

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2-[(*E*)-1-[2-(4-Nitrophenyl)hydrazin-1-ylidene]ethynyl]benzene-1,3-diolR. Alan Howie,^a James L. Wardell,^{b,‡} Solange M. S. V. Wardell^c and Edward R. T. Tiekink^{d*}

^aDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, ^bCentro de Desenvolvimento Tecnológico em Saúde (CDTS), Fundação Oswaldo Cruz (FIOCRUZ), Casa Amarela, Campus de Manguinhos, Avenida Brasil 4365, 21040-900 Rio de Janeiro, RJ, Brazil, ^cCHEMSOL, 1 Harcourt Road, Aberdeen AB15 5NY, Scotland, and ^dDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: edward.tiekink@gmail.com

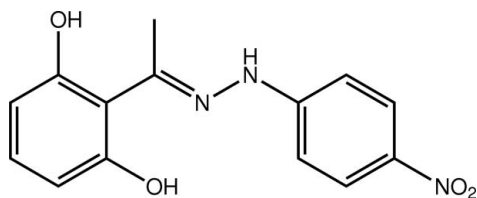
Received 6 February 2012; accepted 7 February 2012

Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.082; wR factor = 0.184; data-to-parameter ratio = 14.9.

The title compound, $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4$, is close to planar, the dihedral angle between the terminal benzene rings being 5.80 (16°); the nitro group is coplanar with the benzene ring to which it is bonded [$\text{O}-\text{N}-\text{C}-\text{C}$ torsion angle = -177.3 (3°)]. The hydroxy group forms an intramolecular hydrogen bond with the imine N atom, and the conformation about the imine bond is *E*. In the crystal, layers in the (101) plane with an undulating topology are formed by $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds along with $\text{C}-\text{H}\cdots\text{O}$ interactions. Centrosymmetrically related layers are connected *via* $\pi-\pi$ interactions [ring centroid-centroid distance = 3.5739 (19) Å] into double layers.

Related literature

For background on the influence of substituents upon the supramolecular structures of hydrazones, see: Glidewell *et al.* (2004); Ferguson *et al.* (2005); Wardell *et al.* (2007); Baddeley, de Souza França *et al.* (2009); Baddeley, Howie *et al.* (2009); de Souza *et al.* (2010); Howie, da Silva Lima *et al.* (2010); Howie, de Souza *et al.* (2010); Nogueira *et al.* (2011); Howie *et al.* (2011).



[‡] Additional correspondence author, e-mail: j.wardell@abdn.ac.uk.

Experimental

Crystal data

$\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_4$
 $M_r = 287.27$
 Monoclinic, $P2_1/n$
 $a = 7.9714$ (3) Å
 $b = 13.5021$ (7) Å
 $c = 12.1081$ (5) Å
 $\beta = 90.186$ (3°)
 $V = 1303.20$ (10) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 120$ K
 $0.10 \times 0.10 \times 0.08$ mm

Data collection

Bruker–Nonius Roper CCD camera
 on κ -goniostat diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2007)
 $T_{\min} = 0.875$, $T_{\max} = 0.991$
 12144 measured reflections
 2984 independent reflections
 1987 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.070$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.082$
 $wR(F^2) = 0.184$
 $S = 1.10$
 2984 reflections
 200 parameters
 3 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1O}\cdots\text{N1}$	0.84 (2)	1.79 (3)	2.534 (4)	147 (4)
$\text{N2}-\text{H2N}\cdots\text{O3}^{\text{i}}$	0.88 (2)	2.18 (3)	3.039 (4)	167 (2)
$\text{O2}-\text{H2O}\cdots\text{O1}^{\text{ii}}$	0.85 (4)	1.99 (4)	2.834 (3)	173 (4)
$\text{C14}-\text{H14}\cdots\text{O4}^{\text{i}}$	0.95	2.50	3.326 (4)	146

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

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: ORTEP-3 (Farrugia, 1997) and DIAMOND (Brandenburg, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

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 CAPES (Brazil). We also thank the Ministry of Higher Education (Malaysia) for funding structural studies through the High-Impact Research scheme (UM.C/HIR/MOHE/SC/12).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5815).

References

- Baddeley, T. C., de Souza França, L., 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.
 Baddeley, T. C., Howie, R. A., da Silva Lima, C. H., Kaiser, C. R., de Souza, M. V. N., Wardell, J. L. & Wardell, S. M. S. V. (2009). *Z. Kristallogr.* **224**, 506–514.
 Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

- Ferguson, G., Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2005). *Acta Cryst.* **C61**, o613–o616.
- Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2004). *Acta Cryst.* **C60**, o19–o23.
- Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Howie, R. A., da Silva Lima, C. H., Kaiser, C. R., de Souza, M. V. N., Wardell, J. L. & Wardell, S. M. S. V. (2010). *Z. Kristallogr.* **225**, 349–358.
- Howie, R. A., de Souza, M. V. N., de Lima Ferreira, M., Kaiser, C. R., Wardell, J. L. & Wardell, S. M. S. V. (2010). *Z. Kristallogr.* **225**, 440–447.
- Howie, R. A., de Souza, M. V. N., Pinheiro, A. C., Kaiser, C. R., Wardell, J. L. & Wardell, S. M. S. V. (2011). *Z. Kristallogr.* **226**, 483–491.
- Nogueira, A., Vasconcelos, T. R. A., Wardell, J. L., Solange, M. S. V. & Wardell, S. M. S. V. (2011). *Z. Kristallogr.* **226**, 846–861.
- 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.
- Souza, M. V. N. de, Howie, R. A., Tiekink, E. R. T., Wardell, J. L., Wardell, S. M. S. V. & Kaiser, C. R. (2010). *Acta Cryst.* **E66**, o698–o699.
- Wardell, S. M. S. V., de Souza, M. V. N., Wardell, J. L., Low, J. N. & Glidewell, C. (2007). *Acta Cryst.* **B63**, 879–895.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supplementary materials

Acta Cryst. (2012). E68, o685–o686 [doi:10.1107/S1600536812005399]

2-*{(E)-1-[2-(4-Nitrophenyl)hydrazin-1-ylidene]ethyl}*benzene-1,3-diol

R. Alan Howie, James L. Wardell, Solange M. S. V. Wardell and Edward R. T. Tiekink

Comment

As a continuation of studies designed to ascertain the influence of substituents upon the supramolecular structures of hydrazones, in particular of those having potential biological activities, the title compound (*E*)-2,6-dihydroxyacetophenone 4-nitrophenylhydrazone (I) was investigated. Previous systematic investigations have included the study of substituted phenylhydrazines with substituted benzaldehydes (Glidewell *et al.*, 2004; Ferguson *et al.*, 2005) and 2-hydroxyacetophenone (Baddeley, de Souza França *et al.*, 2009). Hydrazones derived from substituted benzaldehydes and (pyrazinecarbonyl)hydrazine (Baddeley, Howie *et al.*, 2009; Howie, da Silva Lima *et al.*, 2010), 2-hydrazinyl-benzothiazole (Nogueira *et al.*, 2011), 7-chloroquinoline-4-hydrazide (Howie, de Souza *et al.*, 2010; de Souza *et al.*, 2010) and 2-hydrazinylacyl-*N*-isonicotine (Wardell *et al.*, 2007) have also been investigated along with *L*-serinyl derivatives, (*S*)-2-hydroxy-1-[*N*-(benzylidene)-hydrazinylcarbonyl]ethylcarbamate esters (Howie *et al.*, 2011).

In (I), Fig. 1, the dihedral angle between the benzene rings is 5.80 (16)°, indicating a planar molecule. The nitro group is co-planar with the benzene ring to which it is bonded as seen in the value of the O3—N3—C12—C11 torsion angle of -177.3 (3)°. The hydroxy group forms an intramolecular hydrogen bond with the imine-N1 atom, Table 1. The configuration about the N1=C7 imine bond [1.304 (4) Å] is *E*.

Supramolecular layers with an undulating topology in the (101) plane are formed by O—H···O and N—H···O hydrogen bonds which are reinforced by C—H···O interactions, Fig. 2 and Table 1. Centrosymmetrically related layers are connected *via* π - π interactions occurring between the (C1–C6) and (C9–C14)ⁱ rings [ring centroid···centroid distance = 3.5739 (19) Å, angle between rings = 5.80 (16)° for *i*: -*x*, 1 - *y*, 1 - *z*], Fig. 3. Layers stack without specific interactions between them, Fig. 4.

Experimental

A solution of 4-nitrophenylhydrazine and 2,6-dihydroxyacetophenone (1 mmol each) in ethanol (25 ml) was refluxed for 1 h, rotary evaporated and the residue recrystallized from methanol, *M.pt.*: 501–503 K. IR (KBr, cm⁻¹): ν 3600–2000 (ν br), 3527, 3340, 1625, 1531. Anal. Found: C, 58.81; H, 4.86; N, 14.47. Calculated for C₁₄H₁₃N₃O₄: C, 58.53; H, 4.56; N, 14.62%.

Refinement

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2$ – $1.5U_{\text{eq}}(\text{C})$. The O- and N-bound H atoms were located from a difference map and refined with the distance restraints O—H = 0.84±0.01 and N—H = 0.88±0.01 Å, and with $U_{\text{iso}}(\text{H}) = zU_{\text{eq}}(\text{carrier atom})$; $z = 1.5$ for O and $z = 1.2$ for N.

Computing details

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); program(s) used to solve

structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

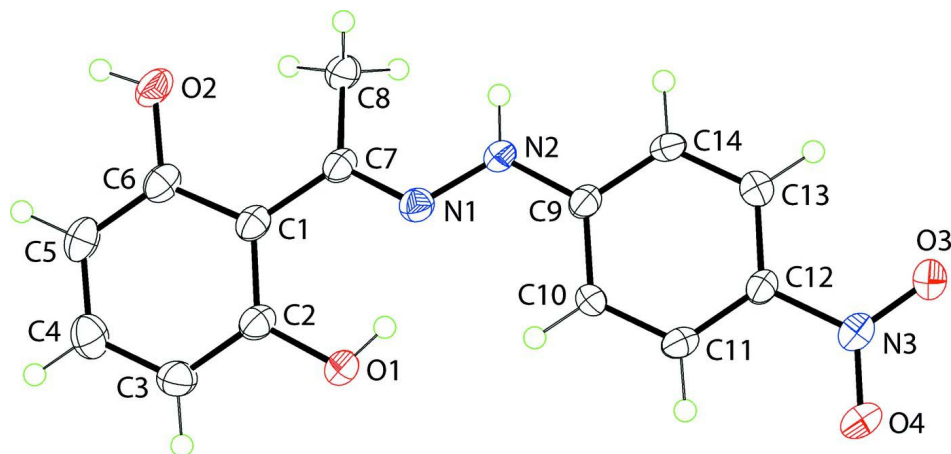


Figure 1

The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

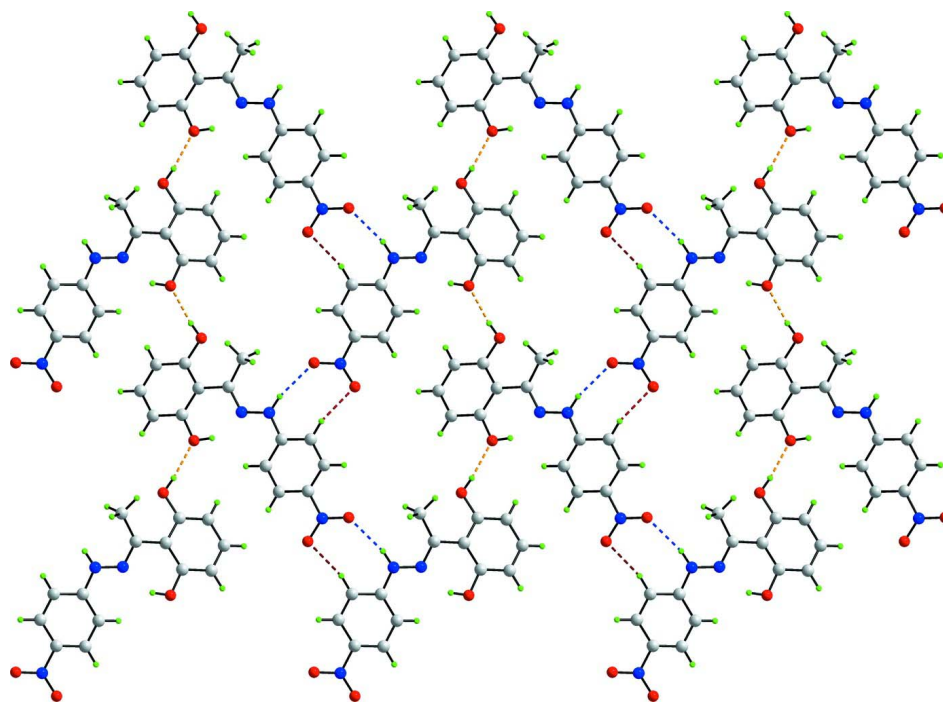
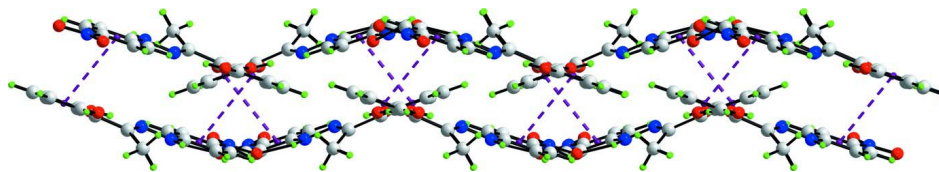
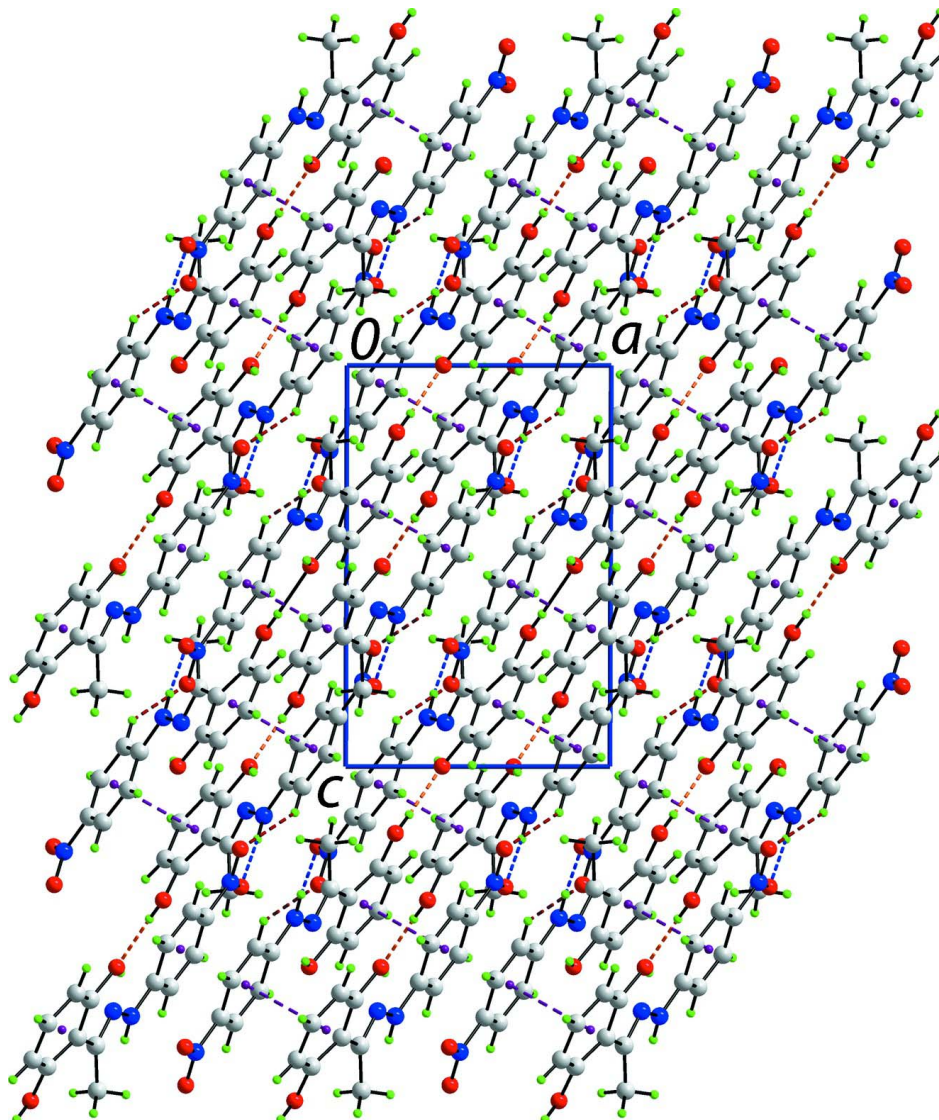


Figure 2

A plan view of the supramolecular layer in (I) sustained by O—H...O (orange dashed lines), N—H...O (blue dashed lines) and C—H...O (brown dashed lines) interactions.

**Figure 3**

A side-on view of two supramolecular layers in (I) connected by π - π interactions (purple dashed lines).

**Figure 4**

A view in projection down the b axis of the packing of supramolecular layers in (I).

2- $\{(E)$ -1-[2-(4-Nitrophenyl)hydrazin-1-ylidene]ethyl}benzene-1,3-diol

Crystal data

$C_{14}H_{13}N_3O_4$
 $M_r = 287.27$

Monoclinic, $P2_1/n$
Hall symbol: -P 2yn

$a = 7.9714$ (3) Å
 $b = 13.5021$ (7) Å
 $c = 12.1081$ (5) Å
 $\beta = 90.186$ (3)°
 $V = 1303.20$ (10) Å³
 $Z = 4$
 $F(000) = 600$
 $D_x = 1.464$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 8454 reflections
 $\theta = 2.9$ – 27.5 °
 $\mu = 0.11$ mm⁻¹
 $T = 120$ K
 Block, orange
 $0.10 \times 0.10 \times 0.08$ mm

Data collection

Bruker–Nonius Roper CCD camera on κ -goniostat diffractometer
 Radiation source: Bruker–Nonius FR591 rotating anode
 Graphite monochromator
 Detector resolution: 9.091 pixels mm⁻¹
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2007)

$T_{\min} = 0.875$, $T_{\max} = 0.991$
 12144 measured reflections
 2984 independent reflections
 1987 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.070$
 $\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.0$ °
 $h = -10 \rightarrow 8$
 $k = -17 \rightarrow 17$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.082$
 $wR(F^2) = 0.184$
 $S = 1.10$
 2984 reflections
 200 parameters
 3 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
 $w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 2.8837P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.30$ e Å⁻³
 $\Delta\rho_{\min} = -0.28$ e Å⁻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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.1354 (3)	0.71070 (18)	0.50069 (19)	0.0328 (6)
H1O	0.150 (5)	0.6502 (11)	0.514 (3)	0.049*
O2	-0.1888 (3)	0.68611 (19)	0.83331 (18)	0.0340 (6)
H2O	-0.241 (5)	0.721 (3)	0.880 (3)	0.051*
O3	0.6044 (3)	0.19192 (18)	0.30034 (19)	0.0360 (6)
O4	0.6016 (3)	0.32888 (19)	0.20547 (18)	0.0360 (6)
N1	0.1233 (3)	0.5509 (2)	0.6101 (2)	0.0257 (6)

N2	0.1909 (4)	0.4583 (2)	0.6225 (2)	0.0276 (6)
H2N	0.167 (4)	0.423 (2)	0.6812 (19)	0.033*
N3	0.5648 (3)	0.2804 (2)	0.2882 (2)	0.0273 (6)
C1	-0.0115 (4)	0.6950 (2)	0.6750 (2)	0.0252 (7)
C2	0.0357 (4)	0.7506 (3)	0.5807 (3)	0.0273 (7)
C3	-0.0168 (5)	0.8477 (3)	0.5650 (3)	0.0334 (8)
H3	0.0214	0.8845	0.5031	0.040*
C4	-0.1245 (5)	0.8902 (3)	0.6400 (3)	0.0357 (8)
H4	-0.1608	0.9566	0.6295	0.043*
C5	-0.1806 (4)	0.8372 (3)	0.7305 (3)	0.0337 (8)
H5	-0.2563	0.8670	0.7810	0.040*
C6	-0.1266 (4)	0.7405 (3)	0.7478 (3)	0.0279 (7)
C7	0.0573 (4)	0.5945 (2)	0.6957 (2)	0.0251 (7)
C8	0.0634 (5)	0.5472 (3)	0.8079 (3)	0.0326 (8)
H8A	-0.0272	0.4984	0.8141	0.049*
H8B	0.0495	0.5981	0.8648	0.049*
H8C	0.1718	0.5141	0.8181	0.049*
C9	0.2810 (4)	0.4167 (2)	0.5372 (2)	0.0235 (7)
C10	0.3233 (4)	0.4699 (2)	0.4419 (2)	0.0239 (7)
H10	0.2865	0.5363	0.4329	0.029*
C11	0.4188 (4)	0.4251 (2)	0.3614 (2)	0.0248 (7)
H11	0.4489	0.4608	0.2968	0.030*
C12	0.4704 (4)	0.3281 (2)	0.3751 (2)	0.0227 (7)
C13	0.4297 (4)	0.2742 (3)	0.4688 (3)	0.0273 (7)
H13	0.4659	0.2076	0.4768	0.033*
C14	0.3360 (4)	0.3191 (2)	0.5497 (2)	0.0260 (7)
H14	0.3084	0.2834	0.6148	0.031*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0374 (14)	0.0285 (13)	0.0327 (13)	0.0032 (11)	0.0141 (10)	0.0013 (11)
O2	0.0387 (14)	0.0374 (15)	0.0258 (12)	0.0003 (12)	0.0129 (10)	-0.0060 (11)
O3	0.0443 (15)	0.0266 (13)	0.0371 (13)	0.0044 (12)	0.0125 (11)	-0.0032 (11)
O4	0.0424 (15)	0.0411 (15)	0.0246 (12)	0.0021 (12)	0.0121 (10)	0.0022 (11)
N1	0.0265 (15)	0.0245 (15)	0.0261 (13)	-0.0025 (12)	0.0036 (11)	-0.0012 (11)
N2	0.0351 (16)	0.0240 (15)	0.0238 (13)	0.0011 (12)	0.0106 (11)	0.0000 (11)
N3	0.0250 (14)	0.0327 (16)	0.0243 (13)	0.0006 (12)	0.0029 (11)	-0.0028 (12)
C1	0.0226 (16)	0.0266 (17)	0.0263 (15)	-0.0051 (13)	0.0035 (12)	-0.0053 (13)
C2	0.0293 (18)	0.0277 (18)	0.0251 (15)	-0.0045 (15)	0.0051 (13)	-0.0038 (13)
C3	0.043 (2)	0.0268 (19)	0.0308 (18)	-0.0026 (16)	0.0061 (15)	0.0012 (14)
C4	0.042 (2)	0.0274 (19)	0.0380 (19)	0.0026 (16)	-0.0010 (16)	-0.0075 (15)
C5	0.034 (2)	0.038 (2)	0.0289 (17)	0.0035 (16)	0.0042 (14)	-0.0112 (15)
C6	0.0280 (18)	0.0318 (19)	0.0239 (15)	-0.0044 (15)	0.0020 (13)	-0.0081 (14)
C7	0.0245 (17)	0.0243 (17)	0.0264 (16)	-0.0064 (13)	0.0061 (13)	-0.0061 (13)
C8	0.045 (2)	0.0270 (18)	0.0264 (17)	-0.0003 (16)	0.0109 (15)	-0.0036 (14)
C9	0.0235 (16)	0.0247 (17)	0.0224 (14)	-0.0024 (13)	0.0041 (12)	-0.0033 (13)
C10	0.0305 (18)	0.0170 (16)	0.0244 (15)	0.0013 (13)	0.0037 (13)	0.0008 (12)
C11	0.0268 (17)	0.0288 (18)	0.0188 (14)	-0.0039 (14)	0.0034 (12)	0.0004 (13)
C12	0.0221 (16)	0.0246 (16)	0.0215 (14)	-0.0011 (13)	0.0033 (12)	-0.0042 (12)

C13	0.0300 (18)	0.0239 (17)	0.0281 (16)	0.0030 (14)	0.0021 (13)	0.0009 (13)
C14	0.0308 (18)	0.0259 (17)	0.0213 (15)	-0.0026 (14)	0.0078 (13)	0.0033 (13)

Geometric parameters (Å, °)

O1—C2	1.366 (4)	C4—H4	0.9500
O1—H1O	0.841 (10)	C5—C6	1.390 (5)
O2—C6	1.364 (4)	C5—H5	0.9500
O2—H2O	0.844 (10)	C7—C8	1.503 (4)
O3—N3	1.244 (4)	C8—H8A	0.9800
O4—N3	1.233 (3)	C8—H8B	0.9800
N1—C7	1.304 (4)	C8—H8C	0.9800
N1—N2	1.369 (4)	C9—C14	1.398 (4)
N2—C9	1.380 (4)	C9—C10	1.401 (4)
N2—H2N	0.880 (10)	C10—C11	1.378 (4)
N3—C12	1.447 (4)	C10—H10	0.9500
C1—C6	1.414 (4)	C11—C12	1.383 (4)
C1—C2	1.418 (4)	C11—H11	0.9500
C1—C7	1.484 (5)	C12—C13	1.387 (4)
C2—C3	1.390 (5)	C13—C14	1.375 (4)
C3—C4	1.377 (5)	C13—H13	0.9500
C3—H3	0.9500	C14—H14	0.9500
C4—C5	1.385 (5)		
C2—O1—H1O	109 (3)	N1—C7—C1	115.4 (3)
C6—O2—H2O	113 (3)	N1—C7—C8	121.0 (3)
C7—N1—N2	119.0 (3)	C1—C7—C8	123.5 (3)
N1—N2—C9	119.7 (3)	C7—C8—H8A	109.5
N1—N2—H2N	120 (2)	C7—C8—H8B	109.5
C9—N2—H2N	120 (2)	H8A—C8—H8B	109.5
O4—N3—O3	123.0 (3)	C7—C8—H8C	109.5
O4—N3—C12	118.7 (3)	H8A—C8—H8C	109.5
O3—N3—C12	118.3 (3)	H8B—C8—H8C	109.5
C6—C1—C2	116.5 (3)	N2—C9—C14	117.8 (3)
C6—C1—C7	122.2 (3)	N2—C9—C10	122.4 (3)
C2—C1—C7	121.4 (3)	C14—C9—C10	119.7 (3)
O1—C2—C3	116.8 (3)	C11—C10—C9	119.6 (3)
O1—C2—C1	121.3 (3)	C11—C10—H10	120.2
C3—C2—C1	122.0 (3)	C9—C10—H10	120.2
C4—C3—C2	119.4 (3)	C10—C11—C12	119.7 (3)
C4—C3—H3	120.3	C10—C11—H11	120.2
C2—C3—H3	120.3	C12—C11—H11	120.2
C3—C4—C5	120.7 (4)	C11—C12—C13	121.6 (3)
C3—C4—H4	119.7	C11—C12—N3	119.4 (3)
C5—C4—H4	119.7	C13—C12—N3	119.0 (3)
C6—C5—C4	120.3 (3)	C14—C13—C12	118.8 (3)
C6—C5—H5	119.9	C14—C13—H13	120.6
C4—C5—H5	119.9	C12—C13—H13	120.6
O2—C6—C5	120.4 (3)	C13—C14—C9	120.6 (3)
O2—C6—C1	118.5 (3)	C13—C14—H14	119.7

C5—C6—C1	121.0 (3)	C9—C14—H14	119.7
C7—N1—N2—C9	-171.3 (3)	C6—C1—C7—C8	-22.2 (5)
C6—C1—C2—O1	-174.7 (3)	C2—C1—C7—C8	157.6 (3)
C7—C1—C2—O1	5.5 (5)	N1—N2—C9—C14	-174.8 (3)
C6—C1—C2—C3	5.3 (5)	N1—N2—C9—C10	7.6 (5)
C7—C1—C2—C3	-174.5 (3)	N2—C9—C10—C11	177.7 (3)
O1—C2—C3—C4	176.7 (3)	C14—C9—C10—C11	0.1 (5)
C1—C2—C3—C4	-3.3 (5)	C9—C10—C11—C12	0.6 (5)
C2—C3—C4—C5	0.1 (5)	C10—C11—C12—C13	-0.5 (5)
C3—C4—C5—C6	1.0 (5)	C10—C11—C12—N3	177.5 (3)
C4—C5—C6—O2	-176.3 (3)	O4—N3—C12—C11	2.4 (4)
C4—C5—C6—C1	1.2 (5)	O3—N3—C12—C11	-177.3 (3)
C2—C1—C6—O2	173.3 (3)	O4—N3—C12—C13	-179.5 (3)
C7—C1—C6—O2	-6.8 (5)	O3—N3—C12—C13	0.9 (4)
C2—C1—C6—C5	-4.2 (5)	C11—C12—C13—C14	-0.2 (5)
C7—C1—C6—C5	175.6 (3)	N3—C12—C13—C14	-178.2 (3)
N2—N1—C7—C1	179.4 (3)	C12—C13—C14—C9	0.8 (5)
N2—N1—C7—C8	3.4 (5)	N2—C9—C14—C13	-178.5 (3)
C6—C1—C7—N1	161.9 (3)	C10—C9—C14—C13	-0.8 (5)
C2—C1—C7—N1	-18.3 (4)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O \cdots N1	0.84 (2)	1.79 (3)	2.534 (4)	147 (4)
N2—H2N \cdots O3 ⁱ	0.88 (2)	2.18 (3)	3.039 (4)	167 (2)
O2—H2O \cdots O1 ⁱⁱ	0.85 (4)	1.99 (4)	2.834 (3)	173 (4)
C14—H14 \cdots O4 ⁱ	0.95	2.50	3.326 (4)	146

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