

Crystal structure of (*E*)-4-hydroxy-6-methyl-3-{1-[2-(4-nitrophenyl)hydrazinylidene]ethyl}-2*H*-pyran-2-one

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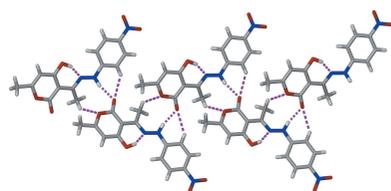
Keywords: crystal structure; HMNP; dehydroacetic acid; hydrogen bonding; thermal stability.**CCDC reference:** 1515036**Supporting information:** this article has supporting information at journals.iucr.org/e^aDepartment of Chemistry, Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh 160 014, India, and^bDepartment of Chemistry, DAV University Jalandhar, Jalandhar 144 001, Punjab, India. *Correspondence e-mail: gkumar@pu.ac.in, rkataria@pu.ac.in

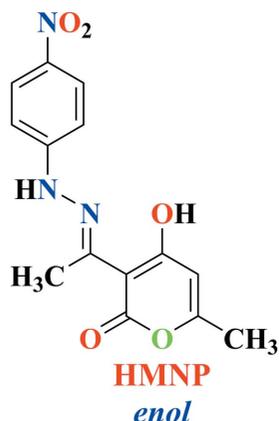
The title compound, C₁₄H₁₃N₃O₅ (HMNP), was synthesized by the simple condensation of *p*-nitrophenylhydrazine with dehydroacetic acid (DHA) in a 1:1 molar ratio in ethanol. HMNP has been characterized by using FT-IR, ¹H and ¹³C NMR and UV-Vis spectroscopic and single-crystal X-ray diffraction techniques. The crystal packing reveals strong hydrogen bonds between the NH group and the carbonyl O atom of dihydropyranone moiety, forming chains along [101]. The thermal stability of the synthesized compound was confirmed by thermogravimetric analysis and it was found to be stable up to 513 K. The UV-Vis spectrum shows the presence of a strong band at λ_{max} 394 nm. ¹H NMR and single-crystal X-ray analyses confirmed the presence of the *enol* form of the ligand and dominance over the *keto* form. The crystal studied was a non-merohedral twin with the refined ratio of the twin components being 0.3720 (19):0.6280 (19).

1. Chemical context

For the last several decades, Schiff bases have remained an important and popular area of research for the scientific community due to their simple synthesis, versatility and extensive range of applications (Cozzi, 2004; Chen *et al.*, 2008). A number of carbonyl compounds and amines have been utilized for the synthesis of Schiff bases (Zheng *et al.*, 2009; Hussain *et al.*, 2014). However, there are only a few reports where dehydroacetic acid (DHA) has been used for the preparation of Schiff bases for various applications (Liu *et al.*, 1991; Luo *et al.*, 1995). In some cases, DHA-based Schiff bases are used for the synthesis of metal complexes, leading to their utilization in various biomedical applications due to their antifungal, antibacterial, antimalarial and anticancer activities (Chan & Wong, 1995; Erkkila *et al.*, 1999; Ganjali *et al.*, 2007; Gupta & Sutar, 2008). In general, the compounds are formed *via* a condensation product of hydrazine and the respective aldehyde or ketone in a 1:1 molar ratio. Structurally, a Schiff base (also known as an imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group.

The reaction between *p*-nitrophenylhydrazine and dehydroacetic acid (DHA) in a 1:1 molar ratio in distilled ethanol afforded the title compound within 4 h. We report herein on its characterization by FT-IR, ¹H and ¹³C NMR and UV-Vis spectroscopic and single-crystal X-ray diffraction techniques.





2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The dihedral angle between the pyran (O2/C9–C13) and benzene (C1–C6) rings is $12.9(1)^\circ$. The approximate planarity of the entire molecule maybe influenced by an intramolecular O1–H1···N3 hydrogen bond, which forms an *S*(6) ring.

3. Supramolecular features

The crystal packing features strong N2–H2···O3ⁱ hydrogen bonds between the NH group and the O_{carbonyl} atom of the DHA moiety of symmetry-related molecules, creating infinite chains along [101] (see Table 1 for symmetry code). This O_{carbonyl} atom is also weakly hydrogen bonded to a symmetry-related hydrogen atom (C5–H5···O3ⁱ), forming a bifurcated N–H, C–H···O hydrogen bond (Fig. 2). In a similar fashion, the O2 atom of the pyran ring forms a weak hydrogen bond to the methyl hydrogen of an adjacent molecule (C7–H7A···O2ⁱ). The chains are arranged in a herringbone pattern in the three-dimensional structure (Fig. 3).

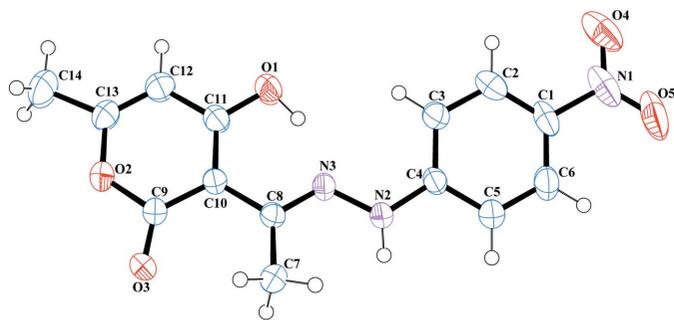


Figure 1
The molecular structure of the title compound, showing the atom-naming scheme. The displacement ellipsoids are shown at the 50% probability level.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1–H1···N3	0.90 (2)	1.64 (2)	2.4760 (18)	154 (2)
N2–H2···O3 ⁱ	0.85 (2)	2.00 (2)	2.8361 (19)	165.2 (19)
C5–H5···O3 ⁱ	0.93	2.60	3.264 (2)	129
C7–H7A···O2 ⁱ	0.96	2.51	3.283 (2)	138

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

4. Hirshfeld surface analysis

The Hirshfeld surface was mapped with d_{norm} to visualize the intermolecular interactions and 2-D fingerprint plots were generated using *Crystal Explorer* (Wolff *et al.*, 2012) (Fig. 4).

5. Spectroscopic and TG analysis

The FT–IR spectrum of the title compound shows a characteristic peak at 1687 cm^{-1} which has been consigned for

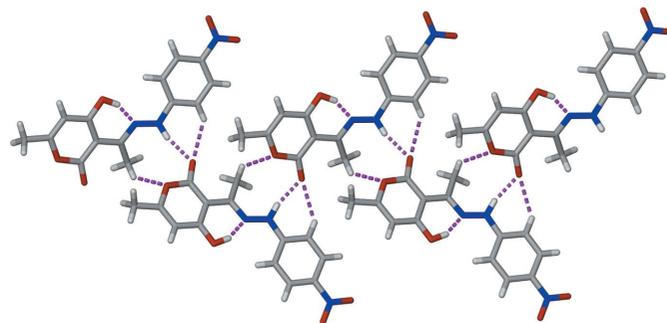


Figure 2
A chain parallel to [101] formed by the intermolecular hydrogen bonding (dashed lines) between the N–H group and carbonyl O atom of the DHA moiety. Weak C–H···O hydrogen bonds are also shown as dashed lines.

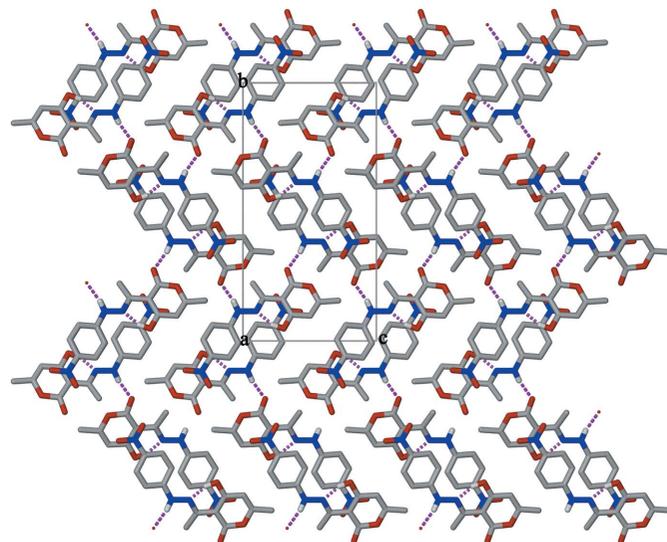


Figure 3
The crystal packing showing the herringbone arrangement of HMNP, viewed along the *a* axis. C-bound H atoms have been omitted for clarity. Hydrogen bonds are shown as dashed lines.

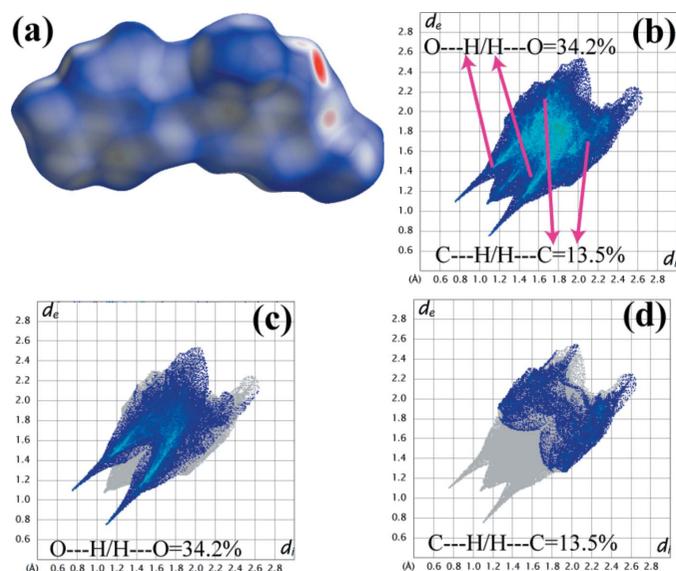


Figure 4
 (a) Hirshfeld surfaces representation for HMNP mapped with d_{norm} . (b)–(d) Fingerprint plots of HMNP resolved into different intermolecular interactions showing the percentages of contacts contributing to the total Hirshfeld surface.

$\nu_{\text{C=N}}$, whereas the broad signal at 3280 cm^{-1} ($\nu_{\text{O-H}}$) indicates the presence of a phenolic group. The ^1H NMR spectrum display a singlet at δ 15.23 ppm, which clearly indicates the dominance of the *enol* form of the title compound over the *keto* form. The absorption spectra for HMNP was recorded in $\text{C}_2\text{H}_5\text{OH}$, and λ_{max} was observed at 394 nm, which is ascribed to the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition of the C=O or C=N group. To probe the thermal stability of HMNP, thermogravimetric analysis (TGA) was undertaken and it was found that HMNP is stable to 513 K.

6. Synthesis and crystallization

Materials and methods: *p*-Nitrophenylhydrazine and dehydroacetic acid were of analytical grade and purchased from Spectrochem and Merck (India), respectively, and used as received. However, analytical grade solvents were purified wherever necessary as per as the standard literature method (Perrin *et al.*, 1980). The FT-IR spectra were recorded with a Perkin-Elmer FTIR-2000 spectrometer. The NMR spectroscopic measurements were carried out with a JEOL AL-400 MHz spectrometer. The thermogravimetric analysis (TGA) measurement was performed on an SDT Q600 (V20.9 Build 20) instrument (Artisan Technology Group, Champaign, IL) under N_2 atmosphere with a heating rate of 10 K min^{-1} . The absorbance spectrum was recorded on a JASCO V-530 UV/vis Spectrophotometer.

Synthesis of (E)-4-hydroxy-6-methyl-3-(1-(2-(4-nitrophenyl)hydrazono) ethyl) 2-H-pyran-2-one (HMNP):

HMNP was synthesized by the reaction of DHA (0.56g, 0.003 mol) with *para*-nitrophenylhydrazine (0.45g, 0.003 mol) in distilled ethanol (15 mL) under reflux condition at 353 K for

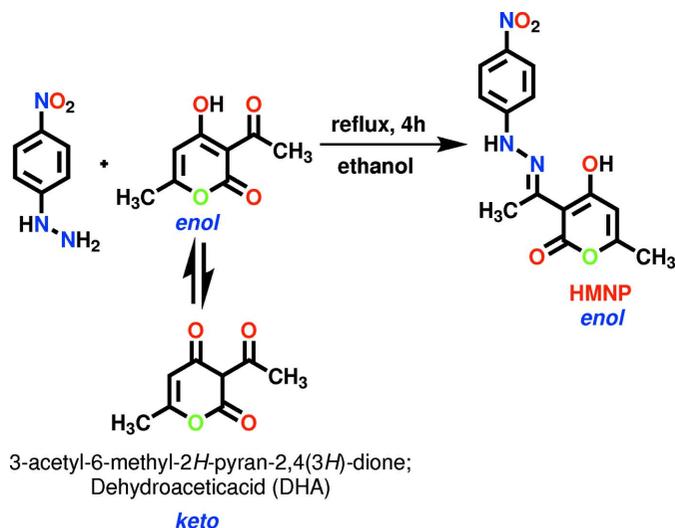


Figure 5
 Synthetic route for the organic ligand HMNP.

3 h (Fig. 5). The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled to room temperature and the yellow crystalline precipitate was filtrated off and washed with cold ethanol and dried [yield: 0.728g (80%)]. Crystals suitable for single crystal X-ray analysis were obtained by the slow evaporation of a THF solution of HMNP for 7–8 d.

Table 2
 Experimental details.

Crystal data	
Chemical formula	$\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_5$
M_r	303.27
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	297
a, b, c (Å)	6.9633 (3), 19.5008 (9), 10.2031 (5)
β (°)	95.196 (2)
V (Å ³)	1379.78 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.16 × 0.13 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (TWINABS; Sheldrick, 2012)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2696, 2696, 2302
R_{int}	0.028
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.121, 1.08
No. of reflections	2696
No. of parameters	208
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.18, -0.20

Computer programs: APEX2 and SAINT (Bruker, 2010), SHELXS2013 (Sheldrick 2008), SHELXL2016 (Sheldrick, 2015), X-SEED (Barbour 2001) and publCIF (Westrip 2010).

FT-IR (selected peaks): 3280 (O–H), 3088 (N–H), 1687 (C=O), 1646 (C=N) cm^{-1} . Absorption spectrum [λ_{max} , nm, $\text{C}_2\text{H}_5\text{OH}$ (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 394 (150), 274 (*sh*, 525). ^1H NMR (CDCl_3 , 400 MHz): δ (ppm): 15.23 (*s*, 1H, H_e), 8.23–8.21 (*d*, 2H, H_a), 7.34 (*1s*, 1H, H_c), 6.94–6.93 (*d*, 2H, H_b), 5.93 (*s*, 1H, H_f), 2.67 (*1s*, 3H, H_g), 2.25 (*1s*, 3H, H_d). ^{13}C NMR ($\text{DMSO-}d_6$, 100 MHz): δ 176.4 (C_8), 167.1 (C_{12}), 163.1 (C_{10}), 150.2 (C_7), 139.5 (C_4), 125.8 (C_1), 111.3 (C_2), 103.3 (C_3), 96.4 (C_9), 79.1 (C_5), 78.7 (C_{11}), 78.3 (C_6).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH and OH hydrogen atoms were located in a difference-Fourier map and freely refined. The C-bound H atoms were included in calculated positions and treated as riding atoms: C–H = 0.93–0.96 Å, O–H = 0.82 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. The crystal studied was a non-merohedral twin with the refined ratio of the twin components being 0.3720 (19): 0.6280 (19) using twin matrix $(\bar{1}0\ 0)$ $(0\ \bar{1}\ 0)$ $(0.265\ 0\ \bar{1})$.

Acknowledgements

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Crystal structure of (*E*)-4-hydroxy-6-methyl-3-{1-[2-(4-nitrophenyl)hydrazinylidene]ethyl}-2*H*-pyran-2-one

Kirandeep, Ahmad Husain, Pooja Negi, Girijesh Kumar and Ramesh Kataria

Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINTE* (Bruker, 2010); data reduction: *SAINTE* (Bruker, 2010); program(s) used to solve structure: *SHELXS2013* (Sheldrick 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *X-SEED* (Barbour 2001); software used to prepare material for publication: *publCIF* (Westrip 2010).

(*E*)-4-Hydroxy-6-methyl-3-{1-[2-(4-nitrophenyl)hydrazin-1-ylidene]ethyl}-2*H*-pyran-2-one

Crystal data

C₁₄H₁₃N₃O₅

M_r = 303.27

Monoclinic, *P*2₁/*n*

a = 6.9633 (3) Å

b = 19.5008 (9) Å

c = 10.2031 (5) Å

β = 95.196 (2)°

V = 1379.78 (11) Å³

Z = 4

F(000) = 632

D_x = 1.460 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 9944 reflections

θ = 2.3–30.3°

μ = 0.11 mm⁻¹

T = 297 K

Block, colourless

0.16 × 0.13 × 0.10 mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(*TWINABS*; Sheldrick, 2012)

2696 measured reflections

2696 independent reflections

2302 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.028

θ_{max} = 26.0°, θ_{min} = 2.3°

h = -8→8

k = 0→24

l = 0→12

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.043

wR(*F*²) = 0.121

S = 1.08

2696 reflections

208 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0606*P*)² + 0.3029*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.18 e Å⁻³

Δρ_{min} = -0.20 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.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.3744 (2)	0.45226 (6)	0.80648 (13)	0.0531 (4)
H1	0.344 (4)	0.4379 (12)	0.7235 (19)	0.080*
O2	0.6082 (2)	0.28918 (6)	1.00744 (12)	0.0469 (3)
O3	0.6119 (3)	0.22490 (6)	0.83226 (13)	0.0663 (5)
O4	0.0188 (3)	0.67218 (8)	0.2507 (2)	0.0812 (6)
O5	-0.0004 (3)	0.61297 (9)	0.07175 (19)	0.0865 (6)
N1	0.0349 (3)	0.61838 (9)	0.1917 (2)	0.0611 (5)
N2	0.3120 (2)	0.38498 (7)	0.46572 (14)	0.0398 (4)
H2	0.268 (3)	0.3474 (11)	0.432 (2)	0.048*
N3	0.3581 (2)	0.38475 (6)	0.60024 (13)	0.0347 (3)
C1	0.1015 (3)	0.55793 (9)	0.2667 (2)	0.0451 (5)
C2	0.1693 (3)	0.56440 (9)	0.3967 (2)	0.0444 (4)
H2A	0.167336	0.606928	0.437835	0.053*
C3	0.2406 (3)	0.50781 (8)	0.46645 (17)	0.0391 (4)
H3	0.289862	0.512366	0.553813	0.047*
C4	0.2383 (2)	0.44367 (8)	0.40531 (16)	0.0337 (4)
C5	0.1636 (3)	0.43827 (9)	0.27327 (18)	0.0462 (5)
H5	0.158976	0.395663	0.232158	0.055*
C6	0.0978 (3)	0.49483 (10)	0.20466 (19)	0.0517 (5)
H6	0.050752	0.491001	0.116717	0.062*
C7	0.5379 (3)	0.27794 (9)	0.57620 (17)	0.0454 (5)
H7A	0.454884	0.238623	0.575635	0.068*
H7B	0.664122	0.265763	0.614883	0.068*
H7C	0.546326	0.293406	0.487576	0.068*
C8	0.4574 (2)	0.33419 (8)	0.65505 (16)	0.0332 (4)
C9	0.5723 (3)	0.28148 (8)	0.87201 (16)	0.0410 (4)
C10	0.4942 (2)	0.33851 (8)	0.79792 (15)	0.0329 (4)
C11	0.4516 (3)	0.39848 (8)	0.86652 (17)	0.0389 (4)
C12	0.4968 (3)	0.40211 (10)	1.00539 (19)	0.0491 (5)
H12	0.472308	0.442214	1.050290	0.059*
C13	0.5736 (3)	0.34866 (9)	1.07078 (17)	0.0451 (4)
C14	0.6316 (4)	0.34367 (13)	1.21487 (19)	0.0689 (7)
H14A	0.564868	0.306098	1.251241	0.103*
H14B	0.599050	0.385539	1.257136	0.103*
H14C	0.768155	0.336166	1.228953	0.103*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0792 (10)	0.0393 (7)	0.0400 (7)	0.0220 (7)	0.0012 (7)	0.0015 (6)
O2	0.0651 (8)	0.0416 (7)	0.0322 (6)	0.0067 (6)	-0.0064 (6)	0.0044 (5)
O3	0.1158 (14)	0.0320 (6)	0.0454 (8)	0.0182 (8)	-0.0238 (8)	-0.0018 (6)
O4	0.0772 (12)	0.0448 (9)	0.1196 (16)	0.0129 (8)	-0.0011 (11)	0.0242 (9)
O5	0.0958 (14)	0.0791 (12)	0.0806 (13)	0.0013 (10)	-0.0138 (11)	0.0484 (10)
N1	0.0438 (9)	0.0498 (10)	0.0889 (15)	0.0011 (8)	0.0009 (9)	0.0340 (10)
N2	0.0555 (9)	0.0297 (7)	0.0317 (8)	-0.0015 (7)	-0.0101 (6)	0.0025 (6)
N3	0.0398 (8)	0.0327 (7)	0.0303 (7)	-0.0018 (6)	-0.0039 (6)	0.0047 (5)
C1	0.0382 (9)	0.0397 (9)	0.0563 (12)	-0.0006 (8)	-0.0016 (8)	0.0210 (8)
C2	0.0436 (10)	0.0312 (8)	0.0587 (12)	-0.0023 (8)	0.0059 (9)	0.0048 (8)
C3	0.0427 (9)	0.0347 (8)	0.0389 (10)	-0.0036 (7)	-0.0017 (8)	0.0025 (7)
C4	0.0349 (8)	0.0308 (8)	0.0345 (9)	-0.0030 (6)	-0.0025 (7)	0.0068 (6)
C5	0.0610 (11)	0.0383 (9)	0.0371 (10)	-0.0013 (9)	-0.0068 (9)	0.0042 (7)
C6	0.0611 (12)	0.0516 (11)	0.0396 (10)	-0.0018 (10)	-0.0102 (9)	0.0134 (8)
C7	0.0601 (12)	0.0401 (9)	0.0342 (9)	0.0088 (9)	-0.0052 (8)	-0.0031 (7)
C8	0.0364 (8)	0.0277 (7)	0.0344 (8)	-0.0031 (6)	-0.0026 (7)	0.0014 (6)
C9	0.0547 (11)	0.0331 (8)	0.0329 (9)	0.0011 (8)	-0.0083 (8)	0.0020 (7)
C10	0.0368 (8)	0.0301 (8)	0.0307 (8)	-0.0006 (6)	-0.0024 (7)	0.0023 (6)
C11	0.0458 (10)	0.0337 (8)	0.0371 (9)	0.0051 (7)	0.0028 (7)	0.0024 (7)
C12	0.0670 (13)	0.0450 (10)	0.0354 (9)	0.0098 (9)	0.0053 (9)	-0.0048 (8)
C13	0.0550 (11)	0.0494 (10)	0.0304 (9)	0.0041 (9)	0.0020 (8)	-0.0008 (8)
C14	0.0965 (18)	0.0774 (15)	0.0312 (10)	0.0156 (14)	-0.0026 (11)	-0.0018 (10)

Geometric parameters (Å, °)

O1—C11	1.305 (2)	C4—C5	1.403 (2)
O1—H1	0.899 (17)	C5—C6	1.363 (2)
O2—C13	1.360 (2)	C5—H5	0.9300
O2—C9	1.390 (2)	C6—H6	0.9300
O3—C9	1.216 (2)	C7—C8	1.499 (2)
O4—N1	1.220 (2)	C7—H7A	0.9600
O5—N1	1.231 (3)	C7—H7B	0.9600
N1—C1	1.458 (2)	C7—H7C	0.9600
N2—C4	1.377 (2)	C8—C10	1.460 (2)
N2—N3	1.3809 (18)	C9—C10	1.424 (2)
N2—H2	0.85 (2)	C10—C11	1.408 (2)
N3—C8	1.301 (2)	C11—C12	1.425 (3)
C1—C2	1.373 (3)	C12—C13	1.324 (3)
C1—C6	1.383 (3)	C12—H12	0.9300
C2—C3	1.381 (2)	C13—C14	1.492 (2)
C2—H2A	0.9300	C14—H14A	0.9600
C3—C4	1.397 (2)	C14—H14B	0.9600
C3—H3	0.9300	C14—H14C	0.9600
C11—O1—H1	104.1 (16)	H7A—C7—H7B	109.5

C13—O2—C9	122.74 (13)	C8—C7—H7C	109.5
O4—N1—O5	123.05 (18)	H7A—C7—H7C	109.5
O4—N1—C1	118.4 (2)	H7B—C7—H7C	109.5
O5—N1—C1	118.5 (2)	N3—C8—C10	115.09 (14)
C4—N2—N3	119.41 (13)	N3—C8—C7	122.27 (14)
C4—N2—H2	115.4 (14)	C10—C8—C7	122.54 (14)
N3—N2—H2	116.0 (14)	O3—C9—O2	113.81 (14)
C8—N3—N2	119.75 (14)	O3—C9—C10	128.22 (15)
C2—C1—C6	120.96 (16)	O2—C9—C10	117.97 (14)
C2—C1—N1	119.85 (18)	C11—C10—C9	118.16 (15)
C6—C1—N1	119.18 (18)	C11—C10—C8	121.23 (14)
C1—C2—C3	120.03 (16)	C9—C10—C8	120.60 (14)
C1—C2—H2A	120.0	O1—C11—C10	122.02 (16)
C3—C2—H2A	120.0	O1—C11—C12	118.12 (15)
C2—C3—C4	119.77 (16)	C10—C11—C12	119.85 (15)
C2—C3—H3	120.1	C13—C12—C11	120.32 (17)
C4—C3—H3	120.1	C13—C12—H12	119.8
N2—C4—C3	123.76 (14)	C11—C12—H12	119.8
N2—C4—C5	117.25 (15)	C12—C13—O2	120.85 (16)
C3—C4—C5	118.95 (15)	C12—C13—C14	127.50 (18)
C6—C5—C4	120.68 (17)	O2—C13—C14	111.65 (16)
C6—C5—H5	119.7	C13—C14—H14A	109.5
C4—C5—H5	119.7	C13—C14—H14B	109.5
C5—C6—C1	119.57 (17)	H14A—C14—H14B	109.5
C5—C6—H6	120.2	C13—C14—H14C	109.5
C1—C6—H6	120.2	H14A—C14—H14C	109.5
C8—C7—H7A	109.5	H14B—C14—H14C	109.5
C8—C7—H7B	109.5		
C4—N2—N3—C8	-168.31 (16)	C13—O2—C9—C10	-0.6 (3)
O4—N1—C1—C2	-9.0 (3)	O3—C9—C10—C11	177.1 (2)
O5—N1—C1—C2	170.29 (19)	O2—C9—C10—C11	-2.2 (3)
O4—N1—C1—C6	172.0 (2)	O3—C9—C10—C8	-2.0 (3)
O5—N1—C1—C6	-8.7 (3)	O2—C9—C10—C8	178.60 (16)
C6—C1—C2—C3	1.9 (3)	N3—C8—C10—C11	-9.8 (2)
N1—C1—C2—C3	-177.08 (17)	C7—C8—C10—C11	166.71 (17)
C1—C2—C3—C4	-1.8 (3)	N3—C8—C10—C9	169.40 (16)
N3—N2—C4—C3	12.9 (3)	C7—C8—C10—C9	-14.1 (3)
N3—N2—C4—C5	-169.53 (16)	C9—C10—C11—O1	-177.92 (17)
C2—C3—C4—N2	177.75 (17)	C8—C10—C11—O1	1.3 (3)
C2—C3—C4—C5	0.2 (3)	C9—C10—C11—C12	3.5 (3)
N2—C4—C5—C6	-176.40 (19)	C8—C10—C11—C12	-177.33 (18)
C3—C4—C5—C6	1.3 (3)	O1—C11—C12—C13	179.38 (19)
C4—C5—C6—C1	-1.2 (3)	C10—C11—C12—C13	-2.0 (3)
C2—C1—C6—C5	-0.4 (3)	C11—C12—C13—O2	-0.9 (3)
N1—C1—C6—C5	178.59 (18)	C11—C12—C13—C14	179.3 (2)
N2—N3—C8—C10	-178.73 (15)	C9—O2—C13—C12	2.3 (3)
N2—N3—C8—C7	4.8 (2)	C9—O2—C13—C14	-177.92 (19)

C13—O2—C9—O3

179.91 (19)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1···N3	0.90 (2)	1.64 (2)	2.4760 (18)	154 (2)
N2—H2···O3 ⁱ	0.85 (2)	2.00 (2)	2.8361 (19)	165.2 (19)
C5—H5···O3 ⁱ	0.93	2.60	3.264 (2)	129
C7—H7A···O2 ⁱ	0.96	2.51	3.283 (2)	138

Symmetry code: (i) $x-1/2, -y+1/2, z-1/2$.