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1,4-Dimethyl-1,4-diazoniabicyclo-[2.2.2]octane diiodide acetonitrile solvate

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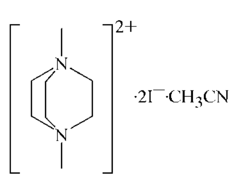
In the crystal structure of the title compound, $C_8H_{18}N_2^{2+}\cdot 2I^-\cdot CH_3CN$, the dication lies on a mirror plane containing the molecular dication threefold axis. The structure displays C—H···I interactions between H atoms of the 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane dication and the iodide anions. The H···I distances are in the range 2.96–3.18 (4) Å. The dications pack forming channels along the *b* axis, which contain the iodide anions and acetonitrile solvent molecules.

Comment

The 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane dication has been used as a non-coordinating divalent cation in salts of mono- and polynuclear transition metal complexes, and as the counter-ion for organic charge-transfer salts. Several structures have been determined that contain the 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane dication, including transition metal complex salts (Christoph & Goedken, 1973; Bond & Willett, 1991), silicate clusters (Breu *et al.*, 2004; Wiebcke *et al.*, 1994) and calixarenes (Mansikkamaki *et al.*, 2002, 2004, 2005), but only one simple salt of any diquaternary alkyldiazabicyclooctane dication has been determined with *n*-octadecyl groups [Cambridge Structural Database (Allen, 2002) refcode QETLEG (Ishioka *et al.*, 2000)]. We report here the structure of the title compound (I), an acetonitrile solvate of 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane diiodide.



(I)

The structure of (I) is presented in Fig. 1. The asymmetric unit consists of part of one 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane dication and two iodide counter-ions. Atoms C1, C2, C5, C6, N1 and N2 all lie on special positions with mirror symmetry. Atoms C3 and C4 are on general positions. The mirror plane generates the third ethylene strap of the dication. Both of the unique I atoms are located on special positions with mirror site symmetry and near the methyl groups of the dication. Additionally, a disordered acetonitrile solvent molecule is present.

Molecules of (I) show intermolecular C—H···I interactions between the H atoms of the dication and the I atoms (Table 1). Fig. 2 shows a view of these interactions. Atoms I1 and I2 each participate in three unique C—H···I interactions with the dication. Atom I1 also participates in a C—H···I interaction with the acetonitrile solvent molecule. Atoms I1 and I2 are each within van der Waals contact of six H atoms. The I atoms are not within van der Waals contact of atoms H1*A*, H1*B*, H2*A* and H2*B* of the ethylene strap that lies on a mirror plane. Note that as the positions of the H atoms bonded to the

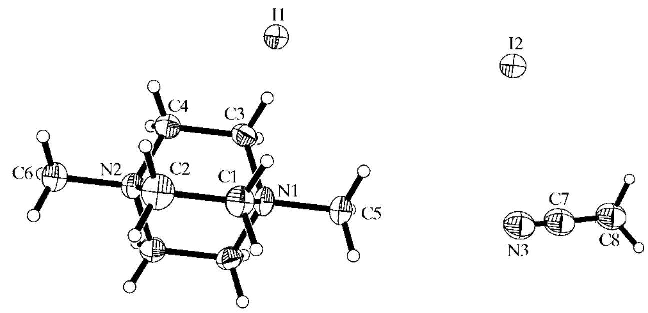


Figure 1
A view of the components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

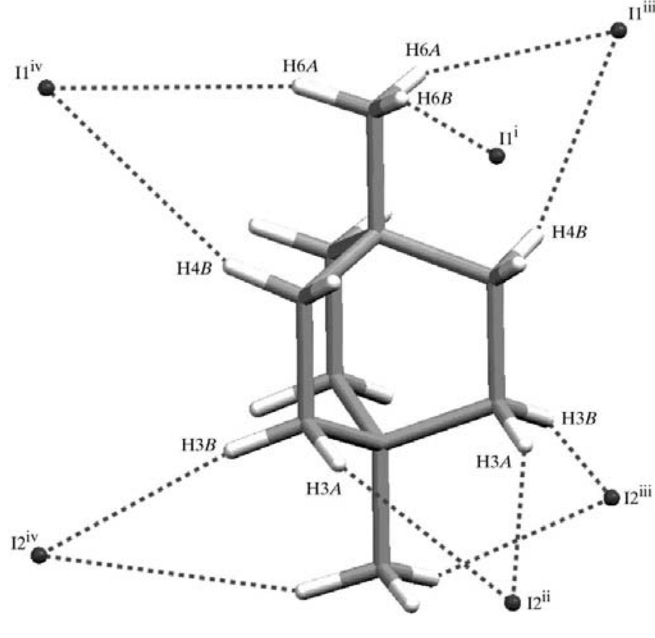
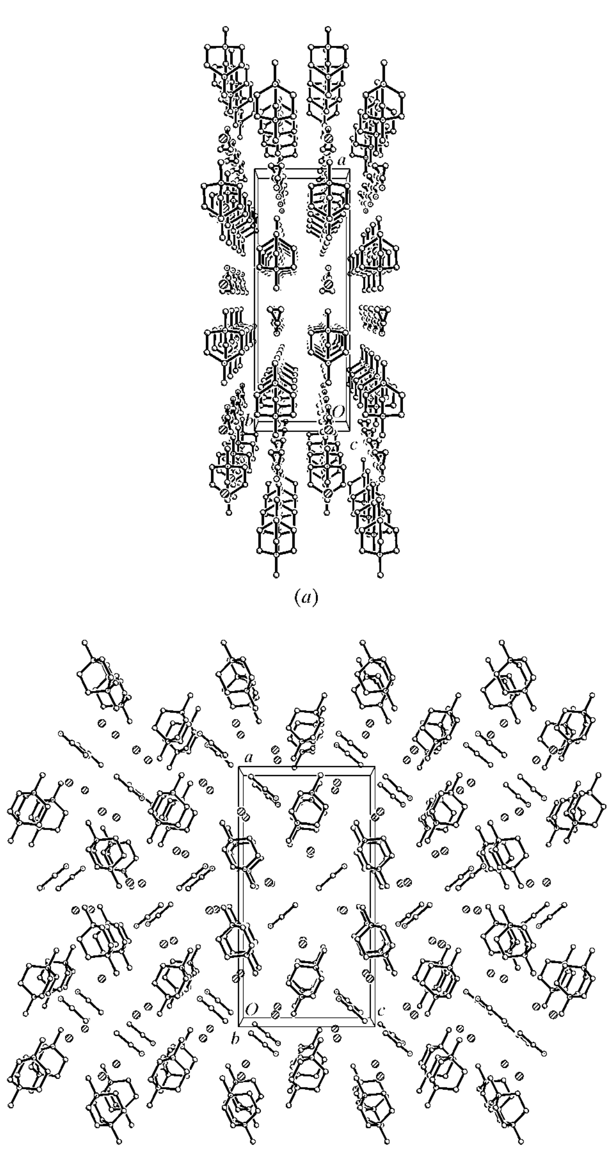


Figure 2
A view of the structure of (I), showing the intermolecular C—H···I interactions. Only H atoms participating in C—H···I interactions are shown with labels. I atoms are labeled with symmetry codes identifying the location relative to the dication asymmetric unit. [Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+1$; (ii) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (iii) $x, y-1, z-1$; (iv) $x, y, z-1$.]

disordered acetonitrile solvent molecule were constrained as riding atoms, the C8—H8B···I1 hydrogen-bonding interaction listed in Table 1 may be suspect.

These C—H···I interactions are considered non-classical hydrogen bonds, as they involve combinations of weak donors (C—H) with strong acceptors (I^-). Comparison of the normalized C—H···I distances of the C—H···I interactions in the structure of (I) (R_{HX} = 0.94–1.01) with the mean normalized distances of C—H···I interactions in the hydrogen-bonding analysis of Brammer *et al.* (2001) (R_{HX} = 0.982) suggests that these interactions are typical of C—H···I hydrogen bonding. The angular relation of the C—H···I interactions [C—H···I = 152–159 (3)°] are also reasonable for C—H···I hydrogen bonding. The proximity of the C-atom donors that form these C—H···I interactions to the positively charged N atoms perhaps enhance their ability to participate in hydrogen bonding (Palusiak *et al.*, 2005).



(*a*)

(*b*)

Figure 3
Packing diagrams of (I) showing (*a*) the layered nature of the packing, viewed down the *c* axis, and (*b*) the channels formed by the dications, viewed down the *b* axis.

A packing diagram of the structure (Fig. 3) reveals that the dications as well as the iodide anions and acetonitrile solvate molecules are packed in layers perpendicular to the *b* axis at 0.25*b* and 0.75*b*. Perpendicular to the layers, the dications form roughly hexagonal channels, though no crystallographic three- or sixfold symmetry is present. Iodide anions and acetonitrile solvent molecules fill these channels in the structure.

Experimental

1,4-Dimethyl-1,4-diazoniabicyclo[2.2.2]octane diiodide was synthesized by the method used to make the analogous *N*-methylpyridinium iodide (Wiley *et al.*, 1972). Crystals of (I) were grown by slow evaporation from a solution containing 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane diiodide, 3′,4′-dibutyl-5,5″-bis(dicyanomethylene)-5,5″-dihydro-2,2′:5′,2″-terthiophene, water and acetonitrile.

Crystal data

$C_8H_{18}N_2^{2+}\cdot 2I^-\cdot C_2H_3N$
M_r = 437.10
Orthorhombic, *Pnma*
a = 20.174 (3) Å
b = 7.343 (1) Å
c = 10.6140 (14) Å
V = 1572.3 (4) Å^3
Z = 4
D_x = 1.846 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2300 reflections
θ = 2.0–25.0°
μ = 3.98 mm^{-1}
T = 173 (2) K
Plate, yellow
0.25 × 0.04 × 0.04 mm

Data collection

Siemens SMART Platform CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
T_{min} = 0.592, T_{max} = 0.85
11185 measured reflections
1508 independent reflections
1297 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 25.0°
$h = -22 \rightarrow 24$
$k = -8 \rightarrow 8$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.045
S = 1.11
1508 reflections
121 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0111P)^2 + 1.9299P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···I2^{vi}	0.99 (4)	3.11 (4)	4.045 (4)	157 (3)
C4—H4*B*···I1^{iv}	0.96 (4)	3.07 (4)	3.980 (4)	159 (3)
C6—H6*A*···I1^{iii}	0.94 (3)	3.04 (4)	3.921 (2)	157 (3)
C6—H6*B*···I1^{i}	0.92 (5)	3.07 (5)	3.940 (7)	159 (4)
C8—H8*B*···I1^{v}	0.98	2.96	3.857 (7)	152
C3—H3*B*···I2^{iv}	0.96 (3)	3.08 (3)	3.981 (4)	157 (2)
C5—H5*A*···I2^{iii}	1.00 (3)	3.18 (4)	4.094 (3)	154 (2)

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

The coordinates of all H atoms were refined [C—H = 0.91 (3)–1.01 (3) Å], except for atoms H8*A*, H8*B* and H8*C*; these H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.98 Å and U_{iso}(H) values of $1.5U_{eq}$(C). Attempts to refine the coordinates of the H atoms of the disordered acetonitrile solvent molecule were unsuccessful; the solvent molecule is disordered over a mirror plane and refinement of this disorder required restraint of the N3—C7 bond length to 1.136 (3) Å, restraint of the C7—C8 bond length to 1.470 (3) Å, and restraint of the total distance between N3 and C8 to 2.606 (3) Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1071). Services for accessing these data are described at the back of the journal.

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