Benzylammonium 2,4-bis(dicyanomethylene)-2,3-dihydroisoindolide

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organic papers

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Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.051
wR factor = 0.127
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.

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The cation and anion of the title salt, $C_7H_{10}N^+ \cdot C_{14}H_4N_5^-$, are both bisected by a crystallographic mirror plane. Extensive hydrogen bonding, with the $R_6^6(28)$ graph-set motif, connects the ions into layers.

Comment

The title compound, (I), is a by-product of the reaction between ammonium salt (II) and benzylamine, producing the amidine, (III), in which the cation of the original salt has been replaced by benzylammonium. The anion and cation of (I), along with indications of the crystallographic symmetry to which they are subject, are shown in Figs. 1 and 2, respectively.

(I)

(I) X = PhCH$_2$NH$_3$

(II) X = NH$_4$

(III)
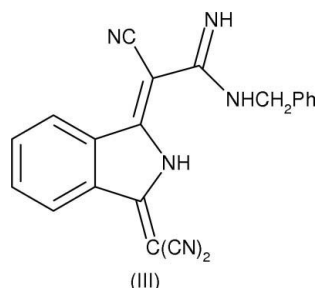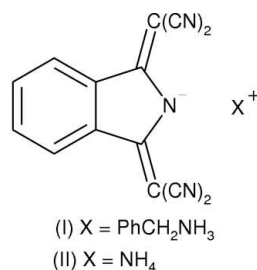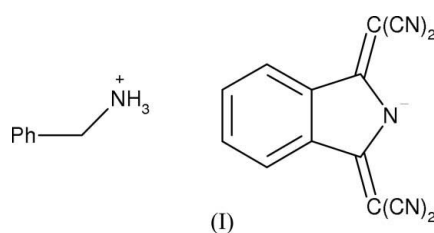
In the anion, the lengths of the N1—C1 and C1—C5 bonds and their symmetry-related equivalents [1.363 (2) and 1.382 (3) Å, respectively] are surprisingly long for their type, which is taken as an indication of their involvement in the delocalization of the negative charge on the anion. Another feature of the structure of the anion is the dihedral angle of 5.77 (15)° between the plane of the five-membered ring and

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Figure 1
A view of the anion of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii. [Symmetry code (i) x, $-y$, z.]
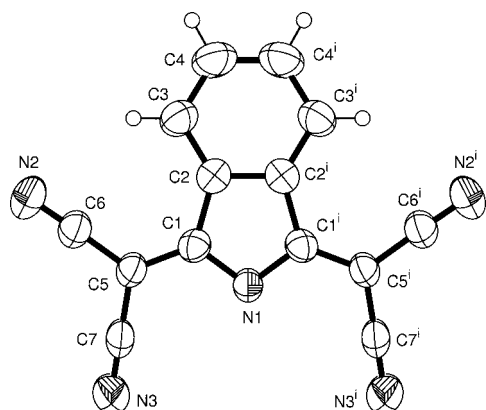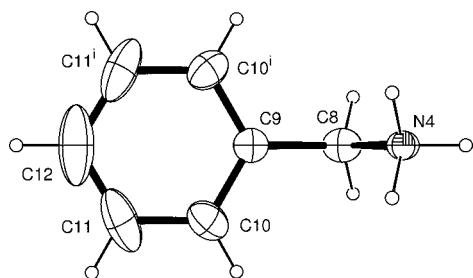

Figure 2
A view of the cation of (I). Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small circles of arbitrary radii. [Symmetry code (i) x, $-y$, z.]
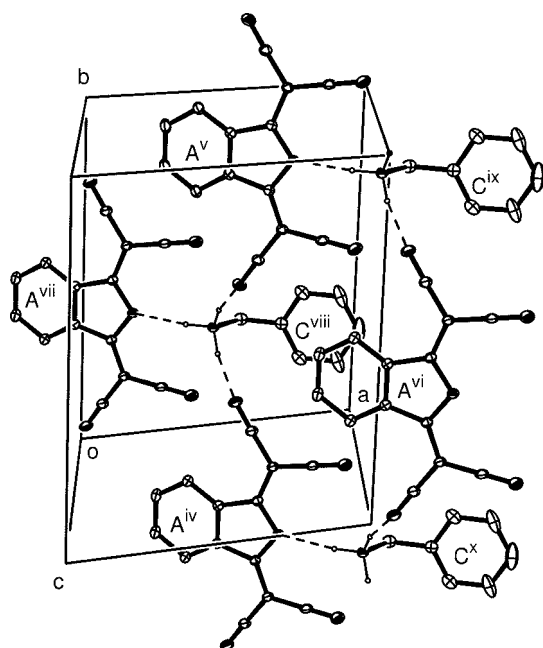

Figure 3
Hydrogen bonding in (I). Displacement ellipsoids are drawn at the 10% probability level. H atoms involved in inter-ion contacts (dashed lines) are shown as small circles of arbitrary radii. Ions are identified according to type as C for cations and A for anions. [Symmetry codes: (iv) $1 - x$, y, $1 - z$; (v) $1 - x$, $1 - y$, $1 - z$; (vi) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$; (vii) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (viii) $\frac{1}{2} + x$, $\frac{1}{2} + y$, $\frac{1}{2} + z$; (ix) $1 + x$, $1 + y$, $1 + z$; (x) $1 + x$, y, $1 + z$.]

that of the $C(CN)_2$ group. In this case, the displacements of the atoms of both $C(CN)_2$ groups are all in the same sense relative to the plane of the five-membered ring. The only notable feature of the structure of the cation is the dihedral angle of 90.00 (11)° between the plane defined by atoms N4/C8/C9 and that of the benzene ring. The most striking feature of the structure of (I) is the inter-ion connectivity created by the N—H···N hydrogen bonds given in Table 1. These hydrogen bonds, which involve all three of the H atoms of the NH_3 group of the benzylammonium cation with three of the five N atoms of the anion as acceptors, create sheets of ions parallel to (10$\bar{1}$), interconnected as shown in Fig. 3. The hydrogen-bond motif, in the graph-set notation of Bernstein *et al.* (1995), which recurs throughout the layer is $R_6^6(28)$ and is exemplified in Fig. 3 by the connectivity of the species $A^{iv}/C^{viii}/A^v/C^{ix}/A^{vi}/C^x$. The disposition of the H atoms in the NH_3 group demands some degree of depth or thickness within the layers, and this requirement is met in such a way as to accommodate the first of the π–π overlaps given in Table 2 and exemplified in Fig. 3 by the situation for C^{viii} and A^{vi}. The second π–π overlap given in Table 2 occurs between layers and involves rings which are related to one another by a crystallographic twofold axis which, because of the crystallographic symmetry of the ring and the anion of which it is part, can be expressed equally as a crystallographic centre of symmetry. This last is also the relationship between neighbouring layers.

Experimental

Crystal data

C$_7$H$_{10}$N$^+$·C$_{14}$H$_4$N$_5^-$	D_x = 1.254 Mg m^{-3}
M_r = 350.38	Mo $K\alpha$ radiation
Monoclinic, $I2/m$	Cell parameters from 14
a = 11.46 (2) Å	reflections
b = 13.094 (5) Å	θ = 8.5–12.4°
c = 13.563 (9) Å	μ = 0.08 mm^{-1}
β = 114.22 (5)°	T = 295 (2) K
V = 1857 (4) Å^3	Block, orange
Z = 4	0.44 × 0.44 × 0.30 mm

Data collection

Nicolet P3 four-circle diffractometer	$\theta_{max} = 25.1°$
ω–2θ scans	$h = 0 \rightarrow 12$
Absorption correction: none	$k = 0 \rightarrow 15$
1803 measured reflections	$l = -16 \rightarrow 14$
1714 independent reflections	2 standard reflections
1044 reflections with $I > 2\sigma(I)$	every 50 reflections
$R_{int} = 0.017$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.99$	$\Delta\rho_{max} = 0.14$ e Å^{-3}
1714 reflections	$\Delta\rho_{min} = -0.15$ e Å^{-3}
138 parameters	Extinction correction: SHELXL97
H atoms treated by a mixture of	Extinction coefficient: 0.0037 (9)
independent and constrained	
refinement	

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N4—H4$B\cdots$N1^i	0.99 (4)	2.28 (4)	3.227 (6)	159 (3)
N4—H4$A\cdots$N2^{ii}	1.02 (2)	2.02 (2)	3.024 (3)	167.2 (19)

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

Table 2
Parameters (Å, °) for π–π contacts in (I).

$CgI\cdots CgJ$	$Cg\cdots Cg$	α	β	γ	CgI_{perp}	CgJ_{perp}
$Cg1\cdots Cg2$	3.551	6.26	2.54	3.72	3.544	3.548
$Cg1\cdots Cg1^{xi}$	3.448	0.00	6.64	6.64	3.424	3.424

Notes: Ring 1, with centroid $Cg1$, is defined by N1/C1/C2/C2^i/C1^i; ring 2, with centroid $Cg2$, is defined by C9/C10/C11/C12/C11^i/C10^i. CgX_{perp} ($X = I$ or J) is the perpendicular distance of the centroid of ring X to the least squares plane of ring Y ($X \neq Y$). α is the dihedral angle between the planes of the rings. β and γ are the angles at CgX between $Cg\cdots Cg$ and CgX_{perp} for $X = I$ and J, respectively. Symmetry codes: (i) $x, -y, z$; (xi) $1 - x, y, -z$.

In this structure, both ions are bisected by a crystallographic mirror plane. The only atoms in general positions and replicated therefore by crystallographic symmetry to complete the ions are, in the benzylammonium counter-cation, one H atom of each of the NH$_3$ group and the methylene group and the C atoms, and the H atoms attached to them, *ortho* and *meta* to the methylene group, and in the anion, all atoms except the N atom in the five-membered ring. The somewhat extreme anisotropic displacement parameters associated with atoms C11 and C12 are attributed to a degree of disorder in these sites which has not been modelled in detail. Difference-map peaks provided approximate positions for the H atoms of the NH$_3$ group. These H atoms were then refined with isotropic displacement parameters in the usual manner. H atoms attached to C atoms were placed in calculated positions, with C—H set at 0.93 and 0.97 Å for aryl and methylene H atoms, respectively, and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C) in both cases.

Data collection: *Nicolet P3 software* (Nicolet, 1980); cell refinement: *Nicolet P3 software*; data reduction: *RDNIC* (Howie, 1980); 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); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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