

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

2-[(*E*)-(1*H*-Pyrrol-2-ylmethylidene)-hydrazinyl]pyridine monohydrateGeraldo M. de Lima,<sup>a</sup> Edward R. T. Tiekink,<sup>b\*</sup> James L. Wardell<sup>c‡</sup> and Solange M. S. V. Wardell<sup>d</sup>

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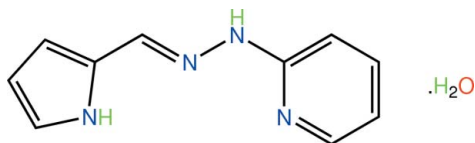
Received 22 November 2009; accepted 23 November 2009

Key indicators: single-crystal X-ray study;  $T = 120$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.040;  $wR$  factor = 0.109; data-to-parameter ratio = 11.3.

The title hydrate,  $\text{C}_{10}\text{H}_{10}\text{N}_4 \cdot \text{H}_2\text{O}$ , shows a small twist in the hydrozone derivative, the dihedral angle between the pyridine and pyrrole rings being  $11.08$  ( $12$ )°. The pyridine and pyrrole N atoms lie to the same side of the molecule being sustained in place by hydrogen-bonding interactions with the water molecule. Further intermolecular  $\text{O}-\text{H} \cdots \text{N}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonding leads to the formation of supramolecular arrays in the *ab* plane.

## Related literature

For related structures of hydrozone derivatives, see: Baddeley *et al.* (2009); Ferguson *et al.* (2005); Wardell, Low & Glidewell (2007); Wardell, Skakle, Low & Glidewell (2007). For additional structural analysis, see: Spek (2003).



## Experimental

## Crystal data

$\text{C}_{10}\text{H}_{10}\text{N}_4 \cdot \text{H}_2\text{O}$   
 $M_r = 204.24$   
 Monoclinic,  $P2_1/c$   
 $a = 5.6479$  (3) Å  
 $b = 7.4383$  (4) Å  
 $c = 24.4233$  (11) Å  
 $\beta = 103.300$  (3)°

$V = 998.52$  (9) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 120$  K  
 $0.24 \times 0.22 \times 0.04$  mm

## Data collection

Nonius KappaCCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2007)  
 $T_{\min} = 0.670$ ,  $T_{\max} = 0.746$

3068 measured reflections  
 1680 independent reflections  
 1636 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.109$   
 $S = 1.07$   
 1680 reflections  
 149 parameters  
 4 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.19$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.24$  e Å<sup>-3</sup>

**Table 1**  
 Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1w}-\text{H1w} \cdots \text{N1}$	0.84 (1)	2.04 (1)	2.870 (2)	170 (3)
$\text{O1w}-\text{H2w} \cdots \text{N3}^i$	0.84 (1)	2.08 (1)	2.899 (3)	166 (3)
$\text{N2}-\text{H2n} \cdots \text{O1w}^{ii}$	0.89 (1)	2.09 (1)	2.959 (3)	166 (2)
$\text{N4}-\text{H4n} \cdots \text{O1w}$	0.88 (1)	1.97 (1)	2.831 (2)	165 (2)

Symmetry codes: (i)  $-x, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ .

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2009).

The use of the EPSRC X-ray crystallographic service at the University of Southampton, England and the valuable assistance of the staff there is gratefully acknowledged. JLW acknowledges support from FAPEMIG (Brazil).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2608).

## References

- Baddeley, T. C., França, L. de S., Howie, R. A., de Lima, G. M., Skakle, J. M. S., de Souza, J. D., Wardell, J. L. & Wardell, S. M. S. V. (2009). *Z. Kristallogr.* **224**, 213–224.
- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Ferguson, G., Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2005). *Acta Cryst.* **C61**, o613–o616.
- Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (2007). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Wardell, J. L., Low, J. N. & Glidewell, C. (2007). *Acta Cryst.* **E63**, o1848–o1850.
- Wardell, J. L., Skakle, J. M. S., Low, J. N. & Glidewell, C. (2007). *Acta Cryst.* **C63**, o462–o467.
- Westrip, S. P. (2009). *pubCIF*. In preparation.

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**supplementary materials**

*Acta Cryst.* (2009). E65, o3241 [ doi:10.1107/S1600536809050296 ]

## 2-[(*E*)-(1*H*-Pyrrol-2-ylmethylidene)hydrazinyl]pyridine monohydrate

G. M. de Lima, E. R. T. Tiekink, J. L. Wardell and S. M. S. V. Wardell

### Comment

In continuation of studies into the supramolecular arrangements of hydrazones (Baddeley *et al.*, 2009; Wardell, Skakle *et al.*, 2007; Wardell, Low *et al.*, 2007; Ferguson *et al.*, 2005), we now report the structure of the title hydrate, (I).

The molecule of (I), Fig. 1, is non-planar owing to a twist about the C6–C7 bond as seen in the C3–C6–C7–N4 torsion angle of  $-11.2(3)^\circ$ . The dihedral angle between the pyrrole and pyridine rings is  $11.08(12)^\circ$ . The conformation about the C6=N3 bond is *E* and the pyrrole- and pyridine-N atoms are *syn*. This arrangement is stabilized by pyrrole-NH $\cdots$ O<sub>water</sub> and water-OH $\cdots$ N<sub>pyridine</sub> hydrogen bonds, Fig. 1 and Table 1.

The water molecule also plays a pivotal role in stabilizing the crystal structure, forming additional donor and acceptor interactions to link three distinct molecules. The molecules stack into columns aligned along the *a* axis and alternate between organic and water molecules along the *b* axis, Fig. 2 and Table 1. The resultant layers stack along the *c* axis, Fig. 3.

### Experimental

A solution of 2-hydrazinopyridine (0.330 g, 3 mmol) in MeOH (15 ml) was added to a solution of 2-pyrrolcarboxaldehyde (0.270 g, 3 mmol) in MeOH (10 ml). The reaction mixture was refluxed for 20 min, and maintained at room temperature. The crystals which slowly formed were collected and recrystallized twice from MeOH. *M. pt.* 449 - 452 K. IR(KBr, cm<sup>-1</sup>):  $\nu$  1603(C=N). Anal. Found, C, 59.13; H, 5.81; N, 27.71. Calc. for C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>.H<sub>2</sub>O: C, 58.82; H, 5.92; N, 27.43%

### Refinement

The C-bound H atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The O- and N-bound H atoms were located from a difference map and included in their idealized positions with O–H =  $0.84 \pm 0.01$  and N–H =  $0.88 \pm 0.01$  Å, and with  $U_{\text{iso}}(\text{H}) = nU_{\text{eq}}(\text{O, N})$ ;  $n = 1.5$  for O and  $n = 1.2$  for N. After analysis with *PLATON* (Spek, 2003), the structure was refined as a twin, with the twin component related by  $-1\ 0\ 0, 0\ -1\ 0, 2\ 0\ 1$ , and with a fractional contribution of 0.4418 (23).

### Figures

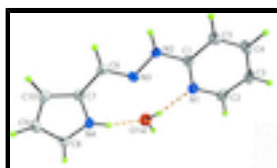


Fig. 1. The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level. The O—H $\cdots$ N and N—H $\cdots$ O hydrogen bonds are shown as orange dashed lines.

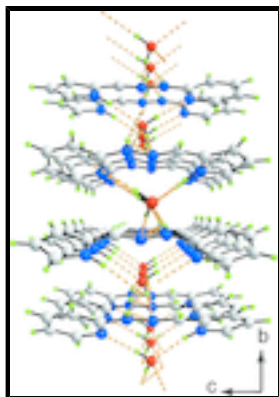


Fig. 2. A side-on view of a supramolecular layer in (I) showing O–H···N and N–H···O hydrogen bonding between the molecules (orange dashed lines). Colour code: O, red; N, blue; C, grey; and H, green.

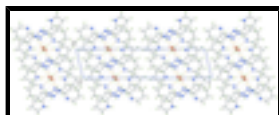


Fig. 3. A view in projection down the *b* axis showing the stacking of layers along the *c* axis in (I). The O–H···N and N–H···O hydrogen bonding is shown as orange dashed lines. Colour code: O, red; N, blue; C, grey; and H, green.

## 2-[(*E*)-(1*H*-Pyrrrol-2-ylmethylidene)hydrazinyl]pyridine monohydrate

### Crystal data

$C_{10}H_{10}N_4 \cdot H_2O$

$M_r = 204.24$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 5.6479$  (3) Å

$b = 7.4383$  (4) Å

$c = 24.4233$  (11) Å

$\beta = 103.300$  (3)°

$V = 998.52$  (9) Å<sup>3</sup>

$Z = 4$

$F(000) = 432$

$D_x = 1.359$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 18744 reflections

$\theta = 2.9$ – $27.5$ °

$\mu = 0.09$  mm<sup>-1</sup>

$T = 120$  K

Block, colourless

$0.24 \times 0.22 \times 0.04$  mm

### Data collection

Nonius KappaCCD area-detector diffractometer

1680 independent reflections

Radiation source: Enraf Nonius FR591 rotating anode

1636 reflections with  $I > 2\sigma(I)$

10 cm confocal mirrors

$R_{int} = 0.027$

Detector resolution: 9.091 pixels mm<sup>-1</sup>

$\theta_{max} = 25.0$ °,  $\theta_{min} = 3.2$ °

$\varphi$  and  $\omega$  scans

$h = -6 \rightarrow 6$

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)

$k = -8 \rightarrow 8$

$T_{min} = 0.670$ ,  $T_{max} = 0.746$

$l = -28 \rightarrow 28$

3068 measured reflections

*Refinement*

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.109$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 0.3833P]$
1680 reflections	where $P = (F_o^2 + 2F_c^2)/3$
149 parameters	$(\Delta/\sigma)_{\max} < 0.001$
4 restraints	$\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O1W	0.0268 (3)	0.5726 (2)	0.74096 (6)	0.0234 (4)
H1W	0.088 (5)	0.635 (3)	0.7695 (7)	0.035*
H2W	-0.071 (4)	0.501 (3)	0.7507 (11)	0.035*
N1	0.2897 (3)	0.7646 (2)	0.83791 (7)	0.0221 (4)
N2	0.5539 (4)	0.8844 (2)	0.78669 (8)	0.0218 (4)
H2N	0.694 (3)	0.935 (3)	0.7844 (10)	0.026*
N3	0.3760 (4)	0.8612 (2)	0.73892 (7)	0.0205 (4)
N4	0.0207 (4)	0.7784 (2)	0.64316 (7)	0.0205 (4)
H4N	0.000 (5)	0.726 (3)	0.6740 (6)	0.025*
C1	0.4955 (4)	0.8541 (3)	0.83784 (8)	0.0193 (4)
C2	0.2360 (4)	0.7344 (3)	0.88823 (8)	0.0238 (5)
H2	0.0904	0.6710	0.8886	0.029*
C3	0.3790 (5)	0.7898 (3)	0.93898 (9)	0.0257 (5)
H3	0.3346	0.7654	0.9735	0.031*
C4	0.5912 (5)	0.8829 (3)	0.93755 (9)	0.0250 (5)
H4	0.6942	0.9245	0.9716	0.030*
C5	0.6526 (4)	0.9152 (3)	0.88711 (9)	0.0229 (5)

## supplementary materials

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H5	0.7981	0.9774	0.8858	0.027*
C6	0.4278 (4)	0.8846 (3)	0.69071 (8)	0.0204 (5)
H6	0.5870	0.9191	0.6882	0.024*
C7	0.2393 (4)	0.8574 (3)	0.64086 (8)	0.0196 (5)
C8	-0.1198 (4)	0.7629 (3)	0.59024 (8)	0.0230 (5)
H8	-0.2775	0.7109	0.5804	0.028*
C9	0.0049 (4)	0.8353 (3)	0.55333 (8)	0.0240 (5)
H9	-0.0522	0.8433	0.5137	0.029*
C10	0.2326 (5)	0.8955 (3)	0.58482 (8)	0.0218 (5)
H10	0.3571	0.9512	0.5705	0.026*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1W	0.0245 (9)	0.0239 (7)	0.0224 (7)	-0.0061 (6)	0.0065 (7)	0.0001 (6)
N1	0.0242 (10)	0.0196 (9)	0.0231 (9)	-0.0003 (8)	0.0066 (8)	0.0013 (7)
N2	0.0194 (10)	0.0269 (10)	0.0200 (8)	-0.0038 (8)	0.0060 (8)	0.0001 (7)
N3	0.0214 (9)	0.0194 (8)	0.0199 (8)	-0.0005 (7)	0.0027 (8)	0.0005 (7)
N4	0.0229 (10)	0.0191 (8)	0.0200 (8)	-0.0011 (8)	0.0062 (7)	0.0014 (7)
C1	0.0202 (11)	0.0159 (9)	0.0217 (10)	0.0028 (9)	0.0048 (9)	0.0013 (8)
C2	0.0269 (12)	0.0195 (9)	0.0278 (10)	0.0027 (9)	0.0120 (10)	0.0032 (9)
C3	0.0361 (13)	0.0211 (10)	0.0215 (9)	0.0040 (10)	0.0102 (10)	0.0029 (9)
C4	0.0335 (13)	0.0191 (10)	0.0198 (10)	0.0034 (10)	0.0007 (10)	-0.0001 (9)
C5	0.0251 (13)	0.0178 (9)	0.0241 (10)	0.0005 (9)	0.0025 (10)	0.0003 (8)
C6	0.0209 (11)	0.0176 (10)	0.0241 (9)	-0.0001 (8)	0.0080 (10)	-0.0016 (8)
C7	0.0221 (12)	0.0166 (9)	0.0210 (10)	0.0006 (9)	0.0069 (9)	0.0005 (8)
C8	0.0226 (12)	0.0209 (10)	0.0243 (9)	-0.0008 (9)	0.0027 (9)	-0.0020 (8)
C9	0.0301 (13)	0.0219 (10)	0.0179 (9)	0.0025 (9)	0.0013 (9)	0.0005 (9)
C10	0.0243 (12)	0.0188 (10)	0.0234 (10)	-0.0005 (9)	0.0080 (9)	-0.0008 (8)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

O1W—H1W	0.842 (10)	C3—C4	1.392 (4)
O1W—H2W	0.840 (10)	C3—H3	0.9500
N1—C1	1.340 (3)	C4—C5	1.375 (3)
N1—C2	1.350 (3)	C4—H4	0.9500
N2—N3	1.364 (3)	C5—H5	0.9500
N2—C1	1.382 (3)	C6—C7	1.435 (3)
N2—H2N	0.886 (10)	C6—H6	0.9500
N3—C6	1.289 (3)	C7—C10	1.390 (3)
N4—C8	1.357 (3)	C8—C9	1.375 (3)
N4—C7	1.380 (3)	C8—H8	0.9500
N4—H4N	0.879 (10)	C9—C10	1.411 (3)
C1—C5	1.396 (3)	C9—H9	0.9500
C2—C3	1.377 (3)	C10—H10	0.9500
C2—H2	0.9500		
H1W—O1W—H2W	107 (2)	C3—C4—H4	119.8
C1—N1—C2	117.39 (19)	C4—C5—C1	118.3 (2)

N3—N2—C1	118.06 (17)	C4—C5—H5	120.9
N3—N2—H2N	119.3 (16)	C1—C5—H5	120.9
C1—N2—H2N	121.9 (16)	N3—C6—C7	118.4 (2)
C6—N3—N2	119.13 (18)	N3—C6—H6	120.8
C8—N4—C7	109.25 (17)	C7—C6—H6	120.8
C8—N4—H4N	127.9 (16)	N4—C7—C10	107.7 (2)
C7—N4—H4N	121.4 (17)	N4—C7—C6	121.43 (19)
N1—C1—N2	118.01 (18)	C10—C7—C6	130.8 (2)
N1—C1—C5	122.68 (19)	N4—C8—C9	108.4 (2)
N2—C1—C5	119.31 (19)	N4—C8—H8	125.8
N1—C2—C3	124.2 (2)	C9—C8—H8	125.8
N1—C2—H2	117.9	C8—C9—C10	107.86 (18)
C3—C2—H2	117.9	C8—C9—H9	126.1
C2—C3—C4	117.1 (2)	C10—C9—H9	126.1
C2—C3—H3	121.4	C7—C10—C9	106.7 (2)
C4—C3—H3	121.4	C7—C10—H10	126.6
C5—C4—C3	120.3 (2)	C9—C10—H10	126.6
C5—C4—H4	119.8		
C1—N2—N3—C6	-178.42 (18)	N2—N3—C6—C7	179.22 (17)
C2—N1—C1—N2	179.37 (18)	C8—N4—C7—C10	1.2 (2)
C2—N1—C1—C5	0.2 (3)	C8—N4—C7—C6	-177.71 (19)
N3—N2—C1—N1	15.4 (3)	N3—C6—C7—N4	-11.2 (3)
N3—N2—C1—C5	-165.42 (17)	N3—C6—C7—C10	170.2 (2)
C1—N1—C2—C3	0.0 (3)	C7—N4—C8—C9	-1.2 (2)
N1—C2—C3—C4	0.2 (3)	N4—C8—C9—C10	0.8 (2)
C2—C3—C4—C5	-0.6 (3)	N4—C7—C10—C9	-0.6 (2)
C3—C4—C5—C1	0.8 (3)	C6—C7—C10—C9	178.1 (2)
N1—C1—C5—C4	-0.6 (3)	C8—C9—C10—C7	-0.1 (2)
N2—C1—C5—C4	-179.75 (18)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1w—H1w...N1	0.842 (10)	2.037 (11)	2.870 (2)	170 (3)
O1w—H2w...N3 <sup>i</sup>	0.840 (10)	2.078 (12)	2.899 (3)	166 (3)
N2—H2n...O1w <sup>ii</sup>	0.886 (10)	2.092 (12)	2.959 (3)	166 (2)
N4—H4n...O1w	0.879 (10)	1.971 (11)	2.831 (2)	165 (2)

Symmetry codes: (i)  $-x, y-1/2, -z+3/2$ ; (ii)  $-x+1, y+1/2, -z+3/2$ .

Fig. 1

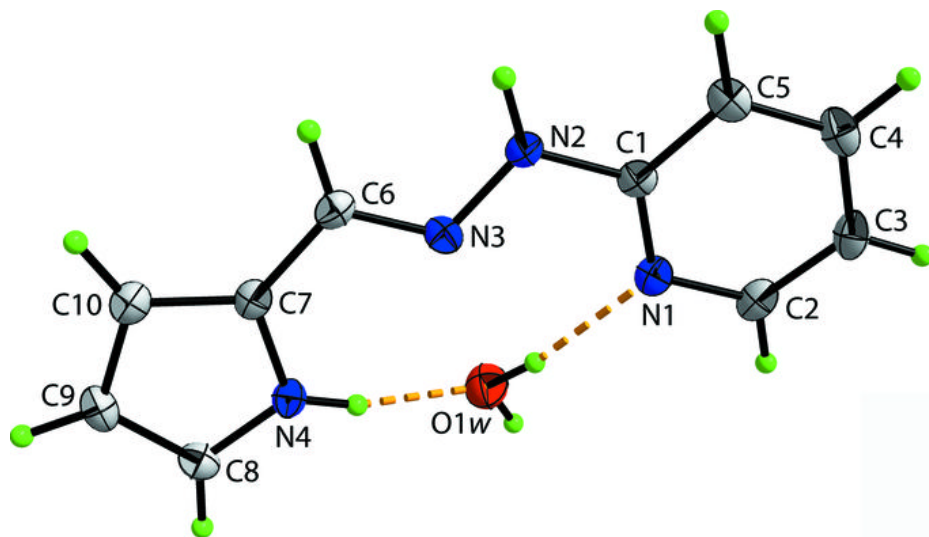




Fig. 2

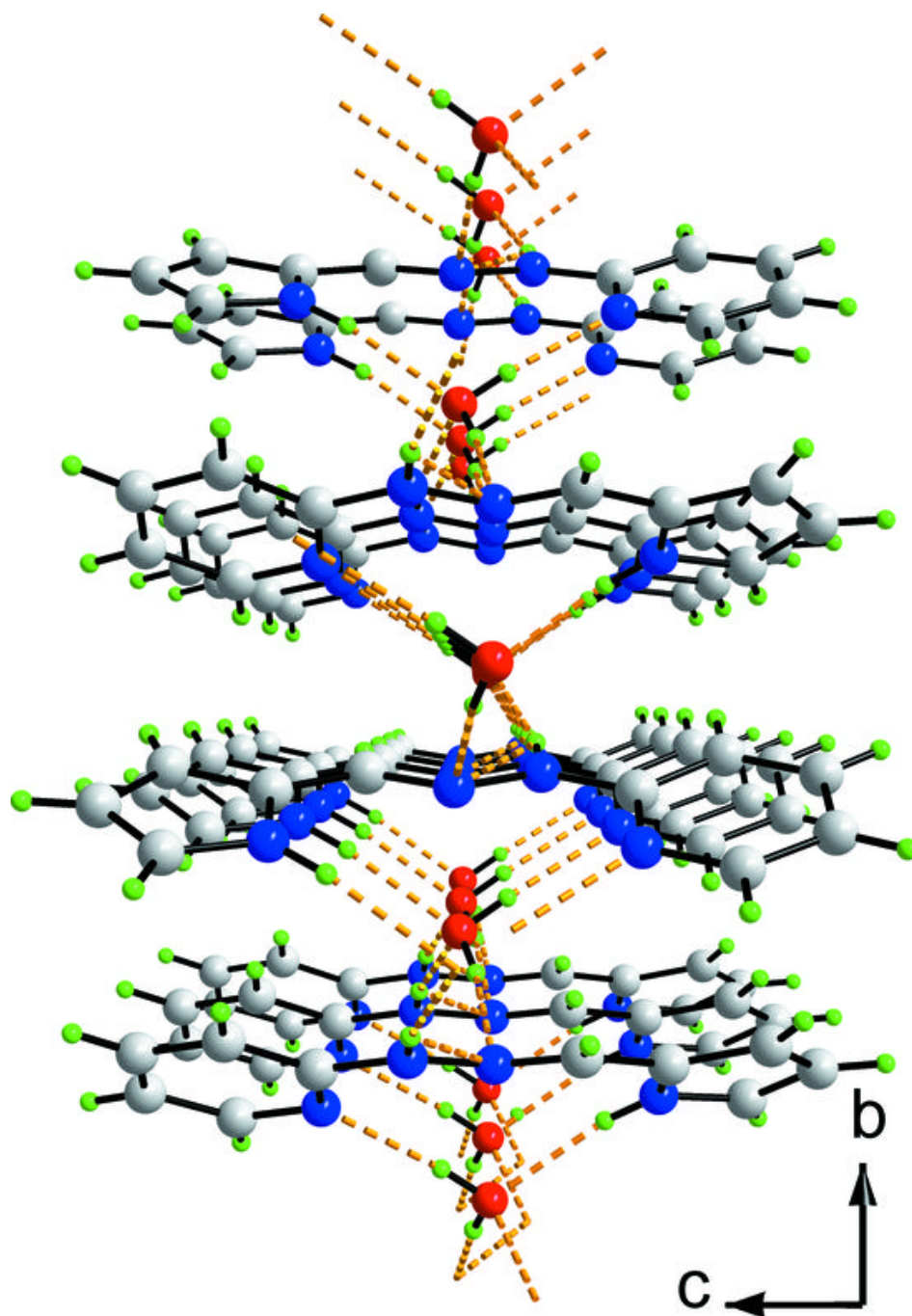


Fig. 3

