

## Synthesis and Reactions of Fluoroalkanesulfonyl Azides and *N,N*-Dichlorofluoroalkanesulfonamides

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Thermolysis or photolysis of fluoroalkanesulfonyl azides  $R_FSO_2N_3$  afforded the corresponding nitrene intermediates  $R_FSO_2N$  which reacted readily with alkanes, alkenes, benzene, dimethyl sulfide, dimethyl sulfoxide, pyridine and triphenylphosphine to give insertion or addition products. Similar results were obtained by the reactions of *N,N*-dichlorofluoroalkanesulfonamides,  $R_FSO_2NCl_2$ , with the same reagents in the presence of zinc powder. Treatment of  $R_FSO_2NCl_2$  with alkene in the absence of zinc powder gave only a 1:1 adduct via a free-radical intermediate  $R_FSO_2NCl$ .

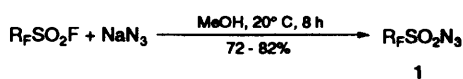
Many azides (e.g. phenyl azide, alkane- or arene-sulfonyl azide and azidoformates, etc.), when heated or irradiated undergo decomposition and react via a nitrene intermediate  $R-N^{1-5}$  ( $R = \text{aryl, } R'OCO, R'SO_2, ArSO_2 \text{ etc.}$ ). The reactions of trifluoromethanesulfonyl azide, first synthesized from the reaction of trifluoromethanesulfonic acid anhydride with sodium azide in 1965,<sup>6</sup> as a trifluoromethanesulfonyl nitrene precursor are little known. The sole report of its reactions concerns those with aromatic compounds.<sup>7</sup>

*N,N*-Dichlorotoluene-*p*-sulfonamide (dichloramine-T) has been reported as a convenient tosyl nitrene precursor.<sup>8</sup> The fluoro-containing analogue *N,N*-dichlorotrifluoromethanesulfonamide  $CF_3SO_2NCl_2$  was first prepared in 1974<sup>9</sup> but its chemistry has been little studied. Recently, Yagupol'skii reported its reactions with diphenyl sulfide<sup>10</sup> and trifluoromethyl phenyl sulfide.<sup>11</sup>

In connection with our studies on the carbene- and nitrene-containing perfluoroalkanesulfonyl functionality,<sup>12-14</sup> we here describe the preparation of fluoroalkanesulfonyl azides  $R_FSO_2N_3$  **1** and *N,N*-dichlorofluoroalkanesulfonamides  $R_FSO_2NCl_2$  **8** and their reactions as fluoroalkanesulfonyl nitrene  $R_FSO_2N$  precursors; other reactions of **8** are also described.

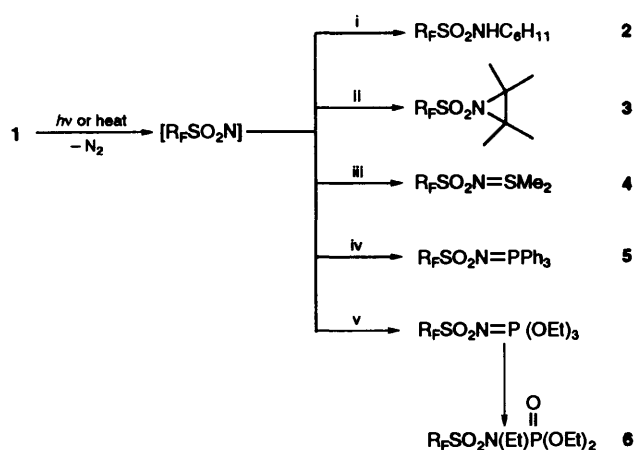
### Results and Discussion

Compounds **1** were conveniently prepared by treatment of perfluoroalkanesulfonyl fluoride with sodium azide in methanol at room temperature,<sup>15</sup> thus:



Perfluoroalkanesulfonyl azides **1**, colourless liquids with a characteristic pungent odour, could be stored unchanged at room temperature but decomposed at ca. 120 °C. When irradiated, compound **1** decomposed readily to form perfluoroalkanesulfonyl nitrene with the elimination of nitrogen (see Scheme 1).

Irradiation of compound **1** in an excess of cyclohexane gave the insertion product *N*-cyclohexylperfluoroalkanesulfonamides **2** together with the minor product  $R_FSO_2NH_2$  **7** (20%). Cycloaddition occurred smoothly with 1,4-dimethylbut-2-ene to yield 2,2,3,3-tetramethylaziridine **3**. It is noteworthy that in this reaction the corresponding insertion product  $R_FSO_2NHCH_2CMe_2$  was absent. In our previous work on the bis(perfluoroalkanesulfonyl)carbene which was formed by photolysis of  $[PhI^+][C(SO_2R_F)_2]^-$ , we found that the carbene intermediate readily added to the C=C bond of



**Scheme 1** Reagents, conditions and yields (%): i, cyclohexane, UV, 52; ii,  $Me_2C=CMe_2$ , UV, 61; iii,  $CH_2Cl_2-SMe_2$ , 25 °C, 78; iv,  $Et_2O-PPh_3$ , 25 °C, 70; v,  $P(OEt)_3$ , 60 °C, 6 h, 67

cyclohexene or 1,4-dimethylbut-2-ene, and did not insert into the allylic carbon-hydrogen bond. The electrophilic perfluoroalkanesulfonyl nitrene intermediate was also easily captured by dimethyl sulfide, triphenylphosphine and triethoxyphosphine giving compounds **4**, **5** and **6**, respectively. Such results indicated that in these reactions the fluoroalkanesulfonyl nitrenes reacted mainly in their singlet state.

Recently, Szonyi reported that,  $R_F C_2 H_4 N=N=N=PPh_3$  was obtained from the reaction of  $R_F C_2 H_4 N_3$  with  $PPh_3$ .<sup>16</sup> In our hands, however, even when the reaction was carried out at 0 °C, addition of compound **1** to a solution of  $PPh_3$  in  $Et_2O$  gave immediate evolution of nitrogen. This is because, compared with  $R_F C_2 H_4 N=PPh_3$ ,<sup>16</sup> the product  $R_F SO_2 N=PPh_3$  **5** is more unstable and, when exposed to air, decomposes readily to  $R_F SO_2 NH_2$  and  $Ph_3 PO$ ; this is similar to the behaviour of the  $CF_3 SO_2 N=BiPh_3$ .<sup>17</sup> In contrast, *N,N*-dimethylsulfoniofluoroalkanesulfonamides  $R_F SO_2 N=SMe_2$  **4**, which were obtained by treatment of **1** with dimethyl sulfide, are stable compounds, remaining unchanged for several weeks at room temperature and capable of being recrystallized ( $CH_2Cl_2-MeCN$ ) to give crystalline material suitable for X-ray structure analysis. Fig. 1 shows the molecular structure of **4b**. It was noteworthy that the  $S^{IV}-N$  bond (1.578 Å) is shorter than the  $S^{IV}-N$  bond (1.619 Å) and both are shorter than the normal  $S-N$  single bond length (1.740 Å).<sup>18,19</sup> The average value of the  $S-O$  bond length (1.424 Å), is very closely similar to that of the  $S-O$  bond length in  $(CF_3 SO_2)_2 CHK$  (1.428 Å), in which the electron is delocalized to the two oxygen atoms.<sup>20</sup> The  $S-N-S$  bond angle is 115.2°,

Table 1 Compounds 1 prepared

Entry	R <sub>F</sub>	Product 1	B.p. (°C/mmHg)	Yield (%)	ν/cm <sup>-1</sup>
1	C <sub>4</sub> F <sub>9</sub>	<b>a</b>	32/4	75	2276, 2150
2	Cl(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub>	<b>b</b>	38/4	75	2252, 2120
3	I(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub>	<b>c</b>	40/4	78	2250, 2120
4	H(CF <sub>2</sub> ) <sub>2</sub> O(CF <sub>2</sub> ) <sub>2</sub>	<b>d</b>	38/4	72	2251, 2130
5	MeO <sub>2</sub> CCF <sub>2</sub>	<b>f</b>	50/4	82	2280, 2140

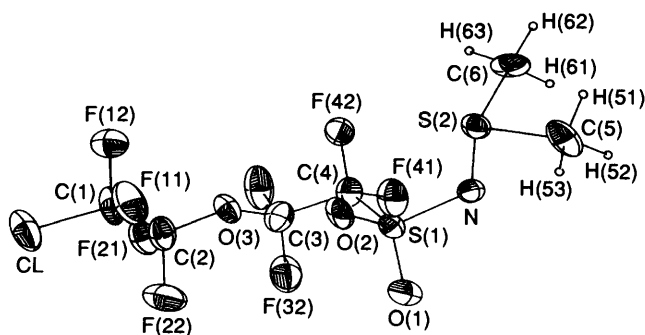
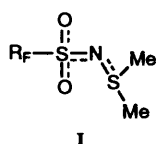
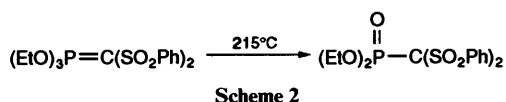


Fig. 1 The structure of compound 4b. Selected bond lengths (Å) and bond angles (°). S(1)–N, 1.578(6); S(2)–N, 1.619(7); S(1)–O(1), 1.413(6); S(1)–O(2), 1.435(5). S(1)–N–S(2), 115.2(4); N–S(2)–C(5), 102.4(5); N–S(1)–C(4), 104.1(4).

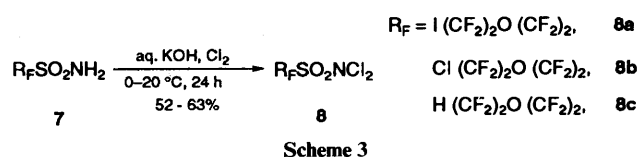
which is smaller than the theoretically expected (120°), an effect arising from the nitrogen's localized lone pair. From these data, it is possible to conclude that the S–N–S group of compound 3 contains a delocalized d–π bond system as shown in structure I.



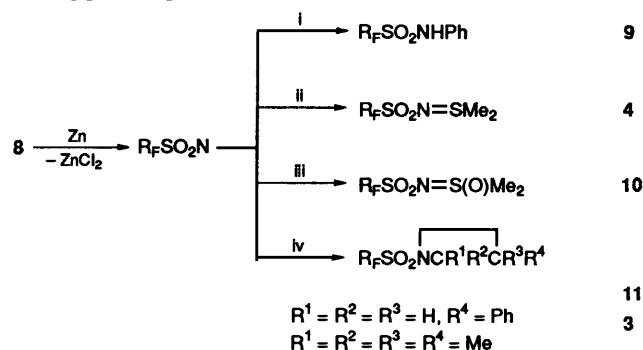
Although, as mentioned above, there was immediate evolution of nitrogen when compound 1 was mixed with PPh<sub>3</sub> at 0 °C, its reaction with (EtO)<sub>3</sub>P was slow; for example, even after the reaction mixture had been stirred at room temperature for 8 h, some azide still remained. The IR spectrum of compound 1 was used to monitor the progress of the reaction. Thus, it was found when the reaction mixture was heated at 60 °C for 7 h, the N<sub>3</sub> absorption peak disappeared completely, the product being R<sub>F</sub>SO<sub>2</sub>N(Et)P(O)(OEt)<sub>2</sub> as a result of the rearrangement of R<sub>F</sub>SO<sub>2</sub>N=P(OEt)<sub>3</sub>. Varvoglis has reported a similar result, although, the isomerization was effected under more vigorous conditions.<sup>21</sup> (Scheme 2).



*N,N*-Dichlorofluoroalkanesulfonamides were conveniently prepared by the one-pot reaction of fluoroalkanesulfonamides with aq. KOH and chlorine gas (Scheme 3).

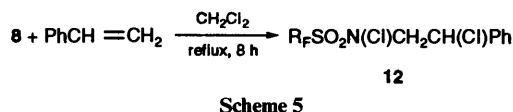


Compounds **8** are unstable, yellowish liquids which after storage at room temperature for 1 week show almost a 50% transformation into the corresponding fluoroalkanesulfonamides. <sup>19</sup>F NMR spectroscopy was used to monitor this transformation, the chemical shifts of CF<sub>2</sub>S in compounds **7** and **8** being at 40 and 29 ppm, respectively (TFA external standard and the upfield is positive). Heating of compound **8** with benzene in the presence of zinc dust afforded 70% of R<sub>F</sub>SO<sub>2</sub>NHC<sub>6</sub>H<sub>5</sub> **9**. Similarly, treatment of compound **8** with dimethyl sulfide or dimethyl sulfoxide gave the sulfonium ylide R<sub>F</sub>SO<sub>2</sub>N=SMe<sub>2</sub> **4** and the sulfoxonium ylide R<sub>F</sub>SO<sub>2</sub>N=S(O)Me<sub>2</sub> **10**, respectively. As already stated, compound 1 undergoes thermal decomposition at ca. 120 °C but when heated under reflux with an excess of cyclohexane or 2,3-dimethylbut-2-ene it failed to react. However, compound **8** when mixed with styrene or 2,3-dimethylbut-2-ene at room temperature in the presence of zinc powder gave the *N*-fluoroalkylsulfonylaziridines R<sub>F</sub>SO<sub>2</sub>NCR<sup>1</sup>R<sup>2</sup>CR<sup>3</sup>R<sup>4</sup> **11** together with R<sub>F</sub>SO<sub>2</sub>NH<sub>2</sub> (ca. 15%). In contrast to the sulfonium ylides **4**, compounds **10** are high boiling point liquids.



Scheme 4 Reagents, conditions and yields: i, C<sub>6</sub>H<sub>6</sub>, reflux, 8 h, 70%; ii, Me<sub>2</sub>S, room temp., 8 h, 68%; iii, Me<sub>2</sub>SO, 60 °C, 8 h, 65%; iv, PhCH=CH<sub>2</sub>, room temp., 8 h, 62% or Me<sub>2</sub>C=CMe<sub>2</sub>, room temp., 8 h, 64%.

These results indicate that, as with the reaction of fluoroalkanesulfonyl azides, fluoroalkanesulfonyl nitrene intermediates are involved in all the above reactions. It was noteworthy that the reaction of **8** with styrene occurred rapidly without zinc powder to give 1 : 1 addition (Scheme 5).



This reaction was shown to be a free-radical process, the radical intermediate R<sub>F</sub>SO<sub>2</sub>NCICH<sub>2</sub>CHPh being captured by Bu'NO. Its ESR spectrum showed the triple doublet peaks (a<sub>N</sub> = 15.18 G, a<sub>H</sub> = 3.04 G, g = 2.0052, see Fig. 2). Reduction of **12** by NaHSO<sub>3</sub>, followed by elimination of HCl by alcoholic NaOH gave *N*-fluoroalkylsulfonylaziridine **11a**.<sup>22,23</sup> It has been reported<sup>24</sup> that C<sub>6</sub>F<sub>5</sub>N=NC<sub>6</sub>F<sub>5</sub> **13** is obtained when C<sub>6</sub>F<sub>5</sub>NCl<sub>2</sub> is heated. It is also formed upon triplet

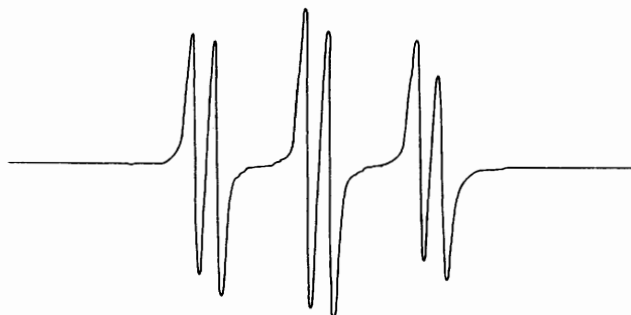
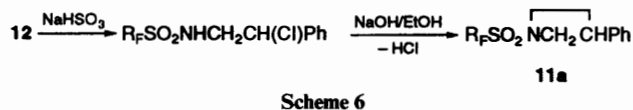


Fig. 2 The ESR spectrum of  $R_FSO_2N(Cl)CH_2CH(Ph)N(Bu')O^*$



photosensitized decomposition of  $C_6F_5N_3$  but not upon direct photolysis.<sup>25</sup> In our hands neither photolysis nor thermolysis of compounds **1** and **8** gave the corresponding dimeric product  $R_FSO_2N=NSO_2R_F$ .

**Conclusions.**—Fluoroalkanesulfonyl azides and *N,N*-dichlorofluoroalkanesulfonamides, prepared in moderate to good yields, are reactive compounds which react with numerous organic reagents under a variety of reaction conditions *via* a fluoroalkanesulfonyl nitrene intermediate. The convenient preparation of these compounds together with their reactive chemical properties make them attractive and useful reagents for the introduction of the  $R_FSO_2N$  functionality into organic molecules.

### Experimental

M.p.s were measured on a Thiele apparatus, and both m.p.s and b.p.s are uncorrected. Solvents were purified before use.  $^1H$  NMR and  $^{19}F$  NMR spectra were recorded on a Varian-360L instrument with  $Me_4Si$  and TFA as an internal and an external standard, respectively.  $^{31}P$  NMR spectra were recorded on a JEOL-XL 90Q instrument with  $H_3PO_4$  (85%) as external standard. Elemental analyses were performed by this Institute. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Low resolution mass spectra were obtained on a Finnigan GC-MS 4021 Instrument. ESR spectra were recorded on a Varian E-112 spectrometer.

**Preparation of Fluoroalkanesulfonyl Azides 1.**—*General procedure.* A mixture of fluoroalkanesulfonyl fluoride (10 mmol), sodium azide (10 mmol) and MeOH (20  $cm^3$ ) was stirred at 20 °C for 8 h. The sodium fluoride was filtered off and the filtrate was poured into ice-water; the oily layer was then separated, dried ( $Na_2SO_4$ ) and distilled *in vacuo* to give **1**. The yields, b.p. and IR results are given in Table 1.

$C_4F_9SO_2N_3$  **1a**.  $\delta_F$ (neat, positive for upfield shift) 5.4 (s,  $CF_3$ ), 37.7 (m,  $CF_2$ ), 45.3 (m,  $CF_2$ ) and 50.2 (s,  $CF_2S$ );  $m/z$  (rel. int.) 325 ( $M^+$ , 1.08), 219 ( $C_4F_9^+$ , 76.38), 90 ( $^+SON_3$ , 14.21) and 69 ( $CF_3^+$ , 100) (Found: C, 14.9; F, 53.0; N, 12.7. Calc. for  $C_4F_9N_3O_2S$ : C, 14.79; F, 52.62; N, 12.92%).

$Cl(CF_2)_2O(CF_2)_2SO_2N_3$  **1b**.  $\delta_F$ (neat) -2.0 (s,  $ClCF_2$ ), 5.3 (m,  $OCF_2$ ), 10.6 (m,  $CF_2O$ ) and 37.3 (s,  $SCF_2$ );  $m/z$  359/357 ( $M^+$ , 0.73/2.30), 90 ( $^+SON_3$ , 100), 87/85 ( $ClCF_2^+$  and 23.56/73.03) (Found: C, 13.7; F, 43.2; N, 11.35. Calc. for  $C_4ClF_8N_3O_3S$ : C, 13.43; F, 42.52; N, 11.75%).

$I(CF_2)_2O(CF_2)_2SO_2N_3$  **1c**.  $\delta_F$ (neat) -11.0 (s,  $ICF_2$ ), 5.0 (m,  $OCF_2$ ), 9.1 (m,  $CF_2O$ ) and 38.2 (s,  $CF_2S$ );  $m/z$  449 ( $M^+$ , 2.25) and 90 ( $^+SON_3$ , 100) (Found: C, 10.7; F, 34.5; N, 9.9;

S, 7.0. Calc. for  $C_4F_8IN_3O_3S$ : C, 10.69; F, 33.87; N, 9.35; S, 7.12%).

$H(CF_2)_2O(CF_2)_2SO_2N_3$  **1d**.  $\delta_F$ (neat) 2.0 (m,  $OCF_2$ ), 9.3 (m,  $CF_2O$ ), 34.3 (s,  $CF_2S$ ) and 58.3 (d,  $HCF_2$ ,  $J_{HF}$  54);  $\delta_H$ (neat, TMS inter.) 6.26 (t,  $HCF_2$ );  $m/z$  323 ( $M^+$ , 2.41), 296 ( $M^+ - N_2$ , 100), 90 ( $^+SON_3$ , 18.07) and 51 ( $HCF_2^+$ , 40.16) (Found: C, 15.0; F, 47.4; N, 12.8. Calc. for  $C_4HF_8N_3O_3S$ : C, 14.86; F, 47.06; N, 13.00%).

$MeO_2CCF_2SO_2N_3$  **1e**.  $\delta_F$ (neat) 29.3 (s,  $CF_2$ );  $\delta_H$  3.82 (s,  $CH_3$ );  $m/z$  215 ( $M^+$ , 1.07), 187 ( $M^+ - N_2$ , 8.33), 109 ( $M^+ - SO_2N_3$ , 14.81) and 43 ( $CH_3CO^+$ , 100) (Found: C, 16.3; H, 1.6; F, 18.1; N, 19.9. Calc. for  $C_3H_3F_2N_3O_2S$ : C, 16.74; H, 1.40; F, 17.67; N, 19.53%).

**Reactions of the Azides 1.**—*Upon irradiation.* A solution of **1d** (1.6 g, 5 mmol) in cyclohexane (5  $cm^3$ ) was subjected to UV irradiation (400 W low-pressure mercury lamp) at room temperature for 6 h, after which the excess of  $C_6H_{12}$  was distilled off. The residue was distilled *in vacuo* to give **2d** (1.0 g, 52%).

$H(CF_2)_2O(CF_2)_2SO_2NHC_6H_{11}$  **2d**, b.p. 85–87 °C/1 mmHg, m.p. 32–34 °C,  $\nu_{max}$ (KBr)/ $cm^{-1}$  3285s, 2920s, 2830s, 1372s, 1320s, 1280s, 1220–1110vs, 978s, 918m, 892s, 860m, 748s and 610s;  $\delta_F$ [( $CD_3$ ) $_2CO$ ] 5.5 (m,  $OCF_2$ ), 12.6 (m,  $CF_2O$ ), 40.6 (s,  $CF_2S$ ) and 62.0 (d,  $HCF_2$ );  $\delta_H$  1.23–2.03 (m,  $C_6H_{11}$ ), 3.70 (br, NH) and 6.40 (t,  $HCF_2$ );  $m/z$  379 ( $M^+$ , 10.29) and 83 ( $C_6H_{11}^+$ , 100) (Found: C, 31.6; H, 3.5; F, 40.0; N, 3.8. Calc. for  $C_{10}H_{13}F_8NO_3S$ : C, 31.66; H, 3.43; F, 40.10; N, 3.69%).

Similar treatment of **1d** with 2,3-dimethylbut-2-ene gave the cycloaddition product  $H(CF_2)_2O(CF_2)_2SO_2\overline{N}C(Me)_2\overline{C}(Me)_2$  **3d**; b.p. 42–44 °C/3 mmHg;  $\nu_{max}$ (film)/ $cm^{-1}$  2985s, 2960m, 2870m, 1461s, 1445m, 1382s, 1330m, 1240m, 1220–1110vs, 975s, 920m, 880s, 750m and 600s;  $\delta_F$  4.5 (m,  $OCF_2$ ), 12.6 (m,  $CF_2O$ ), 41.5 (s,  $CF_2S$ ) and 61.6 (d,  $HCF_2$ );  $\delta_H$  0.8 (s,  $CH_3$ ) and 5.6 (t,  $HCF_2$ );  $m/z$  380 ( $M^+H$ , 74.57), 363 ( $M^+ - O$ , 4.02), 301 ( $M^+ - N - SO_2$ , 8.46), 258 ( $M^+ - N - SO_2 - C_3H_7$ , 3.41), 214 ( $M^+ - HCF_2CF_2SO_2$ , 1.64), 146 ( $M^+ - R_FO$ , 5.43), 101 ( $HC_2F_4^+$ , 96.54), 100 ( $C_2F_4^+$ , 23.84), 83 ( $C_6H_{11}^+$ , 24.74), 57 ( $C_4H_9^+$ , 100), 51 ( $HCF_2^+$ , 4.64) and 43 ( $C_3H_7^+$ , 44.24) (Found: C, 31.4; H, 3.7; F, 40.9; N, 3.9. Calc. for  $C_{10}H_{13}F_8NO_3S$ : C, 31.66; H, 3.43; F, 40.11; N, 3.69%).

*With dimethyl sulfide.* A solution of **1b** (1.8 g, 5 mmol),  $Me_2S$  (0.6 g, 10 mmol) and  $CH_2Cl_2$  (10  $cm^3$ ) was stirred at 25 °C for 8 h after which it was evaporated. The residue was crystallized from MeCN to give the crude product **4b** (2 g, 73%), recrystallization of which from MeCN and  $CH_2Cl_2$  gave crystals suitable for X-ray structure analysis.

$Cl(CF_2)_2O(CF_2)_2SO_2N=SMe_2$  **4b**, m.p. 47 °C;  $\nu_{max}$ (KBr)/ $cm^{-1}$  3017m, 2930w, 1339s, 1304s, 1230s, 1200–1120vs, 982s, 979s, 687m, 665m and 615s;  $\delta_F$  -2.0 (s,  $ClCF_2$ ), 6.0 (m,  $OCF_2$ ), 11.2 (m,  $CF_2O$ ) and 40.5 (s,  $CF_2S$ );  $m/z$  394/392 ( $M^+H$  18.69/42.14) and 140 ( $M^+ - R_F$ , 100) (Found: C, 18.2; H, 1.2; F, 38.9; N, 3.5. Calc. for  $C_6H_6ClF_8NO_3S$ : C, 18.39; H, 1.53; F, 38.93; N, 3.57%).

Similar treatment of **1c** (2.3 g, 5 mmol) with  $Me_2S$  (0.6 g, 10 mmol) gave  $I(CF_2)_2O(CF_2)_2SO_2N=SMe_2$  **4c** (1.7 g, 72%), m.p. 48–49 °C;  $\nu_{max}$ (KBr)/ $cm^{-1}$  1595m, 1412s, 1380s, 1337s, 1298s, 1220–1130vs, 1090s, 912s, 761m, 708s and 598s;  $\delta_F$ ( $CD_3Cl$ ) -11.0 (s,  $ICF_2$ ), 5.1 (m,  $OCF_2$ ), 8.8 (m,  $CF_2O$ ) and 39.5 (s,  $CF_2S$ );  $\delta_H$  2.90 (s,  $2 \times CH_3$ );  $m/z$  484 ( $M^+H$ , 47.31), 483 ( $M^+$ , 21.45), 308 ( $M^+ - I - SO_2$ , 100) and 78 ( $SO_2N^+$ , 47.14) (Found: C, 14.55; H, 0.9; F, 31.7; N, 3.05. Calc. for  $C_6H_6F_8INO_3S_2$ : C, 14.90; H, 1.24; F, 31.47; N, 2.90%).

*With triphenylphosphine.* Compound **1d** (1.6 g, 5 mmol) was added dropwise into a solution of  $Ph_3P$  (1.3 g, 5 mmol) in anhydrous  $Et_2O$  (10  $cm^3$ ) at 25 °C. Upon cessation of  $N_2$  evolution the mixture was evaporated and the residue was sublimed *in vacuo* to give  $H(CF_2)_2O(CF_2)_2SO_2N=PPH_3$  **5d**

(1.9 g, 70%), m.p. 88 °C;  $\nu_{\max}(\text{KCl})/\text{cm}^{-1}$  3030s, 1590m, 1483m, 1438m, 1380m, 1278m, 1210s, 1180–1106vs, 1082m, 995m, 850m, 751s, 720s, 693s and 540s,  $\delta_{\text{F}}$  4.0 (m, OCF<sub>2</sub>), 11.3 (m, CF<sub>2</sub>O), 39.5 (s, CF<sub>2</sub>S) and 60.6 (d, HCF<sub>2</sub>);  $\delta_{\text{H}}$  7.55 (s, 15 H) and 6.13 (t, 1 H);  $m/z$  558 (M<sup>+</sup>H, 1.37), 557 (M<sup>+</sup>, 0.86) and 262 (Ph<sub>3</sub>P<sup>+</sup>, 100).

*With triethyl phosphite.* Compound **1b** (2 g, 5.1 mmol) was added to a solution of (EtO)<sub>3</sub>P (1.7 g, 10 mmol) and CCl<sub>4</sub> (10 cm<sup>3</sup>) and the reaction mixture was heated to 50 °C for 8 h. After this time an IR spectrum of the mixture showed that the N<sub>3</sub> peaks had disappeared. The excess of (EtO)<sub>3</sub>P and CCl<sub>4</sub> were distilled off from the mixture and the residue was distilled *in vacuo* to give H(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>N(Et)P(O)(OEt)<sub>2</sub> **6d** (1 g, 42%);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  2990s, 2910m, 1440w, 1395s, 1320m, 1285s, 1110–1230vs and 920m;  $\delta_{\text{H}}$  5.85 (t, HCF<sub>2</sub>), 3.80 (m, 4 H), 3.12 (m, 2 H) and 0.93 (m, 9 H);  $\delta_{\text{F}}$  4.3 (m, OCF<sub>2</sub>), 10.7 (m, CF<sub>2</sub>O), 38.6 (s, SCF<sub>2</sub>) and 61.8 (d, HCF<sub>2</sub>);  $m/z$  461 (M<sup>+</sup>, 1.85%), 445 (M<sup>+</sup> – O, 7.57), 243 (M<sup>+</sup> – H – R<sub>F</sub>, 47.5), 215 (M<sup>+</sup> – Et – R<sub>F</sub>, 80.65), 188 (M<sup>+</sup> – R<sub>F</sub>–2Et, 100.0), 180 (M<sup>+</sup> – R<sub>F</sub>SO<sub>2</sub>, 64.06), 160 [(HO)<sub>2</sub>P(O)NHSO<sub>2</sub><sup>+</sup>, 83.29], 137 [(EtO)<sub>2</sub>PO, 33.47] and 51 (HCF<sub>2</sub><sup>+</sup>, 14.23);  $\delta_{\text{P}}$  2.03 (s) (Found: C 25.8; H, 3.6; N, 3.3. Calc. for C<sub>10</sub>H<sub>16</sub>F<sub>8</sub>NO<sub>6</sub>PS: C, 26.03; H, 3.47; N, 3.03%).

*Preparation of N,N-Dichloroalkanesulfonamides R<sub>F</sub>SO<sub>2</sub>NCl<sub>2</sub> 8.*—*General procedure.* A mixture of the fluoroalkanesulfonamide I(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>NH<sub>2</sub> **7a** (6.3 g, 15 mmol), KOH (1.7 g, 30 mmol) and water (15 cm<sup>3</sup>) in a 50 cm<sup>3</sup> three-necked flask was stirred at room temperature for 2 h. The flask was then cooled in an ice-bath after which chlorine gas (4.3 g, 60 mmol) was introduced, the reaction temperature being kept in the range 0–5 °C. After this, the mixture was stirred at 20 °C for a further 2 h during which time a yellowish oil separated. This was dried (Na<sub>2</sub>SO<sub>4</sub>) and distilled *in vacuo* to give **8a** (3.8 g, 52%). Similarly, treatment of **7b** (5 g, 15 mmol) or **7c** (4.5 g, 15 mmol) with KOH and chlorine gave **8b** (3.8 g, 63%) or **8c** (3.3 g, 60%), respectively.

Compound **8a**, b.p. 42 °C/2 mmHg;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  1605w, 1420m, 1380s, 1320vs, 1292s, 1220–1120vs, 1092s, 990s, 713s, 600m and 530m;  $\delta_{\text{F}}$  –11.8 (s, ICF<sub>2</sub>), 5.2 (m, OCF<sub>2</sub>), 8.5 (m, CF<sub>2</sub>O) and 29.3 (s, CF<sub>2</sub>S);  $m/z$  492 (M<sup>+</sup>H, 0.62%), 424 (M<sup>+</sup> – F – SO, 1.90), 364 (M<sup>+</sup> – I, 0.96), 343 (M<sup>+</sup> – SO – C<sub>2</sub>F<sub>4</sub>, 5.52), 329 (M<sup>+</sup> – SON – C<sub>2</sub>F<sub>4</sub>, 4.82), 227 (IC<sub>2</sub>F<sub>4</sub><sup>+</sup>, 100.0) and 205 (ISO<sub>2</sub>N<sup>+</sup>, 15.70) (Found: C, 10.0; F, 31.3; N, 3.0. Calc. for C<sub>4</sub>Cl<sub>2</sub>F<sub>8</sub>INO<sub>3</sub>S: C, 9.76; N, 2.85; F, 30.89%).

Compound **8b**, b.p. 40–41 °C/mmHg;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  1602w, 1422m, 1382s, 1324vs, 1300s, 1225–1110vs, 987m, 910s, 721s, 650s and 500s;  $\delta_{\text{F}}$  –2.0 (s, ClCF<sub>2</sub>), 6.0 (m, OCF<sub>2</sub>), 11.8 (m, CF<sub>2</sub>O) and 29.0 (s, CF<sub>2</sub>S) (Found: C, 11.9; Cl, 26.18; F, 38.50; N, 3.8. Calc. for C<sub>4</sub>Cl<sub>3</sub>F<sub>8</sub>NO<sub>3</sub>S: C, 11.98; N, 3.50; Cl, 26.59; F, 37.95%).

Compound **8c**, b.p. 38–39 °C/2 mmHg;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  2998w, 1620m, 1422s, 1320m, 1282s, 1200–1120vs, 1005m, 940m, 850m, 744m and 680m;  $\delta_{\text{H}}$  5.83 (t, HCF<sub>2</sub>);  $\delta_{\text{F}}$  6.3 (m, OCF<sub>2</sub>), 14.3 (m, CF<sub>2</sub>O), 29.3 (s, CF<sub>2</sub>S) and 63.0 (d, HCF<sub>2</sub>) (Found: C, 13.1; N, 4.0; Cl, 19.5; F, 41.91. Calc. for C<sub>4</sub>HCl<sub>2</sub>F<sub>8</sub>NO<sub>3</sub>S: C, 13.11; N, 3.83; Cl, 19.40; F, 41.53%).

*Reactions of Compound 8 in the Presence of Zinc Powder.*—(i)

*Reaction of 8b with benzene.* Compound **8b** (2.0 g, 5 mmol) was added to a mixture of benzene (10 cm<sup>3</sup>) and zinc powder (1 g, 15 mmol) in a 25 cm<sup>3</sup> flask equipped with a magnetic stirring bar at room temperature. The mixture was then stirred at 80 °C for 7 h after which the solid was filtered off and the filtrate was distilled to remove the excess of benzene. The residue when crystallized from MeOH–MeCN to give Cl(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>NHPh **9b** as a white solid (1.3 g, 62%), m.p. 70–72 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3352s, 3340s, 3030w, 1583w, 1500m, 1368vs,

1330s, 1220–1120vs, 990s, 918s, 720s, 675m, 646m and 502s;  $\delta_{\text{H}}$  7.33 (s, 5 H) and 6.23 (s, <sup>1</sup>H);  $\delta_{\text{F}}$  –2.0 (s, ClCF<sub>2</sub>), 6.3 (m, OCF<sub>2</sub>), 12.0 (m, CF<sub>2</sub>O) and 41.3 (s, CF<sub>2</sub>S) (Found: C, 29.4; H, 1.5; N, 3.8; F, 37.1. Calc. for C<sub>10</sub>H<sub>6</sub>ClF<sub>8</sub>NO<sub>3</sub>S: C, 29.45; H, 1.47; F, 37.30; N, 3.44%).

(ii) *Reaction of 8b and 8c with dimethyl sulfide.* Compound **8b** (2.0 g, 5 mmol) was added dropwise to a mixture of Me<sub>2</sub>S (3 g, 48 mmol) and zinc powder (1 g, 15 mmol) at room temperature and the mixture stirred for 7 h at 22 °C. The solid was filtered off and the filtrate was distilled to remove excess of Me<sub>2</sub>S. The residue was crystallized from MeCN to give Cl(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>N=SMe<sub>2</sub> **4b** (1.4 g, 71%). Similarly, H(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>N=SMe<sub>2</sub> **4d** (69%) was prepared. Compound **4b** m.p. 47 °C;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3017m, 2930w, 1339s, 1340s, 1230s, 1200–1120vs, 982s, 979s, 687m, 665m and 615s;  $\delta_{\text{H}}$  2.83 (s, 2 × CH<sub>3</sub>),  $\delta_{\text{F}}$  –2.0 (s, ClCF<sub>2</sub>), 6.0 (m, OCF<sub>2</sub>), 11.2 (m, CF<sub>2</sub>O) and 40.5 (s, CF<sub>2</sub>S);  $m/z$  392/394 (M<sup>+</sup>, 42.14/18.69%) and 140 (M<sup>+</sup> – R<sub>F</sub>, 100.0) (Found: C, 18.2; H, 1.2; F, 39.9; N, 3.5. Calc. for C<sub>6</sub>H<sub>6</sub>F<sub>8</sub>ClNO<sub>3</sub>S<sub>2</sub>: C, 18.39; H, 1.53; F, 38.93; N, 3.57%).

Compound **4d** m.p. 45–47 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3015m, 2992w, 1440m, 1340s, 1310s, 1227s, 1210–1125vs, 973s, 756m, 668m and 610s;  $\delta_{\text{H}}$  5.73 (tt, HCF<sub>2</sub>) and 2.80 (s, 6H);  $\delta_{\text{F}}$  6.70 (m, OCF<sub>2</sub>), 15.0 (m, CF<sub>2</sub>O), 42.3 (s, CF<sub>2</sub>S) and 63.3 (d, HCF<sub>2</sub>);  $m/z$  358 (M<sup>+</sup>H, 2.07%), 357 (M<sup>+</sup>, 1.30), 343 (M<sup>+</sup>H – Me, 7.64), 309 (M<sup>+</sup> – SO, 32.51), 140 (<sup>+</sup>SO<sub>2</sub>N=SMe<sub>2</sub>, 100.0), 124 (Me<sub>2</sub>SNSO<sup>+</sup>, 17.88), 100 (C<sub>2</sub>F<sub>4</sub><sup>+</sup>, 6.95), 76 (Me<sub>2</sub>SN<sup>+</sup>, 42.37), 62 (Me<sub>2</sub>S<sup>+</sup>, 22.51) and 51 (HCF<sub>2</sub><sup>+</sup>, 6.83) (Found: C, 20.5; H, 2.3; N, 3.8; F, 42.1. Calc. for C<sub>6</sub>H<sub>7</sub>F<sub>8</sub>NO<sub>3</sub>S<sub>2</sub>: C, 20.17; H, 1.96; F, 42.58; N, 3.92%).

(iii) *Reaction of 8b and 8c with DMSO.* A mixture of **8b** (2.0 g, 5 mmol), DMSO (10 cm<sup>3</sup>) and zinc powder (1 g, 15 mmol) was stirred for 8 h at 60 °C. After filtration, the filtrate was distilled *in vacuo* to give Cl(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>N=S(O)Me<sub>2</sub> **10b** (1.3 g, 64%). Similarly, treatment of **8c** with DMSO gave H(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>N=S(O)Me<sub>2</sub> **10c** (1.2 g, 63%). Compound **10b** b.p. 98–100 °C/2 mmHg;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  2971s, 2892s, 1580m, 1443m, 1380s, 1370s, 1277s, 1210–1100vs, 1005vs, 980s, 881m, 700m, 653s and 517s;  $\delta_{\text{H}}$  3.50 (s, 6 H);  $\delta_{\text{F}}$  –1.0 (s, ClCF<sub>2</sub>), 6.5 (m, OCF<sub>2</sub>), 11.6 (m, CF<sub>2</sub>O) and 42.3 (s, CF<sub>2</sub>S);  $m/z$  408/410 (M<sup>+</sup>H, 0.75/0.37%), 392/394 (M<sup>+</sup>H – O, 25.96/16.09), 372 (M<sup>+</sup> – Cl, 2.64), 344/346 (M<sup>+</sup>H – SO<sub>2</sub>, 4.34/2.72), 332/334 (M<sup>+</sup>H – SMe<sub>2</sub> – N, 20.22/8.40), 156 (M<sup>+</sup> – R<sub>F</sub>, 11.09), 141 (M<sup>+</sup> – R<sub>F</sub> – Me, 4.99), 140 (M<sup>+</sup> – R<sub>F</sub> – O, 17.32), 135/137 (ClC<sub>2</sub>F<sub>4</sub><sup>+</sup>, 15.39/7.45), 85/87 (ClCF<sub>2</sub><sup>+</sup>, 14.72/6.37), 80 (SOS<sup>+</sup>, 100), 78 (Me<sub>2</sub>SO<sup>+</sup>, 5.74), 64 (SO<sub>2</sub><sup>+</sup>, 85.47), 61 (MeSN<sup>+</sup>, 12.90) and 47 (MeS, 5.14) (Found: C, 18.0; H, 1.8; F, 37.0; N, 3.1. Calc. for C<sub>6</sub>H<sub>6</sub>ClF<sub>8</sub>NO<sub>4</sub>S<sub>2</sub>: C, 17.67; H, 1.47; F, 37.30; N, 3.44%).

Compound **10c**, b.p. 98 °C/2 mmHg;  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  2950s, 2880s, 1588m, 1440m, 1380s, 1325s, 1220–1110vs, 1010vs, 950s, 860m, 750m, 702m, 603s and 500m;  $\delta_{\text{H}}$  5.83 (t, HCF<sub>2</sub>) and 3.50 (s, 6 H);  $\delta_{\text{F}}$  6.60 (m, OCF<sub>2</sub>), 14.6 (m, CF<sub>2</sub>O), 42.3 (s, CF<sub>2</sub>S) and 63.3 (d, HCF<sub>2</sub>);  $m/z$  359 (M<sup>+</sup>H – Me, 0.15%), 353 (M<sup>+</sup>H – F, 0.63), 325 (M<sup>+</sup> – SO, 3.70), 225 (M<sup>+</sup> – SO – C<sub>2</sub>F<sub>4</sub>, 2.78), 223 (M<sup>+</sup> – C<sub>3</sub>F<sub>6</sub>, 3.94), 173 (M<sup>+</sup> – C<sub>2</sub>F<sub>8</sub>, 3.11), 157 (M<sup>+</sup>H – R<sub>F</sub>, 5.73), 141 (M<sup>+</sup>H – R<sub>F</sub> – O, 4.63), 101 (HC<sub>2</sub>F<sub>4</sub><sup>+</sup>, 8.74), 79 (Me<sub>2</sub>S<sup>+</sup>OH, 100.0), 78 (Me<sub>2</sub>SO<sup>+</sup>, 72.07), 63 (MeSO<sup>+</sup>, 41.37), 62 (NSO<sup>+</sup>, 10.07) and 51 (HCF<sub>2</sub><sup>+</sup>, 3.17) (Found: C, 19.1; H, 1.6; F, 40.3; N, 4.1. Calc. for C<sub>6</sub>H<sub>7</sub>F<sub>8</sub>NO<sub>4</sub>S<sub>2</sub>: C, 19.30; H, 1.88; F, 40.75; N, 3.75%).

(iv) *Reaction of 8 with alkenes.* A mixture of **8c** (1.8 g, 5 mmol), 2,3-dimethylbut-2-ene (1 g, 12 mmol) and zinc powder (1 g, 15 mmol) was stirred at room temperature for 8 h and then filtered. The filtrate was distilled *in vacuo* to give H(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>NCMe<sub>2</sub>CMe<sub>2</sub> **3d** (1.2 g, 65%). Similarly, treatment of **8a** with styrene gave I(CF<sub>2</sub>)<sub>2</sub>O(CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>NCH<sub>2</sub>CHC<sub>6</sub>H<sub>5</sub> **11a** (1.6 g, 63%). Compound **11a**, b.p. 132–135 °C/2 mmHg;

$\nu_{\max}$ (film)/ $\text{cm}^{-1}$  3030w, 1585m, 1490m, 1420m, 1378s, 1326m, 1228–1110vs, 1005s, 952m, 862m, 605s and 500s;  $\delta_{\text{H}}$  7.33 (s, 5 H), 4.83 (m, 1 H) and 2.95 (m, 2 H);  $\delta_{\text{F}}$  –11.3 (s,  $\text{ICF}_2$ ), 5.3 (m,  $\text{OCF}_2$ ), 8.3 (m,  $\text{CF}_2\text{O}$ ) and 39.5 (s,  $\text{CF}_2\text{S}$ ) (Found: C, 27.8; H, 2.0; F, 28.6; N, 2.5. Calc. for  $\text{C}_{12}\text{H}_8\text{F}_8\text{INO}_3\text{S}$ : C, 27.43; H, 1.52; F, 28.95; N, 2.67%).

**Reaction of 8a with styrene without zinc powder.** Compound **8a** (2.5 g, 5 mmol) was added to a solution of styrene (2 g, 10 mmol) and  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ). A portion (0.3  $\text{cm}^3$ ) of this reaction mixture was subjected to ESR and gave the spectrum shown in Fig. 2 ( $a_{\text{N}}$  15.18 G,  $a_{\text{H}}$  3.04 G,  $g = 2.0052$ ). The remaining solution was stirred at room temperature for 4 h after which the  $\text{CH}_2\text{Cl}_2$  and excess of styrene were removed and the residue chromatographed ( $\text{CHCl}_3$ –light petroleum) to give **12** (1.8 g, 61%);  $\delta_{\text{H}}$  7.33–7.90 (m, 5 H), 5.7 (m, 1 H) and 2.83 (m, 2 H);  $m/z$  599/597/595 ( $\text{M}^+$ , 0.84/5.01/7.53%);  $\delta_{\text{F}}$  –11.0 (s,  $\text{ICF}_2$ ), 5.3 (m,  $\text{OCF}_2$ ), 8.6 (m,  $\text{CF}_2\text{O}$ ) and 39.0 (s,  $\text{CF}_2\text{S}$ ) (Found: C, 24.4; H, 1.7; Cl, 11.6; F, 25.1; N, 11.6. Calc. for  $\text{C}_{12}\text{H}_8\text{Cl}_2\text{F}_8\text{INO}_3\text{S}$ : C, 24.16; H, 1.34; Cl, 11.91; F, 25.50; N, 2.35%).

**Chemical Transformation of Compound 12.**—A solution of **12** (1.8 g, 3 mmol) in  $\text{CHCl}_3$  (15  $\text{cm}^3$ ) was added to a solution of  $\text{NaHSO}_3$  (0.5 g, 5 mmol) and water (10  $\text{cm}^3$ ) in a 50  $\text{cm}^3$  flask and the mixture was stirred 4 h at room temperature.  $\text{NaOEt}$  (0.4 g, 5 mmol) in  $\text{EtOH}$  (5  $\text{cm}^3$ ) was then added to the mixture which was then further stirred for 4 h after this it was poured into ice–water (25  $\text{cm}^3$ ) and the oily layer was separated, dried ( $\text{Na}_2\text{SO}_4$ ) and distilled *in vacuo* to give **11a** (0.8 g, 49%).

**Crystal data.**  $\text{C}_6\text{H}_6\text{O}_3\text{NF}_8\text{S}_2\text{Cl}$ ,  $M = 391.69$ , monoclinic, space group  $P2_1/a$ ,  $a = 6.667(2)$ ,  $b = 26.840(7)$ ,  $c = 8.372(3)$ ,  $\beta = 112.59(2)$ ,  $V = 1383.2 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.881 \text{ g cm}^{-3}$ ,  $F(000) = 776$ , ( $\text{Mo-K}\alpha$ ) = 6.616 cm, crystal dimensions 0.20  $\times$  0.10  $\times$  0.10 mm, intensity data were collected at 20 °C with an Enraf–Nonius CAD4 diffractometer using graphite-monochromated  $\text{Mo-K}\alpha$  radiation. 2705 Unique reflections were measured in the range  $0^\circ < 2\theta < 50^\circ$  with  $0 < h < 7$ ,  $0 < k < 31$ ,  $\theta < l < 9$ . The correction of LP and absorption was applied for the reflection data. The structure was solved *via* direct methods. The positions for all H atoms were carried out by theoretical calculation.

All positional parameters and anisotropic thermal parameters for non-H atoms were refined by full-matrix least squares technique. The final  $R$ ,  $R_w$  and  $S$  values were 0.075, 0.073, 1.96, respectively, for 1056 observed reflections [ $F^2 > 3\sigma(F)$ ]. All calculations were performed on a MICRO-VAX II computer with SDP, MULTAN82 and ORTEP programs. Scattering factors were taken from International Tables for X-ray Crystallography (1974).

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