

The zwitterion 1-butylimidazolium-3-(*n*-butanesulfonate)

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Key indicators

Single-crystal X-ray study
 $T = 123$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.053
 wR factor = 0.145
 Data-to-parameter ratio = 20.8

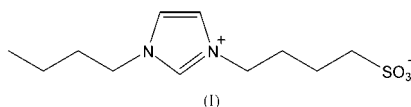
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The molecule of the title compound, $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$, contains a positively charged imidazolium head group and a negatively charged sulfonate tethered together by a four-carbon chain. There is weak intermolecular hydrogen bonding within the structure between the sulfonate O atoms and the H atoms of the imidazolium ring. The sulfonate group causes a twisting of the butyl chain and a decrease in the dihedral angle between the second and third carbon chain compared to the unsubstituted butyl group.

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Comment

Ionic liquids, or room-temperature molten salts, have found recent applications as electrolyte materials as a result of their good conductivity at room temperature. However, when these materials are used as electrolytes in lithium ion batteries it is impossible to realise the required high lithium ion transport number, as the ions of the ionic liquid also migrate on application of a potential gradient. Tethering the anionic and cationic charge together on the same molecule, to form a zwitterion, eliminates the problems of competing ion migration and allows significantly improved lithium transport.



The title compound, (I), has been identified as particularly successful in improving lithium ion conduction in a variety of materials. Single-crystal X-ray data for zwitterions, such as the title compound, that contain either imidazolium or sulfonate groups are relatively scarce, and such information is considered to be invaluable in helping to elucidate the nature of the interactions and thereby the mechanism of lithium ion conduction through these materials.

The title compound crystallizes in the orthorhombic space group *Pbca*, with one complete zwitterion comprising the asymmetric unit. The two butyl groups are orientated *trans* with respect to the plane of the central imidazolium ring and the presence of the sulfonate group results in a twisting of the butyl carbon chain. The dihedral angle between the second and third carbon chain of the butyl group containing the sulfonate substituent is only -67.0 (3)° compared to 176.6 (2)° for the unsubstituted chain, resulting in a *gauche* rather than an *anti* orientation.

The predominant intermolecular interactions within the solid-state structure of the zwitterion are between the sulfonate group and the H atoms on the imidazolium ring. Each sulfonate is surrounded by four zwitterions and forms

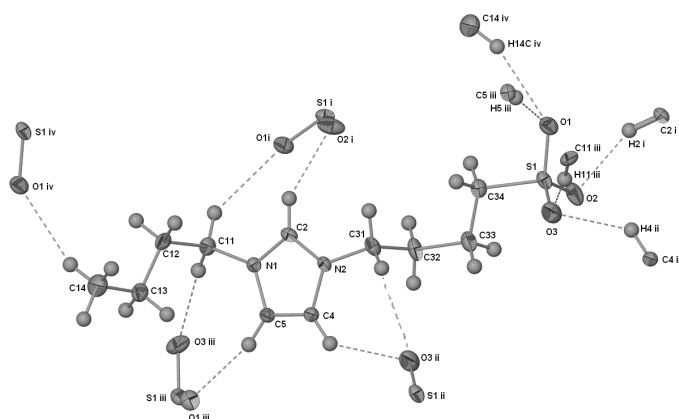


Figure 1
The asymmetric unit of (I), together with some surrounding groups of atoms, showing the weak hydrogen bonds within the structure. Displacement ellipsoids are shown at the 50% probability level.

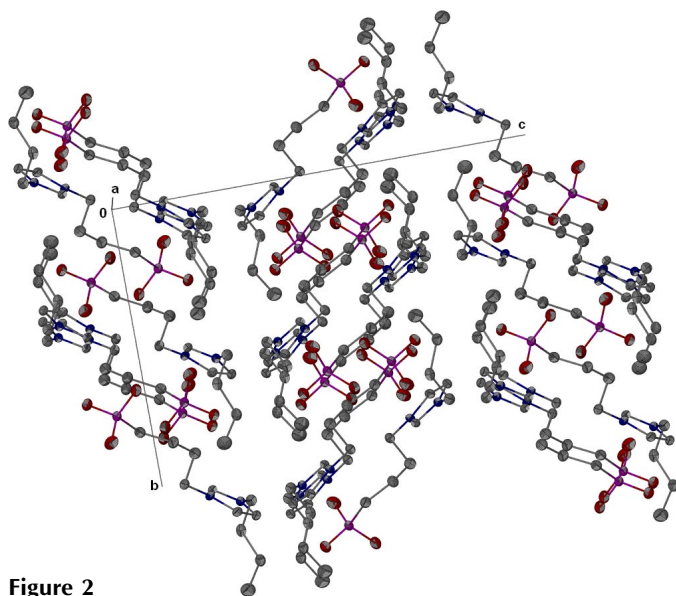


Figure 2
Packing diagram, viewed along the *a* axis, showing the herring-bone structure and the cationic regions.

seven weak hydrogen bonds. The strongest hydrogen bond is to H2, the ring H atom between the two N atoms, *i.e.* the most acidic of the ring H atoms. There are two $R_2^2(8)$ hydrogen-bond rings in the structure, N1—C2—H2···O2ⁱ—S1ⁱ—O1ⁱ···H11B—C11 and N1—C5—H5···O1ⁱⁱⁱ—S1ⁱⁱⁱ—O3ⁱⁱⁱ···H11A—C11, and one $R_2^1(6)$ hydrogen-bond ring, N2—C4—H4···O3ⁱⁱ···H31A—C31 (see Table 2 for symmetry codes). The seventh weak hydrogen bond is between atoms O1 and H14C, the terminal H atom of the butyl-chain substituent.

There are no well defined layers within the structure, but the molecules are aligned in a head-to-tail orientation to maximize anion–cation interaction and minimize the energetically unfavourable anion–anion and cation–cation interactions. This alignment results in a herring-bone arrangement of the molecules, with stacking along the *b* axis, and cationic regions parallel to the *a* axis. This may be of particular importance when considering the mechanism of ion conduction through these materials.

Experimental

The title compound, (I), was synthesized according to the procedure of Yoshizawa *et al.* (2001) for analogous zwitterionic species. 1-Butylimidazole (15 g, 0.1208 mol) was added to a solution of 1,4-butane sultone (12.36 ml, 0.1208 mol) in acetone (50 ml) and the solution stirred under N₂ for 6 d at room temperature, during which time the product slowly formed as a white precipitate. The precipitate was removed by filtration under nitrogen, the product washed three times with acetone (20 ml) and dried under vacuum. The product was obtained as a hygroscopic white powder (m.p. 425 K, yield = 80%). ¹H NMR (300 MHz, *d*₆-DMSO): δ 0.8 (*m*, 3H, CH₃), 1.2 (*m*, 2H, CH₂), 1.5 (*m*, 2H, CH₂), 1.7 (*m*, 2H, CH₂), 1.8 (*m*, 2H, CH₂), 2.4 (*m*, 2H, CH₂), 4.2 (*m*, 4H, N-CH₂), 7.8 (*m*, 2H, H4,H5), 9.2 (*s*, 1H, H2). A colourless single crystal suitable for X-ray diffraction was grown at room temperature by recrystallization from an acetone solution.

Crystal data

C ₁₁ H ₂₀ N ₂ O ₃ S	Mo <i>K</i> α radiation
<i>M_r</i> = 260.35	Cell parameters from 29 344 reflections
Orthorhombic, <i>Pbca</i>	<i>θ</i> = 3.7–28.3°
<i>a</i> = 12.6914 (2) Å	<i>μ</i> = 0.25 mm ^{−1}
<i>b</i> = 11.7483 (2) Å	<i>T</i> = 123 (2) K
<i>c</i> = 17.4988 (2) Å	Prismatic, colourless
<i>V</i> = 2609.11 (7) Å ³	0.30 × 0.30 × 0.25 mm
<i>Z</i> = 8	
<i>D_x</i> = 1.326 Mg m ^{−3}	

Data collection

Nonius KappaCCD diffractometer	<i>R</i> _{int} = 0.063
<i>φ</i> and <i>ω</i> scans (1° frames)	<i>θ</i> _{max} = 28.3°
29 344 measured reflections	<i>h</i> = −16 → 16
3219 independent reflections	<i>k</i> = −15 → 15
2334 reflections with <i>I</i> > 2σ(<i>I</i>)	<i>l</i> = −23 → 23

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2 + 2.971P]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.145$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.06	$\Delta\rho_{\text{max}} = 0.89 \text{ e \AA}^{-3}$
3219 reflections	$\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$
155 parameters	
H-atom parameters constrained	

Table 1

Selected torsion angles (°).

C11—C12—C13—C14	176.6 (2)	C31—C32—C33—C34	−67.0 (3)
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Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C2—H2···O2 ⁱ	0.95	2.21	3.067 (3)	149
C4—H4···O3 ⁱⁱ	0.95	2.51	3.278 (3)	138
C5—H5···O1 ⁱⁱⁱ	0.95	2.31	3.236 (3)	165
C11—H11A···O3 ⁱⁱⁱ	0.99	2.48	3.456 (3)	168
C11—H11B···O1 ⁱ	0.99	2.64	3.515 (3)	147
C14—H14C···O1 ^{iv}	0.98	2.60	3.545 (4)	161
C31—H31A···O3 ⁱⁱ	0.99	2.53	3.259 (3)	130

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *XSeed* (Barbour, 1999) and *POV-Ray*.

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