Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-Dodecyl-3-methylimidazolium bromide monohydrate

Anna Getsis and Anja-Verena Mudring*

Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

Correspondence e-mail:
a.mudring@uni-koeln.de

Key indicators

Single-crystal X-ray study
T = 263 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.026
wR factor = 0.069
Data-to-parameter ratio = 21.9

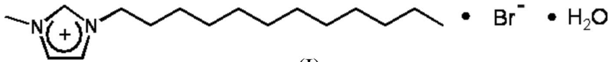
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 8 August 2005
Accepted 11 August 2005
Online 17 August 2005

The asymmetric unit of the title compound, $C_{16}H_{31}N_2^+\cdot Br^-\cdot H_2O$, contains one crystallographically independent 1-dodecyl-3-methylimidazolium cation, one bromide anion, to counterbalance the charge, and one solvent water molecule. The halide anion forms hydrogen bonds with the H atoms of the imidazole ring and with the water H atoms.

Comment

Many 1-alkyl-3-methylimidazolium salts show thermotropic liquid crystalline behaviour (Seddon *et al.*, 1996; Gordon *et al.*, 1998; Hardacre *et al.*, 2001; Bradley *et al.*, 2002). Aside from a large mesophasic range, many of these salts also have a melting point below 373 K and thus belong not only to the class of liquid crystals but also to the class of ionic liquids (Wasserscheid, 2002).



(I)

The liquid crystalline behaviour of 1-dodecyl-3-methylimidazolium bromide, $[C_{12}mim]Br$, and its monohydrate, $[C_{12}mim]Br\cdot H_2O$, (I), has recently been a topic of investigation although the crystal structures had not been established. We were now able to obtain crystals of the monohydrate which were of sufficient quality for structure analysis by recrystallizing the compound from ethyl acetate.

$[C_{12}mim]Br\cdot H_2O$ crystallizes isotypic with $[C_{12}mim]Cl\cdot H_2O$ (Guillet *et al.*, 2004). The bond lengths and angles are well within the expected ranges; the imidazolium head group is planar and the alkyl chain adopts an all-*trans* conformation. The 1-dodecyl-3-methylimidazolium cations form lamellar bilayers parallel to the (022) plane. The orientation of the cations (due to their amphiphilic character) alternates from layer to layer so that separate hydrophobic (alkyl tail groups) and hydrophilic (the imidazolium head group, bromide and water) regions are formed. The alkyl tails of cations with different orientation are interdigitated. The $[C_{12}mim]$ cations

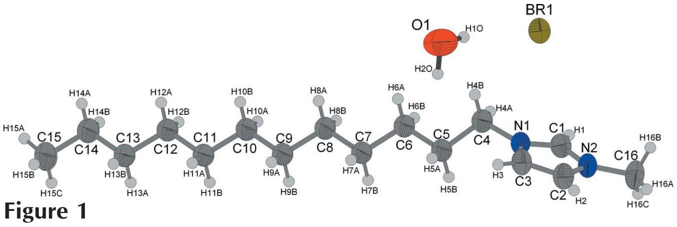


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. Only 1 disorder component is shown.

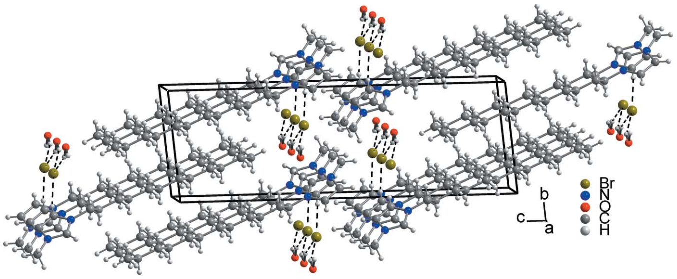


Figure 2
The crystal structure of (I), viewed on to the *bc* plane.

themselves are held together by electrostatic interactions with bromide anions and water molecules. Within each layer a water molecule and a bromide anion are located between two 1-dodecyl-3-methylimidazolium cations. The water–imidazolium O···H1 distance of 2.34 Å is clearly shorter than the mean value for a hydrogen bond between an (*N*,*N*)Csp^2—H group and a water O atom (Steiner, 2002), whereas the interaction of the imidazolium C3—H3 with Br^i of 2.75 Å is about 0.1 Å above the commonly observed mean values. The water hydrogen–bromide distances of 2.61 (2) Å for H1*O*···Br and 2.57 (2) Å for H2*O*···Br are also in the typical range for water hydrogen–bromide hydrogen bonds, whereas unlike in the chloride the ring methyl (C16)–hydrogen halide distances are too long for a significant hydrogen bond (Steiner, 2002); the shortest contact is 2.98 (2) Å. Furthermore, each water molecule is located above or below an imidazolium ring with an oxygen···ring centre distance of 3.699 (8) Å.

Experimental

1-Methylimidazole (16.7 ml, 0.21 mol) was added to 1-bromododecane (72.0 ml, 0.30 mol) (both were freshly distilled before use). After heating the reaction mixture at 373 K for 2 h, a yellow liquid was obtained which was degassed under vacuum at 393 K. After cooling to room temperature, the reaction product solidified. The crude product was washed with ethyl acetate until the ester phase became colourless. After recrystallization from ethyl acetate, white transparent needle-shaped crystals of 1-dodecyl-3-methylimidazolium bromide monohydrate were obtained. Crystals suitable for structure analysis were sealed in glass capillaries (0.3 mm diameter) and their quality checked by Laue photographs. A complete data set was taken of the best specimen. ^{1}H NMR: (300 MHz, DMSO-d_6): δ 0.85 (*t*, 3H, H-15), 1.24 (*br. s*, 20H, H-5–14), 3.85 (*s*, 3H, H-16), 4.15 (*t*, 2H, H-4), 7.71 (*s*, 1H, H-2), 7.78 (*s*, 1H, H-3), 9.15 (*br. s*, 1H, H-1). ^{13}C{^{1}H} NMR: (75.5 MHz, DMSO-d$_6$): δ 13.85 (*s*, C-15), 21.97, 25.38, 28.26, 28.60, 28.71, 28.83, 28.90, 29.27, 31.18, 35.65 (*s*, C-5–14), 38.60 (*s*, C-16), 48.65 (*s*, C-4), 122.15 (*s*, C-3), 123.48 (*s*, C-2).

Crystal data

$C_{16}H_{31}N_2^+\cdot Br^-\cdot H_2O$
M_r = 349.34
Triclinic, $P\bar{1}$
a = 5.500 (5) Å
b = 7.794 (5) Å
c = 22.961 (5) Å
α = 81.893 (5)°
β = 83.761 (5)°
γ = 78.102 (5)°
V = 950.3 (11) Å^3
Z = 2
D_x = 1.221 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 4273 reflections
θ = 2.8–28.3°
μ = 2.16 mm^{-1}
T = 263 (2) K
Needle, white
0.3 × 0.2 × 0.1 mm

Data collection

Stoe IPDS-I diffractometer
φ scans
Absorption correction: numerical [*X-RED32* (Stoe & Cie, 2002) and *X-SHAPE* (Stoe & Cie, 2001)]
T_{min} = 0.585, T_{max} = 0.794
14912 measured reflections
4167 independent reflections
3523 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 27.3°
$h = -6 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.069$
S = 1.04
4167 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.1463P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O—H2*O*···Br^i	0.86 (2)	2.57 (2)	3.386 (3)	159 (3)
O—H1*O*···Br	0.84 (2)	2.61 (2)	3.435 (3)	166 (3)
C3—H3···Br^i	0.93	2.75	3.661 (3)	167
C1—H1···O^{ii}	0.93	2.34	3.193 (4)	152

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

C-bound H atoms were positioned geometrically (C—H = 0.93 (methine), 0.99 (methylene) and 0.98 Å (methyl) and refined with fixed isotropic displacement parameters using a riding model [U_{iso}(H) = 1.5 (methyl C) or 1.2 (methylene, methine C) U_{eq}]. Water H atoms were located in a difference map and refined isotropically with their O—H bond lengths restrained to 0.84 (1) Å. The H atoms of the methyl group bonded to the imidazole ring are equally disordered over two positions. This group was allowed to rotate but not to tip.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXL97*.

References

Bradley, A. E., Hardacre, C., Hobrey, J. D., Johnston, S., McMath, S. E. J. & Nieuwenhuyzen (2002). *Chem. Mater.* **14**, 629–635.
Brandenburg, K. (1996). *DIAMOND*. Release 2.1. Crystal Impact GbR, Bonn, Germany.
Gordon, C. M., Holbrey, J. D., Kennedy, A. R. & Seddon, K. R. (1998). *J. Mater. Chem.* **8**, 2627–2636.
Guillet, E., Imbert, D. Scopelliti, R. & Bünzli, J.-C. G. (2004). *Chem. Mater.* **16**, 4063–4070.
Hardacre, C., Hobrey, J. D., McCormac, P. B., McMath, S. E., Nieuwenhuyzen & Seddon, K . R. (2001). *J. Mater. Chem.* **11**, 346–350.
Seddon, K. R., Bowlas, C. J. & Bruce, D. W. (1996). *Chem. Commun.* pp. 1625–1626.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Steiner, T. (2002). *Angew. Chem.* **114**, 50–80.
Stoe & Cie (2001). *X-SHAPE*. Version 2.01. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (2002). *X-AREA* and *X-RED32*. Version 1.03. Stoe & Cie, Darmstadt, Germany.
Wasserscheid, P. (2002). *Ionic Liquids in Synthesis*. Weinheim: VCH–Wiley.