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Hydrogen-bonding one-dimensional chains containing the $R_4^2(8)$ motif in the ammonium salts 1-naphthylammonium iodide and naphthalene-1,8-diyldiammonium diiodide

Andreas Lemmerer, David G. Billing* and Janine M. Robinson

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, PO Wits 2050, South Africa
Correspondence e-mail: dave.billing@wits.ac.za

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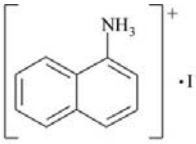
In 1-naphthylammonium iodide, $C_{10}H_{10}N^+\cdot I^-$, and naphthalene-1,8-diyldiammonium diiodide, $C_{10}H_{12}N_2^{2+}\cdot 2I^-$, the predominant hydrogen-bonding pattern can be described using the graph-set notation $R_4^2(8)$. This is the first report of a structure of a diprotonated naphthalene-1,8-diyldiammonium salt.

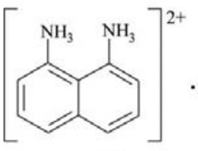
Comment

As part of a continuing investigation into the hydrogen-bonding motifs exhibited by simple organic ammonium halide salts (Lemmerer & Billing, 2006*a*,*b*,*c*,*d*, 2007), the crystal structures of two naphthalene–ammonium salts are reported. The unprotonated cases of the title compounds have been reported previously, *viz.* 1,8-diaminonaphthalene twice [Cambridge Structural Database (CSD; Version 5.29, November 2007 release; Allen, 2002) refcodes JISVEM (Llamas-Saiz *et al.*, 1991) and JISVEM01 (Basaran *et al.*, 1993)] and 1-naphthylamine once (ZZZOZQ; Kitaigorodskii, 1945). In the diaminonaphthalene case, monoprotonated salts are more common. Counter-ions in these structures include dichloroacetate (LECCIF; Basaran *et al.*, 1993), trichloroacetate (LECCOL; Basaran *et al.*, 1993) and maleate (YEWRIB; Bartoszak *et al.*, 1995). No diprotonated 1,8-diaminonaphthalene salts are reported in the CSD. The 1-naphthylammonium salts have two different counter-ions, namely cyclohexaphosphate (HUNDAV; Nasr *et al.*, 2001), cyclohexaphosphate and hexane-1,6-diammonium together (MAVQEF; Marouani *et al.*, 1998), and trichloroacetate (LECCUR; Basaran *et al.*, 1993). In the current report, we compare the packing arrangements and hydrogen-bonding motifs exhibited by the two title salts, (I) and (II).

The molecular structure of (I) and the packing arrangement in the unit cell, viewed along the *c* axis, are shown in Figs. 1(*a*) and 2, respectively. All the C atoms and the N atom lie in a well defined plane and deviate from it by no more than 0.051 (8) Å. The structure consists of ionic pillars, extending along the *c* axis, that are surrounded by a hydrocarbon framework. There are two complete ionic pillars per unit cell, each centred around inversion centres, one at the centre of the unit cell at ($\frac{1}{2}$, $\frac{1}{2}$, *z*) and another at the four corners of the unit cell at (0, 0, *z*), (1, 0, *z*), (0, 1, *z*) and (1, 1, *z*). The ionic pillars consist of four I^- anions and four NH_3^+ ammonium groups, arranged tetrahedrally on the vertices of a distorted cube (Fig. 3). Each ionic pillar is surrounded by four naphthalene molecules that interact with the π systems of adjacent naphthalene molecules by C—H$\cdots\pi$ interactions (Fig. 2). The H7$\cdots$*Cg*2 distance is 2.94 Å and the C7—H7$\cdots$*Cg*2 angle is 130°, where *Cg*2 is the centroid of the aromatic ring described by atoms C4*B*, C4*A*, C5, C6, C7 and C8.



(I)



(II)

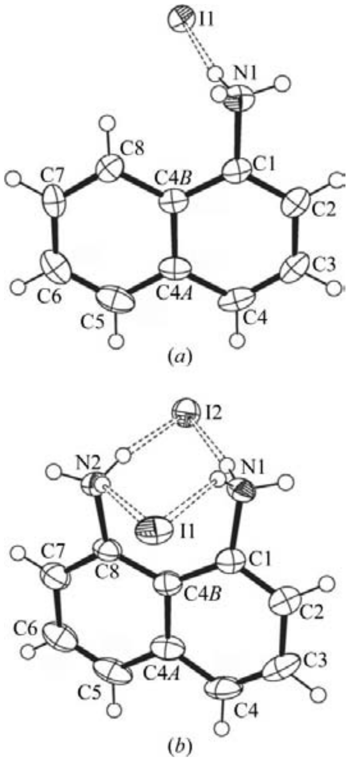


Figure 1
The asymmetric unit of (*a*) (I) and (*b*) (II). Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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The hydrogen-bonding interactions within the ionic pillar form extended one-dimensional chains (Fig. 4 and Table 1) consisting of four unique hydrogen-bonded rings. The basic hydrogen-bonding scheme can be described as the ring motif $R_4^2(8)$ when using graph-set notation (Bernstein *et al.*, 1995). The first ring, designated R', describes the sequence N1—H1*C*···I1···H1*A*—N1—H1*C*···I1···H1*A*–; the H1*C*···I1 and H1*A*···I1 distances are 2.68 and 2.69 Å, respectively. The second ring, R'', is adjacent to R' and contains the sequence N1—H1*B*···I1···H1*A*—N1—H1*B*···I1···H1*A*–; the H1*B*···I1 and H1*A*···I1 distances are 3.13 and 2.69 Å, respectively. Atom H1*A* is common to both rings. These two rings lie parallel to the *ac* plane and extend in the direction of the crystallographic *c* axis. Two of these joined rings are present in the ionic pillar and are joined along the crystallographic *b* direction by a third hydrogen-bonded ring, R''', with the sequence N1—H1*A*···I1···H1*B*—N1—H1*A*···I1···H1*B*–; the H1*A*···I1 and H1*B*···I1 distances are 2.69 and 3.01 Å, respectively. The last ring, R'''', lies parallel to the *ab* plane and has a different bonding motif. R'''' has a bifurcated hydrogen bond and hence the notation is $R_3^2(6)$. The sequence is N1—H1*B*···I1···H1*B*···I1···H1*C*–. All four rings are combined in the form of a distorted cube, with one face each of R' and R'', and two faces each of R''' and R'''' (Fig. 4). The N1 donor and I1 acceptor atoms sit at the eight vertices of the distorted cube.

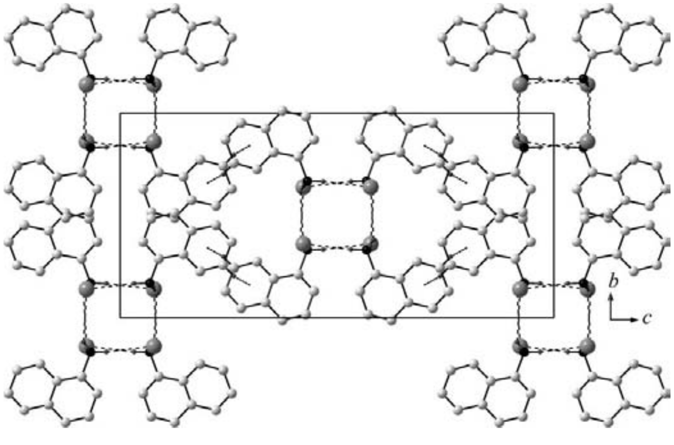

Figure 2
The packing of (I). Intermolecular hydrogen bonds within the ionic pillars form chains along the *c* axis and C—H···π interactions join the naphthalene framework along the *c* axis. H atoms have been omitted for clarity, except for those involved in hydrogen bonds and C—H···π interactions (shown as dashed lines).

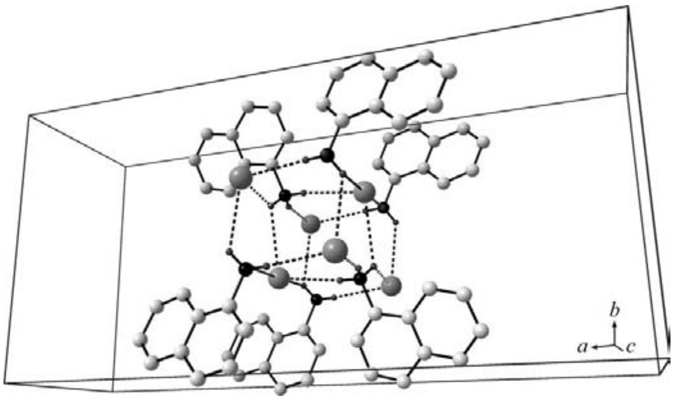

Figure 3
A perspective view of an ionic pillar and the one-dimensional chain of hydrogen bonds of (I).

The atomic numbering scheme of (II) is shown in Fig. 1(*b*). The crystal structure has a bidimensional arrangement, in which a double layer of naphthalene-1,8-diyldiammonium cations is embedded between two consecutive ionic layers, forming an alternating hydrocarbon–ionic structure along the *c* axis (Fig. 5). The X-ray structure reveals that the N atoms are slightly bent out of the plane of the C atoms of the naphthalene ring. Atoms N1 and N2 deviate from the plane defined by atoms C1–C8 by 0.214 (6) and −0.278 (6) Å, respectively. Associated with this is a dihedral angle of 7.7 (2)° between the two joined rings, the common edge comprising atoms C4*A* and C4*B*. The N atoms themselves lean away from each other, as seen in Fig. 1(*b*). This bending has been described in the literature as the *peri* interaction (Balasubramaniyan, 1966) and is also observed in the crystal structure of the unprotonated 1,8-diaminonaphthalene molecule (Llamas-Saiz *et al.*, 1991). In the latter case, the repulsion is partly countered by an attractive intramolecular hydrogen bond, and the N···N distances are 2.72 and 2.74 Å for the two molecules in the asymmetric unit. In the monoprotonated salts, the distances are 2.72 Å for both LECCIF and LECCOL (Basaran *et al.*, 1993) and 2.67 Å for YEWRIB (Bartoszak *et al.*, 1995). Compound (II) has no intramolecular hydrogen bond and the N1···N2 distance is thus longer at 2.92 (1) Å.

The two N atoms on the naphthalene-1,8-diyldiammonium cation again form hydrogen bonds to the I2 atoms using the

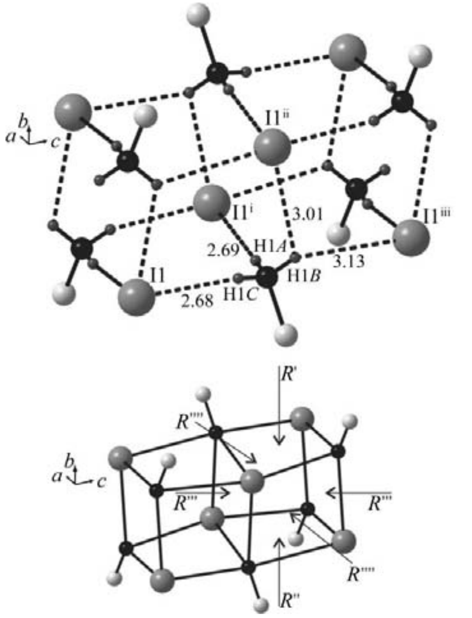

Figure 4
A magnified view of the one-dimensional chain of hydrogen bonds of (I). Only the C atoms to which the N atoms are attached are shown. The schematic shows the four different hydrogen-bonded rings forming a distorted cube. [Symmetry codes: (i) $-x+1, y, -z+\frac{1}{2}$; (ii) $x, -y+1, z+\frac{1}{2}$; (iii) $x, y, z+1$.]

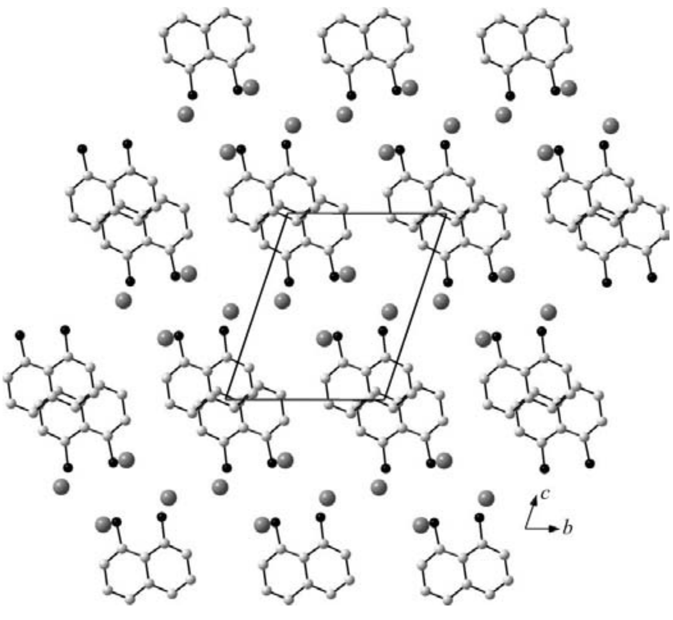

Figure 5
The packing of (II). H atoms have been omitted for clarity.

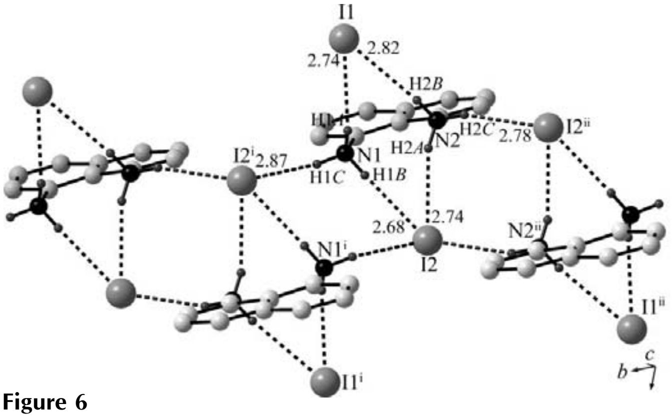

Figure 6
A magnified view of the hydrogen-bonded chain of (II). The intermolecular hydrogen bonds that form chains along the *c* axis are shown as dashed lines. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z + 1$.]

same $R_4^2(8)$ ring motif seen in (I). Atom N1 has the following sequence of hydrogen bonds: N1—H1*B*···I2···H1*C*—N1—H1*B*···I2···H1*C*–; similarly, atom N2 has the sequence N2—H2*C*···I2···H2*A*—N2—H2*C*···I2···H2*A*–. The rings are centrosymmetric, being centred around $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. These two rings have the same acceptor atom I2. One final hydrogen-bonded ring is found in the structure. This ring also has an $R_4^2(8)$ motif, but has both I1 and I2 as acceptor atoms and N1 and N2 as donor atoms: N1—H1*A*···I1···H2*B*—N2—H2*A*···I2···H1*B*– (Figs. 1 and 6). These three rings also describe extended one-dimensional chains in the *b* direction (Fig. 6).

Experimental

All chemicals were purchased from commercial sources and used as received. Compound (I) was prepared by the slow evaporation of a solution of 1-aminonaphthalene (0.015 g, 0.105 mmol) in 5 ml of 48% aqueous HI. Compound (II) was prepared by slow cooling of a solution containing 1,8-diaminonaphthalene (0.010 g, 0.063 mmol) in 7 ml of 48% aqueous HI. The solution was kept at 373 K for 12 h and then cooled to room temperature at a rate of 2 K h^{-1}.

Compound (I)

Crystal data

$C_{10}H_{10}N^+\cdot I^-$
$M_r = 271.09$
Orthorhombic, *Pbcn*
$a = 24.259$ (4) Å
$b = 11.469$ (2) Å
$c = 7.1937$ (12) Å
$V = 2001.5$ (6) Å^3
$Z = 8$
Mo *Kα* radiation
$\mu = 3.15$ mm^{-1}
$T = 293$ (2) K
0.5 × 0.23 × 0.09 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: integration (*XPREP*; Bruker, 1999)
$T_{\min} = 0.293$, $T_{\max} = 0.706$
10172 measured reflections
1870 independent reflections
1646 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.077$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.139$
$S = 1.33$
1870 reflections
110 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.05$ e Å^{-3}
$\Delta\rho_{\min} = -1.33$ e Å^{-3}

Compound (II)

Crystal data

$C_{10}H_{12}N_2^{2+}\cdot 2I^-$
$M_r = 414.02$
Triclinic, $P\overline{1}$
$a = 7.2529$ (13) Å
$b = 9.1586$ (17) Å
$c = 10.897$ (2) Å
$\alpha = 68.082$ (3)°
$\beta = 75.764$ (3)°
$\gamma = 68.867$ (3)°
$V = 621.2$ (2) Å^3
$Z = 2$
Mo *Kα* radiation
$\mu = 5.03$ mm^{-1}
$T = 293$ (2) K
0.28 × 0.2 × 0.04 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: integration (*XPREP*; Bruker, 1999)
$T_{\min} = 0.119$, $T_{\max} = 0.814$
3479 measured reflections
2288 independent reflections
1901 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.114$
$S = 1.03$
2288 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.44$ e Å^{-3}
$\Delta\rho_{\min} = -1.54$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···I1$^{\rm i}$	0.89	2.69	3.570 (6)	172
N1—H1*B*···I1$^{\rm ii}$	0.89	3.01	3.538 (7)	120
N1—H1*B*···I1$^{\rm iii}$	0.89	3.13	3.699 (6)	124
N1—H1*C*···I1	0.89	2.68	3.539 (6)	162

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

For both compounds, all H atoms were refined using a riding model, with C—H distances of 0.93 Å and N—H distances of 0.89 Å,

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯I1	0.89	2.74	3.517 (5)	146
N1—H1B⋯I2	0.89	2.68	3.568 (5)	172
N1—H1C⋯I2^{i}	0.89	2.87	3.615 (5)	143
N2—H2A⋯I2	0.89	2.74	3.556 (5)	153
N2—H2B⋯I1	0.89	2.82	3.668 (5)	161
N2—H2C⋯I2^{ii}	0.89	2.78	3.634 (5)	161

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y, -z+1$.

and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C) or $1.5U_{\rm eq}$(N). The highest residual peak was 1.25 Å from atom H7 in (I) and 1.21 Å from I1 in (II). It is worth noting that the H atoms at N2 in compound (II) were not well resolved in difference maps, and as a consequence may not be accurately placed.

For both compounds, data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); 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: DN3092). Services for accessing these data are described at the back of the journal.

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