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3,3′-Diethyl-1,1′-butylenedi[5(6)-methylbenzimidazolium] diiodide dihydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
Disorder in main residue
R factor = 0.057
wR factor = 0.114
Data-to-parameter ratio = 21.5

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

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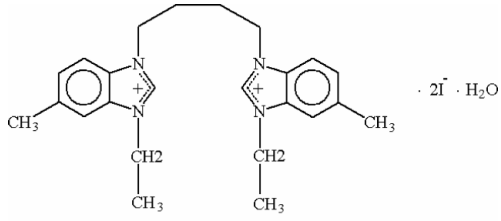
The molecule of the title compound, $C_{24}H_{32}N_4^{2+}\cdot 2I^-\cdot 2H_2O$, possesses C_i symmetry with the inversion center at the midpoint of the central C—C bond between two benzimidazolium rings. In the crystal structure, the molecules stack along the *a* axis, forming channels occupied by a chain of I^- ions bridged by water molecules *via* O—H···I hydrogen bonds.

Comment

Bis-benzimidazoles constitute a family of heterocycles that have begun to attract particular interest because of their potential use in cancer therapy by DNA binding and blocking, and their use as ligands for metals (Rezende *et al.*, 2001). A previous study of bis-benzimidazoles differing in the number of cationic groups and benzimidazole sub-units suggested that, although electrostatic interactions and hydrogen bonding provided some binding energy, the single most important factor for DNA binding is the van der Waals interactions within the minor groove of DNA (Cazarny *et al.*, 1995).



(I)

In light of the general importance of benzimidazole compounds, the study of benzimidazoles and bis-benzimidazole derivatives remains an active area of research, in spite of previous extensive investigations. Benzimidazole itself and the 5- or 6-substituted derivatives can show a tautomerism of the imidazole ring (Elderfield, 1957). Following our work on the synthesis and antibacterial activity of bis-benzimidazole compounds (Küçükbay *et al.*, 2003), we studied the crystal structure of the title compound, (I), in order to determine whether the same tautomerism could exist in this type of bis-benzimidazole derivative.

The structure of (I) has a step-like non-planar conformation (Fig. 1), and the benzimidazolium rings are planar, within experimental error. The tautomerism of the imidazole ring is found to be present. Atom C13*A* is bonded to atom C3, and atom C13*B* to atom C4, with site occupancies of 0.45 (1) and 0.55 (1), respectively. The bond lengths and angles in (I) agree with the corresponding values in bis(1-methyl-3-ethylbenzimidazolidine-2-ylium) tetrafluoroborate (Aydın *et al.*, 1998), in 1,3-dimethylbenzimidazole-2-selenone (Aydın *et al.*,

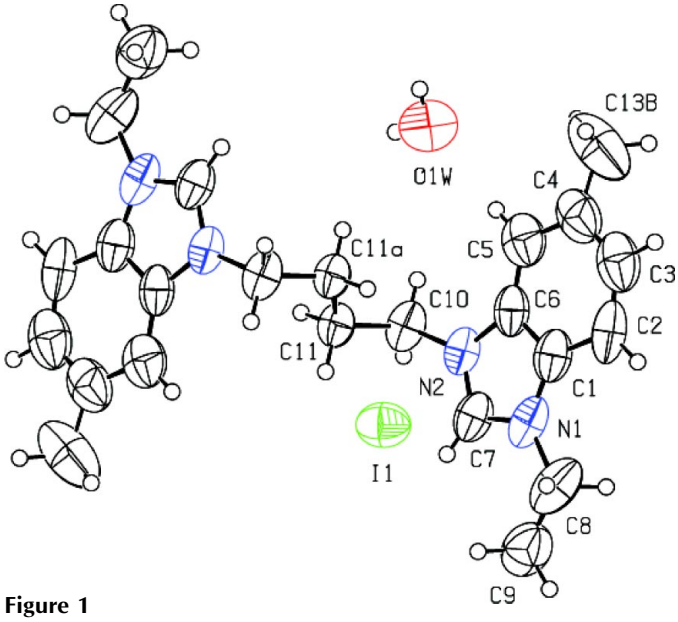


Figure 1
The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme. The minor disorder component is omitted.

1999), in 1-(2-ethoxyethyl)-3-(2-methoxyethyl)benzimidazolium chloride monohydrate (Öztürk *et al.*, 2001), and in 3,3′-bis(3-cyanopropyl)-1,1′-propylenedi(benzimidazolium) dichloride dihydrate (Akkurt *et al.*, 2003).

In the crystal structure, the molecules stack along the *a* axis, forming channels occupied by a chain of I^- ions bridged by water molecules *via* O—H···I hydrogen bonds (Fig. 2). There are also two C—H···*X* hydrogen bonds involving the benzimidazolium cation with the water molecule and the I^- anion (Table 2).

Experimental

All experiments were performed under argon using freshly distilled dry solvents. ^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Bruker DPX-400 high-performance digital FT–NMR (Bruker WM360, Bruker Instruments, Inc., Billercia, USA) spectrometer. Melting points were recorded using an Electrothermal melting point apparatus (Electrothermal 9200, Electrothermal Engineering Ltd, Essex, UK) and are uncorrected. The starting reactant 1,1′-butylenedi[5(6)-methylbenzimidazole] was synthesized from 5(6)-methylbenzimidazole and 1,4-dibromobutane, according to a literature procedure (Küçükbay *et al.*, 2003). 5(6)-Methylbenzimidazole shows tautomerism of the imidazole ring, as indicated in the literature (Elderfield, 1957). Hence, the starting compound is a mixture of both 5-methyl- and 6-methylbenzimidazole. The title compound, (I), was synthesized by adding ethyl iodide (0.4 ml, 4.95 mmol) to a solution of 1,1′-butylenedi[5(6)-methylbenzimidazole] (0.78 g, 2.47 mmol) in DMF (2 ml). The mixture was refluxed for 5 h. All the volatiles were then driven off and the crude product was recrystallized from EtOH/Et_2O (3:1), giving yellow crystals (yield: 1.48 g, 96%; m.p.: 506–507 K).

^{1}H NMR (DMSO): δ 1.57 (*t*, CH_2CH_3, 6H), 2.07 (*s*, $NCH_2CH_2CH_2$-CH_2N, 4H), 2.55 (*s*, CH_3, 6H), 4.50 (*q*, NCH_2CH_3, 4H), 4.53 (*s*, $NCH_2CH_2CH_2CH_2N$, 4H), 7.49–8.03 (*m*, Ar—H, 6H), 9.77 (*s*, CH, 2H). ^{13}C NMR (DMSO): δ 15.90, 22.93, 27.32, 47.94, 48.03, 114.84, 115.04, 129.83, 131.17, 133.10, 138.74, 143.09. Analysis calculated for $C_{24}H_{32}N_4I_2$: C 45.71, H 5.08, N 8.89%; found: C 45.60, H 5.02, N 8.84%.

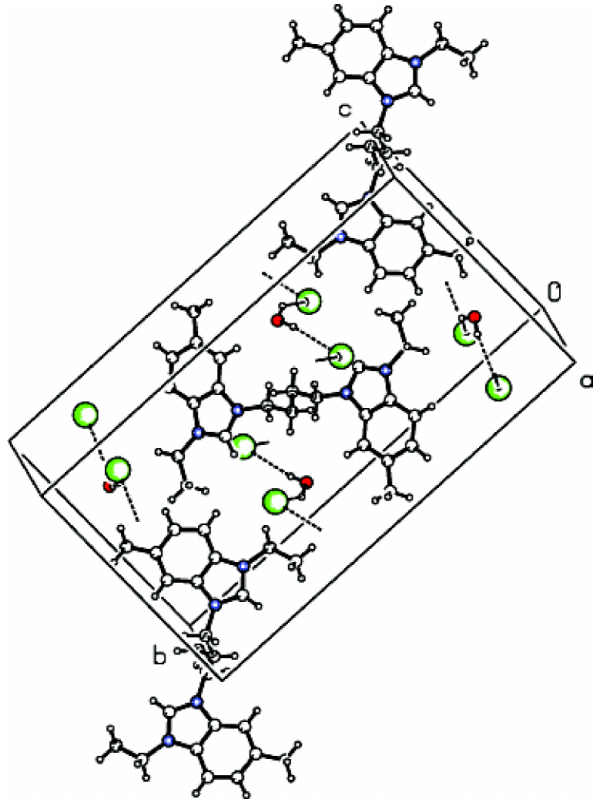


Figure 2
A view of the molecular packing and the hydrogen-bond contacts of (I).

Crystal data

$C_{24}H_{32}N_4^{2+}\cdot 2I^-\cdot 2H_2O$
M_r = 666.37
Monoclinic, $P2_1/c$
a = 5.4761 (3) Å
b = 21.7289 (12) Å
c = 12.2512 (6) Å
β = 104.156 (2)°
V = 1413.50 (13) Å^3
Z = 2
D_x = 1.566 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3391 reflections
θ = 2.5–28.3°
μ = 2.25 mm^{-1}
T = 293 (2) K
Prism, yellow
0.40 × 0.26 × 0.24 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.442, T_{max} = 0.583
8590 measured reflections
3391 independent reflections
2496 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 28.3°
$h = -7 \rightarrow 7$
$k = -28 \rightarrow 25$
$l = -12 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.114
S = 0.97
3391 reflections
158 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2 + 4.7667P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.77 e Å^{-3}
$\Delta\rho_{min}$ = −0.79 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C7	1.340 (8)	N2—C7	1.323 (8)
N1—C8	1.477 (8)	C3—C13*A*	1.521 (17)
N1—C1	1.382 (8)	C4—C13*B*	1.40 (2)
N2—C10	1.485 (6)	C10—C11	1.509 (7)
N2—C6	1.389 (7)	C11—C11^{i}	1.494 (7)
C1—N1—C7	108.5 (5)	N1—C1—C2	131.5 (6)
C7—N1—C8	126.3 (5)	N2—C6—C1	106.8 (5)
C1—N1—C8	125.1 (5)	N2—C6—C5	132.2 (6)
C6—N2—C7	108.6 (5)	N1—C7—N2	109.5 (5)
C7—N2—C10	124.5 (5)	N1—C8—C9	113.4 (6)
C6—N2—C10	126.9 (5)	N2—C10—C11	112.2 (4)
N1—C1—C6	106.6 (5)	C10—C11—C11^{i}	114.1 (4)
C1—N1—C8—C9	−172.5 (6)	N1—C1—C2—C3	178.6 (6)
C7—N1—C8—C9	11.8 (10)	C2—C3—C4—C13*B*	179.8 (9)
C7—N2—C6—C5	179.2 (6)	C13*B*—C4—C5—C6	−178.9 (10)
C6—N2—C10—C11	−102.8 (6)	N2—C10—C11—C11^{i}	63.4 (5)
C7—N2—C10—C11	78.0 (6)	C10—C11—C11^{i}—C10^{i}	180.0 (4)
C2—C1—C6—C5	−0.2 (9)		

Symmetry code: (i) $1-x, 1-y, 1-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···I1^{i}	0.85	2.74	3.573 (6)	169
O1*W*—H2*W*···I1^{ii}	0.85	3.04	3.671 (6)	133
C5—H5*A*···O1*W*	0.93	2.35	3.276 (8)	175
C7—H7*A*···I1^{iii}	0.93	2.95	3.853 (6)	165

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $2-x, 1-y, 1-z$; (iii) $x-1, y, z$.

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. The U_{iso} values of the H atoms of the water molecule and the methyl groups were made equal to $1.5U_{eq}$(parent atom).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 1990) and *WinGX* (Farrugia, 1999).

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