

2-[Bis(5-chloro-2-pyridylamino)methyl]pyridine monohydrate

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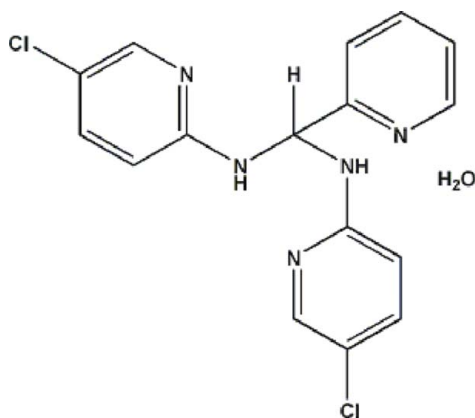
Received 20 October 2008; accepted 3 November 2008

Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.039; wR factor = 0.101; data-to-parameter ratio = 17.4.

In the title compound, the dihedral angles between the 2-amino-5-chloropyridyl rings and the pyridine ring are 56.26 (6°) and 78.83 (5°); the angle between the 2-amino-5-chloropyridyl rings is 72.42 (5°). The solvent water molecules are linked to the organic compound by $\text{N}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{N}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds. $\pi\cdots\pi$ Stacking interactions are also observed between the 2-amino-5-chloropyridyl rings (centroid \cdots centroid distance = 3.243 Å).

Related literature

For related crystallographic studies, see: Makowska-Grzyska *et al.* (2003); Li *et al.* (2008); Peori *et al.* (2008).



Experimental

Crystal data

$\text{C}_{16}\text{H}_{13}\text{Cl}_2\text{N}_5\cdot\text{H}_2\text{O}$
 $M_r = 364.23$
 Monoclinic, $C2/c$
 $a = 34.414$ (3) Å
 $b = 4.4337$ (3) Å
 $c = 26.236$ (2) Å
 $\beta = 124.778$ (1°)

$V = 3288.0$ (4) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.41$ mm⁻¹
 $T = 150$ (2) K
 $0.35 \times 0.10 \times 0.05$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.870$, $T_{\max} = 0.980$

14914 measured reflections
 3778 independent reflections
 2830 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.101$
 $S = 1.04$
 3778 reflections

217 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2N}\cdots\text{N5}^i$	0.87	2.15	2.994 (2)	165
$\text{N4}-\text{H4N}\cdots\text{O1}^{ii}$	0.87	2.18	2.993 (2)	156
$\text{O1}-\text{H1O}\cdots\text{N1}$	0.82	1.98	2.773 (2)	164
$\text{O1}-\text{H2O}\cdots\text{O1}^{iii}$	0.82	1.96	2.758 (2)	163

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

We are grateful to the Research Council of Sharif University of Technology, and Loughborough University for their financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2287).

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 Peori, M. B., Vaughan, K. & Bertolasi, V. (2008). *J. Chem. Crystallogr.* **38**, 61–64.
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supplementary materials

Acta Cryst. (2008). E64, o2428 [doi:10.1107/S1600536808035940]

2-[Bis(5-chloro-2-pyridylamino)methyl]pyridine monohydrate

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Comment

Primary amines add to imines to form aminal compounds; these are not stable (Peori *et al.*, 2008). The title compound, $C_{16}H_{13}Cl_2N_5 \cdot H_2O$, was synthesized by the reaction of 2-amino-5-chloropyridine with 2-pyridinecarbaldehyde in ethanol. Tris(pyridyl)amines are very common ligands and many complexes containing such ligands have been reported (Makowska-Grzyska *et al.*, 2003; Li *et al.*, 2008).

In the title compound, intermolecular N—H \cdots O and N—H \cdots N hydrogen bonds involving amine NH and pyridyl groups form a two dimensional network (Table 1 and Fig. 3). π – π stacking interactions are also observed between the 2-amino-5-chloropyridyl rings [centroid \cdots centroid distance = 3.243 Å]. The dihedral angles between the 2-amino-5-chloropyridyl rings and the pyridine ring are 56.26 (6) $^\circ$ and 78.83 (5) $^\circ$; the angle between the 2-amino-5-chloropyridyl rings is 72.42 (5) $^\circ$.

Experimental

The title compound was synthesized by adding 2-pyridinecarbaldehyde (1 mmol, 107 mg) to a solution of 2-amino-5-chloropyridine (3 mmol, 386 mg) and manganese acetate (0.02 mmol, 4.90 mg) in ethanol (20 ml). The mixture was refluxed with stirring for 7 h. The resultant yellow solution was filtered. Colourless single crystals of the title compound suitable for X-ray structure determination were recrystallized from a mixture of ethanol / water (5/1) by slow evaporation of the solvents at room temperature over several days.

Refinement

The H atoms bonded to C atoms were positioned geometrically and refined using the riding model with $U_{iso}(H) = 1.2U_{eq}(\text{parent atom})$; C—H = 0.95 and 1.00 Å for aromatic and methine C atoms, respectively. The H atoms bonded to N and O atoms were found in the difference Fourier map and refined with the following *DFIX* restraints: 0.87 (2) Å for N—H and 0.82 (2) Å for O—H. In the final refinement stages the *AFIX3* constraint was used for these H atoms.

Figures

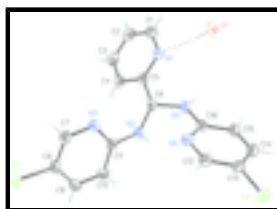


Fig. 1. View of the molecular structure of the title compound, with displacement ellipsoids for non-H atoms drawn at the 50% probability level. The hydrogen atoms are represented by spheres of arbitrary radius. The hydrogen bond is shown as a dashed line.

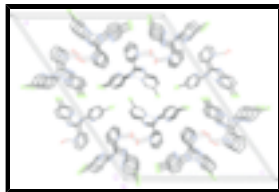


Fig. 2. View of the crystal structure packing scheme. The dashed lines indicate hydrogen bonds. H atoms have been omitted.

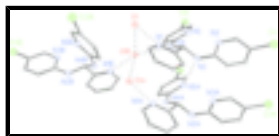


Fig. 3. View of the hydrogen bonding (dashed lines) scheme. H atoms have been omitted.

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Crystal data

$C_{16}H_{13}Cl_2N_5 \cdot H_2O$

$M_r = 364.23$

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Hall symbol: $-C 2yc$

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$b = 4.4337 (3) \text{ \AA}$

$c = 26.236 (2) \text{ \AA}$

$\beta = 124.778 (1)^\circ$

$V = 3288.0 (4) \text{ \AA}^3$

$Z = 8$

$F_{000} = 1504$

$D_x = 1.472 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2781 reflections

$\theta = 2.4\text{--}26.1^\circ$

$\mu = 0.41 \text{ mm}^{-1}$

$T = 150 (2) \text{ K}$

Lath, colourless

$0.35 \times 0.10 \times 0.05 \text{ mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 150(2) \text{ K}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 2003)

$T_{\min} = 0.870$, $T_{\max} = 0.980$

14914 measured reflections

3778 independent reflections

2830 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 1.9^\circ$

$h = -44 \rightarrow 44$

$k = -5 \rightarrow 5$

$l = -34 \rightarrow 34$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.101$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 1.3212P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$S = 1.04$ $(\Delta/\sigma)_{\max} < 0.001$
 3778 reflections $\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$
 217 parameters $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$
 Primary atom site location: structure-invariant direct methods Extinction correction: none

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.25729 (5)	0.5318 (4)	0.15040 (7)	0.0272 (3)
C1	0.30054 (7)	0.4226 (5)	0.17347 (9)	0.0308 (4)
H1	0.3259	0.4888	0.2134	0.037*
C2	0.31028 (7)	0.2185 (4)	0.14231 (9)	0.0317 (4)
H2	0.3414	0.1436	0.1606	0.038*
C3	0.27344 (7)	0.1266 (5)	0.08383 (9)	0.0330 (4)
H3	0.2789	-0.0104	0.0607	0.040*
C4	0.22844 (7)	0.2366 (4)	0.05934 (9)	0.0279 (4)
H4	0.2026	0.1759	0.0192	0.033*
C5	0.22143 (6)	0.4366 (4)	0.09407 (8)	0.0232 (4)
C6	0.17286 (6)	0.5693 (4)	0.06964 (8)	0.0235 (4)
H6	0.1720	0.7800	0.0554	0.028*
N2	0.13502 (5)	0.4001 (4)	0.01720 (6)	0.0244 (3)
H2N	0.1224	0.2485	0.0239	0.029*
N3	0.13945 (5)	0.6845 (3)	-0.05317 (7)	0.0254 (3)
C7	0.12129 (7)	0.7555 (4)	-0.11245 (9)	0.0279 (4)
H7	0.1368	0.9051	-0.1206	0.033*
C8	0.08131 (6)	0.6224 (5)	-0.16202 (8)	0.0286 (4)
C11	0.06183 (2)	0.72387 (14)	-0.23748 (2)	0.04370 (16)
C9	0.05738 (6)	0.4096 (5)	-0.15136 (8)	0.0296 (4)
H9	0.0295	0.3165	-0.1850	0.035*
C10	0.07470 (6)	0.3361 (4)	-0.09131 (8)	0.0255 (4)
H10	0.0588	0.1919	-0.0825	0.031*
C11	0.11634 (6)	0.4768 (4)	-0.04267 (8)	0.0224 (4)
N4	0.16586 (5)	0.5834 (4)	0.11881 (7)	0.0273 (4)
H4N	0.1839	0.4738	0.1518	0.033*
N5	0.10283 (5)	0.9191 (4)	0.06534 (7)	0.0267 (3)
C12	0.06679 (6)	1.0659 (4)	0.06110 (9)	0.0288 (4)
H12	0.0479	1.1975	0.0269	0.035*
C13	0.05617 (6)	1.0341 (4)	0.10388 (9)	0.0275 (4)
C12	0.008985 (17)	1.23175 (12)	0.09516 (3)	0.03644 (14)
C14	0.08384 (7)	0.8454 (5)	0.15457 (9)	0.0298 (4)
H14	0.0773	0.8215	0.1849	0.036*
C15	0.12065 (7)	0.6949 (4)	0.16002 (9)	0.0281 (4)
H15	0.1401	0.5650	0.1943	0.034*
C16	0.12928 (6)	0.7355 (4)	0.11388 (8)	0.0238 (4)
O1	0.27352 (5)	0.8741 (3)	0.24925 (6)	0.0359 (3)
H1O	0.2644	0.7974	0.2157	0.043*
H2O	0.2570	1.0234	0.2418	0.043*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0274 (8)	0.0316 (9)	0.0225 (8)	-0.0008 (7)	0.0142 (7)	0.0010 (7)
C1	0.0266 (10)	0.0366 (11)	0.0260 (10)	0.0014 (8)	0.0130 (8)	0.0040 (8)
C2	0.0286 (10)	0.0339 (11)	0.0381 (11)	0.0057 (8)	0.0224 (9)	0.0095 (9)
C3	0.0399 (11)	0.0315 (10)	0.0387 (11)	0.0032 (9)	0.0290 (10)	0.0017 (9)
C4	0.0304 (10)	0.0306 (10)	0.0253 (9)	-0.0008 (8)	0.0174 (8)	-0.0014 (8)
C5	0.0267 (9)	0.0239 (9)	0.0213 (8)	-0.0014 (7)	0.0150 (7)	0.0029 (7)
C6	0.0246 (9)	0.0281 (10)	0.0182 (8)	-0.0004 (7)	0.0125 (7)	-0.0008 (7)
N2	0.0275 (8)	0.0275 (8)	0.0187 (7)	-0.0047 (6)	0.0134 (6)	0.0003 (6)
N3	0.0272 (8)	0.0288 (8)	0.0216 (8)	-0.0025 (6)	0.0146 (7)	-0.0003 (6)
C7	0.0306 (10)	0.0302 (10)	0.0272 (9)	0.0009 (8)	0.0191 (8)	0.0033 (8)
C8	0.0303 (10)	0.0363 (11)	0.0195 (9)	0.0068 (8)	0.0144 (8)	0.0037 (8)
C11	0.0461 (3)	0.0610 (4)	0.0212 (2)	0.0011 (3)	0.0175 (2)	0.0074 (2)
C9	0.0245 (9)	0.0343 (11)	0.0235 (9)	0.0007 (8)	0.0099 (8)	-0.0018 (8)
C10	0.0210 (9)	0.0279 (10)	0.0268 (9)	-0.0003 (7)	0.0133 (8)	0.0004 (8)
C11	0.0235 (9)	0.0237 (9)	0.0222 (9)	0.0028 (7)	0.0144 (7)	-0.0010 (7)
N4	0.0276 (8)	0.0366 (9)	0.0191 (7)	0.0049 (7)	0.0142 (7)	0.0034 (7)
N5	0.0260 (8)	0.0317 (9)	0.0246 (8)	-0.0011 (7)	0.0157 (7)	0.0010 (7)
C12	0.0254 (9)	0.0319 (10)	0.0279 (10)	-0.0020 (8)	0.0145 (8)	0.0012 (8)
C13	0.0241 (9)	0.0293 (10)	0.0331 (10)	-0.0039 (8)	0.0186 (8)	-0.0062 (8)
C12	0.0296 (3)	0.0394 (3)	0.0465 (3)	-0.0015 (2)	0.0254 (2)	-0.0073 (2)
C14	0.0352 (10)	0.0333 (10)	0.0288 (10)	-0.0056 (8)	0.0229 (9)	-0.0045 (8)
C15	0.0320 (10)	0.0318 (10)	0.0222 (9)	-0.0009 (8)	0.0165 (8)	-0.0011 (8)
C16	0.0258 (9)	0.0256 (9)	0.0206 (8)	-0.0045 (7)	0.0137 (7)	-0.0049 (7)
O1	0.0438 (8)	0.0344 (8)	0.0245 (7)	0.0003 (6)	0.0165 (6)	-0.0050 (6)

Geometric parameters (\AA , $^\circ$)

N1—C1	1.337 (2)	C8—C9	1.381 (3)
N1—C5	1.343 (2)	C8—C11	1.7484 (18)
C1—C2	1.383 (3)	C9—C10	1.368 (3)
C1—H1	0.9500	C9—H9	0.9500
C2—C3	1.381 (3)	C10—C11	1.409 (2)
C2—H2	0.9500	C10—H10	0.9500
C3—C4	1.383 (3)	N4—C16	1.368 (2)
C3—H3	0.9500	N4—H4N	0.8698
C4—C5	1.388 (3)	N5—C16	1.338 (2)
C4—H4	0.9500	N5—C12	1.348 (2)
C5—C6	1.526 (2)	C12—C13	1.372 (3)
C6—N4	1.442 (2)	C12—H12	0.9500
C6—N2	1.452 (2)	C13—C14	1.389 (3)
C6—H6	1.0000	C13—C12	1.7418 (19)
N2—C11	1.358 (2)	C14—C15	1.365 (3)
N2—H2N	0.8699	C14—H14	0.9500
N3—C7	1.342 (2)	C15—C16	1.413 (2)
N3—C11	1.344 (2)	C15—H15	0.9500

C7—C8	1.375 (3)	O1—H1O	0.8206
C7—H7	0.9500	O1—H2O	0.8206
C1—N1—C5	118.11 (16)	C9—C8—C11	121.13 (15)
N1—C1—C2	123.50 (18)	C10—C9—C8	118.51 (17)
N1—C1—H1	118.3	C10—C9—H9	120.7
C2—C1—H1	118.3	C8—C9—H9	120.7
C3—C2—C1	118.10 (18)	C9—C10—C11	119.16 (17)
C3—C2—H2	121.0	C9—C10—H10	120.4
C1—C2—H2	121.0	C11—C10—H10	120.4
C2—C3—C4	119.16 (18)	N3—C11—N2	117.63 (15)
C2—C3—H3	120.4	N3—C11—C10	122.19 (16)
C4—C3—H3	120.4	N2—C11—C10	120.16 (16)
C3—C4—C5	119.22 (18)	C16—N4—C6	123.43 (15)
C3—C4—H4	120.4	C16—N4—H4N	117.7
C5—C4—H4	120.4	C6—N4—H4N	118.5
N1—C5—C4	121.90 (16)	C16—N5—C12	117.83 (15)
N1—C5—C6	116.09 (15)	N5—C12—C13	123.00 (18)
C4—C5—C6	121.98 (16)	N5—C12—H12	118.5
N4—C6—N2	110.65 (14)	C13—C12—H12	118.5
N4—C6—C5	110.04 (14)	C12—C13—C14	119.23 (17)
N2—C6—C5	111.98 (15)	C12—C13—Cl2	120.28 (15)
N4—C6—H6	108.0	C14—C13—Cl2	120.48 (14)
N2—C6—H6	108.0	C15—C14—C13	118.88 (17)
C5—C6—H6	108.0	C15—C14—H14	120.6
C11—N2—C6	122.92 (15)	C13—C14—H14	120.6
C11—N2—H2N	117.7	C14—C15—C16	118.96 (18)
C6—N2—H2N	119.3	C14—C15—H15	120.5
C7—N3—C11	117.36 (15)	C16—C15—H15	120.5
N3—C7—C8	123.29 (17)	N5—C16—N4	118.68 (16)
N3—C7—H7	118.4	N5—C16—C15	122.09 (17)
C8—C7—H7	118.4	N4—C16—C15	119.23 (16)
C7—C8—C9	119.47 (17)	H1O—O1—H2O	106.9
C7—C8—C11	119.40 (15)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N \cdots N5 ⁱ	0.87	2.15	2.994 (2)	165
N4—H4N \cdots O1 ⁱⁱ	0.87	2.18	2.993 (2)	156
O1—H1O \cdots N1	0.82	1.98	2.773 (2)	164
O1—H2O \cdots O1 ⁱⁱⁱ	0.82	1.96	2.758 (2)	163

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

Fig. 1

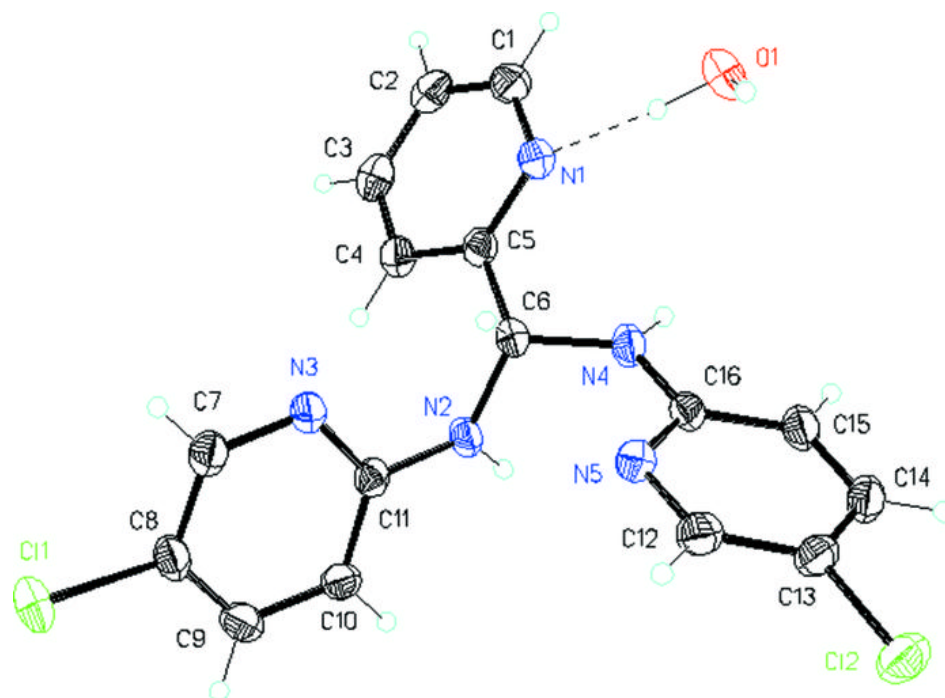


Fig. 2

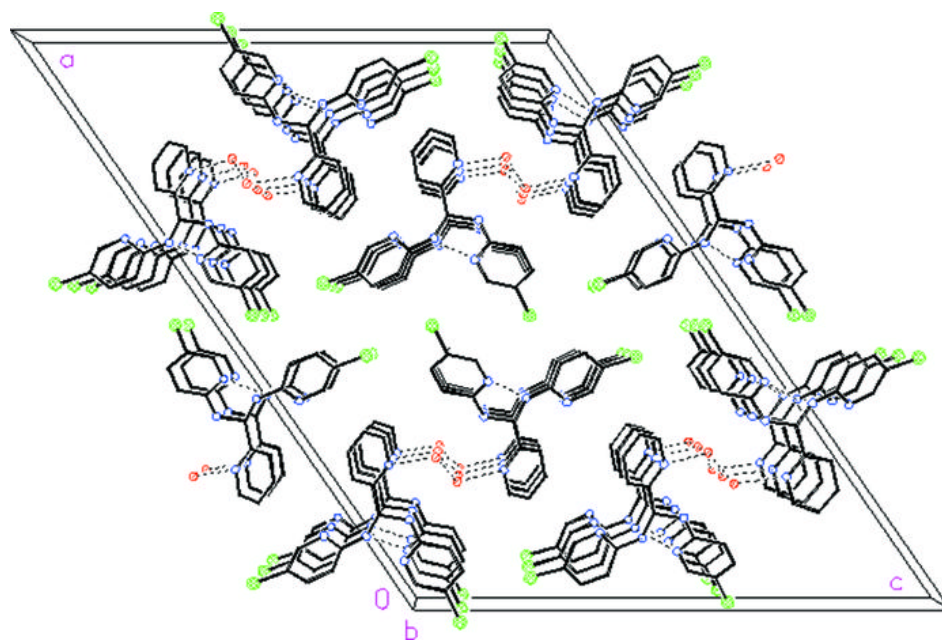


Fig. 3

