

# 1,2-Bis(*N*-fluoro-*p*-toluenesulfonamido)ethane chloroform solvate

Khazaei Ardeshir,<sup>a</sup> R. Eric Banks,<sup>b</sup> Mohammed K. Besheesh,<sup>b</sup> Alan K. Brisdon<sup>b\*</sup> and Robin G. Pritchard<sup>b</sup>

<sup>a</sup>Chemistry Department, Bu-Ali Sina University, Hamadan, Iran, and <sup>b</sup>Department of Chemistry, UMIST, PO Box 88, Manchester M60 1QD, England  
Correspondence e-mail: alan.brisdon@umist.ac.uk

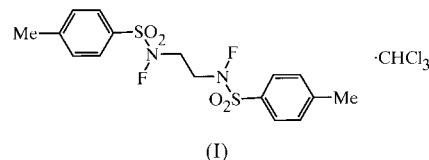
Received 3 April 2001  
Accepted 14 May 2001

The title compound, *N,N'*-difluoro-*N,N'*-ethylenedi-*p*-toluenesulfonamide, C<sub>16</sub>H<sub>18</sub>F<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>·CHCl<sub>3</sub>, is a novel stable compound of the N—F class of reagents containing two R<sub>2</sub>N—F functionalities. The compound, as the chloroform solvate, is the first such bis(N—F) compound to be structurally characterized. It adopts a solid-state structure in which the two aromatic rings are antiperiplanar and a combination of weak C—H···F and C—H···O hydrogen bonds [distances and angles range from 3.265 (4) to 3.439 (4) Å and 150 to 170°, respectively] and  $\pi$ -stacking between the rings of different molecules (separations of 3.717 and 3.926 Å) results in a solid-state structure containing well defined channels in which CHCl<sub>3</sub> solvent molecules are located. The N—F distances are 1.428 (3) and 1.433 (3) Å.

## Comment

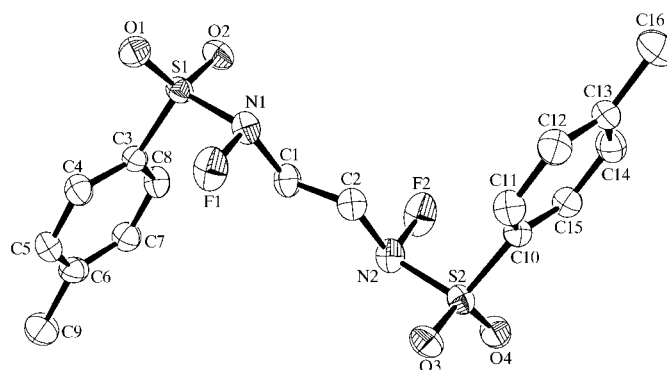
Fluorine and fluorine-containing substituents can exert a profound influence on the activity and selectivity of bio-organic molecules. This realisation has lead to much work in identifying reagents which can be used as site-selective fluorinating agents, and many of the more recent advances in this area have involved compounds in which fluorine is bound to an N atom. Included in this class of compounds are reagents featuring neutral N atoms of the type R<sub>2</sub>NF, for example, *N*-fluoro-*N*-alkylsulfonamides (Barnett, 1984) and the electrophilic fluorine-delivery agents [R<sub>3</sub>N<sup>+</sup>F], such as 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Banks *et al.*, 1996; Banks, 1998). However, the amount of structural data for such N—F-containing systems is quite limited. There are just 12 crystal structures in the Cambridge Structural Database (Allen & Kennard, 1993) for organic compounds containing N—F bonds, six of which are NF<sub>2</sub>-containing materials, *i.e.* formally organic derivatives of NF<sub>3</sub>. Of the remaining six structures, three compounds contain neutral N—F moieties and the other three contain the <sup>+</sup>N—F group. There are no structures of compounds which contain two separate single N—F moieties (neutral or charged) within the same organic molecule. Recent work (Ardeshir & Abbas,

1999) has shown that bis(*N*-halogeno) compounds, such as 1,2-bis(*N*-bromo-2,5-dimethylbenzenesulfamido)ethane, are good selective brominating agents and relatively accessible. We report here an extension of that work to give the fluorinated analogue, which has resulted in the first structural characterization of an organic bis(N—F)-containing compound.



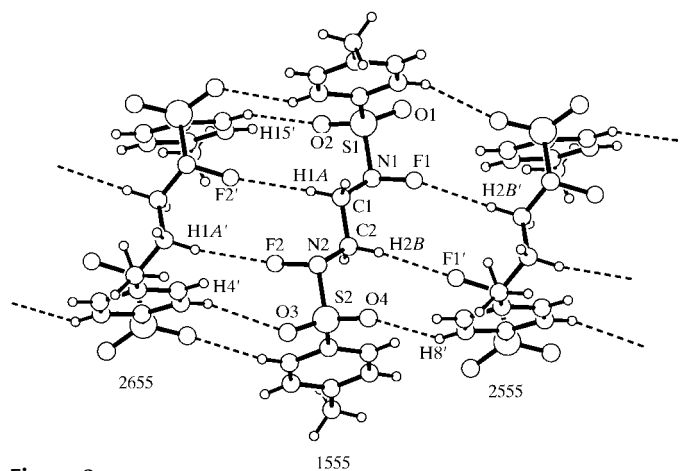
The title compound, (I), may be synthesized by passing dilute elemental fluorine through a CHCl<sub>3</sub> solution of 1,2-bis(benzenesulfonamido)ethane at low temperature. Crystallization of (I) from a CHCl<sub>3</sub> solution resulted in crystals of (I) as the CHCl<sub>3</sub> solvate which crystallizes in the space group *P2*<sub>1</sub>/*n*. A view of molecule (I) with the atomic numbering scheme is shown in Fig. 1 and selected geometric parameters are given in Table 1. The bond lengths obtained for compound (I) are mostly in accord with anticipated values (Orpen *et al.*, 1994). Of particular interest are the two N—F distances in this molecule, which are the same within experimental limits, *viz.* 1.428 (3) and 1.433 (3) Å. These distances are comparable with those found in related neutral N—F-containing organic systems, *i.e.* 1.435 (3) (Kakuda *et al.*, 1997), 1.420 (4) (Davis *et al.*, 1998) and 1.437 (6) Å (Batail *et al.*, 1974), with an average of 1.431 (7) Å. However, as expected, the N—F distances are longer than the distances found in molecules which formally contain <sup>+</sup>N—F bonds, *i.e.* 1.106 (2) (Klapötke *et al.*, 1993), 1.37 (2) (Banks, Pritchard & Sharif, 1993) and 1.406 (3) Å (Banks, Sharif & Pritchard, 1993), with an average of 1.29 (2) Å. However, this average figure is distorted by the very short N—F distance observed by Klapötke for the hexafluoroarsenate salt of *N*-fluoro-2,4,6-trichlorotriazine, which the authors describe as being unreliable due to severe disorder problems.

The molecule is symmetric about the central C—C bond; this results in an overall Z-like shape and the two N—F moieties are located on opposite sides of the molecule. The

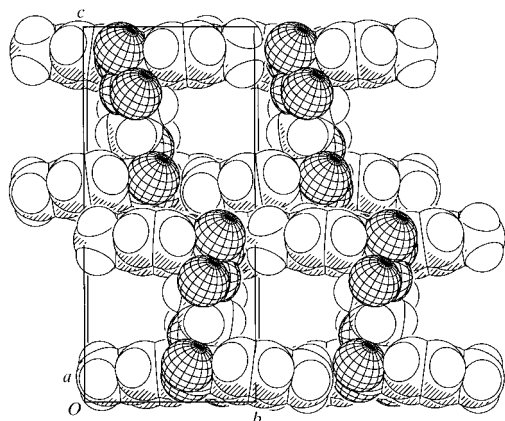


**Figure 1**  
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

two aromatic rings are antiperiplanar, with torsion angles of  $C3-S1-N1-C1 = 50.4 (3)^\circ$ ,  $N1-C1-C2-N2 = 179.4 (3)^\circ$  and  $C2-N2-S2-C10 = -52.2 (2)^\circ$ . In the solid state, there are weak hydrogen bonds between the electronegative F1 and F2 atoms and the H atoms attached to the carbon centres C2 and C1, respectively, of the central aliphatic chain (Fig. 2). The average  $C-H \cdots F$  distance is  $3.429 (6) \text{ \AA}$  and the angle is



**Figure 2**  
A view of the intermolecular hydrogen bonds in the crystal structure of (I).



**Figure 3**  
A view of the crystal packing illustrating the resulting channels formed in the solid-state structure of (I).

$170^\circ$ . Hydrogen bonding also occurs between the O atoms of the  $SO_2$  groups and the *ortho* H atoms of the aromatic rings with  $(C-H \cdots O)_{av}$  values of  $3.330 (7) \text{ \AA}$  and  $153^\circ$ . These two features result in a two-dimensional stack of molecules in an alternate head-to-tail fashion in the *a*-axis direction. The aromatic rings of one stack interweave with those of a second stack, resulting in the generation of an approximately square arrangement when viewed down the *a* axis. The next pair of stacks is separated in the *c* direction by a distance of *ca*  $3.8 \text{ \AA}$  between the aromatic rings and is offset (Fig. 3); the offset and short distance are indicative of  $\pi$ -interactions between the aromatic rings.

This combination of intermolecular interactions results in the generation of channels running parallel to the *a* axis in which solvent molecules may be located. In this case, molecules of  $CHCl_3$  solvent are located in the channels but are disordered over two equally populated sites.

## Experimental

The title compound was synthesized in two stages. 1,2-Bis(benzenesulfanamido)ethane was obtained by the dropwise addition of diethylamine (6.21 g, 0.085 mol) to benzenesulfonyl chloride (30.0 g, 0.170 mol) at room temperature with vigorous stirring. The reaction mixture was heated to 353 K for 30 min and then cooled and washed with water (100 ml). The resulting white solid was filtered and recrystallized from boiling ethanol. 1,2-Bis(benzenesulfanamido)ethane (0.5 g, 1.5 mmol) was dissolved in chloroform (180 ml) and the solution cooled to 195 K. Elemental fluorine (15 mmol, 5% in  $N_2$ ) was bubbled through the cold stirred solution for 15 min. After warming to room temperature, the solvent was removed under vacuum and the crude solid was washed with diethyl ether. Crystals suitable for X-ray diffraction studies were grown by slow evaporation of the solvent from a  $CHCl_3$  solution.

### Crystal data

$C_{16}H_{18}F_2N_2O_4S_2 \cdot CHCl_3$   
 $M_r = 523.81$   
 Monoclinic,  $P2_1/n$   
 $a = 10.9948 (10) \text{ \AA}$   
 $b = 9.6922 (10) \text{ \AA}$   
 $c = 21.381 (5) \text{ \AA}$   
 $\beta = 94.815 (10)^\circ$   
 $V = 2270.4 (6) \text{ \AA}^3$   
 $Z = 4$

$D_x = 1.532 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 12.7-17.2^\circ$   
 $\mu = 0.63 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Plate, colourless  
 $0.35 \times 0.30 \times 0.10 \text{ mm}$

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 Non-profiled  $\omega$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{min} = 0.810$ ,  $T_{max} = 0.940$   
 4222 measured reflections  
 3999 independent reflections  
 2572 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.017$   
 $\theta_{max} = 25.0^\circ$   
 $h = 0 \rightarrow 13$   
 $k = 0 \rightarrow 11$   
 $l = -25 \rightarrow 25$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 3%

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

|             |              |              |             |
|-------------|--------------|--------------|-------------|
| S1—O1       | 1.417 (2)    | S2—C10       | 1.739 (3)   |
| S1—O2       | 1.418 (2)    | N1—F1        | 1.428 (3)   |
| S1—N1       | 1.712 (3)    | N1—C1        | 1.451 (4)   |
| S1—C3       | 1.740 (3)    | N2—F2        | 1.433 (3)   |
| S2—O4       | 1.417 (2)    | N2—C2        | 1.456 (4)   |
| S2—O3       | 1.419 (2)    | C1—C2        | 1.507 (5)   |
| S2—N2       | 1.706 (3)    | C3—C4        | 1.382 (5)   |
| O1—S1—O2    | 121.33 (16)  | O4—S2—C10    | 109.75 (16) |
| O1—S1—N1    | 105.35 (15)  | O3—S2—C10    | 110.72 (16) |
| O2—S1—N1    | 101.20 (14)  | N2—S2—C10    | 106.13 (15) |
| O1—S1—C3    | 110.51 (16)  | F1—N1—C1     | 105.0 (3)   |
| O2—S1—C3    | 110.60 (16)  | F1—N1—S1     | 105.22 (18) |
| N1—S1—C3    | 106.26 (15)  | C1—N1—S1     | 114.6 (2)   |
| O4—S2—O3    | 121.78 (16)  | F2—N2—C2     | 105.2 (3)   |
| O4—S2—N2    | 105.39 (15)  | F2—N2—S2     | 105.10 (19) |
| O3—S2—N2    | 101.51 (14)  | C2—N2—S2     | 115.6 (2)   |
| O2—S1—N1—F1 | −179.94 (19) | C10—S2—N2—F2 | 63.4 (2)    |
| C3—S1—N1—C1 | 50.4 (3)     | N1—C1—C2—N2  | 179.4 (3)   |
| O3—S2—N2—F2 | 179.1 (2)    |              |             |

## Refinement

Refinement on  $F^2$

$R(F) = 0.050$

$wR(F^2) = 0.142$

$S = 1.04$

3999 reflections

309 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.3412P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.026$$

$$\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$$

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

| $D-H\cdots A$          | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------|-------|-------------|-------------|---------------|
| $C1-H1A\cdots F2^i$    | 0.97  | 2.46        | 3.418 (4)   | 169           |
| $C2-H2B\cdots F1^{ii}$ | 0.97  | 2.48        | 3.439 (4)   | 170           |
| $C4-H4\cdots O3^{ii}$  | 0.93  | 2.47        | 3.311 (4)   | 150           |
| $C8-H8\cdots O4^i$     | 0.93  | 2.56        | 3.415 (4)   | 152           |
| $C15-H15\cdots O2^i$   | 0.93  | 2.39        | 3.265 (4)   | 157           |

Symmetry codes: (i)  $\frac{3}{2} - x, y, \frac{1}{2} - z$ ; (ii)  $\frac{1}{2} - x, y, \frac{1}{2} - z$ .

Molecule (I) crystallized in the monoclinic system; space group  $P2_1/n$  or  $Pn$  from the systematic absences.  $P2_1/n$  was chosen and confirmed by the successful refinement. H atoms were treated as riding ( $C-H = 0.93$  and  $0.97 \text{ \AA}$ ). The solvent molecules located in the channels within the structure exist as disordered pairs (50:50 occupancy) around the crystallographic twofold axis. This leads to the Cl atoms nearly coalescing with another from a symmetry-related molecule, so distorting the vibrational ellipsoids for these atoms.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

KA thanks the Research and Postgraduate Committee of Bu-Ali Sina University for funding in order to visit UMIST.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1055). Services for accessing these data are described at the back of the journal.

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