3-(1-Methyl-3-imidazolio)propanesulfonate: a precursor to a Brønsted acid ionic liquid

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The title compound, C7H12N2O3S, is a zwitterion precursor to a Brønsted acid ionic liquid with potential as an acid catalyst. The C—N—C—C torsion angle of 100.05 (8)° allows the positively charged imidazolium head group and the negatively charged sulfonate group to interact with neighboring zwitterions, forming a C—H⋯O hydrogen-bonding network; the shortest among these interactions is 2.9512 (9) Å. The C—H⋯O interactions can be described by graph-set notation as two $R_2^2(16)$ and one $R_2^2(5)$ hydrogen-bonded rings.

Related literature

For the use of functionalized ionic liquids (ILs) as Brønsted acid catalysts for organic reactions, see: Cole et al. (2002); Yoshizawa et al. (2001). The local structure of ILs is often conserved on transition from the solid state to the liquid state, see: Henderson et al. (2007); Reichert et al. (2007); Triolo et al. (2006). For a related structure, see: Pringle et al. (2003). For polymorphs of ionic liquids, see: Holbrey et al. (2003) and for the applications of ionic liquids, see: Plechкова & Seddon (2008).

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Experimental

Crystal data
C7H12N2O3S
$\mu = 0.33 \text{ mm}^{-1}$
$T = 296 \text{ K}$
$0.29 \times 0.28 \times 0.13 \text{ mm}$

Data collection
Bruker SMART CCD area-detector diffractometer
Absorption correction: for a sphere (SADABS; Bruker, 2007)
$T_{\text{min}} = 0.910, T_{\text{max}} = 0.958$

Refinement
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.120$
$S = 1.03$
$8299$ reflections

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

$D$—H⋯$A$ $D$—H $H$⋯$A$ $D$⋯$A$ $D$—H⋯$A$

C2—H2A⋯O2i 0.923 (14) 2.197 (14) 2.9512 (9) 138.4 (12)
C5—H5A⋯O1ii 0.899 (14) 2.381 (15) 3.1573 (10) 144.6 (12)
C4—H4A⋯O1iii 0.961 (14) 2.528 (14) 3.3268 (11) 140.5 (11)
C4—H4B⋯O3iv 0.961 (14) 2.541 (14) 3.4364 (11) 155.0 (11)
C7—H7B⋯O3v 0.961 (12) 2.613 (12) 3.1693 (10) 117.2 (9)
C8—H8B⋯O3v 0.990 (14) 2.621 (13) 3.2086 (11) 118.1 (9)

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

Data collection: SMART (Bruker, 2007); cell refinement: SMART; program(s) used to solve structure: SHELX97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2241).

References

**3-(1-Methyl-3-imidazolio) Propane-sulfonate: A Precursor To A Bronsted Acid Ionic Liquid**

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supplementary materials
supplementary materials


3-(1-Methyl-3-imidazoliio)propanesulfonate: a precursor to a Brønsted acid ionic liquid

W. M. Reichert, P. C. Trulove and H. C. De Long

Comment

Ionic liquids (ILs) have proven to be highly versatile materials with an ever expanding suite of chemical applications. An application that has recently shown great promise is the use of functionalized ILs as Brønsted acid catalysts for organic reactions (Cole et al., 2002). These IL catalysts are most commonly prepared by the reaction of 1-methylimidazolium-3-alkyl sulfonate zwitterion with an acid that has a pKa low enough to protonate the sulfonate group (Yoshizawa et al., 2001; Cole et al., 2002). The activity of the IL (e.g. the effectiveness of proton transfer) is significantly impacted by the structure and interactions of the zwitterion. It has been shown that the local structure of ILs is often conserved on transition from the solid state to the liquid state (Triolo et al., 2006; Henderson et al., 2007; Reichert et al., 2007). Thus, a structural analysis of the zwitterion, 1-methylimidazolium-3-propanesulfonate (I) might provide valuable insight into the activity of the Brønsted acid IL catalyst.

The asymmetric unit of the title compound is presented in Figure 1. The dominant intermolecular interactions are Coulombic in nature and are through the charged centers of the zwitterion: the imidazolium ring and the sulfonate group (Fig. 2). The negative charged sulfonate group is surrounded by four imidazolium head groups forming six close contacts (Table 1). The interactions of the imidazolium ring hydrogen atoms with the sulfonate group establish two three-dimensional R22(16) rings. The packing along the b axis (Fig. 3) shows the zwitterions arranged in columns along the c axis. The head-to-tail orientation maximizes the polar interaction and minimizes cation-cation and anion-anion repulsions.

Experimental

Compound I was synthesized following the procedure for similar zwitterionic compounds published by (Yoshizawa et al., 2001). 1,3-Propane sultone (25 g, 0.122 mol) was added dropwise to a solution of 1-methylimidazole (10 g, 0.122 mol) in acetone (40 ml) and stirred, then cooled on an ice bath overnight. A white precipitate was recovered from the reaction solution through filtration and washing with acetone. The product was then dried under vacuum giving a white solid (m.p. 482 K). A colourless crystal suitable for single crystal X-ray diffraction was retrieved from the dried product.

Refinement

(type here to add refinement details)

Figures

Fig. 1. The thermal ellipsoid plot of the asymmetric unit of (I). The displacement ellipsoids are shown at the 50% probability level.
supplementary materials

Fig. 2. Close contacts in compound I.

Fig. 3. Packing diagram along the $b$ axis.

Fig. 4. Reaction scheme.

3-(1-Methyl-3-imidazolio)propanesulfonate

Crystal data

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>C$<em>7$H$</em>{12}$N$_2$O$_3$S</td>
<td></td>
</tr>
<tr>
<td>$M_r$</td>
<td>204.25</td>
</tr>
<tr>
<td>Monoclinic, $P2_1/c$</td>
<td></td>
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<tr>
<td>Hall symbol: -P 2ybc</td>
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</tr>
<tr>
<td>$a$</td>
<td>9.8164 (4) Å</td>
</tr>
<tr>
<td>$b$</td>
<td>11.7421 (5) Å</td>
</tr>
<tr>
<td>$c$</td>
<td>7.9769 (3) Å</td>
</tr>
<tr>
<td>$\beta$</td>
<td>94.878 (2)$^\circ$</td>
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<tr>
<td>$V$</td>
<td>916.13 (6) Å$^3$</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
</tbody>
</table>

$F(000) = 432$

$D_x = 1.481$ Mg m$^{-3}$

Melting point: 482 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4851 reflections

$0 = 3.1$–$41.1^\circ$

$\mu = 0.33$ mm$^{-1}$

Plate, colourless

0.29 × 0.28 × 0.13 mm

Data collection

Bruker SMART CCD area-detector
diffractometer

8299 independent reflections

Radiation source: fine-focus sealed tube

graphite

5726 reflections with $I > 2\sigma(I)$

$R_{int} = 0.033$

$h = -20\rightarrow 13$

$\theta_{max} = 47.1^\circ$, $\theta_{min} = 3.1^\circ$

Absorption correction: for a sphere
(SADABS; Bruker, 2007)

$T_{min} = 0.910$, $T_{max} = 0.958$

21327 measured reflections

$k = -19\rightarrow 24$

$l = -16\rightarrow 16$
**Supplementary Materials**

**Refinement**

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.120$

$S = 1.03$

8299 reflections

166 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

All $H$-atom parameters refined

$S = 1.03$

$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2 + 0.0483P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.55 \text{ e Å}^{-3}$

$\Delta\rho_{min} = -0.47 \text{ e Å}^{-3}$

**Special details**

**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 $F^2 > \sigma(F^2)$ 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 ($\text{Å}^2$)**

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{iso}/U_{eq}$</th>
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<td>S1</td>
<td>0.288447 (16)</td>
<td>0.459431 (14)</td>
<td>0.711035 (19)</td>
<td>0.01929 (4)</td>
</tr>
<tr>
<td>O1</td>
<td>0.18103 (7)</td>
<td>0.54452 (5)</td>
<td>0.71911 (8)</td>
<td>0.02993 (12)</td>
</tr>
<tr>
<td>O2</td>
<td>0.42331 (6)</td>
<td>0.50523 (8)</td>
<td>0.76230 (9)</td>
<td>0.03616 (15)</td>
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<td>O3</td>
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<td>0.35528 (5)</td>
<td>0.79823 (8)</td>
<td>0.03407 (14)</td>
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<tr>
<td>N3</td>
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<td>0.51000 (5)</td>
<td>0.16133 (7)</td>
<td>0.01989 (9)</td>
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<tr>
<td>N1</td>
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<td>0.65793 (5)</td>
<td>0.08981 (8)</td>
<td>0.02208 (9)</td>
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<td>C2</td>
<td>0.29151 (7)</td>
<td>0.54584 (6)</td>
<td>0.11322 (8)</td>
<td>0.02096 (10)</td>
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<tr>
<td>H2A</td>
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<td>0.5037 (13)</td>
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<tr>
<td>C4</td>
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<td>0.60254 (6)</td>
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<td>0.2077 (16)</td>
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<td>0.69513 (7)</td>
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<td>H5A</td>
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<td>0.7688 (12)</td>
<td>0.1137 (17)</td>
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<td>C6</td>
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<td>0.72763 (8)</td>
<td>0.03336 (12)</td>
<td>0.03149 (15)</td>
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<td>H6A</td>
<td>0.3932 (15)</td>
<td>0.8024 (14)</td>
<td>0.0813 (19)</td>
<td>0.044 (4)*</td>
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<tr>
<td>H6B</td>
<td>0.4809 (19)</td>
<td>0.6923 (15)</td>
<td>0.063 (2)</td>
<td>0.061 (5)*</td>
</tr>
<tr>
<td>H6C</td>
<td>0.3820 (17)</td>
<td>0.7417 (17)</td>
<td>0.081 (2)</td>
<td>0.067 (5)*</td>
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<tr>
<td>C7</td>
<td>0.14604 (8)</td>
<td>0.39419 (6)</td>
<td>0.21968 (8)</td>
<td>0.02303 (11)</td>
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<tr>
<td>H7A</td>
<td>0.0552 (13)</td>
<td>0.3717 (11)</td>
<td>0.1696 (15)</td>
<td>0.027 (3)*</td>
</tr>
</tbody>
</table>
supplementary materials

H7B  0.2156 (12)  0.3490 (11)  0.1741 (15)  0.026 (3)*
C8    0.1526 (7)  0.38976 (6)  0.41105 (8)  0.02112 (10)
H8A   0.0853 (14)  0.4389 (12)  0.4510 (18)  0.033 (3)*
H8B   0.1301 (13)  0.3105 (12)  0.4405 (17)  0.036 (3)*
C9    0.29159 (7)  0.42456 (8)  0.49418 (9)  0.02574 (12)
H9A   0.3243 (16)  0.4859 (13)  0.444 (2)  0.043 (4)*
H9B   0.3600 (16)  0.3658 (13)  0.4885 (18)  0.043 (4)*

Atomic displacement parameters (Å²)

\[
\begin{array}{cccccc}
S1 & U^{11} & U^{22} & U^{33} & U^{12} & U^{13} \\
O1 & 0.01791 (6) & 0.02075 (7) & 0.01894 (6) & -0.00086 (5) & 0.00002 (4) \\
O2 & 0.0218 (2) & 0.0569 (4) & 0.0287 (3) & -0.0109 (3) & -0.0044 (2) \\
O3 & 0.0510 (4) & 0.0231 (2) & 0.0281 (2) & -0.0029 (2) & 0.0032 (2) \\
N3 & 0.0201 (2) & 0.01929 (19) & 0.0339 (3) & 0.0023 (2) & 0.0011 (2) \\
N1 & 0.0201 (2) & 0.0222 (2) & 0.0233 (2) & -0.0089 (18) & 0.00037 (18) \\
C4 & 0.0200 (3) & 0.0237 (3) & 0.0361 (3) & 0.0030 (2) & 0.0014 (2) \\
C5 & 0.0245 (3) & 0.0121 (3) & 0.0039 (2) & -0.0069 (3) & 0.0048 (3) \\
C6 & 0.0295 (4) & 0.0310 (3) & 0.0347 (4) & -0.00069 (3) & 0.0068 (3) \\
C7 & 0.0289 (3) & 0.0190 (2) & 0.0207 (2) & -0.0029 (2) & -0.0088 (2) \\
C8 & 0.0208 (2) & 0.0220 (2) & 0.0204 (2) & -0.00162 (19) & 0.00092 (18) \\
C9 & 0.0180 (2) & 0.0392 (4) & 0.0020 (2) & 0.00188 (18) & -0.0015 (2)
\end{array}
\]

Geometric parameters (Å, °)

\[
\begin{array}{cccc}
S1—O3 & 1.4529 (6) & C5—H5A & 0.899 (14) \\
S1—O2 & 1.4550 (6) & C6—H6A & 0.959 (16) \\
S1—O1 & 1.4580 (6) & C6—H6B & 0.945 (19) \\
S1—C9 & 1.7805 (7) & C6—H6C & 0.924 (19) \\
N3—C2 & 1.3298 (9) & C7—C8 & 1.5233 (9) \\
N3—C4 & 1.3825 (9) & C7—H7A & 0.982 (13) \\
N3—C7 & 1.4673 (9) & C7—H7B & 0.961 (12) \\
N1—C2 & 1.3301 (9) & C8—C9 & 1.5207 (10) \\
N1—C5 & 1.3791 (10) & C8—H8A & 0.952 (14) \\
N1—C6 & 1.4607 (10) & C8—H8B & 0.990 (14) \\
C2—H2A & 0.923 (14) & C9—H9A & 0.898 (16) \\
C4—C5 & 1.3562 (11) & C9—H9B & 0.967 (16) \\
C4—H4A & 0.961 (14) & \\
C3—S1—O2 & 113.68 (5) & H6A—C6—H6B & 110.8 (14) \\
C3—S1—O1 & 111.84 (4) & N1—C6—H6C & 110.7 (11) \\
C2—S1—O1 & 112.24 (5) & H6A—C6—H6C & 102.9 (15) \\
C3—S1—C9 & 107.06 (4) & H6B—C6—H6C & 112.0 (15) \\
C2—S1—C9 & 105.52 (4) & N3—C7—C8 & 110.85 (5) \\
O1—S1—C9 & 105.84 (4) & N3—C7—H7A & 107.3 (7) \\
C2—N3—C4 & 108.62 (6) & C8—C7—H7A & 111.0 (7) \\
C2—N3—C7 & 124.60 (6) & N3—C7—H7B & 104.0 (7)
\end{array}
\]
supplementary materials

C4—N3—C7  126.28 (6)  C8—C7—H7B  112.9 (7)
C2—N1—C5  108.65 (6)  H7A—C7—H7B  110.4 (10)
C2—N1—C6  124.78 (7)  C9—C8—C7  112.84 (6)
C5—N1—C6  126.54 (7)  C9—C8—H8A  108.3 (8)
N3—C2—N1  108.77 (6)  C7—C8—H8A  110.0 (8)
N3—C2—H2A  127.3 (9)  C9—C8—H8B  111.1 (8)
N1—C2—H2A  123.6 (9)  C7—C8—H8B  106.2 (8)
C5—C4—N3  106.86 (7)  H8A—C8—H8B  108.4 (11)
C5—C4—H4A  128.8 (8)  C8—C9—S1  113.36 (5)
N3—C4—H4A  124.1 (8)  C8—C9—H9A  111.2 (10)
C4—C5—N1  107.09 (7)  S1—C9—H9A  106.8 (10)
C4—C5—H5A  130.7 (9)  C8—C9—H9B  112.9 (9)
N1—C5—H5A  122.2 (9)  S1—C9—H9B  106.2 (9)
N1—C6—H6A  110.2 (9)  H9A—C9—H9B  105.9 (13)
N1—C6—H6B  110.1 (11)
C2—N3—C7—C8  100.05 (8)  C4—N3—C7—C8  −70.97 (8)
N3—C7—C8—C9  −60.48 (8)  N3—C7—C8—C9  −60.48 (8)
C7—C8—C9—S1  163.00 (5)

Hydrogen-bond geometry (Å, °)

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
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<tbody>
<tr>
<td>C2—H2A···O2i</td>
<td>0.923 (14)</td>
<td>2.197 (14)</td>
<td>2.9512 (9)</td>
<td>138.4 (12)</td>
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<td>C5—H5A···O1ii</td>
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<td>144.6 (12)</td>
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<tr>
<td>C4—H4A···O1iii</td>
<td>0.961 (14)</td>
<td>2.528 (14)</td>
<td>3.3268 (11)</td>
<td>140.5 (11)</td>
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<tr>
<td>C4—H4A···O3iii</td>
<td>0.961 (14)</td>
<td>2.541 (14)</td>
<td>3.4364 (11)</td>
<td>155.0 (11)</td>
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<tr>
<td>C7—H7B···O3iv</td>
<td>0.961 (12)</td>
<td>2.613 (12)</td>
<td>3.1693 (10)</td>
<td>117.2 (9)</td>
</tr>
<tr>
<td>C8—H8B···O3iv</td>
<td>0.990 (14)</td>
<td>2.621 (13)</td>
<td>3.2086 (9)</td>
<td>118.1 (9)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) x, −y+3/2, z−1/2; (iii) −x, −y+1, −z+1; (iv) x, −y+1/2, z−1/2.
Fig. 4

\[ \text{NCH}_3 + \text{OSO}_4 \rightarrow \text{H}_3\text{C-N} \text{H}_2 \text{C-N} \text{C} \text{H}_2 \text{SO}_4 \text{I} \]