

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## Bis[2,6-bis[(2-hydroxy-5-methylphenyl)-iminomethyl]pyridine] monohydrate

Muhammet Kose\* and Vickie McKee

Department of Chemistry, Loughborough University, Loughborough LE11 3TU, England

Correspondence e-mail: m.kose@lboro.ac.uk

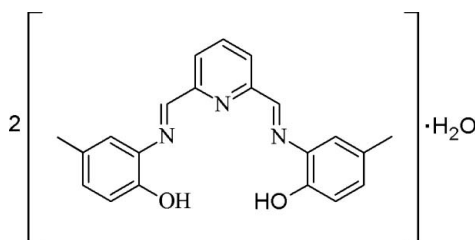
Received 30 September 2011; accepted 28 October 2011

Key indicators: single-crystal X-ray study;  $T = 150$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.042;  $wR$  factor = 0.124; data-to-parameter ratio = 19.9.

The title compound,  $2\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2 \cdot \text{H}_2\text{O}$ , was synthesized by a Schiff base condensation of 2,6-diformylpyridine with 2-amino-4-methylphenol in ethanol. In the crystal, two molecules of 2,6-bis[(2-hydroxy-5-methylphenyl)iminomethyl]pyridine dimerize *via* hydrogen bonding to a water molecule, which lies on a twofold axis. There are also intramolecular phenol-imine hydrogen bonds. The dimers are further linked *via*  $\pi$ - $\pi$  (phenyl-pyridine) [centroid-centroid distance =  $3.707(2)$  Å] and  $\pi$ - $\pi$  edge-to-edge [ $3.392(2)$  Å] interactions. The dihedral angles between the central ring and the two pendant rings are  $11.46(8)$  and  $2.06(8)^\circ$  while the pendant rings make a dihedral angle of  $10.14(8)^\circ$ .

## Related literature

For related structures, see: Gonzalez *et al.* (2008); Sun *et al.* (2006).



## Experimental

## Crystal data

 $2\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2 \cdot \text{H}_2\text{O}$  $M_r = 708.80$ 

Monoclinic,  $C2/c$   
 $a = 23.8510(13)$  Å  
 $b = 12.9688(7)$  Å  
 $c = 12.3835(7)$  Å  
 $\beta = 114.077(1)^\circ$   
 $V = 3497.2(3)$  Å<sup>3</sup>

$Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 150$  K  
 $0.60 \times 0.28 \times 0.11$  mm

## Data collection

Bruker APEXII CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2008)  
 $T_{\min} = 0.947$ ,  $T_{\max} = 0.991$

19364 measured reflections  
 5005 independent reflections  
 3919 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.124$   
 $S = 1.06$   
 5005 reflections  
 251 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.36$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.23$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                          | $D-H$      | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---|------------|--------------|--------------|----------------|
| $\text{O2}-\text{H2A} \cdots \text{O3}$ | 0.836 (17) | 1.960 (17)   | 2.7592 (12)  | 159.6 (15)     |
| $\text{O2}-\text{H2A} \cdots \text{N3}$ | 0.836 (17) | 2.347 (15)   | 2.7624 (12)  | 111.3 (12)     |
| $\text{O1}-\text{H1A} \cdots \text{N1}$ | 0.86 (2)   | 2.120 (19)   | 2.6722 (13)  | 121.7 (16)     |
| $\text{O3}-\text{H3D} \cdots \text{N2}$ | 0.812 (16) | 2.187 (16)   | 2.9865 (12)  | 168.0 (16)     |
| $\text{O3}-\text{H3D} \cdots \text{N3}$ | 0.812 (16) | 2.569 (16)   | 3.0142 (9)   | 115.9 (14)     |

Data collection: APEX2 (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); 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 Turkish Government for the award of a postgraduate scholarship (to MK).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AA2032).

## References

- Bruker (1998). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Gonzalez, A., Gomez, E., Cortes-Lozada, A., Hernandez, S., Ramirez-Apan, T. & Nieto-Camacho, A. (2008). *Chem. Pharm. Bull.* **57**, 5–15.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Sun, X. X., Qi, C. M., Ma, S. L., Huang, H. B., Zhu, W. & Liu, Y. C. (2006). *Inorg. Chem. Commun.* **9**, 911–914.

**supplementary materials**

*Acta Cryst.* (2011). E67, o3193 [ doi:10.1107/S1600536811045399 ]

## Bis{2,6-bis[(2-hydroxy-5-methylphenyl)iminomethyl]pyridine} monohydrate

M. Kose and V. McKee

### Comment

The molecules crystallize as dimers, assembled by hydrogen bonding around a water molecule. The water molecule sits on a twofold axis and makes four strong hydrogen bonds, as donor to the pyridine nitrogen atoms, and as acceptor from the phenol groups (Table 1). There are also weaker hydrogen bond interactions with one of the imine nitrogen atoms of each molecule. Additionally, there are phenol-imine intramolecular hydrogen bonds in each molecule. The azomethine (C8=N1 and C14=N3) linkage distances are 1.278 (14) and 1.273 (14) Å respectively and within the normal C=N values.

The geometry is *cis* at the C8=N1 imine group and *trans* at C14=N3 group. The molecule is close to planar with interplanar angles between the pyridine and phenol groups, 11.46 (8)° and 2.06 (8)° for the rings containing O1 and O2 respectively.

The hydrogen bond geometry at the water molecule is approximately tetrahedral but the angle between the two H-bonded Schiff base molecules is not close to the ideal 90°; the angle between the N2/O3/O2 plane and its equivalent under twofold rotation is 60.52 (4)°. This is possibly a consequence of the intermolecular interactions in the lattice. The Schiff base molecules show two sets of interactions with neighbouring dimeric units. On the more open face (that nearest to the H-bonded phenol of the second molecule), there is a  $\pi$ - $\pi$  interaction involving the pyridine ring and the phenolimine group H-bonded to central water molecule. The average interplanar distance between this section and its neighbour under symmetry operation  $1 - x, -y, -z$  is 3.354 (1) Å and phenol-pyridine centroid-centroid distance is 3.707 (2) Å. On the other face (partially blocked by the non-bonded phenol of the second molecule), there is a less extensive edge to edge interaction C10 to C11 of a neighbouring dimer under symmetry operation  $1 - x, 1 - y, -z$  is 3.392 (2) Å. These result in columns formed by alternating  $\pi$ - $\pi$  and edge to edge interactions extending through the lattice.

### Experimental

A solution of 2,6-diformylpyridine (0.405 g, 3 mmol) in ethanol (15 ml) was added dropwise to an ethanolic solution (30 ml) of 2-amino-4-methylphenol (0.740 g, 6 mmol). A yellow colour appeared and a precipitate was formed in a few minutes. The mixture was stirred for two hours, and then the yellow product was collected by filtration, washed with ethanol-diethylether mixture (1:1) and dried in air. Yield: 0.852 g, 80%, m.p 173–177 °C. Analysis Calc. for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>·0.5(H<sub>2</sub>O): C, 71.17; H, 5.69; N, 11.86%. Found: C, 71.03; H, 5.65; N, 11.70%.

### Refinement

H atoms bonded to C atoms were inserted at calculated positions with C—H distances of 0.95 and 0.99 Å for non-saturated and saturated C atoms, respectively. They were refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The H-atoms bonded to O1, O2 and O3 are taken directly from the difference Fourier and were refined with temperature factors riding on the carrier atom.

## Figures

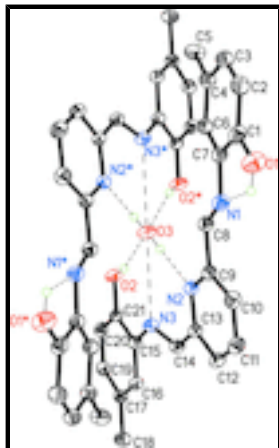


Fig. 1. The structure of the dimeric compound, thermal ellipsoid 50% probability, hydrogen atoms bonded to carbon atoms are omitted for clarity, hydrogen bonds are shown as dash lines, symmetry operation \* 1 - x, y, 1/2 - z.

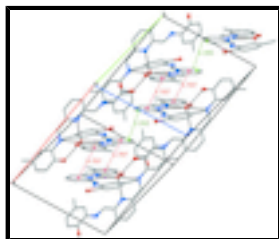


Fig. 2.  $\pi$ - $\pi$  (phenyl-pyridine) and  $\pi$ - $\pi$  edge to edge interactions in the lattice.

## Bis{2,6-bis[(2-hydroxy-5-methylphenyl)iminomethyl]pyridine} monohydrate

### Crystal data

$2C_{21}H_{19}N_3O_2 \cdot H_2O$

$M_r = 708.80$

Monoclinic,  $C2/c$

Hall symbol: -C 2yc

$a = 23.8510$  (13) Å

$b = 12.9688$  (7) Å

$c = 12.3835$  (7) Å

$\beta = 114.077$  (1)°

$V = 3497.2$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 1496$

$D_x = 1.346$  Mg m<sup>-3</sup>

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

Cell parameters from 5957 reflections

$\theta = 2.3$ – $29.8$ °

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

$T = 150$  K

Block, yellow

$0.60 \times 0.28 \times 0.11$  mm

### Data collection

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\phi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2008)

5005 independent reflections

3919 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.024$

$\theta_{max} = 29.8$ °,  $\theta_{min} = 1.8$ °

$h = -33 \rightarrow 33$

$T_{\min} = 0.947$ ,  $T_{\max} = 0.991$   
19364 measured reflections

$k = -17 \rightarrow 18$   
 $l = -17 \rightarrow 17$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.124$

$S = 1.06$

5005 reflections

251 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2 + 1.5272P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

### 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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )

|     | $x$         | $y$          | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|--------------|--------------|----------------------------------|
| O1  | 0.33231 (5) | 0.57957 (7)  | 0.14787 (9)  | 0.0363 (2)                       |
| H1A | 0.3535 (9)  | 0.5552 (15)  | 0.1120 (17)  | 0.054*                           |
| C1  | 0.32840 (6) | 0.50007 (9)  | 0.21682 (10) | 0.0263 (2)                       |
| C2  | 0.29313 (6) | 0.51152 (9)  | 0.28174 (11) | 0.0295 (3)                       |
| H2  | 0.2724      | 0.5747       | 0.2792       | 0.035*                           |
| C3  | 0.28826 (5) | 0.43063 (9)  | 0.35006 (11) | 0.0285 (2)                       |
| H3  | 0.2641      | 0.4391       | 0.3944       | 0.034*                           |
| C4  | 0.31806 (5) | 0.33642 (9)  | 0.35549 (10) | 0.0259 (2)                       |
| C5  | 0.30934 (6) | 0.24734 (10) | 0.42542 (12) | 0.0344 (3)                       |
| H5A | 0.3220      | 0.1832       | 0.4000       | 0.052*                           |
| H5B | 0.2660      | 0.2426       | 0.4119       | 0.052*                           |
| H5C | 0.3344      | 0.2584       | 0.5098       | 0.052*                           |
| C6  | 0.35360 (5) | 0.32612 (9)  | 0.29095 (10) | 0.0243 (2)                       |
| H6  | 0.3744      | 0.2630       | 0.2942       | 0.029*                           |
| C7  | 0.35935 (5) | 0.40707 (9)  | 0.22099 (9)  | 0.0232 (2)                       |

## supplementary materials

|      |             |              |               |              |
|------|-------------|--------------|---------------|--------------|
| N1   | 0.39157 (5) | 0.40486 (7)  | 0.14721 (8)   | 0.0250 (2)   |
| C8   | 0.42258 (5) | 0.32597 (9)  | 0.14243 (9)   | 0.0231 (2)   |
| H8   | 0.4261      | 0.2691       | 0.1931        | 0.028*       |
| C9   | 0.45300 (5) | 0.32110 (8)  | 0.06030 (9)   | 0.0209 (2)   |
| C10  | 0.44553 (5) | 0.39831 (9)  | -0.02331 (10) | 0.0250 (2)   |
| H10  | 0.4218      | 0.4580       | -0.0268       | 0.030*       |
| C11  | 0.47345 (6) | 0.38588 (9)  | -0.10081 (10) | 0.0274 (2)   |
| H11  | 0.4695      | 0.4372       | -0.1582       | 0.033*       |
| C12  | 0.50726 (5) | 0.29722 (9)  | -0.09334 (10) | 0.0251 (2)   |
| H12  | 0.5265      | 0.2866       | -0.1461       | 0.030*       |
| C13  | 0.51268 (5) | 0.22380 (8)  | -0.00723 (9)  | 0.0205 (2)   |
| N2   | 0.48638 (4) | 0.23536 (7)  | 0.06979 (8)   | 0.02020 (19) |
| C14  | 0.54842 (5) | 0.12966 (8)  | -0.00076 (9)  | 0.0219 (2)   |
| H14  | 0.5582      | 0.1125       | -0.0657       | 0.026*       |
| N3   | 0.56667 (4) | 0.07051 (7)  | 0.08909 (8)   | 0.02191 (19) |
| C15  | 0.60324 (5) | -0.01660 (8) | 0.09325 (9)   | 0.0199 (2)   |
| C16  | 0.63466 (5) | -0.03133 (8) | 0.02040 (9)   | 0.0210 (2)   |
| H16  | 0.6319      | 0.0200       | -0.0362       | 0.025*       |
| C17  | 0.66968 (5) | -0.11873 (8) | 0.02855 (9)   | 0.0218 (2)   |
| C18  | 0.70282 (5) | -0.13137 (9) | -0.05144 (10) | 0.0276 (2)   |
| H18A | 0.6833      | -0.0877      | -0.1215       | 0.041*       |
| H18B | 0.7008      | -0.2036      | -0.0758       | 0.041*       |
| H18C | 0.7459      | -0.1109      | -0.0090       | 0.041*       |
| C19  | 0.67339 (5) | -0.19289 (8) | 0.11334 (10)  | 0.0242 (2)   |
| H19  | 0.6969      | -0.2536      | 0.1200        | 0.029*       |
| C20  | 0.64359 (5) | -0.17978 (9) | 0.18780 (10)  | 0.0240 (2)   |
| H20  | 0.6471      | -0.2309      | 0.2452        | 0.029*       |
| C21  | 0.60848 (5) | -0.09168 (8) | 0.17862 (9)   | 0.0212 (2)   |
| O2   | 0.57884 (4) | -0.08313 (7) | 0.25167 (7)   | 0.02766 (19) |
| H2A  | 0.5591 (7)  | -0.0281 (13) | 0.2415 (13)   | 0.033*       |
| O3   | 0.5000      | 0.07316 (9)  | 0.2500        | 0.0278 (3)   |
| H3D  | 0.4959 (8)  | 0.1100 (13)  | 0.1942 (14)   | 0.042*       |

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

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$    |
|-----|------------|------------|------------|------------|------------|-------------|
| O1  | 0.0520 (6) | 0.0268 (4) | 0.0359 (5) | 0.0110 (4) | 0.0239 (4) | 0.0038 (4)  |
| C1  | 0.0301 (6) | 0.0243 (5) | 0.0224 (5) | 0.0038 (4) | 0.0088 (4) | -0.0028 (4) |
| C2  | 0.0304 (6) | 0.0275 (6) | 0.0300 (6) | 0.0074 (5) | 0.0119 (5) | -0.0056 (5) |
| C3  | 0.0263 (5) | 0.0334 (6) | 0.0272 (6) | 0.0027 (5) | 0.0122 (5) | -0.0071 (5) |
| C4  | 0.0242 (5) | 0.0290 (6) | 0.0251 (5) | 0.0010 (4) | 0.0106 (4) | -0.0033 (4) |
| C5  | 0.0364 (7) | 0.0364 (7) | 0.0386 (7) | 0.0026 (5) | 0.0236 (6) | 0.0021 (5)  |
| C6  | 0.0242 (5) | 0.0247 (5) | 0.0241 (5) | 0.0043 (4) | 0.0099 (4) | -0.0023 (4) |
| C7  | 0.0237 (5) | 0.0249 (5) | 0.0205 (5) | 0.0026 (4) | 0.0084 (4) | -0.0036 (4) |
| N1  | 0.0278 (5) | 0.0258 (5) | 0.0226 (5) | 0.0032 (4) | 0.0115 (4) | -0.0022 (4) |
| C8  | 0.0235 (5) | 0.0252 (5) | 0.0210 (5) | 0.0021 (4) | 0.0097 (4) | -0.0007 (4) |
| C9  | 0.0203 (5) | 0.0229 (5) | 0.0193 (5) | 0.0002 (4) | 0.0077 (4) | -0.0021 (4) |
| C10 | 0.0268 (5) | 0.0223 (5) | 0.0249 (5) | 0.0021 (4) | 0.0098 (4) | 0.0009 (4)  |

|     |            |            |            |             |            |             |
|-----|------------|------------|------------|-------------|------------|-------------|
| C11 | 0.0315 (6) | 0.0270 (5) | 0.0241 (5) | 0.0007 (4)  | 0.0117 (5) | 0.0056 (4)  |
| C12 | 0.0270 (5) | 0.0302 (6) | 0.0199 (5) | 0.0012 (4)  | 0.0115 (4) | 0.0021 (4)  |
| C13 | 0.0207 (5) | 0.0242 (5) | 0.0168 (4) | 0.0003 (4)  | 0.0079 (4) | -0.0007 (4) |
| N2  | 0.0205 (4) | 0.0226 (4) | 0.0182 (4) | 0.0003 (3)  | 0.0086 (3) | -0.0012 (3) |
| C14 | 0.0232 (5) | 0.0267 (5) | 0.0185 (5) | 0.0021 (4)  | 0.0110 (4) | -0.0009 (4) |
| N3  | 0.0248 (4) | 0.0221 (4) | 0.0224 (4) | 0.0006 (3)  | 0.0133 (4) | -0.0004 (3) |
| C15 | 0.0224 (5) | 0.0201 (5) | 0.0182 (5) | 0.0001 (4)  | 0.0093 (4) | -0.0011 (4) |
| C16 | 0.0231 (5) | 0.0215 (5) | 0.0203 (5) | 0.0003 (4)  | 0.0109 (4) | 0.0008 (4)  |
| C17 | 0.0217 (5) | 0.0225 (5) | 0.0223 (5) | -0.0011 (4) | 0.0102 (4) | -0.0031 (4) |
| C18 | 0.0295 (6) | 0.0278 (6) | 0.0307 (6) | 0.0032 (5)  | 0.0176 (5) | -0.0011 (4) |
| C19 | 0.0235 (5) | 0.0218 (5) | 0.0268 (5) | 0.0022 (4)  | 0.0097 (4) | 0.0000 (4)  |
| C20 | 0.0263 (5) | 0.0232 (5) | 0.0215 (5) | -0.0003 (4) | 0.0086 (4) | 0.0034 (4)  |
| C21 | 0.0230 (5) | 0.0246 (5) | 0.0171 (5) | -0.0023 (4) | 0.0093 (4) | -0.0008 (4) |
| O2  | 0.0370 (5) | 0.0287 (4) | 0.0239 (4) | 0.0042 (4)  | 0.0191 (4) | 0.0038 (3)  |
| O3  | 0.0386 (7) | 0.0270 (6) | 0.0266 (6) | 0.000       | 0.0223 (5) | 0.000       |

*Geometric parameters (Å, °)*

|           |             |             |             |
|-----------|-------------|-------------|-------------|
| O1—C1     | 1.3660 (15) | C11—H11     | 0.9500      |
| O1—H1A    | 0.86 (2)    | C12—C13     | 1.3957 (15) |
| C1—C2     | 1.3884 (16) | C12—H12     | 0.9500      |
| C1—C7     | 1.4040 (15) | C13—N2      | 1.3467 (13) |
| C2—C3     | 1.3821 (18) | C13—C14     | 1.4725 (15) |
| C2—H2     | 0.9500      | C14—N3      | 1.2731 (14) |
| C3—C4     | 1.4012 (16) | C14—H14     | 0.9500      |
| C3—H3     | 0.9500      | N3—C15      | 1.4153 (13) |
| C4—C6     | 1.3885 (15) | C15—C16     | 1.4013 (14) |
| C4—C5     | 1.5083 (17) | C15—C21     | 1.4048 (14) |
| C5—H5A    | 0.9800      | C16—C17     | 1.3870 (15) |
| C5—H5B    | 0.9800      | C16—H16     | 0.9500      |
| C5—H5C    | 0.9800      | C17—C19     | 1.3998 (15) |
| C6—C7     | 1.4030 (16) | C17—C18     | 1.5072 (15) |
| C6—H6     | 0.9500      | C18—H18A    | 0.9800      |
| C7—N1     | 1.4139 (14) | C18—H18B    | 0.9800      |
| N1—C8     | 1.2778 (14) | C18—H18C    | 0.9800      |
| C8—C9     | 1.4721 (15) | C19—C20     | 1.3853 (15) |
| C8—H8     | 0.9500      | C19—H19     | 0.9500      |
| C9—N2     | 1.3445 (14) | C20—C21     | 1.3934 (15) |
| C9—C10    | 1.3985 (15) | C20—H20     | 0.9500      |
| C10—C11   | 1.3827 (16) | C21—O2      | 1.3610 (13) |
| C10—H10   | 0.9500      | O2—H2A      | 0.836 (17)  |
| C11—C12   | 1.3857 (16) | O3—H3D      | 0.812 (16)  |
| C1—O1—H1A | 104.5 (13)  | C12—C11—H11 | 120.6       |
| O1—C1—C2  | 119.56 (10) | C11—C12—C13 | 119.14 (10) |
| O1—C1—C7  | 120.15 (10) | C11—C12—H12 | 120.4       |
| C2—C1—C7  | 120.28 (11) | C13—C12—H12 | 120.4       |
| C3—C2—C1  | 119.70 (10) | N2—C13—C12  | 122.72 (10) |
| C3—C2—H2  | 120.2       | N2—C13—C14  | 118.71 (9)  |
| C1—C2—H2  | 120.2       | C12—C13—C14 | 118.57 (9)  |

## supplementary materials

---

|               |              |                 |              |
|---------------|--------------|-----------------|--------------|
| C2—C3—C4      | 121.56 (11)  | C9—N2—C13       | 117.41 (9)   |
| C2—C3—H3      | 119.2        | N3—C14—C13      | 122.07 (9)   |
| C4—C3—H3      | 119.2        | N3—C14—H14      | 119.0        |
| C6—C4—C3      | 118.25 (11)  | C13—C14—H14     | 119.0        |
| C6—C4—C5      | 121.09 (10)  | C14—N3—C15      | 119.91 (9)   |
| C3—C4—C5      | 120.61 (10)  | C16—C15—C21     | 118.89 (9)   |
| C4—C5—H5A     | 109.5        | C16—C15—N3      | 124.68 (9)   |
| C4—C5—H5B     | 109.5        | C21—C15—N3      | 116.42 (9)   |
| H5A—C5—H5B    | 109.5        | C17—C16—C15     | 121.93 (10)  |
| C4—C5—H5C     | 109.5        | C17—C16—H16     | 119.0        |
| H5A—C5—H5C    | 109.5        | C15—C16—H16     | 119.0        |
| H5B—C5—H5C    | 109.5        | C16—C17—C19     | 117.90 (10)  |
| C4—C6—C7      | 121.31 (10)  | C16—C17—C18     | 120.18 (10)  |
| C4—C6—H6      | 119.3        | C19—C17—C18     | 121.92 (10)  |
| C7—C6—H6      | 119.3        | C17—C18—H18A    | 109.5        |
| C6—C7—C1      | 118.89 (10)  | C17—C18—H18B    | 109.5        |
| C6—C7—N1      | 126.84 (10)  | H18A—C18—H18B   | 109.5        |
| C1—C7—N1      | 114.20 (10)  | C17—C18—H18C    | 109.5        |
| C8—N1—C7      | 121.58 (10)  | H18A—C18—H18C   | 109.5        |
| N1—C8—C9      | 121.61 (10)  | H18B—C18—H18C   | 109.5        |
| N1—C8—H8      | 119.2        | C20—C19—C17     | 121.49 (10)  |
| C9—C8—H8      | 119.2        | C20—C19—H19     | 119.3        |
| N2—C9—C10     | 123.29 (10)  | C17—C19—H19     | 119.3        |
| N2—C9—C8      | 114.60 (9)   | C19—C20—C21     | 120.05 (10)  |
| C10—C9—C8     | 122.07 (10)  | C19—C20—H20     | 120.0        |
| C11—C10—C9    | 118.58 (10)  | C21—C20—H20     | 120.0        |
| C11—C10—H10   | 120.7        | O2—C21—C20      | 118.06 (9)   |
| C9—C10—H10    | 120.7        | O2—C21—C15      | 122.20 (10)  |
| C10—C11—C12   | 118.84 (10)  | C20—C21—C15     | 119.72 (9)   |
| C10—C11—H11   | 120.6        | C21—O2—H2A      | 112.5 (10)   |
| O1—C1—C2—C3   | 178.93 (11)  | C11—C12—C13—C14 | 179.63 (10)  |
| C7—C1—C2—C3   | -0.42 (18)   | C10—C9—N2—C13   | -1.22 (16)   |
| C1—C2—C3—C4   | -0.16 (18)   | C8—C9—N2—C13    | 176.55 (9)   |
| C2—C3—C4—C6   | 0.66 (18)    | C12—C13—N2—C9   | 1.05 (15)    |
| C2—C3—C4—C5   | -176.69 (12) | C14—C13—N2—C9   | -178.70 (9)  |
| C3—C4—C6—C7   | -0.61 (17)   | N2—C13—C14—N3   | -15.80 (16)  |
| C5—C4—C6—C7   | 176.73 (11)  | C12—C13—C14—N3  | 164.44 (11)  |
| C4—C6—C7—C1   | 0.06 (17)    | C13—C14—N3—C15  | -177.17 (9)  |
| C4—C6—C7—N1   | -176.84 (11) | C14—N3—C15—C16  | 16.85 (16)   |
| O1—C1—C7—C6   | -178.88 (10) | C14—N3—C15—C21  | -164.27 (10) |
| C2—C1—C7—C6   | 0.47 (17)    | C21—C15—C16—C17 | 1.35 (16)    |
| O1—C1—C7—N1   | -1.61 (16)   | N3—C15—C16—C17  | -179.79 (10) |
| C2—C1—C7—N1   | 177.74 (10)  | C15—C16—C17—C19 | -0.49 (16)   |
| C6—C7—N1—C8   | -3.83 (18)   | C15—C16—C17—C18 | -179.90 (10) |
| C1—C7—N1—C8   | 179.15 (10)  | C16—C17—C19—C20 | -0.50 (16)   |
| C7—N1—C8—C9   | 176.17 (10)  | C18—C17—C19—C20 | 178.90 (10)  |
| N1—C8—C9—N2   | 176.83 (10)  | C17—C19—C20—C21 | 0.60 (17)    |
| N1—C8—C9—C10  | -5.37 (17)   | C19—C20—C21—O2  | 178.48 (10)  |
| N2—C9—C10—C11 | 0.45 (17)    | C19—C20—C21—C15 | 0.29 (16)    |



|                 |              |                 |              |
|-----------------|--------------|-----------------|--------------|
| C8—C9—C10—C11   | -177.16 (10) | C16—C15—C21—O2  | -179.34 (10) |
| C9—C10—C11—C12  | 0.52 (17)    | N3—C15—C21—O2   | 1.71 (15)    |
| C10—C11—C12—C13 | -0.68 (17)   | C16—C15—C21—C20 | -1.24 (15)   |
| C11—C12—C13—N2  | -0.12 (17)   | N3—C15—C21—C20  | 179.82 (10)  |

*Hydrogen-bond geometry (Å, °)*

| <i>D—H...A</i> | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|----------------|------------|--------------|--------------|----------------|
| O2—H2A...O3    | 0.836 (17) | 1.960 (17)   | 2.7592 (12)  | 159.6 (15)     |
| O2—H2A...N3    | 0.836 (17) | 2.347 (15)   | 2.7624 (12)  | 111.3 (12)     |
| O1—H1A...N1    | 0.86 (2)   | 2.120 (19)   | 2.6722 (13)  | 121.7 (16)     |
| O3—H3D...N2    | 0.812 (16) | 2.187 (16)   | 2.9865 (12)  | 168.0 (16)     |
| O3—H3D...N3    | 0.812 (16) | 2.569 (16)   | 3.0142 (9)   | 115.9 (14)     |

Fig. 1

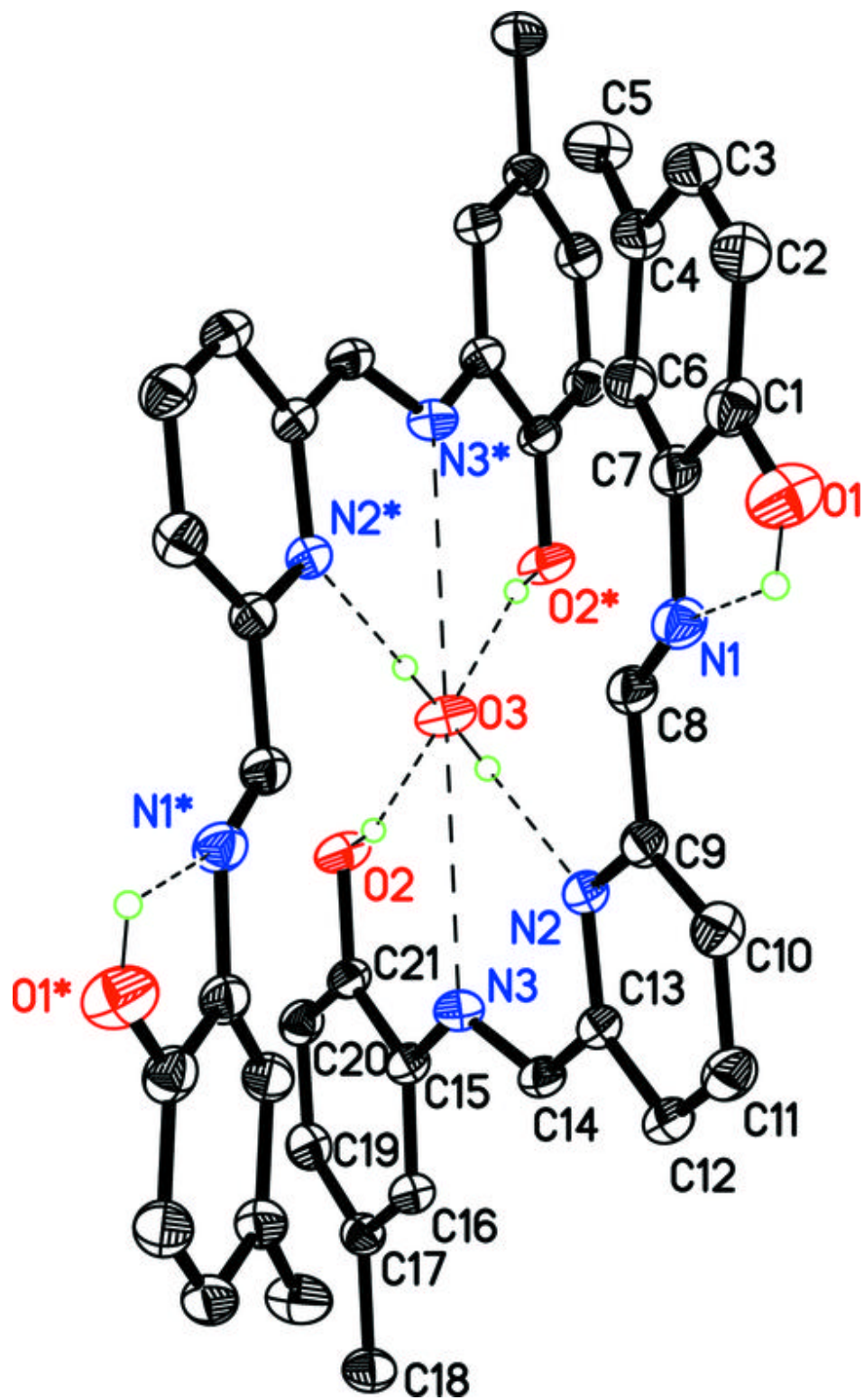


Fig. 2

