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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$

R factor = 0.044

wR factor = 0.123

Data-to-parameter ratio = 28.7

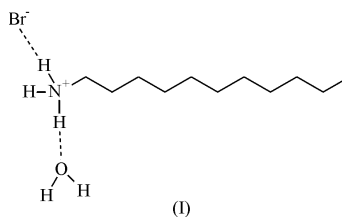
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.*n*-Undecylammonium bromide monohydrate*n*-Undecylammonium bromide crystallizes from solution as the monohydrate, $\text{C}_{11}\text{H}_{23}\text{NH}_3^+\cdot\text{Br}^-\cdot\text{H}_2\text{O}$, the structure containing alternating ionic and hydrocarbon layers. The water molecules are incorporated into the ionic layer and they interact, *via* hydrogen bonds, with the bromide anions and the terminal ammonium groups. The non-polar methylene chains are fully extended with all-*trans* conformations. The molecules pack as parallel and interdigitated cylinders, roughly perpendicular to the layers.

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Comment

Long-chain *n*-alkylammonium halides are widely used as surfactants (Aratono *et al.*, 1998; Törnblom *et al.*, 2000) and as models for biological membranes (Ringsdorf *et al.*, 1988). They exhibit polymorphism at room temperature (Gilson *et al.*, 1976; Schenk *et al.*, 1989; Terreros *et al.*, 2000) and a complex sequence of solid–solid phase transitions at higher temperatures (Tsau & Gilson, 1968; Kind *et al.*, 1982; Reynhardt *et al.*, 1998). Only four crystal structures of *n*-alkylammonium halides have been reported previously. They are the three anhydrous compounds *n*-decylammonium chloride ($\text{C}_{10}\text{H}_{21}\text{NH}_3^+\cdot\text{Cl}^-$; Schenk & Chapuis, 1986; Pinto *et al.*, 1987), *n*-dodecylammonium chloride ($\text{C}_{12}\text{H}_{25}\text{NH}_3^+\cdot\text{Cl}^-$; Pinto *et al.*, 1987; Silver *et al.*, 1995) and *n*-dodecylammonium bromide ($\text{C}_{12}\text{H}_{25}\text{NH}_3^+\cdot\text{Br}^-$; Lundén, 1974), and the solvate (sometimes also called a pseudo-polymorph) *n*-undecylammonium chloride monohydrate ($\text{C}_{11}\text{H}_{23}\text{NH}_3^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$; Silver *et al.*, 1996). They all exhibit alternating hydrocarbon and ionic layers, with hydrogen bonding in the ionic layer.In this study, we have established that *n*-undecylammonium bromide monohydrate, $\text{C}_{11}\text{H}_{23}\text{NH}_3^+\cdot\text{Br}^-\cdot\text{H}_2\text{O}$, (I), is isostructural with *n*-undecylammonium chloride monohydrate, $\text{C}_{11}\text{H}_{23}\text{NH}_3^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$, (Silver *et al.*, 1996). The crystal structure of the chloride has to be transformed, however, to be consistent with $P2_1/c$ symmetry, as it was reported in space group $P2_1/a$, with $a = 7.701(2) \text{ \AA}$, $b = 40.020(5) \text{ \AA}$, $c = 4.6437(6) \text{ \AA}$ and $\beta = 107.34(1)^\circ$. The two monohydrate structures exhibit similar molecular conformations and crystal packing. The only obvious effect of the change in anion is to expand the bromide cell, by an increase in all three unit-cell

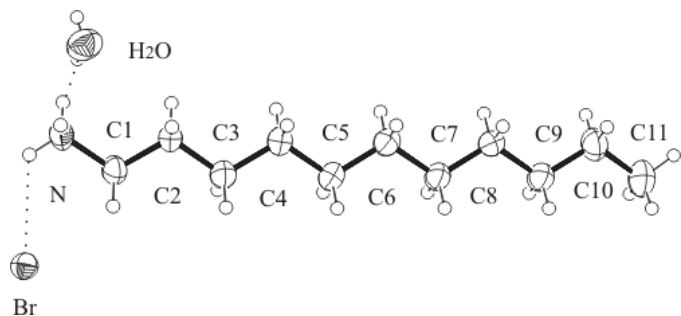


Figure 1
The molecular structure of (I), illustrating the hydrogen bonds (dotted lines) between the N atom, the anion, and the water of crystallization. Displacement ellipsoids are drawn at the 50% probability level (ORTEP-3; Farrugia, 1997).

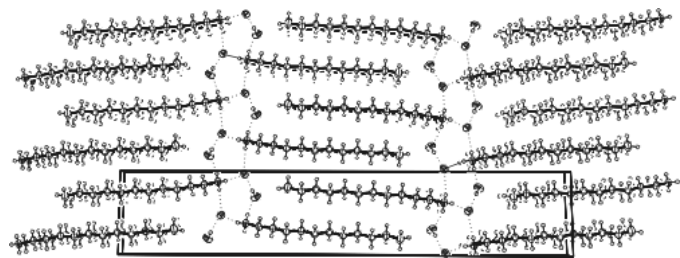


Figure 2
A packing diagram of (I), viewed down the a axis, showing the interdigitated packing of the molecules and the alternating ionic and hydrocarbon layers.

lengths. The cell volumes of the chloride and bromide are 1366.1 (4) and 1473 (3) Å³, respectively, indicating that a volume increase of approximately 27 Å³ is required to accommodate the larger bromide anion.

The molecular structure of (I) is illustrated in Fig. 1. The methylene chain has the extended all-*trans* conformation, but it is slightly curved in the vicinity of the ammonium group, probably to accommodate the hydrogen-bonding interactions. The extent of the curvature is illustrated by the deviation from planarity of the carbon backbone of the molecule, which is found to be dependent on the size of the anion. In both monohydrate structures, atoms C2–C11 are coplanar, while N and C1 are displaced significantly from these ideal carbon zigzag planes; the r.m.s. deviations of the fitted atoms from the least-squares planes are 0.029 and 0.026 Å for the chloride and the bromide, respectively. Atoms N and C1 are out of plane by 0.392 and 0.341 Å for the chloride, and 0.314 (5) and 0.317 (5) Å for the bromide, respectively. An alternative measure of the curvature is the deviation of torsion angles from their ideal values. Only torsion angle C1–C2–C3–C4 deviates significantly from 180°, with a value of 170.0 (1)° for the chloride and 170.8 (3)° for the bromide.

The interdigitated packing displayed by (I) is illustrated in Fig. 2. In the hydrocarbon layer, the chains are parallel to one another and interact *via* van der Waals forces. The molecular plane (calculated through atoms C2–C11) is at an angle of 87.07 (8)° to the ionic plane, indicating that the molecules are almost perpendicular to the layers. The type of packing exhibited by the methylene chains (C2–C11) can be classified

as the polymethylene subcell ' M_2 perpendicular' (Segerman, 1965), with subcell parameters $a_s = 4.809$ Å, $b_s = 8.050$ Å, $c_s \sim 2.54$ Å, $\gamma_s = 109.47^\circ$ and space group $A2/m$, with c_s chosen to be in the direction of the long axis. The calculated cross-sectional area per chain, 18.3 Å², indicates dense chain packing.

The ionic layer of (I) consists of ammonium groups, bromide anions and water molecules, all interacting *via* hydrogen bonds (Table 1 and Fig. 2). Each ammonium group is hydrogen bonded to two bromide anions and one O atom of a water molecule. Each water molecule is, in turn, hydrogen bonded to two bromide anions. The hydrogen-bonding N···halide and O···halide distances are shorter for the chloride than for the bromide [3.209 (1) and 3.235 (2) Å compared to 3.366 (4) and 3.392 (5) Å], but the distances of the N···O interaction, where the anion does not play a role, are similar, 2.845 (2) and 2.828 (5) Å. Likewise, the water-to-halide-anion interactions are shorter for the chloride than for the bromide [3.180 (1) and 3.226 (1) Å compared to 3.535 (4) and 3.384 (4) Å].

A property that *n*-undecylammonium bromide shares with other *n*-alkylammonium halides is that of polymorphism. A different crystal form of the bromide, as characterized by differential scanning calorimetry (DSC), crystallizes from the melt, as opposed to the crystallization from solvent of the monohydrate reported here. The hydrate exhibits three solid–solid phase transitions on heating before melting, as determined by DSC measurements. The transitions were named according to the established phase sequence nomenclature reported for *n*-alkylammonium chlorides (Schenk & Chapuis, 1986), except that we have called the initial monohydrate phase the *m* phase. The following transition temperatures were observed: *m* phase to β phase, 319.86 K; β phase to α phase, 341.52 K; α phase to liquid crystal phase, 467.60 K and liquid crystal phase to the melt, 536.96 K.

Experimental

n-Undecylammonium bromide was prepared by the addition of HBr to an ethanol solution of *n*-undecylamine. The resulting precipitate was filtered off and recrystallized several times from chloroform. Single crystals were obtained by slow evaporation of a chloroform solution at room temperature. DSC curves were measured on a Mettler–Toledo 822 instrument. The temperature scale and heat-flow values were calibrated to the known values of indium and zinc. The DSC samples, weighing between 1 and 2 mg, were sealed in 40 μ l aluminium pans with holes punched into the lids to prevent pressure build-up due to desolvation. The samples were heated from room temperature at a constant rate of 5 K min⁻¹.

Crystal data

$C_{11}H_{26}N^+Br^- \cdot H_2O$
 $M_r = 270.25$
 Monoclinic, $P2_1/c$
 $a = 4.809$ (6) Å
 $b = 40.353$ (5) Å
 $c = 7.882$ (9) Å
 $\beta = 105.65$ (2)°
 $V = 1473$ (3) Å³
 $Z = 4$

$D_x = 1.219$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1024 reflections
 $\theta = 3.0$ – 22.4°
 $\mu = 2.77$ mm⁻¹
 $T = 293$ (2) K
 Thin plate, colourless
 0.11 \times 0.09 \times 0.03 mm

Data collection

Bruker SMART CCD area-detector diffractometer 3647 independent reflections
 1923 reflections with $I > 2\sigma(I)$
 ω scans $R_{\text{int}} = 0.060$
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $\theta_{\text{max}} = 28.3^\circ$
 $T_{\text{min}} = 0.751$, $T_{\text{max}} = 0.922$ $h = -6 \rightarrow 6$
 10404 measured reflections $k = -53 \rightarrow 33$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2 H-atom parameters constrained
 $R[F^2 > 2\sigma(F^2)] = 0.044$ $w = 1/[\sigma^2(F_o^2) + (0.0571P)^2]$
 $wR(F^2) = 0.123$ where $P = (F_o^2 + 2F_c^2)/3$
 $S = 0.94$ $(\Delta/\sigma)_{\text{max}} = 0.003$
 3647 reflections $\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{\AA}^{-3}$
 127 parameters $\Delta\rho_{\text{min}} = -0.54 \text{ e } \text{\AA}^{-3}$

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N-H12A \cdots Br^i$	0.89	2.50	3.366 (4)	165
$N-H12B \cdots O^{ii}$	0.89	1.96	2.828 (5)	164
$N-H12C \cdots Br$	0.89	2.55	3.392 (5)	159
$O-H13A \cdots Br^{iii}$	0.84	2.517	3.353 (4)	180
$O-H13B \cdots Br$	0.82	2.567	3.384 (4)	179

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

The H atoms of the water molecule were fixed in position at a distance of 0.82 \AA from the O atom on the $O \cdots Br$ vectors. All other H atoms were positioned geometrically and refined using a riding model, with rotation in the case of the terminal ammonium and methyl groups.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); program(s) used to solve structure:

SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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