Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

6-Methoxycarbonyl-2-methyl-1*H*-benzimidazol-3-ium nitrate hemihydrate

Cai-Feng Ding,[a] Shu-Sheng Zhang,[b]* Xue-Mei Li,[b] Hong Xu[a] and Ping-Kai Ouyang[a]

[a]College of Life Science and Pharmaceutical Engineering, Nanjing University of Technology, 210093 Nanjing, Jiangsu, People's Republic of China, and [b]College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, 266042 Qingdao, Shandong, People's Republic of China

Correspondence e-mail: zhangshush@public.qd.sd.cn

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.078
wR factor = 0.249
Data-to-parameter ratio = 12.8

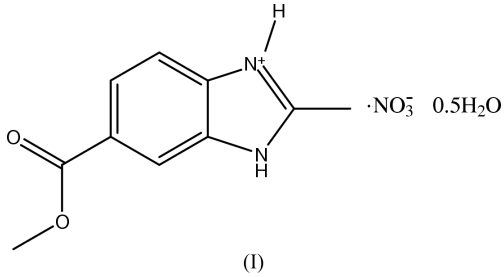
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{10}H_{11}N_2O_2^+\cdot NO_3^-\cdot 0.5H_2O$, crystallizes in a monoclinic unit cell with two benzimidazolium cations, two NO_3^- anions and one water molecule in the asymmetric unit. Intermolecular hydrogen bonds link the cations, anions and water molecules into two-dimensional layers.

Received 16 November 2004
Accepted 19 November 2004
Online 27 November 2004

Comment

Benzimidazole derivatives and their metal complexes are of considerable interest due to their biological activities (Matthews *et al.*, 1998), and are widely used for medicaments (David *et al.*, 1993). Benzimidazole derivatives are also used as metal antiseptics, photosensitizers, surfactants, fluorescence whitening agents and photosensitive dyes (Matthews *et al.*, 1996; Raban *et al.*, 1985). In this paper, we report the synthesis and crystal structure of the title compound, (I).



(I)

The asymmetric unit of (I) contains two crystallographically independent benzimidazolium cations *A* and *B*, two NO_3^- anions and one water molecule (Fig. 1). The cations are parallel to each other, with a dihedral angle of 2.5 (2)° between the mean planes of the two benzimidazole moieties.

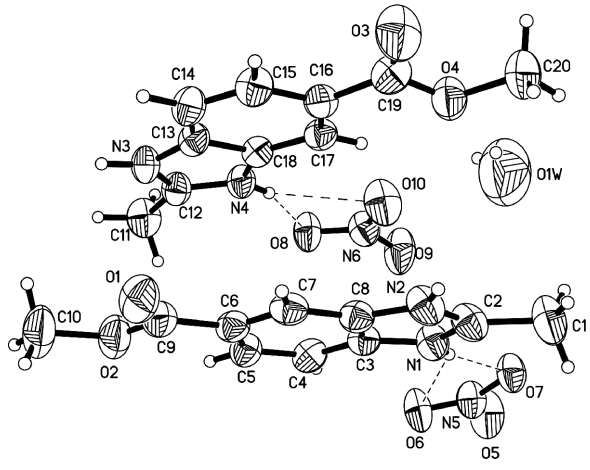


Figure 1
View of the asymmetric unit of (I), showing 50% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

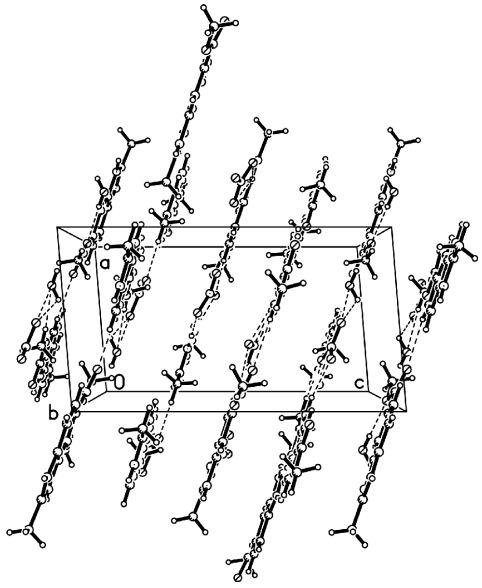


Figure 2
Packing diagram of (I), showing the layers. Dashed lines denote short-contact interactions.

Compound (I) is a hemihydrated nitrate salt.

The bond lengths in the benzimidazole skeleton (Table 1) show a character intermediate between single and double bonds, implying a highly π-conjugated delocalization effect, comparable with those observed in other benzimidazole derivatives (Bei *et al.*, 2004; Ozbey *et al.*, 1998). Each cation is almost planar, with dihedral angles of 1.6 (3) and 0.6 (3)° between the benzene ring and the five-membered ring in *A* and *B*, respectively.

Within the asymmetric unit, the water molecule is linked to the cation and anion, acting as a hydrogen-bond donor *via* O1*W*—H1*W*1···O4 and O1*W*—H2*W*1···O10 interactions (Table 2). In the crystal packing, the cations, anions and water molecules are connected into two-dimensional layers, which are stacked along the *c* axis (Fig. 2).

Experimental

A solution of ethyl 3,4-diaminobenzoate (1 g, 6 mmol) in acetic acid (30 ml) was heated under reflux for 10 h. The mixture was then poured into a beaker containing 50 ml ice water, yielding quantities of precipitate. After filtration, the residue was dissolved in ethanol (30 ml) and $Cu(NO_3)_2{\cdot}9H_2O$ (3.5 g, 10 mmol) was added. The mixture was stirred at 351 K for 2 h. The yellow solution was left to stand at room temperature, and single crystals of the title compound were obtained unexpectedly.

Crystal data

$C_{10}H_{11}N_2O_2^+{\cdot}NO_3^-{\cdot}0.5H_2O$
M_r = 262.23
Monoclinic, $P2_1/c$
a = 7.9107 (6) Å
b = 21.5276 (17) Å
c = 14.2691 (11) Å
β = 94.573 (2)°
V = 2422.3 (3) Å^3
Z = 8
D_x = 1.438 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 937 reflections
θ = 2.4–25.0°
μ = 0.12 mm^{-1}
T = 293 (2) K
Block, brown–yellow
0.20 × 0.15 × 0.09 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.977, T_{max} = 0.989
12579 measured reflections
4284 independent reflections
1703 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
θ_{max} = 25.0°
$h = -5 \rightarrow 9$
$k = -25 \rightarrow 25$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.078
$wR(F^2)$ = 0.249
S = 0.97
4284 reflections
334 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1161P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—C9	1.354 (7)	N2—C2	1.321 (6)
O2—C10	1.474 (6)	N3—C12	1.327 (6)
O4—C19	1.329 (6)	N3—C13	1.384 (6)
O4—C20	1.455 (6)	N4—C12	1.321 (5)
N1—C2	1.318 (6)	N4—C18	1.383 (6)
N1—C3	1.385 (6)		
C2—N1—C3	110.1 (5)	C8—C3—N1	105.8 (5)
C2—N2—C8	109.4 (5)	C3—C8—N2	106.1 (5)
C12—N3—C13	110.4 (4)	N4—C12—N3	107.8 (5)
C12—N4—C18	110.2 (4)	C14—C13—C18	122.0 (5)
N1—C2—N2	108.7 (5)	N4—C18—C13	106.2 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*A*···O6	0.86	2.34	3.040 (6)	138
N1—H1*A*···O7	0.86	2.07	2.906 (6)	163
N2—H2*A*···O8^{i}	0.86	2.36	3.120 (6)	148
N2—H2*A*···O9^{i}	0.86	2.00	2.804 (7)	154
N3—H3*A*···O5^{ii}	0.86	2.43	3.135 (6)	139
N3—H3*A*···O7^{ii}	0.86	2.04	2.868 (5)	160
N4—H4*A*···O8	0.86	2.01	2.839 (6)	163
N4—H4*A*···O10	0.86	2.40	3.090 (6)	138
O1*W*—H1*W*1···O4	0.85	2.43	3.28 (2)	173
O1*W*—H2*W*1···O10	0.85	2.15	2.72 (2)	124
C1—H1*B*···O9^{i}	0.96	2.55	3.350 (8)	140
C5—H5*A*···O3^{iii}	0.93	2.49	3.140 (7)	127
C10—H10*A*···O1*W*^{ii}	0.96	2.47	3.42 (2)	173
C15—H15*A*···O6^{iv}	0.93	2.56	3.359 (7)	145
C17—H17*A*···O10	0.93	2.55	3.258 (7)	133

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

After their location in a difference Fourier map, all H atoms were positioned geometrically (O—H = 0.95, N—H = 0.86 and C—H = 0.93–0.96 Å) and refined as riding, with U_{iso}(H) = 1.2 or 1.5 times U_{eq}(parent atom).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

This project was supported by the National Natural Science Foundation of China (No. 20275020 and 20475030) and the

Outstanding Adult-Young Scientific Research Encouraging Foundation of Shandong Province (No. 03BS081).

References

Bei, F. L., Chen, H. Q., Yang, X. J., Lu, L. D. & Wang, X. (2004). *Chin. J. Org. Chem.* **24**, 300–305.
David, S. S., Abhijit, M. & David, M. P. (1993). *Chem. Rev.* **93**, 2295–2316.
Matthews, C. J., Clegg, W., Elsegood, M. R. J., Leese, T. A., Thorp, D., Thornton, P. & Lockhart, J. C. (1996). *J. Chem. Soc. Dalton Trans.* pp. 1531–1538.
Matthews, C. J., Clegg, W., Heath, S. L., Martin, N. C. & Hill, M. N. S. (1998). *Inorg. Chem.* **37**, 199–207.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Ozbey, S., Ide, S. & Kendi, E. (1998). *J. Mol. Struct.* **442**, 23–30.
Raban, M., Chang, H., Craine, L. & Hortelano, E. (1985). *J. Org. Chem.* **50**, 2205–2210.
Sheldrick, G. M. (1996). *SADABS.* University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL.* Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.