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2,2'-(Iminodimethylene)dibenzimidazolium bis(perchlorate) methanol solvate

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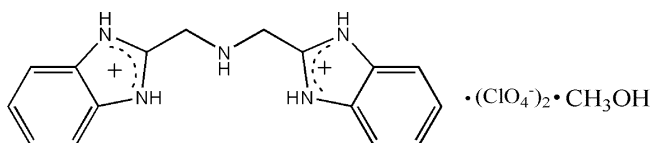
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 Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.058; wR factor = 0.169; data-to-parameter ratio = 15.6.

In the title compound, $\text{C}_{16}\text{H}_{17}\text{N}_5^{2+} \cdot 2\text{ClO}_4^- \cdot \text{CH}_3\text{OH}$, the dihedral angle between the two benzimidazolium ring systems is 34.6 (1°). The anions and solvent molecules are linked to the cation by $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. In the crystal structure, the combination of $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds results in two-dimensional layers running parallel to the (010) plane; these are in turn linked by $\pi-\pi$ interactions, forming a three-dimensional network.

Related literature

For related literature, see: Adams *et al.* (1990); Allen (2002); Berends & Stephan (1984); Bernstein *et al.* (1995); Bruno *et al.* (2002); Girasolo *et al.* (2000); Liao *et al.* (2001); Liu *et al.* (2004); Meng *et al.* (2005, 2006a,b); Spek (2003); Tarazon Navarro & McKee (2003); Xu *et al.* (2007); Young *et al.* (1995); Zheng *et al.* (2005).



Experimental

Crystal data

 $\text{C}_{16}\text{H}_{17}\text{N}_5^{2+} \cdot 2\text{ClO}_4^- \cdot \text{CH}_4\text{O}$
 $M_r = 510.29$

 Monoclinic, $P2_1/n$
 $a = 8.3359$ (4) Å

 $b = 18.0323$ (8) Å

 $c = 14.8532$ (7) Å

 $\beta = 102.944$ (1°)

 $V = 2175.89$ (18) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.36$ mm⁻¹
 $T = 295$ (2) K

 $0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1997)

 $T_{\min} = 0.900$, $T_{\max} = 0.932$

 24553 measured reflections
 4957 independent reflections

 3479 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.069$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.169$
 $S = 1.02$

4957 reflections

317 parameters

5 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.26$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1} \cdots \text{O7}^i$	0.86 (3)	2.42 (3)	3.200 (3)	150 (2)
$\text{N2}-\text{H2A} \cdots \text{O8}$	0.831 (16)	2.15 (2)	2.895 (3)	150 (3)
$\text{N2}-\text{H2A} \cdots \text{O9}$	0.831 (16)	2.489 (19)	3.233 (3)	150 (2)
$\text{N3}-\text{H3A} \cdots \text{O1}$	0.831 (16)	1.996 (17)	2.799 (3)	162 (2)
$\text{N4}-\text{H4A} \cdots \text{O1}$	0.857 (16)	1.985 (17)	2.823 (3)	166 (2)
$\text{N5}-\text{H5A} \cdots \text{O4}$	0.824 (16)	2.46 (2)	3.197 (4)	150 (2)
$\text{N5}-\text{H5A} \cdots \text{O5}$	0.824 (16)	2.21 (2)	2.939 (3)	147 (2)
$\text{O1}-\text{H1C} \cdots \text{O6}^{ii}$	0.805 (17)	2.00 (2)	2.765 (3)	159 (3)

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

Table 2

 Table 2 $\pi-\pi$ Stacking interactions ($^\circ$, Å).

C_{g_i}	C_{g_j}	Dihedral angle	CCD	Interplanar spacing
C_{g1}	C_{g2}^{iv}	0.42	3.854 (2)	3.349 (2)
C_{g1}	C_{g4}^{iv}	0.35	3.557 (2)	3.354 (2)
C_{g3}	C_{g2}^{iv}	0.85	3.612 (2)	3.360 (2)
C_{g3}	C_{g4}^v	0.36	3.929 (2)	3.453 (2)

CCD is the centroid-to-centroid distance; C_{g1} is the centroid of atoms N2/N3/C2/C3/C8; C_{g2} is the centroid of atoms N4/N5/C10/C11/C16; C_{g3} is the centroid of atoms C3-C8; C_{g4} is the centroid of atoms C11-C16. Symmetry codes: (iv) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (v) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2246).

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supplementary materials

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2,2'-(Iminodimethylene)dibenzimidazolium bis(perchlorate) methanol solvate

C.-S. Zhou, X.-Y. Huang and X.-G. Meng

Comment

Bis[N-(benzimidazol-2-ylmethyl)]amine (IDB) and its analogs have been utilized extensively in the synthesis of various metal complexes to mimic certain biological activities; these include superoxide dismutase (Liao *et al.*, 2001), DNA probe (Girasolo *et al.*, 2000), alkaline phosphatase (Young *et al.*, 1995). In IDB, each benzimidazole (bzim) arm possesses one imine N atom, one amine NH group and, at the centre, an NH group. The two imine N atoms can chelate metal ions, while the three NH groups can act as hydrogen bond donors. In the absence of metal coordination, the two imine N atoms can also act as hydrogen bond acceptors. The easily formed coordination and hydrogen-bonding interactions allow the central acyclic —CH₂—NH—CH₂— unit to possess various steric arrangements. In our and other reported organic complex analogs (Meng *et al.*, 2006a; Meng *et al.*, 2006b; Meng *et al.*, 2005; Zheng *et al.*, 2005; Liu *et al.*, 2004; Tarazon Navarro *et al.*, 2003) we find that IDB preferentially adopts a more extended conformation, with the two bzim groups pointing away from each other. However, in most examples of metal-complexes it adopts a more crowded conformation, with the two bzim units bending towards the same side of the central acyclic linkage (Berends & Stephan, 1984; Xu *et al.*, 2007; Adams *et al.*, 1990). With the aim of gaining more insight into the influence of solvents and anions on the crystal structure, we have synthesized H₂IDB²⁺·2ClO₄⁻·CH₃OH and report its molecular and supramolecular structure in this communication.

The two imine N atoms on both bzim arms are protonated, as confirmed by the residual electron peaks around the imine N atoms during the structure refinement. The positive charge on each imine N atom is delocalized in the imidazole ring, as evidenced by the near equivalence of bonds C2—N2/C2—N3 [1.323 (3)/1.320 (3) Å] and C10—N4/C10—N5 [1.330 (3)/1.326 (3) Å]. These values lie within the range of C—N single bond [1.357 (2) Å] and C=N double bond [1.318 (2) Å] determined at low temperature by Tarazon Navarro & McKee (2003). In the title compound, the dication adopts a somewhat folded conformation and the dihedral angle between two bzim groups is 34.6 (1)°. This angle is comparable with those in (IDB)·(H₂O)₄ [36.2 (1)° and 39.7 (1)°; Meng *et al.* (2006a)] and (IDB)₂·(H₂O)₂·C₂H₅OH [26.8 (1)° and 25.8 (1)°; Meng *et al.* (2006b)], but considerably larger than those in IDB [0.0°; Tarazon Navarro & McKee (2003)], HIDB⁺·Cl⁻ [5.4 (1)°; Zheng *et al.* (2005)], HIDB⁺·ClO₄⁻ [3.7 (1)°; Liu *et al.* (2004)] and H₂IDB²⁺·SO₄²⁻ [3.3 (1)°; Meng *et al.* (2005)].

Two imine N atoms (N2 and N5) act as hydrogen bond donors, *via* atoms H2A and H5A, respectively, to atoms O8/O9 and O4/O5, thereby generating four hydrogen bonds, each two forming an R²₁(4) (Fig.1) motif (Bernstein *et al.*, 1995). The other two N atoms (N3 and N4) on bzim also act as hydrogen bond donors, forming intermolecular hydrogen bonds of R¹₂(10) motif, to the methanol solvent molecule. The methanol molecule donates its hydroxyl H atom to atom O6, forming a relatively strong O—H···O hydrogen bond. There is a pseudo-mirror plane passing through the central NH group and the solvent C and O atoms.

In the crystal structure, the component ions are assembled into a three-dimensional network by a combination of N—H···O, O—H···O hydrogen bonds and π - π interactions which can be analyzed in terms of several substructures. Firstly, by the six cooperative hydrogen-bonding interactions (Table 1), the discrete dications, anions and methanol molecules are

supplementary materials

joined together, forming a relatively independent neutral unit. These neutral units are linked together by $N1\cdots O7$ ($-1/2 + x, 1/2 - y, -1/2 + z$) and $O1\cdots O6$ ($1/2 + x, 1/2 - y, -1/2 + z$) hydrogen bonds related by the n -glide plane at $y = 1/4$, forming a two-dimensional layer parallel to the (010) plane in the domain of $-0.259 < y < 0.759$ (Fig.2). Secondly, by π - π stacking interactions, adjacent two-dimensional layers are interlinked into a simple three-dimensional network. The geometric details of the π - π stacking interactions are listed in Table 2. A CSD (Version 1.9, September 2006 release; Allen, 2002; Bruno *et al.*, 2002) study indicates that π - π stacking interactions play a critical role in stabilizing the crystal structures of organic and metal-organic compounds containing poly-bzim groups. For instance, in $HIDB^+ \cdot ClO_4^-$ (Liu *et al.*, 2004), the $N-H\cdots N$ and $N-H\cdots O$ hydrogen bonds link the component ions into one-dimensional chains. However, π - π stacking interactions between adjacent bzim groups link the molecules into a three-dimensional network.

Experimental

All the reagents and solvents were used as obtained without further purification. Bis(benzimidazol-2-yl-methyl)amine (IDB) was prepared according to the method described by Adams *et al.* (1990). 2 g of the powdered title compound were dissolved in 15 ml methanol and adjusted to pH 5 using $HClO_4$. Colorless crystals were obtained as blocks by slowly evaporating the solvent over a period of several days.

Refinement

H atoms bonded to C atoms were located in difference maps and subsequently treated as riding, with C—H distances of 0.93 Å (aromatic), 0.97 Å (methylene) and 0.96 Å (methyl); $U_{iso}(H) = 1.2U_{eq}(\text{aromatic and methylene C})$ or $1.5U_{eq}(\text{methyl C})$. H atoms bonded to N and methanol O atoms were also found in difference maps, and refined with restraints of $N-H = 0.86(2)$ Å and $O-H = 0.82(2)$ Å; $U_{iso}(H)$ values were set equal to k times those of their carrier atoms ($k=1.2$ for N and 1.5 for O atoms)

Figures

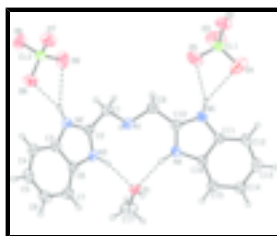


Fig. 1. Molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms as spheres of arbitrary radius. Hydrogen bonds are shown as dashed lines.

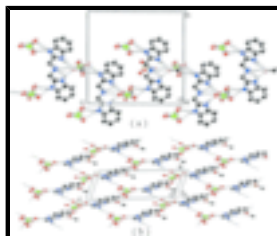


Fig. 2. Part of the crystal structure of the title compound, showing the formation of the two-dimensional network parallel to the (010) plane, built from $N-H\cdots O$ and $O-H\cdots O$ hydrogen bonds which are shown as dashed lines. (a) the view along the a axis and (b) the view along the b axis. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

2,2'-(Iminodimethylene)dibenzimidazolium bis(perchlorate) methanol solvate

Crystal data

$C_{16}H_{17}N_5^{2+} \cdot 2ClO_4^- \cdot CH_4O$	$F_{000} = 1056$
$M_r = 510.29$	$D_x = 1.558 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
Hall symbol: -P 2yn	$\lambda = 0.71073 \text{ \AA}$
$a = 8.3359 (4) \text{ \AA}$	Cell parameters from 7139 reflections
$b = 18.0323 (8) \text{ \AA}$	$\theta = 2.3\text{--}25.2^\circ$
$c = 14.8532 (7) \text{ \AA}$	$\mu = 0.36 \text{ mm}^{-1}$
$\beta = 102.944 (1)^\circ$	$T = 295 (2) \text{ K}$
$V = 2175.89 (18) \text{ \AA}^3$	Block, colorless
$Z = 4$	$0.30 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer	4957 independent reflections
Radiation source: fine focus sealed Siemens Mo tube	3479 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.069$
$T = 295(2) \text{ K}$	$\theta_{\text{max}} = 27.5^\circ$
0.3° wide ω exposures scans	$\theta_{\text{min}} = 1.8^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.900, T_{\text{max}} = 0.932$	$k = -23 \rightarrow 21$
24553 measured reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.057$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.169$	$w = 1/[\sigma^2(F_o^2) + (0.1086P)^2]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
4957 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
317 parameters	$\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
5 restraints	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

supplementary materials

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2809 (3)	0.30786 (14)	0.38370 (17)	0.0497 (6)
H1A	0.1809	0.2888	0.3983	0.060*
H1B	0.3586	0.3183	0.4414	0.060*
C2	0.3517 (3)	0.25067 (13)	0.33135 (15)	0.0396 (5)
C3	0.4580 (3)	0.14439 (14)	0.29713 (16)	0.0426 (5)
C4	0.5154 (3)	0.07295 (14)	0.29609 (19)	0.0519 (6)
H4	0.5108	0.0394	0.3430	0.062*
C5	0.5799 (3)	0.05391 (15)	0.2218 (2)	0.0582 (7)
H5	0.6225	0.0065	0.2190	0.070*
C6	0.5829 (4)	0.10337 (16)	0.1514 (2)	0.0605 (7)
H6	0.6244	0.0875	0.1015	0.073*
C7	0.5271 (3)	0.17525 (15)	0.15176 (17)	0.0520 (6)
H7	0.5315	0.2085	0.1045	0.062*
C8	0.4636 (3)	0.19489 (13)	0.22791 (15)	0.0411 (5)
C9	0.2625 (4)	0.44157 (14)	0.38863 (18)	0.0543 (7)
H9A	0.3339	0.4307	0.4482	0.065*
H9B	0.1560	0.4563	0.3987	0.065*
C10	0.3339 (3)	0.50353 (14)	0.34394 (15)	0.0418 (5)
C11	0.4340 (3)	0.61419 (13)	0.32023 (16)	0.0409 (5)
C12	0.4887 (3)	0.68676 (14)	0.32554 (17)	0.0499 (6)
H12	0.4805	0.7175	0.3746	0.060*
C13	0.5561 (3)	0.71112 (15)	0.25419 (18)	0.0541 (7)
H13	0.5960	0.7594	0.2555	0.065*
C14	0.5658 (3)	0.66542 (15)	0.18039 (18)	0.0531 (6)
H14	0.6096	0.6845	0.1329	0.064*
C15	0.5131 (3)	0.59301 (14)	0.17489 (17)	0.0489 (6)
H15	0.5213	0.5625	0.1256	0.059*
C16	0.4468 (3)	0.56799 (13)	0.24711 (15)	0.0393 (5)
C17	0.2881 (5)	0.3822 (2)	0.0512 (2)	0.0840 (11)
H17A	0.1777	0.3890	0.0588	0.126*
H17B	0.2965	0.3352	0.0223	0.126*
H17C	0.3151	0.4212	0.0132	0.126*
Cl1	0.24642 (8)	0.62635 (4)	0.59521 (4)	0.0481 (2)

Cl2	0.31148 (8)	0.10820 (3)	0.57634 (4)	0.0464 (2)
N1	0.2440 (3)	0.37571 (11)	0.33106 (14)	0.0445 (5)
H1	0.145 (4)	0.3694 (14)	0.2981 (19)	0.053*
N2	0.3856 (3)	0.18181 (11)	0.36014 (13)	0.0445 (5)
H2A	0.358 (3)	0.1635 (15)	0.4057 (14)	0.053*
N3	0.3963 (2)	0.26023 (11)	0.25234 (13)	0.0418 (5)
H3A	0.388 (3)	0.3016 (10)	0.2272 (16)	0.050*
N4	0.3827 (2)	0.49959 (11)	0.26472 (13)	0.0430 (5)
H4A	0.380 (3)	0.4598 (11)	0.2328 (15)	0.052*
N5	0.3622 (3)	0.57129 (12)	0.37846 (13)	0.0445 (5)
H5A	0.326 (3)	0.5852 (15)	0.4229 (14)	0.053*
O1	0.3990 (2)	0.38398 (9)	0.13891 (12)	0.0471 (4)
H1C	0.493 (2)	0.3935 (16)	0.138 (2)	0.071*
O2	0.3285 (3)	0.62766 (13)	0.68957 (15)	0.0858 (7)
O3	0.0789 (3)	0.63840 (17)	0.58637 (17)	0.1044 (9)
O4	0.3121 (3)	0.67790 (18)	0.5420 (2)	0.1118 (10)
O5	0.2696 (4)	0.55666 (15)	0.55727 (18)	0.1208 (11)
O6	0.1832 (3)	0.06270 (12)	0.59527 (17)	0.0829 (7)
O7	0.4415 (3)	0.11275 (12)	0.65578 (14)	0.0788 (7)
O8	0.3685 (3)	0.07408 (13)	0.50223 (13)	0.0738 (6)
O9	0.2500 (3)	0.17971 (12)	0.54776 (17)	0.0911 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0628 (17)	0.0430 (14)	0.0466 (13)	-0.0040 (12)	0.0194 (12)	0.0000 (11)
C2	0.0370 (12)	0.0417 (13)	0.0399 (11)	-0.0063 (10)	0.0083 (9)	0.0020 (10)
C3	0.0385 (13)	0.0436 (14)	0.0443 (12)	-0.0009 (10)	0.0063 (10)	0.0023 (10)
C4	0.0530 (16)	0.0385 (14)	0.0611 (15)	-0.0012 (12)	0.0063 (12)	0.0027 (12)
C5	0.0556 (17)	0.0457 (16)	0.0699 (18)	0.0077 (13)	0.0071 (14)	-0.0067 (13)
C6	0.0521 (17)	0.0680 (19)	0.0644 (17)	0.0004 (14)	0.0195 (14)	-0.0169 (15)
C7	0.0494 (15)	0.0573 (17)	0.0523 (14)	-0.0034 (12)	0.0179 (12)	-0.0014 (12)
C8	0.0393 (13)	0.0391 (13)	0.0448 (12)	-0.0058 (10)	0.0090 (10)	-0.0014 (10)
C9	0.0732 (18)	0.0445 (15)	0.0523 (14)	0.0051 (13)	0.0293 (13)	0.0020 (11)
C10	0.0393 (13)	0.0446 (14)	0.0425 (11)	0.0077 (10)	0.0111 (9)	0.0020 (10)
C11	0.0379 (13)	0.0408 (13)	0.0434 (12)	0.0064 (10)	0.0080 (10)	-0.0020 (10)
C12	0.0479 (15)	0.0427 (14)	0.0573 (15)	0.0036 (11)	0.0077 (12)	-0.0119 (11)
C13	0.0505 (16)	0.0418 (15)	0.0689 (17)	-0.0020 (12)	0.0110 (13)	0.0017 (12)
C14	0.0544 (16)	0.0513 (16)	0.0579 (15)	0.0056 (12)	0.0217 (12)	0.0084 (12)
C15	0.0526 (16)	0.0464 (15)	0.0514 (14)	0.0049 (12)	0.0199 (12)	-0.0006 (11)
C16	0.0389 (12)	0.0353 (13)	0.0444 (12)	0.0070 (9)	0.0108 (10)	-0.0002 (9)
C17	0.073 (2)	0.125 (3)	0.0535 (17)	0.0090 (19)	0.0120 (16)	0.0070 (17)
Cl1	0.0421 (4)	0.0612 (4)	0.0436 (3)	-0.0032 (3)	0.0155 (3)	-0.0038 (3)
Cl2	0.0510 (4)	0.0450 (4)	0.0454 (3)	0.0006 (3)	0.0152 (3)	0.0041 (2)
N1	0.0399 (12)	0.0494 (13)	0.0428 (11)	0.0018 (9)	0.0065 (9)	0.0017 (9)
N2	0.0504 (12)	0.0419 (12)	0.0428 (10)	-0.0047 (9)	0.0136 (9)	0.0048 (9)
N3	0.0438 (11)	0.0364 (11)	0.0450 (11)	-0.0017 (9)	0.0099 (9)	0.0074 (8)
N4	0.0492 (12)	0.0371 (11)	0.0450 (10)	0.0043 (9)	0.0157 (9)	-0.0054 (8)

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N5	0.0499 (12)	0.0450 (12)	0.0419 (11)	0.0085 (9)	0.0171 (9)	-0.0037 (9)
O1	0.0502 (11)	0.0517 (11)	0.0431 (9)	-0.0006 (8)	0.0184 (8)	0.0030 (7)
O2	0.0842 (17)	0.118 (2)	0.0479 (12)	-0.0101 (13)	-0.0010 (11)	-0.0106 (11)
O3	0.0471 (14)	0.181 (3)	0.0882 (17)	0.0107 (15)	0.0230 (12)	0.0009 (16)
O4	0.0934 (19)	0.131 (2)	0.1124 (19)	-0.0257 (16)	0.0253 (16)	0.0449 (17)
O5	0.195 (3)	0.090 (2)	0.0883 (17)	0.0224 (19)	0.0562 (19)	-0.0256 (14)
O6	0.0794 (15)	0.0663 (15)	0.1205 (18)	-0.0110 (11)	0.0595 (14)	-0.0011 (12)
O7	0.0794 (16)	0.0883 (16)	0.0576 (12)	0.0054 (12)	-0.0081 (11)	-0.0067 (10)
O8	0.0842 (15)	0.0842 (15)	0.0617 (12)	-0.0034 (12)	0.0350 (11)	-0.0092 (11)
O9	0.119 (2)	0.0498 (13)	0.0938 (17)	0.0148 (13)	0.0018 (14)	0.0128 (11)

Geometric parameters (Å, °)

N1—C1	1.448 (3)	C11—C16	1.392 (3)
N1—C9	1.451 (3)	C12—C13	1.378 (3)
N2—C2	1.323 (3)	C12—H12	0.9300
N2—C3	1.396 (3)	C13—C14	1.388 (4)
N3—C2	1.320 (3)	C13—H13	0.9300
N3—C8	1.388 (3)	C14—C15	1.374 (4)
N4—C10	1.330 (3)	C14—H14	0.9300
N4—C16	1.392 (3)	C15—C16	1.388 (3)
N5—C10	1.326 (3)	C15—H15	0.9300
N5—C11	1.392 (3)	C17—O1	1.419 (4)
C1—C2	1.491 (3)	C17—H17A	0.9600
C1—H1A	0.9700	C17—H17B	0.9600
C1—H1B	0.9700	C17—H17C	0.9600
C3—C4	1.375 (3)	C11—O3	1.390 (2)
C3—C8	1.382 (3)	C11—O4	1.408 (2)
C4—C5	1.375 (4)	C11—O5	1.408 (2)
C4—H4	0.9300	C11—O2	1.416 (2)
C5—C6	1.379 (4)	C12—O7	1.414 (2)
C5—H5	0.9300	C12—O9	1.417 (2)
C6—C7	1.377 (4)	C12—O6	1.425 (2)
C6—H6	0.9300	C12—O8	1.4320 (19)
C7—C8	1.398 (3)	N1—H1	0.86 (3)
C7—H7	0.9300	N2—H2A	0.831 (16)
C9—C10	1.490 (3)	N3—H3A	0.831 (16)
C9—H9A	0.9700	N4—H4A	0.857 (16)
C9—H9B	0.9700	N5—H5A	0.824 (16)
C11—C12	1.382 (3)	O1—H1C	0.805 (17)
N1—C1—C2	111.35 (19)	C14—C13—H13	119.2
N1—C1—H1A	109.4	C15—C14—C13	122.4 (2)
C2—C1—H1A	109.4	C15—C14—H14	118.8
N1—C1—H1B	109.4	C13—C14—H14	118.8
C2—C1—H1B	109.4	C14—C15—C16	116.1 (2)
H1A—C1—H1B	108.0	C14—C15—H15	121.9
N3—C2—N2	109.1 (2)	C16—C15—H15	121.9
N3—C2—C1	126.7 (2)	C15—C16—C11	121.5 (2)
N2—C2—C1	124.2 (2)	C15—C16—N4	132.0 (2)

C4—C3—C8	122.6 (2)	C11—C16—N4	106.50 (19)
C4—C3—N2	131.6 (2)	O1—C17—H17A	109.5
C8—C3—N2	105.8 (2)	O1—C17—H17B	109.5
C5—C4—C3	116.3 (2)	H17A—C17—H17B	109.5
C5—C4—H4	121.9	O1—C17—H17C	109.5
C3—C4—H4	121.9	H17A—C17—H17C	109.5
C4—C5—C6	121.6 (3)	H17B—C17—H17C	109.5
C4—C5—H5	119.2	O3—C11—O4	110.65 (18)
C6—C5—H5	119.2	O3—C11—O5	109.08 (19)
C7—C6—C5	122.8 (3)	O4—C11—O5	105.00 (19)
C7—C6—H6	118.6	O3—C11—O2	110.09 (15)
C5—C6—H6	118.6	O4—C11—O2	112.49 (16)
C6—C7—C8	115.5 (2)	O5—C11—O2	109.37 (16)
C6—C7—H7	122.2	O7—C12—O9	110.80 (14)
C8—C7—H7	122.2	O7—C12—O6	109.72 (15)
C3—C8—N3	106.4 (2)	O9—C12—O6	110.25 (16)
C3—C8—C7	121.1 (2)	O7—C12—O8	110.00 (14)
N3—C8—C7	132.5 (2)	O9—C12—O8	108.70 (14)
N1—C9—C10	110.6 (2)	O6—C12—O8	107.30 (13)
N1—C9—H9A	109.5	C1—N1—C9	113.1 (2)
C10—C9—H9A	109.5	C1—N1—H1	104.8 (17)
N1—C9—H9B	109.5	C9—N1—H1	113.8 (17)
C10—C9—H9B	109.5	C2—N2—C3	109.28 (19)
H9A—C9—H9B	108.1	C2—N2—H2A	123.9 (19)
N5—C10—N4	109.1 (2)	C3—N2—H2A	126.5 (19)
N5—C10—C9	125.0 (2)	C2—N3—C8	109.43 (19)
N4—C10—C9	125.9 (2)	C2—N3—H3A	120.5 (18)
C12—C11—N5	132.3 (2)	C8—N3—H3A	129.9 (18)
C12—C11—C16	122.0 (2)	C10—N4—C16	109.0 (2)
N5—C11—C16	105.7 (2)	C10—N4—H4A	123.9 (17)
C13—C12—C11	116.4 (2)	C16—N4—H4A	127.0 (17)
C13—C12—H12	121.8	C10—N5—C11	109.64 (19)
C11—C12—H12	121.8	C10—N5—H5A	121.6 (19)
C12—C13—C14	121.6 (2)	C11—N5—H5A	127.9 (19)
C12—C13—H13	119.2	C17—O1—H1C	115 (2)
N1—C1—C2—N3	7.9 (4)	C12—C11—C16—C15	-1.0 (4)
N1—C1—C2—N2	-174.9 (2)	N5—C11—C16—C15	179.7 (2)
C8—C3—C4—C5	0.2 (4)	C12—C11—C16—N4	179.1 (2)
N2—C3—C4—C5	179.7 (2)	N5—C11—C16—N4	-0.1 (2)
C3—C4—C5—C6	-1.5 (4)	C2—C1—N1—C9	-148.2 (2)
C4—C5—C6—C7	2.1 (4)	C10—C9—N1—C1	142.0 (2)
C5—C6—C7—C8	-1.2 (4)	N3—C2—N2—C3	0.7 (3)
C4—C3—C8—N3	-179.8 (2)	C1—C2—N2—C3	-176.9 (2)
N2—C3—C8—N3	0.6 (2)	C4—C3—N2—C2	179.7 (3)
C4—C3—C8—C7	0.7 (4)	C8—C3—N2—C2	-0.8 (3)
N2—C3—C8—C7	-178.9 (2)	N2—C2—N3—C8	-0.3 (3)
C6—C7—C8—C3	-0.2 (4)	C1—C2—N3—C8	177.2 (2)
C6—C7—C8—N3	-179.5 (3)	C3—C8—N3—C2	-0.2 (3)
N1—C9—C10—N5	178.4 (2)	C7—C8—N3—C2	179.2 (2)

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N1—C9—C10—N4	-3.2 (4)	N5—C10—N4—C16	0.3 (3)
N5—C11—C12—C13	179.4 (2)	C9—C10—N4—C16	-178.2 (2)
C16—C11—C12—C13	0.3 (4)	C15—C16—N4—C10	-179.9 (2)
C11—C12—C13—C14	1.0 (4)	C11—C16—N4—C10	-0.1 (3)
C12—C13—C14—C15	-1.6 (4)	N4—C10—N5—C11	-0.4 (3)
C13—C14—C15—C16	0.9 (4)	C9—C10—N5—C11	178.1 (2)
C14—C15—C16—C11	0.4 (4)	C12—C11—N5—C10	-178.8 (3)
C14—C15—C16—N4	-179.8 (2)	C16—C11—N5—C10	0.4 (3)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O7 ⁱ	0.86 (3)	2.42 (3)	3.200 (3)	150 (2)
N2—H2A \cdots O8	0.831 (16)	2.15 (2)	2.895 (3)	150 (3)
N2—H2A \cdots O9	0.831 (16)	2.489 (19)	3.233 (3)	150 (2)
N3—H3A \cdots O1	0.831 (16)	1.996 (17)	2.799 (3)	162 (2)
N4—H4A \cdots O1	0.857 (16)	1.985 (17)	2.823 (3)	166 (2)
N5—H5A \cdots O4	0.824 (16)	2.46 (2)	3.197 (4)	150 (2)
N5—H5A \cdots O5	0.824 (16)	2.21 (2)	2.939 (3)	147 (2)
O1—H1C \cdots O6 ⁱⁱ	0.805 (17)	2.00 (2)	2.765 (3)	159 (3)

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

Table 2

Table 2 π - π Stacking interactions ($^\circ$, \AA)

Cg _i	Cg _j	Dihedral angle	CCD	Interplanar spacing
Cg1	Cg2 ^{iv}	0.42	3.854 (2)	3.349 (2)
Cg1	Cg4 ^{iv}	0.35	3.557 (2)	3.354 (2)
Cg3	Cg2 ^{iv}	0.85	3.612 (2)	3.360 (2)
Cg3	Cg4 ^v	0.36	3.929 (2)	3.453 (2)

CCD is the centroid-to-centroid distance; Cg1 is the centroid of atoms N2/N3/C2/C3/C8; Cg2 is the centroid of atoms N4/N5/C10/C11/C16; Cg3 is the centroid of atoms C3-C8; Cg4 is the centroid of atoms C11-C16. symmetry codes: (iv) $1/2 - x, -1/2 + y, 1/2 - z$; (v) $1/2 - x, -1/2 + y, 1/2 - z$.

Fig. 1

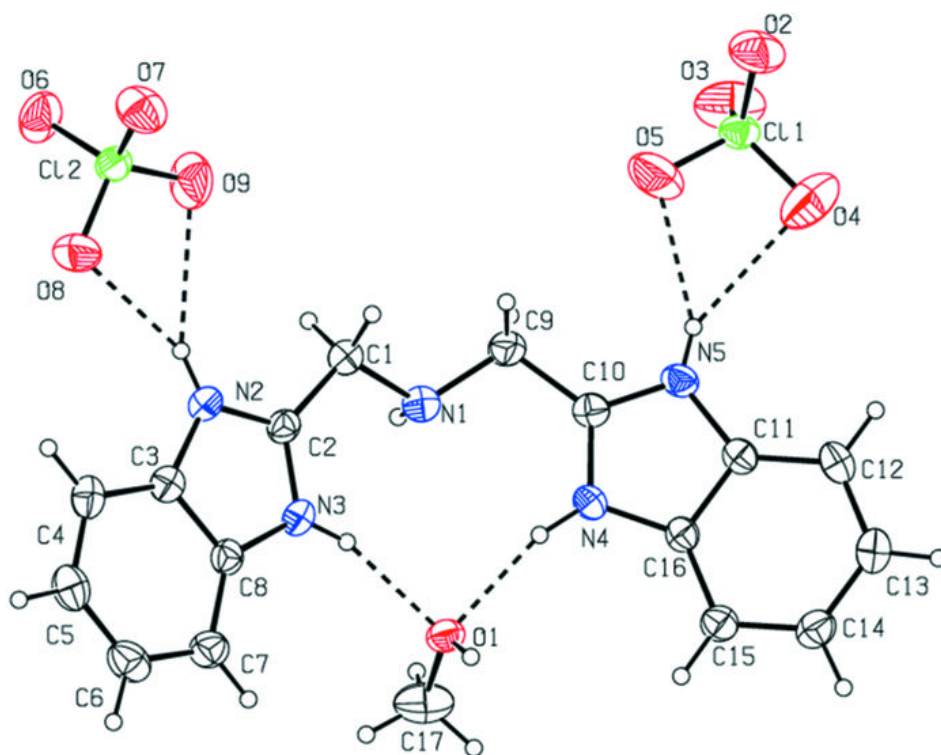


Fig. 2

