

Naphthalene-1,5-diammonium diiodide dihydrate

Andreas Lemmerer* and
David G. BillingSchool of Chemistry, University of the
Witwatersrand, Private Bag 3, PO Wits 2050,
South AfricaCorrespondence e-mail:
andy@hobbes.gh.wits.ac.zaReceived 3 March 2006
Accepted 6 March 2006

Naphthalene-1,5-diammonium diiodide crystallizes as the dihydrate, $C_{10}H_{12}N_2^{2+} \cdot 2I^- \cdot 2H_2O$, and the crystal structure exhibits ionic layers separated by hydrocarbon layers. The naphthalene-1,5-diammonium cations in the hydrocarbon layers do not pack parallel to each other but alternate. In the ionic layer, the ammonium groups, the water molecules and the I^- anions interact *via* hydrogen-bond bridges to form two infinite hydrogen-bonded chains.

Key indicators

Single-crystal X-ray study
 $T = 293$ K
 Mean $\sigma(C-C) = 0.003$ Å
 R factor = 0.016
 wR factor = 0.041
 Data-to-parameter ratio = 16.3

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. While synthesizing the red-coloured hybrid perovskite $(H_3NC_{10}H_6NH_3)PbI_4$ (Billing & Lemmerer, 2006), colourless crystals of the title compound, (I), appeared on cooling. For comparison, we decided to prepare a separate solution without the lead iodide. A search of the Cambridge Structural Database (Version 5.24, February 2003 release; Allen, 2002) showed that the crystal structure of the non-protonated $NH_2C_{10}H_6NH_2$ case has been studied only recently (Bernès *et al.*, 2004). In that compound, the asymmetric unit of 1,5-diaminonaphthalene contains one and a half molecules, one on an inversion centre and the other in a general position, to give $Z' = 1.5$. The dihedral angle between these two ring systems is $73.30(4)^\circ$ and not the ideal expected value of 0° .

The title compound displays a lesser degree of ‘poor’ packing (Bernès *et al.*, 2004), with a dihedral angle of $37.10(5)^\circ$ and a centroid-to-centroid distance of 4.326 Å. The naphthalene-1,5-diammonium cation sits on a centre of inversion and hence the asymmetric unit contains only one-half of the cation, together with one anion and one water molecule. The atomic numbering scheme is shown in Fig. 1.

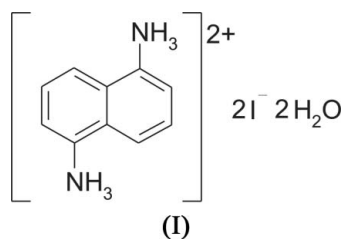
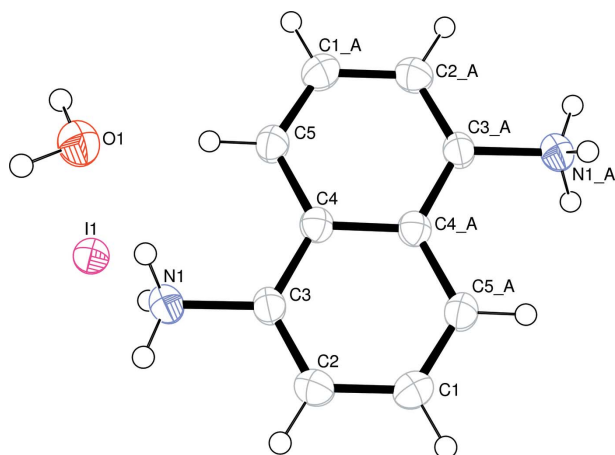
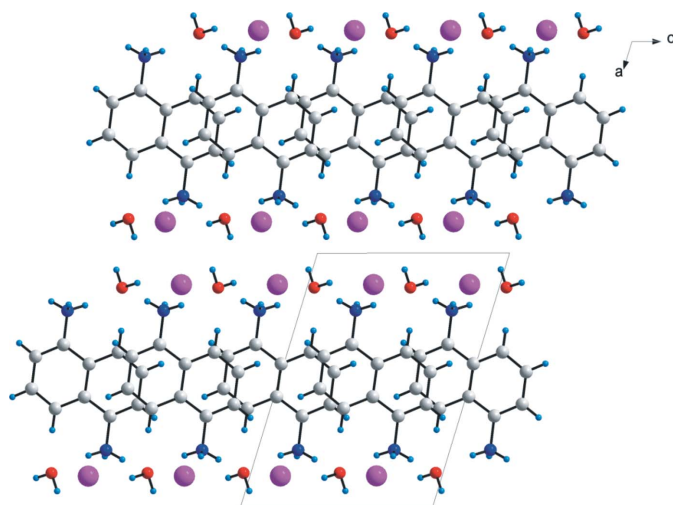


Fig. 2 clearly indicates a monodimensional arrangement in which a single layer of naphthalene-1,5-diammonium cations is embedded between two consecutive ionic layers, forming an alternating hydrocarbon–ionic structure. Within the ionic layer, the I^- anions and water molecules alternate.

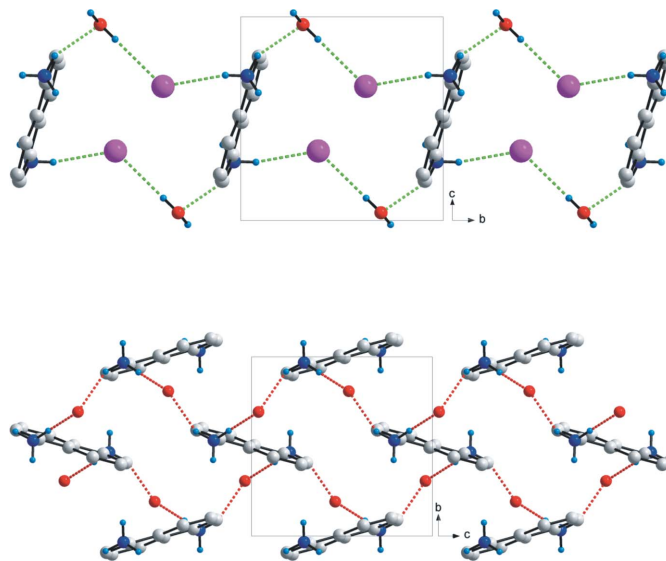
**Figure 1**

The asymmetric unit plus the symmetry-related half of the cation of (I), showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. Atoms labelled with the suffix A are at the symmetry position $(-x + 1, -y + 1, -z)$.

**Figure 2**

A packing diagram for (I), viewed along the b axis.

There is no evidence of π - π interactions in either crystal structure. However, other intermolecular contacts exist in (I) which are not found in 1,5-diaminonaphthalene. Compound (I) has an extensive network of hydrogen bonding due to numerous acceptor and donor atoms. In the crystal structure, the naphthalene-1,5-diammonium cations are linked together by $N1-H1A \cdots O1 \cdots H1B-N1$ hydrogen-bond bridges, forming infinite chains in the crystallographic c direction. At the same time, the components of the structure are linked in the crystallographic b direction by $N1-H1C \cdots I1 \cdots H1E-O1 \cdots H1B-N1$ hydrogen-bond bridges to form a second set of infinite chains. The former chain connects alternating cations, *i.e.* these are related by the twofold screw axis, whereas the latter chain connects cations that are related by translation along the c axis, *i.e.* at $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 1)$. The hydrogen-bond bridge $N1-H1B \cdots I1$ is common to both chains. Atom $H1D$ of the water molecule is not involved in any chains and simply bridges to the I^- anion.

**Figure 3**

The hydrogen-bonding interactions (red and green lines) between the ammonium cations, the water molecules and the I^- anions of (I).

Experimental

For the preparation of (I), $C_{10}H_{10}N_2$ (0.015 g, 0.098 mmol) was added to 47% HI (6 ml) and the precipitate which formed was dissolved by refluxing at 388 K for 12 h. The solution was cooled slowly to room temperature at 2 K h^{-1} to give colourless single crystals of (I) suitable for X-ray diffraction analysis. Analysis calculated for $C_{10}H_{16}I_2N_2O_2$: C 26.69, H 3.58, N 6.22%; found: C 26.39, H 3.72, N 5.90%.

Crystal data

$C_{10}H_{12}N_2^{2+} \cdot 2I^- \cdot 2H_2O$
 $M_r = 450.05$
 Monoclinic, $P2_1/c$
 $a = 11.353(4) \text{ \AA}$
 $b = 7.827(3) \text{ \AA}$
 $c = 8.217(3) \text{ \AA}$
 $\beta = 106.921(5)^\circ$
 $V = 698.6(4) \text{ \AA}^3$
 $Z = 2$

$D_x = 2.14 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 1014 reflections
 $\theta = 3.7\text{--}28.2^\circ$
 $\mu = 4.49 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Plate, white
 $0.38 \times 0.26 \times 0.02 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: integration (*XPREP*; Bruker, 1999)
 $T_{\min} = 0.294$, $T_{\max} = 0.912$
 7024 measured reflections

1306 independent reflections
 1190 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 25.5^\circ$
 $h = -13 \rightarrow 13$
 $k = -9 \rightarrow 9$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.016$
 $wR(F^2) = 0.041$
 $S = 1.14$
 1306 reflections
 80 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0184P)^2 + 0.2375P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

C1—C5 ⁱ	1.358 (4)	C3—N1	1.466 (3)
C1—C2	1.397 (4)	C4—C5	1.411 (3)
C2—C3	1.354 (3)	C4—C4 ⁱ	1.425 (4)
C3—C4	1.414 (3)		

Symmetry code: (i) $-x + 1, -y + 1, -z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1C \cdots I1	0.89	2.65	3.522 (2)	167
N1—H1A \cdots O1	0.89	1.94	2.820 (3)	172
N1—H1B \cdots O1 ⁱⁱ	0.89	2.14	2.954 (3)	151
O1—H1D \cdots I1 ⁱⁱⁱ	0.89 (2)	3.02 (3)	3.653 (2)	129 (2)
O1—H1E \cdots I1 ^{iv}	0.89 (2)	2.64 (2)	3.507 (2)	165 (3)

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

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

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).

The University of the Witwatersrand is thanked for the award of a research grant and for providing the infrastructure required to carry out this work.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bernès, S., Pastrana, M. R., Sánchez, E. H. & Pérez, R. G. (2004). *Acta Cryst.* **E60**, o45–o47.
- Billing, D. G. & Lemmerer, A. (2006). Unpublished results.
- Brandenburg, K. (1999). *DIAMOND*. Release 2.1c. Crystal Impact GbR, Bonn, Germany.
- Bruker (1998). *SMART-NT*. Version 5.050. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SAINT-Plus*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.