

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

Puvaneswary Subramaniam,* Yatimah Alias and Kumuthini Chandrasekaram

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia
Correspondence e-mail: puvanes5881@yahoo.com

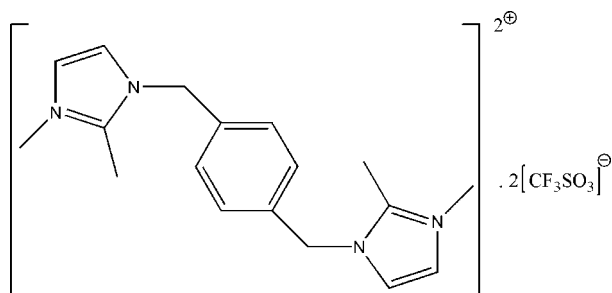
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.042; wR factor = 0.103; data-to-parameter ratio = 13.1.

In the solid form of the title imidazolium-based ionic liquid salt, $\text{C}_{18}\text{H}_{24}\text{N}_4^{2+} \cdot 2\text{CF}_3\text{SO}_3^-$, 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 = $85.11(11)^\circ$]. In the crystal, the components are linked by $\text{C}-\text{H}\cdots\text{O}$ interactions.

Related literature

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



Experimental

Crystal data

$\text{C}_{18}\text{H}_{24}\text{N}_4^{2+} \cdot 2\text{CF}_3\text{O}_3\text{S}^-$
 $M_r = 594.55$
Triclinic, $P\bar{1}$

$a = 7.3054(1)$ Å
 $b = 8.0645(2)$ Å
 $c = 11.3548(2)$ Å

$\alpha = 89.946(1)^\circ$
 $\beta = 76.653(1)^\circ$
 $\gamma = 75.213(1)^\circ$
 $V = 628.14(2)$ Å³
 $Z = 1$

Mo $K\alpha$ radiation
 $\mu = 0.30$ mm⁻¹
 $T = 100$ K
 $0.31 \times 0.19 \times 0.04$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.912$, $T_{\max} = 0.988$

5105 measured reflections
2273 independent reflections
1982 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.103$
 $S = 1.16$
2273 reflections

174 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C6}-\text{H6A}\cdots\text{O2}^{\text{ii}}$	0.99	2.35	3.251 (3)	152
$\text{C3}-\text{H3A}\cdots\text{O2}^{\text{ii}}$	0.98	2.59	3.424 (4)	144
$\text{C1}-\text{H1C}\cdots\text{O2}^{\text{ii}}$	0.98	2.49	3.296 (3)	139
$\text{C1}-\text{H1B}\cdots\text{O1}^{\text{iii}}$	0.98	2.36	3.293 (3)	159
$\text{C1}-\text{H1A}\cdots\text{O1}^{\text{iv}}$	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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2702).

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supplementary materials

Acta Cryst. (2010). E66, o2455 [doi:10.1107/S1600536810033490]

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P. Subramaniam, Y. Alias and K. Chandrasekaram

Comment

Crystal structures of similar symmetrical compounds 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 compound are held together *via* C–H···O hydrogen bonds in opposite directions through imidazole rings to CF₃SO₃[−] anions and these hydrogen bonds stabilize the crystal structure.

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).

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 1.5 $U_{eq}(C)$.

Figures

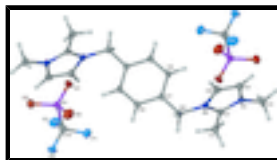


Fig. 1. Thermal ellipsoid plot of the title compound at the 50% probability level. H atoms are drawn as spheres of arbitrary radius.

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Crystal data

C₁₈H₂₄N₄²⁺·2CF₃O₃S[−]

$M_r = 594.55$

Triclinic, $P\bar{1}$

$Z = 1$

$F(000) = 306$

$D_x = 1.572 \text{ Mg m}^{-3}$

supplementary materials

Hall symbol: -P 1
 $a = 7.3054$ (1) Å
 $b = 8.0645$ (2) Å
 $c = 11.3548$ (2) Å
 $\alpha = 89.946$ (1)°
 $\beta = 76.653$ (1)°
 $\gamma = 75.213$ (1)°
 $V = 628.14$ (2) Å³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1992 reflections
 $\theta = 2.6$ – 29.0 °
 $\mu = 0.30$ mm⁻¹
 $T = 100$ K
Plate, colourless
 $0.31 \times 0.19 \times 0.04$ mm

Data collection

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

Refinement

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^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)

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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, °)

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 codes: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, °)

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

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

Fig. 1

