organic papers

Benzylammonium nitrate

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The crystal structure of benzylammonium nitrate, $C_7H_{10}N^+ \cdot NO_3^-$, exhibits ionic layers separated by hydrocarbon layers. The hydrocarbon layer contains the interdigitated benzyl groups, but no π–π interactions are observed. In the inorganic layer, the ammonium groups and nitrate ions interact *via* hydrogen-bonding.

Comment

As part of a study on the effect of anions on the crystal structures in organic–inorganic layered compounds, the crystal structure of benzylammonium nitrate, (I), has been determined. Only one other structure containing a benzylammonium cation and a polyatomic anion could be located in the literature, namely that of benzylammonium dihydrogen phosphate (Aakeroy *et al.*, 1989). Even though a layered structure is formed for both compounds, the packing of the benzylammonium cations in the two structures differs.

(I)
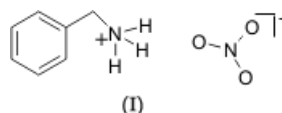
The molecular structure of (I), and the atomic numbering used, is illustrated in Fig. 1. All bond distances and angles are within the ranges of accepted values.

A layered structure composed of alternating ionic and hydrocarbon layers is formed. The layers extend parallel to the *ab* plane. Fig. 2 illustrates the layered packing viewed down the *a* axis. The organic layer is formed by interdigitated benzyl moieties. For this part of the cation, the atoms constituting the aromatic ring and C7 are coplanar, with a standard uncertainty of 0.002 Å. The maximum absolute deviation from this plane is 0.015 (2) Å for atom C1. No intermolecular π–π interactions are observed in the organic layer, and the shortest centroid-to-centroid distance between aromatic rings is 4.978 (5) Å.
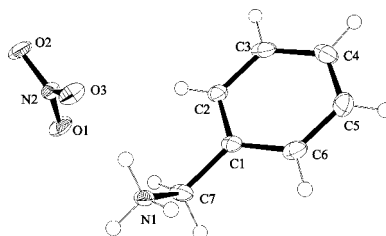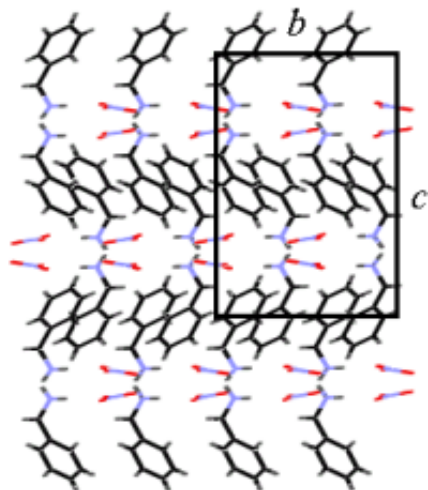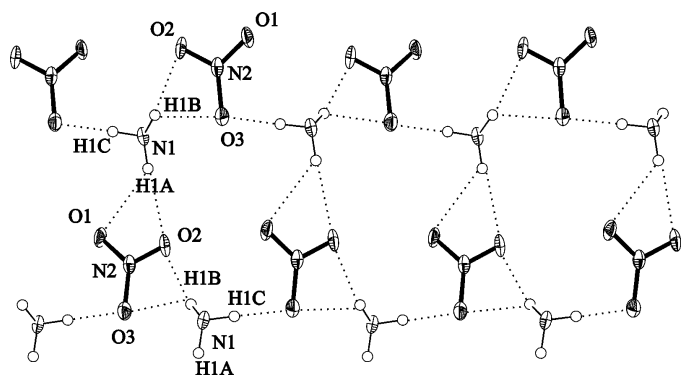
Figure 1
The molecular structure of (I), showing the atomic numbering scheme and ellipsoids at the 50% probability level (*ORTEP*-3; Farrugia, 1997).

Figure 2
Packing diagram for (I), viewed down the *a* axis, showing the layered packing and interdigitation (*MERCURY*; Bruno *et al.*, 2002).

Figure 3
Hydrogen-bonding network in the ionic layer (*ORTEP*-3; Farrugia, 1997).

The ionic layer contains the ammonium groups and planar nitrate ions. In this layer, a complex hydrogen-bonding network is formed, where each ammonium N atom is hydrogen bonded to five O atoms through one normal and four bifurcated hydrogen bonds. N···O donor–acceptor distances range from 2.609 (2) to 3.286 (3) Å, and H···O interactions range from 1.72 (3) to 2.46 (3) Å. Hydrogen-bonding parameters are listed in Table 1 and Fig. 3 shows these interactions in the inorganic layer.

In the nitrate ion, the N—O bond distances differ significantly, with values of 1.181 (2) (N2—O2), 1.216 (2) (N2—O1) and 1.402 (3) Å (N2—O3). It is clear that the the N—O bond for the O atom engaged in strong hydrogen bonding, O3 [H1C···O3 hydrogen-bonding interaction of 1.72 (3) Å], is elongated.

Experimental

Benzylammonium nitrate was prepared by the dropwise addition of concentrated nitric acid (70%, Aldrich) to a solution of benzylamine (99%, Saarchem) in chloroform. The resulting precipitate was filtered off and recrystallized from ethanol. Single crystals were obtained by slow evaporation of a solution of (I) in ethanol at room temperature.

Crystal data

$C_7H_{10}N^+ \cdot NO_3^-$	Mo $K\alpha$ radiation
$M_r = 170.17$	Cell parameters from 944
Orthorhombic, $Pbca$	reflections
$a = 9.817$ (2) Å	$\theta = 2$–$32°$
$b = 11.043$ (3) Å	$\mu = 0.10$ mm^{-1}
$c = 15.819$ (4) Å	$T = 120$ (2) K
$V = 1714.9$ (7) Å^3	Block, colourless
$Z = 8$	$0.20 \times 0.20 \times 0.15$ mm
$D_x = 1.318$ Mg m^{-3}	

Data collection

Oxford Excalibur2 diffractometer	$R_{int} = 0.037$
ω–2θ scans	$\theta_{max} = 28.0°$
Absorption correction: none	$h = -12 \rightarrow 11$
13 426 measured reflections	$k = -14 \rightarrow 14$
2060 independent reflections	$l = -20 \rightarrow 18$
1792 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.069$	independent and constrained
$wR(F^2) = 0.172$	refinement
$S = 1.29$	$w = 1/[\sigma^2(F_o^2) + (0.085P)^2]$
2060 reflections	where $P = (F_o^2 + 2F_c^2)/3$
121 parameters	$(\Delta/\sigma)_{max} = 0.026$
	$\Delta\rho_{max} = 0.29$ e Å^{-3}
	$\Delta\rho_{min} = -0.31$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O2^i	0.99 (4)	2.15 (3)	3.071 (3)	154 (3)
N1—H1C···O3	0.89 (3)	1.72 (3)	2.609 (2)	178 (3)
N1—H1A···O2^{ii}	0.96 (3)	2.33 (3)	3.286 (3)	175 (2)
N1—H1A···O1^{ii}	0.96 (3)	2.46 (3)	3.221 (3)	136 (2)
N1—H1B···O3^i	0.99 (4)	2.08 (3)	2.772 (2)	126 (3)

Symmetry codes: (i) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, z$.

H atoms bonded to C atoms were placed in calculated positions and refined using a riding model. For the ammonium group, H atoms were placed as observed in a Fourier map and refined. C—C bond lengths in the phenyl ring were restrained to similar values.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

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