

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 2-(4-*tert*-Butylphenyl)-1*H*-imidazo[4,5-*f*]-[1,10]phenanthroline sesquihydrate

Chun-Yang Zheng\* and Ting-Quan Sun

Hubei Key Laboratory of Pollutant Analysis and Reuse Technology, Hubei Normal University, Huangshi 435002, People's Republic of China  
Correspondence e-mail: chunyangzheng@yahoo.com.cn

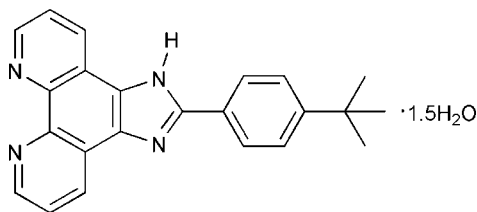
Received 16 May 2009; accepted 27 May 2009

Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å; disorder in main residue;  $R$  factor = 0.068;  $wR$  factor = 0.167; data-to-parameter ratio = 8.8.

In the title compound,  $\text{C}_{23}\text{H}_{20}\text{N}_4 \cdot 1.5\text{H}_2\text{O}$ , the mean planes of the imidazo[4,5-*f*][1,10]phenanthroline system and the benzene ring make a dihedral angle of  $21.76(2)^\circ$ . One water O atom lies on a twofold rotation axis. The organic molecules and water molecules are linked *via*  $\text{N}-\text{H} \cdots \text{O}$ ,  $\text{O}-\text{H} \cdots \text{N}$  and  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds. Weak intermolecular  $\text{C}-\text{H} \cdots \text{N}$  hydrogen bonds and  $\pi-\pi$  stacking interactions between inversion-related phenanthroline rings complete the three-dimensional hydrogen-bonding network in the crystal structure. The stacking distance is short at  $3.513(2)$  Å and the perpendicular distance between the rings is  $3.355$  Å. The three methyl groups are disordered over two positions, with a site-occupancy ratio of  $0.875(14):0.125(14)$ .

### Related literature

For 1,10-phenanthroline derivatives as ligands, see: Cardinaels *et al.* (2005); Liu *et al.* (2005). For the crystal structures of 1,10-phenanthroline derivatives, see: Bian *et al.* (2002); Wu *et al.* (1998). For aromatic  $\pi-\pi$  stacking interactions, see: Janiak (2000).



### Experimental

#### Crystal data

$\text{C}_{23}\text{H}_{20}\text{N}_4 \cdot 1.5\text{H}_2\text{O}$   
 $M_r = 379.46$   
Tetragonal,  $P4_32_12$   
 $a = 14.809(4)$  Å

$c = 18.281(6)$  Å  
 $V = 4009.1(19)$  Å<sup>3</sup>  
 $Z = 8$   
Mo  $K\alpha$  radiation

$\mu = 0.08$  mm<sup>-1</sup>  
 $T = 298$  K

$0.16 \times 0.13 \times 0.10$  mm

#### Data collection

Bruker SMART CCD area-detector diffractometer  
Absorption correction: none  
46858 measured reflections  
2670 independent reflections  
2508 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.054$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$   
 $wR(F^2) = 0.167$   
 $S = 1.28$   
2670 reflections  
304 parameters  
53 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.30$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.15$  e Å<sup>-3</sup>

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

| $D-\text{H} \cdots A$                          | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|--|--------------|---------------------|--------------|-----------------------|
| $\text{O1}-\text{H1A} \cdots \text{N1}^i$      | 0.83 (3)     | 2.45 (3)            | 3.193 (5)    | 151 (5)               |
| $\text{O1}-\text{H1A} \cdots \text{N2}^j$      | 0.83 (3)     | 2.19 (4)            | 2.853 (4)    | 137 (5)               |
| $\text{O1}-\text{H1B} \cdots \text{O2}^{ii}$   | 0.83 (3)     | 2.065 (16)          | 2.878 (3)    | 168 (5)               |
| $\text{O2}-\text{H2A} \cdots \text{N4}$        | 0.82 (3)     | 2.15 (2)            | 2.914 (4)    | 156 (5)               |
| $\text{N3}-\text{H3} \cdots \text{O1}$         | 0.86 (3)     | 1.90 (3)            | 2.754 (4)    | 176 (4)               |
| $\text{C12}-\text{H12} \cdots \text{N4}^{iii}$ | 0.93         | 2.53                | 3.346 (4)    | 147                   |

Symmetry codes: (i)  $-y + \frac{3}{2}, x - \frac{1}{2}, z - \frac{1}{4}$ ; (ii)  $y + \frac{1}{2}, -x + \frac{1}{2}, z + \frac{1}{4}$ ; (iii)  $y, x, -z + 2$ .

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; 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* and *PLATON* (Spek, 2009).

The authors are grateful to the Postgraduate Programme of Hubei Normal University for financial support under grant No. 2008D53.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2177).

### References

- Bian, Z. Q., Wang, K. Z. & Jin, L. P. (2002). *Polyhedron*, **21**, 313–319.  
Bruker (1997). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.  
Bruker (1999). *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.  
Cardinaels, T., Ramaekers, J., Guillon, D., Donnio, B. & Binnemans, K. (2005). *J. Am. Chem. Soc.* **127**, 17602–17603.  
Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.  
Liu, Y., Duan, Z. Y., Zhang, H. Y., Jiang, X. L. & Han, J. R. (2005). *J. Org. Chem.* **70**, 1450–1455.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.  
Wu, J. Z., Yang, G., Chen, S., Ji, L. N., Zhou, J. Y. & Xu, Y. (1998). *Inorg. Chim. Acta*, **283**, 17–23.

**supplementary materials**

*Acta Cryst.* (2009). E65, o1471 [ doi:10.1107/S1600536809020261 ]

## 2-(4-*tert*-Butylphenyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline sesquihydrate

C.-Y. Zheng and T.-Q. Sun

### Comment

1,10-Phenanthroline and its derivatives are commonly used as ligands in metal complexes (Bian *et al.* 2002; Cardinaels *et al.* 2005; Liu *et al.* 2005; Wu *et al.* 1998). We report here the structure of the title compound (I) (Fig. 1), which was synthesized from [4,5-*f*]1,10-phenanthroline. The mean plane of the [4,5-*f*]1,10-phenanthroline moiety and the benzene ring (C14 - C19) make a dihedral angle of 21.76 (2)°. The water oxygen atom O2 occupies a twofold rotation axis, generating a symmetric four-centre hydrogen bond system that link two imidazo groups and two water molecules O1 *via* O—H···N and O—H···O bonds (Fig. 2). The other water molecules O1 link the two phenanthroline N-atoms through bifurcated O—H···N hydrogen bonds (Table 1). Intermolecular C—H···N hydrogen bonds and  $\pi$ — $\pi$  stacking interactions (Janiak, 2000) between inversion related phenanthroline rings complete the hydrogen bonding network in the crystal structure. The short stacking distance  $Cg_i$ — $Cg_j$  is 3.513 (2) Å, the perpendicular distance between the rings is 3.355 Å, and the dihedral angle between the rings is 2.48°.  $Cg$  is the centroid of ring (N2, C5, C4, C12, C11, C10), a symmetry code for  $Cg_j$  was given as (1 - *y*, 1 - *x*, 5/2 - *z*). The three methyl groups are disordered over two positions, with a site occupancy ratio of *ca* 7:1.

### Experimental

1,10-Phenanthroline-5,6-dione (0.84 g, 0.004 mol) and ammonium acetate (3.1 g, 0.04 mmol) were dissolved in 40 ml of hot glacial acetic acid. While the mixture was stirred, a solution of 4-*tert*-butylbenzaldehyde (0.65 g, 0.004 mmol) in 10 ml of glacial acetic acid was added dropwise to the mixture. The mixture was heated at 363 K for 3 h and was then poured in 200 ml of water. The solution was neutralized with ammonia to pH=8 and was then cooled to room temperature. The precipitate was filtered off and recrystallized from dilute ethanol solution to give the title compound (I). Crystals suitable for X-ray diffraction were grown by slow evaporation of the EtOH solutions at room temperature.

### Refinement

The methyl groups were found to be disordered over two orientations. The occupancies of the disordered positions C21/C21', C22/C22' and C23/C23' were refined to 0.875 (14)/0.125 (14). Suitable restraints were applied to the C—C distances involving the disordered atoms. The methyl H atoms were constrained to an ideal geometry with C—H distances of 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ , but each group was allowed to rotate freely about its C—C bond. Other H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms, with C—H distances of 0.93 to 0.97 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ . All H atoms on N atoms were positioned geometrically and refined as riding atoms, with N—H = 0.86 Å and  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$ . The H atoms of the waters were located in a Fourier map following isotropic refinement. In the absence of significant anomalous scattering effects, Friedel related intensity reflections were averaged.

## Figures

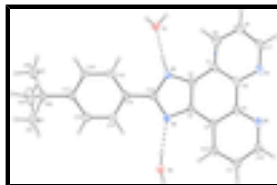


Fig. 1. View of the molecular structure of (I), showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are indicated by dashed lines. The three disordered methyl groups were omitted for clarity.

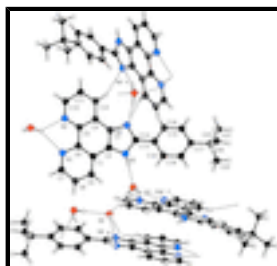


Fig. 2. A section of the structure of (I) with intermolecular hydrogen bonds indicated as dashed lines.

## 2-(4-*tert*-Butylphenyl)-1*H*-imidazo[4,5-*f*][1,10] phenanthroline sesquihydrate

### Crystal data

$C_{23}H_{20}N_4 \cdot 1.5H_2O$

$M_r = 379.46$

Tetragonal,  $P4_32_12$

Hall symbol: P4nw 2abw

$a = 14.809 (4) \text{ \AA}$

$b = 14.809 (4) \text{ \AA}$

$c = 18.281 (6) \text{ \AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 4009.1 (19) \text{ \AA}^3$

$Z = 8$

$F_{000} = 1608$

$D_x = 1.257 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

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

Cell parameters from 5405 reflections

$\theta = 2.2\text{--}22.5^\circ$

$\mu = 0.08 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Block, yellow

$0.16 \times 0.13 \times 0.10 \text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298 \text{ K}$

$\varphi$  and  $\omega$  scans

Absorption correction: none

46858 measured reflections

2670 independent reflections

2508 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

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

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

$h = -19 \rightarrow 19$

$k = -19 \rightarrow 19$

$l = -23 \rightarrow 23$

Refinement

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map                   |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites               |
| $R[F^2 > 2\sigma(F^2)] = 0.068$                                | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.167$  | $w = 1/[\sigma^2(F_o^2) + (0.0765P)^2 + 0.9688P]$                      |
| $S = 1.28$   | where $P = (F_o^2 + 2F_c^2)/3$   |
| 2670 reflections   | $(\Delta/\sigma)_{\max} < 0.001$                                       |
| 304 parameters   | $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$                  |
| 53 restraints  | $\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$                 |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none  |

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 ( $\text{\AA}^2$ )

|     | $x$        | $y$        | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|------------|------------|--------------|----------------------------------|-----------|
| C1  | 0.7310 (2) | 0.4019 (2) | 1.19064 (17) | 0.0436 (7)                       |           |
| C2  | 0.6832 (2) | 0.3733 (2) | 1.12626 (16) | 0.0412 (7)                       |           |
| C3  | 0.6074 (2) | 0.4156 (2) | 1.10102 (16) | 0.0392 (7)                       |           |
| C4  | 0.5709 (2) | 0.4934 (2) | 1.13671 (16) | 0.0399 (7)                       |           |
| C5  | 0.6151 (2) | 0.5242 (2) | 1.20079 (17) | 0.0424 (7)                       |           |
| C6  | 0.6959 (2) | 0.4778 (2) | 1.22760 (17) | 0.0453 (8)                       |           |
| N1  | 0.7345 (2) | 0.5111 (2) | 1.28912 (17) | 0.0593 (9)                       |           |
| C7  | 0.8061 (3) | 0.4692 (3) | 1.3142 (2)   | 0.0723 (13)                      |           |
| H7  | 0.8325     | 0.4915     | 1.3567       | 0.087*                           |           |
| C8  | 0.8453 (3) | 0.3944 (4) | 1.2822 (3)   | 0.0760 (14)                      |           |
| H8  | 0.8961     | 0.3676     | 1.3027       | 0.091*                           |           |
| C9  | 0.8074 (3) | 0.3605 (3) | 1.2194 (2)   | 0.0623 (10)                      |           |
| H9  | 0.8325     | 0.3104     | 1.1965       | 0.075*                           |           |
| N2  | 0.5840 (2) | 0.5952 (2) | 1.23928 (16) | 0.0505 (7)                       |           |
| C10 | 0.5114 (3) | 0.6373 (3) | 1.2156 (2)   | 0.0538 (9)                       |           |
| H10 | 0.4901     | 0.6860     | 1.2428       | 0.065*                           |           |

## supplementary materials

---

|      |              |              |              |             |            |
|------|--------------|--------------|--------------|-------------|------------|
| C11  | 0.4647 (3)   | 0.6138 (3)   | 1.1531 (2)   | 0.0569 (9)  |            |
| H11  | 0.4139       | 0.6460       | 1.1385       | 0.068*      |            |
| C12  | 0.4950 (2)   | 0.5420 (2)   | 1.11298 (19) | 0.0504 (8)  |            |
| H12  | 0.4654       | 0.5254       | 1.0702       | 0.060*      |            |
| C13  | 0.6348 (2)   | 0.3069 (2)   | 1.02710 (16) | 0.0416 (7)  |            |
| C14  | 0.6341 (2)   | 0.2461 (2)   | 0.96339 (16) | 0.0426 (7)  |            |
| C15  | 0.5563 (2)   | 0.2359 (2)   | 0.92178 (18) | 0.0480 (8)  |            |
| H15  | 0.5038       | 0.2657       | 0.9359       | 0.058*      |            |
| C16  | 0.5553 (3)   | 0.1825 (2)   | 0.85987 (18) | 0.0500 (8)  |            |
| H16  | 0.5020       | 0.1764       | 0.8335       | 0.060*      |            |
| C17  | 0.6319 (3)   | 0.1377 (2)   | 0.83626 (18) | 0.0510 (9)  |            |
| C18  | 0.7096 (3)   | 0.1491 (3)   | 0.8774 (2)   | 0.0616 (11) |            |
| H18  | 0.7623       | 0.1202       | 0.8627       | 0.074*      |            |
| C19  | 0.7112 (3)   | 0.2021 (3)   | 0.93992 (19) | 0.0566 (10) |            |
| H19  | 0.7646       | 0.2082       | 0.9663       | 0.068*      |            |
| C20  | 0.6326 (3)   | 0.0806 (3)   | 0.76548 (19) | 0.0646 (11) |            |
| C21  | 0.5375 (4)   | 0.0646 (6)   | 0.7367 (4)   | 0.110 (3)   | 0.875 (14) |
| H21A | 0.5404       | 0.0291       | 0.6928       | 0.165*      | 0.875 (14) |
| H21B | 0.5094       | 0.1216       | 0.7262       | 0.165*      | 0.875 (14) |
| H21C | 0.5028       | 0.0331       | 0.7729       | 0.165*      | 0.875 (14) |
| C22  | 0.6769 (8)   | -0.0099 (5)  | 0.7785 (4)   | 0.122 (4)   | 0.875 (14) |
| H22A | 0.6722       | -0.0460      | 0.7351       | 0.183*      | 0.875 (14) |
| H22B | 0.6472       | -0.0401      | 0.8182       | 0.183*      | 0.875 (14) |
| H22C | 0.7394       | -0.0010      | 0.7904       | 0.183*      | 0.875 (14) |
| C23  | 0.6840 (7)   | 0.1327 (6)   | 0.7075 (3)   | 0.125 (4)   | 0.875 (14) |
| H23A | 0.7410       | 0.1519       | 0.7269       | 0.188*      | 0.875 (14) |
| H23B | 0.6495       | 0.1846       | 0.6929       | 0.188*      | 0.875 (14) |
| H23C | 0.6940       | 0.0945       | 0.6658       | 0.188*      | 0.875 (14) |
| C21' | 0.565 (3)    | 0.003 (3)    | 0.765 (3)    | 0.13 (2)    | 0.125 (14) |
| H21D | 0.5711       | -0.0303      | 0.7199       | 0.188*      | 0.125 (14) |
| H21E | 0.5047       | 0.0268       | 0.7680       | 0.188*      | 0.125 (14) |
| H21F | 0.5762       | -0.0362      | 0.8054       | 0.188*      | 0.125 (14) |
| C22' | 0.7261 (17)  | 0.040 (4)    | 0.752 (3)    | 0.099 (17)  | 0.125 (14) |
| H22D | 0.7216       | -0.0080      | 0.7169       | 0.149*      | 0.125 (14) |
| H22E | 0.7490       | 0.0154       | 0.7976       | 0.149*      | 0.125 (14) |
| H22F | 0.7664       | 0.0853       | 0.7347       | 0.149*      | 0.125 (14) |
| C23' | 0.612 (4)    | 0.140 (3)    | 0.6995 (18)  | 0.12 (2)    | 0.125 (14) |
| H23D | 0.6390       | 0.1146       | 0.6565       | 0.174*      | 0.125 (14) |
| H23E | 0.6365       | 0.1996       | 0.7076       | 0.174*      | 0.125 (14) |
| H23F | 0.5479       | 0.1446       | 0.6929       | 0.174*      | 0.125 (14) |
| N3   | 0.70020 (19) | 0.30431 (19) | 1.07917 (14) | 0.0433 (6)  |            |
| H3   | 0.734 (2)    | 0.2580 (17)  | 1.086 (2)    | 0.052*      |            |
| N4   | 0.57632 (19) | 0.37297 (18) | 1.03858 (13) | 0.0417 (6)  |            |
| O1   | 0.8076 (2)   | 0.1575 (2)   | 1.11023 (13) | 0.0661 (9)  |            |
| H1A  | 0.852 (2)    | 0.159 (4)    | 1.0831 (19)  | 0.099*      |            |
| H1B  | 0.824 (3)    | 0.140 (4)    | 1.1511 (13)  | 0.099*      |            |
| O2   | 0.38586 (17) | 0.38586 (17) | 1.0000       | 0.0487 (8)  |            |
| H2A  | 0.4347 (17)  | 0.366 (3)    | 1.014 (3)    | 0.073*      |            |

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

|      | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| C1   | 0.0486 (18) | 0.0470 (18) | 0.0354 (14) | -0.0038 (15) | -0.0049 (13) | 0.0075 (13)  |
| C2   | 0.0490 (18) | 0.0405 (16) | 0.0341 (14) | -0.0017 (14) | -0.0012 (13) | 0.0037 (12)  |
| C3   | 0.0475 (17) | 0.0393 (15) | 0.0307 (13) | -0.0020 (13) | -0.0058 (12) | 0.0041 (12)  |
| C4   | 0.0453 (17) | 0.0405 (16) | 0.0340 (14) | -0.0022 (13) | -0.0008 (13) | 0.0001 (12)  |
| C5   | 0.0510 (18) | 0.0420 (17) | 0.0342 (14) | -0.0069 (14) | 0.0002 (13)  | 0.0027 (12)  |
| C6   | 0.0514 (18) | 0.0490 (18) | 0.0355 (15) | -0.0111 (15) | -0.0054 (14) | 0.0018 (13)  |
| N1   | 0.064 (2)   | 0.069 (2)   | 0.0451 (15) | -0.0063 (17) | -0.0158 (15) | -0.0029 (15) |
| C7   | 0.079 (3)   | 0.081 (3)   | 0.057 (2)   | -0.006 (3)   | -0.031 (2)   | -0.004 (2)   |
| C8   | 0.069 (3)   | 0.086 (3)   | 0.072 (3)   | 0.010 (3)    | -0.031 (2)   | 0.002 (3)    |
| C9   | 0.062 (2)   | 0.064 (2)   | 0.061 (2)   | 0.005 (2)    | -0.0200 (19) | -0.0030 (19) |
| N2   | 0.0604 (18) | 0.0486 (16) | 0.0425 (14) | -0.0071 (13) | -0.0021 (14) | -0.0057 (13) |
| C10  | 0.061 (2)   | 0.0452 (18) | 0.0552 (19) | -0.0009 (16) | 0.0023 (18)  | -0.0122 (17) |
| C11  | 0.060 (2)   | 0.048 (2)   | 0.062 (2)   | 0.0087 (17)  | -0.0095 (18) | -0.0069 (17) |
| C12  | 0.058 (2)   | 0.0471 (18) | 0.0459 (17) | 0.0003 (16)  | -0.0133 (16) | -0.0037 (15) |
| C13  | 0.0492 (17) | 0.0409 (16) | 0.0347 (14) | 0.0019 (14)  | -0.0003 (13) | 0.0050 (13)  |
| C14  | 0.0523 (18) | 0.0408 (16) | 0.0349 (14) | 0.0042 (14)  | -0.0006 (14) | 0.0033 (13)  |
| C15  | 0.0472 (19) | 0.0515 (19) | 0.0452 (16) | 0.0083 (15)  | 0.0009 (15)  | -0.0064 (15) |
| C16  | 0.058 (2)   | 0.051 (2)   | 0.0408 (16) | 0.0000 (17)  | -0.0041 (16) | -0.0042 (15) |
| C17  | 0.073 (2)   | 0.0489 (19) | 0.0317 (14) | 0.0097 (17)  | 0.0009 (16)  | -0.0007 (14) |
| C18  | 0.066 (2)   | 0.074 (3)   | 0.0446 (18) | 0.029 (2)    | -0.0004 (18) | -0.0092 (18) |
| C19  | 0.056 (2)   | 0.069 (2)   | 0.0449 (18) | 0.0161 (19)  | -0.0064 (16) | -0.0076 (17) |
| C20  | 0.090 (3)   | 0.069 (3)   | 0.0340 (17) | 0.016 (2)    | -0.0018 (19) | -0.0102 (18) |
| C21  | 0.111 (5)   | 0.131 (7)   | 0.088 (5)   | -0.003 (5)   | -0.016 (4)   | -0.068 (5)   |
| C22  | 0.194 (10)  | 0.100 (6)   | 0.072 (4)   | 0.064 (6)    | -0.030 (5)   | -0.038 (4)   |
| C23  | 0.169 (9)   | 0.162 (8)   | 0.044 (3)   | -0.053 (7)   | 0.024 (4)    | -0.020 (4)   |
| C21' | 0.13 (3)    | 0.12 (3)    | 0.13 (3)    | -0.006 (19)  | -0.007 (19)  | -0.019 (19)  |
| C22' | 0.11 (2)    | 0.10 (2)    | 0.09 (2)    | 0.019 (17)   | -0.012 (17)  | -0.026 (18)  |
| C23' | 0.13 (3)    | 0.11 (3)    | 0.11 (2)    | 0.003 (19)   | -0.011 (19)  | -0.014 (18)  |
| N3   | 0.0484 (16) | 0.0451 (15) | 0.0363 (13) | 0.0073 (12)  | -0.0044 (12) | 0.0032 (12)  |
| N4   | 0.0514 (15) | 0.0418 (14) | 0.0319 (11) | 0.0064 (12)  | -0.0039 (12) | -0.0008 (11) |
| O1   | 0.0715 (19) | 0.086 (2)   | 0.0412 (12) | 0.0343 (17)  | 0.0099 (13)  | 0.0085 (14)  |
| O2   | 0.0519 (12) | 0.0519 (12) | 0.0422 (17) | -0.0066 (17) | 0.0024 (11)  | -0.0024 (11) |

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

|        |           |          |            |
|--------|-----------|----------|------------|
| C1—C9  | 1.390 (5) | C17—C18  | 1.384 (6)  |
| C1—C6  | 1.411 (5) | C17—C20  | 1.545 (5)  |
| C1—C2  | 1.437 (4) | C18—C19  | 1.387 (5)  |
| C2—N3  | 1.360 (4) | C18—H18  | 0.9300     |
| C2—C3  | 1.366 (4) | C19—H19  | 0.9300     |
| C3—N4  | 1.383 (4) | C20—C22  | 1.511 (6)  |
| C3—C4  | 1.431 (5) | C20—C23  | 1.516 (6)  |
| C4—C12 | 1.403 (5) | C20—C21  | 1.522 (6)  |
| C4—C5  | 1.418 (4) | C20—C21' | 1.524 (10) |
| C5—N2  | 1.346 (4) | C20—C23' | 1.527 (10) |

## supplementary materials

---

|           |           |               |            |
|-----------|-----------|---------------|------------|
| C5—C6     | 1.465 (5) | C20—C22'      | 1.532 (10) |
| C6—N1     | 1.354 (4) | C21—H21A      | 0.9600     |
| N1—C7     | 1.312 (6) | C21—H21B      | 0.9600     |
| C7—C8     | 1.381 (7) | C21—H21C      | 0.9600     |
| C7—H7     | 0.9300    | C22—H22A      | 0.9600     |
| C8—C9     | 1.372 (6) | C22—H22B      | 0.9600     |
| C8—H8     | 0.9300    | C22—H22C      | 0.9600     |
| C9—H9     | 0.9300    | C23—H23A      | 0.9600     |
| N2—C10    | 1.316 (5) | C23—H23B      | 0.9600     |
| C10—C11   | 1.382 (5) | C23—H23C      | 0.9600     |
| C10—H10   | 0.9300    | C21'—H21D     | 0.9600     |
| C11—C12   | 1.367 (5) | C21'—H21E     | 0.9600     |
| C11—H11   | 0.9300    | C21'—H21F     | 0.9600     |
| C12—H12   | 0.9300    | C22'—H22D     | 0.9600     |
| C13—N4    | 1.323 (4) | C22'—H22E     | 0.9600     |
| C13—N3    | 1.359 (4) | C22'—H22F     | 0.9600     |
| C13—C14   | 1.472 (4) | C23'—H23D     | 0.9600     |
| C14—C19   | 1.383 (5) | C23'—H23E     | 0.9600     |
| C14—C15   | 1.389 (5) | C23'—H23F     | 0.9600     |
| C15—C16   | 1.381 (5) | N3—H3         | 0.86 (3)   |
| C15—H15   | 0.9300    | O1—H1A        | 0.83 (3)   |
| C16—C17   | 1.383 (5) | O1—H1B        | 0.83 (3)   |
| C16—H16   | 0.9300    | O2—H2A        | 0.82 (3)   |
| C9—C1—C6  | 118.0 (3) | C19—C18—H18   | 119.0      |
| C9—C1—C2  | 125.5 (3) | C14—C19—C18   | 120.5 (4)  |
| C6—C1—C2  | 116.4 (3) | C14—C19—H19   | 119.7      |
| N3—C2—C3  | 106.4 (3) | C18—C19—H19   | 119.7      |
| N3—C2—C1  | 130.4 (3) | C22—C20—C23   | 110.0 (5)  |
| C3—C2—C1  | 123.2 (3) | C22—C20—C21   | 108.5 (5)  |
| C2—C3—N4  | 110.1 (3) | C23—C20—C21   | 107.6 (5)  |
| C2—C3—C4  | 121.7 (3) | C23—C20—C21'  | 135 (2)    |
| N4—C3—C4  | 128.2 (3) | C22—C20—C23'  | 136.5 (19) |
| C12—C4—C5 | 117.4 (3) | C21'—C20—C23' | 107.3 (10) |
| C12—C4—C3 | 125.1 (3) | C21—C20—C22'  | 136.1 (18) |
| C5—C4—C3  | 117.5 (3) | C21'—C20—C22' | 107.1 (9)  |
| N2—C5—C4  | 121.7 (3) | C23'—C20—C22' | 106.7 (9)  |
| N2—C5—C6  | 118.1 (3) | C22—C20—C17   | 110.9 (3)  |
| C4—C5—C6  | 120.2 (3) | C23—C20—C17   | 108.1 (4)  |
| N1—C6—C1  | 122.2 (3) | C21—C20—C17   | 111.7 (4)  |
| N1—C6—C5  | 116.9 (3) | C21'—C20—C17  | 115 (2)    |
| C1—C6—C5  | 121.0 (3) | C23'—C20—C17  | 110.1 (19) |
| C7—N1—C6  | 117.4 (4) | C22'—C20—C17  | 110.7 (17) |
| N1—C7—C8  | 124.8 (4) | C20—C21—H21A  | 109.5      |
| N1—C7—H7  | 117.6     | C20—C21—H21B  | 109.5      |
| C8—C7—H7  | 117.6     | C20—C21—H21C  | 109.5      |
| C9—C8—C7  | 118.5 (4) | C20—C22—H22A  | 109.5      |
| C9—C8—H8  | 120.8     | C20—C22—H22B  | 109.5      |
| C7—C8—H8  | 120.8     | C20—C22—H22C  | 109.5      |
| C8—C9—C1  | 119.2 (4) | C20—C23—H23A  | 109.5      |

|             |           |                |            |
|-------------|-----------|----------------|------------|
| C8—C9—H9    | 120.4     | C20—C23—H23B   | 109.5      |
| C1—C9—H9    | 120.4     | C20—C23—H23C   | 109.5      |
| C10—N2—C5   | 118.5 (3) | C20—C21'—H21D  | 109.5      |
| N2—C10—C11  | 124.2 (3) | C20—C21'—H21E  | 109.5      |
| N2—C10—H10  | 117.9     | H21D—C21'—H21E | 109.5      |
| C11—C10—H10 | 117.9     | C20—C21'—H21F  | 109.5      |
| C12—C11—C10 | 118.4 (4) | H21D—C21'—H21F | 109.5      |
| C12—C11—H11 | 120.8     | H21E—C21'—H21F | 109.5      |
| C10—C11—H11 | 120.8     | C20—C22'—H22D  | 109.5      |
| C11—C12—C4  | 119.7 (3) | C20—C22'—H22E  | 109.5      |
| C11—C12—H12 | 120.1     | H22D—C22'—H22E | 109.5      |
| C4—C12—H12  | 120.1     | C20—C22'—H22F  | 109.5      |
| N4—C13—N3   | 112.1 (3) | H22D—C22'—H22F | 109.5      |
| N4—C13—C14  | 125.0 (3) | H22E—C22'—H22F | 109.5      |
| N3—C13—C14  | 122.8 (3) | C20—C23'—H23D  | 109.5      |
| C19—C14—C15 | 117.7 (3) | C20—C23'—H23E  | 109.5      |
| C19—C14—C13 | 121.8 (3) | H23D—C23'—H23E | 109.5      |
| C15—C14—C13 | 120.4 (3) | C20—C23'—H23F  | 109.5      |
| C16—C15—C14 | 121.3 (3) | H23D—C23'—H23F | 109.5      |
| C16—C15—H15 | 119.4     | H23E—C23'—H23F | 109.5      |
| C14—C15—H15 | 119.4     | C13—N3—C2      | 106.9 (3)  |
| C15—C16—C17 | 121.5 (3) | C13—N3—H3      | 123 (3)    |
| C15—C16—H16 | 119.3     | C2—N3—H3       | 128 (3)    |
| C17—C16—H16 | 119.3     | C13—N4—C3      | 104.5 (3)  |
| C16—C17—C18 | 117.0 (3) | C13—N4—H2A     | 124.9 (13) |
| C16—C17—C20 | 121.9 (4) | C3—N4—H2A      | 121.2 (13) |
| C18—C17—C20 | 121.1 (3) | H3—O1—H1A      | 107 (4)    |
| C17—C18—C19 | 122.1 (4) | H3—O1—H1B      | 128 (4)    |
| C17—C18—H18 | 119.0     | H1A—O1—H1B     | 109 (4)    |

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

| $D-H\cdots A$                      | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| O1—H1A $\cdots$ N1 <sup>i</sup>    | 0.83 (3) | 2.45 (3)    | 3.193 (5)   | 151 (5)       |
| O1—H1A $\cdots$ N2 <sup>i</sup>    | 0.83 (3) | 2.19 (4)    | 2.853 (4)   | 137 (5)       |
| O1—H1B $\cdots$ O2 <sup>ii</sup>   | 0.83 (3) | 2.065 (16)  | 2.878 (3)   | 168 (5)       |
| O2—H2A $\cdots$ N4                 | 0.82 (3) | 2.15 (2)    | 2.914 (4)   | 156 (5)       |
| N3—H3 $\cdots$ O1                  | 0.86 (3) | 1.90 (3)    | 2.754 (4)   | 176 (4)       |
| C12—H12 $\cdots$ N4 <sup>iii</sup> | 0.93     | 2.53        | 3.346 (4)   | 147           |

Symmetry codes: (i)  $-y+3/2, x-1/2, z-1/4$ ; (ii)  $y+1/2, -x+1/2, z+1/4$ ; (iii)  $y, x, -z+2$ .

Fig. 1

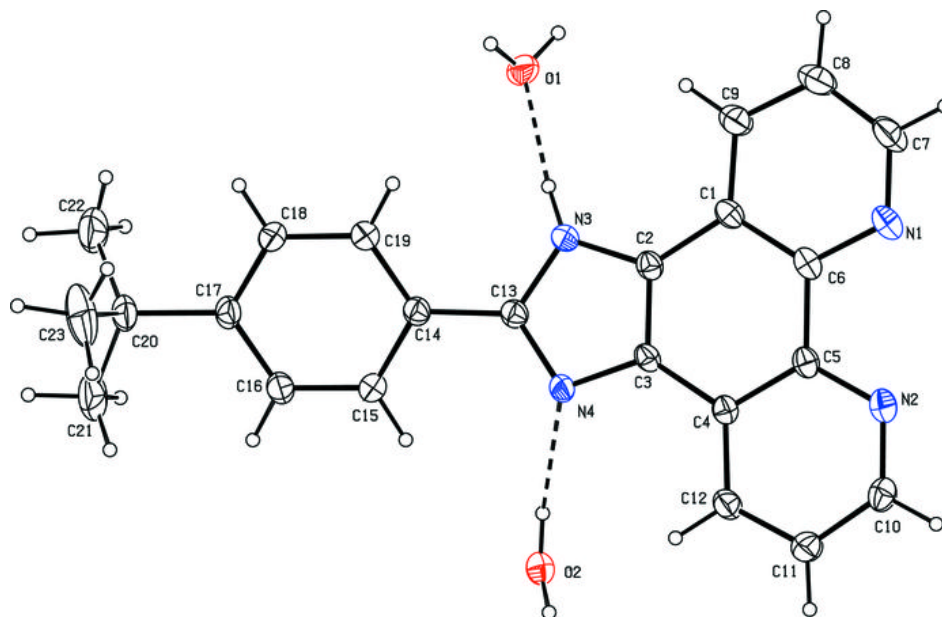


Fig. 2

