Crystal structure, DFT and Hirshfeld surface analysis of (E)-N'-[(1-chloro-3,4-dihydronaphthalen-2-yl)methylidene]benzohydrazide monohydrate

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In the title compound, $C_{18}H_{15}ClN_2O \cdot H_2O$, a benzohydrazide derivative, the dihedral angle between the mean plane of the dihydronaphthalene ring system and the phenyl ring is 17.1 (2)°. In the crystal, O—H⋯O, N—H⋯O and C—H⋯O hydrogen bonds link the benzohydrazide and water molecules, forming a layer parallel to the bc plane. Hirshfeld surface analysis and two-dimensional fingerprint plots indicate that the most important contributions to the crystal packing are from H⋯H (45.7%) and H⋯C/C⋯H (20.2%) contacts.

1. Chemical context

Benzohydrazides are versatile compounds in medicinal chemistry that are used for the development of new drugs (Veeramanikandan *et al.*, 2015). Benzohydrazide derivatives are potent inhibitors of prostate cancer (Arjun *et al.*, 2019) and show anti-inflammatory (Todeschini *et al.*, 1998), anti-malarial (Melnyk *et al.*, 2006), entamoeba histolyica (Inam *et al.*, 2016) and anti-tuberculosis (Bedia *et al.*, 2006) activities. Herein we describe the molecular and crystal structures of the title compound, which can act as a potential multidrug ligand for various biological activities. The molecular packing was further studied with Hirshfeld surface analysis and PIXEL methods (Sowmya *et al.*, 2018).
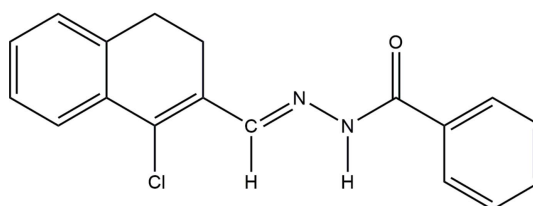
2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The benzohydrazide molecule adopts an *E* configuration with respect to the C8=N2 bond. The cyclohexene ring (C9–C12/C17/C18) adopts nearly a half-chair conformation, as indicated by the total puckering amplitude Q_T of 0.431 (3) Å and spherical polar angle θ = 115.6 (3)° with φ = 264.4 (4)°; atom C10 shows a maximum deviation of 0.282 (4) Å from the mean plane. The phenyl ring (C1–C6) and the mean plane of the dihydronaphthalene ring system (C9–C18) are inclined to
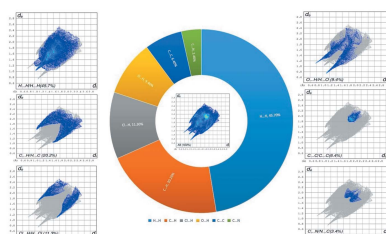
Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2A$\cdots$O1^{i}	0.78 (5)	2.06 (5)	2.829 (4)	166 (5)
O2—H2B$\cdots$O1	0.96 (6)	1.90 (6)	2.858 (4)	171 (5)
N6—H6$\cdots$O2^{ii}	0.93 (5)	1.98 (5)	2.869 (4)	159 (4)
C1—H1$\cdots$O2^{ii}	0.93	2.47	3.350 (5)	158
C8—H8$\cdots$O2^{ii}	0.93	2.48	3.261 (5)	142

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

each other by 17.1 (2)°. The central hydrazine fragment (C8/ N2/N6/C7/O1) is almost planar, making dihedral angles of 11.0 (2) and 8.49 (18)°, respectively, with the phenyl ring and the mean plane of the dihydronaphthalene ring system.

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, the water molecule forms five hydrogen bonds with three benzohydrazide molecules. The benzohydrazide molecules are stacked in a column along the b-axis direction through O—H$\cdots$O hydrogen bonds (O2—H2A$\cdots$O1^{i} and O2—H2B$\cdots$O1; symmetry code as in Table 1) between the H atoms of the water molecule and the carbonyl O atoms of two
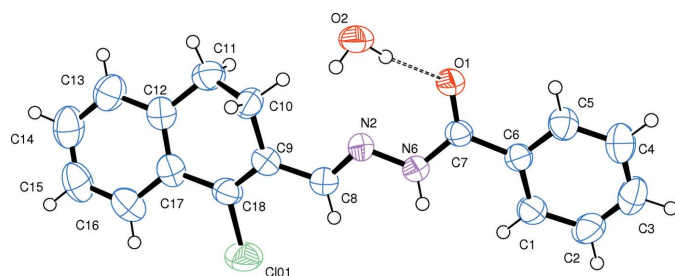

Figure 1
The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The O—H$\cdots$O hydrogen bond is indicated by a dashed line.
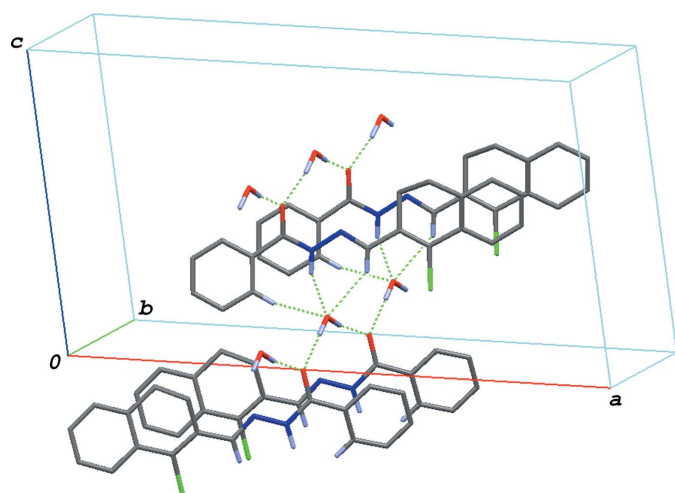

Figure 2
A packing diagram of the title compound, showing the O—H$\cdots$O, N—H$\cdots$O and C—H$\cdots$O hydrogen bonds (dashed lines). H atoms not involved in these interactions have been omitted.
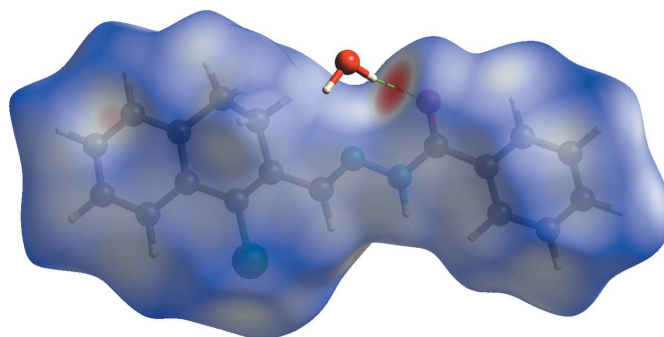

Figure 3
Hirshfeld surface mapped over d_{norm} (range -0.575 to 1.326 a.u.) for the title compound showing the O—H$\cdots$O hydrogen bond.

adjacent benzohydrazide molecules (Fig. 2). The water molecule also acts as a hydrogen-bond acceptor from other benzohydrazide molecules: N—H$\cdots$O and C—H$\cdots$O hydrogen bonds (N6—H6$\cdots$O2^{ii}, C1—H1$\cdots$O2^{ii} and C8—H8$\cdots$O2^{ii}; Table 1) link the molecules, forming a layer parallel to the bc plane.

Hirshfeld surface analysis was performed using *CrystalExplorer17.5* (Spackman & Jayatilaka, 2009) to quantify and visualize the various intermolecular contacts in the crystal. The Hirshfeld surface for the title compound mapped over d_{norm} is shown in Fig. 3, where the dark-red spot represents a close contact of the water molecule, corresponding to the O—H$\cdots$O interactions. Two-dimensional fingerprint plots are shown in Fig. 4. The most important contributions to the crystal packing are from H$\cdots$H/H$\cdots$H (45.7%), C$\cdots$H/H$\cdots$C (20.2%), O$\cdots$H/H$\cdots$O (9.4%), Cl$\cdots$H/H$\cdots$Cl (11.3%), C$\cdots$C(6.4%) and C$\cdots$N/N$\cdots$C(3.4%) interactions.

4. Interaction energies and theoretical calculations

The various intermolecular interaction energies of the title crystal were calculated using the PIXEL-CLP module (Gavezzotti, 2003). The lattice energy of the crystal structure
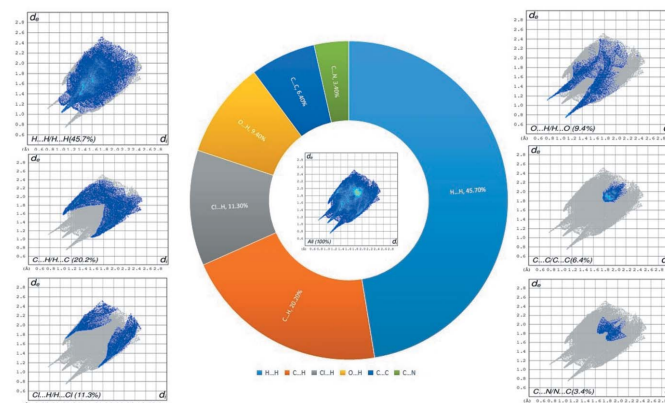

Figure 4
Two-dimensional fingerprint plots for the title compound with the percentage contribution of the intermolecular contacts. The d_i and d_e values are the closest internal and external distances (Å) from given points on the Hirshfeld surface.

Table 2
List of intermolecular interaction energies (kJ mol^{-1}) in the crystal of the title compound.

Code	Symmetry	Centroid distance	E_{col}	E_{pol}	$E_{energy-dispersive}$	E_{rep}	E_{total}	Interaction
A	$x, y + 1, z$	4.812	−37.4	−14.2	−64.3	88.7	−27.1	O—H···O
B	$-x + 1, -y + 1, z - \frac{1}{2}$	7.513	−6.7	−4.3	−20.9	15.9	−16.0	C—H···O
C	$-x + 1, -y + \frac{1}{2}, z$	9.210	−2.2	−4.2	−16.1	6.6	−15.9	Cl···H
D	$-x + \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$	11.475	−1.9	−0.9	−8.9	3.8	−7.9	H···H
E	x, y, z	5.924	−33.1	−11.6	−12.3	33.1	−23.9	O—H···O
F	$x, y - 1, z$	4.077	−38.5	−12.0	−13.0	30.7	−32.8	N—H···O

Table 3
HUMO–LUMO energies and quantum-chemical parameters (eV) for the title compound.

HOMO energy: E_H	−5.7777
LUMO energy: E_L	−2.1428
Energy gap: $E_g = E_H - E_L$	3.6349
Chemical hardness: $\eta = |E_H - E_L|/2$	1.8174
Softness: $\zeta = 1/2\eta$	0.2751
Electrophilicity index: $\omega = \mu^2/2\eta$	4.3148
Chemical Potential: $\mu = -(E_H + E_L/2)$	−3.9602
Electronegativity: $\chi = -\mu$	3.9602

HOMO and LUMO energies. The electrophilicity index (ω) of 4.3148 eV, which measures the energy lowering due to the electron flow between the donor and acceptor, also supports the soft nature of the title compound. The lower chemical potential (μ) of −3.9602 eV signifies the lesser resistance towards the deformation or polarization of the electron cloud of the atoms or molecule under a small perturbation of chemical reaction.

is found to be −67.2 kJ mol^{-1} with the energy partitioned into Coulombic, polarization, dispersion and repulsion energy components of −68.4, −30.7, −95.3 and 128.1 kJ mol^{-1}, respectively. The important molecular pairs (motifs A–F) and their interaction energies are shown in Fig. 5, and the partitioned intermolecular energies along with the above interactions are given in Table 2. The N—H···O interaction energy in motif F (−32.8 kJ mol^{-1}) is strongest followed by the O—H···O interactions in motifs A and E (−27.1 and −23.9 kJ mol^{-1}, respectively), and the C—H···O interaction in motif B (−16 kJ mol^{-1}).

Density functional theory (DFT) calculations using the *B3LYP* (Becke, 1993) method at the 6-31++G(d,p) level were performed using *GAUSSIAN09* (Frisch *et al.*, 2009). The DFT-optimized structure of the title compound is found to be in good agreement with the experimental geometry. Frontier molecular orbitals are plotted to specify the distribution of electronic densities (Fig. 6); the HOMO–LUMO gap of 3.6349 eV indicates that the nature of molecule is soft. The quantum-chemical parameters, such as hardness (η), softness (ζ), chemical potential (μ), electrophilicity (ω) and electronegativity (χ), were also calculated (Table 3), using the

5. Database Survey

A search of the Cambridge Structural Database (Version 5.39; Groom *et al.*, 2016) gave 1579 hits for the benzohydrazides with different substituents and 260 hits for their hydrate compounds. The water molecules mediate strong hydrogen bonds in hydrate compounds such as (E)-3,4,5-trimethoxy-N-[(6-methoxy-4-oxo-4H-chromen-3-yl)methylidene]benzohydrazide monohydrate (Ishikawa & Watanabe, 2014a), (E)-4-methoxy-N-[(6-methyl-4-oxo-4H-chromen-3-yl)methylidene]benzohydrazide monohydrate (Ishikawa & Watanabe, 2014b), N-[(E)-(3-fluoropyridin-2-yl)methylidene]benzohydrazide monohydrate (Nair *et al.*, 2012), (E)-4-methoxy-N-(2,3,4-trimethoxybenzylidene)benzohydrazide monohydrate (Veeramanikandan *et al.*, 2016), 4-chloro-N-[(E)-2-

Figure 5
Important molecular pairs in the crystal of the title compound and their interaction energies.

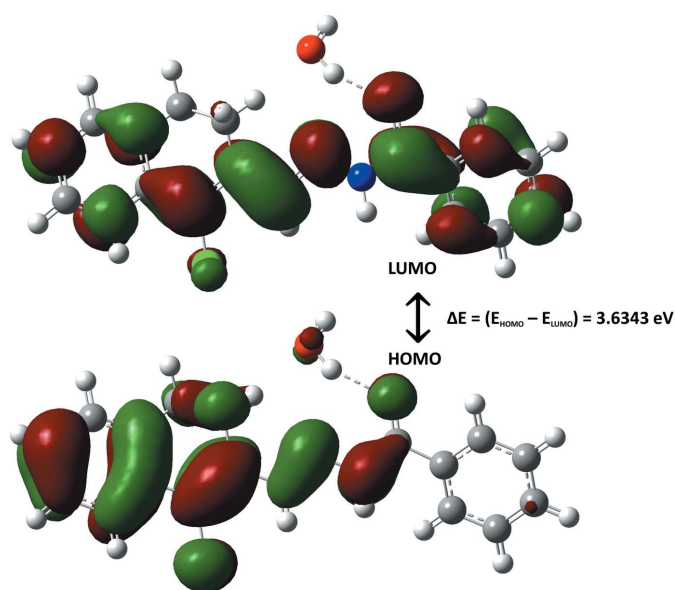$\Delta E = (E_{HOMO} - E_{LUMO}) = 3.6343$ eV

Figure 6
The frontier molecular orbitals, highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO), calculated for the title compound.

Table 4
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{15}ClN_2O \cdot H_2O$
M_r	328.78
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	301
a, b, c (Å)	26.2059 (18), 4.8119 (3), 12.8084 (9)
V (Å^3)	1615.14 (19)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.25
Crystal size (mm)	$0.28 \times 0.22 \times 0.21$
Data collection	
Diffractometer	Bruker APEXII microsource
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.890, 0.915
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	51179, 4917, 3162
R_{int}	0.069
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.151, 1.03
No. of reflections	4917
No. of parameters	220
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})	0.18, −0.30
Absolute structure	Flack x determined using 1242 quotients [$(I^+)−(I^-)]/[(I^+)+(I^-)$] (Parsons *et al.*, 2013)
Absolute structure parameter	−0.04 (2)

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SIR2011* (Burla *et al.*, 2012), *SHELXL2018* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

chlorobenzylidene]benzohydrazide monohydrate (Mague *et al.*, 2014), 4-chloro-*N*-[(*Z*)-4-(dimethylamino)benzylidene]-benzohydrazide monohydrate (Fun *et al.*, 2008), (*E*)-*N*-(4-butoxy-3-methoxybenzylidene)benzohydrazide (Zhen & Han, 2005) and (*E*)-4-hydroxy-*N*-(3-hydroxybenzylidene)benzo-hydrazide monohydrate (Harrison *et al.*, 2014). The presence of O—H···N hydrogen bonds in addition to water-mediated O—H···O interactions is a common feature in many of the reported structures, but such an O—H···N interaction is not observed in the title compound.

6. Synthesis and crystallization

Phosphoryl chloride (POCl$_3$) (0.171mol) was slowly added to dry dimethyl formamide at 273 K, and then 3,4-dihydro-naphthalen-1(2*H*)-one (0.174 mol) was added. The mixture was stirred at 353 K for 1.5 h. The reaction mixture was then poured into aqueous sodium acetate (3 mol l^{-1}) and the product was extracted with ethyl acetate. Evaporating the ethyl acetate gave an oil, which on cooling solidified to yield 1-chloro-3,4-dihydronaphthalene-2-carbaldehyde. The title compound was prepared by refluxing 1-chloro-3,4-dihydro-naphthalene-2-carbaldehyde (0.01 mol) with benzohydrazide (0.01 mol) in ethanol (5 ml) and few drops of acetic acid for 8 h. The reaction mixture was then cooled to room temperature, excess ethanol was removed under vacuum and the residue was quenched with ice. The precipitate was filtered, dried and crystallized from ethanol. The completion of the reaction was monitored by thin layer chromatography. Single crystals suitable for X-ray diffraction study were grown from an *N*,*N*-dimethylformamide solution by slow evaporation. Yield: 86%; m.p.: 438–440 K, colourless solid. ^{1}H NMR (DMSO-*d*$_6$, 400 MHz, ppm): δ 12.10 (*s*, 1H, NH), 8.77 (*s*, 1H), 7.87 (*d*, *J* = 7.2, 2H), 7.64–7.25 (*m*, 7H), 2.808–2.764 (*m*, 4H). ^{13}C NMR: δ 163.34, 143.77, 144.5, 136.97, 132.72, 132.63, 131.65, 130.73, 129.80, 129.49, 128.16, 128.00, 127.41, 124.94, 29.50, 26.54, 23.65, 21.51. Mass calculated for $C_{18}H_{15}ClN_2O$ [*M*+H]$^+$: 310.08; found: 310.9758.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The N-bound H atom (H6) and water H atoms (H2*A* and H2*B*) were located in a difference-Fourier map and refined isotropically. All C-bound H atoms were placed in idealized positions (C—H = 0.93 or 0.97 Å) and treated as riding with U_{iso}(H) = 1.2U_{eq}(C).

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supporting information

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Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SIR2011* (Burla *et al.*, 2012); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

(*E*)-*N*′-[(1-Chloro-3,4-dihydronaphthalen-2-yl)methylidene]\ benzohydrazide monohydrate

Crystal data

$C_{18}H_{15}ClN_2O \cdot H_2O$	$F(000) = 688$
$M_r = 328.78$	$D_x = 1.352$ Mg m^{-3}
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2c -2n	Cell parameters from 689 reflections
$a = 26.2059$ (18) Å	$\theta = 2.2$–30.1°
$b = 4.8119$ (3) Å	$\mu = 0.25$ mm^{-1}
$c = 12.8084$ (9) Å	$T = 301$ K
$V = 1615.14$ (19) Å^3	Block, white
$Z = 4$	$0.28 \times 0.22 \times 0.21$ mm

Data collection

Bruker APEXII microsource diffractometer	51179 measured reflections
Radiation source: microfocus sealed X-ray tube	4917 independent reflections
Mirror optics monochromator	3162 reflections with $I > 2\sigma(I)$
Detector resolution: 7.9 pixels mm^{-1}	$R_{int} = 0.069$
ω and φ scans	$\theta_{max} = 30.6°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (SADABS; Bruker, 2012)	$h = -37 \rightarrow 36$
	$k = -6 \rightarrow 6$
$T_{min} = 0.890$, $T_{max} = 0.915$	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.045$	
$wR(F^2) = 0.151$	
$S = 1.03$	Hydrogen site location: mixed
4917 reflections	H atoms treated by a mixture of independent and constrained refinement
220 parameters	
1 restraint	

$w = 1/[\sigma^2(F_o^2) + (0.0735P)^2 + 0.2866P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Absolute structure: Flack x determined using 1242 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.04 (2)

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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Cl01	0.64431 (5)	0.3485 (3)	0.24491 (8)	0.0815 (4)
O1	0.48097 (11)	−0.3470 (5)	0.58021 (18)	0.0577 (6)
O2	0.48890 (14)	0.1565 (7)	0.6974 (2)	0.0676 (8)
N6	0.50596 (11)	−0.2027 (6)	0.4205 (2)	0.0463 (6)
N2	0.54124 (11)	−0.0257 (5)	0.4646 (2)	0.0469 (6)
C1	0.44073 (17)	−0.6214 (7)	0.3284 (3)	0.0589 (9)
H1	0.464242	−0.537211	0.284202	0.071*
C2	0.40586 (19)	−0.8116 (8)	0.2890 (3)	0.0699 (11)
H2	0.405810	−0.852699	0.218085	0.084*
C3	0.37164 (16)	−0.9389 (9)	0.3536 (4)	0.0677 (11)
H3	0.348710	−1.067883	0.326756	0.081*
C4	0.37102 (15)	−0.8766 (9)	0.4583 (4)	0.0661 (10)
H4	0.347389	−0.961795	0.501996	0.079*
C5	0.40541 (13)	−0.6878 (8)	0.4987 (3)	0.0543 (8)
H5	0.405023	−0.648210	0.569795	0.065*
C6	0.44038 (12)	−0.5569 (6)	0.4347 (2)	0.0440 (7)
C7	0.47695 (12)	−0.3606 (6)	0.4845 (2)	0.0429 (6)
C8	0.57029 (13)	0.1000 (8)	0.3996 (3)	0.0514 (8)
H8	0.566552	0.073299	0.328142	0.062*
C9	0.60942 (13)	0.2864 (7)	0.4405 (3)	0.0500 (7)
C10	0.61014 (14)	0.3515 (8)	0.5571 (3)	0.0546 (8)
H10A	0.593193	0.203807	0.595282	0.066*
H10B	0.591853	0.523334	0.570138	0.066*
C11	0.66436 (15)	0.3790 (9)	0.5944 (3)	0.0603 (9)
H11A	0.664204	0.450456	0.665242	0.072*
H11B	0.679939	0.196212	0.595934	0.072*
C12	0.69626 (13)	0.5672 (8)	0.5273 (3)	0.0548 (8)
C13	0.73640 (15)	0.7232 (10)	0.5674 (4)	0.0703 (11)
H13	0.743717	0.714146	0.638323	0.084*
C14	0.76533 (16)	0.8898 (10)	0.5042 (5)	0.0796 (14)
H14	0.791894	0.993296	0.532615	0.096*
C15	0.75553 (16)	0.9049 (10)	0.4007 (5)	0.0771 (13)
H15	0.775202	1.020496	0.358664	0.093*
C16	0.71653 (16)	0.7501 (10)	0.3565 (4)	0.0692 (11)

H16	0.710430	0.759136	0.285089	0.083*
C17	0.68627 (13)	0.5795 (8)	0.4204 (3)	0.0549 (8)
C18	0.64461 (13)	0.4061 (8)	0.3791 (3)	0.0536 (8)
H2A	0.4899 (19)	0.281 (11)	0.658 (4)	0.068 (14)*
H2B	0.4887 (19)	−0.005 (13)	0.653 (4)	0.082 (15)*
H6	0.4993 (18)	−0.204 (10)	0.349 (4)	0.071 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl01	0.0854 (7)	0.1131 (10)	0.0460 (5)	−0.0167 (6)	0.0052 (5)	0.0096 (6)
O1	0.0824 (17)	0.0516 (13)	0.0391 (11)	−0.0173 (12)	−0.0005 (11)	0.0002 (10)
O2	0.107 (2)	0.0580 (17)	0.0377 (12)	−0.0104 (15)	−0.0058 (13)	0.0033 (13)
N6	0.0548 (15)	0.0444 (14)	0.0396 (13)	−0.0079 (12)	−0.0029 (12)	0.0010 (11)
N2	0.0532 (15)	0.0418 (13)	0.0456 (13)	−0.0061 (11)	−0.0046 (11)	0.0014 (11)
C1	0.082 (2)	0.0491 (19)	0.0460 (18)	−0.0105 (17)	−0.0023 (17)	−0.0016 (15)
C2	0.099 (3)	0.056 (2)	0.054 (2)	−0.009 (2)	−0.017 (2)	−0.0074 (18)
C3	0.063 (2)	0.052 (2)	0.088 (3)	−0.0062 (18)	−0.016 (2)	−0.009 (2)
C4	0.051 (2)	0.063 (2)	0.085 (3)	−0.0085 (17)	0.0055 (19)	−0.004 (2)
C5	0.0508 (18)	0.0550 (19)	0.057 (2)	−0.0037 (15)	0.0072 (15)	−0.0048 (16)
C6	0.0511 (17)	0.0363 (13)	0.0445 (15)	0.0031 (12)	−0.0035 (13)	−0.0007 (12)
C7	0.0513 (16)	0.0380 (14)	0.0393 (15)	0.0017 (12)	−0.0007 (12)	0.0007 (12)
C8	0.0556 (18)	0.0532 (18)	0.0454 (17)	−0.0059 (15)	0.0009 (14)	0.0022 (14)
C9	0.0533 (18)	0.0493 (17)	0.0475 (18)	0.0011 (14)	0.0012 (14)	0.0040 (14)
C10	0.0507 (17)	0.064 (2)	0.0495 (18)	−0.0105 (16)	0.0004 (14)	−0.0084 (15)
C11	0.063 (2)	0.064 (2)	0.054 (2)	0.0048 (18)	−0.0070 (17)	0.0023 (17)
C12	0.0467 (17)	0.0496 (17)	0.068 (2)	0.0052 (14)	−0.0017 (16)	−0.0001 (17)
C13	0.055 (2)	0.073 (3)	0.083 (3)	−0.0009 (19)	−0.008 (2)	−0.008 (2)
C14	0.050 (2)	0.072 (3)	0.117 (5)	−0.0076 (19)	−0.003 (2)	−0.001 (3)
C15	0.056 (2)	0.069 (3)	0.107 (4)	−0.009 (2)	0.010 (2)	0.015 (2)
C16	0.062 (2)	0.069 (2)	0.077 (3)	0.0004 (19)	0.009 (2)	0.016 (2)
C17	0.0453 (17)	0.0497 (18)	0.070 (2)	0.0026 (14)	−0.0001 (15)	0.0058 (17)
C18	0.0548 (18)	0.0603 (19)	0.0457 (17)	−0.0032 (15)	0.0027 (15)	0.0074 (16)

Geometric parameters (Å, º)

Cl01—C18	1.741 (4)	C8—H8	0.9300
O1—C7	1.233 (4)	C9—C18	1.342 (5)
O2—H2A	0.79 (6)	C9—C10	1.527 (5)
O2—H2B	0.96 (6)	C10—C11	1.505 (5)
N6—C7	1.352 (4)	C10—H10A	0.9700
N6—N2	1.378 (4)	C10—H10B	0.9700
N6—H6	0.93 (5)	C11—C12	1.502 (6)
N2—C8	1.280 (4)	C11—H11A	0.9700
C1—C2	1.389 (6)	C11—H11B	0.9700
C1—C6	1.396 (5)	C12—C13	1.390 (6)
C1—H1	0.9300	C12—C17	1.396 (5)
C2—C3	1.365 (7)	C13—C14	1.368 (7)

C2—H2	0.9300	C13—H13	0.9300
C3—C4	1.374 (7)	C14—C15	1.352 (7)
C3—H3	0.9300	C14—H14	0.9300
C4—C5	1.381 (5)	C15—C16	1.385 (7)
C4—H4	0.9300	C15—H15	0.9300
C5—C6	1.381 (5)	C16—C17	1.404 (6)
C5—H5	0.9300	C16—H16	0.9300
C6—C7	1.489 (4)	C17—C18	1.472 (5)
C8—C9	1.459 (5)		
H2A—O2—H2B	104 (5)	C9—C10—H10A	109.7
C7—N6—N2	118.4 (3)	C11—C10—H10A	109.7
C7—N6—H6	119 (3)	C9—C10—H10B	109.7
N2—N6—H6	122 (3)	C11—C10—H10B	109.7
C8—N2—N6	115.1 (3)	H10A—C10—H10B	108.2
C2—C1—C6	119.8 (4)	C12—C11—C10	113.4 (3)
C2—C1—H1	120.1	C12—C11—H11A	108.9
C6—C1—H1	120.1	C10—C11—H11A	108.9
C3—C2—C1	120.5 (4)	C12—C11—H11B	108.9
C3—C2—H2	119.7	C10—C11—H11B	108.9
C1—C2—H2	119.7	H11A—C11—H11B	107.7
C4—C3—C2	120.1 (4)	C13—C12—C17	118.7 (4)
C4—C3—H3	120.0	C13—C12—C11	122.4 (4)
C2—C3—H3	120.0	C17—C12—C11	118.9 (3)
C3—C4—C5	120.1 (4)	C14—C13—C12	121.2 (5)
C3—C4—H4	119.9	C14—C13—H13	119.4
C5—C4—H4	119.9	C12—C13—H13	119.4
C6—C5—C4	120.7 (4)	C13—C14—C15	120.4 (4)
C6—C5—H5	119.7	C13—C14—H14	119.8
C4—C5—H5	119.7	C15—C14—H14	119.8
C5—C6—C1	118.8 (3)	C14—C15—C16	120.8 (4)
C5—C6—C7	117.5 (3)	C14—C15—H15	119.6
C1—C6—C7	123.6 (3)	C16—C15—H15	119.6
O1—C7—N6	121.7 (3)	C15—C16—C17	119.6 (4)
O1—C7—C6	121.0 (3)	C15—C16—H16	120.2
N6—C7—C6	117.3 (3)	C17—C16—H16	120.2
N2—C8—C9	118.4 (3)	C16—C17—C12	119.4 (4)
N2—C8—H8	120.8	C16—C17—C18	122.8 (4)
C9—C8—H8	120.8	C12—C17—C18	117.9 (3)
C18—C9—C8	122.4 (3)	C9—C18—C17	122.8 (3)
C18—C9—C10	118.5 (3)	C9—C18—Cl01	120.5 (3)
C8—C9—C10	119.1 (3)	C17—C18—Cl01	116.6 (3)
C9—C10—C11	109.9 (3)		
C7—N6—N2—C8	174.4 (3)	C10—C11—C12—C13	149.3 (4)
C6—C1—C2—C3	−0.8 (6)	C10—C11—C12—C17	−32.7 (5)
C1—C2—C3—C4	0.9 (7)	C17—C12—C13—C14	1.0 (6)
C2—C3—C4—C5	−0.8 (6)	C11—C12—C13—C14	179.0 (4)

C3—C4—C5—C6	0.7 (6)	C12—C13—C14—C15	−0.4 (7)
C4—C5—C6—C1	−0.7 (5)	C13—C14—C15—C16	−0.7 (8)
C4—C5—C6—C7	−178.7 (3)	C14—C15—C16—C17	1.1 (7)
C2—C1—C6—C5	0.8 (5)	C15—C16—C17—C12	−0.5 (6)
C2—C1—C6—C7	178.6 (3)	C15—C16—C17—C18	−179.1 (4)
N2—N6—C7—O1	0.9 (5)	C13—C12—C17—C16	−0.6 (5)
N2—N6—C7—C6	−178.0 (3)	C11—C12—C17—C16	−178.7 (4)
C5—C6—C7—O1	10.7 (5)	C13—C12—C17—C18	178.2 (4)
C1—C6—C7—O1	−167.2 (3)	C11—C12—C17—C18	0.1 (5)
C5—C6—C7—N6	−170.5 (3)	C8—C9—C18—C17	−175.8 (3)
C1—C6—C7—N6	11.6 (5)	C10—C9—C18—C17	5.0 (5)
N6—N2—C8—C9	−178.7 (3)	C8—C9—C18—Cl01	1.3 (5)
N2—C8—C9—C18	173.5 (3)	C10—C9—C18—Cl01	−177.9 (3)
N2—C8—C9—C10	−7.3 (5)	C16—C17—C18—C9	−166.5 (4)
C18—C9—C10—C11	−36.7 (5)	C12—C17—C18—C9	14.8 (5)
C8—C9—C10—C11	144.1 (3)	C16—C17—C18—Cl01	16.3 (5)
C9—C10—C11—C12	49.2 (5)	C12—C17—C18—Cl01	−162.4 (3)

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O2—H2*A*⋯O1[i]	0.78 (5)	2.06 (5)	2.829 (4)	166 (5)
O2—H2*B*⋯O1	0.96 (6)	1.90 (6)	2.858 (4)	171 (5)
N6—H6⋯O2[ii]	0.93 (5)	1.98 (5)	2.869 (4)	159 (4)
C1—H1⋯O2[ii]	0.93	2.47	3.350 (5)	158
C8—H8⋯O2[ii]	0.93	2.48	3.261 (5)	142

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