Tris(1,9-diethyladeninium) triiodide diiodide

Elizabeth F. Day,[a]* Norman S. Dean[b] and Andreas H. Franz[a]

[a]Department of Chemistry, University of the Pacific, 3601 Pacific Avenue, Stockton, CA 95211, USA, and [b]Department of Chemistry, California State University Northridge, 18111 Nordhoff Street, Northridge, CA 91330, USA

Correspondence e-mail: eday@pacific.edu

X-ray analysis of the title compound reveals three crystallographically distinct cations of 1,9-diethyladeninium, two iodide anions and one triiodide anion in the asymmetric unit, giving six residues and the formula $3C_9H_{14}N_5^+ \cdot I_3^- \cdot 2I^-$. Standard purine nomenclature is used to identify the atoms of each adenine moiety. Hydrogen bonding is observed between atoms N6 and N7 of a pair of cations $[N \cdots N = 2.885 (4)/2.902 (3)$ and $2.854 (3)/2.854 (3)$ Å], with additional hydrogen bonding to I^- anions via the other N6 H atom $[N \cdots I = 3.708 (3), 3.738 (3)$ and $3.638 (3)$ Å]. The triiodide anion is not involved in hydrogen bonding. The bond lengths and angles of the 1,9-diethyladeninium cations are compared with literature values and confirm the formation of the imine tautomer.

Comment

Derivatized nucleobases have long been studied, due to the biological activity of the many compounds that contain them. Nucleoside analogues and substituted nucleobases are used as antiviral and anticancer therapeutic agents (Galmarini *et al.*, 2002; Mitsuya *et al.*, 1990). Additionally, modified nucleobases, including those with N1 alkylation, are present in natural systems such as tRNA (McCloskey & Nishimura, 1977; Rich, 1977). As a result, a detailed understanding of the structures and reactivity of nucleobase derivatives remains an important topic of research.

The title compound, (I), has three independent cations, *viz.* A, B and C, in the asymmetric unit. Fig. 1 shows the independent components of (I) with the atom-numbering scheme. Selected bond distances and angles for the three cations are presented in Table 1, using the standard purine numbering shown in the scheme.

The amine tautomeric form dominates for N9-substituted adenine derivatives under normal conditions, with <0.01% of the imine form in 9-ethyladenine and adenosine (Lippert *et al.*, 1992, and references therein). However, alkylation of the 1

position leads to imine stabilization (Dreyfus *et al.*, 1977). Notable parameters to support imine formation in (I) are the shortening of the C6—N6 bond distance [1.314 (4), 1.318 (4) and 1.314 (4) Å in cations A, B and C, respectively] compared

(I)
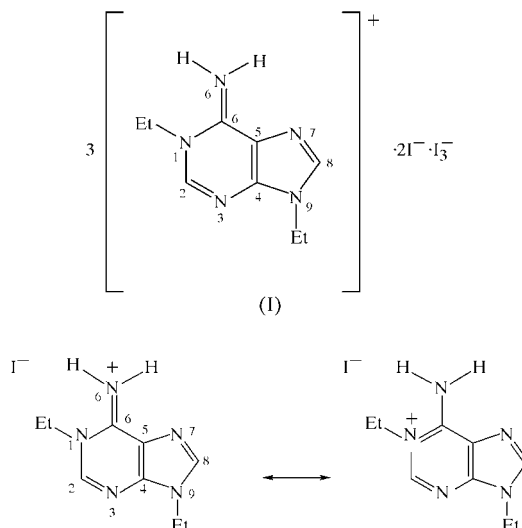
with 9-MeAH [1.329 (2) Å], and the lengthening of the C6—N1 bond [1.369 (4), 1.373 (4) and 1.374 (4) Å in cations A, B and C, respectively] compared with 1.357 (2) Å obtained from the crystal structure of 9-MeAH (Kistenmacher & Rossi, 1977; Clowney *et al.*, 1996). Although the differences are just at the limit of statistical significance, the clear trend supports the bonding description of the nucleobase derivative as the imine form. The enhanced internal C6—N1—C2 angle [121.9 (3), 121.6 (3) and 121.3 (3)° for cations A, B and C, respectively] clearly shows the effects of a substituent on N1, compared with an angle of 118.7 (1)° for 9-MeAH. As expected, comparison between the purine parameters of the three cations of (I) shows that they have the same dimensions within experimental error. Also, comparison of the geometric values for the cations of (I) with those for the cations of 1,9-dimethyladeninium chloride shows that the parameters of the purine ring are all within calculated error (Chiang *et al.*, 1979).
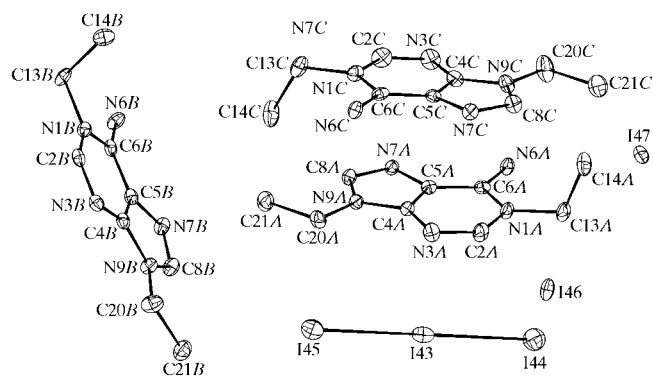

Figure 1
The independent components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

organic compounds

The three unique cations in the asymmetric unit of (I) form two sets of hydrogen-bonded dimers (Fig. 2). Cations *A* and *C* form a hydrogen-bonded dimer *via* atoms N6 and N7 to give a ten-membered ring with two donors and two acceptors (N6*A*···N7*C* and N6*C*···N7*A*) [graph set $R_2^2(10)$; Bernstein *et al.*, 1995]. Cation *B* similarly dimerizes with a neighbouring cation *B*^{i} at $(-x, -y + 1, -z + 1)$ (N7*B*···N6*B*^{i} and N6*B*^{i}···N7*B*). This pair lies on a crystallographic centre of symmetry, with the two hydrogen bonds having the same length. The angle between the planes of the two hydrogen-bonded dimers is 53.53 (6)°. There is additional hydrogen
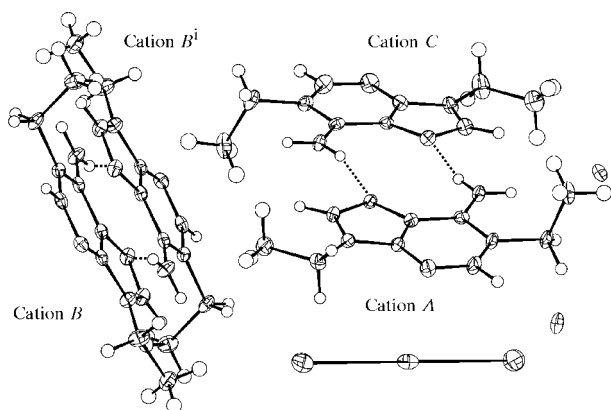
bonding to I$^-$ anions *via* the other N6 H atom (N6*A*···I47, N6*B*···I47 and N6*C*···I46). The triiodide anion is not involved in hydrogen bonding. Details of the hydrogen bonds are given in Table 2. A packing diagram is presented in Fig. 3 and illustrates the presence of alternating layers of *B* dimers and *A*–*C* dimers, as viewed down the *b* axis. Additionally, the hydrogen bonds to the anions are shown.

The triiodide anion is proposed to be a result of air oxidation of the I$^-$ anions present in the reaction mixture. This is a well documented reaction known to occur in acidic environments. According to a review by Svensson & Kloo (2003, and references therein), the triiodide parameters of (I) are well within the expected range. Using these published parameters, the triiodide ion in (I) is defined as essentially linear [I44−I43−I45 = 178.980 (11)°] and symmetric [I44−I43 = 2.9079 (4) Å and I43−I45 = 2.9186 (4) Å]. The triiodide anions in (I) do not have close contacts with any components of the unit cell.

Figure 2
The asymmetric unit of (I), including an extra congener of cation *B*^{i} at $(-x, -y + 1, -z + 1)$, showing the formation of the hydrogen-bonded dimers (dotted lines).

Experimental

The addition of equimolar quantities of 1,9-diethyladeninium iodide (Itaya *et al.*, 1972) and Re$_2$(CH$_3$COO)$_2$Cl$_4$·2H$_2$O (Chakravarty *et al.*, 1986) in ethanol resulted in a purple precipitate. The precipitate was treated with 0.2 molar equivalents of Re$_2$(CH$_3$CH$_2$COO)$_4$Cl$_2$ (Brignole & Cotton, 1971) in acetonitrile. The resulting purple solid was removed by filtration and slow evaporation of the filtrate gave red crystals of (I) suitable for X-ray diffraction analysis.

Crystal data

3C$_9$H$_{14}$N$_5$$^+$·I$_3$$^-$·2I$^-$	$Z = 4$
$M_r = 1211.26$	$D_x = 2.020$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.3570 (9)$ Å	$\mu = 3.95$ mm^{-1}
$b = 10.3185 (7)$ Å	$T = 100 (2)$ K
$c = 31.305 (2)$ Å	Prism, red
$\beta = 93.8760 (10)°$	$0.25 \times 0.20 \times 0.18$ mm
$V = 3982.4 (5)$ Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	31380 measured reflections
	8826 independent reflections
φ and ω scans	7819 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	$R_{int} = 0.031$
$T_{min} = 0.439$, $T_{max} = 0.537$	$\theta_{max} = 27.5°$
(expected range = 0.402–0.492)	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 5.0719P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.062$	$(\Delta/\sigma)_{max} = 0.022$
$S = 1.04$	$\Delta\rho_{max} = 0.95$ e Å^{-3}
8826 reflections	$\Delta\rho_{min} = -0.59$ e Å^{-3}
424 parameters	
H-atom parameters constrained	

Displacement ellipsoids did not show any abnormalities. H atoms were positioned geometrically after each cycle. All H atoms were included in the refinement in calculated positions using a riding model, with N—H = 0.88 Å, and C—H = 0.95 for aromatic, 0.99 for CH$_2$, and 0.98 Å for methyl H atoms, and with U_{iso}(H) = 1.2U_{eq}(C,N) or 1.5U_{eq}(methyl C).
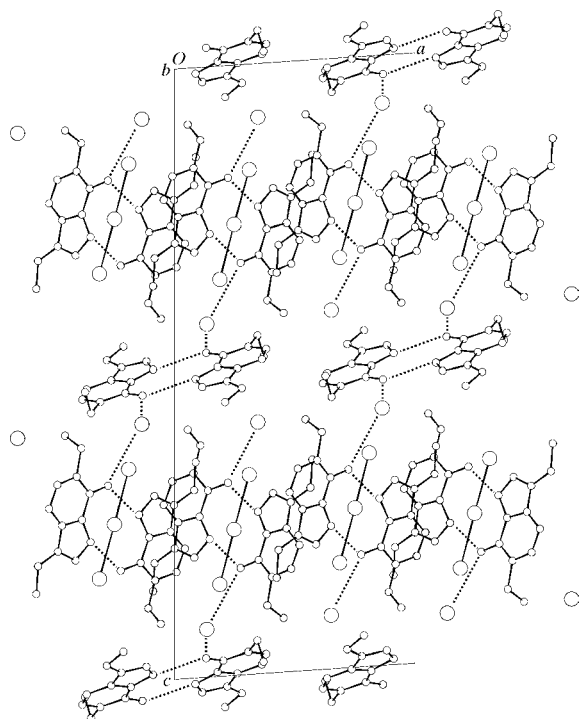

Figure 3
A packing diagram of (I), viewed down the *b* axis, showing the hydrogen bonding (dotted lines) and the alternating layers of cation *B* hydrogen-bonded dimers and cation *A*–*C* hydrogen-bonded dimers (the latter roughly in the plane of the drawing).

Table 1
Comparison of the geometric parameters of the independent 1,9-diethyladeninium cations of (I) (Å, °), using standard purine numbering.

	Cation A	Cation B	Cation C
N1—C2	1.380 (4)	1.376 (4)	1.379 (4)
C2—N3	1.299 (4)	1.293 (4)	1.294 (4)
N3—N4	1.347 (4)	1.346 (4)	1.352 (4)
C4—C5	1.380 (4)	1.376 (4)	1.376 (4)
C5—C6	1.405 (4)	1.402 (4)	1.399 (4)
C6—N6	1.314 (4)	1.318 (4)	1.314 (4)
C6—N1	1.369 (4)	1.373 (4)	1.374 (4)
C5—N7	1.376 (4)	1.380 (4)	1.378 (4)
N7—C8	1.313 (4)	1.313 (4)	1.317 (4)
C8—N9	1.367 (4)	1.363 (4)	1.368 (4)
N9—C4	1.355 (4)	1.362 (4)	1.364 (4)
N1–C2–N3	126.1 (3)	126.0 (3)	126.5 (3)
C2–N3–C4	112.1 (3)	112.5 (3)	112.2 (3)
N3–C4–C5	127.2 (3)	127.1 (3)	126.8 (3)
C4–C5–C6	118.6 (3)	118.4 (3)	119.0 (3)
C5–C6–N1	114.0 (3)	114.3 (3)	114.2 (3)
C6–N1–C2	121.9 (3)	121.6 (3)	121.3 (3)
N6–C6–N1	121.8 (3)	121.5 (3)	121.7 (3)
C4–C5–N7	110.8 (3)	110.6 (3)	110.4 (3)
C5–N7–C8	103.4 (2)	103.6 (3)	103.9 (3)
N7–C8–N9	113.8 (3)	113.8 (3)	113.6 (3)
C8–N9–C4	105.8 (2)	105.7 (3)	105.5 (2)
N9–C4–C5	106.2 (3)	106.3 (3)	106.6 (3)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N6C—H6C2⋯N7A	0.88	2.05	2.902 (3)	162
N6B—H6B1⋯I47[i]	0.88	2.90	3.738 (3)	160
N6C—H6C1⋯I46[ii]	0.88	2.82	3.638 (3)	155
N6A—H6A1⋯I47	0.88	2.89	3.708 (3)	156
N6B—H6B2⋯N7B[iii]	0.88	2.00	2.854 (3)	164
N6A—H6A2⋯N7C	0.88	2.03	2.885 (4)	165

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

Data collection: *SMART* (Siemens, 1993); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material

for publication: *CRYSTALS* (Betteridge *et al.*, 2003).

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