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A new synthetic route to aryl bis(perfluoroalkanesulfonyl) methanes; structures of tolyldiazonium bis(trifluoromethanesulfonyl)methide and 4-nitrophenylhydrazono bis(trifluoromethanesulfonyl)methane

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Abstract

Aryl bis(perfluoroalkanesulfonyl)methanes have been prepared in high yield by the pyrolysis of arenediazonium bis(perfluoroalkanesulfonyl)methides obtained from the reaction of arenediazonium chlorides with potassium bis(perfluoroalkanesulfonyl)methides. Heating *p*-nitrophenyldiazonium bis(trifluoromethanesulphonyl)methide resulted in a rearrangement to 4-nitrophenylhydrazono bis(trifluoromethanesulfonyl)methane. The X-ray structure analyses of $4\text{-}CH_3C_6H_4N_2^+(CF_3SO_2)_2CH^-$ and $4\text{-}NO_2C_6H_4NHN{=}C(SO_2CF_3)_2$ are presented.

Introduction

Bis(trifluoromethanesulfonyl)methane, $(CF_3SO_2)_2CH_2$ (**1**), was first synthesized more than 30 years ago [1]; since Korsh reported an improved method for preparing this compound, many of its derivatives have been synthesized. Because of the low reactivity of $(R_fSO_2)_2CH^-$, its alkylation could only be accomplished through the use of reactive halides such as allyl and benzyl iodide or bromide [2, 3]. Its arylation, however, has not been reported to date. Recently, in our studies on phenyliodonium bis(perfluoroalkanesulfonyl)methides, $PhI^+\text{–}\bar{C}(SO_2CF_3)_2$, (**2**), as a carbene precursor, we found that photolysis of **2** in benzene or toluene afforded aryl bis(trifluoromethanesulfonyl)methanes [4] [eqn. (1)].

$$\underset{(\mathbf{2})}{PhI^+\text{–}\bar{C}(SO_2CF_3)_2} + RC_6H_5 \xrightarrow[-PhI]{h\nu} 4\text{-}RC_6H_4CH(SO_2CF_3)_2 \ (R{=}H,\ CH_3) \qquad (1)$$

However, upon heating or photolysis of **2** in fluorobenzene or nitrobenzene, no corresponding aryl bis(trifluoromethanesulfonyl)methane was formed [5]. This may be attributed to the electrophilic properties of the bis(trifluoromethanesulfonyl)carbene intermediate. Here, we would like to report a general method for the preparation of the title compound.

Results and discussion

The synthesis of the title compounds involves a two-step reaction sequence; treatment of aryldiazonium chloride with potassium

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bis(perfluoroalkanesulfonyl)methide gave aryldiazonium bis(perfluoroalkanesulfonyl)methides $ArN_2^+\ \bar{C}H(SO_2R_f)_2$ (**4**), pyrolysis of **4** affording aryl bis(perfluoroalkanesulfonyl)methanes with the elimination of nitrogen gas [eqn. (2)].

$$\begin{gathered} ArN_2^+\ Cl^- + K^+\ \bar{C}H(SO_2R_f)_2 \xrightarrow[H_2O]{0\ ^\circ C-r.t.} \underset{\textbf{(4)}}{ArN_2^+\ \bar{C}H(SO_2R_f)_2} \\ ArN_2^+\ \bar{C}H(SO_2R_f)_2 \xrightarrow[-N_2]{\Delta} \underset{\textbf{(5)}}{ArCH(SO_2R_f)_2} \end{gathered} \qquad (2)$$

As mentioned above, the reactivity of bis(perfluoroalkanesulfonyl)methides, $(R_fSO_2)_2CH^-$, is low, due to steric hindrance and electron delocalization. However, it reacted readily with phenyldiazonium chloride; thus, when a solution of $K^+\ \bar{C}H(SO_2R_f)_2$ was added to a clear solution of $PhN_2^+\ Cl^-$, a yellow precipitate was formed. After filtration and vacuum drying, the crude product (**4**) was obtained in high yield (see Table 1). These new diazo compounds are more stable than $PhN_2^+\ Cl^-$ [6] and can be stored at room temperature for several weeks without alteration.

Recrystallization of **4** from acetone and acetonitrile (1:1) gave fine yellowish crystals. The X-ray structure analysis of **4b** (see Fig. 1) shows that the N(1)–N(2)–C(3)–C(6) arrangement is linear and that the arenediazonium cation is planar with an N–N bond length equal to that in nitrogen gas. Every N_2 group is surrounded by four sulfonyl oxygen atoms, the bond distances between the nitrogen and oxygen atoms being nearly equal (*c.* 3 Å) indicating that the positive charge is shared by the two nitrogen atoms [7]. Pyrolysis of **4** (with the exception of **4e**) at a temperature of *c.* 75–95 °C gave aryl bis(perfluoroalkanesulfonyl)methanes (**5**). If the pyrolysis was carried out in a polar solvent such as in acetone or acetonitrile, compound **4** decomposed at *c.* 50 °C.

We have previously reported that pyrolysis of phenyldiazonium tris(trifluoromethanesulfonyl)methide gives two products [eqn. (3)] [8]:

TABLE 1

Aryldiazonium bis(perfluoroalkanesulfonyl)methide compounds (**4**) prepared

Entry No.	R_f	Ar	Product **4**	Yield (%)[a]
1	CF_3	C_6H_5	**4a**	95
2	CF_3	p-$CH_3C_6H_4$	**4b**	92
3	CF_3	p-FC_6H_4	**4c**	92
4	CF_3	p-IC_6H_4	**4d**	90
5	CF_3	p-$NO_2C_6H_4$	**4e**	90
6	C_4F_9	C_6H_5	**4f**	90
7	[b]	C_6H_5	**4g**	88

[a] Isolated yield.
[b] See eqn. (4).

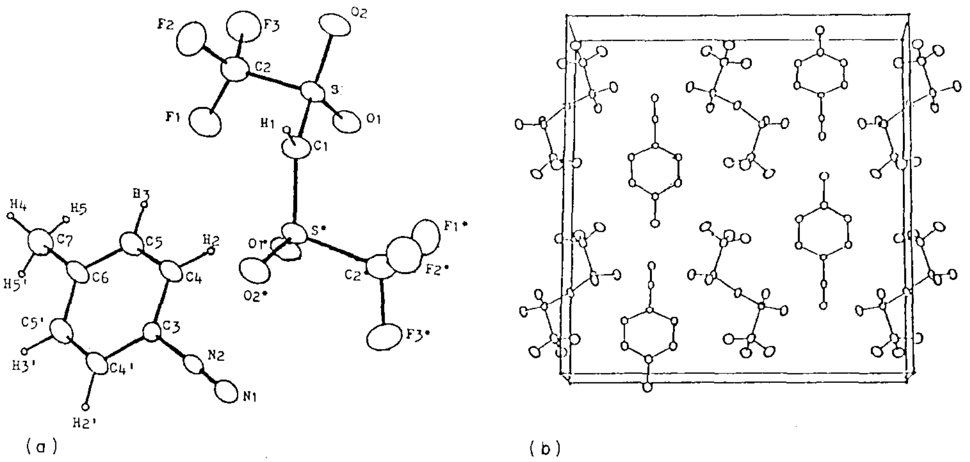


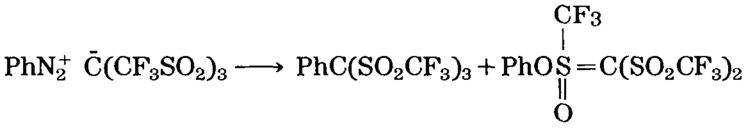
Fig. 1. (a) The structure of compound **4b** and (b) the stereoview of the unit cell contained therein.

TABLE 2

Products arising from the pyrolysis of aryldiazonium bis(perfluoroalkanesulfonyl)methides (**4**)

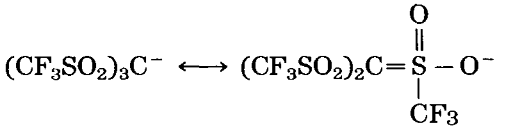
Entry No.	Reactant	Product	Yield (%)[a]	M.p. (°C)
1	**4a**	**5a**	76	104
2	**4b**	**5b**	70	92
3	**4c**	**5c**	68	135
4	**4d**	**5d**	68	126
5	**4e**	**6**	75	153
6	**4f**	**5f**	70	152
7	**4g**	**5g**	75	136

[a] Isolated yield.



$$PhN_2^+\ \bar{C}(CF_3SO_2)_3 \longrightarrow PhC(SO_2CF_3)_3 + PhO\overset{\overset{\displaystyle CF_3}{|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{=}C(SO_2CF_3)_2 \qquad (3)$$

In this reaction, the phenyl cation formed attacks the tris(trifluoromethanesulfonyl)methide anion at both the carbon and the oxygen atom.



$$(CF_3SO_2)_3C^- \longleftrightarrow (CF_3SO_2)_2C{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CF_3}{|}}{S}}-O^-$$

In the pyrolysis of **4**, only the carbon arylation product **5** was obtained (see Table 2), even though the X-ray structure analysis of **4b** shows that the positive nitrogen is closer to the oxygen than to the carbon atom. Similarly, treatment of potassium 1,1,3,3-tetraoxothiohexafluorocyclohexide with $PhN_2^+\ Cl^-$ gave phenyldiazonium 1,1,3,3-tetraoxothiohexafluorocyclohexide (**4g**); heat treatment of **4g** led to the formation of 2-phenyl-1,1,3,3-tetraoxythiohexafluorocyclohexane (**5g**) in 75% yield [eqn. (5)]:

$$PhN_2^+\ Cl^- + K^+\ \overline{\bar{C}HSO_2(CF_2)_3SO_2} \longrightarrow \underset{\textbf{(4g)}}{PhN_2^+\ \overline{\bar{C}HSO_2(CF_2)_3SO_2}} \qquad (4)$$

$$\textbf{4g} \longrightarrow \underset{\textbf{(5g)}}{Ph\overline{CHSO_2(CF_2)_3SO_2}} \qquad (5)$$

It is interesting to note that even on heating **4e** to the melting point no nitrogen was released. After purification, the pyrolysis product was shown to be 4-nitrophenylhydrazono bis(trifluoromethanesulfonyl)methane (**6**) by IR, NMR and X-ray structure analyses (see Fig. 2). This demonstrates that tautomerization presumably occurs in the pyrolysis of **4e**:

$$\underset{\textbf{(4e)}}{4\text{-}NO_2C_6H_4N_2^+\ \bar{C}H(SO_2CF_3)_2} \longrightarrow \underset{\textbf{(6)}}{4\text{-}NO_2C_6H_4NHN{=}C(SO_2CF_3)_2} \qquad (6)$$

X-Ray analysis revealed that the 4-nitrophenyl group, and the N, N and C atoms are planar, the lengths of the C(1)–S(1) and C(1)–S(2) bonds (1.755

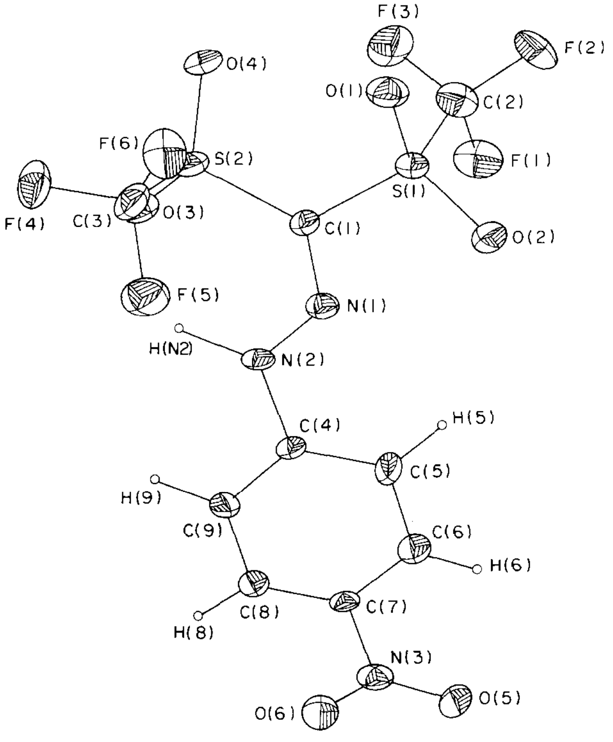
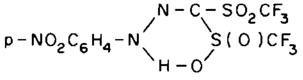


Fig. 2. The structure of compound **6**.

Å) are longer than in the diazonium compound **4b** (1.659 Å), and that the bond distances H(N2)–N(2), H(N2)–N(1), H(N2)–C(1) and H(N2)–O(3) are 1.238 Å, 2.205 Å, 2.987 Å and 2.134 Å, respectively. Consistent with these data and the IR spectra, another possible tautomer **6a** and an intramolecular six-membered ring structure **6b** may be ruled out.

$p\text{-}NO_2C_6H_4\text{-}N{=}NCH(SO_2CF_3)_2$

(**6a**)



(**6b**)

All these results are summarized in Tables 3–6. The positional and general displacement parameters for compounds **4** and **6** are listed in Tables 7–10, respectively.

TABLE 3

Compound **4b**: bond distances in Ångstrom

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S	O(1)	1.428(4)[a]	C(3)	C(4)	1.380(6)
S	O(2)	1.423(4)	C(4)	C(5)	1.368(8)
S	C(1)	1.66(4)	C(5)	C(6)	1.378(7)
S	C(2)	1.811(7)	C(6)	C(7)	1.50(1)
F(1)	C(2)	1.334(8)	N(1)	O(1)	2.988(4)
F(2)	C(2)	1.324(8)	N(1)	O(2)	3.043(7)
F(3)	C(2)	1.319(7)	N(2)	O(1)	3.024(4)
N(1)	N(2)	1.091(9)	N(2)	O(2)	2.939(7)
N(2)	C(3)	1.40(2)			

[a] Numbers in parentheses are estimated standard deviations for the last digits.

TABLE 4

Compound **4b**: bond angles in degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O(1)	S	O(2)	120.0(2)[a]	S	C(2)	F(3)	111.8(5)
O(1)	S	C(1)	113.2(3)	F(1)	C(2)	F(2)	106.9(6)
O(1)	S	C(2)	102.7(3)	F(1)	C(2)	F(3)	105.7(6)
O(2)	S	C(1)	110.5(4)	F(2)	C(2)	F(3)	107.1(6)
O(2)	S	C(2)	101.7(4)	N(2)	C(3)	C(4)	118.0(4)
C(1)	S	C(2)	107.0(2)	C(4)	C(3)	C(4*)	123.9(8)
N(1)	N(2)	C(3)	180(1)	C(3)	C(4)	C(5)	116.3(5)
S	C(1)	S*	123.0(5)	C(4)	C(5)	C(6)	123.4(6)
S	C(2)	F(1)	112.6(5)	C(5)	C(6)	C(5*)	116.9(8)
S	C(2)	F(2)	112.4(5)	C(5)	C(6)	C(7)	121.5(4)

[a] Numbers in parentheses are estimated standard deviations for the last digits.

TABLE 5

Compound **6**: bond distances in Ångstrom

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S(1)	O(1)	1.425(4)[a]	F(4)	C(3)	1.339(7)	C(4)	C(9)	1.382(8)
S(1)	O(2)	1.414(5)	F(5)	C(3)	1.330(8)	C(5)	C(6)	1.382(8)
S(1)	C(1)	1.755(6)	F(6)	C(3)	1.278(8)	C(5)	H(5)	1.021(7)
S(1)	C(2)	1.848(8)	O(5)	N(3)	1.222(7)	C(6)	C(7)	1.361(8)
S(2)	O(3)	1.426(4)	O(6)	N(3)	1.211(7)	C(6)	H(6)	0.939(7)
S(2)	O(4)	1.413(4)	N(1)	N(2)	1.289(7)	C(7)	C(8)	1.368(8)
S(2)	C(1)	1.755(5)	N(1)	C(1)	1.312(7)	C(8)	C(9)	1.391(8)
S(2)	C(3)	1.812(8)	N(2)	C(4)	1.438(7)	C(8)	H(8)	1.141(6)
F(1)	C(2)	1.307(9)	N(2)	H(N2)	1.238(5)	C(9)	H(9)	1.091(6)
F(2)	C(2)	1.323(8)	N(3)	C(7)	1.487(7)			
F(3)	C(2)	1.293(9)	C(4)	C(5)	1.396(8)			

[a] Numbers in parentheses are estimated standard deviations for the last digits.

It is also noteworthy that, in contrast to other diazonium bis(perfluoroalkanesulfonyl)methides, no $M-N_2$ fragment peak occurs in the mass spectrum of **4e**. Gorvin and Ayling suggested that substituents exerting electron-withdrawing effects on the diazonium ion group increase the covalency of the C—N bond and hence the stability of the molecule [9, 10]. This present work confirms this point. Another tautomerization of a phenyl diazo compound has been reported by Meyer [11, 12], who found that the product obtained via coupling of diazobenzene with malonic acid is the phenylhydrazone of mesoxalic acid [eqn. (7)]:

$$PhN_2^+\ \bar{C}H(CO_2H)_2 \longrightarrow PhNHN{=}C(CO_2H)_2 \qquad (7)$$

Attempts to extend this method to prepare diphenyl bis(perfluoroalkanesulfonyl)methanes failed. Under similar reaction conditions, treatment of $K^+\ \bar{C}(Ph)(SO_2CF_3)_2$ with $PhN_2^+\ Cl^-$ did not give the expected $PhN_2^+\ \bar{C}(Ph)(SO_2CF_3)_2$ product.

In view of the convenience of preparation of the diazonium salt **4** and the high yields (in both reaction steps), this present method provides an easy synthesis of the title compounds.

Experimental

Melting points were measured on a Thiele apparatus and are reported uncorrected. ^1H NMR and ^{19}F NMR spectra were recorded on a Varian 360L instrument using Me_4Si and CF_3Cl as internal or external standards, respectively. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Low-resolution mass spectra were obtained on a Finnigan GC–MS 4021 instrument. Elemental analyses were performed by the Analysis Department of this Institute. Bis(perfluoroalkanesulfonyl)methanes were prepared according to literature methods [2, 3].

TABLE 6

Compound **6**: bond angles in degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O(1)	S(1)	O(2)	121.1(3)[a]	O(5)	N(3)	O(6)	135.1(5)	C(5)	C(6)	H(6)	120.5(6)
O(1)	S(1)	C(1)	109.5(3)	O(5)	N(3)	C(7)	117.2(8)	C(7)	C(6)	H(6)	119.8(6)
O(1)	S(1)	C(2)	106.6(3)	O(6)	N(3)	C(7)	117.7(6)	N(3)	C(7)	C(6)	117.8(5)
O(2)	S(1)	C(1)	109.7(3)	F(1)	C(2)	F(2)	108.0(8)	N(3)	C(7)	C(8)	119.0(5)
O(2)	S(1)	C(2)	105.4(3)	F(1)	C(2)	F(3)	109.5(7)	C(6)	C(7)	C(8)	123.3(5)
C(1)	S(1)	C(2)	102.8(3)	F(2)	C(2)	F(3)	109.8(6)	C(7)	C(8)	C(9)	118.3(5)
O(3)	S(2)	O(4)	120.6(3)	F(4)	C(3)	F(5)	106.5(7)	C(7)	C(8)	H(8)	125.1(5)
O(3)	S(2)	C(1)	106.2(3)	F(4)	C(3)	F(6)	109.1(6)	C(9)	C(8)	H(8)	115.1(5)
O(3)	S(2)	C(3)	106.9(3)	F(5)	C(3)	F(6)	107.7(6)	C(4)	C(9)	C(8)	118.5(5)
O(4)	S(2)	C(1)	112.0(3)	N(2)	C(4)	C(5)	120.8(5)	C(4)	C(9)	H(9)	118.5(5)
O(4)	S(2)	C(3)	107.4(3)	N(2)	C(4)	C(9)	116.6(5)	C(8)	C(9)	H(9)	121.7(5)
C(1)	S(2)	C(3)	102.3(3)	C(5)	C(4)	C(9)	122.6(5)	S(1)	C(1)	C(9)	121.2(3)
N(2)	N(1)	C(1)	125.7(5)	C(4)	C(5)	C(6)	117.9(6)	S(1)	C(1)	N(1)	112.5(4)
N(1)	N(2)	C(4)	117.2(5)	C(4)	C(5)	H(5)	126.0(6)	S(2)	C(1)	N(1)	126.3(5)
N(1)	N(2)	H(N2)	121.5(4)	C(6)	C(5)	H(5)	115.9(5)				
C(1)	N(2)	H(N2)	115.4(4)	C(5)	C(6)	C(7)	119.3(6)				

[a] Numbers in parentheses are estimated standard deviations for the last digits.

TABLE 7

Compound **4b**: positional parameters and their estimated standard deviations

Atom	x	y	z	B (Å^2)[a]
S	0.7351(4)	0.57176(9)	0.2937(1)	3.70(3)
F(1)	0.550(1)	0.4752(3)	0.3927(3)	8.3(1)
F(2)	0.918(1)	0.5247(3)	0.4196(3)	8.4(2)
F(3)	0.575(1)	0.5936(3)	0.4270(3)	8.3(2)
O(1)	0.4739(9)	0.5823(3)	0.2696(3)	4.8(1)
O(2)	0.901(1)	0.6381(3)	0.3023(3)	5.4(1)
N(1)	0.361(2)	0.750	0.3061(5)	4.6(2)
N(2)	0.293(2)	0.750	0.2497(5)	3.9(2)
C(1)	0.889(2)	0.500	0.250	3.7(2)
C(2)	0.694(2)	0.5400(5)	0.3873(4)	5.4(2)
C(3)	0.203(2)	0.750	0.1774(5)	4.1(3)
C(4)	0.156(2)	0.6785(4)	0.1445(4)	5.2(3)
C(5)	0.067(2)	0.6810(4)	0.0743(4)	6.7(3)
C(6)	0.016(3)	0.750	0.0377(6)	5.3(3)
C(7)	−0.100(4)	0.750	−0.0376(7)	8.5(5)
H(1)	0.082	0.500	0.250	4.0*
H(4)	0.250	0.365	0.332	4.0*
H(5)	0.041	0.365	0.449	4.0*
H(71)	0.957	0.750	0.416	4.0*
H(72)	0.125	0.699	0.449	4.0*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a2B(1,1)+b2B(2,2)+c2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

Preparation of arenediazonium bis(trifluoromethanesulfonyl)methides (4)

A typical procedure for preparing the arenediazonium bis(trifluoromethanesulfonyl)methide **4a** was as follows. A solution consisting of water (10 ml) and potassium bis(trifluoromethanesulfonyl)methide (1.6 g, 5 mmol), synthesized from the reaction of bis(trifluoromethanesulfonyl)methane with potassium carbonate, was added dropwise to a 50 ml round-bottomed flask charged with a solution of phenyldiazonium chloride in water prepared by treatment of aniline (0.5 g, 5.5 mmol), water (10 ml), hydrochloric acid (1 N, 6 ml) and sodium nitrite (0.4 g, 6 mmol) at 0 °C. After addition, the reaction mixture was warmed to room temperature and stirred for 1 h. The yellow precipitate was filtered off and dried under vacuum giving compound **4a** (1.8 g, 95%). Recrystallization from acetone gave the pure product.

Compound **4a**: ^{1}H NMR ($CDCl_3$) δ: 3.30 (s, 1H); 8.05 (m, 2H); 8.30 (m, 3H) ppm. ^{19}F NMR δ: 5.30 (s, $2\times CF_3$) ppm. IR (ν_{max}) (KBr) (cm^{-1}): 3065 (s); 2270 (m); 1572 (s); 1461 (s); 1360 (vs); 1220–1120 (vs); 1070 (vs); 955 (s); 830 (m); 750 (s); 648 (m); 600 (vs). MS (70 eV) (*m/e*): 384 (M^+, 0.11); 357 (M^+H-N_2, 28.08); 315 (M^+-CF_3, 2.00); 287 ($M^+-CF_3-N_2$, 14.16); 239 ($M^+-N_2-CF_3SO$, 9.44); 223 ($M^+-N_2-CF_3SO_2$, 6.14); 105 ($C_6H_5N_2^+$, 10.97); 77 ($C_6H_5^+$, 100). Analysis: Calc. for $C_9H_6F_6N_2O_4S_2$: C,

TABLE 8

Compound **4b**: general displacement parameters and their estimated standard deviations[a]

Atom	*U*(1,1)	*U*(2,2)	*U*(3,3)	*U*(1,2)	*U*(1,3)	*U*(2,3)
S	0.0417(8)	0.0324(6)	0.0667(9)	−0.001(1)	−0.000(1)	−0.0065(9)
F(1)	0.143(5)	0.084(3)	0.088(3)	−0.039(4)	0.020(4)	0.004(3)
F(2)	0.122(5)	0.103(4)	0.093(3)	0.016(4)	−0.034(4)	0.002(3)
F(3)	0.134(5)	0.095(3)	0.087(3)	0.015(4)	0.029(4)	−0.027(3)
O(1)	0.045(3)	0.044(2)	0.091(4)	0.013(3)	−0.010(3)	−0.012(3)
O(2)	0.060(3)	0.044(3)	0.099(4)	−0.011(3)	0.007(4)	−0.015(3)
N(1)	0.076(6)	0.037(4)	0.062(6)	0	−0.006(6)	0
N(2)	0.071(6)	0.023(3)	0.053(5)	0	0.004(6)	0
C(1)	0.027(5)	0.042(5)	0.070(6)	0	0	−0.014(5)
C(2)	0.074(6)	0.056(4)	0.076(5)	0.004(5)	0.004(5)	−0.016(4)
C(3)	0.091(9)	0.036(4)	0.029(5)	0	0.001(6)	0
C(4)	0.114(7)	0.034(3)	0.050(4)	0.011(5)	−0.013(5)	−0.001(3)
C(5)	0.16(1)	0.039(4)	0.056(5)	−0.008(6)	−0.0066(7)	−0.008(4)
C(6)	0.11(1)	0.036(5)	0.058(7)	0	−0.012(8)	0
C(7)	0.21(2)	0.056(6)	0.054(7)	0	−0.03(1)	0

[a] The form of the anisotropic displacement parameter is: exp[−2*P*[2{*h*2*a*2*U*(1,1)+*k*2*b*2*U*(2,2)+12*c*2*U*(3,3)+2*hkabU*(1,2)+2*hlacU*(1,3)+2*klbcU*(2,3)}]] where *a*, *b* and *c* are reciprocal lattice constants.

28.13; H, 1.56; N, 7.29; F, 29.69%. Found: C, 28.41; H, 1.57; N, 7.37; F, 29.31%.

Compound **4b**: ^{1}H NMR δ: 2.65 (s, CH_3); 3.40 (s, 1H); 7.81–8.80 (AA'BB', $4H_{arom}$) ppm. ^{19}F NMR δ: 5.10 (s, $2\times CF_3$) ppm. IR (ν_{max}) (cm^{-1}): 3060 (m); 3030 (m); 2249 (m); 1580 (s); 1322 (vs); 1303 (s); 1216–1120 (vs); 1090 (s); 942 (s); 842 (m); 811 (s); 600 (vs). MS (*m/e*): 398 (M^+, 0.54); 371 (M^+-N_2, 43.44); 355 ($M^+-N_2-CH_3$, 6.01); 253 ($M^+-N_2-CF_3SO$, 14.89); 237 ($M^+-N_2-CF_3SO_2$, 3.89); 151 ($CH_3C_6H_4CSO^+$, 6.86); 119 ($CH_3C_6H_4N_2{}^+$, 6.69); 107 ($CH_3C_6H_4O^+$, 100); 91 ($CH_3C_6H_4{}^+$, 18.40). Analysis: Calc. for $C_{10}H_8F_6N_2O_4S_2$: C, 30.15; H, 2.01; N, 7.04; F, 28.64%. Found: C, 30.40; H, 2.07; N, 7.16; F, 28.27%.

Compound **4c**: ^{1}H NMR δ: 3.20 (s, 1H); 7.85–9.15 (AA'BB', $4H_{arom}$) ppm. ^{19}F NMR δ: 11.0 (s, $2\times CF_3$); 15.3 (s, 1F) ppm. IR (ν_{max}) (cm^{-1}): 3080 (m); 2450 (m); 1580 (s); 1481 (m); 1325 (vs); 1258 (m); 1200–1160 (vs); 1091 (s); 960 (s); 840 (s); 600 (s). MS (*m/e*): 402 (M^+, 1.35); 401 (M^+-1, 8.54); 374 (M^+-N_2, 0.67); 312 ($M^+-N_2-SO_2$, 3.35); 268 ($M^+-H-CF_3SO_2$, 10.60); 110 ($FC_6H_4NH^+$, 52.94); 95 ($FC_6H_4{}^+$, 18.48); 69 ($CF_3{}^+$, 100). Analysis: Calc. for $C_9H_5F_7N_2O_4S_2$: C, 26.87; H, 1.24; N, 6.97; F, 33.08%. Found: C, 26.67; H, 1.09; N, 6.81; F, 33.71%.

Compound **4d**: ^{1}H NMR δ: 3.40 (s, 1H); 7.83–8.88 (AA'BB', $4H_{arom}$) ppm. ^{19}F NMR δ: 5.30 (s, $2\times CF_3$) ppm. IR (ν_{max}) (cm^{-1}): 3063 (w); 3033 (m); 2260 (m); 1581 (s); 1320 (vs); 1305 (s); 1240–1140 (s); 1088 (s); 948 (m); 840 (m); 600 (s). MS (*m/e*): 510 (M^+, 0.22); 482 (M^+-N_2, 1.05); 406 ($M^+-N_2-C_6H_4$, 6.29); 349 ($M^+-N_2-CF_3SO_2$, 10.80); 330 (M^+-

TABLE 9

Compound **6**: positional parameters and their estimated standard deviations

Atom	x	y	z	B (Å^2)^a
S(1)	0.8779(2)	0.3060(2)	0.7185(2)	3.27(5)
S(2)	0.8185(2)	0.4457(2)	0.5157(2)	3.43(5)
F(1)	1.1058(5)	0.3443(6)	0.7097(6)	6.7(2)
F(2)	0.9959(6)	0.4873(5)	0.7007(6)	1.0(2)
F(3)	0.9896(6)	0.3821(6)	0.5512(5)	6.8(2)
F(4)	0.6172(6)	0.0349(5)	0.4519(5)	6.5(2)
F(5)	0.6900(6)	0.0245(6)	0.6352(5)	6.7(2)
F(6)	0.5962(5)	0.1665(6)	0.5686(6)	6.8(2)
O(1)	0.7670(6)	0.3578(5)	0.6664(6)	4.8(2)
O(2)	0.9183(6)	0.3030(5)	0.8421(5)	4.0(1)
O(3)	0.8770(6)	0.0554(5)	0.4761(5)	4.3(2)
O(4)	0.7887(7)	0.2402(5)	0.4451(5)	5.2(2)
O(5)	1.3297(7)	−0.1843(6)	1.1405(6)	5.6(2)
O(6)	1.3220(7)	−0.3196(5)	1.0189(6)	5.8(2)
N(1)	0.9555(7)	0.1102(6)	0.7301(6)	3.3(2)
N(2)	0.9743(7)	0.0082(6)	0.7105(6)	3.6(2)
N(3)	1.2918(7)	−0.2296(7)	1.0471(7)	3.9(2)
C(1)	0.8890(9)	0.1773(7)	0.6575(9)	3.3(2)
C(2)	1.000(1)	0.3947(8)	0.6646(9)	5.1(3)
C(3)	0.6700(9)	0.0933(9)	0.5446(8)	4.5(2)
C(4)	1.0513(8)	−0.0514(7)	0.8011(7)	2.9(2)
C(5)	1.1119(9)	0.0013(7)	0.8996(8)	4.2(2)
C(6)	1.1883(9)	−0.0593(8)	0.9812(8)	3.9(2)
C(7)	1.2038(8)	−0.1678(7)	0.9606(7)	3.0(2)
C(8)	1.1438(8)	−0.2217(7)	0.86343(7)	3.3(2)
C(9)	1.0649(8)	−0.1621(7)	0.7819(7)	3.3(2)
H(N2)	0.971	−0.027	0.609	4.0*
H(5)	1.109	0.094	0.916	4.0*
H(6)	1.221	−0.029	1.055	4.0*
H(8)	1.168	−0.307	0.834	4.0*
H(9)	1.029	−0.195	0.695	4.0*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a2B(1,1)+b2B(2,2)+c2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

$N_2-F-CF_3SO_2$, 100); 279 ($M^+-N_2-C_6H_4I$, 10.00); 203 ($C_6H_4I^+$, 22.29); 127 (I^+, 5.11). Analysis: Calc. for $C_9H_5F_6IN_2O_4S_2$: C, 21.18; H, 0.98; N, 5.49; F, 22.35%. Found: C, 21.20; H, 1.04; N, 5.64; F, 21.98%.

Compound **4e**: ^1H NMR δ: 3.15 (s, 1H); 8.75–9.35 (AA'BB', $4H_{arom}$) ppm. ^{19}F NMR δ: 6.0 (s, $2\times CF_3$) ppm. IR (ν_{max}) (cm^{-1}): 3080 (m); 2280 (m); 1600 (m); 1540 (s); 1392 (m); 1325 (vs); 1220–1100 (s); 962 (s); 858 (m); 730 (m); 600 (s). MS (m/e): 429 (M^+, 1.89); 307 ($M^+-O_2NC_6H_4$, 1.34); 295 ($M^+-H-CF_3SO_2$, 3.90); 150 ($O_2NC_6H_4N_2{}^+$, 2.29); 122 ($O_2NC_6H_4{}^+$, 7.14); 117 (CF_3SO^+, 5.11); 69 ($CF_3{}^+$, 100). Analysis: Calc. for $C_9H_5F_6N_3O_6S_2$: C, 25.17; H, 1.17; N, 9.79; F, 26.57%. Found: C, 25.43; H, 1.39; N, 10.08; F, 25.97%.

TABLE 10

Compound **6**: general displacement parameters and their estimated standard deviations[a]

Atom	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
S(1)	0.045(1)	0.033(1)	0.044(1)	0.006(1)	0.002(1)	0.006(1)
S(2)	0.051(1)	0.042(1)	0.034(1)	0.011(1)	−0.004(1)	0.008(1)
F(1)	0.055(4)	0.086(4)	0.116(5)	0.003(4)	0.015(4)	0.021(4)
F(2)	0.100(5)	0.044(3)	0.121(5)	−0.017(4)	0.020(4)	−0.000(4)
F(3)	0.104(5)	0.096(5)	0.061(3)	−0.026(4)	0.024(3)	0.017(3)
F(4)	0.072(4)	0.086(4)	0.079(4)	−0.007(4)	−0.020(3)	−0.019(4)
F(5)	0.079(4)	0.096(4)	0.076(4)	−0.026(4)	−0.001(4)	0.023(4)
F(6)	0.055(4)	0.092(4)	0.107(5)	0.016(4)	0.005(4)	−0.023(4)
O(1)	0.056(4)	0.034(3)	0.068(4)	0.012(3)	−0.001(3)	0.012(3)
O(2)	0.065(4)	0.044(3)	0.039(3)	0.003(4)	−0.000(3)	0.000(3)
O(3)	0.060(4)	0.055(4)	0.044(3)	0.021(4)	0.001(3)	0.002(3)
O(4)	0.097(5)	0.047(4)	0.041(3)	0.008(4)	−0.020(4)	0.013(3)
O(5)	0.085(5)	0.058(4)	0.053(4)	0.007(4)	−0.040(4)	0.004(4)
O(6)	0.084(5)	0.046(4)	0.078(5)	0.023(4)	−0.019(4)	0.009(4)
N(1)	0.043(4)	0.034(4)	0.044(4)	0.007(4)	−0.905(4)	0.009(3)
N(2)	0.057(5)	0.036(4)	0.039(4)	0.015(4)	−0.007(4)	0.008(4)
N(3)	0.044(4)	0.041(4)	0.056(4)	0.008(4)	0.007(4)	0.018(4)
C(1)	0.059(6)	0.034(5)	0.027(4)	0.012(5)	−0.011(4)	−0.001(4)
C(2)	0.079(7)	0.051(6)	0.065(6)	0.006(6)	0.019(6)	0.010(5)
C(3)	0.056(6)	0.065(6)	0.042(5)	0.012(6)	−0.011(5)	−0.001(5)
C(4)	0.042(5)	0.029(4)	0.037(5)	0.007(4)	−0.008(4)	0.004(4)
C(5)	0.073(7)	0.028(5)	0.047(5)	0.008(5)	−0.023(5)	−0.005(4)
C(6)	0.059(6)	0.041(5)	0.038(5)	0.003(5)	−0.018(5)	−0.004(4)
C(7)	0.037(5)	0.031(4)	0.039(4)	0.006(4)	−0.011(4)	0.010(4)
C(8)	0.045(5)	0.028(4)	0.042(5)	0.006(4)	−0.009(4)	−0.002(4)
C(9)	0.048(5)	0.028(4)	0.042(5)	−0.000(4)	−0.010(4)	0.002(4)

[a] The form of the anisotropic displacement parameter is: $\exp[-2P[2\{h2a2U(1,1)+k2b2U(2,2)+12c2U(3,3)+2hkabU(1,3)+2hlacU(1,3)+2klbcU(2,3)\}]]$ where a, b and c are reciprocal lattice constants.

Compound **4f**: ^{1}H NMR δ: 3.20 (s, 1H); 8.00 (m, 2H); 8.25 (m, 3H) ppm. ^{19}F NMR δ: 6.2 (s, $2\times CF_3$); 34.7 (m, $2\times CF_2$); 45.5 (m, $2\times CF_2$); 50.8 (s, $2\times CF_2S$) ppm. IR (ν_{max}) (cm^{-1}): 3064 (m); 2270 (m); 1590 (m); 1462 (s); 1360 (vs); 1240–1100 (vs); 1058 (s); 960 (s); 828 (m); 751 (s); 645 (m); 600 (s). MS (*m/e*): 684 (M^+, 0.22); 657 ($MH^+ - N_2$, 12.07); 437 ($M^+ - C_4F_9 - N_2$, 24.58); 373 ($M^+ - C_4F_9SO_2 - N_2$, 11.31); 105 ($C_6H_5N_2^+$, 10.86); 77 ($C_6H_5^+$, 100); 69 (CF_3^+, 31.59). Analysis: Calc. for $C_{15}H_6F_{18}N_2O_4S_2$: C, 26.32; H, 0.88; F, 50.00%. Found: C, 1.00; H, 1.02; F, 49.86%.

Compound **4g**: ^{1}H NMR δ: 4.62 (s, 1H); 7.93–8.33 (m, 5ArH) ppm. ^{19}F NMR δ: 41.0 (s, $2\times CF_2S$); 45.8 (s, CF_2) ppm. IR (ν_{max}) (cm^{-1}): 3063 (m); 2265 (m); 1582 (s); 1460 (m); 1328 (vs); 1220–1160 (vs); 1083 (s); 966 (s); 831 (m); 747 (s); 650 (s); 595 (s). MS (*m/e*): 397 (M^+H, 1.70); 396 (M^+, 0.89); 368 ($M^+ - N_2$, 1.34); 304 ($M^+ - N_2 - SO_2$, 12.10); 140 ($M^+ - N_2 - 2SO_2 - C_2F_4$, 87.21); 105 ($C_6H_5N_2^+$, 11.63); 100 ($C_2F_4^+$, 23.67);

77 ($C_6H_5^+$, 100). Analysis: Calc. for $C_{10}H_6F_6N_2O_4S_2$: C, 30.30; H, 1.52; F, 28.79%. Found: C, 30.42; H, 1.78; F, 28.34%.

*Preparation of compounds **5** by pyrolysis of arenediazonium bis(trifluoromethanesulfonyl)methides (**4**)*

A typical procedure was as follows. Compound **4a** (1.9 g, 5 mmol) was placed in a 5 ml flask equipped with a drying tube. After heating about 10 min, the release of N_2 ceased. The residue was sublimed under vacuum giving 1.3 g of **5a** as a crude product. Recrystallization from CH_3CN and $(CH_3)_2CO$ (1:1) gave colourless needles. Other aryl bis(perfluoroalkanesulfonyl)methanes (**5**) were prepared similarly.

Compound **5a**: ^{1}H NMR δ: 4.70 (s, 1H); 7.80–8.20 (m, 5H) ppm. ^{19}F NMR δ: -2.0 (s, $2\times CF_3$) ppm. IR (ν_{max}) (cm^{-1}): 3030 (w); 2950 (w); 1500 (m); 1450 (w); 1380 (vs); 1370 (s); 1240–1170 (s); 1100 (vs); 805 (m); 700 (m); 605 (m); 580 (m); 510 (s). MS (*m/e*): 356 (M^+, 0.75); 287 (M^+-CF_3, 1.20); 223 ($M^+-CF_3SO_2$, 49.37); 154 ($C_6H_4CHSO_2^+$, 4.36); 106 ($C_6H_5CHO^+$, 100); 90 ($C_7H_6^+$, 52.81); 77 ($C_6H_5^+$, 43.65); 69 (CF_3^+, 19.91). Analysis: Calc. for $C_9H_6F_6O_4S_2$: C, 30.34; H, 1.68; F, 32.02%. Found: C, 30.61; H, 1.77; F, 32.21%.

Compound **5b**: ^{1}H NMR δ: 2.65 (s, CH_3); 4.73 (s, 1H); 7.80–8.80 (AA'BB', $4H_{arom}$) ppm. ^{19}F NMR δ: -2.1 (s, $2\times CF_3$) ppm. IR (ν_{max}) (cm^{-1}): 3030 (m); 2950 (w); 1600 (w); 1498 (m); 1378 (vs); 1315 (s); 1250–1120 (vs); 990 (s); 892 (s); 808 (s); 760 (m); 708 (m); 610 (s). MS (*m/e*): 301 (M^+-CF_3, 4.59); 253 (M^+-CF_3SO, 3.63); 237 ($M^+-CF_3SO_2$, 4.72); 167 ($CH_3C_6H_4CSO_2^+$, 5.25); 155 ($CH_3C_6H_4SO_2$, 4.72); 133 ($CF_3SO_2^+$, 2.85); 107 ($CH_3C_6H_4O^+$, 100); 91 ($CH_3C_6H_4^+$, 7.82); 69 (CF_3^+, 37.86). Analysis: Calc. for $C_{10}H_8F_6O_4S_2$: C, 32.42; H, 2.16; F, 30.81%. Found: C, 32.02; H, 1.75; F, 30.69%.

Compound **5c**: ^{1}H NMR δ: 4.90 (s, 1H); 7.85–9.05 (AA'BB', $4H_{arom}$) ppm. ^{19}F NMR δ: 48.0 (s, 1F); -2.0 (s, $2\times CF_3$) ppm. IR (ν_{max}) (cm^{-1}): 3033 (m); 2960 (w); 1587 (w); 1498 (m); 1380 (vs); 1310 (s); 1240–1140 (vs); 1100 (s); 980 (s); 845 (s); 600 (s). MS (*m/e*): 374 (M^+, 0.44); 355 (M^+-F, 1.79); 305 (M^+-CF_3, 6.52); 257 (M^+-CF_3SO, 3.17); 241 ($M^+-CF_3SO_2$, 42.16); 117 (CF_3SO^+, 12.38); 95 ($FC_6H_4^+$, 52.34); 69 (CF_3^+, 100). Analysis, Calc. for $C_9H_5F_7O_4S_2$: C, 28.88; H, 1.34; F, 35.56%. Found: C, 28.59; H, 1.07; F, 35.01%.

Compound **5d**: ^{1}H NMR δ: 4.74 (s, 1H); 7.78–8.85 (AA'BB', $4H_{arom}$) ppm. ^{19}F NMR δ: -2.3 (s, $2\times CF_3$) ppm. IR (ν_{max}) (cm^{-1}): 3026 (m); 2948 (m); 1600 (w); 1495 (m); 1380 (vs); 1365 (s); 1245–1100 (vs); 875 (m); 800 (s); 600 (s); 510 (s). MS (*m/e*): 483 (M^+H, 6.21); 482 (M^+, 3.04); 413 (M^+-CF_3, 1.64); 365 (M^+-CF_3SO, 12.37); 355 (M^+-I), 24.85); 267 ($IC_6H_4SO_2$, 11.37); 203 ($IC_6H_4^+$, 78.31); 127 (I^+, 5.27); 69 (CF_3^+, 100). Analysis: Calc. for $C_9H_5IF_6O_4S_2$: C, 22.41; H, 1.04; F, 23.65%. Found: C, 22.08; H, 1.27; F, 23.27%.

Compound **5f**: ^{1}H NMR δ: 4.63 (s, 1H); 7.83–8.23 (m, 5H) ppm. ^{19}F NMR δ: 0.3 (s, $2\times CF_3$); 30.2 (m, $2\times CF_2$); 40.5 (m, $2\times CF_2$); 44.2 (m,

$2 \times CF_2S$) ppm. IR (ν_{max}) (cm^{-1}): 3030 (m); 2979 (w); 1590 (w); 1497 (m); 1371 (s); 1244–1110 (vs); 1060 (s); 978 (s); 830 (m); 763 (m); 640 (m); 595 (s). MS (*m/e*): 657 (M^+H, 1.07); 656 (M^+, 0.54); 637 ($M^+ - F$, 7.63); 587 ($M^+ - CF_3$, 2.28); 580 ($M^+H - C_6H_5$, 18.94); 437 ($M^+ - C_4F_9$, 2.33); 389 ($M^+ - C_4F_9SO$, 11.88); 219 ($C_4F_9^+$, 63.17); 77 ($C_6H_5^+$, 100); 69 (CF_3^+, 24.87). Analysis: Calc. for $C_{15}H_6F_{19}O_4S_2$: C, 27.44; H, 0.91; F, 55.03%. Found: C, 27.04; H, 1.17; F, 54.88%.

Compound **5g**: ^1H NMR δ: 5.72 (s, 1H); 7.26–7.82 (m, C_6H_5) ppm. ^{19}F NMR δ: 32.1 (AB, F^a CF_2C, $^2J_{FF} = 278$ Hz); 40.9 (AB, $2F^a$ CF_2S, $^2J_{FF} = 286$ Hz); 55.0 (AB, F^e CF_2C); 56.1 (AB, $2F^e$ CF_2S) ppm. IR (ν_{max}) (cm^{-1}): 3030 (vw); 2919 (m); 1491 (m); 1450 (m); 1390 (vs); 1375 (s); 1285 (m); 1205 (m); 1185 (s); 1163 (s); 1150 (s); 1060 (m); 990 (m); 905 (s); 850 (m); 800 (m); 693 (m); 650 (m). MS (*m/e*): 368 (M^+, 1.90); 304 ($M^+ - SO_2$, 1.60); 140 ($M^+ - 2SO_2 - C_2F_4$, 100); 90 ($C_6H_5CH^+$, 58.21); 77 ($C_6H_5^+$, 28.84). Analysis: Calc. for $C_{10}H_6F_6O_4S_2$: C, 32.61; H, 1.63; F, 30.98%. Found: C, 32.49; H, 1.84; F, 30.67%.

Tautomerization of ***4e***

Compound **4e** (1.1 g, 2.6 mmol), placed in a 5 ml flask equipped with a drying tube, was heated to 90 °C in an oil bath for 30 min. No N_2 was released. The product was sublimed under vacuum and then purified by crystallization from CH_3CN and C_6H_6 (1:1) to give pure **6** (0.8 g, 72%).

Compound **6**: ^1H NMR δ: 6.37 (broad, 1H); 7.85–8.50 (AA'BB', $4H_{arom}$) ppm. ^{19}F NMR δ: 0.7 (s, $2 \times CF_3$) ppm. IR (ν_{max}) (cm^{-1}): 3200 (m); 3105 (w); 1620 (m); 15809 (w); 1543 (s); 1440 (s); 1395 (s); 1370 (m); 1342 (s); 1240–1180 (vs); 1120 (s); 990 (s); 860 (s); 838 (s); 705 (s); 650 (s); 505 (s).

Crystal data

Compound **4b**: $C_{10}H_8F_6N_2O_4S_2$, M = 398.30, orthorhombic, space group *Pcmb*, $a = 5.153(1)$, $b = 17.017(3)$, $c = 18.330(2)$ Å, $V = 1607.2$ Å^3, $Z = 4$; $D_c = 1.646$ g cm^{-3}, $F(000) = 800$, $\mu(MoK\alpha) = 3.970$ cm^{-1}; crystal dimension $0.2 \times 0.1 \times 0.1$ mm. Intensity data were collected at 20 °C with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated MoKα radiation. 1693 unique reflections were measured in the range $2° < 2\theta < 50°$ with $0 < h < 6$, $0 < k < 20$, $0 < l < 21$. LP and absorption corrections were applied to the reflection data. The structure was solved by direct methods using MULTAN 11/82. The positions of the H atoms were defined via theoretical calculation. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by a full-matrix least-squares technique. Final *R*, *Rw* and *S* values were 0.039, 0.047, 1.85, respectively, for 621 observed reflections ($F^2 > 3\sigma(F^2)$). All computations were performed on a MICROVAX II computer with SDP, MULTAN 11/82 and ORTEP programs. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Compound **6**: $C_9HF_6N_2O_4S_2$, M = 429.28, monoclinic, space group *P2l/n*, $a = 11.206(2)$, $b = 12.209(2)$, $c = 11.522(4)$ Å, $\beta = 99.47(2)°$, $V = 1554.9$

Å^3, $Z = 4$; $D_c = 1.829$ g cm^{-3}; $F(000) = 856$, $\mu(\text{MoK}\alpha) = 4.276$ cm^{-1}; crystal dimension $0.1 \times 0.3 \times 0.1$ mm. Intensity data were collected at 20 °C with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated MoKα radiation. 2885 unique reflections were measured in the range $2° < 2\theta < 50°$ with $0 < h < 13$, $0 < k < 14$, $-13 < l < 13$. The LP correction factor was applied to the reflection data. The structure was solved by direct methods. All H atoms were defined by difference Fourier synthesis. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by a full-matrix least-squares technique. Final R, Rw and S values were 0.058, 0.065, 2.33, respectively, for 1357 observed reflections ($F^2 > 3\sigma(F^2)$). All computations were performed on a MICROVAX II computer with SDP, MULTAN 11/82 and ORTEP programs. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

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References

1 T. Gramsted and R.N. Haszeldine, *J. Chem. Soc.*, (1957) 4069.

2 R.J. Koshar and R.A. Mitsch, *J. Org. Chem.*, *38* (1978) 3358.

3 S.-Z. Zhu and D.D. DesMarteau, *12th Int. Fluorine Symp.*, Santa Cruz, CA, Aug. 7–12, 1988.

4 S.-Z. Zhu and Q.Y. Chen, *J. Chem. Soc., Chem. Commun.*, (1990) 1459.

5 S.-Z. Zhu, unpublished results.

6 K.H. Saunders and R.L.M. Allen, *Aromatic Diazo Compounds*, 3rd edn., Edward Arnold, London.

7 C. Romming, *Acta Chem. Scand.*, *17* (1963) 1444.

8 S.-Z. Zhu and D.D. DesMarteau, *Inorg. Chem.*, *32* (1993) 223.

9 E.E. Ayling, J.H. Gorvin and L.E. Hinkel, *J. Chem. Soc.*, (1941) 613.

10 J.H. Gorvin, *J. Chem. Soc.*, (1951) 1693.

11 R. Meyer, *Ber. Dtsch. Chem. Ges.*, *21* (1884) 118.

12 R. Meyer, *Ber. Dtsch. Chem. Ges.*, *24* (1891) 241.