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Crystal structure and Hirshfeld surface analysis of (±)-*N*′-(2-hydroxy-3-methoxybenzylidene)-2-(4-isobutylphenyl)propionohydrazide

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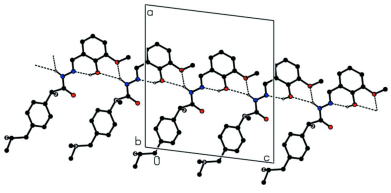
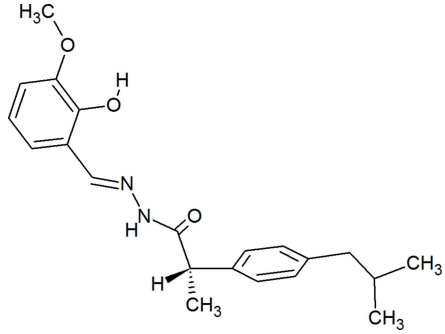
The title molecule, $C_{21}H_{26}N_2O_3$, adopts a V-shaped conformation and is chiral at the C atom with methyl group attached at the common cut of the edges of the V-conformation and crystallizes as a racemate. It also contains an intramolecular O—H···N hydrogen bond. In the crystal, N—H···O hydrogen bonds form chains of molecules extending along the *c*-axis direction, together with normal van der Waals contacts. The roles of the various intermolecular interactions were clarified by Hirshfeld surface analysis, which reveals that the most important contributions to the crystal packing are from H···H (62.6%), C···H/H···C (15.8%) and O···H/H···O (15.3%) contacts.

1. Chemical context

Non-steroidal anti-inflammatory drugs (NSAIDs) are commonly used as analgesics and antipyretics to manage pain and inflammation in people with chronic pain, osteoarthritis, rheumatoid arthritis, postoperative surgical conditions, and menstrual cramps (Manzano *et al.*, 2018; Gupta & Bah, 2016; Budoff, 1979). Azo-methine structure-based ibuprofen core compounds in particular have been used as anti-viral and anti-bacterial agents (El Bakri *et al.*, 2022). Based on such significant activity, we herein report the crystal structure of a member of this family, namely (±)-*N*′-(2-hydroxy-3-methoxybenzylidene)-2-(4-isobutylphenyl)propionohydrazide.





2. Structural commentary

In the solid state, the molecule adopts a wide, V-shaped conformation (Fig. 1) with a dihedral angle of 1.08 (11)° between the mean plane of the C1–C6 ring and the chain

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H*O*1···N1	0.85 (1)	1.83 (1)	2.5914 (13)	149 (2)
N2—H*N*2···O1^{i}	0.90 (1)	2.40 (1)	3.2470 (14)	157 (1)
N2—H*N*2···O2^{i}	0.90 (1)	2.18 (1)	2.8745 (14)	133 (1)

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

Table 2
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
H*O*1···H7*C*	2.49	$1-x, -\frac{1}{2}+y, \frac{3}{2}-z$
O2···H*N*2	2.18	$x, \frac{3}{2}-y, \frac{1}{2}+z$
H13···H7*C*	2.47	$1-x, 2-y, 1-z$
H11*B*···C2	2.95	$1-x, 1-y, 1-z$
C6···H19*A*	2.90	$1+x, \frac{3}{2}-y, \frac{1}{2}+z$
H6···C13	2.98	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
H7*A*···H20*D*	2.26	$1+x, y, 1+z$
H11*A*···H20*F*	2.05	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$
H20*C*···H14	2.58	$-x, 2-y, -z$
H21*D*···H21*A*	2.02	$-x, 1-y, -z$

defined by C8, C9, N1 and N2. This is likely due to the intramolecular O1—H1···N1 hydrogen bond (Table 1 and Fig. 1). The dihedral angle between the latter chain and the mean plane of the C12–C17 ring is 59.34 (6)°. There is one stereogenic center in the racemic title compound and the chirality of the C10 atom is *S* in the chosen asymmetric unit. All bond distances and angles appear as expected.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, N2—H2···O2 and weaker N2—H2···O1 hydrogen bonds (Table 1) form chains of molecules extending along the *c*-axis direction (Fig. 2). The molecular packing is provided by normal van der Waals interactions between chains.

Hirshfeld surfaces and their related two-dimensional fingerprint plots were generated using *CrystalExplorer17.5* (Turner *et al.*, 2017) to visually represent the intermolecular interactions in the crystal structure of the title compound. The Hirshfeld surface plotted over d_{norm} in the range −0.3801 to +1.4738 a.u. is shown in Fig. 3. The interactions shown in Tables 1 and 2 are important in the molecular packing of the title compound.

The overall two-dimensional fingerprint plot is illustrated in Fig. 4*a*, and those delineated into the major contacts: H···H (62.6%; Fig. 4*b*), C···H/H···C (15.8%; Fig. 4*c*), O···H/H···O and (15.3%; Fig. 4*d*). The other contacts are negligible with individual contributions of less than 2.2% [N···H/H···N (2.2%), N···C/C···N (2.1%), C···C (1.3%) and N···C/C···N (0.7%)].

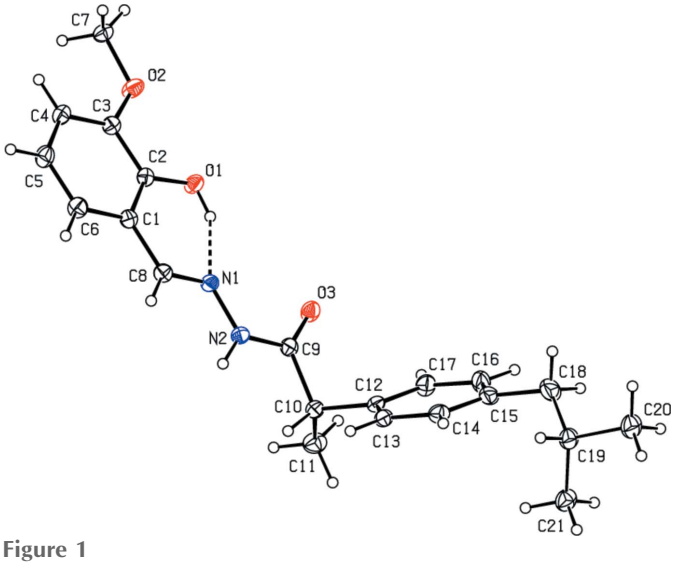


Figure 1
The title molecule with labeling scheme and 30% probability level ellipsoids. The intramolecular O—H···N hydrogen bond is depicted by a dashed line. Only the major component of the disorder is shown.

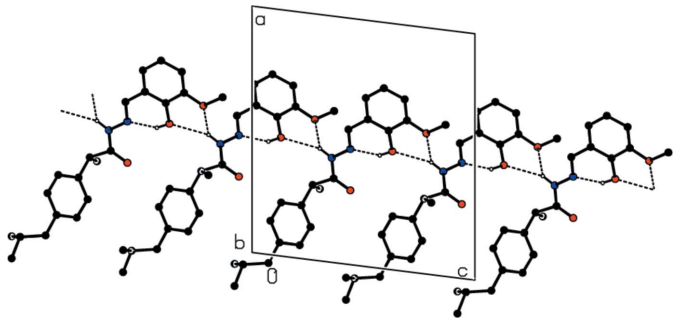


Figure 2
A portion of one chain viewed along the *b*-axis with the O—H···N and N—H···O hydrogen bonds depicted by dashed lines and non-interacting hydrogen atoms omitted for clarity.

4. Database survey

Six related compounds were found in a search of the Cambridge Structural Database (CSD, version 5.42, update of

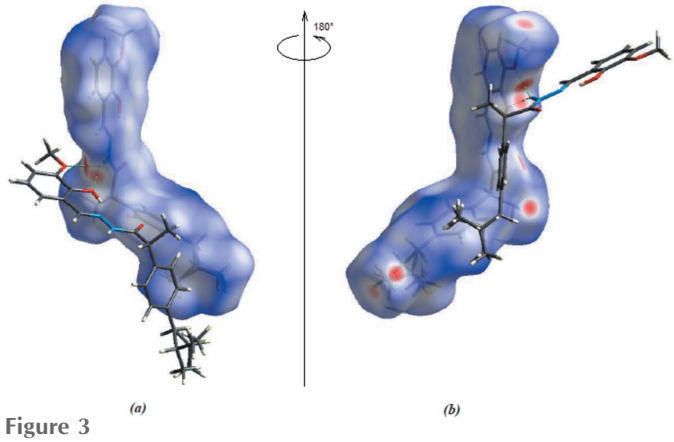


Figure 3
(*a*) Front view and (*b*) back view of the three-dimensional Hirshfeld surface of the title compound plotted over d_{norm} in the range −0.3801 to +1.4738 a.u. The red, white and blue regions visible on the d_{norm} surfaces indicate contacts with distances shorter, longer and equal to the van der Waals separations, respectively. The red spots highlight the interatomic contacts, including the O—H···N and N—H···O hydrogen bonds.

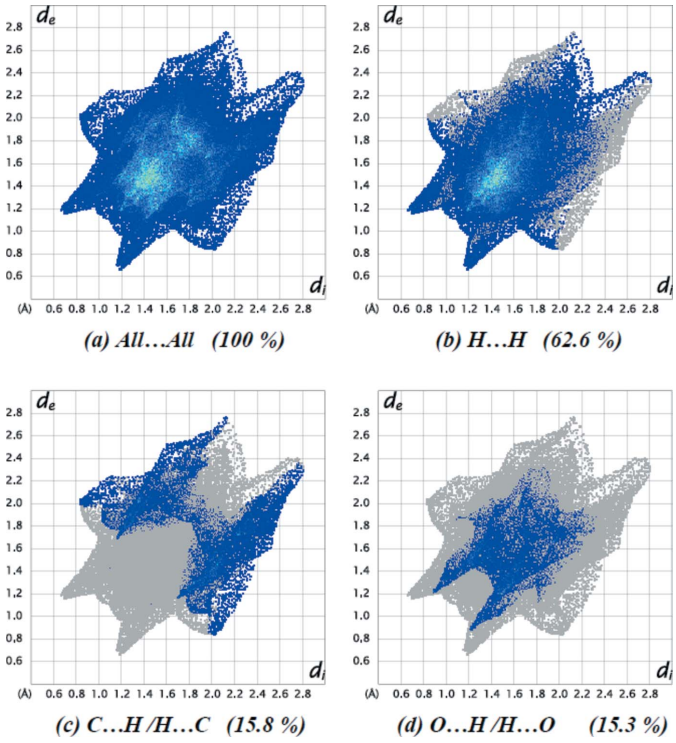


Figure 4
Two-dimensional fingerprint plots for the title compound, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) C···H/H···C and (*d*) O···H/H···O interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

September 2021; Groom *et al.*, 2016), *viz.* *N*′-benzylidene-2-({5-[(4-chlorophenoxy)methyl]-4-phenyl-4*H*-1,2,4-triazol-3-yl}sulfanyl)acetohydrazide hemihydrate [CSD refcode ULARIK (**I**); Mague *et al.*, 2016], *N*′-[(3-cyanophenyl)methylidene]-*N*-methyl-2-(thiophen-2-yl)acetohydrazide [ECOWEB (**II**); Cardoso *et al.*, 2017], *N*′-[(4-methoxyphenyl)methylidene]-*N*-methyl-2-(thiophen-2-yl)acetohydrazide [ECOWIF (**III**); Cardoso *et al.*, 2017], *N*′-[(1*Z*)-1-(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)ethyl]-2-[(4-methylphenyl)sulfanyl]acetohydrazide [GEMQIB (**IV**); Mohamed *et al.*, 2017], (*E*)-*N*′-(4-fluorobenzylidene)-2-(3-methylphenyl)-acetohydrazide [MEWMUY (**V**); Praveen *et al.*, 2013] and *N*′-[4-(dimethylamino)benzylidene]-2-(4-methylphenoxy)acetohydrazide [ZIYSOR (**VI**); Usha *et al.*, 2014].

In (**I**), three independent molecules in the asymmetric unit and two water molecules of crystallization are observed. The three unique organic molecules differ in the conformations of the substituents on the pyrazole ring. In the crystal, extensive O—H···O, O—H···N, N—H···O and C—H···O hydrogen bonding generates a three-dimensional network and C—H···π interactions are also observed. Compounds (**II**) and (**III**) crystallize with two molecules in the asymmetric unit, with generally similar conformations that approximate to L-shapes. The packing for (**II**) features short C—H···O interactions arising from the C—H adjacent to the cyanide group and C—H···N_c (c = cyanide) links arising from the methine groups to generate [110] double chains. Weak C—H···π interactions interlink the chains into a three-dimensional network. The packing for (**III**) features numerous C—H···O and C—H···π interactions arising from different donor groups to generate a three-dimensional network. In (**IV**), the molecular conformation is influenced by intramolecular N—H···O and C—H···O hydrogen bonds. In the crystal, N—H···O hydrogen bonds plus C—H···π and π–π stacking interactions lead to the formation of chains extending in the *a*-axis direction. The chains are linked by complementary pairs of C—H···π interactions. Compound (**V**) has four independent molecules in the asymmetric unit. In the crystal, N—H—O hydrogen bonds involving the hydrazide and acetyl groups, which form $R_2^2(18)$ ring motifs, link the molecules into dimers, which form columns along the [010] plane. In the crystal of (**VI**), the molecules are linked by C—H···O and N—H···O hydrogen bonds, as well as weak C—H···π contacts, forming a three-dimensional supramolecular architecture.

5. Synthesis and crystallization

The title compound was synthesized by mixing 1.101g (5 mmol) of ibuprofen hydrazide in 15 mL of chloroform with 0.76 g (5 mmol) of 2-hydroxy-3-methoxybenzaldehyde in 15 mL of methanol. A few drops of acetic acid were added to the reaction mixture as catalyst and the mixture was refluxed at 333 K for 1 h. The reaction progress was monitored by TLC until completion. The crude product as a pale-yellow precipitate was filtered off, washed, recrystallized from ethanol and dried under vacuum over anhydrous $CaCl_2$ under vacuum. M.p. 444.15 K; 87% yield.

The product was characterized by different spectroscopic analyses. Empirical formula, $C_{21}H_{26}N_2O_3$ (354.33 g mol^{-1}); IR (cm^{-1}); 3280 (NH), 1704 (C=O), 1612 (C=N), and 1248 (C—O). ^{1}H NMR (400 MHz, $CDCl_3$) ppm δ = 0.83–0.86 (*d*, *J* = 6.6 Hz, 6H), 1.37–1.43 (*d*, *J* = 7.0 Hz, 3H), 1.45–1.84 (*m*, 1H), 2.37–2.52 (*d*, *J* = 7.1 Hz, 2H), 3.65–3.70 (*q*, *J* = 7.0 Hz, 3H), 3.80–3.82 (*s*, 3H), 6.81–7.30 (*m*, 7H), 8.41 (*s*, 1H), 10.82 (*s*, 1H), 11.73 (*s*, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 18.88, 19.10, 22.64, 30.10, 39.55, 39.97, 40.38, 44.70, 56.28, 113.19, 114.12, 118.34, 119.68, 121.12, 127.68, 129.46, 139.72, 140.14, 146.31, 148.34, 170.12.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms attached to carbon were placed in calculated positions (C—H = 0.95–1.00 Å) and were included as riding contributions with isotropic displacement parameters 1.2–1.5 times those of the attached atoms. Those attached to nitrogen and to oxygen were placed in locations derived from a difference map and refined freely with DFIX 0.91 0.01 and DFIX 0.84 0.01 instructions, respectively. The atoms of the propane group are disordered over two sets of sites with an occupancy ratio of 0.929 (3):0.071 (3).

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{26}N_2O_3$
M_r	354.44
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	125
a, b, c (Å)	14.5241 (7), 10.0718 (5), 13.2710 (7)
β (°)	97.042 (2)
V (Å^3)	1926.69 (17)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.66
Crystal size (mm)	0.20 × 0.20 × 0.03
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 3 CPAD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.90, 0.98
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38584, 3758, 3400
R_{int}	0.035
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.109, 1.06
No. of reflections	3758
No. of parameters	259
No. of restraints	8
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.21

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/1* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

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Author contributions to this paper are as follows: synthesis and organic chemistry parts preparation, MAH, MRA; EAAT; conceptualization and study guide, LHAR, SKM; financial support, EAA; crystal data production and validation, JTM; paper preparation and Hirshfeld study, MA, SKM.

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supporting information

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Crystal structure and Hirshfeld surface analysis of (±)-*N*′-(2-hydroxy-3-methoxybenzylidene)-2-(4-isobutylphenyl)propionohydrazide

Shaaban K. Mohamed, Joel T. Mague, Mehmet Akkurt, Laila H. Abdel-Rahman, Mohamed Abdel-Hameed, Mustafa R. Albayati and Elham A. Al-Taif

Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2018/1* (Sheldrick, 2015*b*); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

(±)-*N*′-(2-Hydroxy-3-methoxybenzylidene)-2-(4-isobutylphenyl)propionohydrazide

Crystal data

$C_{21}H_{26}N_2O_3$
M_r = 354.44
Monoclinic, $P2_1/c$
a = 14.5241 (7) Å
b = 10.0718 (5) Å
c = 13.2710 (7) Å
β = 97.042 (2)°
V = 1926.69 (17) Å^3
Z = 4
$F(000)$ = 760
D_x = 1.222 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9778 reflections
θ = 5.5–72.4°
μ = 0.66 mm^{-1}
T = 125 K
Plate, colourless
0.20 × 0.20 × 0.03 mm

Data collection

Bruker D8 VENTURE PHOTON 3 CPAD diffractometer
Radiation source: INCOATEC IμS micro—-focus source
Mirror monochromator
Detector resolution: 7.3910 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.90, T_{max} = 0.98
38584 measured reflections
3758 independent reflections
3400 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 72.4°, θ_{min} = 5.5°
h = −17→17
k = −12→12
l = −14→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.109
S = 1.06
3758 reflections
259 parameters
8 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.694P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Special details

Experimental. The diffraction data were obtained from 15 sets of frames, each of width 0.5° in ω or φ, collected with scan parameters determined by the "strategy" routine in *APEX4*. The scan time was 10 sec/frame.

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}	Occ. (<1)
O1	0.48117 (6)	0.83125 (10)	0.62950 (7)	0.0328 (2)	
HO1	0.4586 (13)	0.7973 (19)	0.5735 (10)	0.061 (6)*	
O2	0.57158 (7)	0.95029 (10)	0.78175 (7)	0.0378 (2)	
O3	0.30167 (6)	0.64479 (10)	0.44100 (7)	0.0353 (2)	
N1	0.46923 (7)	0.75956 (10)	0.44081 (8)	0.0276 (2)	
N2	0.42448 (7)	0.69530 (11)	0.35782 (8)	0.0291 (2)	
HN2	0.4561 (10)	0.6800 (17)	0.3046 (10)	0.041 (4)*	
C1	0.59869 (9)	0.88043 (12)	0.51948 (9)	0.0272 (3)	
C2	0.56349 (8)	0.88651 (12)	0.61296 (9)	0.0259 (3)	
C3	0.61408 (9)	0.95151 (12)	0.69520 (9)	0.0276 (3)	
C4	0.69830 (9)	1.01023 (13)	0.68500 (10)	0.0310 (3)	
H4	0.732144	1.054394	0.741015	0.037*	
C5	0.73341 (9)	1.00426 (15)	0.59170 (11)	0.0364 (3)	
H5	0.791294	1.044688	0.584278	0.044*	
C6	0.68465 (9)	0.94019 (14)	0.51054 (10)	0.0341 (3)	
H6	0.709452	0.936307	0.447606	0.041*	
C7	0.61541 (9)	1.02016 (14)	0.86811 (10)	0.0343 (3)	
H7A	0.675774	0.979590	0.890582	0.051*	
H7B	0.576255	1.015696	0.923125	0.051*	
H7C	0.624321	1.113185	0.849937	0.051*	
C8	0.54787 (9)	0.81416 (13)	0.43243 (9)	0.0289 (3)	
H8	0.572764	0.811269	0.369529	0.035*	
C9	0.34188 (9)	0.63537 (13)	0.36611 (9)	0.0277 (3)	
C10	0.30483 (9)	0.55529 (13)	0.27208 (9)	0.0293 (3)	
H10	0.352167	0.557419	0.223374	0.035*	
C11	0.29224 (12)	0.41096 (14)	0.30427 (12)	0.0427 (4)	
H11A	0.250084	0.407883	0.356498	0.064*	
H11B	0.352538	0.373853	0.331631	0.064*	
H11C	0.266064	0.358829	0.245264	0.064*	
C12	0.21646 (8)	0.61920 (12)	0.22138 (9)	0.0268 (3)	
C13	0.21756 (9)	0.68811 (13)	0.13073 (9)	0.0287 (3)	
H13	0.273825	0.694597	0.101326	0.034*	
C14	0.13798 (10)	0.74751 (13)	0.08254 (10)	0.0340 (3)	
H14	0.140562	0.794801	0.021011	0.041*	
C15	0.05427 (10)	0.73865 (15)	0.12330 (10)	0.0377 (3)	
C16	0.05360 (10)	0.66893 (17)	0.21379 (11)	0.0419 (4)	
H16	−0.002864	0.660731	0.242608	0.050*	

C17	0.13317 (10)	0.61141 (16)	0.26259 (10)	0.0364 (3)	
H17	0.130938	0.566028	0.324999	0.044*	
C18	−0.03439 (12)	0.80231 (19)	0.07374 (12)	0.0507 (4)	
H18A	−0.087137	0.761937	0.103331	0.061*	
H18B	−0.032812	0.897690	0.091900	0.061*	
C19	−0.05346 (11)	0.79118 (15)	−0.04059 (12)	0.0363 (4)	0.929 (3)
H19	−0.002595	0.838797	−0.070091	0.044*	0.929 (3)
C20	−0.14474 (15)	0.8607 (2)	−0.07853 (17)	0.0478 (5)	0.929 (3)
H20A	−0.196295	0.813447	−0.053316	0.072*	0.929 (3)
H20B	−0.153574	0.860749	−0.152939	0.072*	0.929 (3)
H20C	−0.142860	0.952371	−0.053670	0.072*	0.929 (3)
C21	−0.05494 (17)	0.6501 (2)	−0.07825 (16)	0.0410 (5)	0.929 (3)
H21A	0.004431	0.607334	−0.054798	0.062*	0.929 (3)
H21B	−0.064915	0.649641	−0.152632	0.062*	0.929 (3)
H21C	−0.105315	0.601541	−0.051829	0.062*	0.929 (3)
C19A	−0.1011 (12)	0.7500 (17)	−0.0070 (13)	0.0363 (4)	0.071 (3)
H19A	−0.140915	0.702544	0.037706	0.044*	0.071 (3)
C20A	−0.172 (2)	0.852 (3)	−0.047 (3)	0.0478 (5)	0.071 (3)
H20D	−0.224290	0.807511	−0.087183	0.072*	0.071 (3)
H20E	−0.143533	0.914905	−0.090648	0.072*	0.071 (3)
H20F	−0.193809	0.899507	0.009485	0.072*	0.071 (3)
C21A	−0.064 (3)	0.629 (3)	−0.054 (3)	0.0410 (5)	0.071 (3)
H21D	−0.072593	0.551247	−0.010781	0.062*	0.071 (3)
H21E	0.001967	0.640502	−0.059041	0.062*	0.071 (3)
H21F	−0.097861	0.614437	−0.121356	0.062*	0.071 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0293 (5)	0.0422 (5)	0.0276 (5)	−0.0105 (4)	0.0059 (4)	−0.0063 (4)
O2	0.0384 (5)	0.0494 (6)	0.0260 (5)	−0.0148 (4)	0.0054 (4)	−0.0083 (4)
O3	0.0315 (5)	0.0495 (6)	0.0245 (5)	−0.0024 (4)	0.0017 (4)	−0.0011 (4)
N1	0.0287 (5)	0.0295 (5)	0.0238 (5)	0.0024 (4)	−0.0005 (4)	−0.0023 (4)
N2	0.0290 (5)	0.0352 (6)	0.0225 (5)	0.0011 (4)	0.0012 (4)	−0.0047 (4)
C1	0.0279 (6)	0.0265 (6)	0.0270 (6)	0.0017 (5)	0.0025 (5)	0.0029 (5)
C2	0.0246 (6)	0.0252 (6)	0.0278 (6)	−0.0002 (5)	0.0025 (5)	0.0027 (5)
C3	0.0291 (6)	0.0278 (6)	0.0257 (6)	0.0003 (5)	0.0024 (5)	0.0020 (5)
C4	0.0291 (6)	0.0307 (6)	0.0315 (6)	−0.0022 (5)	−0.0028 (5)	0.0013 (5)
C5	0.0287 (6)	0.0412 (7)	0.0395 (7)	−0.0078 (6)	0.0052 (5)	0.0017 (6)
C6	0.0330 (7)	0.0397 (7)	0.0306 (7)	−0.0043 (6)	0.0080 (5)	0.0022 (5)
C7	0.0349 (7)	0.0394 (7)	0.0275 (6)	−0.0025 (6)	−0.0008 (5)	−0.0065 (5)
C8	0.0308 (6)	0.0306 (6)	0.0255 (6)	0.0013 (5)	0.0039 (5)	0.0016 (5)
C9	0.0286 (6)	0.0309 (6)	0.0226 (6)	0.0050 (5)	−0.0005 (5)	0.0015 (5)
C10	0.0290 (6)	0.0327 (7)	0.0255 (6)	0.0021 (5)	0.0000 (5)	−0.0024 (5)
C11	0.0522 (9)	0.0326 (7)	0.0414 (8)	0.0032 (6)	−0.0021 (7)	−0.0002 (6)
C12	0.0277 (6)	0.0281 (6)	0.0235 (6)	−0.0009 (5)	−0.0009 (5)	−0.0044 (5)
C13	0.0287 (6)	0.0303 (6)	0.0270 (6)	−0.0027 (5)	0.0029 (5)	−0.0034 (5)
C14	0.0414 (7)	0.0330 (7)	0.0265 (6)	0.0032 (6)	−0.0002 (5)	0.0003 (5)

C15	0.0359 (7)	0.0467 (8)	0.0289 (7)	0.0122 (6)	−0.0025 (5)	−0.0095 (6)
C16	0.0296 (7)	0.0668 (10)	0.0297 (7)	0.0047 (6)	0.0059 (5)	−0.0063 (6)
C17	0.0333 (7)	0.0531 (8)	0.0230 (6)	−0.0013 (6)	0.0036 (5)	0.0009 (6)
C18	0.0439 (9)	0.0652 (11)	0.0409 (8)	0.0229 (8)	−0.0032 (7)	−0.0096 (7)
C19	0.0341 (8)	0.0353 (8)	0.0376 (8)	0.0053 (6)	−0.0039 (6)	0.0017 (6)
C20	0.0424 (11)	0.0441 (9)	0.0527 (12)	0.0110 (8)	−0.0112 (8)	0.0018 (9)
C21	0.0414 (10)	0.0356 (10)	0.0431 (13)	0.0014 (8)	−0.0066 (9)	0.0022 (8)
C19A	0.0341 (8)	0.0353 (8)	0.0376 (8)	0.0053 (6)	−0.0039 (6)	0.0017 (6)
C20A	0.0424 (11)	0.0441 (9)	0.0527 (12)	0.0110 (8)	−0.0112 (8)	0.0018 (9)
C21A	0.0414 (10)	0.0356 (10)	0.0431 (13)	0.0014 (8)	−0.0066 (9)	0.0022 (8)

Geometric parameters (Å, º)

O1—C2	1.3609 (15)	C13—C14	1.3863 (19)
O1—HO1	0.847 (9)	C13—H13	0.9500
O2—C3	1.3690 (15)	C14—C15	1.393 (2)
O2—C7	1.4265 (15)	C14—H14	0.9500
O3—C9	1.2167 (16)	C15—C16	1.392 (2)
N1—C8	1.2847 (17)	C15—C18	1.5146 (19)
N1—N2	1.3706 (14)	C16—C17	1.381 (2)
N2—C9	1.3594 (17)	C16—H16	0.9500
N2—HN2	0.902 (9)	C17—H17	0.9500
C1—C2	1.3999 (17)	C18—C19A	1.453 (8)
C1—C6	1.4042 (18)	C18—C19	1.513 (2)
C1—C8	1.4545 (17)	C18—H18A	0.9900
C2—C3	1.4011 (17)	C18—H18B	0.9900
C3—C4	1.3802 (18)	C19—C21	1.505 (3)
C4—C5	1.397 (2)	C19—C20	1.529 (2)
C4—H4	0.9500	C19—H19	1.0000
C5—C6	1.3751 (19)	C20—H20A	0.9800
C5—H5	0.9500	C20—H20B	0.9800
C6—H6	0.9500	C20—H20C	0.9800
C7—H7A	0.9800	C21—H21A	0.9800
C7—H7B	0.9800	C21—H21B	0.9800
C7—H7C	0.9800	C21—H21C	0.9800
C8—H8	0.9500	C19A—C21A	1.50 (3)
C9—C10	1.5272 (17)	C19A—C20A	1.50 (3)
C10—C12	1.5174 (17)	C19A—H19A	1.0000
C10—C11	1.5324 (19)	C20A—H20D	0.9800
C10—H10	1.0000	C20A—H20E	0.9800
C11—H11A	0.9800	C20A—H20F	0.9800
C11—H11B	0.9800	C21A—H21D	0.9800
C11—H11C	0.9800	C21A—H21E	0.9800
C12—C17	1.3896 (18)	C21A—H21F	0.9800
C12—C13	1.3907 (18)		
C2—O1—HO1	106.1 (14)	C13—C14—H14	119.6
C3—O2—C7	117.83 (10)	C15—C14—H14	119.6

C8—N1—N2	118.14 (11)	C16—C15—C14	117.78 (12)
C9—N2—N1	118.74 (10)	C16—C15—C18	119.51 (14)
C9—N2—HN2	121.8 (11)	C14—C15—C18	122.71 (14)
N1—N2—HN2	118.3 (11)	C17—C16—C15	121.48 (13)
C2—C1—C6	118.76 (12)	C17—C16—H16	119.3
C2—C1—C8	121.27 (11)	C15—C16—H16	119.3
C6—C1—C8	119.97 (11)	C16—C17—C12	120.70 (13)
O1—C2—C1	123.27 (11)	C16—C17—H17	119.6
O1—C2—C3	116.91 (11)	C12—C17—H17	119.6
C1—C2—C3	119.82 (11)	C19A—C18—C15	128.4 (7)
O2—C3—C4	125.61 (11)	C19—C18—C15	116.46 (13)
O2—C3—C2	113.71 (11)	C19—C18—H18A	108.2
C4—C3—C2	120.68 (12)	C15—C18—H18A	108.2
C3—C4—C5	119.52 (12)	C19—C18—H18B	108.2
C3—C4—H4	120.2	C15—C18—H18B	108.2
C5—C4—H4	120.2	H18A—C18—H18B	107.3
C6—C5—C4	120.36 (12)	C21—C19—C18	113.35 (14)
C6—C5—H5	119.8	C21—C19—C20	110.26 (15)
C4—C5—H5	119.8	C18—C19—C20	109.95 (14)
C5—C6—C1	120.86 (12)	C21—C19—H19	107.7
C5—C6—H6	119.6	C18—C19—H19	107.7
C1—C6—H6	119.6	C20—C19—H19	107.7
O2—C7—H7A	109.5	C19—C20—H20A	109.5
O2—C7—H7B	109.5	C19—C20—H20B	109.5
H7A—C7—H7B	109.5	H20A—C20—H20B	109.5
O2—C7—H7C	109.5	C19—C20—H20C	109.5
H7A—C7—H7C	109.5	H20A—C20—H20C	109.5
H7B—C7—H7C	109.5	H20B—C20—H20C	109.5
N1—C8—C1	119.85 (11)	C19—C21—H21A	109.5
N1—C8—H8	120.1	C19—C21—H21B	109.5
C1—C8—H8	120.1	H21A—C21—H21B	109.5
O3—C9—N2	123.24 (12)	C19—C21—H21C	109.5
O3—C9—C10	123.52 (12)	H21A—C21—H21C	109.5
N2—C9—C10	113.23 (11)	H21B—C21—H21C	109.5
C12—C10—C9	109.42 (10)	C18—C19A—C21A	111.2 (18)
C12—C10—C11	113.75 (11)	C18—C19A—C20A	112.3 (16)
C9—C10—C11	108.38 (11)	C21A—C19A—C20A	132 (2)
C12—C10—H10	108.4	C18—C19A—H19A	96.7
C9—C10—H10	108.4	C21A—C19A—H19A	96.7
C11—C10—H10	108.4	C20A—C19A—H19A	96.7
C10—C11—H11A	109.5	C19A—C20A—H20D	109.5
C10—C11—H11B	109.5	C19A—C20A—H20E	109.5
H11A—C11—H11B	109.5	H20D—C20A—H20E	109.5
C10—C11—H11C	109.5	C19A—C20A—H20F	109.5
H11A—C11—H11C	109.5	H20D—C20A—H20F	109.5
H11B—C11—H11C	109.5	H20E—C20A—H20F	109.5
C17—C12—C13	118.13 (12)	C19A—C21A—H21D	109.5
C17—C12—C10	122.10 (11)	C19A—C21A—H21E	109.5

C13—C12—C10	119.77 (11)	H21D—C21A—H21E	109.5
C14—C13—C12	121.14 (12)	C19A—C21A—H21F	109.5
C14—C13—H13	119.4	H21D—C21A—H21F	109.5
C12—C13—H13	119.4	H21E—C21A—H21F	109.5
C13—C14—C15	120.75 (13)		

C8—N1—N2—C9	179.02 (11)	O3—C9—C10—C11	−58.49 (16)
C6—C1—C2—O1	−179.68 (12)	N2—C9—C10—C11	121.52 (12)
C8—C1—C2—O1	0.51 (19)	C9—C10—C12—C17	−73.14 (15)
C6—C1—C2—C3	0.03 (18)	C11—C10—C12—C17	48.22 (17)
C8—C1—C2—C3	−179.78 (11)	C9—C10—C12—C13	106.89 (13)
C7—O2—C3—C4	2.85 (19)	C11—C10—C12—C13	−131.75 (13)
C7—O2—C3—C2	−176.72 (11)	C17—C12—C13—C14	−0.01 (19)
O1—C2—C3—O2	−0.43 (16)	C10—C12—C13—C14	179.96 (11)
C1—C2—C3—O2	179.84 (11)	C12—C13—C14—C15	−0.6 (2)
O1—C2—C3—C4	179.97 (11)	C13—C14—C15—C16	0.3 (2)
C1—C2—C3—C4	0.25 (18)	C13—C14—C15—C18	179.73 (13)
O2—C3—C4—C5	−179.74 (13)	C14—C15—C16—C17	0.7 (2)
C2—C3—C4—C5	−0.20 (19)	C18—C15—C16—C17	−178.79 (14)
C3—C4—C5—C6	−0.1 (2)	C15—C16—C17—C12	−1.3 (2)
C4—C5—C6—C1	0.4 (2)	C13—C12—C17—C16	1.0 (2)
C2—C1—C6—C5	−0.4 (2)	C10—C12—C17—C16	−179.00 (13)
C8—C1—C6—C5	179.46 (13)	C16—C15—C18—C19A	−96.1 (12)
N2—N1—C8—C1	−178.45 (11)	C14—C15—C18—C19A	84.4 (13)
C2—C1—C8—N1	−0.19 (18)	C16—C15—C18—C19	−139.06 (16)
C6—C1—C8—N1	180.00 (12)	C14—C15—C18—C19	41.5 (2)
N1—N2—C9—O3	6.17 (18)	C15—C18—C19—C21	56.4 (2)
N1—N2—C9—C10	−173.84 (10)	C15—C18—C19—C20	−179.71 (16)
O3—C9—C10—C12	66.06 (16)	C15—C18—C19A—C21A	−11 (3)
N2—C9—C10—C12	−113.93 (12)	C15—C18—C19A—C20A	−170.6 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H*O*1···N1	0.85 (1)	1.83 (1)	2.5914 (13)	149 (2)
N2—H*N*2···O1^{i}	0.90 (1)	2.40 (1)	3.2470 (14)	157 (1)
N2—H*N*2···O2^{i}	0.90 (1)	2.18 (1)	2.8745 (14)	133 (1)
C10—H10···O1^{i}	1.00	2.63	3.5545 (16)	155

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