Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N-Methylbenzimidazole *N*-methylbenzimidazolium hexafluorophosphate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.038
wR factor = 0.106
Data-to-parameter ratio = 12.9

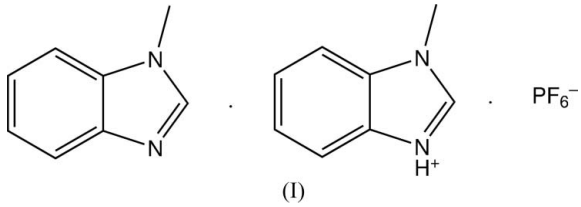
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 25 November 2005
Accepted 28 November 2005
Online 7 December 2005

In the title compound, $C_8H_8N_2{\cdot}C_8H_9N_2^+{\cdot}PF_6^-$, 50% of the *N*-methylbenzimidazole residues are protonated. An N—H$\cdots$N$^+$ hydrogen bond with a $D\cdots A$ distance of 2.641 (2) Å is formed. The organic molecules are located on crystallographic mirror planes and the PF_6^- counter-ions are located on crystallographic 2/*m* sites.

Comment

During our investigations of ruthenium–bipyridine complexes with DNA model bases (Velders *et al.*, 1999, 2000), we obtained crystals of both *cis*-[Ru(bipyridine)$_2$(*N*-methylbenzimidazole)$_2$](PF$_6$)$_2$ (Velders *et al.*, 2005) and the title compound, (I), which contains a partly protonated *N*-methylbenzimidazole. The Cambridge Structural Database (Version 5.26 of November 2004, Updates 1 and 2; Allen, 2002) reports no other protonated *N*-methylbenzimidazole structures.



(I)

The asymmetric unit of (I) contains an *N*-methylbenzimidazole molecule located on a crystallographic mirror plane and a hexafluorophosphate counter-ion positioned on a crystallographic 2/*m* site. At 2.641 (2) Å from atom N3, a symmetry-related N3 atom is located. The short N$\cdots$N distance and the electron-density maps strongly suggest the presence of an [N—H$\cdots$N]$^+$ hydrogen bond, where the H atom displays symmetry-induced disorder (see refinement details and Fig. 2). Atom N3 turns out to be protonated in 50% of the *N*-methylbenzimidazole residues, meaning that the title compound is a co-crystal of neutral *N*-methylbenzimidazole and the hexafluorophosphate salt of protonated *N*-methylbenzimidazole.

The crystal packing of (I) displays layers of partly protonated *N*-methylbenzimidazole and PF_6^- counter-ions (Fig. 3). Due to their location on special positions, the centroids of all residues are located exactly in the *ac* plane. Short C—H$\cdots$F contacts (Table 2) further stabilize these layers.

Experimental

In a concentrated solution of *cis*-[Ru(bipyridine)$_2$(*N*-methylbenzimidazole)$_2$](PF$_6$)$_2$ (0.5 g, 0.5 mol), *N*-methylbenzimidazole (1.1 g,

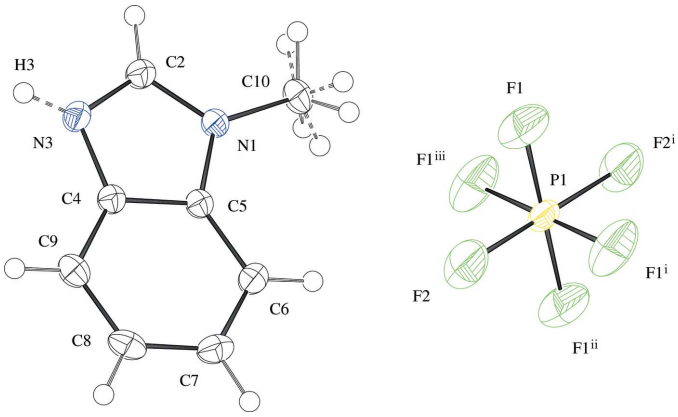


Figure 1
A view of the title compound, showing 50% probability displacement ellipsoids. Atom H3 and the disordered methyl H atoms have site-occupancy factors of 0.5. [Symmetry codes: (i) $-x$, y, $1-z$ (ii) $-x$, $-y$,$1-z$ (iii) x, $-y$, z.]

8 mmol) and NH_4PF_6 (3.1 g, 19 mmol) in a water–acetone mixture (1:2 *v*/*v*), transparent crystals of the title compound formed after a few weeks at 277 K. The crystalline material was isolated by filtration and washed with water.

Crystal data

$C_8H_8N_2{\cdot}C_8H_9N_2^+{\cdot}PF_6^-$
M_r = 410.31
Monoclinic, $C2/m$
a = 14.930 (4) Å
b = 6.6524 (12) Å
c = 9.0261 (12) Å
β = 90.214 (17)°
V = 896.5 (3) Å^3
Z = 2
D_x = 1.520 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 263 reflections
θ = 2.0–25.0°
μ = 0.22 mm^{-1}
T = 150 K
Block, colourless
0.3 × 0.2 × 0.2 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans and ω scans with κ offset
Absorption correction: none
3017 measured reflections
1072 independent reflections
986 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.4°
$h = -19 \rightarrow 17$
$k = -7 \rightarrow 8$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.106
S = 1.03
1072 reflections
83 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.93P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.339 (2)	N3—C2	1.321 (2)
N1—C5	1.380 (2)	N3—C4	1.390 (2)
N1—C10	1.462 (2)		
C2—N1—C10	126.30 (15)	C2—N3—C4	106.44 (15)
C2—N1—C5	107.56 (15)	N1—C2—N3	112.18 (16)
C5—N1—C10	126.13 (15)		

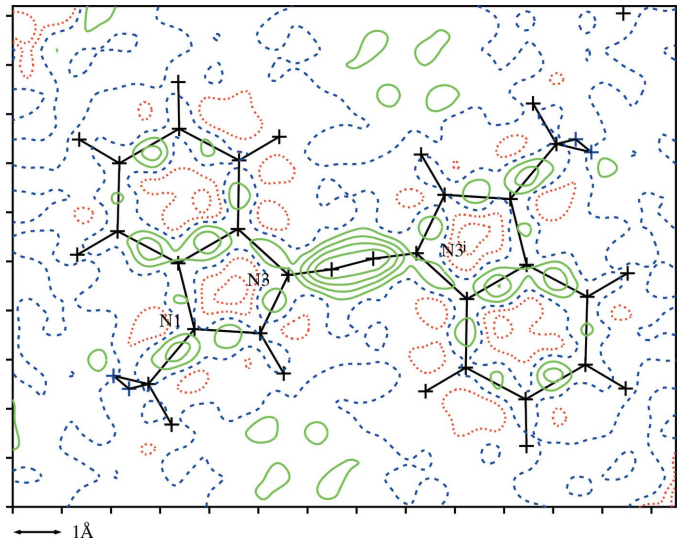


Figure 2
Difference Fourier map of the *ac* plane, calculated without the contribution of atom H3. Green contours represent positive residual density, red contours represent negative residual density and the blue contours represent the zero level. Contour increment is 0.10 e Å^{-3}.

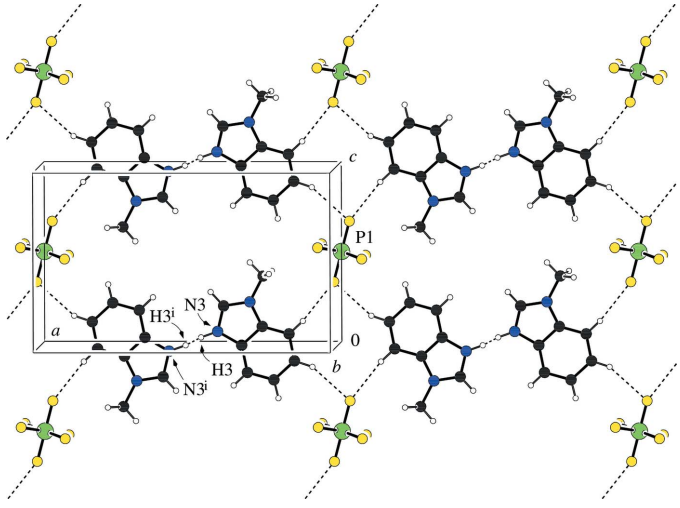


Figure 3
The crystal packing of (I) in the *ac* plane. Due to their location at special positions, the centroids of all displayed residues are located in the *ac* plane. The H atom in the $[N{-}H{\cdots}N]^+$ hydrogen bond is disordered over positions H3 and H3^i, as indicated in the plot. [Symmetry code: (i) $1-x$, y, $-z$.]

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···N3^i	0.89 (5)	1.76 (5)	2.641 (2)	176 (5)
C6—H6···F2	0.95	2.52	3.463 (3)	171
C7—H7···F2^{ii}	0.95	2.54	3.428 (3)	156

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

The short N3···N3($1-x$, y, $-z$) distance strongly suggests the presence of a hydrogen bond, either a symmetric $[N{\cdots}H{\cdots}N]^+$ bond or an asymmetric $[N{-}H{\cdots}N]^+$ hydrogen bond, where the H atom

displays symmetry-induced disorder. A difference Fourier map calculated without the contribution of atom H3 displays an elongated area of residual electron density between the two symmetry-related N3 atoms (Fig. 2). This density cannot be resolved into two separate H-atom positions. Refinement of the coordinates of a disordered asymmetrically located H atom, rather then an ordered symmetrically located H atom, resulted in a stable position for the H atom, with an N—H bond length of 0.89 (5) Å. The methyl group of *N*-methylbenzimidazole was refined as a rigid group, allowing for rotation around the N—C bond and displaying disorder over the crystallographic mirror plane in which N—C is located. All other H atoms were introduced in calculated positions, riding on their carrier atoms, with C—H = 0.95–0.98 Å. The constraint U_{iso}(H) = 1.2 U_{eq}(carrier) was applied for all H atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

This work was supported in part (ALS) by the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO). Professor Dr Jan Reedijk (Leiden Institute of Chemistry) is thanked for financial support and for critically reading the manuscript.

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