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Crystal structure and Hirshfeld surface analysis of 3-(hydroxymethyl)-3-methyl-2,6-diphenylpiperidin-4-one

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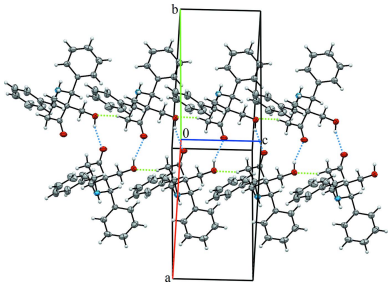
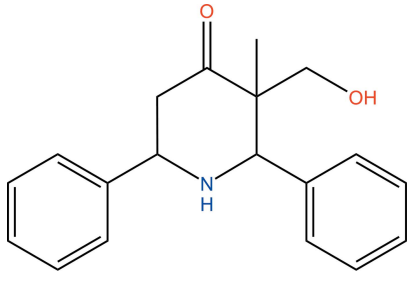
A new synthesis of the title compound, $C_{19}H_{21}NO_2$, was developed with good yield and purity using the reaction of 4-hydroxy-3-methyl-2-butanone, benzaldehyde and ammonium acetate in glacial acetic acid as a solvent. The central piperidine ring adopts a chair conformation, and its least-squares basal plane forms dihedral angles of 85.71 (11) and 77.27 (11)° with the terminal aromatic rings. In the crystal, the molecules are linked by O—H···O and C—H···O hydrogen bonds into double ribbons. The Hirshfeld surface analysis shows that the most important contributions are from H···H (68%), C···H/H···C (19%) and O···H/H···O (12%) interactions.

1. Chemical context

Many piperidine derivatives are found to possess pharmacological activity and are constituents of important drugs. Numerous biological effects including antiviral, antitumor, bactericidal, fungicidal and anti-inflammatory activities have been reported for these compounds (Kappe, 2000; Rameshkumar *et al.*, 2003; Sasitha & John, 2021). In this work, a new protocol for the synthesis of diphenylpiperidin-4-one from 4-hydroxy-3-methyl-2-butanone, benzaldehyde and ammonium acetate under mild reaction conditions was developed. In addition, 3-(hydroxymethyl)-3-methyl-2,6-diphenylpiperidin-4-one was characterized by single crystal X-ray diffraction and studied by Hirshfeld surface analysis.





2. Structural commentary

The title compound, $C_{19}H_{21}NO_2$, crystallizes in the space group $Pna2_1$ with one molecule in the asymmetric unit of the

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1^{i}	0.82	2.05	2.8194 (18)	156
C8—H8A···O2^{ii}	0.97	2.47	3.379 (3)	155
N1—H1···C3^{iii}	0.90 (3)	2.75 (3)	3.605 (2)	161 (3)

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

cell. As shown in Fig. 1, it involves two terminal aromatic rings (C1–C6 and C14–C19) and a central piperidinone fragment (N1/C7–C10/Cl3/O1). The piperidine ring adopts a chair conformation, with the carbonyl O1 and the N-bound H1 atoms being in the equatorial positions. The least-squares basal plane of the piperidine ring (C7, C8, C10, C13) makes dihedral angles of 85.71 (11) and 77.27 (11)°, respectively, with the planes of the C1–C6 and C14–C19 aromatic rings.

3. Supramolecular features

In the crystal, molecules of the title compound are linked by strong O—H···O and weak C—H···O hydrogen bonds (Table 1) into double ribbons stretched along the *c*-axis direction (Fig. 2). Neighbouring molecules in the ribbon are related by the 2_1 screw axis. Besides this, the molecules are connected by N1—H1···C3 contacts into chains along the *b*-axis direction, thus layers perpendicular to the *a* axis are formed. No π–π or C—H···π interactions are present in this structure.

4. Database survey

A search of the Cambridge Structural Database (CSD Version 5.42, update of May 2021; Groom *et al.*, 2016) revealed several related structures, *viz*. dimethyl-3-(2-hydroxyethyl)-9-oxo-7-phenylethyl-6,8-diphenyl-3,7-diazabicyclo(3.3.1)nonane-1,5-dicarboxylate (BACLUM; Caujolle *et al.*, 1981), dimethyl-3-methyl-2,4-bis(4-nitrophenyl)-9-oxo-7-(1-phenylethyl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate (DEZTEK; Rossetti *et al.*, 2018) and dimethyl-2,4-bis(2-methoxyphenyl)-3,7-dimethyl-3,7-diazabicyclo(3.3.1)nonan-9-one-1,5-dicarboxylate (REXNUD; Comba *et al.*, 1997). In these three structures, the piperidine rings adopt a chair conformation, as in the title compound.

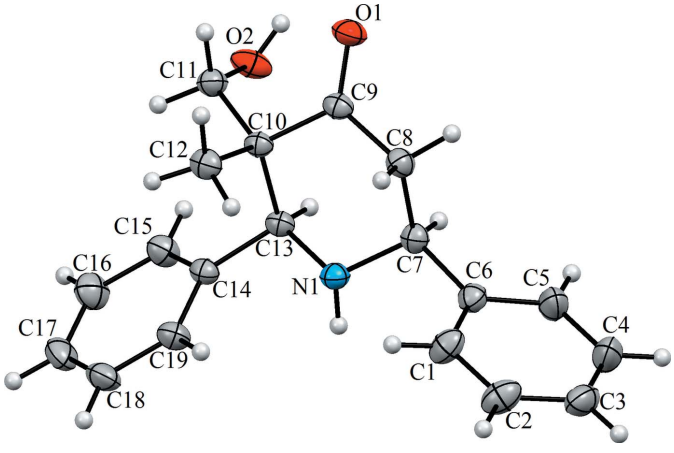


Figure 1
The molecular structure of 3-(hydroxymethyl)-3-methyl-2,6-diphenylpiperidin-4-one with the atom labelling. Displacement ellipsoids are drawn at the 40% probability level.

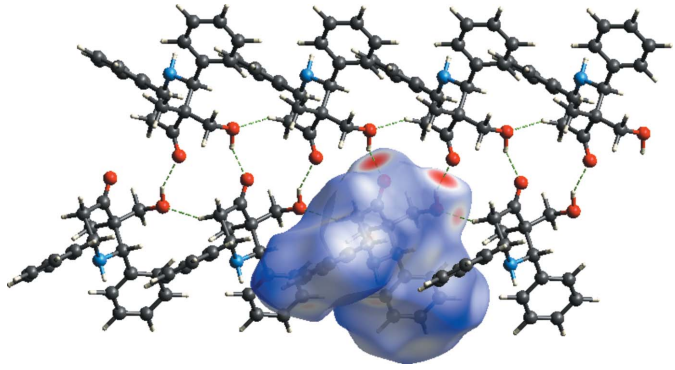


Figure 3
The red spots on the d_{norm} surface of the title structure represent the O—H···O and C—H···O intermolecular interactions.

5. Hirshfeld surface analysis

The Hirshfeld surface analysis of the title compound was performed using *Crystal Explorer 17* (Turner *et al.*, 2017; Spackman & Jayatilaka, 2009). Fig. 3 shows the 3D surface mapped over $d_{\rm norm}$ over the range −0.5456 (red) to 1.6913 (blue) a.u. The large and small red spots indicate the O—H···O and C—H···O interactions. The two-dimensional fingerprint plots, shown in Fig. 4, present all interactions and those delineated into H···H (68%), C···H/H···C (19%) and O···H/H···O (12%) components.

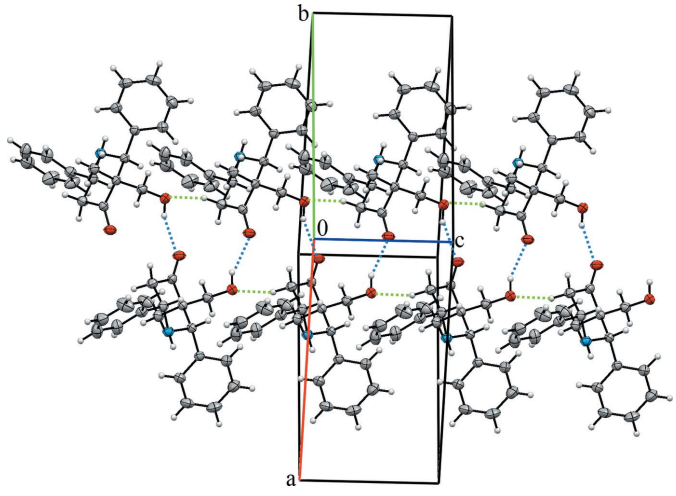


Figure 2
View of the hydrogen-bonded double ribbon in the title structure showing C8—H8A···O2 hydrogen bonds as green dashed lines and O2—H2···O1 hydrogen bonds as blue dashed lines.

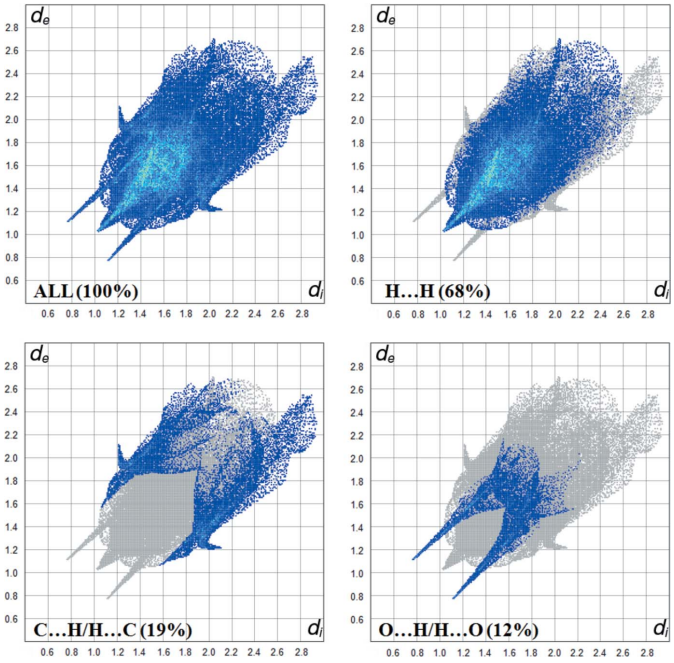


Figure 4
The view of the two-dimensional fingerprint plots for the title structure.

6. Synthesis and crystallization

The title compound was prepared (Fig. 5) according to the procedure reported in the literature for preparation of diphenylpiperidin-4-one (Kim & Tulemisova, 1997). To a mixture of 3.03 g (0.03 mol) of 4-hydroxy-3-methyl-2-butanone and 6.04 g (0.06 mol) of benzaldehyde in glacial acetic acid as a solvent, kept at 293–298 K until the initial keto alcohol disappears as indicated by TLC (1.5 h), 2.3 g (0.03 mol) of ammonium acetate was added. Then the mixture was stirred at the same temperature for 6–7 h. The formed white precipitate was separated and after acidification of the solution with 5% hydrochloric acid to pH 4, the hydrochlorides were converted to bases by neutralization with K_2CO_3 in a strongly basic reaction. After the extraction with diethyl ether of the by-product base (control of the completeness of extraction by TLC), the title compound was extracted with chloroform. After drying the chloroform extracts and distilling off the solvent, a white crystalline compound was obtained (5.95 g, 70%), readily soluble in chloroform, acetone, and hot ethanol (Fig. 5).

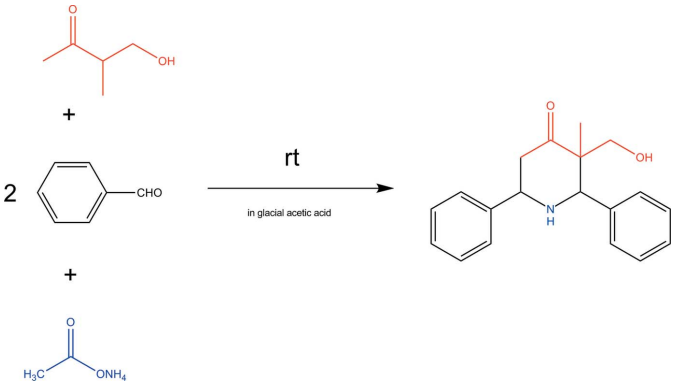


Figure 5
The synthesis of 3-(hydroxymethyl)-3-methyl-2,6-diphenylpiperidin-4-one.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{21}NO_2$
M_r	295.37
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	296
a, b, c (Å)	17.3298 (8), 14.1856 (7), 6.5857 (3)
V (Å^3)	1618.99 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.72 × 0.57 × 0.33
Data collection	
Diffractometer	Stoe IPDS 2
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2002)
T_{min}, T_{max}	0.958, 0.973
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17314, 4763, 3441
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.729
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.096, 1.01
No. of reflections	4763
No. of parameters	204
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.19
Absolute structure	Flack x determined using 1072 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter	0.8 (5)

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 2002), *SHELXT2017/1* (Sheldrick, 2015*a*), *SHELXL2017/1* (Sheldrick, 2015*b*), *PLATON* (Spek, 2020), *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N-bound H atom was refined freely. The O-bound H atom was located in a difference-Fourier map and refined with O—H = 0.82 Å, and with U_{iso}(H) = 1.5U_{eq}(O). The C-bound H atoms were positioned geometrically (C—H = 0.93, 0.96, 0.97 and 0.98 Å for sp^2-hybridized, methyl, methylene and methine C atoms, respectively) and refined using a riding model, with U_{iso}(H) = 1.5U_{eq}(C) and 1.2U_{eq}(C) for methyl and other H atoms, respectively.

Acknowledgements

Author contributions are as follows. Conceptualization, MKG, SK, and ES; synthesis, MKG and GBT; writing (review and

editing of the manuscript) MKG and SK; formal analysis, MKG, SK and ND; crystal-structure determination, MKG, SK and ND; validation, MKG, GBT and ES; project administration, MKG and SK. MKG thanks the Ministry of Education and Science of the Republic of Kazakhstan for financial support as a visiting professor at Atyrau State University.

References

Caujolle, R., Lattes, A., Jaud, J. & Galy, J. (1981). *Acta Cryst.* B**37**, 1699–1703.
Comba, P., Nuber, B. & Ramlow, A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 347–352.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Kappe, C. O. (2000). *Eur. J. Med. Chem.* **35**, 1043–1052.
Kim, D. G. & Tulemisova, G. B. (1997). *Russ. J. Org. Chem.* **33**, 1337–1340.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Rameshkumar, N., Veena, A., Ilavarasan, R., Adiraj, M., Shanmugapandiyan, P. & Sridhar, S. K. (2003). *Biol. Pharm. Bull.* **26**, 188–193.
Rossetti, A., Landoni, S., Meneghetti, F., Castellano, C., Mori, M., Colombo Dugoni, G. & Sacchetti, A. (2018). *New J. Chem.* **42**, 12072–12081.
Sasitha, T. & John, W. J. (2021). *Heliyon*, **7**, e06127.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.
Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie GmbH, Darmstadt, Germany.
Turner, M. J., MacKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *Crystal Explorer 17.5*. University of Western Australia. http://hirshfeldsurface.net.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

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Crystal structure and Hirshfeld surface analysis of 3-(hydroxymethyl)-3-methyl-2,6-diphenylpiperidin-4-one

Mustafa Kemal Gümüş, Sevgi Kansiz, Gulzhamal Bagitovna Tulemisova, Necmi Dege and Eiad Saif

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXT2017/1* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2017/1* (Sheldrick, 2015b); molecular graphics: *PLATON* (Spek, 2020); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

3-(Hydroxymethyl)-3-methyl-2,6-diphenylpiperidin-4-one

Crystal data

$C_{19}H_{21}NO_2$
M_r = 295.37
Orthorhombic, $Pna2_1$
a = 17.3298 (8) Å
b = 14.1856 (7) Å
c = 6.5857 (3) Å
V = 1618.99 (13) Å^3
Z = 4
$F(000)$ = 632
D_x = 1.212 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 17006 reflections
θ = 1.9–31.5°
μ = 0.08 mm^{-1}
T = 296 K
Prism, colorless
0.72 × 0.57 × 0.33 mm

Data collection

Stoe IPDS 2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)
T_{min} = 0.958, T_{max} = 0.973
17314 measured reflections
4763 independent reflections
3441 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 31.2°, θ_{min} = 1.9°
h = −24→25
k = −20→20
l = −7→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.096
S = 1.01
4763 reflections
204 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Absolute structure: Flack *x* determined using 1072 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter: 0.8 (5)

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}
O1	−0.52068 (8)	−0.46901 (9)	−0.4103 (2)	0.0600 (4)
O2	−0.60074 (9)	−0.40945 (10)	−0.0228 (2)	0.0610 (4)
H2	−0.565229	−0.447609	−0.026638	0.091*
N1	−0.58527 (9)	−0.20075 (10)	−0.4826 (2)	0.0446 (3)
C14	−0.69489 (10)	−0.21260 (11)	−0.2492 (3)	0.0421 (4)
C9	−0.54765 (10)	−0.39351 (11)	−0.4587 (3)	0.0417 (4)
C13	−0.61836 (10)	−0.25456 (10)	−0.3131 (3)	0.0396 (3)
H13	−0.582802	−0.250220	−0.197803	0.048*
C6	−0.47125 (11)	−0.16339 (12)	−0.6872 (3)	0.0483 (4)
C10	−0.62508 (9)	−0.36075 (11)	−0.3756 (3)	0.0388 (3)
C11	−0.64790 (12)	−0.42148 (12)	−0.1929 (3)	0.0482 (4)
H11A	−0.700646	−0.406616	−0.155468	0.058*
H11B	−0.646451	−0.487258	−0.233009	0.058*
C7	−0.50597 (10)	−0.22790 (12)	−0.5292 (3)	0.0453 (4)
H7	−0.474939	−0.224784	−0.404983	0.054*
C19	−0.74209 (11)	−0.16475 (13)	−0.3861 (3)	0.0515 (4)
H19	−0.725854	−0.156467	−0.519485	0.062*
C8	−0.50769 (11)	−0.32968 (13)	−0.6060 (3)	0.0484 (4)
H8A	−0.534221	−0.331932	−0.735585	0.058*
H8B	−0.455272	−0.351604	−0.626845	0.058*
C12	−0.68510 (11)	−0.37561 (13)	−0.5433 (3)	0.0508 (4)
H12A	−0.674874	−0.333097	−0.653506	0.076*
H12B	−0.735741	−0.363652	−0.490172	0.076*
H12C	−0.682287	−0.439401	−0.591446	0.076*
C15	−0.72036 (12)	−0.22177 (14)	−0.0520 (3)	0.0555 (5)
H15	−0.688985	−0.251458	0.043011	0.067*
C18	−0.81260 (13)	−0.12956 (14)	−0.3257 (4)	0.0638 (6)
H18	−0.843205	−0.097262	−0.418500	0.077*
C1	−0.51207 (14)	−0.13749 (15)	−0.8595 (4)	0.0630 (5)
H1A	−0.562927	−0.157131	−0.875089	0.076*
C17	−0.83831 (13)	−0.14174 (16)	−0.1288 (4)	0.0692 (6)
H17	−0.886403	−0.119157	−0.089324	0.083*
C3	−0.40316 (15)	−0.05295 (15)	−0.9865 (4)	0.0730 (7)
H3	−0.379964	−0.017017	−1.087645	0.088*

C16	−0.79174 (14)	−0.18768 (16)	0.0075 (4)	0.0687 (6)
H16	−0.808210	−0.195995	0.140665	0.082*
C2	−0.47809 (16)	−0.08286 (16)	−1.0084 (4)	0.0717 (6)
H2A	−0.505992	−0.066302	−1.123614	0.086*
C5	−0.39677 (12)	−0.13063 (17)	−0.6673 (5)	0.0715 (7)
H5	−0.368693	−0.145511	−0.551306	0.086*
C4	−0.36317 (14)	−0.07616 (19)	−0.8164 (5)	0.0847 (9)
H4	−0.312707	−0.055149	−0.800405	0.102*
H1	−0.5902 (17)	−0.140 (2)	−0.450 (5)	0.102*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0654 (9)	0.0459 (7)	0.0686 (9)	0.0199 (6)	0.0128 (8)	0.0080 (6)
O2	0.0811 (10)	0.0618 (7)	0.0400 (7)	0.0271 (7)	−0.0050 (7)	0.0015 (6)
N1	0.0489 (8)	0.0368 (6)	0.0480 (9)	0.0024 (6)	0.0031 (7)	0.0004 (6)
C14	0.0454 (9)	0.0369 (7)	0.0439 (9)	0.0037 (7)	−0.0020 (8)	−0.0021 (6)
C9	0.0468 (9)	0.0383 (7)	0.0399 (8)	0.0044 (7)	−0.0039 (7)	−0.0052 (6)
C13	0.0428 (9)	0.0376 (7)	0.0383 (8)	0.0038 (6)	−0.0031 (7)	0.0005 (7)
C6	0.0484 (10)	0.0428 (8)	0.0537 (11)	−0.0033 (7)	0.0038 (9)	−0.0028 (8)
C10	0.0424 (8)	0.0370 (7)	0.0372 (8)	0.0030 (6)	−0.0040 (7)	0.0002 (6)
C11	0.0524 (10)	0.0425 (8)	0.0495 (10)	0.0046 (7)	0.0047 (9)	0.0050 (7)
C7	0.0448 (9)	0.0468 (8)	0.0441 (9)	−0.0011 (7)	−0.0013 (8)	−0.0006 (8)
C19	0.0549 (11)	0.0475 (9)	0.0521 (10)	0.0092 (8)	−0.0043 (9)	0.0034 (8)
C8	0.0478 (10)	0.0465 (9)	0.0509 (10)	0.0044 (8)	0.0061 (8)	−0.0008 (8)
C12	0.0536 (11)	0.0482 (9)	0.0507 (10)	0.0017 (8)	−0.0117 (9)	−0.0064 (8)
C15	0.0594 (11)	0.0600 (10)	0.0471 (11)	0.0121 (9)	0.0023 (9)	0.0022 (9)
C18	0.0584 (12)	0.0527 (10)	0.0803 (16)	0.0175 (9)	−0.0110 (11)	0.0034 (11)
C1	0.0735 (14)	0.0611 (11)	0.0544 (12)	−0.0208 (10)	−0.0075 (11)	0.0033 (10)
C17	0.0518 (12)	0.0604 (11)	0.0954 (19)	0.0141 (10)	0.0101 (13)	−0.0121 (12)
C3	0.0806 (16)	0.0533 (10)	0.0851 (18)	0.0009 (10)	0.0272 (14)	0.0154 (12)
C16	0.0682 (13)	0.0748 (13)	0.0632 (14)	0.0105 (11)	0.0176 (12)	−0.0050 (11)
C2	0.0980 (17)	0.0631 (12)	0.0540 (13)	−0.0150 (12)	−0.0030 (12)	0.0060 (11)
C5	0.0459 (12)	0.0746 (14)	0.0940 (19)	−0.0035 (10)	−0.0049 (12)	0.0283 (14)
C4	0.0533 (13)	0.0824 (16)	0.119 (3)	−0.0099 (11)	0.0055 (15)	0.0365 (17)

Geometric parameters (Å, º)

O1—C9	1.211 (2)	C19—H19	0.9300
O2—C11	1.397 (2)	C8—H8A	0.9700
O2—H2	0.8200	C8—H8B	0.9700
N1—C7	1.460 (2)	C12—H12A	0.9600
N1—C13	1.469 (2)	C12—H12B	0.9600
N1—H1	0.90 (3)	C12—H12C	0.9600
C14—C15	1.378 (3)	C15—C16	1.385 (3)
C14—C19	1.394 (3)	C15—H15	0.9300
C14—C13	1.513 (2)	C18—C17	1.382 (4)
C9—C8	1.497 (3)	C18—H18	0.9300

C9—C10	1.522 (2)	C1—C2	1.381 (3)
C13—C10	1.566 (2)	C1—H1A	0.9300
C13—H13	0.9800	C17—C16	1.372 (4)
C6—C5	1.378 (3)	C17—H17	0.9300
C6—C1	1.387 (3)	C3—C4	1.358 (4)
C6—C7	1.511 (3)	C3—C2	1.374 (4)
C10—C12	1.532 (3)	C3—H3	0.9300
C10—C11	1.531 (2)	C16—H16	0.9300
C11—H11A	0.9700	C2—H2A	0.9300
C11—H11B	0.9700	C5—C4	1.379 (4)
C7—C8	1.530 (3)	C5—H5	0.9300
C7—H7	0.9800	C4—H4	0.9300
C19—C18	1.379 (3)		

C11—O2—H2	109.5	C9—C8—C7	111.45 (15)
C7—N1—C13	112.98 (14)	C9—C8—H8A	109.3
C7—N1—H1	113.2 (19)	C7—C8—H8A	109.3
C13—N1—H1	107 (2)	C9—C8—H8B	109.3
C15—C14—C19	117.87 (17)	C7—C8—H8B	109.3
C15—C14—C13	120.38 (16)	H8A—C8—H8B	108.0
C19—C14—C13	121.74 (17)	C10—C12—H12A	109.5
O1—C9—C8	121.79 (16)	C10—C12—H12B	109.5
O1—C9—C10	121.04 (16)	H12A—C12—H12B	109.5
C8—C9—C10	117.15 (14)	C10—C12—H12C	109.5
N1—C13—C14	110.43 (13)	H12A—C12—H12C	109.5
N1—C13—C10	109.24 (13)	H12B—C12—H12C	109.5
C14—C13—C10	112.72 (13)	C14—C15—C16	121.3 (2)
N1—C13—H13	108.1	C14—C15—H15	119.3
C14—C13—H13	108.1	C16—C15—H15	119.3
C10—C13—H13	108.1	C19—C18—C17	120.7 (2)
C5—C6—C1	117.8 (2)	C19—C18—H18	119.6
C5—C6—C7	120.78 (19)	C17—C18—H18	119.6
C1—C6—C7	121.40 (17)	C2—C1—C6	120.8 (2)
C9—C10—C12	107.29 (14)	C2—C1—H1A	119.6
C9—C10—C11	109.78 (14)	C6—C1—H1A	119.6
C12—C10—C11	108.28 (15)	C16—C17—C18	118.9 (2)
C9—C10—C13	108.82 (13)	C16—C17—H17	120.5
C12—C10—C13	111.86 (13)	C18—C17—H17	120.5
C11—C10—C13	110.75 (14)	C4—C3—C2	119.6 (2)
O2—C11—C10	114.21 (15)	C4—C3—H3	120.2
O2—C11—H11A	108.7	C2—C3—H3	120.2
C10—C11—H11A	108.7	C17—C16—C15	120.4 (2)
O2—C11—H11B	108.7	C17—C16—H16	119.8
C10—C11—H11B	108.7	C15—C16—H16	119.8
H11A—C11—H11B	107.6	C3—C2—C1	120.1 (3)
N1—C7—C6	111.10 (15)	C3—C2—H2A	119.9
N1—C7—C8	107.46 (14)	C1—C2—H2A	119.9
C6—C7—C8	110.59 (16)	C4—C5—C6	121.1 (2)

N1—C7—H7	109.2	C4—C5—H5	119.4
C6—C7—H7	109.2	C6—C5—H5	119.4
C8—C7—H7	109.2	C3—C4—C5	120.5 (2)
C18—C19—C14	120.7 (2)	C3—C4—H4	119.7
C18—C19—H19	119.7	C5—C4—H4	119.7
C14—C19—H19	119.7		

C7—N1—C13—C14	170.51 (14)	C1—C6—C7—N1	−44.8 (2)
C7—N1—C13—C10	−64.98 (17)	C5—C6—C7—C8	−103.5 (2)
C15—C14—C13—N1	−152.01 (17)	C1—C6—C7—C8	74.5 (2)
C19—C14—C13—N1	28.7 (2)	C15—C14—C19—C18	−1.2 (3)
C15—C14—C13—C10	85.5 (2)	C13—C14—C19—C18	178.07 (17)
C19—C14—C13—C10	−93.80 (19)	O1—C9—C8—C7	−133.78 (19)
O1—C9—C10—C12	−102.5 (2)	C10—C9—C8—C7	47.8 (2)
C8—C9—C10—C12	75.99 (19)	N1—C7—C8—C9	−54.0 (2)
O1—C9—C10—C11	15.0 (2)	C6—C7—C8—C9	−175.41 (15)
C8—C9—C10—C11	−166.55 (15)	C19—C14—C15—C16	2.3 (3)
O1—C9—C10—C13	136.33 (17)	C13—C14—C15—C16	−177.03 (19)
C8—C9—C10—C13	−45.2 (2)	C14—C19—C18—C17	−0.6 (3)
N1—C13—C10—C9	50.76 (17)	C5—C6—C1—C2	1.8 (3)
C14—C13—C10—C9	173.93 (15)	C7—C6—C1—C2	−176.3 (2)
N1—C13—C10—C12	−67.59 (18)	C19—C18—C17—C16	1.4 (4)
C14—C13—C10—C12	55.57 (19)	C18—C17—C16—C15	−0.4 (4)
N1—C13—C10—C11	171.52 (14)	C14—C15—C16—C17	−1.5 (3)
C14—C13—C10—C11	−65.32 (18)	C4—C3—C2—C1	−1.0 (4)
C9—C10—C11—O2	67.49 (18)	C6—C1—C2—C3	−0.4 (4)
C12—C10—C11—O2	−175.68 (14)	C1—C6—C5—C4	−1.8 (4)
C13—C10—C11—O2	−52.70 (19)	C7—C6—C5—C4	176.2 (2)
C13—N1—C7—C6	−173.39 (15)	C2—C3—C4—C5	1.0 (4)
C13—N1—C7—C8	65.51 (18)	C6—C5—C4—C3	0.5 (4)
C5—C6—C7—N1	137.2 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.82	2.05	2.8194 (18)	156
C8—H8*A*···O2^{ii}	0.97	2.47	3.379 (3)	155
N1—H1···C3^{iii}	0.90 (3)	2.75 (3)	3.605 (2)	161 (3)

Symmetry codes: (i) −*x*−1, −*y*−1, *z*+1/2; (ii) *x*, *y*, *z*−1; (iii) −*x*−1, −*y*, *z*+1/2.