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1,3-Diethylbenzimidazolium iodide

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Key indicators

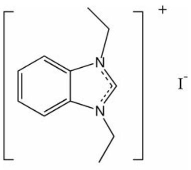
Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.008 Å
R factor = 0.041
wR factor = 0.114
Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title salt, $C_{11}H_{15}N_2^+\cdot I^-$, crystallizes with two formula units in the asymmetric unit. The two crystallographically unique cations form alternating columns along the *a* axis, linked by protruding ethyl groups and interspersed with iodide counter-ions. Cations in a given column stack in centrosymmetrically related pairs with interionic C···C and C···N distances consistent with substantial π–π bonding. One of the iodide ions appears to form a weak hydrogen bond with the most acidic proton in one of the cations.

Comment

Our long-standing interest in imidazole and benzimidazole chemistry has led us to prepare ionic salts (Stibrany, Potenza, & Schugar, 2002), catalysts (Patil *et al.*, 2003; Stibrany, Schulz *et al.*, 2003; Stibrany, Matturo *et al.*, 2002), geometrically constraining ligands (Knapp *et al.*, 1990; Stibrany, Lobanov *et al.*, 2003), and proton sponges (Stibrany, Schugar & Potenza, 2002) based on these species. The title salt, (I), whose structure we report here, was obtained as a side product in the alkylation of benzimidazole as part of a larger synthetic procedure.



(I)

The structure of (I) contains two 1,3-diethylbenzimidazolium cations and two iodide ions in the asymmetric unit (Fig. 1). The benzimidazole fragments in both unique cations are planar to within 0.01 Å, while the terminal

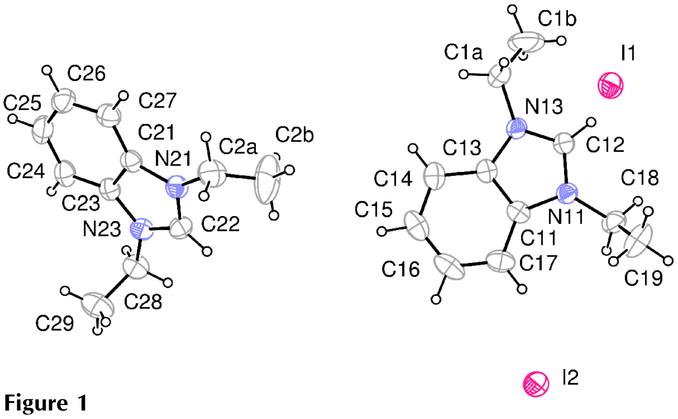
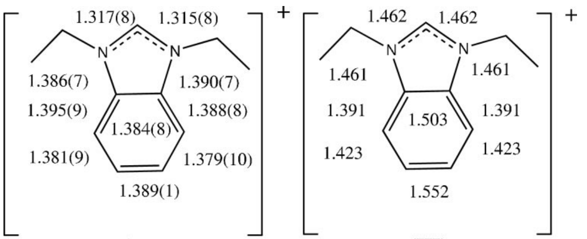


Figure 1
The contents of the asymmetric unit, showing 30% probability displacement ellipsoids.

methyl groups lie on opposite sides of the plane, conferring upon each cation a *trans* conformation. Corresponding bond distances and angles within the two unique cations give r.m.s. fits of 0.011 Å and 0.40°, respectively, demonstrating the extent to which the cations are equivalent. Despite these similarities, they do not appear to be related by either crystallographic or non-crystallographic symmetry. Supporting this view is the observation that the largest correlation coefficient in the structure refinement is 0.52.

Qualitatively, bond distances in the imidazolium fragments of the cations show the typical short (N11—C12 and N13—C12) and long (N11—C11, N13—C13 and C11—C13) variation characteristic of imidazolium and benzimidazolium species. The N11—C12 and N13—C12 distances are equal within experimental error, consistent with electron delocalization over the benzimidazolium imidazole fragments. A search of the Cambridge Structural Database (Version 5.24; Allen, 2002) revealed two additional structures containing 1,3-diethylbenzimidazolium cations [refcodes KEKQAS, (II) (Wang *et al.*, 1999), and CILFUY (III) (Gritsenko *et al.*, 1999)].



(II)

(III)

Metric parameters in the benzimidazolium fragments in (I) agree well with those reported for (II), but not with those for (III). In particular, corresponding bond distances in the planar imidazolium fragments of (I) and (II) agree with each other within experimental error. In contrast, structure (III) exhibits an unusual non-planar benzimidazolium unit with several anomalously long bond distances, including all of the C—N distances in the imidazolium fragment and several of the C—C distances in the benzene ring. These derived parameters are so unusual that they suggest the structure might be in error.

In the crystal structure (Fig. 2), the cations form columns along the *a* axis; these are linked by protruding ethyl groups and interspersed with columns of iodide ions centered approximately along $[a, \frac{1}{4}, \frac{1}{4}]$, and similar axes. One of the iodide ions, I1, appears to form a weak hydrogen bond with the H22—C22 unit (Table 2) which contains the most acidic proton in the cation. The comparable D—H···A unit involving I2, C12—H12···I2, exhibits metric parameters just outside the range considered acceptable for hydrogen bonding. Each column of cations contains only one of the unique cations in the asymmetric unit and is linked *via* its ethyl groups to four columns containing only cations of the second type. Cations in a given column (Fig. 3) stack head-to-tail in centrosymmetrically related pairs. One pair exhibits interionic C···C and C···N distances ranging from 3.439 (7) to 3.565 (7) Å for nine contacts, while the second exhibits seven comparable contacts ranging from 3.397 (8) to 3.559 (6) Å. These observations are consistent with substantial interionic π–π bonding similar to that noted previously by Wang *et al.* (1999).

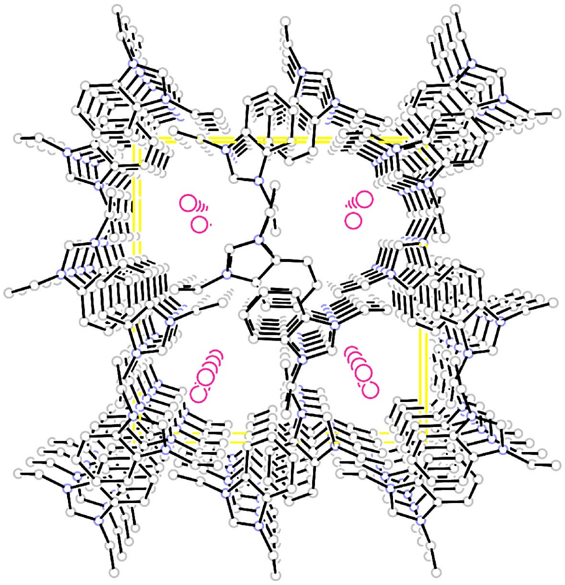


Figure 2
View of the structure along the *a* axis. The origin is at the upper left and the *b* and *c* axes are horizontal and vertical, respectively. H atoms have been omitted for clarity.

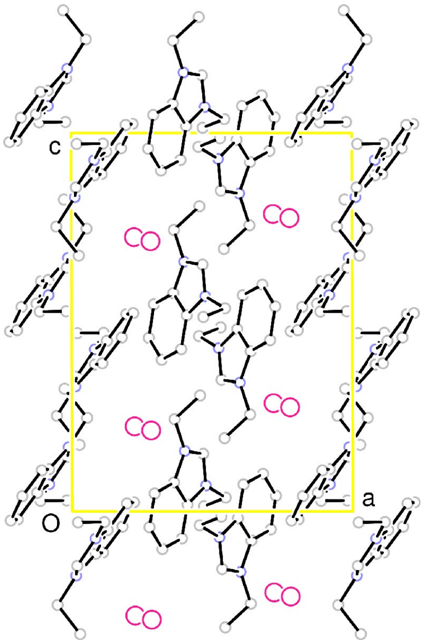


Figure 3
Projection of the structure along the *b* axis. H atoms have been omitted for clarity.

Experimental

A modified procedure for the alkylation of benzimidazoles was utilized for the preparation of *N*-ethylbenzimidazole (Stibrany Lobanov *et al.*, 2003). In this procedure 1.05 molar equivalents of iodoethane per equivalent of benzimidazole were used to alkylate benzimidazole. Upon work-up, a small number of crystals of the title salt, (I), were obtained as a side product.

Acta Cryst. (2004). E**60**, o28–o30 Robert T. Stibrany *et al.* • $C_{11}H_{15}N_2^+ \cdot I^-$ **o29**

Crystal data

$C_{11}H_{15}N_2^+\cdot I^-$
$M_r = 302.15$
Monoclinic, $P2_1/c$
$a = 11.2578$ (5) Å
$b = 14.6014$ (7) Å
$c = 15.1903$ (5) Å
$\beta = 90.212$ (3)°
$V = 2496.96$ (18) Å^3
$Z = 8$

$D_x = 1.607$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 900 reflections
$\theta = 2.7$–22.5°
$\mu = 2.53$ mm^{-1}
$T = 297$ (1) K
Rod, colorless
0.50 × 0.10 × 0.04 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.690$, $T_{\max} = 0.904$
17742 measured reflections

4368 independent reflections
3384 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\max} = 25.0°$
$h = -12 \rightarrow 13$
$k = -16 \rightarrow 17$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.114$
$S = 1.00$
4368 reflections
257 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 2.1072P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

N11—C12	1.323 (6)	N21—C22	1.322 (6)
N13—C12	1.321 (6)	N23—C22	1.328 (6)
N11—C11	1.394 (6)	N21—C21	1.387 (6)
N13—C13	1.392 (6)	N23—C23	1.382 (6)
C11—C13	1.375 (7)	C21—C23	1.393 (7)
C11—C17	1.385 (7)	C21—C27	1.395 (7)
C13—C14	1.389 (7)	C23—C24	1.387 (7)
C14—C15	1.393 (10)	C24—C25	1.378 (9)
C15—C16	1.381 (10)	C25—C26	1.380 (9)
C16—C17	1.364 (9)	C26—C27	1.372 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
C22—H22···I2$^{\rm i}$	0.93	2.99	3.820 (5)	149

Symmetry code: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

During refinement, the ethyl groups C1a—C1b and C2a—C2b exhibited relatively large displacement parameters and anomalously short C—C distances. In the final refinement cycles, these two C—C distances were restrained, leading to more reasonable distances. H atoms were included in ideal positions, with Csp^3—H and Csp^2—H distances set at 0.97 and 0.93 Å, respectively. Attempts to refine H-atom coordinates did not lead to significant improvement in the structure. H-atom displacement parameters were set as $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The largest five peaks in the final difference map ranged from 0.64 to 1.18 e Å^{-3} and were located between 0.68 and 0.81 Å from the iodide ions. The next highest residual had an electron density of 0.40 Å^{-3}.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *ORTEP*32 (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

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o30 Robert T. Stibrany *et al.* • $C_{11}H_{15}N_2^+\cdot I^-$ *Acta Cryst.* (2004). E**60**, o28–o30