

4,4'-Bipyridinium bis(perchlorate)–4-aminobenzoic acid–4,4'-bipyridine–water (1/4/2/2)

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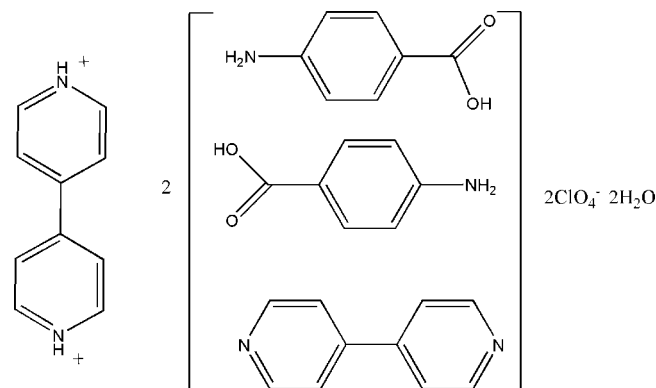
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; disorder in solvent or counterion; R factor = 0.066; wR factor = 0.198; data-to-parameter ratio = 11.5.

In the structure of the title compound, $\text{C}_{10}\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{ClO}_4^- \cdot 4\text{C}_7\text{H}_7\text{NO}_2 \cdot 2\text{C}_{10}\text{H}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$, the 4,4'-bipyridinium cation has a crystallographically imposed centre of symmetry. The cation is linked by $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds to adjacent 4,4'-bipyridine molecules, which in turn interact *via* $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds with 4-aminobenzoic acid molecules, forming chains running parallel to $[30\bar{2}]$. The chains are further connected into a three-dimensional network by $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen-bonding interactions involving the perchlorate anion, the water molecules and the 4-aminobenzoic acid molecules. In addition, $\pi-\pi$ stacking interactions with centroid-centroid distances ranging from 3.663 (6) to 3.695 (6) Å are present. The O atoms of the perchlorate anion are disordered over two sets of positions, with refined site occupancies of 0.724 (9) and 0.276 (9).

Related literature

For details of the hydrogen-bonding networks formed by 4-aminobenzoic acid and 4,4'-bipyridine, see: Clemente & Marzotto (2004); Hu *et al.* (2003); Yang *et al.* (2004).



Experimental

Crystal data

$\text{C}_{10}\text{H}_{10}\text{N}_2^{2+} \cdot 2\text{ClO}_4^- \cdot 4\text{C}_7\text{H}_7\text{NO}_2 \cdot 2\text{C}_{10}\text{H}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 1254.04$
 Triclinic, $P\bar{1}$
 $a = 10.1007$ (3) Å
 $b = 10.1105$ (4) Å
 $c = 16.5830$ (6) Å
 $\alpha = 91.487$ (2)°
 $\beta = 98.529$ (3)°
 $\gamma = 118.500$ (2)°
 $V = 1462.68$ (10) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.19$ mm⁻¹
 $T = 296$ (2) K
 $0.20 \times 0.18 \times 0.15$ mm

Data collection

Bruker APEXII area-detector diffractometer
 Absorption correction: none
 18132 measured reflections

5242 independent reflections
 3142 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.198$
 $S = 1.04$
 5242 reflections
 455 parameters
 74 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.41$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1}-\text{H1C} \cdots \text{N2}^{\text{i}}$	0.89 (4)	1.78 (4)	2.673 (4)	174 (5)
$\text{O3}-\text{H3C} \cdots \text{O5}^{\text{ii}}$	0.90 (5)	1.72 (4)	2.609 (4)	168 (5)
$\text{O5}-\text{H5B} \cdots \text{O4}^{\text{iii}}$	0.86 (4)	1.93 (4)	2.775 (4)	171 (4)
$\text{O5}-\text{H5A} \cdots \text{O2}^{\text{iv}}$	0.852 (11)	1.903 (13)	2.739 (4)	167 (3)
$\text{N5}-\text{H5C} \cdots \text{N1}$	0.90 (5)	1.78 (5)	2.680 (4)	175 (5)
$\text{N3}-\text{H3A} \cdots \text{O6}$	0.86	2.24	3.079 (6)	166
$\text{N3}-\text{H3A} \cdots \text{O7}'$	0.86	2.31	3.113 (15)	156
$\text{N3}-\text{H3B} \cdots \text{O6}^{\text{v}}$	0.86	2.25	3.085 (8)	166
$\text{N3}-\text{H3B} \cdots \text{O6}^{\text{v}}$	0.86	2.09	2.917 (18)	162
$\text{N4}-\text{H4A} \cdots \text{O8}^{\text{vi}}$	0.86	2.22	3.028 (10)	157
$\text{N4}-\text{H4A} \cdots \text{O8}^{\text{vi}}$	0.86	2.55	3.351 (19)	156
$\text{N4}-\text{H4B} \cdots \text{O8}$	0.86	2.57	3.174 (13)	129
$\text{N4}-\text{H4B} \cdots \text{O8}'$	0.86	2.57	3.25 (2)	136

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in

SHELXTL (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2274).

References

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supplementary materials

Acta Cryst. (2009). E65, o132-o133 [doi:10.1107/S1600536808042207]

4,4'-Bipyridinium bis(perchlorate)-4-aminobenzoic acid-4,4'-bipyridine-water (1/4/2/2)

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Comment

Hydrogen-bonding interactions between ligands are specific and directional. In this sense, 4-aminobenzoic acid and 4,4'-bipyridine are the excellent candidates for the construction of three-dimensional network motifs, as they form regular hydrogen bonds functioning as both hydrogen-bond donors and acceptors (Clemente & Marzotto, 2004; Hu *et al.*, 2003; Yang *et al.*, 2004). Recently, we obtained the title compound under hydrothermal conditions and report its crystal structure herein.

In the title compound (Fig. 1), all bond lengths and angles are unexceptional. The 4,4'-bipyridinium cation, which is located on a centre of symmetry, acts as a N—H hydrogen bond donor on both sides to unprotonated 4,4'-bipyridine molecules, which in turn act as O—H hydrogen bond acceptors from one of the two independent 4-aminobenzoic acid molecules. Two 4-aminobenzoic acid molecules, two 4,4'-bipyridine molecules and the cation are thus connected by hydrogen bonding interactions to form a linear centrosymmetric chain running parallel to the $[3\ 0\ \bar{2}]$ direction. These chains are further connected by O—H...O and N—H...O hydrogen bonds (Table 1) *via* the interstitial solvate water molecules, the perchlorate anions and the other 4-aminobenzoic acid molecules, forming a three-dimensional network (Fig. 2). The crystal packing is stabilized by π - π stacking interactions involving both pyridine rings of the unprotonated 4,4'-bipyridine molecule, the N5/C25-C29 pyridine ring of the cation and the C12-C17 benzene ring of one 4-aminobenzoic acid molecule: $Cg1\cdots Cg2^i = 3.695\ (6)\ \text{\AA}$; $Cg1\cdots Cg3 = 3.663\ (6)\ \text{\AA}$; $Cg3\cdots Cg4^{ii} = 3.674\ (7)\ \text{\AA}$ [$Cg1$, $Cg2$, $Cg3$ and $Cg4$ are the centroids of the N1/C1-C5, N2/C6-C10, C12-CC17 and N5/C25-C29 rings, respectively. Symmetry codes: (i) = 1-x, 1-y, -z; (ii) = 1-x, y, z].

Experimental

4-Aminobenzoic acid (1 mmol, 0.137 g), 4,4'-bipyridine (1 mmol, 0.156 g) and sodium perchlorate (1 mmol, 0.123 g) were dissolved in hot water with stirring. Colourless single crystals were obtained at room temperature by slow evaporation of the solvent over a period of several days.

Refinement

The disordered perchlorate ion was refined into two sites with refined occupancies of 0.724 (9) and 0.276 (9). The Cl...O and O...O distances were restrained to be 1.44 (1) and 2.35 (1) Å, respectively. Water H atoms were located in a difference Fourier map and refined with distance restraints of O—H = 0.86 Å and H...H = 1.39 Å. The H atom bound to the N5 nitrogen atom in the cation and the carboxylic H atoms were refined with N—H and O—H distance restraints of 0.90 Å. All other H atoms were placed at calculated positions and treated as riding on the parent atoms, with C—H = 0.93 Å, N—H = 0.86 Å, and with $U_{iso}(H) = 1.2 U_{eq}(C, N)$.

Figures

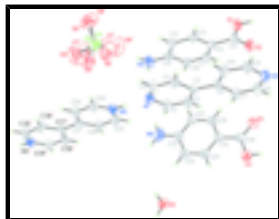


Fig. 1. The molecular structure showing the atomic-numbering scheme. Displacement ellipsoids drawn at the 30% probability level. Symmetry codes: (i)-x, 1-y, 1-z.

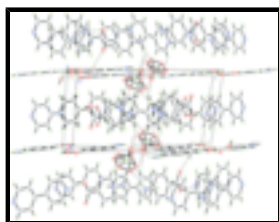


Fig. 2. Packing diagram of the title compound viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

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Crystal data

$C_{10}H_{10}N_2^{2+} \cdot 2ClO_4^- \cdot 4C_7H_7NO_2 \cdot 2C_{10}H_8N_2 \cdot 2H_2O$	$Z = 1$
$M_r = 1254.04$	$F_{000} = 654$
Triclinic, $P\bar{1}$	$D_x = 1.424 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 10.1007 (3) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 10.1105 (4) \text{ \AA}$	Cell parameters from 2787 reflections
$c = 16.5830 (6) \text{ \AA}$	$\theta = 2.4\text{--}21.0^\circ$
$\alpha = 91.487 (2)^\circ$	$\mu = 0.19 \text{ mm}^{-1}$
$\beta = 98.529 (3)^\circ$	$T = 296 (2) \text{ K}$
$\gamma = 118.500 (2)^\circ$	Block, colourless
$V = 1462.68 (10) \text{ \AA}^3$	$0.20 \times 0.18 \times 0.15 \text{ mm}$

Data collection

Bruker APEXII area-detector diffractometer	3142 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{\text{int}} = 0.058$
Monochromator: graphite	$\theta_{\text{max}} = 25.2^\circ$
$T = 296(2) \text{ K}$	$\theta_{\text{min}} = 2.3^\circ$
φ and ω scans	$h = -12 \rightarrow 11$
Absorption correction: None	$k = -11 \rightarrow 12$
18132 measured reflections	$l = -18 \rightarrow 19$
5242 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.066$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.198$	$w = 1/[\sigma^2(F_o^2) + (0.0835P)^2 + 0.5543P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
5242 reflections	$(\Delta/\sigma)_{\max} < 0.001$
455 parameters	$\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
74 restraints	$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.4592 (5)	0.5702 (4)	0.2272 (2)	0.0780 (12)	
H1	0.4688	0.6561	0.2552	0.094*	
C2	0.5531 (5)	0.5894 (4)	0.1716 (2)	0.0718 (11)	
H2	0.6235	0.6866	0.1627	0.086*	
C3	0.5438 (3)	0.4659 (3)	0.12897 (17)	0.0445 (7)	
C4	0.4368 (4)	0.3262 (4)	0.1468 (2)	0.0621 (9)	
H4	0.4256	0.2382	0.1204	0.075*	
C5	0.3468 (4)	0.3170 (4)	0.2035 (2)	0.0667 (10)	
H5	0.2758	0.2216	0.2145	0.080*	
C6	0.6445 (3)	0.4829 (3)	0.06907 (17)	0.0454 (7)	
C7	0.7468 (4)	0.6237 (4)	0.0504 (2)	0.0640 (10)	
H7	0.7552	0.7104	0.0767	0.077*	
C8	0.8361 (4)	0.6363 (4)	-0.0067 (2)	0.0681 (10)	
H8	0.9044	0.7329	-0.0176	0.082*	
C9	0.7333 (5)	0.3836 (5)	-0.0301 (2)	0.0774 (12)	
H9	0.7272	0.2990	-0.0576	0.093*	

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C10	0.6398 (5)	0.3613 (4)	0.0269 (2)	0.0716 (11)
H10	0.5731	0.2634	0.0368	0.086*
C11	1.0179 (4)	0.5687 (4)	0.1962 (2)	0.0570 (9)
C12	0.9160 (4)	0.5534 (4)	0.25473 (18)	0.0504 (8)
C13	0.8008 (4)	0.4134 (4)	0.26858 (19)	0.0529 (8)
H13	0.7875	0.3258	0.2406	0.064*
C14	0.7066 (4)	0.4019 (4)	0.32255 (19)	0.0556 (8)
H14	0.6304	0.3070	0.3307	0.067*
C15	0.7238 (4)	0.5309 (4)	0.3653 (2)	0.0566 (9)
C16	0.8404 (4)	0.6714 (4)	0.3531 (2)	0.0647 (10)
H16	0.8550	0.7588	0.3820	0.078*
C17	0.9340 (4)	0.6819 (4)	0.2984 (2)	0.0601 (9)
H17	1.0108	0.7767	0.2904	0.072*
C18	0.8014 (5)	0.0246 (4)	0.0816 (2)	0.0625 (9)
C19	0.7278 (4)	0.0094 (3)	0.1525 (2)	0.0573 (9)
C20	0.8008 (4)	0.0010 (4)	0.2290 (2)	0.0653 (10)
H20	0.8963	0.0066	0.2340	0.078*
C21	0.7339 (5)	-0.0152 (4)	0.2969 (2)	0.0713 (11)
H21	0.7847	-0.0200	0.3473	0.086*
C22	0.5911 (5)	-0.0244 (4)	0.2912 (3)	0.0735 (11)
C23	0.5181 (5)	-0.0161 (4)	0.2145 (3)	0.0747 (11)
H23	0.4226	-0.0216	0.2094	0.090*
C24	0.5850 (4)	0.0000 (4)	0.1471 (2)	0.0644 (10)
H24	0.5341	0.0047	0.0966	0.077*
C25	0.2424 (5)	0.5900 (5)	0.3916 (2)	0.0785 (12)
H25	0.3251	0.6733	0.3770	0.094*
C26	0.1654 (5)	0.6129 (4)	0.4471 (2)	0.0716 (11)
H26	0.1951	0.7107	0.4689	0.086*
C27	0.0433 (3)	0.4902 (4)	0.47059 (17)	0.0466 (7)
C28	0.0067 (4)	0.3484 (4)	0.4352 (2)	0.0657 (10)
H28	-0.0737	0.2620	0.4491	0.079*
C29	0.0886 (4)	0.3356 (5)	0.3799 (2)	0.0709 (11)
H29	0.0623	0.2396	0.3567	0.085*
N1	0.3567 (3)	0.4374 (3)	0.24310 (16)	0.0579 (7)
N2	0.8310 (3)	0.5191 (4)	-0.04737 (17)	0.0607 (8)
N3	0.6272 (4)	0.5201 (4)	0.41820 (18)	0.0758 (9)
H3A	0.5550	0.4328	0.4251	0.091*
H3B	0.6389	0.6007	0.4443	0.091*
N4	0.5226 (5)	-0.0444 (5)	0.3583 (2)	0.1091 (13)
H4A	0.5680	-0.0514	0.4049	0.131*
H4B	0.4342	-0.0499	0.3540	0.131*
N5	0.2031 (4)	0.4537 (4)	0.35815 (17)	0.0598 (8)
O1	0.9981 (3)	0.4406 (3)	0.16264 (16)	0.0718 (7)
O2	1.1150 (3)	0.6913 (3)	0.18048 (17)	0.0787 (8)
O3	0.7226 (3)	0.0324 (3)	0.01186 (18)	0.0793 (8)
O4	0.9250 (3)	0.0302 (3)	0.08352 (18)	0.0848 (8)
O5	0.1553 (3)	0.9533 (3)	0.11791 (17)	0.0720 (7)
H1C	1.058 (4)	0.451 (5)	0.126 (2)	0.119 (17)*
H3C	0.776 (5)	0.039 (6)	-0.028 (2)	0.122 (19)*

H5A	0.128 (4)	0.866 (2)	0.133 (2)	0.078 (13)*	
H5B	0.079 (3)	0.970 (4)	0.111 (3)	0.12 (2)*	
H5C	0.251 (5)	0.442 (6)	0.319 (2)	0.14 (2)*	
O6	0.3808 (7)	0.2312 (5)	0.4742 (4)	0.153 (3)	0.724 (9)
O7	0.2540 (10)	0.0812 (8)	0.3516 (3)	0.158 (3)	0.724 (9)
O8	0.2998 (12)	-0.0234 (8)	0.4681 (6)	0.155 (4)	0.724 (9)
O9	0.1258 (8)	0.0621 (9)	0.4610 (6)	0.190 (4)	0.724 (9)
C11	0.26368 (13)	0.08898 (12)	0.43474 (8)	0.0877 (4)	0.724 (9)
O6'	0.265 (2)	0.1766 (19)	0.5022 (7)	0.158 (7)	0.276 (9)
O7'	0.3803 (16)	0.1791 (19)	0.3902 (11)	0.175 (8)	0.276 (9)
O8'	0.264 (2)	-0.0437 (14)	0.4533 (12)	0.109 (7)	0.276 (9)
O9'	0.1148 (13)	0.0416 (13)	0.3755 (9)	0.115 (6)	0.276 (9)
C11'	0.26368 (13)	0.08898 (12)	0.43474 (8)	0.0877 (4)	0.276 (9)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.101 (3)	0.059 (2)	0.088 (3)	0.041 (2)	0.048 (2)	0.007 (2)
C2	0.087 (3)	0.048 (2)	0.086 (3)	0.029 (2)	0.045 (2)	0.0136 (19)
C3	0.0441 (17)	0.0503 (19)	0.0398 (16)	0.0236 (15)	0.0071 (13)	0.0044 (13)
C4	0.068 (2)	0.050 (2)	0.067 (2)	0.0218 (18)	0.0303 (18)	0.0017 (16)
C5	0.065 (2)	0.057 (2)	0.071 (2)	0.0190 (18)	0.0278 (18)	0.0058 (18)
C6	0.0450 (17)	0.0509 (19)	0.0415 (16)	0.0240 (15)	0.0085 (13)	0.0076 (14)
C7	0.062 (2)	0.051 (2)	0.070 (2)	0.0167 (17)	0.0244 (18)	0.0000 (17)
C8	0.057 (2)	0.062 (2)	0.068 (2)	0.0113 (18)	0.0246 (18)	0.0100 (19)
C9	0.099 (3)	0.066 (3)	0.084 (3)	0.043 (2)	0.051 (2)	0.014 (2)
C10	0.088 (3)	0.051 (2)	0.086 (3)	0.033 (2)	0.050 (2)	0.0181 (19)
C11	0.051 (2)	0.067 (2)	0.053 (2)	0.0286 (19)	0.0115 (16)	0.0133 (18)
C12	0.0505 (19)	0.058 (2)	0.0458 (17)	0.0287 (17)	0.0082 (14)	0.0096 (15)
C13	0.057 (2)	0.055 (2)	0.0496 (18)	0.0293 (17)	0.0115 (15)	0.0056 (15)
C14	0.054 (2)	0.059 (2)	0.0524 (19)	0.0248 (17)	0.0139 (15)	0.0097 (16)
C15	0.056 (2)	0.074 (2)	0.0492 (19)	0.0380 (19)	0.0113 (16)	0.0105 (17)
C16	0.073 (2)	0.063 (2)	0.066 (2)	0.039 (2)	0.0136 (19)	0.0012 (18)
C17	0.059 (2)	0.054 (2)	0.065 (2)	0.0247 (17)	0.0153 (17)	0.0110 (17)
C18	0.066 (2)	0.047 (2)	0.077 (3)	0.0274 (18)	0.018 (2)	0.0114 (17)
C19	0.056 (2)	0.0402 (18)	0.074 (2)	0.0217 (16)	0.0126 (17)	0.0086 (16)
C20	0.062 (2)	0.057 (2)	0.077 (3)	0.0304 (19)	0.0102 (19)	0.0050 (18)
C21	0.084 (3)	0.059 (2)	0.069 (2)	0.034 (2)	0.011 (2)	0.0068 (18)
C22	0.082 (3)	0.050 (2)	0.089 (3)	0.027 (2)	0.034 (2)	0.014 (2)
C23	0.061 (2)	0.064 (2)	0.103 (3)	0.031 (2)	0.023 (2)	0.019 (2)
C24	0.061 (2)	0.056 (2)	0.079 (3)	0.0292 (18)	0.0149 (19)	0.0149 (18)
C25	0.090 (3)	0.067 (3)	0.083 (3)	0.032 (2)	0.050 (2)	0.017 (2)
C26	0.088 (3)	0.053 (2)	0.083 (3)	0.033 (2)	0.047 (2)	0.0095 (18)
C27	0.0489 (18)	0.0546 (19)	0.0420 (16)	0.0294 (16)	0.0090 (13)	0.0066 (14)
C28	0.060 (2)	0.056 (2)	0.078 (2)	0.0229 (18)	0.0246 (18)	-0.0046 (18)
C29	0.066 (2)	0.063 (2)	0.077 (3)	0.026 (2)	0.021 (2)	-0.0122 (19)
N1	0.0571 (17)	0.067 (2)	0.0516 (16)	0.0300 (15)	0.0159 (13)	0.0041 (14)
N2	0.0552 (17)	0.074 (2)	0.0550 (17)	0.0302 (16)	0.0203 (13)	0.0093 (15)

supplementary materials

N3	0.073 (2)	0.093 (2)	0.072 (2)	0.0439 (19)	0.0284 (17)	0.0050 (18)
N4	0.125 (3)	0.118 (3)	0.103 (3)	0.062 (3)	0.060 (3)	0.037 (3)
N5	0.0637 (19)	0.077 (2)	0.0497 (16)	0.0412 (18)	0.0156 (14)	0.0034 (15)
O1	0.0788 (18)	0.0675 (17)	0.0739 (17)	0.0323 (14)	0.0395 (14)	0.0093 (14)
O2	0.0747 (17)	0.0691 (17)	0.0948 (19)	0.0289 (15)	0.0418 (15)	0.0247 (15)
O3	0.0734 (18)	0.095 (2)	0.0739 (19)	0.0426 (16)	0.0169 (15)	0.0200 (15)
O4	0.0781 (19)	0.101 (2)	0.098 (2)	0.0563 (17)	0.0312 (16)	0.0246 (16)
O5	0.0724 (18)	0.0648 (18)	0.0782 (18)	0.0317 (15)	0.0163 (14)	0.0169 (14)
O6	0.165 (5)	0.067 (3)	0.187 (6)	0.018 (3)	0.060 (4)	-0.015 (3)
O7	0.213 (8)	0.156 (5)	0.086 (4)	0.072 (5)	0.043 (4)	0.021 (3)
O8	0.199 (8)	0.095 (5)	0.177 (7)	0.077 (5)	0.030 (6)	0.017 (4)
O9	0.148 (6)	0.210 (7)	0.237 (8)	0.084 (5)	0.114 (6)	0.047 (6)
O11	0.0960 (9)	0.0596 (7)	0.1150 (10)	0.0368 (6)	0.0438 (7)	0.0144 (6)
O6'	0.195 (12)	0.143 (10)	0.156 (10)	0.094 (9)	0.056 (8)	-0.036 (7)
O7'	0.172 (11)	0.162 (11)	0.170 (12)	0.048 (8)	0.082 (9)	0.058 (9)
O8'	0.115 (9)	0.063 (9)	0.145 (11)	0.045 (7)	-0.003 (7)	0.037 (7)
O9'	0.095 (8)	0.096 (8)	0.139 (10)	0.051 (6)	-0.030 (7)	-0.010 (6)
O11'	0.0960 (9)	0.0596 (7)	0.1150 (10)	0.0368 (6)	0.0438 (7)	0.0144 (6)

Geometric parameters (Å, °)

C1—N1	1.310 (5)	C18—C19	1.456 (5)
C1—C2	1.371 (5)	C19—C24	1.388 (5)
C1—H1	0.9300	C19—C20	1.396 (5)
C2—C3	1.376 (5)	C20—C21	1.372 (5)
C2—H2	0.9300	C20—H20	0.9300
C3—C4	1.382 (4)	C21—C22	1.388 (6)
C3—C6	1.481 (4)	C21—H21	0.9300
C4—C5	1.378 (5)	C22—N4	1.366 (5)
C4—H4	0.9300	C22—C23	1.397 (6)
C5—N1	1.321 (4)	C23—C24	1.365 (5)
C5—H5	0.9300	C23—H23	0.9300
C6—C10	1.375 (5)	C24—H24	0.9300
C6—C7	1.380 (4)	C25—N5	1.318 (5)
C7—C8	1.371 (5)	C25—C26	1.371 (5)
C7—H7	0.9300	C25—H25	0.9300
C8—N2	1.323 (5)	C26—C27	1.385 (5)
C8—H8	0.9300	C26—H26	0.9300
C9—N2	1.322 (5)	C27—C28	1.387 (5)
C9—C10	1.381 (5)	C27—C27 ⁱ	1.472 (6)
C9—H9	0.9300	C28—C29	1.365 (5)
C10—H10	0.9300	C28—H28	0.9300
C11—O2	1.224 (4)	C29—N5	1.312 (5)
C11—O1	1.308 (4)	C29—H29	0.9300
C11—C12	1.475 (5)	N3—H3A	0.8600
C12—C17	1.390 (5)	N3—H3B	0.8600
C12—C13	1.391 (5)	N4—H4A	0.8600
C13—C14	1.368 (4)	N4—H4B	0.8600
C13—H13	0.9300	N5—H5C	0.90 (5)

C14—C15	1.390 (5)	O1—H1C	0.89 (4)
C14—H14	0.9300	O3—H3C	0.90 (5)
C15—N3	1.375 (4)	O5—H5A	0.852 (11)
C15—C16	1.391 (5)	O5—H5B	0.86 (4)
C16—C17	1.376 (5)	O6—C11	1.412 (4)
C16—H16	0.9300	O7—C11	1.365 (4)
C17—H17	0.9300	O8—C11	1.448 (5)
C18—O4	1.218 (4)	O9—C11	1.424 (5)
C18—O3	1.329 (4)		
N1—C1—C2	123.6 (3)	C24—C19—C20	118.0 (3)
N1—C1—H1	118.2	C24—C19—C18	122.5 (3)
C2—C1—H1	118.2	C20—C19—C18	119.5 (3)
C1—C2—C3	120.4 (3)	C21—C20—C19	121.0 (4)
C1—C2—H2	119.8	C21—C20—H20	119.5
C3—C2—H2	119.8	C19—C20—H20	119.5
C2—C3—C4	115.7 (3)	C20—C21—C22	120.8 (4)
C2—C3—C6	121.7 (3)	C20—C21—H21	119.6
C4—C3—C6	122.6 (3)	C22—C21—H21	119.6
C5—C4—C3	120.2 (3)	N4—C22—C21	120.8 (4)
C5—C4—H4	119.9	N4—C22—C23	121.0 (4)
C3—C4—H4	119.9	C21—C22—C23	118.2 (4)
N1—C5—C4	123.0 (3)	C24—C23—C22	120.9 (4)
N1—C5—H5	118.5	C24—C23—H23	119.5
C4—C5—H5	118.5	C22—C23—H23	119.5
C10—C6—C7	115.7 (3)	C23—C24—C19	121.1 (4)
C10—C6—C3	122.9 (3)	C23—C24—H24	119.4
C7—C6—C3	121.4 (3)	C19—C24—H24	119.4
C8—C7—C6	120.3 (3)	N5—C25—C26	122.2 (4)
C8—C7—H7	119.8	N5—C25—H25	118.9
C6—C7—H7	119.8	C26—C25—H25	118.9
N2—C8—C7	123.9 (3)	C25—C26—C27	119.9 (3)
N2—C8—H8	118.1	C25—C26—H26	120.0
C7—C8—H8	118.1	C27—C26—H26	120.0
N2—C9—C10	123.3 (3)	C26—C27—C28	116.4 (3)
N2—C9—H9	118.4	C26—C27—C27 ⁱ	121.7 (4)
C10—C9—H9	118.4	C28—C27—C27 ⁱ	121.9 (4)
C6—C10—C9	120.5 (3)	C29—C28—C27	120.0 (3)
C6—C10—H10	119.8	C29—C28—H28	120.0
C9—C10—H10	119.8	C27—C28—H28	120.0
O2—C11—O1	122.0 (3)	N5—C29—C28	122.5 (4)
O2—C11—C12	123.2 (3)	N5—C29—H29	118.8
O1—C11—C12	114.8 (3)	C28—C29—H29	118.8
C17—C12—C13	117.9 (3)	C1—N1—C5	117.1 (3)
C17—C12—C11	119.8 (3)	C9—N2—C8	116.4 (3)
C13—C12—C11	122.3 (3)	C15—N3—H3A	120.0
C14—C13—C12	121.3 (3)	C15—N3—H3B	120.0
C14—C13—H13	119.3	H3A—N3—H3B	120.0
C12—C13—H13	119.3	C22—N4—H4A	120.0

supplementary materials

C13—C14—C15	120.6 (3)	C22—N4—H4B	120.0
C13—C14—H14	119.7	H4A—N4—H4B	120.0
C15—C14—H14	119.7	C29—N5—C25	119.1 (3)
N3—C15—C14	120.8 (3)	C29—N5—H5C	120 (4)
N3—C15—C16	120.6 (3)	C25—N5—H5C	121 (4)
C14—C15—C16	118.6 (3)	C11—O1—H1C	114 (3)
C17—C16—C15	120.4 (3)	C18—O3—H3C	108 (3)
C17—C16—H16	119.8	H5A—O5—H5B	110 (4)
C15—C16—H16	119.8	O7—C11—O6	111.8 (4)
C16—C17—C12	121.2 (3)	O7—C11—O9	114.1 (5)
C16—C17—H17	119.4	O6—C11—O9	107.3 (4)
C12—C17—H17	119.4	O7—C11—O8	110.9 (4)
O4—C18—O3	120.9 (4)	O6—C11—O8	106.6 (5)
O4—C18—C19	124.5 (4)	O9—C11—O8	105.7 (5)
O3—C18—C19	114.6 (3)		
N1—C1—C2—C3	-0.3 (7)	C13—C12—C17—C16	-0.5 (5)
C1—C2—C3—C4	-0.5 (6)	C11—C12—C17—C16	179.7 (3)
C1—C2—C3—C6	-179.4 (4)	O4—C18—C19—C24	-178.5 (3)
C2—C3—C4—C5	0.6 (5)	O3—C18—C19—C24	1.6 (5)
C6—C3—C4—C5	179.5 (3)	O4—C18—C19—C20	0.3 (5)
C3—C4—C5—N1	0.1 (6)	O3—C18—C19—C20	-179.6 (3)
C2—C3—C6—C10	178.6 (3)	C24—C19—C20—C21	-0.3 (5)
C4—C3—C6—C10	-0.3 (5)	C18—C19—C20—C21	-179.2 (3)
C2—C3—C6—C7	-3.3 (5)	C19—C20—C21—C22	0.3 (5)
C4—C3—C6—C7	177.8 (3)	C20—C21—C22—N4	178.3 (4)
C10—C6—C7—C8	-0.2 (5)	C20—C21—C22—C23	-0.3 (5)
C3—C6—C7—C8	-178.4 (3)	N4—C22—C23—C24	-178.3 (4)
C6—C7—C8—N2	0.4 (6)	C21—C22—C23—C24	0.3 (6)
C7—C6—C10—C9	-0.1 (6)	C22—C23—C24—C19	-0.4 (6)
C3—C6—C10—C9	178.1 (3)	C20—C19—C24—C23	0.4 (5)
N2—C9—C10—C6	0.1 (7)	C18—C19—C24—C23	179.2 (3)
O2—C11—C12—C17	-3.6 (5)	N5—C25—C26—C27	1.0 (7)
O1—C11—C12—C17	175.5 (3)	C25—C26—C27—C28	0.0 (6)
O2—C11—C12—C13	176.5 (3)	C25—C26—C27—C27 ⁱ	-179.4 (4)
O1—C11—C12—C13	-4.3 (5)	C26—C27—C28—C29	-0.5 (5)
C17—C12—C13—C14	0.8 (5)	C27 ⁱ —C27—C28—C29	178.9 (4)
C11—C12—C13—C14	-179.3 (3)	C27—C28—C29—N5	0.1 (6)
C12—C13—C14—C15	-0.1 (5)	C2—C1—N1—C5	1.0 (6)
C13—C14—C15—N3	178.5 (3)	C4—C5—N1—C1	-0.9 (6)
C13—C14—C15—C16	-1.1 (5)	C10—C9—N2—C8	0.0 (6)
N3—C15—C16—C17	-178.2 (3)	C7—C8—N2—C9	-0.3 (6)
C14—C15—C16—C17	1.4 (5)	C28—C29—N5—C25	0.9 (6)
C15—C16—C17—C12	-0.6 (5)	C26—C25—N5—C29	-1.5 (6)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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O1—H1C…N2 ⁱⁱ	0.89 (4)	1.78 (4)	2.673 (4)	174 (5)
O3—H3C…O5 ⁱⁱⁱ	0.90 (5)	1.72 (4)	2.609 (4)	168 (5)
O5—H5B…O4 ^{iv}	0.86 (4)	1.93 (4)	2.775 (4)	171 (4)
O5—H5A…O2 ^v	0.852 (11)	1.903 (13)	2.739 (4)	167 (3)
N5—H5C…N1	0.90 (5)	1.78 (5)	2.680 (4)	175 (5)
N3—H3A…O6	0.86	2.24	3.079 (6)	166
N3—H3A…O7'	0.86	2.31	3.113 (15)	156
N3—H3B…O6 ^{vi}	0.86	2.25	3.085 (8)	166
N3—H3B…O6 ^{vi}	0.86	2.09	2.917 (18)	162
N4—H4A…O8 ^{vii}	0.86	2.22	3.028 (10)	157
N4—H4A…O8 ^{vii}	0.86	2.55	3.351 (19)	156
N4—H4B…O8	0.86	2.57	3.174 (13)	129
N4—H4B…O8'	0.86	2.57	3.25 (2)	136

Symmetry codes: (ii) $-x+2, -y+1, -z$; (iii) $-x+1, -y+1, -z$; (iv) $x-1, y+1, z$; (v) $x-1, y, z$; (vi) $-x+1, -y+1, -z+1$; (vii) $-x+1, -y, -z+1$.

Fig. 1

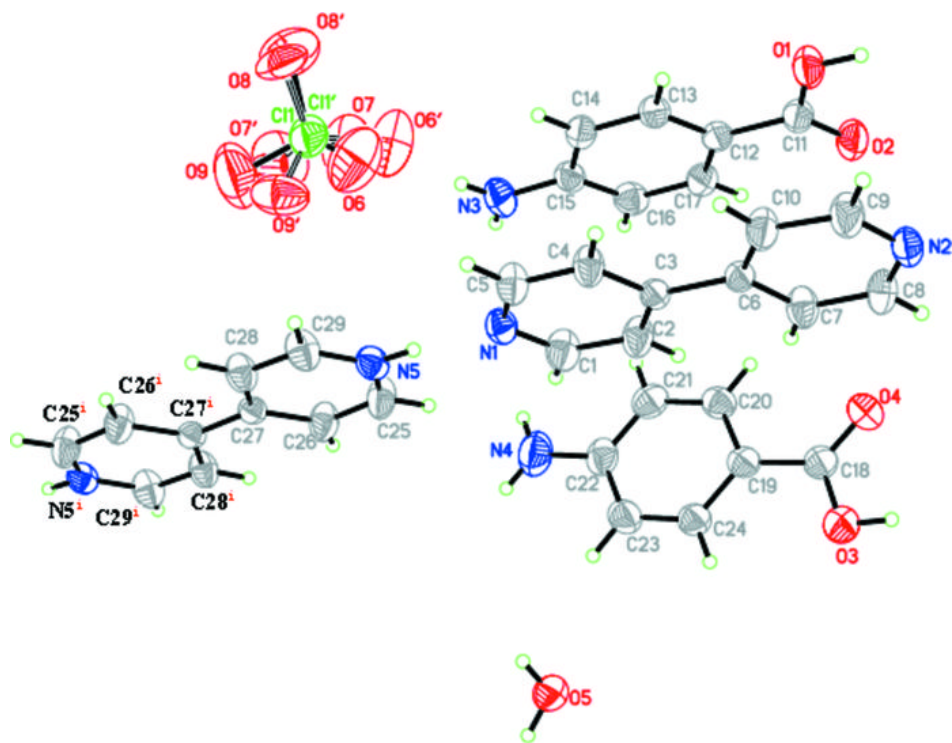


Fig. 2

