organic compounds

1,1',2,2'-Tetramethyl-3,3'-(p-phenyl-enedimethylene)diimidazol-1-ium bis(trifluoromethanesulfonate)

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In the solid form of the title imidazolium-based ionic liquid salt, $C_{18}H_{24}N_4{}^{2+} \cdot 2CF_3SO_3{}^-$, the complete cation is generated by a crystallographic inversion centre. The five-membered imidazole ring is approximately perpendicular to the six-membered phenylene ring [dihedral angle = 85.11 (11)°]. In the crystal, the components are linked by C—H···O interactions.

Related literature

For background to imidazolium-based ionic liquid salts, see: Ganesan *et al.* (2008); Puvaneswary *et al.* (2009*a*,*b*,*c*).
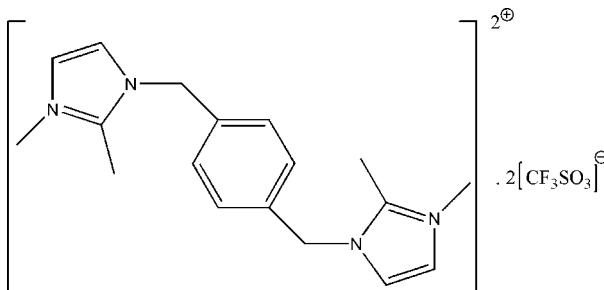
Experimental

Crystal data

$C_{18}H_{24}N_4{}^{2+} \cdot 2CF_3O_3S^-$	a = 7.3054 (1) Å
M_r = 594.55	b = 8.0645 (2) Å
Triclinic, $P\bar{1}$	c = 11.3548 (2) Å
α = 89.946 (1)°	Mo $K\alpha$ radiation
β = 76.653 (1)°	μ = 0.30 mm^{-1}
γ = 75.213 (1)°	T = 100 K
V = 628.14 (2) Å^3	0.31 × 0.19 × 0.04 mm
Z = 1	

Data collection

Bruker APEXII CCD diffractometer	5105 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2273 independent reflections
T_{min} = 0.912, T_{max} = 0.988	1982 reflections with $I > 2\sigma(I)$
	R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042	174 parameters
$wR(F^2)$ = 0.103	H-atom parameters constrained
S = 1.16	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
2273 reflections	$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6A···O2^i	0.99	2.35	3.251 (3)	152
C3—H3A···O2^{ii}	0.98	2.59	3.424 (4)	144
C1—H1C···O2^{ii}	0.98	2.49	3.296 (3)	139
C1—H1B···O1^{iii}	0.98	2.36	3.293 (3)	159
C1—H1A···O1^{iv}	0.98	2.52	3.164 (3)	123

Symmetry codes: (i) $-x+2, -y, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $x-1, y, z$; (iv) $-x+1, -y+1, -z+1$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Ganesan, K., Alias, Y. & Ng, S. W. (2008). *Acta Cryst.* C**64**, o478–o480.
Puvaneswary, S., Alias, Y. & Ng, S. W. (2009*a*). *Acta Cryst.* E**65**, o1828.
Puvaneswary, S., Alias, Y. & Ng, S. W. (2009*b*). *Acta Cryst.* E**65**, o1829.
Puvaneswary, S., Alias, Y. & Ng, S. W. (2009*c*). *Acta Cryst.* E**65**, o1830.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

1,1′,2,2′-Tetramethyl-3,3′-(*p*-phenylenedimethylene)diimidazol-1-ium bis(trifluoromethanesulfonate)

Puvaneswary Subramaniam, Yatimah Alias and Kumuthini Chandrasekaram

S1. Comment

Crystal structures of similar symmetrical compunds have been reported from our previous studies (Ganesan, *et al.*, 2008; Puvaneswary *et al.*, 2009*a*; 2009*b*; 2009*c*). As part of our ongoing research into imidazolium-based ionic liquids, we have synthesized 1,1′,2,2′-tetramethyl-3,3′-(*p*-phenylenedimethylene)diimidazolium salt with trifluoromethanesulfonate anion.

The neighbouring cations in the title compund are held together *via* C–H⋯O hydrogen bonds in opposite directions through imidazole rings to $CF_3SO_3^-$ anions and these hydrogen bonds stabilize the crystal structure.

S2. Experimental

α,α-Dibromo-*p*-xylene (1.26 g, 4.77 mmol) and 1,2-dimethylimidazole (0.96 g, 9.99 mmol) were refluxed in DMF (50 ml) for 3 h. The product that separated from solution was collected and washed with ether. Crystals of the bromide salt were grown from its solution in water (Puvaneswary *et al.*, 2009*a*).

The bromide salt (0.50 g, 1.10 mmol) and lithium trifluoromethanesulfonate (0.36 g, 2.31 mmol) were stirred in water (100 ml) for 24 h. Colourless crystals were obtained by slow evaporation of the solution (Melting point: 92–94°C).

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 to 0.99Å)and were included in the refinement in the riding model approximation, with U(H) set to 1.2 to 1.5U_{eq}(C).
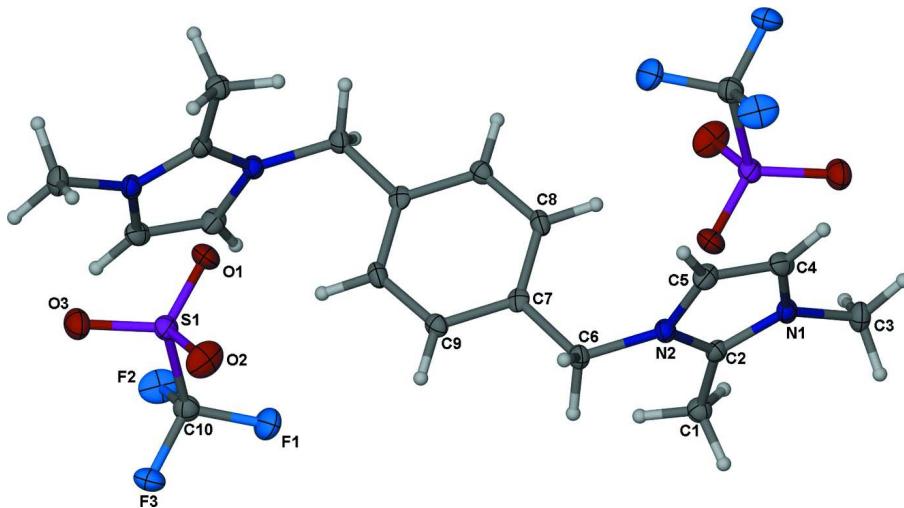
Figure 1

Thermal ellipsoid plot of the title compund at the 50% probability level. H atoms are drawn as spheres of arbitrary radius.

1,1′,2,2′-Tetramethyl-3,3′-(*p*-phenylenedimethylene)diimidazol-1-ium bis(trifluoromethanesulfonate)

Crystal data
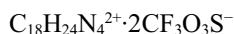
$C_{18}H_{24}N_4^{2+} \cdot 2CF_3O_3S^-$	$Z = 1$
$M_r = 594.55$	$F(000) = 306$
Triclinic, $P\overline{1}$	$D_x = 1.572$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.3054$ (1) Å	Cell parameters from 1992 reflections
$b = 8.0645$ (2) Å	$\theta = 2.6$–29.0°
$c = 11.3548$ (2) Å	$\mu = 0.30$ mm^{-1}
$\alpha = 89.946$ (1)°	$T = 100$ K
$\beta = 76.653$ (1)°	Plate, colourless
$\gamma = 75.213$ (1)°	$0.31 \times 0.19 \times 0.04$ mm
$V = 628.14$ (2) Å^3	

Data collection

Bruker APEXII CCD diffractometer	5105 measured reflections
Radiation source: fine-focus sealed tube	2273 independent reflections
Graphite monochromator	1982 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.021$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.3°$, $\theta_{min} = 1.9°$
$T_{min} = 0.912$, $T_{max} = 0.988$	$h = -8 \rightarrow 8$
	$k = -9 \rightarrow 9$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.042$	
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.16$	$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 1.0056P]$ where $P = (F_o^2 + 2F_c^2)/3$
2273 reflections	
174 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.33$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.37$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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	$U_{iso}*/U_{eq}$
N1	0.1441 (3)	0.2762 (3)	0.18655 (19)	0.0160 (5)

N2	0.3402 (3)	0.2113 (3)	0.30441 (19)	0.0154 (5)
C1	−0.0172 (4)	0.3018 (3)	0.4080 (2)	0.0184 (6)
H1A	−0.1168	0.4026	0.3949	0.028*
H1B	0.0251	0.3241	0.4810	0.028*
H1C	−0.0718	0.2022	0.4184	0.028*
C2	0.1513 (4)	0.2664 (3)	0.3023 (2)	0.0153 (5)
C3	−0.0369 (4)	0.3301 (4)	0.1445 (3)	0.0214 (6)
H3A	−0.1169	0.2498	0.1703	0.032*
H3B	−0.0050	0.3304	0.0558	0.032*
H3C	−0.1093	0.4459	0.1793	0.032*
C4	0.3304 (4)	0.2260 (3)	0.1129 (2)	0.0192 (6)
H4	0.3651	0.2214	0.0268	0.023*
C5	0.4525 (4)	0.1851 (3)	0.1863 (2)	0.0191 (6)
H5	0.5906	0.1454	0.1620	0.023*
C6	0.4164 (4)	0.1924 (3)	0.4137 (2)	0.0165 (6)
H6A	0.5389	0.0992	0.3970	0.020*
H6B	0.3214	0.1575	0.4796	0.020*
C7	0.4564 (3)	0.3550 (3)	0.4568 (2)	0.0144 (5)
C8	0.4553 (4)	0.4977 (3)	0.3878 (2)	0.0166 (6)
H8	0.4247	0.4974	0.3109	0.020*
C9	0.5011 (4)	0.3589 (3)	0.5692 (2)	0.0155 (5)
H9	0.5018	0.2624	0.6173	0.019*
S1	1.07181 (10)	0.18928 (9)	0.76648 (6)	0.01802 (18)
F1	0.7150 (2)	0.1636 (2)	0.78601 (16)	0.0331 (4)
F2	0.7393 (2)	0.3543 (2)	0.91048 (16)	0.0334 (4)
F3	0.8292 (2)	0.0858 (2)	0.94182 (14)	0.0272 (4)
O1	1.0372 (3)	0.3265 (3)	0.68688 (17)	0.0283 (5)
O2	1.1362 (3)	0.0188 (3)	0.70802 (19)	0.0332 (5)
O3	1.1741 (3)	0.2164 (3)	0.85592 (18)	0.0262 (5)
C10	0.8268 (4)	0.1991 (3)	0.8556 (2)	0.0204 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0189 (12)	0.0156 (11)	0.0150 (11)	−0.0052 (9)	−0.0060 (9)	−0.0006 (9)
N2	0.0154 (11)	0.0174 (12)	0.0136 (11)	−0.0046 (9)	−0.0035 (9)	0.0001 (9)
C1	0.0180 (14)	0.0191 (14)	0.0177 (13)	−0.0044 (11)	−0.0039 (11)	0.0009 (11)
C2	0.0188 (13)	0.0130 (13)	0.0162 (13)	−0.0063 (11)	−0.0059 (11)	0.0002 (10)
C3	0.0221 (15)	0.0233 (15)	0.0215 (14)	−0.0053 (12)	−0.0111 (12)	0.0003 (11)
C4	0.0247 (15)	0.0190 (14)	0.0136 (13)	−0.0081 (12)	−0.0009 (11)	−0.0017 (10)
C5	0.0173 (14)	0.0215 (14)	0.0174 (14)	−0.0062 (11)	−0.0007 (11)	−0.0032 (11)
C6	0.0160 (13)	0.0192 (14)	0.0157 (13)	−0.0050 (11)	−0.0060 (10)	0.0020 (10)
C7	0.0073 (12)	0.0192 (13)	0.0151 (13)	−0.0022 (10)	−0.0011 (10)	−0.0011 (10)
C8	0.0150 (13)	0.0227 (14)	0.0123 (12)	−0.0038 (11)	−0.0047 (10)	0.0009 (10)
C9	0.0131 (13)	0.0171 (13)	0.0155 (13)	−0.0022 (10)	−0.0041 (10)	0.0029 (10)
S1	0.0180 (4)	0.0213 (4)	0.0143 (3)	−0.0061 (3)	−0.0019 (3)	−0.0007 (3)
F1	0.0283 (10)	0.0448 (11)	0.0367 (10)	−0.0189 (8)	−0.0182 (8)	0.0115 (8)
F2	0.0254 (9)	0.0241 (9)	0.0409 (11)	0.0004 (7)	0.0038 (8)	−0.0048 (8)

F3	0.0329 (10)	0.0300 (9)	0.0213 (9)	−0.0150 (8)	−0.0044 (7)	0.0088 (7)
O1	0.0382 (12)	0.0340 (12)	0.0190 (10)	−0.0182 (10)	−0.0098 (9)	0.0098 (9)
O2	0.0293 (12)	0.0287 (12)	0.0355 (13)	−0.0059 (9)	0.0024 (10)	−0.0137 (10)
O3	0.0222 (11)	0.0357 (12)	0.0227 (11)	−0.0089 (9)	−0.0081 (8)	0.0034 (9)
C10	0.0216 (15)	0.0187 (14)	0.0209 (14)	−0.0047 (11)	−0.0060 (12)	0.0023 (11)

Geometric parameters (Å, º)

N1—C2	1.329 (3)	C6—C7	1.520 (4)
N1—C4	1.382 (3)	C6—H6A	0.9900
N1—C3	1.471 (3)	C6—H6B	0.9900
N2—C2	1.343 (3)	C7—C9	1.390 (4)
N2—C5	1.386 (3)	C7—C8	1.391 (4)
N2—C6	1.466 (3)	C8—C9^i	1.392 (4)
C1—C2	1.475 (4)	C8—H8	0.9500
C1—H1A	0.9800	C9—C8^i	1.392 (4)
C1—H1B	0.9800	C9—H9	0.9500
C1—H1C	0.9800	S1—O1	1.438 (2)
C3—H3A	0.9800	S1—O3	1.439 (2)
C3—H3B	0.9800	S1—O2	1.442 (2)
C3—H3C	0.9800	S1—C10	1.824 (3)
C4—C5	1.339 (4)	F1—C10	1.338 (3)
C4—H4	0.9500	F2—C10	1.331 (3)
C5—H5	0.9500	F3—C10	1.338 (3)
C2—N1—C4	109.9 (2)	N2—C6—C7	113.6 (2)
C2—N1—C3	124.5 (2)	N2—C6—H6A	108.8
C4—N1—C3	125.6 (2)	C7—C6—H6A	108.8
C2—N2—C5	109.0 (2)	N2—C6—H6B	108.8
C2—N2—C6	125.6 (2)	C7—C6—H6B	108.8
C5—N2—C6	125.3 (2)	H6A—C6—H6B	107.7
C2—C1—H1A	109.5	C9—C7—C8	118.8 (2)
C2—C1—H1B	109.5	C9—C7—C6	118.2 (2)
H1A—C1—H1B	109.5	C8—C7—C6	123.0 (2)
C2—C1—H1C	109.5	C7—C8—C9^i	120.3 (2)
H1A—C1—H1C	109.5	C7—C8—H8	119.8
H1B—C1—H1C	109.5	C9^i—C8—H8	119.8
N1—C2—N2	107.0 (2)	C7—C9—C8^i	120.9 (2)
N1—C2—C1	126.3 (2)	C7—C9—H9	119.5
N2—C2—C1	126.6 (2)	C8^i—C9—H9	119.5
N1—C3—H3A	109.5	O1—S1—O3	115.23 (12)
N1—C3—H3B	109.5	O1—S1—O2	115.05 (13)
H3A—C3—H3B	109.5	O3—S1—O2	114.61 (13)
N1—C3—H3C	109.5	O1—S1—C10	102.57 (13)
H3A—C3—H3C	109.5	O3—S1—C10	103.71 (12)
H3B—C3—H3C	109.5	O2—S1—C10	103.25 (13)
C5—C4—N1	106.8 (2)	F2—C10—F3	107.4 (2)
C5—C4—H4	126.6	F2—C10—F1	107.8 (2)

N1—C4—H4	126.6	F3—C10—F1	107.1 (2)
C4—C5—N2	107.3 (2)	F2—C10—S1	111.33 (19)
C4—C5—H5	126.4	F3—C10—S1	111.72 (19)
N2—C5—H5	126.4	F1—C10—S1	111.34 (19)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6*A*···O2ii	0.99	2.35	3.251 (3)	152
C3—H3*A*···O2iii	0.98	2.59	3.424 (4)	144
C1—H1*C*···O2iii	0.98	2.49	3.296 (3)	139
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C1—H1*A*···O1i	0.98	2.52	3.164 (3)	123

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+2, −*y*, −*z*+1; (iii) −*x*+1, −*y*, −*z*+1; (iv) *x*−1, *y*, *z*.