 moiety was easily verified not only by GC–MS but also by ^{19}F NMR spectroscopy (a prototypical AB_4 spin pattern with an asymmetric nonet at ca. 80–83 ppm and a doublet of multiplets at ca. 63–65 ppm with a coupling constant of ca. 150–152 Hz [50]).

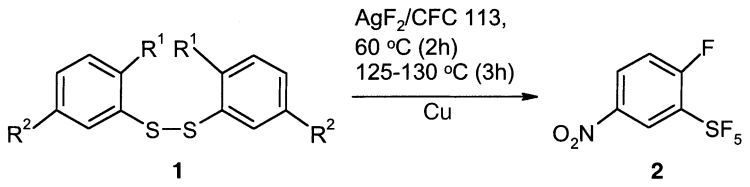
Table 1
Preparation of disulfides **1a–e**

Compound **1**	Reaction time (h)	Yield (%)	mp (°C)
a	24	82	124–126
b	24	84	40–41
c	36	85	142–144 (143–143.5) [58]
d	36	90	157–159 (159–161) [59]
e	24	86	187–188.5

Our study revealed evidence of a SF_5-containing derivative only in the case of disulfide **1a** (see Scheme 1). Evidently, the presence of the NO_2 group on the aromatic ring during the fluorination turns out to be essential, as the fluorination of disulfide **1b**, which contains a Br atom instead of a NO_2 group, gave no evidence of any SF_5-containing products under identical reaction conditions to those used for **1a**. In all other reactions, complex product mixtures were obtained

Table 2
Spectral data of compounds **1a–e**

Compound	^1H NMR (δ)	^{13}C NMR (δ)	MS *m/z* (%)	HRMS		
				Calculated	Formula	Found
a	7.27 (1H, m), 81.19 (1H, m), 8.53 (1H, m)	117.0 (d, J = 24.3 Hz), 125.3 (d, J = 19.7 Hz), 125.8 (d, J = 9.4 Hz), 126.5, 144.7 (broad s), 163.7 (d, J = 257.8 Hz)	344 (M^+, 92), 173 ($M^+/2$ + 1, 100), 172 ($M^+/2$, 32), 126 (95)	343.974	$C_{12}H_6F_2O_4S_2$	343.974
b	6.96 (1H, t, J = 8.8 Hz), 7.38 (1H, m), 7.69 (1H, dd, J = 2.4, 6.6 Hz)	117.2 (d, J = 3.5 Hz), 117.5 (d, J = 23.2 Hz), 125.4 (d, J = 18.8 Hz), 132.8 (d, J = 7.7 Hz), 133.4, 159.6 (d, J = 248.0 Hz)	414 (M^+ + 4, 41), 412 (M^+ + 2, 75), 410 (M^+, 40), 252 (11), 207 ($M^+/2$ + 2, 27), 205 ($M^+/2$, 26), 126 (100)	409.825	$C_{12}H_6{}^{75}Br_2F_2S_2$	409.826
				413.821	$C_{12}H_6{}^{81}Br_2F_2S_2$	413.822
c	7.60 (1H, d, J = 8.5 Hz), 8.06 (1H, dd, J = 2.5, 8.5 Hz), 8.44 (1H, d, J = 2.5 Hz)		376 (M^+, 100), 360 (12), 346 (6), 298 (9), 267 (19), 237 (34), 189 ($M^+/2$ + 1, 71), 188 ($M^+/2$, 64)	375.915	$C_{12}H_6{}^{35}Cl_2O_4S_2$	375.914
d	7.77 (1H, d, J = 8.5 Hz), 7.96 (1H, dd, J = 2.4, 8.5 Hz), 8.40 (1H, d, J = 2.4 Hz)		466 (M^+, 100), 450 (8), 306 (34), 283 (8), 260 (18), 234 (28), 233 $M^+/2$, 35), 232 (28), 230 (24), 214 (24)	465.812	$C_{12}H_6{}^{79}Br^{81}BrO_4S_2$	465.812
e	7.46 (1H, d, J = 8.4 Hz), 7.62 (2H, m), 8.16 (1H, dd, J = 2.2, 8.4 Hz), 8.40 (2H, m), 8.43 (1H, d, J = 2.2 Hz)	121.0, 122.4, 124.1, 130.2, 131.3, 136.5, 143.3, 145.0, 148.4, 148.6	550 (M^+, 31), 534 (5), 518 (6), 276 ($M^+/2$ + 1, 100), 275 ($M^+/2$, 43), 259 (35), 258 (31), 244 (27)	550.025	$C_{24}H_{14}N_4O_8S_2$	550.025



1 2

1	R^1	R^2
a	F	NO_2
b	F	Br
c	Cl	NO_2
d	Br	NO_2
e	*p*-NO_2-C_6H_4	NO_2

Scheme 1.

that did not give any evidence of the presence of a SF_5-containing product. Perhaps the fluorinations were halted at the stage of the SF_3 derivative, which would have been easily hydrolyzed during work up with the aqueous $NaHCO_3$. However, compounds **1b–d** can interact with AgF_2 in other ways. For instance, fluorination of the benzene ring could occur as well as intramolecular and/or intermolecular oxidation–reduction processes with NO_2 groups [4].

The successful fluorination of disulfide **1a** was carried out as described, and compound **2** was isolated in 18.4% yield. Its structure was confirmed by spectroscopic and analytical analyses (see Section 3 and Tables 3–5). For example, the ^{19}F NMR spectrum of **2** reveals three multiplets: two belong to the resonances of the SF_5 group at 77.95 ppm (axial fluorine) and 67.80 ppm (equatorial fluorines, dd, $^2J = 151.6$ Hz, $^4J = 24.7$ Hz), while the third multiplet belonging to the resonance of the ring fluorine is a quintet at −97.41 ppm ($^4J = 24.7$ Hz). In comparison to the usual ^{19}F NMR spectra of SF_5-benzenes, this spectrum shows the additional coupling between the ring fluorine and the equatorial fluorine atom. The *ortho* ring fluorine atom also shifts the resonances of the equatorial fluorine atoms to stronger field by about 3–5 ppm.

In the ^{13}C NMR spectrum of compound **2**, the resonance of the ipso carbon to the SF_5 group appears as a doublet of quintets as a result of spin–spin coupling with both the *ortho* ring fluorine atom and the four equatorial fluorine atoms of the SF_5 group. The downfield doublet with $J = 271.5$ Hz belongs to the C-1 carbon atom, and the broad signal at δ 143.5 ppm can be assigned to the C-4 carbon atom connected to the NO_2 group. The other three resonances: a doublet at δ 129.0 ppm ($J = 11.2$ Hz), multiplet at δ 125.2 ppm, and strongfield doublet at δ 119.3 ppm ($J = 26.0$ Hz) can be assigned to C-5, C-3 and C-6, respectively.

The ^1H NMR spectrum of compound **2** displays three sets of signals of equal intensity. The signal at 8.71 ppm is a

Table 3
^1H and ^{19}F NMR spectral data for compounds **2–7**

Compound	^1H NMR (δ, ppm)				^{19}F NMR (δ, ppm)		
	Benzene protons			Others	SF_5		Others
	H-6	H-5	H-3		Axial	Equatorial	
2	7.47 (m, $J = 8.7$, 5.9 Hz)	8.47 (m)	8.71 (dd, $J =$ 5.9, 2.7 Hz)		77.95 (m, $J =$ 151.6 Hz)	67.84 (dm, $J =$ 151.6, 24.7 Hz)	−97.41 (m, J = 24.7 Hz)
3a	7.44 (d, $J = 8.9$ Hz)	8.26 (dd, $J =$ 8.9, 2.2 Hz)	8.69 (d, $J =$ 2.2 Hz)	2.63 (3H, s)	81.90 (m, $J =$ 152.0 Hz)	65.07 (dm, $J =$ 152.0 Hz)	
3b	7.28 (d, $J = 9.0$ Hz)	8.13 (dd, $J =$ 8.8, 2.3 Hz)	8.76 (d, $J =$ 2.4 Hz)	7.66 (2H, d, $J = 8.9$ Hz)	82.13 (m, $J =$ 150.5 Hz)	66.95 (dm, $J =$ 150.5 Hz)	
4	7.14 (d, $J = 9.2$ Hz)	8.35 (dd, $J =$ 9.2, 2.7 Hz)	8.68 (d, $J =$ 2.7 Hz)	1.53 (3H, t, $J = 7.0$ Hz), 4.28 (2H, q, $J = 7.0$ Hz)	82.04 (m, $J =$ 151.8 Hz)	67.61 (dm, $J =$ 151.8 Hz)	
5	7.63 (d, $J = 8.8$ Hz)	8.35 (dd, $J =$ 8.8, 2.4 Hz)	8.70 (d, $J =$ 2.4 Hz)	1.61 (2H, m), 1.73 (4H, t, $J =$ 5.7 Hz), 2.8 (4H, t, $J = 4.8$ Hz)	80.95 (m, $J =$ 153.2 Hz)	66.13 (dm, $J =$ 153.2 Hz)	
6	7.41 (d, $J = 8.7$ Hz)	8.22 (dd, $J =$ 8.7, 2.3 Hz)	8.82 (d, $J =$ 2.3 Hz)		80.78 (m, $J =$ 151.0 Hz)	66.77 (dm, $J =$ 151.0 Hz)	
7	6.82 (d, $J = 9.1$ Hz)	8.10 (dd, $J =$ 9.1, 2.0 Hz)	8.57 (d, $J =$ 2.2 Hz)	5.25 (2H, broad s)	85.83 (m, $J =$ 150.0 Hz)	65.45 (dm, $J =$ 150.0 Hz)	

Table 4
^{13}C NMR spectral data for compounds **2–7**

Compound	Benzene carbons						Others
	C-1	C-2	C-3	C-4	C-5	C-6	
2	159.5 (d, J = 271.5 Hz)	140.1 (d-qu, J = 26.0, 20.0 Hz)	125.2 (m)	143.5	129.0 (d, J = 11.2 Hz)	119.3 (d, J = 26.0 Hz)	
3a	146.8	151.2 (qu, J = 18.8 Hz)	124.8 (m, J = 5.7 Hz)	143.5	126.5	125.3	16.6
3b[a]	147.7	151.3 (qu, J = 18.0 Hz)	125.0 (m, J = 5.8 Hz)	140.1	127.1	134.5	125.1, 133.8, 140.0, 145.8
4	148.4	141.4 (qu, J = 20.0 Hz)	126.0 (m, J = 5.5 Hz)	139.8	128.3	114.2	14.4, 66.4
5	157.5	151.3 (qu, J = 14.0 Hz)	125.3 (qu, J = 5.2 Hz)	144.4	127.1	128.3	24.0, 26.1, 55.0
6	146.7	154.5 (qu, J = 18.5 Hz)	125.2	140.6	126.4	136.5	
7	146.9	137.0 (qu, J = 18.0 Hz)	126.1 (qu, J = 5.5 Hz)	137.1	127.6	118.7	

[a] Spectrum was recorded in DMSO-d_6.

doublet of doublets (J_1 = 2.7 Hz, J_2 = 5.9 Hz) and can be assigned to H-3. The couplings J_1 and J_2 were assigned as *meta*-H_a–H_b and H–F couplings, respectively. The next multiplet at δ 8.47 ppm is the result of a hydrogen atom coupling with two other hydrogen atoms and a fluorine atom and can be attributed to H-5. Finally, the multiplet at δ 7.47 ppm is a result of H-6 coupling with H-5 (*ortho*) and the ring fluorine atom (*ortho*). Additional evidence for structure **2** was obtained by IR, mass spectrometer (MS) and high resolution mass spectra (HRMS).

The ring fluorine atom in compound **2** is located *ortho* and *para* with respect to the electron-withdrawing SF_5 and NO_2 groups, respectively. Normally, such a fluorine atom should be susceptible to nucleophilic aromatic substitution. But since this fluorine atom is *ortho* to such a bulky group, nucleophilic substitution was expected to be more difficult, especially when compared to similar reactions of 2,4-dinitrofluorobenzene [51]. Only moderate yields (40–60%) of the desired products were obtained when reactions of **2** were carried out, even under more forcing conditions than those used with 1-chloro-2-nitro-4-pentafluorosulfanylbenzene [52]. On the other hand, these reactions did allow us to prepare a number of novel SF_5-benzenes with *ortho*-heteroatom bonded substituents (see Scheme 2).

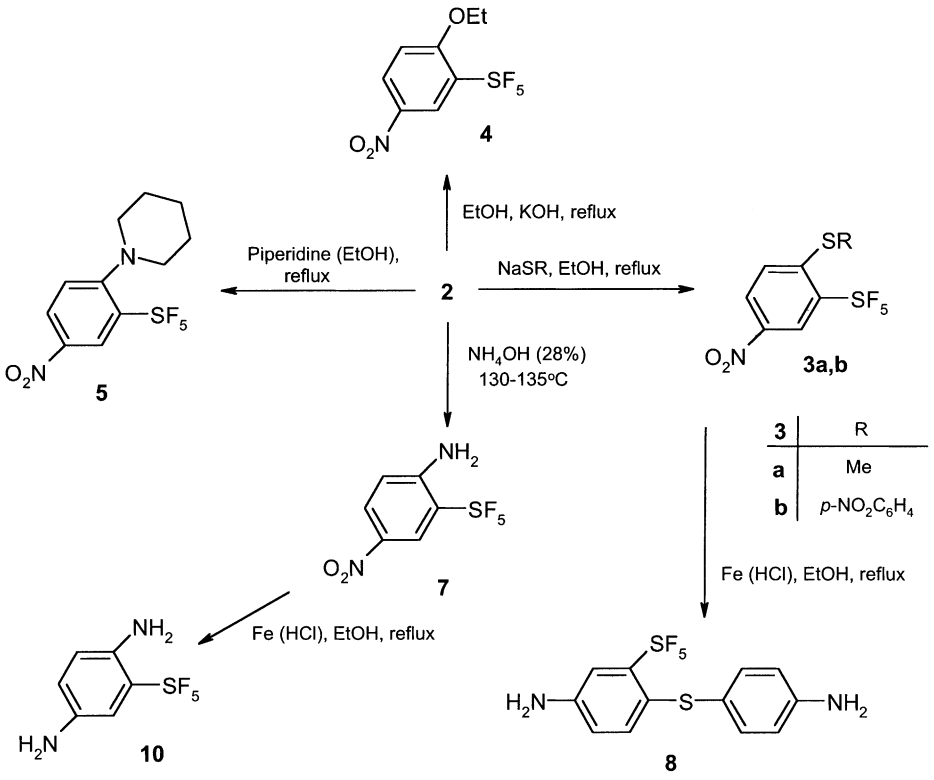
Compound **2** also reacts with the sodium salt of *para*-nitrothiophenol as well as potassium ethyl xanthate in boiling ethanol to give the asymmetric and symmetric dinitrodiphenylsulfides **3b** and **6**, respectively. The synthetic route to compound **6** is shown in Scheme 3 [53].

Heating a mixture of compound **2** and concentrated aqueous ammonia in a sealed ampule at 130–135 °C led to substitution of the fluorine atom and the formation of the amino derivative **7**. The dinitrodiphenylsulfide **3b** was oxidized into the sulfone (**11**) using $KMnO_4$ in boiling acetic acid according to Scheme 4 [54].

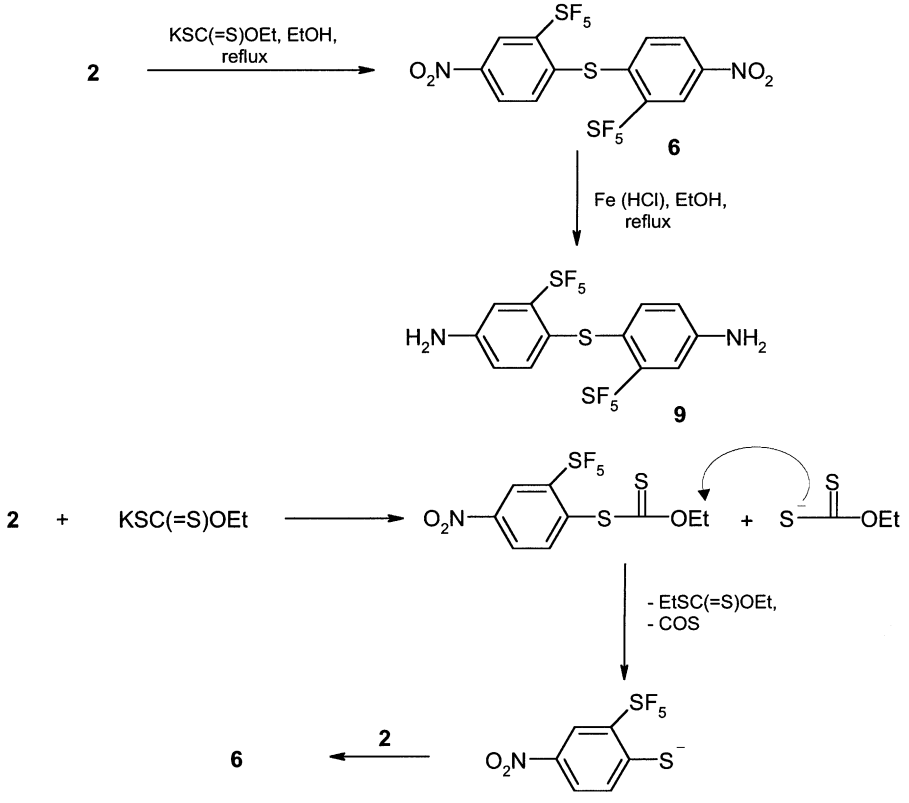
All dinitro derivatives **3b**, **7**, and **11** were reduced to their corresponding diamines **8**, **9**, and **12** with iron powder in the presence of hydrochloric acid in ethanol. This method was

Table 5
IR, MS and HRMS data for compounds **2–7**

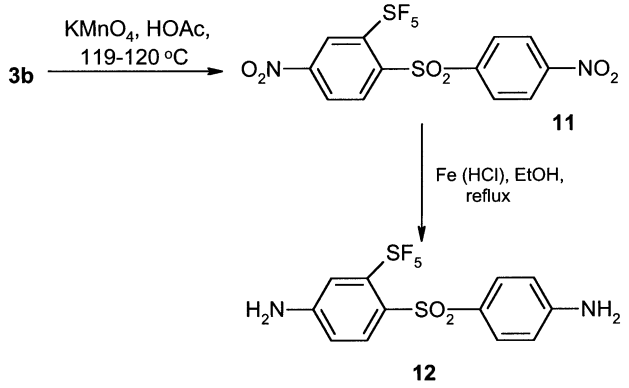
Compound	IR (cm^{-1})	MS m/z (%)	HRMS		
			Calculated	Formula	Found
2	3125, 3097 (C–N), 1625, 1593, 1546, 1489, 1361 (N–O), 1263 (C–F), 908, 861, 833, 811 (S–F)	267 (M^+, 72), 248 ([M − F]$^+$, 27), 237 ([M − NO]$^+$, 11), 221 ([M − NO_2]$^+$, 27), 207 (24), 205 (25), 189 (30), 149 (58)	266.979	$C_6H_3F_6NO_2S$	266.980
3a	1583 (N–O), 900, 870, 850, 830 (S–F)	295 (M^+, 100), 276 ([M − F]$^+$, 9), 265 ([M − NO]$^+$, 20), 245 (7)	294.975	$C_7H_6F_5NO_2S_2$	294.976
3b	1517, 1457 (N–O), 856 (S–F)	402 (M^+, 100), 309 ([M − 2NO_2 − H]$^+$, 5), 229 ([M − NO_2 − SF_5]$^+$, 5)	401.977	$C_{12}H_7F_5N_2O_4S_2$	401.978
4	899, 859, 806 (S–F)	293 (M^+, 37), 265 ([M − C_2H_4]$^+$, 35), 245 ([M − C_2H_4 − HF]$^+$, 100), 229 ([M − OC_2H_5 − F]$^+$, 13), 208 (5)	293.015	$C_8H_8F_5N_2O_2S$	293.016
5	3123, 3091 (C–N), 1596 (N–O), 913, 894, 848, 815 (S–F)	332 (M^+, 46), 331 ([M − H]$^+$, 100), 291 ([M − C_3H_5]$^+$, 14), 285 (18), 276 ([M − C_4H_8]$^+$, 23)	332.062	$C_{11}H_{13}F_5N_2O_2S$	332.064
6	1606, 1584, 1534, 1513 (N–O), 908, 866, 844 (S–F)	528 (M^+, 100), 498 ([M − NO]$^+$, 12), 400 ([M − SF_5 − H]$^+$, 8), 355 ([M − NO_2 − SF_5]$^+$, 9)	527.933	$C_{12}H_6F_{10}N_2O_4S_3$	527.932
7	3550, 3531, 3368 (NH), 1643, 1610, 1590 (N–O), 830 (S–F)	264 (M^+, 100), 244 ([M − HF]$^+$, 15), 137 ([M − SF_5]$^+$, 10)	263.999	$C_6H_5F_5N_2O_2S$	263.998



Scheme 2.



Scheme 3.



Scheme 4.

also employed for the reduction of nitroaniline **7** and the *para*-phenylenediamine **10**. The reduction of the nitro group of compound **2** by this same method gave a good yield of the aniline **13**. The amino group of the latter compound was exchanged for a bromine atom according to the Sandmeyer reaction. As a result, we have obtained a new bromo derivative of *ortho*-fluoro-SF_5-benzene **14** that was not available by the direct fluorination of disulfide **1e** (see Scheme 5).

Structures of new products **3a**, **b** and **4** have been confirmed by NMR, IR, MS and HRMS (see Tables 3–5). As expected, substitution of the ring fluorine atom with some other substituents lead to a disappearance of the additional splitting of the resonances for the equatorial fluorines of SF_5 group in the ^{19}F NMR spectrum. The NMR chemical shift data for compounds **2**, **3a**, **b**, and **4** are shown in Tables 3 and 4. The use of empirical additivity parameters [6,55] and the extra coupling observed to the four equatorial fluorine atoms of the SF_5 group make the assignment of ^{13}C NMR spectra very straightforward.

3. Experimental

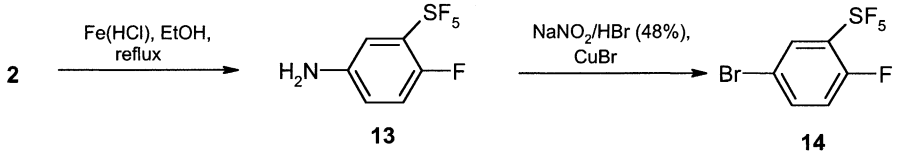
Melting points were determined in open capillaries and are uncorrected. Column chromatography was performed on silica gel 60, 230–400 mesh (Merck), with the solvents indicated. TLC was run on silica gel 60 F_{254} plates (Merck). ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on either a Bruker AM 360 or 500 spectrometer, using TMS and $CFCl_3$ as internal standards, respectively, and $CDCl_3$ or acetone-d_6 as solvent unless otherwise stated. Chemical shifts are reported in ppm. Infrared spectra were recorded on a BioRad FTS-40 FT-IR spectrometer; frequencies are reported in cm^{-1}. GC–MS analyses were carried out on a Hewlett-Packard 5890 GC–MS (70 eV) using a 30 m capillary column coated with HP1 stationary phase. HRMS were recorded on a VG Autospec MS, and the uncertainty in the mass measurements was ±0.002 Da. Elemental analyses were performed by Galbraith Laboratories Inc., in Knoxville, TN.

3.1. Preparation of aromatic disulfides *1a–e*

Each starting aromatic disulfide **1a–e** was obtained by a two-step synthesis. The first step was the transformation of the corresponding aniline into the benzene sulfonyl chloride by means of the Sandmeyer reaction [56,57], and the second step was the reduction of the latter with an HBr solution in glacial acetic acid in presence of phenol [58]. For example, 0.25 mol of the corresponding benzene sulfonyl chloride was gradually dissolved in 1.25 l of glacial acetic acid saturated with 125 g of gaseous HBr. Phenol (25.9 g, 0.275 mol) was added to the reaction mixture, which was then heated carefully under stirring to 55–60 °C (exothermic reaction). After 24–36 h at this temperature, the reaction mixture was cooled to room temperature and diluted with water. The resulting precipitate was separated by filtration, washed with water, dried in air, and recrystallized from ethanol or acetic acid. The disulfides **1a–e** were obtained in 80–90% yield as white or yellow-white fine crystals (see Tables 1 and 2).

3.2. Fluorination of aromatic disulfides

All reactions with AgF_2 were performed in a stainless steel reactor previously been passivated with elemental fluorine. While being passivated, the reactor contained six copper sheets (10 mm × 100 mm × 0.2 mm) which would later be used in the reactions. In a typical reaction, the reactor was charged with 0.037 mol of disulfide, 1.0 mol of AgF_2, and the copper strips, with all manipulations being carried out within a dry box. The vessel was then sealed, evacuated on a vacuum line, cooled to 0 °C, and 90–100 ml of CFC 113 was added by vacuum transfer. After warming to room temperature, the vessel was held at 60 °C for 2 h and then at 125–130 °C for 3 h, under intermittent shaking. The reactor was then cooled to room temperature, and the reaction mixture was extracted three times with 150 ml portions of chloroform. The extract was filtered, washed with an aqueous $NaHCO_3$ solution, and dried over $CaCl_2$. After removal of the



Scheme 5.

Table 6
Preparation of compounds **3–7**

Compound	Compound **2**	Reagent	Solvent	Temperature (°C)	*t* (h)	Eluent for chromatography	Yield (%)	mp (°C)
3a	0.13 g (0.49 mmol)	0.05 g (0.71 mmol) CH_3SNa	EtOH, 5 ml	RT, reflux	5	Benzene:hexane, 1:1.5	45.3	106–107 (yellow solid)
3b	3.45 g (12.9 mmol)	4 g (25.8 mmol) 4-nitrothiophenol 1.03 g (25.8 mmol), NaOH	EtOH, 30 ml	Reflux	2	Benzene:ethylacetate, 4:1	46.0	148–150[a] (from ethanol) (yellow solid)
4	0.13 g (0.49 mmol)	0.065 (1 mmol) KOH	EtOH, 5 ml	RT, reflux	3	Benzene:hexane, 1:2	49.1	62–63 (white solid)
5	0.1 g (0.375 mmol)	0.07 (0.82 mmol) piperidine	EtOH, 3 ml	Reflux	4	Benzene:hexane, 1:2	64.3	70–71 (orange solid)
6	3.2 g (12 mmol)	2 g (12.5 mmol) KSC(=S)OEt	EtOH, 6 ml	Reflux	24		44.3	225–227 (from ethanol) (yellowish solid)
7	3 g (10.9 mmol)	l5 ml 28% NH_4OH		130–135	5	Benzene	61.3	127–129 (yellow solid)

[a] Sample contains 40–45% of 4,4′-bis-(nitrophenyl) disulfide.

chloroform, the resulting oil was analyzed by GC–MS, and any SF_5-containing product was separated by column chromatography (silica, hexane:benzene 4:1).

3.2.1. 1-Fluoro-4-nitro-2-pentafluorosulfanylbenzene (2)

Compound **2** was prepared according to the general procedure. Yield: 18.4% as a yellow oil, $n_D^{22} = 1.4565$. Anal. calcd. for $C_6H_3F_6NO_2S$: C, 26.97; H, 1.12; N, 5.24. Found: C, 27.34; H, 1.10; N, 5.18.

3.3. Nucleophilic substitution reactions of compound 2

1-Fluoro-4-nitro-2-pentafluorosulfanylbenzene (**2**) was dissolved in ethanol, and the nucleophilic reagent was added under stirring (see Table 6). After the reaction was complete, the solvent was stripped from the reaction mixture under vacuum, and the resulting residue was mixed with water and extracted with benzene. The organic layer was dried over Na_2SO_4 and filtered. The solvent was then evaporated, and the product was purified either on a column packed with silica gel or by recrystallization from ethanol. The characterization data for compounds **2–7** are shown in Tables 3–5.

3.3.1. 1-Ethoxy-4-nitro-2-pentafluorosulfanylbenzene (4)

Anal. calcd. for $C_8H_8F_5NO_2S$: C, 32.77; H, 2.75; N, 4.78. Found: C, 34.35; H, 3.05; N, 4.63.

3.3.2. 4′-Nitro-2′-pentafluorosulfanyl-1-phenylpiperidine (5)

Anal. calcd. for $C_{11}H_{13}F_5N_2O_2S$: C, 39.76; H, 3.94; N, 8.43. Found: C, 40.69; H, 4.32; N, 8.39.

3.4. Reduction of nitro compounds 2, 3b, 6, 7, 11

Iron powder (4–5 mmol per mmol of NO_2 groups) was added in portions to a refluxing solution of the corresponding nitro compound in 5 ml of ethanol and 0.2 ml of concentrated hydrochloric acid, under stirring. After refluxing for 2–3 h, the mixture was decolorized with activated charcoal, filtered, cooled to room temperature, and made slightly basic by the addition of NH_4OH. The solvent was evaporated in vacuum, and the remaining residue was washed with water and extracted with benzene or chloroform. The organic layer was dried over Na_2SO_4 and filtered. The solvent was then evaporated, and the product was purified either by recrystallization or column chromatography.

3.4.1. 4,4′-Diamino-2-pentafluorosulfanyldiphenyl sulfide (8)

Compound **3b** (1.21 g, 3.0 mmol) was reduced according to the general method. The product was purified by column chromatography (silica, benzene). Yield: 0.80 g (78%) as yellowish solid, mp 76–77 °C. ^{1}H NMR ($CDCl_3$) δ 3.72 (4H, broad s), 6.55 (1H, dd, $J = 8.6$, 2.4 Hz), 6.63 (2H, d, $J = 8.6$ Hz), 6.90 (1H, d, $J = 8.6$ Hz), 7.08 (1H, d, $J = 2.5$ Hz), 7.23 (2H, d, $J = 8.4$ Hz); ^{19}F NMR δ 67.46 (m, $^2J_{SF_4-SF} = 151.7$ Hz), 86.91 (m, $^2J_{SF-SF_4} = 151.7$ Hz); ^{13}C NMR δ 114.5 (qu, $^3J_{C-SF_4} = 5.0$ Hz), 115.9, 118.4, 121.7, 124.6, 133.4, 135.8, 144.2, 147.1, 153.2 (qu, $^2J_{C-SF_4} = 18.0$ Hz). IR (Nujol) 3418, 3312, 3208 (N–H), 850 (S–F) cm^{-1}. GC–MS *m/z* (relative intensity) 342 (M^+, 100), 214 ($[M - SF_5 - H]^+$, 42), 199 ($[M - SF_5 - NH_2]^+$, 30), 171 ($M^+/2$, 17), 124 ($C_6H_6NS^+$, 42). HRMS calcd. for $C_{12}H_{11}F_5N_2S_2$ 342.028. Found: 342.028. Anal. calcd. for $C_{12}H_{11}F_5N_2S_2$: C, 42.10; H, 3.24; N, 8.18. Found: C, 42.34; H, 3.23; N, 7.97.

3.4.2. Bis-(4-amino-2-pentafluorosulfanylphenyl) sulfide (9)

Dinitro compound **6** (1.37 g, 2.6 mmol) was converted into the diamino derivative **9** by the general method. The product was separated by column chromatography (silica, benzene). Yield: 1.04 g (85%) as white-yellow solid, mp 169–170 °C. ^{1}H NMR ($CDCl_3$) δ 4.76 (2H, broad s), 6.62 (1H, dd, $J = 8.5$, 2.4 Hz), 6.99 (1H, d, $J = 8.5$ Hz), 7.12 (1H, d, $J = 2.4$ Hz); ^{19}F NMR δ 67.78 (m, $^2J_{SF_4-SF} = 151.8$ Hz) 86.23 (m, $^2J_{SF-SF_4} = 151.8$ Hz); ^{13}C NMR δ 112.0, 114.6, 118.6, 136.8, 145.6, 155.2 (C-2, qu, $^2J_{C-SF_4} = 14.6$ Hz). IR (Nujol) 3473, 3344 (N–H), 911, 849, 803 (S–F) cm^{-1}. MS *m/z* (relative intensity) 468 (M^+, 100), 360 ($[M - SF_4]^+$, 5), 340 ($[M - SF_5 - H]^+$, 9), 232 ($[M - SF_5 - SF_4 - H]^+$, 9), 214 ($[M - 2SF_5]^+$, 48), 186 ($C_{12}H_{10}S^+$, 13). HRMS calcd. for $C_{12}H_{10}F_{10}N_2S_3$ 467.985.

Found: 467.983. Anal. calcd. for $C_{12}H_{10}F_{10}N_2S_3$: C, 30.77; H, 2.15; N, 5.98. Found: C, 30.84; H, 2.25; N, 5.95.

3.4.3. 2-Pentafluorosulfanyl-1,4-phenylenediamine (**10**)

Compound **7** (1.0 g, 3.8 mmol) was reduced with iron powder by the general method. The product was purified by recrystallization from hexane. Yield: 0.67 g (75%) as ivory colored solid, mp 106–108 °C. ^{1}H NMR ($CDCl_3$) δ 3.35 (2H, broad s), 4.04 (2H, broad s), 6.62 (1H, d, $J = 8.63$ Hz), 6.69 (1H, dd, $J = 8.5, 2.3$ Hz), 6.95 (1H, d, $J = 2.5$ Hz); ^{19}F NMR δ 65.62 (m, $^2J_{SF_4-SF} = 148.5$ Hz), 88.93 (m, $^2J_{SF-SF_4} = 148.5$ Hz); ^{13}C NMR δ 114.1 (C-3, qu, $^3J_{C-SF_4} = 5.5$ Hz), 120.6, 121.2, 134.0, 137.1, 140.4 (C-2, qu, $^2J_{C-SF_4} = 14.6$ Hz). IR (Nujol) 3470, 3422, 3318, 3208 (N–H), 824 (S–F) cm^{-1}. GC–MS *m/z* (relative intensity) 234 (M^+, 100), 125 ($[M - SF_4 - H]^+$, 9), 106 ($[M - SF_5 - H]^+$, 57). HRMS calcd. for $C_6H_7F_5N_2S$ 234.025. Found: 234.023. Anal. calcd. for $C_6H_7F_5N_2S$: C, 30.77; H, 3.01; N, 11.96. Found: C, 31.15; H, 3.39; N, 11.55.

3.4.4. 4,4′-Dinitro-2-pentafluorosulfanyldiphenyl sulfone (**11**)

Potassium permanganate (1.85 g) in 12 ml of hot water was added dropwise with stirring to 1.6 g (4.0 mmol) of compound **3b** dissolved in boiling acetic acid (30 ml). When the addition was complete, water (30 ml) was added, and the cooled mixture was decolorized with SO_2. The precipitate was separated by filtration and purified by column chromatography (silica, benzene:ethylacetate 4:1). Yield: 1.04 g (60%) as a yellowish solid, mp 164–166 °C. ^{1}H NMR (acetone-d_6) δ 8.21 (2H, d, $J = 8.9$ Hz), 8.66 (2H, d, $J = 8.9$ Hz), 8.83 (1H, dd, $J = 8.8, 2.1$ Hz), 8.88 (1H, d, $J = 2.1$ Hz), 9.08 (1H, d, $J = 8.8$ Hz); ^{19}F NMR δ 71.40 (m, $^2J_{SF_4-SF} = 150.8$ Hz), 79.24 (m, $^2J_{SF-SF_4} = 150.8$ Hz); ^{13}C NMR δ 125.6, 126.6 (qu, $^3J_{C-SF_4} = 6.7$ Hz), 128.9, 130.2, 137.6, 142.5, 146.6, 151.5, 151.9, 152.4 (C-2, qu, $^2J_{C-SF_4} = 22.2$ Hz). IR (Nujol) 3120 (C–H), 1613, 1542 (N–O), 870 (S–F) cm^{-1}. GC–MS *m/z* (relative intensity) 434 (M^+, 2), 415 ($[M - F]^+$, 2.5), 308 ($[M - SF_5 + H]^+$, 2.5), 296 ($C_6H_3F_5NO_3S_2^+$, 84), 229 ($C_{12}H_7F_5NO_2S^+$, 10), 207 (7), 186 ($C_6H_4NO_4S^+$, 85), 122 ($C_6H_4NO_2^+$, 100). HRMS calcd. for $C_{12}H_7F_5N_2O_6S_2$ 433.967. Found: 433.969. Anal. calcd. for $C_{12}H_7F_5N_2O_6S_2$: C, 33.19; H, 1.62; N, 6.45. Found: C, 33.40; H, 1.72; N, 6.38.

3.4.5. 4,4′-Diamino-2-pentafluorosulfanyldiphenyl sulfone (**12**)

The dinitro compound **11** (1.3 g, 3.0 mmol) was reduced according to the general procedure. The product was purified by recrystallization from toluene. Yield: 0.90 g (80%) as white-yellow solid, mp 191–193 °C. ^{1}H NMR (acetone-d_6) δ 5.53 (2H, broad s), 6.03 (2H, broad s), 6.70 (2H, d, $J = 8.7$ Hz), 6.97 (1H, dd, $J = 8.9, 2.2$ Hz), 7.33 (1H, d, $J = 2.2$ Hz), 7.43 (2H, d, $J = 8.7$ Hz), 8.26 (1H, d, $J = 8.9$ Hz); ^{19}F NMR δ 70.95 (m, $^2J_{SF_4-SF} = 150.0$ Hz), 83.90 (m, $^2J_{SF-SF_4} = 150.0$ Hz); ^{13}C NMR δ 113.8, 115.4, 115.8, 126.1, 129.0, 130.1, 136.6, 153.37 (C-2, qu, $^3J_{C-SF_4} = 18.0$ Hz), 153.45, 153.5. IR (Nujol) 3505, 3479, 3378 (N–H), 862 (S–F) cm^{-1}. GC–MS *m/z* (relative intensity) 374 (M^+, 100), 281 ($[M - C_6H_5NH_2]^+$, 40), 207 (90), 191 (12), 156 ($C_6H_6NO_2S^+$, 84), 140 ($C_6H_4O_2S^+$, 23). HRMS calcd. for $C_{12}H_{11}F_5N_2O_2S_2$ 374.018. Found: 374.016. Anal. calcd. for $C_{12}H_{11}F_5N_2O_2S_2$: C, 38.50; H, 2.96; N, 7.48. Found: C, 38.92; H, 3.08; N, 7.38.

3.4.6. 4-Fluoro-3-pentafluorosulfanylaniline (**13**)

Compound **2** (5.6 g, 21 mmol) was transformed into the amino derivative by the standard method. For purification, compound **13** was passed through a column (silica, benzene). Yield: 3.9 g (78%) as yellow oil, $n_D^{22} = 1.4710$. ^{1}H NMR ($CDCl_3$) δ 3.60 (2H, broad s), 6.76 (1H, m), 6.96–6.99 (2H, m); ^{19}F NMR δ −123.27 (qu-m, $^4J_{SF-SF_4} = 24.9$ Hz), 67.37 (m, $^2J_{SF_4-SF} = 151.2$ Hz, $^4J_{CF-SF_4} = 24.9$ Hz), 81.82 (m, $^2J_{SF-SF_4} = 151.2$ Hz, $^4J_{SF-CF} = 1.7$ Hz); ^{13}C NMR δ 113.6 (C-2, qu, $J = 4.8$ Hz), 118.2 (C-5, d, $J = 25.0$ Hz), 119.7 (C-6, d, $J = 7.8$ Hz), 140.0 (C-3, d-qu), 142.3 (C-1, s), 149.0 (C-4, d, $^1J_{C-F} = 250.2$ Hz). IR (film) 3482, 3400 (N–H), 3228, 865, 818 (S–F) cm^{-1}. GC–MS *m/z* (relative intensity) 237 (M^+, 100), 129 ($[M - SF_4]^+$, 27), 110 ($[M - SF_5]^+$, 50), 83 (57). HRMS calcd. for $C_6H_5F_6NS$ 237.005. Found: 237.003.

3.5. 1-Bromo-4-fluoro-3-pentafluorosulfanylbenzene (**14**)

Compound **13** (3.2 g, 12 mmol), dissolved in 100 ml of 48% HBr, was diazotized at 0–5 °C with 1.02 g of $NaNO_2$ dissolved in 2.5 ml H_2O. The resulting solution was gradually added to a boiling mixture of 10 ml HBr (48%) and 2 g of CuBr in a vessel with a steam inlet. After steam distillation, the liquid product was separated with a funnel, dried, and then purified by column chromatography (silica, hexane). Yield of colorless liquid: 1.6 g (44%), $n_D^{22} = 1.4680$. ^{1}H NMR ($CDCl_3$) δ 7.12 (1H, m), 7.63 (1H, m), 7.88 (1H, dd, $J = 6.0$, 2.5 Hz); ^{19}F NMR δ −109.09 (qu, $^4J_{CF-SF_4} = 26.0$ Hz), 68.92 (m, $^2J_{SF_4-SF} = 151.6$ Hz, $^4J_{SF_4-CF} = 26.0$ Hz), 80.81 (m, $^2J_{SF-SF_4} = 151.6$ Hz, $^4J_{SF-CF} = 2.1$ Hz); ^{13}C NMR δ 116.2 (C-1, s), 119.6 (C-5, d, $J = 25.2$ Hz), 131.4 (C-2, qu, $J = 4.4$ Hz), 136.7 (C-6, d, $J = 8.7$ Hz), 140.9 (C-3, d-qu), 155.1 (C-4, d, $^1J_{C-F} = 261.4$ Hz). IR (film) 3108 (C–H), 863 (S–F), 813 (S–F) cm^{-1}. GC–MS *m/z* (relative intensity) 302/300 (M^+, 100), 283/281 ($[M - F]^+$, 10), 194/192 ($[M - SF_4]^+$, 60), 113 ($C_6H_3F_2^+$, 50), 94 ($C_6H_3F^+$, 50). HRMS calcd. for $C_6H_3{}^{81}BrF_6S$ and $C_6H_3{}^{79}BrF_6S$ 301.902 and 299.904. Found: 301.902 and 299.904.

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