Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure, DFT and MEP study of (*E*)-2-[(2-hydroxy-5-methoxybenzylidene)amino]benzonitrile

Md. Serajul Haque Faizi,[a] Necmi Dege,[b] Ceren Çiçek,[c] Erbil Agar[c] and Igor O. Fritsky[d]*

[a]PG Department of Chemistry, Langat Singh College, B. R. A. Bihar University, Muzaffarpur, Bihar-842001, India, [b]Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Physics, 55139, Kurupelit, Samsun, Turkey, [c]Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Chemistry, 55139, Kurupelit, Samsun, Turkey, and [d]National Taras Shevchenko University, Department of Chemistry, Volodymyrska str., 64, 01601 Kyiv, Ukraine. *Correspondence e-mail: faizichemiitg@gmail.com,ifritsky@univ.kiev.ua

Received 13 May 2019
Accepted 5 June 2019

Edited by A. J. Lough, University of Toronto, Canada

Keywords: crystal structure; 2-hydroxy-5-methoxybenzaldehyde; weak hydrogen bonding; 2-aminobenzonitrile.

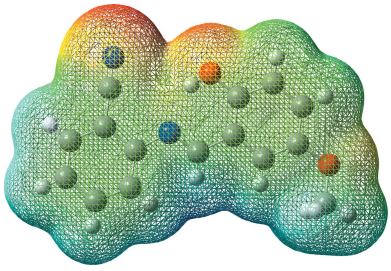
CCDC reference: 1912294

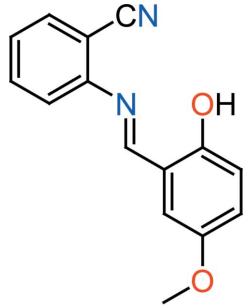
Supporting information: this article has supporting information at journals.iucr.org/e

The asymmetric unit of the title compound, $C_{15}H_{12}N_2O_2$, contains two crystallographically independent molecules in which the dihedral angles between the benzene rings in each are 13.26 (5) and 7.87 (5)°. An intramolecular O—H···N hydrogen bonds results in the formation of an *S*(6) ring motif. In the crystal, molecules are linked by weak C—H···O and C—H···N hydrogen bonds, forming layers parallel to (011). In addition, π–π stacking interactions with centroid–centroid distances in the range 3.693 (2)–3.931 (2) Å complete the three-dimensional network.

1. Chemical context

Most Schiff bases have antibacterial, anticancer, anti inflammatory and antitoxic properties (Williams, 1972). In addition, Schiff bases are important in diverse fields of chemistry and biochemistry owing to their biological activities (Lozier *et al.*, 1975). On the industrial scale, they have a wide range of applications, such as in dyes and pigments, and Schiff bases have also been employed as ligands for the complexation of metal ions (Taggi *et al.*, 2002). Photochromism and thermochromism are also characteristics of these materials and arise *via* H-atom transfer from the hydroxy O atom to the N atom (Hadjoudis *et al.*, 1987). In NLO studies, Schiff base provide the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical interconnections (Geskin *et al.*, 2003). The present work is a part of an ongoing structural study of Schiff bases and their utilization in the synthesis of quinoxaline derivatives (Faizi *et al.*, 2016*a*), fluorescence sensors (Faizi *et al.*, 2016*b*) and coordination compounds (Faizi & Prisyazhnaya, 2015).





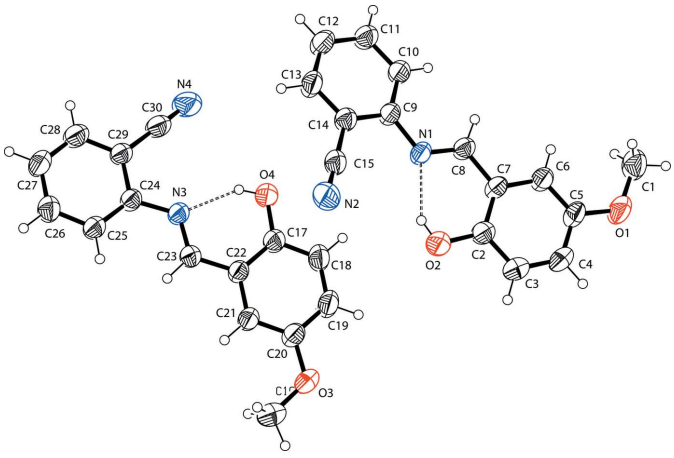


Figure 1
The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. The intramolecular O—H···N hydrogen bonds (Table 1) are shown as dashed lines.

We report herein on the synthesis, crystal structure and DFT computational calculation of the new title Schiff base compound, (I). The results of calculations by density functional theory (DFT) on (I) carried out at the B3LYP/6–311G(d,p) level are compared with the experimentally determined molecular structure in the solid state.

2. Structural commentary

The asymmetric unit of the title compound contains two crystallographically independent molecules (Fig. 1; r.m.s. deviation of overlay of the two molecules = 0.035 Å) in which the bond lengths (Allen *et al.*, 1987) and angles are normal and in good agreement with those reported for 5-chloro-2-(2-hydroxybenzylideneamino)benzonitrile (Cheng *et al.*, 2006) and 2-(2-hydroxybenzylideneamino) benzonitrile (Xia *et al.*, 2008). The benzene rings in the two independent molecules [*A* (C2–C7)/*B* (C9–C14) and *C* (C17–C22)/*D* (C24–C29)] subtend dihedral angles *A*/*B* = 13.26 (5) and *C*/*D* = 7.87 (5)°. The title compound displays a *trans* configuration with respect to the C8═N1 and C23═N3 double bonds. In each independent molecule, an intramolecular O—H···N hydrogen bond (Table 1) results in the formation of a planar six-membered ring [*G* (N1/H2/O2/C2/C7/C8) and *H* (O4/H4/N3/C23/C22/C17)]; these are oriented at dihedral angles of *A*/*G* = 1.31 (5) and *C*/*H* = 0.42 (5)° with respect to the adjacent benzene rings.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···N3	0.82	1.92	2.637 (3)	146
O2—H2···N1	0.82	1.92	2.635 (3)	145
C23—H23···N2^{i}	0.93	2.57	3.446 (4)	158
C8—H8···N4^{ii}	0.93	2.60	3.444 (4)	152
C12—H12···O1^{iii}	0.93	2.46	3.391 (3)	176
C27—H27···O3^{iii}	0.93	2.52	3.444 (3)	175

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

3. Supramolecular features

In the crystal, weak C—H···O hydrogen bonds link both types of independent molecule into chains along [010] while weak C—H···N hydrogen bonds link the chains into a two-dimensional network parallel to (011) (Fig. 2 and Table 1). In addition, three types of π–π stacking interactions occur between benzene rings: $Cg1\cdots Cg3(-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z)$ = 3.860 (2) Å, $Cg2\cdots Cg2(1-x, 1-y, -z)$ = 3.693 (2) Å and $Cg2\cdots Cg4(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$ = 3.931 (2) Å; where *Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of the C2–C7, C9–C14, C17–C22 and C24–C29 rings, respectively (Fig. 3).

4. Frontier molecular orbital analysis

The highest occupied molecular orbitals (HOMOs) and the lowest lying unoccupied molecular orbitals (LUMOs) are termed frontier molecular orbitals (FMOs), which play an important role in the optical and electric properties of

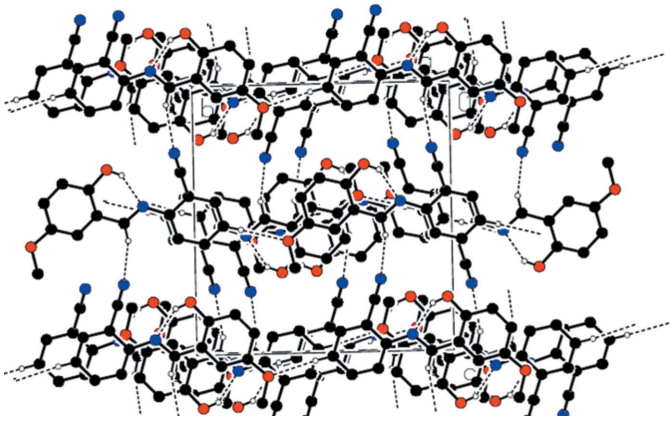


Figure 2
Part of the crystal structure with weak C—H···O and C—H···N hydrogen bonds shown as dashed lines.

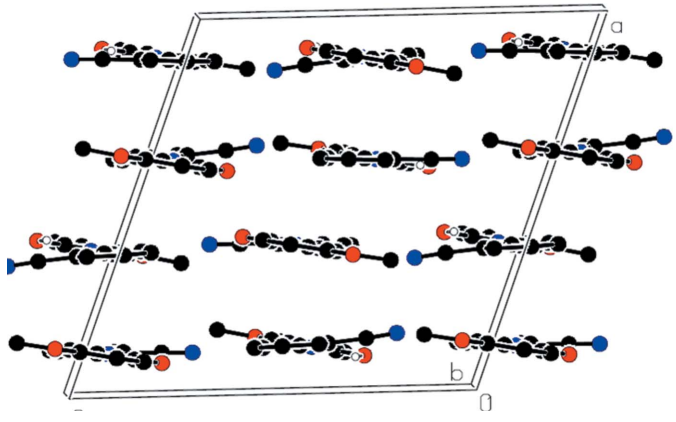


Figure 3
Part of the crystal structure viewed along the *b* axis to illustrate the π–π stacking interactions in the crystal. **label for c axis not visible**

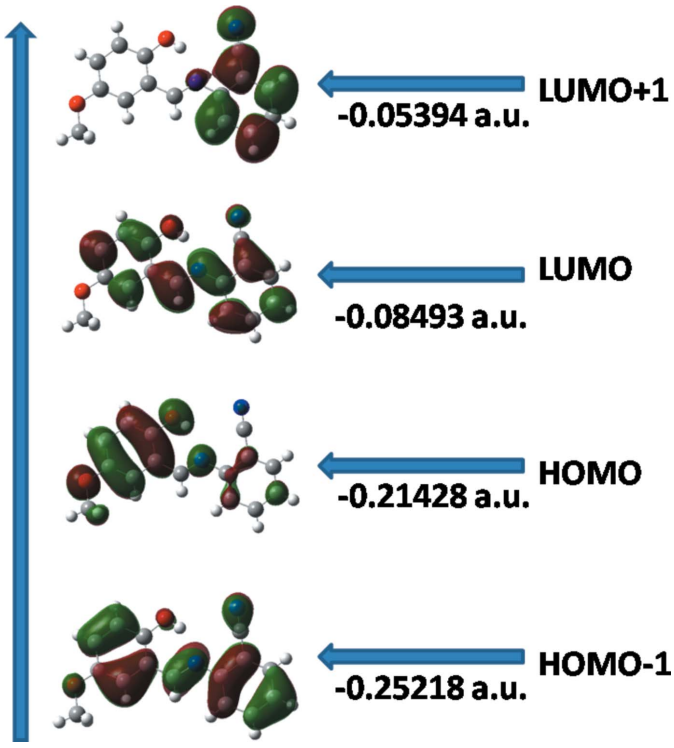


Figure 4
Molecular orbital surfaces and energies of HOMO−1, HOMO, LUMO and LUMO+1 for (I).

compounds, as well as in their quantum chemistry and UV–vis spectra. According to molecular orbital theory, an interaction between HOMO and LUMO orbitals of a structure gives rise to a π–π^* type transition. The frontier orbital gap helps to characterize the chemical reactivity and the kinetic stability of the molecule. A molecule with a small frontier orbital gap is generally associated with a high chemical reactivity, low kinetic stability and is also termed a soft molecule. DFT quantum-chemical calculations for the title compound were performed at the B3LYP/6–311G(d,p) level (Becke, 1993) as implemented in *GAUSSIAN09* (Frisch *et al.*, 2009). The DFT structure optimization started from the X-ray geometry and the experimental bond lengths and bond angles were found to match with theoretical values indicating that the 6-311G(d,p) basis set is well suited in its approach to the experimental data. The DFT study of (I) shows that the HOMO and LUMO are localized in the plane extending from the whole phenol ring to the cyano benzene ring. The electron distribution of the HOMO−1, HOMO, LUMO and the LUMO+1 energy levels are shown in Fig. 4. The HOMO molecular orbital exhibits both σ and π character, whereas HOMO−1 is dominated by π-orbital density. The LUMO is mainly composed of π density while LUMO+1 has both σ and π electronic density. The HOMO–LUMO gap is 0.12935 a.u. and the frontier molecular orbital energies, $E_{\rm HOMO}$ and $E_{\rm LUMO}$ are −0.21428 and −0.08493 a.u., respectively.

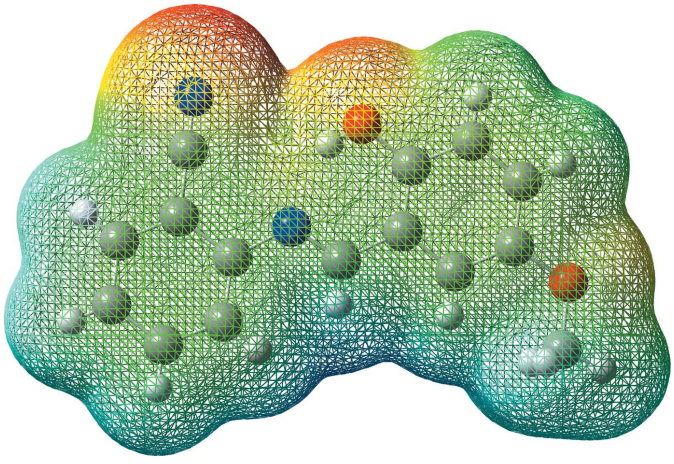


Figure 5
Total electron density mapped over the molecular electrostatic potential surface.

5. Molecular electrostatic potential surface analysis

Molecular electrostatic potential (MEP) surface analysis is a technique of mapping electrostatic potential onto the iso-electron density surface, providing information about the reactive sites. The surface simultaneously displays molecular size and shape and the electrostatic potential value. In the colour scheme adopted, red indicates an electron-rich region with a partially negative charge and blue an electron-deficient region with partially positive charge, light blue indicates a slightly electron-deficient region, yellow a slightly electron-rich region and green a neutral region (Politzer *et al.*, 2002). In addition to these, in the majority of the MEPs, the maximum positive region, which is the preferred site for nucleophilic attack, is shown in blue and the maximum negative region, which is preferred site for electrophilic attack, is red. A three-dimensional plot of the MEP surface of one of the two independent molecules of the title compound is shown in Fig. 5. According to this, the negative regions of the molecule are located on the donor oxygen atom, the acceptor nitrogen atom and the benzonitrile group of N2 atom (red region). The positive regions over the methoxy hydrogen atoms and all other hydrogen atoms indicate that these sites are most probably involved in nucleophilic processes.

6. Database survey

A search of the Cambridge Structural Database (CSD, version 5.39; Groom *et al.*, 2016) gave eight hits for the (*E*)-2-[(2-hydroxy-5-methoxybenzylidene)amino]benzonitrile moiety: (*Z*)-2-[(2-hydroxy-1-naphthyl)methyleneamino]benzonitrile (FOVRUE; Zhou *et al.*, 2009*c*), (*E*)-2-[(5-bromo-2-hydroxybenzylidene)amino]benzonitrile (FOWXOF; Zhou *et al.*, 2009*b*), 5-chloro-2-(2-hydroxybenzylideneamino)benzonitrile (GEJGAE; Cheng *et al.*, 2006), *trans*-2-(2-hydroxybenzylideneamino)benzonitrile(LOCBOV; Xia *et al.*, 2008), 2-[(2-hydroxy-6-methoxybenzylidene)amino]benzonitrile (LOVDUX; Demircioğlu *et al.*, 2015), (*E*)-2-(2,4-dihydroxybenzylideneamino)benzonitrile (MOZPAT; Liu 2009), (*E*)-2-(4-diethylamino-2-hydroxybenzylideneamino)benzonitrile (PUJDOO;

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{12}N_2O_2$
M_r	252.27
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, b, c (Å)	14.3173 (11), 13.0633 (9), 14.5450 (11)
β (°)	110.264 (6)
V (Å^3)	2552.0 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	0.77 × 0.51 × 0.28
Data collection	
Diffractometer	Stoe IPDS 2
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2002)
T_{min}, T_{max}	0.944, 0.981
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16144, 4514, 1853
R_{int}	0.065
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.106, 0.80
No. of reflections	4514
No. of parameters	347
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.10, −0.14

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2002), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

Wang *et al.*, 2010) and (*E*)-2-[(3,5-di-*tert*-butyl-2-hydroxybenzylidene)amino]benzonitrile (YOVBUH; Zhou *et al.*, 2009*a*). In all of these compounds, an intramolecular O—H···N hydrogen bond forms an *S*(6) ring motif, similar to title compound.

7. Synthesis and crystallization

The title compound was prepared by refluxing mixed solutions of 2-hydroxy-5-methoxybenzaldehyde (38.0 mg, 0.25 mmol) in ethanol (15 ml) and 2-aminobenzonitrile (29.5 mg, 0.25 mmol) in ethanol (15 ml). The reaction mixture was stirred for 5 h under reflux. Single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution (yield 60%, m.p. 414–416 K).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2). H atoms were positioned geometrically (O—H = 0.82, C—H = 0.93–0.96 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(O,C-methyl).

Funding information

This study was supported by Ondokuz Mayıs University under project No. PYO·FEN.1906.19.001.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orphen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
Becke, A. D. (1993). *J. Chem. Phys.* **98**, 5648–5652.
Cheng, K., Zhu, H.-L., Li, Z.-B. & Yan, Z. (2006). *Acta Cryst.* E**62**, o2417–o2418.
Demircioğlu, Z., Kaştaş, Ç. A. & Büyükgüngör, O. (2015). *Spectrochim. Acta A*, **139**, 539–548.
Faizi, M. S. H., Ali, A. & Potaskalov, V. A. (2016*a*). *Acta Cryst.* E**72**, 1366–1369.
Faizi, M. S. H., Gupta, S., Mohan, V. K., Jain, K. V. & Sen, P. (2016*b*). *Sens. Actuators B Chem.* **222**, 15–20.
Faizi, M. S. H. & Prisyazhnaya, E. V. (2015). *Acta Cryst.* E**71**, m175–m176.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Frisch, M. J., *et al.* (2009). *GAUSSIAN09*. Gaussian Inc., Wallingford, CT, USA.
Geskin, V. M., Lambert, C. & Bredas, J. L. (2003). *J. Am. Chem. Soc.* **125**, 15651–15658.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Hadjoudis, E., Vittorakis, M. & Moustakali-Mavridis, I. (1987). *Tetrahedron*, **43**, 1345–1360.
Liu, T. (2009). *Acta Cryst.* E**65**, o1502.
Lozier, R., Bogomolni, R. A. & Stoeckenius, W. (1975). *Biophys. J.* **15**, 955–962.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Politzer, P. & Murray, J. S. (2002). *Theor. Chim. Acta*, **108**, 134–142.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Stoe & Cie (2002). *X-AREA*, *X-RED32* and *X-SHAPE*. Stoe & Cie GmbH, Darmstadt, Germany.
Taggi, A. E., Hafez, A. M., Wack, H., Young, B., Ferraris, D. & Lectka, T. (2002). *J. Am. Chem. Soc.* **124**, 6626–6635.
Wang, X.-C., Xu, H. & Qian, K. (2010). *Acta Cryst.* E**66**, o528.
Williams, D. R. (1972). *Chem. Rev.* **72**, 203–213.
Xia, R., Xu, H.-J. & Gong, X.-X. (2008). *Acta Cryst.* E**64**, o1047.
Zhou, J.-C., Li, N.-X., Zhang, C.-M. & Zhang, Z.-Y. (2009*a*). *Acta Cryst.* E**65**, o1416.
Zhou, J.-C., Li, N.-X., Zhang, C.-M. & Zhang, Z.-Y. (2009*b*). *Acta Cryst.* E**65**, o1949.
Zhou, J.-C., Zhang, C.-M., Li, N.-X. & Zhang, Z.-Y. (2009*c*). *Acta Cryst.* E**65**, o1700.

supporting information

Acta Cryst. (2019). E**75**, 987-990 [https://doi.org/10.1107/S2056989019008077]

Crystal structure, DFT and MEP study of (*E*)-2-[(2-hydroxy-5-methoxybenzylidene)amino]benzonitrile

Md. Serajul Haque Faizi, Necmi Dege, Ceren Çiçek, Erbil Agar and Igor O. Fritsky

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015b), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

(*E*)-2-[(2-Hydroxy-5-methoxybenzylidene)amino]benzonitrile

Crystal data

$C_{15}H_{12}N_2O_2$
$M_r = 252.27$
Monoclinic, $P2_1/n$
$a = 14.3173$ (11) Å
$b = 13.0633$ (9) Å
$c = 14.5450$ (11) Å
$\beta = 110.264$ (6)°
$V = 2552.0$ (3) Å^3
$Z = 8$
$F(000) = 1056$
$D_x = 1.313$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 12734 reflections
$\theta = 1.7$–30.0°
$\mu = 0.09$ mm^{-1}
$T = 293$ K
Stick, yellow
0.77 × 0.51 × 0.28 mm

Data collection

Stoe IPDS 2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Plane graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)
$T_{min} = 0.944$, $T_{max} = 0.981$
16144 measured reflections
4514 independent reflections
1853 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$
$\theta_{max} = 25.1°$, $\theta_{min} = 2.2°$
$h = -17\rightarrow17$
$k = -15\rightarrow15$
$l = -17\rightarrow17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.106$
$S = 0.80$
4514 reflections
347 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.10$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O4	0.58870 (18)	0.47768 (14)	0.30079 (13)	0.0819 (6)
H4	0.593839	0.419694	0.323603	0.123*
O3	0.63712 (16)	0.77448 (13)	0.58275 (15)	0.0824 (6)
O1	0.35678 (17)	1.13841 (14)	−0.08120 (17)	0.0898 (7)
N3	0.61295 (16)	0.33843 (16)	0.43837 (15)	0.0558 (6)
N1	0.37945 (17)	0.70036 (16)	0.05960 (15)	0.0570 (6)
O2	0.4072 (2)	0.83829 (15)	0.19874 (14)	0.0917 (7)
H2	0.409316	0.780745	0.177052	0.138*
C22	0.61829 (19)	0.51807 (19)	0.47001 (19)	0.0527 (7)
C24	0.61766 (19)	0.2355 (2)	0.47037 (19)	0.0540 (7)
C23	0.62435 (19)	0.4118 (2)	0.49956 (19)	0.0569 (7)
H23	0.636936	0.396297	0.565171	0.068*
C9	0.37421 (19)	0.59730 (19)	0.02685 (19)	0.0549 (7)
C8	0.3682 (2)	0.7747 (2)	−0.0008 (2)	0.0589 (7)
H8	0.354897	0.759991	−0.066688	0.071*
C14	0.3677 (2)	0.5226 (2)	0.09280 (19)	0.0587 (7)
C7	0.37551 (19)	0.8803 (2)	0.02964 (19)	0.0553 (7)
C29	0.6146 (2)	0.1611 (2)	0.39996 (19)	0.0581 (7)
C17	0.6007 (2)	0.5471 (2)	0.3733 (2)	0.0617 (7)
C6	0.36283 (19)	0.95656 (19)	−0.0412 (2)	0.0612 (7)
H6	0.350350	0.937718	−0.105985	0.073*
N2	0.3453 (2)	0.57423 (19)	0.25515 (18)	0.0911 (9)
C20	0.6261 (2)	0.6952 (2)	0.5172 (2)	0.0632 (8)
C10	0.3776 (2)	0.56611 (19)	−0.06333 (19)	0.0635 (8)
H10	0.381228	0.614757	−0.108635	0.076*
C21	0.63063 (19)	0.59328 (19)	0.54172 (19)	0.0598 (7)
H21	0.641935	0.574221	0.606288	0.072*
C5	0.3684 (2)	1.0581 (2)	−0.0173 (2)	0.0662 (8)
C25	0.6209 (2)	0.20343 (19)	0.5621 (2)	0.0643 (8)
H25	0.622114	0.251235	0.609905	0.077*
C15	0.3572 (2)	0.5527 (2)	0.1837 (2)	0.0652 (8)
C2	0.3940 (2)	0.9085 (2)	0.1262 (2)	0.0651 (8)
C11	0.3755 (2)	0.4634 (2)	−0.0860 (2)	0.0708 (8)
H11	0.376934	0.443640	−0.146878	0.085*
C13	0.3682 (2)	0.4193 (2)	0.0698 (2)	0.0693 (8)
H13	0.366432	0.369901	0.115268	0.083*
C19	0.6079 (2)	0.7230 (2)	0.4211 (2)	0.0749 (9)
H19	0.603749	0.791933	0.404294	0.090*
C28	0.6149 (2)	0.0575 (2)	0.4218 (2)	0.0725 (9)

H28	0.612046	0.008688	0.374315	0.087*
C26	0.6224 (2)	0.0999 (2)	0.5823 (2)	0.0720 (8)
H26	0.625365	0.078738	0.644307	0.086*
C12	0.3712 (2)	0.3899 (2)	−0.0199 (2)	0.0730 (9)
H12	0.370435	0.320812	−0.035801	0.088*
C30	0.6120 (3)	0.1939 (2)	0.3053 (2)	0.0780 (10)
C18	0.5957 (2)	0.6504 (2)	0.3502 (2)	0.0773 (9)
H18	0.584003	0.670547	0.285793	0.093*
C27	0.6195 (2)	0.0277 (2)	0.5129 (2)	0.0738 (9)
H27	0.620696	−0.041524	0.528119	0.089*
N4	0.6109 (3)	0.2189 (2)	0.2296 (2)	0.1178 (12)
C3	0.4003 (2)	1.0116 (2)	0.1505 (2)	0.0839 (10)
H3	0.413366	1.031176	0.215218	0.101*
C4	0.3873 (2)	1.0848 (2)	0.0794 (2)	0.0790 (9)
H4A	0.391329	1.153637	0.096722	0.095*
C16	0.6543 (2)	0.7483 (2)	0.6815 (2)	0.0889 (10)
H16A	0.599599	0.708154	0.685334	0.133*
H16B	0.660293	0.809549	0.719536	0.133*
H16C	0.714693	0.709297	0.706679	0.133*
C1	0.3355 (3)	1.1138 (2)	−0.1815 (2)	0.0939 (10)
H1A	0.328552	1.175673	−0.218800	0.141*
H1B	0.274610	1.075385	−0.205212	0.141*
H1C	0.388875	1.073549	−0.188179	0.141*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O4	0.1348 (19)	0.0579 (12)	0.0586 (12)	0.0127 (13)	0.0407 (13)	0.0018 (10)
O3	0.1213 (18)	0.0449 (12)	0.0829 (15)	−0.0003 (12)	0.0377 (13)	−0.0080 (12)
O1	0.1321 (19)	0.0433 (12)	0.0982 (17)	−0.0020 (12)	0.0454 (15)	0.0078 (12)
N3	0.0731 (16)	0.0453 (14)	0.0549 (14)	0.0019 (12)	0.0296 (12)	−0.0004 (12)
N1	0.0792 (17)	0.0386 (14)	0.0591 (14)	0.0006 (12)	0.0315 (12)	0.0003 (12)
O2	0.156 (2)	0.0615 (14)	0.0606 (13)	0.0064 (15)	0.0410 (14)	0.0006 (11)
C22	0.0614 (18)	0.0438 (16)	0.0571 (17)	0.0037 (14)	0.0259 (14)	0.0014 (14)
C24	0.063 (2)	0.0453 (18)	0.0580 (18)	0.0012 (14)	0.0272 (15)	−0.0011 (15)
C23	0.074 (2)	0.0490 (18)	0.0517 (16)	−0.0013 (15)	0.0267 (14)	0.0016 (14)
C9	0.0687 (19)	0.0421 (16)	0.0589 (18)	0.0007 (14)	0.0286 (15)	−0.0004 (15)
C8	0.082 (2)	0.0456 (17)	0.0568 (17)	0.0022 (15)	0.0343 (16)	−0.0030 (15)
C14	0.0743 (19)	0.0505 (17)	0.0574 (17)	0.0002 (14)	0.0304 (14)	0.0022 (14)
C7	0.067 (2)	0.0416 (17)	0.0649 (19)	−0.0010 (15)	0.0320 (16)	−0.0052 (15)
C29	0.074 (2)	0.0483 (18)	0.0567 (17)	−0.0024 (14)	0.0286 (15)	−0.0040 (14)
C17	0.078 (2)	0.0522 (18)	0.0600 (18)	0.0069 (15)	0.0306 (15)	0.0017 (15)
C6	0.076 (2)	0.0463 (17)	0.0664 (18)	0.0008 (15)	0.0318 (15)	0.0000 (14)
N2	0.135 (2)	0.0836 (19)	0.0666 (16)	0.0089 (17)	0.0510 (17)	0.0067 (15)
C20	0.073 (2)	0.0480 (19)	0.072 (2)	0.0020 (15)	0.0300 (16)	−0.0031 (16)
C10	0.090 (2)	0.0508 (18)	0.0568 (17)	0.0030 (16)	0.0339 (16)	0.0013 (14)
C21	0.078 (2)	0.0442 (17)	0.0616 (18)	0.0010 (15)	0.0300 (16)	0.0015 (14)
C5	0.081 (2)	0.0401 (18)	0.082 (2)	−0.0014 (15)	0.0343 (18)	0.0036 (16)

C25	0.091 (2)	0.0470 (18)	0.0618 (19)	0.0014 (16)	0.0349 (16)	−0.0023 (14)
C15	0.090 (2)	0.0519 (17)	0.0593 (18)	0.0033 (15)	0.0325 (16)	0.0088 (14)
C2	0.087 (2)	0.0524 (18)	0.0605 (18)	−0.0021 (16)	0.0314 (16)	−0.0030 (16)
C11	0.099 (2)	0.0550 (19)	0.0659 (19)	0.0016 (17)	0.0384 (17)	−0.0044 (16)
C13	0.093 (2)	0.0448 (18)	0.077 (2)	0.0010 (16)	0.0384 (17)	0.0082 (15)
C19	0.103 (3)	0.0473 (18)	0.082 (2)	0.0093 (16)	0.041 (2)	0.0135 (17)
C28	0.094 (2)	0.055 (2)	0.075 (2)	−0.0056 (17)	0.0380 (18)	−0.0113 (17)
C26	0.097 (2)	0.058 (2)	0.0692 (19)	0.0004 (18)	0.0383 (18)	0.0091 (16)
C12	0.097 (2)	0.0472 (19)	0.082 (2)	−0.0035 (17)	0.0399 (19)	−0.0055 (17)
C30	0.120 (3)	0.055 (2)	0.069 (2)	−0.0126 (18)	0.045 (2)	−0.0138 (17)
C18	0.114 (3)	0.059 (2)	0.0673 (19)	0.0143 (18)	0.0419 (19)	0.0152 (17)
C27	0.093 (2)	0.0448 (19)	0.085 (2)	−0.0026 (16)	0.0335 (19)	0.0019 (17)
N4	0.211 (4)	0.083 (2)	0.075 (2)	−0.029 (2)	0.069 (2)	−0.0150 (16)
C3	0.117 (3)	0.060 (2)	0.071 (2)	0.0035 (19)	0.0285 (19)	−0.0132 (18)
C4	0.107 (3)	0.0425 (18)	0.086 (2)	−0.0008 (17)	0.032 (2)	−0.0097 (18)
C16	0.117 (3)	0.070 (2)	0.081 (2)	−0.002 (2)	0.037 (2)	−0.0194 (18)
C1	0.129 (3)	0.070 (2)	0.093 (2)	0.007 (2)	0.052 (2)	0.021 (2)

Geometric parameters (Å, º)

O4—C17	1.356 (3)	C20—C21	1.374 (3)
O4—H4	0.8200	C20—C19	1.379 (4)
O3—C20	1.380 (3)	C10—C11	1.379 (3)
O3—C16	1.413 (3)	C10—H10	0.9300
O1—C5	1.373 (3)	C21—H21	0.9300
O1—C1	1.420 (3)	C5—C4	1.382 (4)
N3—C23	1.279 (3)	C25—C26	1.383 (3)
N3—C24	1.417 (3)	C25—H25	0.9300
N1—C8	1.282 (3)	C2—C3	1.387 (4)
N1—C9	1.421 (3)	C11—C12	1.375 (4)
O2—C2	1.361 (3)	C11—H11	0.9300
O2—H2	0.8200	C13—C12	1.376 (4)
C22—C17	1.393 (3)	C13—H13	0.9300
C22—C21	1.399 (3)	C19—C18	1.367 (4)
C22—C23	1.447 (3)	C19—H19	0.9300
C24—C25	1.384 (3)	C28—C27	1.361 (4)
C24—C29	1.401 (3)	C28—H28	0.9300
C23—H23	0.9300	C26—C27	1.371 (4)
C9—C10	1.390 (3)	C26—H26	0.9300
C9—C14	1.394 (3)	C12—H12	0.9300
C8—C7	1.442 (3)	C30—N4	1.143 (3)
C8—H8	0.9300	C18—H18	0.9300
C14—C13	1.392 (3)	C27—H27	0.9300
C14—C15	1.436 (4)	C3—C4	1.373 (4)
C7—C2	1.386 (3)	C3—H3	0.9300
C7—C6	1.398 (3)	C4—H4A	0.9300
C29—C28	1.390 (3)	C16—H16A	0.9600
C29—C30	1.430 (4)	C16—H16B	0.9600

C17—C18	1.388 (3)	C16—H16C	0.9600
C6—C5	1.367 (3)	C1—H1A	0.9600
C6—H6	0.9300	C1—H1B	0.9600
N2—C15	1.145 (3)	C1—H1C	0.9600
C17—O4—H4	109.5	C26—C25—H25	120.2
C20—O3—C16	117.3 (2)	C24—C25—H25	120.2
C5—O1—C1	117.1 (2)	N2—C15—C14	177.2 (3)
C23—N3—C24	120.2 (2)	O2—C2—C7	122.2 (2)
C8—N1—C9	120.6 (2)	O2—C2—C3	118.5 (3)
C2—O2—H2	109.5	C7—C2—C3	119.3 (3)
C17—C22—C21	119.6 (2)	C12—C11—C10	121.0 (3)
C17—C22—C23	122.1 (2)	C12—C11—H11	119.5
C21—C22—C23	118.3 (2)	C10—C11—H11	119.5
C25—C24—C29	118.5 (2)	C12—C13—C14	120.2 (3)
C25—C24—N3	125.8 (2)	C12—C13—H13	119.9
C29—C24—N3	115.6 (2)	C14—C13—H13	119.9
N3—C23—C22	122.1 (2)	C18—C19—C20	120.8 (3)
N3—C23—H23	118.9	C18—C19—H19	119.6
C22—C23—H23	118.9	C20—C19—H19	119.6
C10—C9—C14	118.5 (2)	C27—C28—C29	119.7 (3)
C10—C9—N1	125.4 (2)	C27—C28—H28	120.1
C14—C9—N1	116.1 (2)	C29—C28—H28	120.1
N1—C8—C7	122.4 (2)	C27—C26—C25	121.5 (3)
N1—C8—H8	118.8	C27—C26—H26	119.3
C7—C8—H8	118.8	C25—C26—H26	119.3
C13—C14—C9	120.4 (2)	C11—C12—C13	119.4 (3)
C13—C14—C15	119.8 (2)	C11—C12—H12	120.3
C9—C14—C15	119.7 (2)	C13—C12—H12	120.3
C2—C7—C6	119.2 (2)	N4—C30—C29	179.0 (4)
C2—C7—C8	122.3 (3)	C19—C18—C17	120.6 (3)
C6—C7—C8	118.6 (2)	C19—C18—H18	119.7
C28—C29—C24	120.8 (3)	C17—C18—H18	119.7
C28—C29—C30	120.6 (3)	C28—C27—C26	120.0 (3)
C24—C29—C30	118.7 (2)	C28—C27—H27	120.0
O4—C17—C18	118.7 (2)	C26—C27—H27	120.0
O4—C17—C22	122.3 (2)	C4—C3—C2	120.3 (3)
C18—C17—C22	119.1 (3)	C4—C3—H3	119.8
C5—C6—C7	121.5 (3)	C2—C3—H3	119.8
C5—C6—H6	119.2	C3—C4—C5	121.2 (3)
C7—C6—H6	119.2	C3—C4—H4A	119.4
C21—C20—C19	119.6 (3)	C5—C4—H4A	119.4
C21—C20—O3	124.4 (3)	O3—C16—H16A	109.5
C19—C20—O3	116.0 (3)	O3—C16—H16B	109.5
C11—C10—C9	120.4 (3)	H16A—C16—H16B	109.5
C11—C10—H10	119.8	O3—C16—H16C	109.5
C9—C10—H10	119.8	H16A—C16—H16C	109.5
C20—C21—C22	120.3 (2)	H16B—C16—H16C	109.5

C20—C21—H21	119.8	O1—C1—H1A	109.5
C22—C21—H21	119.8	O1—C1—H1B	109.5
C6—C5—O1	125.9 (3)	H1A—C1—H1B	109.5
C6—C5—C4	118.5 (3)	O1—C1—H1C	109.5
O1—C5—C4	115.6 (3)	H1A—C1—H1C	109.5
C26—C25—C24	119.6 (3)	H1B—C1—H1C	109.5
C23—N3—C24—C25	9.1 (4)	C23—C22—C21—C20	179.6 (3)
C23—N3—C24—C29	−173.6 (2)	C7—C6—C5—O1	−179.8 (3)
C24—N3—C23—C22	−178.8 (2)	C7—C6—C5—C4	0.2 (4)
C17—C22—C23—N3	−0.7 (4)	C1—O1—C5—C6	1.1 (4)
C21—C22—C23—N3	179.3 (3)	C1—O1—C5—C4	−178.9 (3)
C8—N1—C9—C10	13.8 (4)	C29—C24—C25—C26	0.8 (4)
C8—N1—C9—C14	−167.8 (3)	N3—C24—C25—C26	178.1 (3)
C9—N1—C8—C7	−178.4 (2)	C6—C7—C2—O2	−180.0 (3)
C10—C9—C14—C13	2.3 (4)	C8—C7—C2—O2	0.4 (4)
N1—C9—C14—C13	−176.2 (3)	C6—C7—C2—C3	−0.5 (4)
C10—C9—C14—C15	−175.7 (3)	C8—C7—C2—C3	179.9 (3)
N1—C9—C14—C15	5.8 (4)	C9—C10—C11—C12	−0.8 (5)
N1—C8—C7—C2	−0.8 (4)	C9—C14—C13—C12	−2.5 (5)
N1—C8—C7—C6	179.6 (3)	C15—C14—C13—C12	175.5 (3)
C25—C24—C29—C28	0.0 (4)	C21—C20—C19—C18	−1.0 (5)
N3—C24—C29—C28	−177.6 (3)	O3—C20—C19—C18	−180.0 (3)
C25—C24—C29—C30	−179.5 (3)	C24—C29—C28—C27	−0.8 (4)
N3—C24—C29—C30	2.9 (4)	C30—C29—C28—C27	178.7 (3)
C21—C22—C17—O4	179.6 (3)	C24—C25—C26—C27	−0.8 (5)
C23—C22—C17—O4	−0.4 (4)	C10—C11—C12—C13	0.6 (5)
C21—C22—C17—C18	0.0 (4)	C14—C13—C12—C11	1.1 (5)
C23—C22—C17—C18	179.9 (3)	C20—C19—C18—C17	0.6 (5)
C2—C7—C6—C5	0.1 (4)	O4—C17—C18—C19	−179.7 (3)
C8—C7—C6—C5	179.7 (3)	C22—C17—C18—C19	0.0 (5)
C16—O3—C20—C21	0.1 (4)	C29—C28—C27—C26	0.9 (5)
C16—O3—C20—C19	179.0 (3)	C25—C26—C27—C28	−0.1 (5)
C14—C9—C10—C11	−0.7 (4)	O2—C2—C3—C4	−179.9 (3)
N1—C9—C10—C11	177.6 (3)	C7—C2—C3—C4	0.7 (5)
C19—C20—C21—C22	1.0 (4)	C2—C3—C4—C5	−0.4 (5)
O3—C20—C21—C22	179.8 (3)	C6—C5—C4—C3	−0.1 (5)
C17—C22—C21—C20	−0.4 (4)	O1—C5—C4—C3	180.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···N3	0.82	1.92	2.637 (3)	146
O2—H2···N1	0.82	1.92	2.635 (3)	145
C23—H23···N2^{i}	0.93	2.57	3.446 (4)	158
C8—H8···N4^{ii}	0.93	2.60	3.444 (4)	152

C12—H12···O1^{iii}	0.93	2.46	3.391 (3)	176
C27—H27···O3^{iii}	0.93	2.52	3.444 (3)	175

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*; (iii) *x*, *y*−1, *z*.