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The crystal structure of *p*-nitroaniline hydrobromide, $C_6H_7N_2O_2^+ \cdot Br^-$ or $O_2NC_6H_4NH_3^+ \cdot Br^-$, exhibits ionic layers separated by hydrocarbon layers. The hydrocarbon layers stack head-to-tail but no π - π interactions are observed. In the inorganic layer, the ammonium group, Br^- anion and nitro group interact to form a three-dimensional hydrogen-bonded network. The structure is compared with that of the related compound $O_2NC_6H_4NH_3^+ \cdot Cl^-$.

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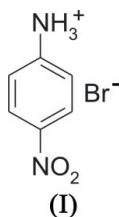
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(C-C) = 0.006$ Å
 R factor = 0.024
 wR factor = 0.056
Data-to-parameter ratio = 12.4

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

Comment

Organic-inorganic hybrid perovskites have been studied extensively. We are interested in determining the crystal structures of simple monoammonium or diammonium hydrocarbons that are aromatic. The protonated amine *para*-nitroanilinium has been incorporated into the hybrid perovskites $(O_2NC_6H_4NH_3)_2CuCl_4$ (Sekine *et al.*, 1996) and $(O_2NC_6H_4NH_3)_2CdCl_4$ (Azumi *et al.*, 1995).



While attempting to synthesize a hybrid perovskite with $PbBr_2$ and *para*-nitroaniline, green crystals of the title compound, (I), crystallized out with no evidence of the desired organic-inorganic hybrid. The crystal structure of the related material *p*-nitroaniline hydrochloride was studied 24 years ago (Ploug-Sørensen & Andersen, 1982). That compound crystallizes in the monoclinic space group $P2_1/c$. The *p*-nitroanilinium ions pack parallel to the *bc* plane and are separated

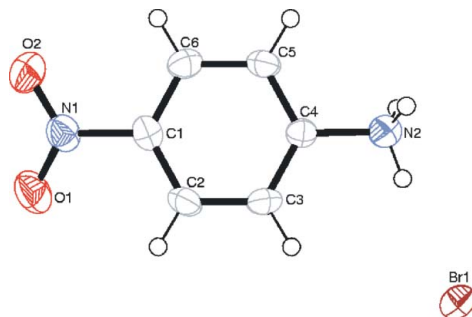


Figure 1
The asymmetric unit of (I) showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

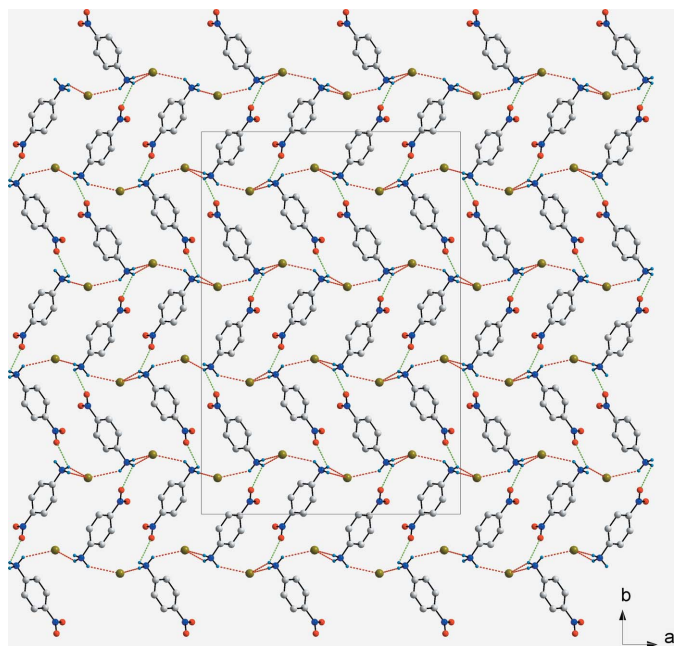


Figure 2

Packing diagram of (I) viewed along the c axis. N—H \cdots O hydrogen bonds are shown as dashed green lines and N—H \cdots Br hydrogen bonds as dashed red lines.

by a layer of Cl^- ions. The two layers interact *via* coulombic forces and hydrogen bonds between the ammonium group and the Cl^- ions.

In contrast, the title compound crystallizes in the orthorhombic space group $Fdd2$. Fig. 2 clearly shows an arrangement in which layers of *p*-nitroanilinium cations are embedded between ionic layers of Br^- ions, forming an alternating hydrocarbon–ionic structure. Adjacent molecules pack head-to-tail. The ammonium groups all point along the positive c axis, with an angle of $75.52(8)^\circ$ between the C–N vector and the c axis, and hence the crystal packing is polar.

No intermolecular π – π interactions are evident in the hydrocarbon layer in either crystal structure, the shortest centroid-to-centroid distance being $5.080(5) \text{ \AA}$ in (I).

Compound (I) has an extensive network of hydrogen bonding involving the two acceptor atoms, Br and O. In the ac plane, the ions are linked together by N2—H2A \cdots Br1 \cdots H2B—N2—H2C \cdots Br1 hydrogen bonds. This hydrogen-bonding sequence is repeated to form a ring. The ring is shaped like a hexagon and has three N2 and three Br1 atoms at the vertices, leading to a hydrogen-bond network defining cyclic motifs denoted $R_3^3(12)$ in the notation of Etter *et al.* (1990). The vertices are shared with neighbouring hexagons to form an infinite two-dimensional network of hydrogen bonds in the ac plane. The network is not unlike the pattern of chicken wire (Fig. 3). The Br^- ions act as acceptor atoms for three different ammonium head groups. Within a single hexagon, two *p*-nitroanilinium cations are above the network and a single one below. At the same time, the two-dimensional network of hydrogen bonds is linked to adjacent networks by additional N2—H2B \cdots O1 hydrogen bonds in the

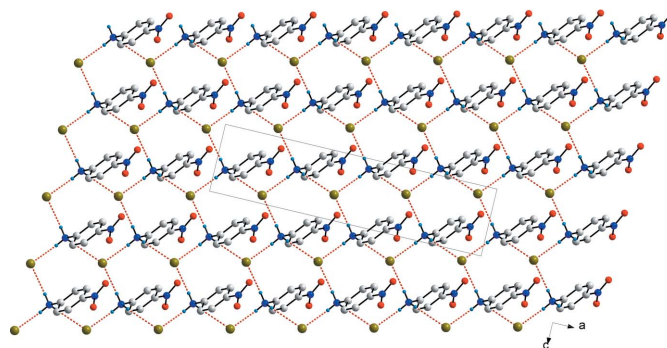


Figure 3

The two-dimensional network of hydrogen bonds (dashed red lines) between the ammonium heads and the bromide anions.

crystallographic b direction *via* the O atom on the nitro group (Fig. 2). The *p*-nitroanilinium cations interdigitate and so form a three-dimensional system of hydrogen bonds. The structure with Cl^- as the counter-ion displays the same two-dimensional pattern of hydrogen bonds, this time in the ac plane. The authors did not mention any N—H \cdots O hydrogen bonds in their paper. The distance between the N and O atoms is 3.590 \AA and so can be considered a weak interaction compared with that in (I), with a distance of $2.915(5) \text{ \AA}$.

Experimental

For the preparation of (I), PbBr_2 (0.424 g, 1.16 mmol) and $(\text{C}_6\text{H}_6\text{N}_2\text{O}_2)$ (0.311 g, 2.24 mmol) were added to a mixture of 48% HBr (8 ml) and H_2O (3 ml). The solution was heated to dissolve the precipitate and then left to stand at room temperature. The crystals, grown by slow evaporation, were harvested after one month.

Crystal data

$\text{C}_6\text{H}_7\text{N}_2\text{O}_2^+\cdot\text{Br}^-$
 $M_r = 219.05$
 Orthorhombic, $Fdd2$
 $a = 20.625(5) \text{ \AA}$
 $b = 30.408(5) \text{ \AA}$
 $c = 5.080(5) \text{ \AA}$
 $V = 3186(3) \text{ \AA}^3$
 $Z = 16$
 $D_x = 1.827 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 898 reflections
 $\theta = 3.3\text{--}26.9^\circ$
 $\mu = 5.11 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Plate, green
 $0.4 \times 0.21 \times 0.04 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.290$, $T_{\max} = 0.810$
 4378 measured reflections

1254 independent reflections
 1157 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\text{max}} = 25.5^\circ$
 $h = -24 \rightarrow 24$
 $k = -36 \rightarrow 30$
 $l = -6 \rightarrow 5$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.056$
 $S = 1.08$
 1254 reflections
 101 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + 2.6422P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 425 Friedel pairs
 Flack parameter: 0.022 (16)

Table 1

Selected bond lengths (Å).

C1—N1	1.474 (5)	N1—O1	1.218 (6)
C4—N2	1.468 (5)	N1—O2	1.236 (7)

Table 2

Hydrogen-bond 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>
N2—H2A...Br1	0.89	2.37	3.253 (4)	174
N2—H2B...O1 ⁱ	0.89	2.48	2.915 (5)	110
N2—H2B...Br1 ⁱⁱ	0.89	2.63	3.402 (5)	146
N2—H2C...Br1 ⁱⁱⁱ	0.89	2.79	3.535 (4)	142

Symmetry codes: (i) $-x + \frac{3}{4}, y + \frac{1}{4}, z - \frac{1}{4}$; (ii) $x, y, z - 1$; (iii) $x + \frac{1}{4}, -y + \frac{3}{4}, z - \frac{1}{4}$.

H atoms were refined in idealized positions in the riding-model approximation, with C—H = 0.93 Å and N—H = 0.89 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{N})$. The NH₃ group was allowed to rotate but not to tip.

Data collection: *SMART-NT* (Bruker (1998)); cell refinement: *SMART-NT*; data reduction: *SAINT-Plus* (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) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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