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Crystal structure of dimethylformamidium bis(trifluoromethanesulfonyl)amide: an ionic liquid

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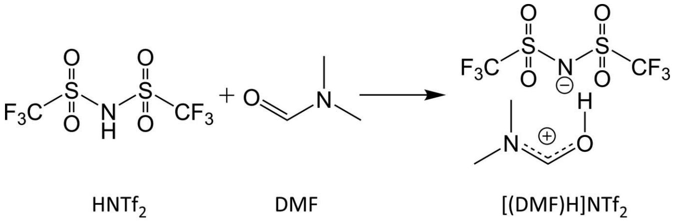
At 100 K, the title molecular salt, $C_3H_8NO^+\cdot C_2F_6NO_4S_2^-$, has orthorhombic ($P2_12_12_1$) symmetry; the amino H atom of bis(trifluoromethanesulfonyl)amine ($HNTf_2$) was transferred to the basic O atom of dimethylformamide (DMF) when the ionic liquid components were mixed. The structure displays an O—H···N hydrogen bond, which links the cation to the anion, which is reinforced by a non-conventional C—H···O interaction, generating an $R_2^2(7)$ loop. A further very weak C—H···O interaction generates an [001] chain.

1. Chemical context

A ionic liquid, also known as a liquid electrolyte, is a salt or an ion pair that remains in a liquid state below 373 K (Ghandi, 2014): such species extend the selection of solvents or media of chemical processes. The study of its solid-state structure can facilitate the exploration of other intermolecular forces of attraction besides electrostatic forces that govern the properties of these ionic liquids such as melting point, acidity, ion mobility, diffusion and viscosity. In this study we report the crystal structure of an organic liquid salt formed by a proton-transfer reaction between bis(trifluoromethanesulfonyl)amine and dimethylformamide. This protic ionic liquid has been used as a solvent, an electrolyte and a substrate for electrocatalysis (Hou *et al.*, 2014).



2. Structural commentary

The asymmetric unit consists of one bis(trifluoromethanesulfonyl)amide anion and one dimethylformamidium cation (Fig. 1): when the components were mixed, the acidic N—H proton of $HNTf_2$ was transfered to the formyl group of dimethylformamide. The dimethylformamidium C4—O5 and N2—C4 bond lengths are 1.2983 (16) and 1.2888 (15) Å respectively, which reflect the delocalization of charge *via* π-electrons. The N2—C4—O5 angle does not deviate from the expected 120° of an sp^2-hybridized carbon atom [120.37 (11)°]. The bis(trifluoromethanesulfonyl)amide anion features S1—N1 and S2—N1 bond distances of 1.6035 (11) and 1.5947 (11) Å, respectively.

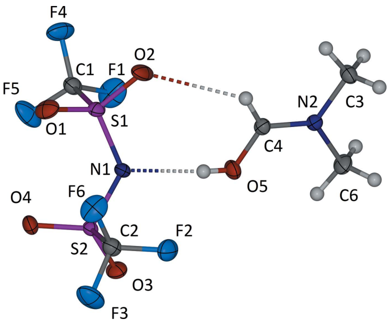


Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O5—H5⋯N1	0.74 (3)	1.98 (3)	2.7139 (14)	172 (2)
C4—H4⋯O2	0.93	2.57	3.2694 (16)	132
C4—H4⋯O4^{i}	0.93	2.63	3.4773 (16)	152

Symmetry code: (i) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$.

3. Supramolecular features

The ion pair features two hydrogen bonds (Table 1). One is between the acidic hydrogen atom attached to the formyl oxygen atom of the dimethylformamidium cation and the nitrogen atom of the bis(trifluoromethanesulfonyl)amide anion: the H⋯N distance is 1.98 (3) Å. The other is a non-conventional C—H⋯O hydrogen bond between the formyl hydrogen atom of the dimethylformamidium cation and one of the sulfoxide oxygen atoms of the anion (Desiraju, 1991). The C4—H⋯O2 distance is 2.57 Å (Table 1). Together, these generate an $R_2^2(7)$ loop. A further very weak C—H⋯O interaction links the ion pairs into an [001] chain.

4. Database survey

A CSD search (Web CSD version 1.1.1; May 4, 2016) found no structures that have the same ion pairing. Some structures feature the same bis(trifluoromethanesulfonyl)amide anion but different cations, which are usually metal complexes.

5. Synthesis and crystallization

A literature procedure was followed to synthesize [(DMF)H]NTf$_2$ (I) (Hou *et al.*, 2014). Equimolar amounts of of dimethylformamide (17.6 mmol, 1.29 g) and bis(trifluoromethanesulfonyl)amine (17.8 mmol, 5.0g) were mixed together after cooling each reagent to 238 K. The solution was stirred at room temperature until it formed a light-yellow viscous solution. The solution was then left to stand undisturbed at room temperature and colorless blocks of (I) were isolated.

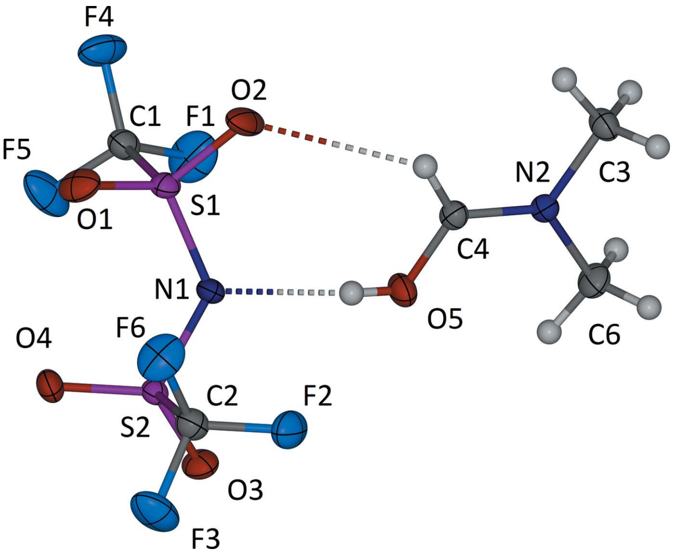


Figure 1
The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_3H_8NO^+ \cdot C_2F_6NO_4S_2^-$
M_r	354.25
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	9.0254 (9), 11.4601 (12), 12.3621 (14)
V (Å^3)	1278.6 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.51
Crystal size (mm)	0.40 × 0.30 × 0.30
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.582, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15926, 4274, 3989
R_{int}	0.033
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.739
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.066, 1.06
No. of reflections	4274
No. of parameters	187
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.30
Absolute structure	Flack (1983)
Absolute structure parameter	−0.01 (4)

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically and allowed to ride on their parent atoms: C—H = 0.93–0.96 Å with $U_{iso}(H) = 1.5U_{eq}$(C-methyl) and $1.2U_{eq}$(C) for other H atoms. The methyl groups were refined as rotating groups.

Acknowledgements

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Crystal structure of dimethylformamidium bis(trifluoromethanesulfonyl)amide: an ionic liquid

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Dimethylformamidium bis(trifluoromethanesulfonyl)amide

Crystal data

$C_3H_8NO^+\cdot C_2F_6NO_4S_2^-$
$M_r = 354.25$
Orthorhombic, $P2_12_12_1$
$a = 9.0254\ (9)$ Å
$b = 11.4601\ (12)$ Å
$c = 12.3621\ (14)$ Å
$V = 1278.6\ (2)$ Å^3
$Z = 4$
$F(000) = 712$
$D_x = 1.840$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9937 reflections
$\theta = 2.4$–$31.5°$
$\mu = 0.51$ mm^{-1}
$T = 100$ K
Block, colourless
0.40 × 0.30 × 0.30 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
$T_{\min} = 0.582$, $T_{\max} = 0.746$
15926 measured reflections
4274 independent reflections
3989 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.033$
$\theta_{\max} = 31.7°$, $\theta_{\min} = 2.4°$
$h = -13\rightarrow12$
$k = -16\rightarrow16$
$l = -17\rightarrow18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.066$
$S = 1.06$
4274 reflections
187 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Absolute structure: Flack (1983)

Absolute structure parameter: −0.01 (4)

Special details

Experimental. Absorption correction: SADABS-2014/5 (Bruker,2014/5) was used for absorption correction. wR2(int) was 0.0777 before and 0.0530 after correction. The Ratio of minimum to maximum transmission is 0.7795. The $\lambda/2$ correction factor is 0.00150.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.95481 (3)	0.01794 (3)	0.22331 (2)	0.02018 (7)
S2	1.05136 (3)	−0.05314 (3)	0.43097 (2)	0.01784 (6)
C3	1.44513 (14)	0.35694 (12)	0.10155 (11)	0.0239 (2)
H3A	1.3456	0.3670	0.0757	0.036*
H3B	1.5095	0.3401	0.0417	0.036*
H3C	1.4774	0.4272	0.1366	0.036*
F1	1.14157 (11)	−0.10684 (12)	0.11057 (9)	0.0507 (3)
F2	1.09712 (11)	0.15500 (8)	0.51280 (8)	0.0352 (2)
F3	0.97455 (13)	0.03798 (10)	0.61557 (7)	0.0455 (3)
F4	0.92510 (12)	−0.09329 (9)	0.04146 (7)	0.0428 (3)
F5	0.96239 (14)	−0.20423 (8)	0.17885 (9)	0.0472 (3)
F6	0.86942 (10)	0.11845 (9)	0.47659 (8)	0.0413 (2)
O1	0.80609 (10)	−0.00178 (9)	0.25752 (9)	0.0324 (3)
O2	0.99064 (13)	0.11860 (9)	0.16080 (8)	0.0338 (3)
O3	1.19216 (10)	−0.08639 (9)	0.47431 (8)	0.0276 (2)
O4	0.92949 (10)	−0.13268 (9)	0.43684 (8)	0.0250 (2)
N1	1.07837 (11)	0.00592 (10)	0.31584 (9)	0.0210 (2)
N2	1.44952 (11)	0.25990 (9)	0.17894 (8)	0.01757 (19)
O5	1.33633 (10)	0.11905 (9)	0.27429 (9)	0.0260 (2)
C1	0.99834 (15)	−0.10436 (13)	0.13368 (11)	0.0246 (3)
C2	0.99431 (14)	0.07208 (13)	0.51356 (11)	0.0253 (3)
C6	1.59693 (13)	0.22881 (13)	0.22087 (12)	0.0275 (3)
H6A	1.5879	0.1646	0.2703	0.041*
H6B	1.6389	0.2947	0.2578	0.041*
H6C	1.6602	0.2068	0.1618	0.041*
C4	1.33073 (12)	0.20433 (11)	0.20528 (10)	0.0193 (2)
H4	1.2405	0.2254	0.1747	0.023*
H5	1.265 (3)	0.0923 (19)	0.2902 (16)	0.051 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02305 (12)	0.01838 (15)	0.01912 (13)	0.00063 (11)	−0.00390 (11)	0.00356 (11)
S2	0.01587 (10)	0.01937 (14)	0.01828 (12)	−0.00017 (10)	−0.00079 (10)	0.00504 (11)
C3	0.0222 (5)	0.0239 (7)	0.0257 (6)	−0.0006 (5)	0.0031 (5)	0.0054 (5)
F1	0.0329 (5)	0.0708 (8)	0.0485 (6)	0.0044 (5)	0.0119 (4)	−0.0170 (6)
F2	0.0436 (5)	0.0245 (5)	0.0374 (5)	−0.0066 (4)	−0.0092 (4)	−0.0004 (4)
F3	0.0703 (7)	0.0429 (6)	0.0232 (4)	−0.0029 (6)	0.0124 (5)	0.0005 (4)
F4	0.0657 (7)	0.0352 (5)	0.0276 (4)	−0.0002 (5)	−0.0181 (5)	−0.0046 (4)
F5	0.0837 (8)	0.0191 (4)	0.0389 (5)	−0.0046 (5)	0.0122 (6)	0.0027 (4)
F6	0.0301 (4)	0.0410 (6)	0.0530 (6)	0.0141 (4)	−0.0011 (4)	−0.0103 (5)
O1	0.0185 (4)	0.0475 (7)	0.0310 (5)	0.0074 (4)	−0.0046 (4)	0.0018 (5)
O2	0.0586 (7)	0.0185 (5)	0.0244 (5)	−0.0065 (5)	−0.0123 (5)	0.0063 (4)
O3	0.0198 (4)	0.0349 (6)	0.0282 (5)	0.0041 (4)	−0.0056 (4)	0.0067 (4)
O4	0.0234 (4)	0.0233 (5)	0.0282 (5)	−0.0052 (3)	0.0004 (4)	0.0070 (4)
N1	0.0199 (4)	0.0258 (6)	0.0174 (4)	−0.0036 (4)	−0.0020 (4)	0.0069 (4)
N2	0.0162 (4)	0.0197 (5)	0.0167 (4)	0.0011 (4)	0.0015 (4)	−0.0013 (4)
O5	0.0199 (4)	0.0285 (5)	0.0295 (5)	−0.0032 (4)	0.0019 (4)	0.0088 (4)
C1	0.0294 (5)	0.0225 (7)	0.0220 (6)	−0.0014 (5)	0.0003 (5)	0.0024 (5)
C2	0.0275 (5)	0.0252 (7)	0.0231 (6)	−0.0001 (5)	0.0006 (5)	0.0013 (5)
C6	0.0166 (5)	0.0322 (8)	0.0336 (7)	−0.0001 (5)	−0.0030 (5)	0.0034 (6)
C4	0.0172 (4)	0.0223 (6)	0.0184 (5)	−0.0003 (4)	0.0013 (4)	−0.0011 (5)

Geometric parameters (Å, º)

S1—O1	1.4253 (10)	F2—C2	1.3282 (16)
S1—O2	1.4256 (11)	F3—C2	1.3321 (16)
S1—N1	1.6035 (11)	F4—C1	1.3239 (16)
S1—C1	1.8293 (15)	F5—C1	1.3141 (17)
S2—O3	1.4307 (9)	F6—C2	1.3273 (16)
S2—O4	1.4304 (9)	N2—C6	1.4716 (15)
S2—N1	1.5947 (11)	N2—C4	1.2888 (15)
S2—C2	1.8349 (15)	O5—C4	1.2983 (16)
C3—H3A	0.9600	O5—H5	0.74 (2)
C3—H3B	0.9600	C6—H6A	0.9600
C3—H3C	0.9600	C6—H6B	0.9600
C3—N2	1.4675 (16)	C6—H6C	0.9600
F1—C1	1.3242 (16)	C4—H4	0.9300
O1—S1—O2	120.18 (7)	C4—O5—H5	116.8 (16)
O1—S1—N1	115.44 (6)	F1—C1—S1	110.90 (11)
O1—S1—C1	105.10 (7)	F4—C1—S1	109.94 (10)
O2—S1—N1	107.36 (6)	F4—C1—F1	107.68 (12)
O2—S1—C1	104.06 (7)	F5—C1—S1	110.91 (10)
N1—S1—C1	102.53 (6)	F5—C1—F1	108.30 (13)
O3—S2—N1	108.15 (6)	F5—C1—F4	109.03 (13)
O3—S2—C2	104.43 (6)	F2—C2—S2	111.07 (9)

O4—S2—O3	119.62 (6)	F2—C2—F3	108.06 (11)
O4—S2—N1	115.68 (6)	F3—C2—S2	109.56 (10)
O4—S2—C2	104.73 (6)	F6—C2—S2	111.09 (9)
N1—S2—C2	101.98 (6)	F6—C2—F2	107.72 (12)
H3A—C3—H3B	109.5	F6—C2—F3	109.25 (12)
H3A—C3—H3C	109.5	N2—C6—H6A	109.5
H3B—C3—H3C	109.5	N2—C6—H6B	109.5
N2—C3—H3A	109.5	N2—C6—H6C	109.5
N2—C3—H3B	109.5	H6A—C6—H6B	109.5
N2—C3—H3C	109.5	H6A—C6—H6C	109.5
S2—N1—S1	124.53 (6)	H6B—C6—H6C	109.5
C3—N2—C6	115.95 (10)	N2—C4—O5	120.37 (11)
C4—N2—C3	121.11 (11)	N2—C4—H4	119.8
C4—N2—C6	122.92 (11)	O5—C4—H4	119.8

C3—N2—C4—O5	−179.64 (11)	O4—S2—N1—S1	21.78 (11)
O1—S1—N1—S2	14.69 (11)	O4—S2—C2—F2	−178.35 (9)
O1—S1—C1—F1	−169.55 (11)	O4—S2—C2—F3	62.34 (10)
O1—S1—C1—F4	71.48 (11)	O4—S2—C2—F6	−58.47 (11)
O1—S1—C1—F5	−49.18 (12)	N1—S1—C1—F1	−48.50 (12)
O2—S1—N1—S2	151.76 (9)	N1—S1—C1—F4	−167.47 (9)
O2—S1—C1—F1	63.26 (12)	N1—S1—C1—F5	71.88 (11)
O2—S1—C1—F4	−55.70 (11)	N1—S2—C2—F2	−57.43 (10)
O2—S1—C1—F5	−176.36 (10)	N1—S2—C2—F3	−176.74 (9)
O3—S2—N1—S1	159.07 (8)	N1—S2—C2—F6	62.45 (11)
O3—S2—C2—F2	55.11 (11)	C1—S1—N1—S2	−98.96 (9)
O3—S2—C2—F3	−64.20 (10)	C2—S2—N1—S1	−91.20 (9)
O3—S2—C2—F6	174.99 (10)	C6—N2—C4—O5	2.30 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···N1	0.74 (3)	1.98 (3)	2.7139 (14)	172 (2)
C4—H4···O2	0.93	2.57	3.2694 (16)	132
C4—H4···O4$^{\mathrm{i}}$	0.93	2.63	3.4773 (16)	152

Symmetry code: (i) $-x+2, y+1/2, -z+1/2$.