

Hydrogen bonding in isomorphous 2-methyl-4-nitroanilinium bromide and iodide

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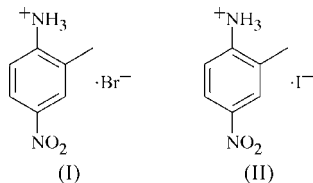
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The isomorphous structures of 2-methyl-4-nitroanilinium bromide, $C_7H_9N_2O_2^+ \cdot Br^-$, and 2-methyl-4-nitroanilinium iodide, $C_7H_9N_2O_2^+ \cdot I^-$, exhibit ionic layers separated by hydrocarbon layers. The hydrocarbon layer stacks head-to-head, while in the ionic layer, the ammonium groups and halide anions interact *via* hydrogen bonds to form infinite chains.

Comment

As part of a study of the effect of anions on the crystal structures of anilinium halide salts, the crystal structures of two protonated 2-methyl-4-nitroaniline molecules are reported. The unprotonated case, $O_2NC_7H_6NH_2$, has been studied previously (Ferguson *et al.*, 2001). The authors were investigating the effect that the substituents on the ring had on the packing arrangement and the hydrogen bonding, and they found that the molecules act as double donors and double acceptors of $N-H \cdots O$ hydrogen bonds. The introduction of a halide anion has a significant effect on the packing, as the ammonium groups form $N-H \cdots X$ hydrogen bonds only in the title compounds. We report here the isostructural salts 2-methyl-4-nitroanilinium bromide, (I), and 2-methyl-4-nitroanilinium iodide, (II). The detailed packing of (I) will be discussed, as well as the hydrogen bonding of (II).



The atomic numbering schemes of both compounds are shown in Fig. 1. Fig. 2 shows the one-dimensional arrangement of (I), in which a single layer of cations is embedded between two ionic layers, forming an alternating hydrocarbon–ionic structure. Within the ionic layer, the Br^- atoms and ammonium groups interact *via* hydrogen bonds. The cations pack

head-to-head in layers parallel to the *ab* plane. In contrast, the unsubstituted 4-nitroanilinium bromide has a head-to-tail packing arrangement (Lemmerer & Billing, 2006).

Compound (II) has the same packing arrangement as (I) but differs only in the identity of the counter-ion, I1. The volume of the unit cell is unexpectedly less by 2.2 \AA^3 for the iodide case, even though the I^- ion has a larger ionic radius (2.20 \AA) than bromide (1.96 \AA) (Shannon, 1976). To compensate, the cations pack closer together.

Compound (II) has an extensive network of hydrogen bonding. In the crystal structure, the ions are linked together by $N2-H2C \cdots I1 \cdots H2B-N2-H2C \cdots I1$ hydrogen bonds,

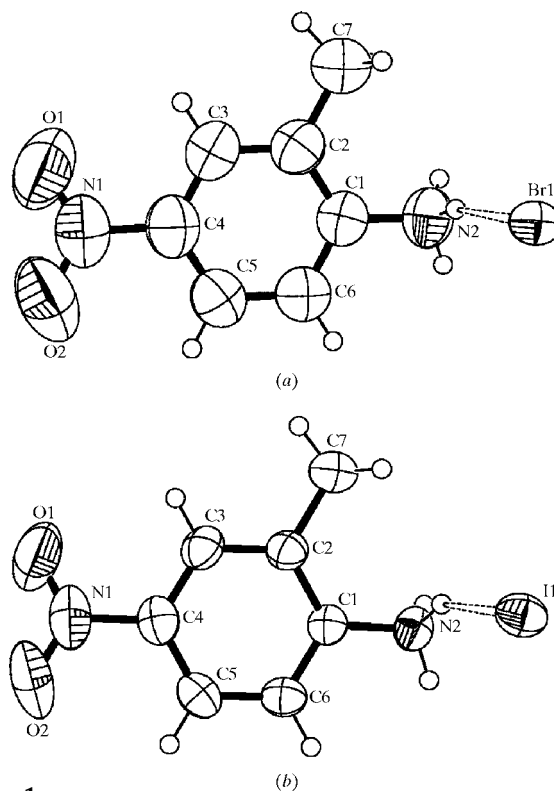


Figure 1
The asymmetric units of (a) (I) and (b) (II), showing the atomic numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

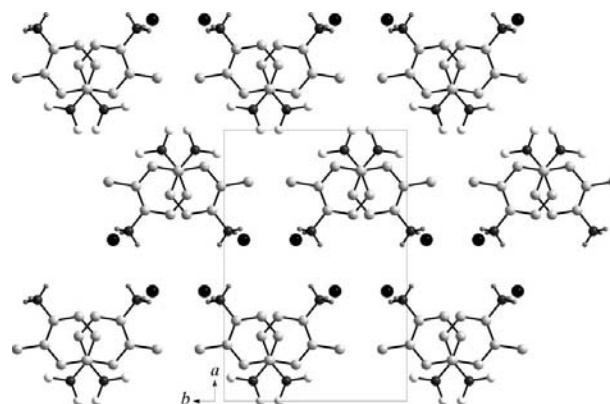


Figure 2
A packing diagram for (I), viewed along the *c* axis.

forming infinite chains parallel to [001]. At the same time, two adjacent chains are linked in the [100] direction by N2—H2A···I1 hydrogen bonds to form a connected set of infinite chains (Fig. 3). Overall, the hydrogen-bonding scheme is $R_2^2(8)$ (Bernstein *et al.*, 1995). The hydrogen-bonded rings connect I[−] ions and 2-methyl-4-nitroanilinium cations, which are related by a twofold screw axis. The chains form ladders, which are parallel to the *ac* plane. These ladders are then stacked perpendicular to this plane and are connected to the I[−] ions of adjacent ladders by I1···H2C—N2—H2B···I1 hydrogen bonds, *i.e.* atoms H2C and H2B have bifurcated hydrogen bonds. These interactions are weaker, as the hydrogen-acceptor (H···A) distances are 3.245 (1) and 3.238 (1) Å.

Compound (I) has the same hydrogen-bonding sequence in the *c* direction. However, due to the smaller van der Waals radius of Br, the ladders are connected by a single Br1···H2C—N2 hydrogen bond. The H···A distance is

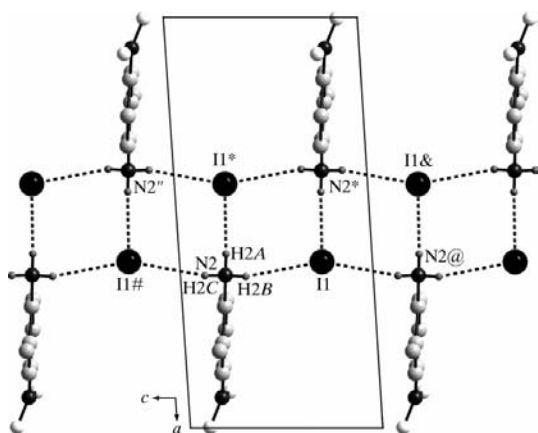


Figure 3
The one-dimensional chains of hydrogen bonds (dashed lines) between the ammonium heads and the I[−] anions in (II). Atoms marked with an asterisk (*), hash (#), ampersand (&), 'at' sign (@) or double prime (") are at the symmetry positions $(1-x, 1-y, 1-z)$, $(x, y, 1+z)$, $(1-x, 1-y, -z)$, $(x, y, -1+z)$ and $(1-x, 1-y, 2-z)$, respectively.

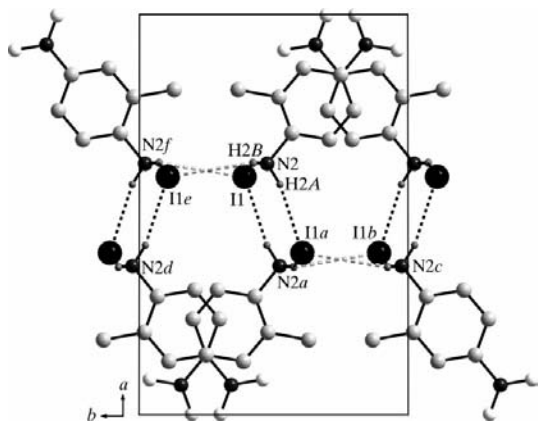


Figure 4
The weak hydrogen-bonding interactions (light-grey dashed lines) and strong interactions (black dashed lines) which stabilize the overall structure in (II). Atoms marked with the suffixes *a, b, c, d, e* and *f* are at the symmetry positions $(1-x, 1-y, 1-z)$, $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, $(1-x, -\frac{1}{2}+y, \frac{3}{2}-z)$, $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$, $(x, \frac{3}{2}-y, \frac{1}{2}+z)$ and $(x, \frac{3}{2}-y, -\frac{1}{2}+z)$, respectively.

3.12 Å. Subsequently, there is only one bifurcated and three simple hydrogen bonds in (I), compared with three simple and two bifurcated hydrogen bonds in (II).

Experimental

For the preparation of (I), 2-methyl-4-nitroaniline (0.196 g, 1.29 mmol) was added to 48% HBr (18 ml) and the precipitate dissolved by heating the solution. The solution was then cooled to room temperature and yellow crystals of (I) were grown by slow evaporation. Analysis calculated for C₇H₉BrN₂O₂: C 36.1, H 3.9, N 12.0%; found: C 36.8, H 3.9, N 12.7%. For the preparation of (II), 2-methyl-4-nitroaniline (0.204 g, 1.34 mmol) was added to 47% HI (1 ml) and the precipitate dissolved with ethanol (10 ml). Yellow crystals of (II) were grown by slow evaporation of the solution. Elemental analysis was not deemed necessary.

Compound (I)

Crystal data

C ₇ H ₉ N ₂ O ₂ ⁺ ·Br [−]	<i>Z</i> = 4
<i>M_r</i> = 233.07	<i>D_x</i> = 1.561 Mg m ^{−3}
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 14.687 (5) Å	<i>μ</i> = 4.11 mm ^{−1}
<i>b</i> = 9.840 (5) Å	<i>T</i> = 293 (2) K
<i>c</i> = 6.877 (5) Å	Needle, light yellow
<i>β</i> = 93.836 (5)°	0.24 × 0.08 × 0.04 mm
<i>V</i> = 991.6 (9) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	5290 measured reflections
<i>φ</i> and <i>ω</i> scans	1798 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1435 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.565, <i>T_{max}</i> = 0.850	<i>R_{int}</i> = 0.027
	<i>θ_{max}</i> = 25.3°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.1324P)^2 + 1.4593P]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.220$	(Δ/σ) _{max} = 0.006
<i>S</i> = 1.21	$\Delta\rho_{max} = 0.77 \text{ e } \text{Å}^{-3}$
1798 reflections	$\Delta\rho_{min} = -0.96 \text{ e } \text{Å}^{-3}$
99 parameters	
H-atom parameters constrained	

Table 1

Hydrogen-bond geometry (Å, °) for (I).

<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>
N2—H2A···Br1 ⁱ	0.89	2.64	3.490 (10)	159
N2—H2B···Br1	0.89	2.71	3.579 (8)	165
N2—H2C···Br1 ⁱⁱ	0.89	2.89	3.563 (9)	134
N2—H2C···Br1 ⁱⁱⁱ	0.89	3.12	3.677 (10)	122

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

Compound (II)

Crystal data

C ₇ H ₉ N ₂ O ₂ ⁺ ·I [−]	<i>Z</i> = 4
<i>M_r</i> = 280.06	<i>D_x</i> = 1.88 Mg m ^{−3}
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 14.671 (4) Å	<i>μ</i> = 3.20 mm ^{−1}
<i>b</i> = 9.830 (3) Å	<i>T</i> = 293 (2) K
<i>c</i> = 6.875 (2) Å	Needle, yellow
<i>β</i> = 93.782 (7)°	0.14 × 0.06 × 0.03 mm
<i>V</i> = 989.4 (5) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	5499 measured reflections
φ and ω scans	1846 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1047 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.664$, $T_{\max} = 0.911$	$R_{\text{int}} = 0.073$
	$\theta_{\text{max}} = 25.5^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.070$	$w = 1/[\sigma^2(F_o^2) + (0.1138P)^2]$
$wR(F^2) = 0.187$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.94$	$(\Delta/\sigma)_{\text{max}} = 0.004$
1846 reflections	$\Delta\rho_{\text{max}} = 4.27 \text{ e } \text{\AA}^{-3}$
99 parameters	$\Delta\rho_{\text{min}} = -0.85 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2A\cdots I1^i$	0.89	2.62	3.495 (10)	166
$N2-H2C\cdots I1^{ii}$	0.89	2.77	3.568 (9)	150
$N2-H2B\cdots I1$	0.89	2.78	3.568 (8)	148
$N2-H2B\cdots I1^{iii}$	0.89	3.24	3.662 (10)	112
$N2-H2C\cdots I1^{iii}$	0.89	3.24	3.662 (10)	112

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

H atoms bonded to C and N atoms were refined in idealized positions in the riding-model approximation, with $C-H = 0.93 \text{ \AA}$ and $N-H = 0.89 \text{ \AA}$, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{N})$. The NH_3 group was allowed to rotate but not to tip. The highest residual peak was 1.92 \AA from atom Br1 in (I) and 1.90 \AA from I1 in (II).

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-*

Plus; 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) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3015). Services for accessing these data are described at the back of the journal.

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