



Crystal structure and Hirshfeld surface analysis of a Schiff base: (Z)-6-[(5-chloro-2-methoxyanilino)-methylidene]-2-hydroxycyclohexa-2,4-dien-1-one

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The title compound, C₁₄H₁₂ClNO₃, is a Schiff base that exists in the keto-enamine tautomeric form and adopts a *Z* configuration. In the crystal, the dihedral angle between the planes of the benzene rings is 5.34 (15)°. The roughly planar geometry of the molecule is stabilized by a strong intramolecular N—H···O hydrogen bond. In the crystal, pairs of centrosymmetrically related molecules are linked by O—H···O hydrogen bonds, forming R₂²(10) rings. Besides this, the molecules form stacks along the [001] direction with C—H···π and C—H···Cl contacts between the stacks. The intermolecular interactions in the crystal were analysed using Hirshfeld surfaces. The most significant contribution to the crystal packing is from H···H contacts (30.8%).

1. Chemical context

Schiff bases are widely used as ligands in coordination chemistry (Calligaris & Randaccio, 1987) and they are also of interest in various fields because of their diverse biological activity (Lozier *et al.*, 1975; Costamagna *et al.*, 1992). Some Schiff bases derived from salicylaldehyde have attracted the interest of chemists and physicists because they show thermochromism and photochromism in the solid state (Cohen *et al.*, 1964; Hadjoudis *et al.*, 1987). The origin of their photo- and thermochromism is related to the reversible intramolecular proton transfer associated with a change in the electronic structure (Hadjoudis *et al.*, 1987). The *o*-hydroxy Schiff bases obtained by the condensation of *o*-hydroxyaldehydes with aniline have been extensively examined in this context. Such compounds can exist in two tautomeric forms, *viz.* keto-enamine (N—H···O) and phenol-imine (N···H—O) (Stewart & Lingafelter, 1959; Petek *et al.*, 2010). We report herein the synthesis and the crystal and molecular structures of the title compound, as well as an analysis of its Hirshfeld surfaces.

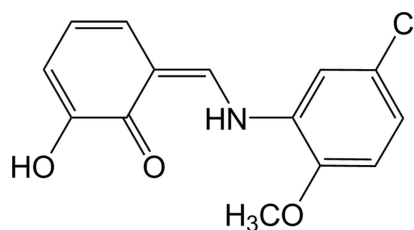
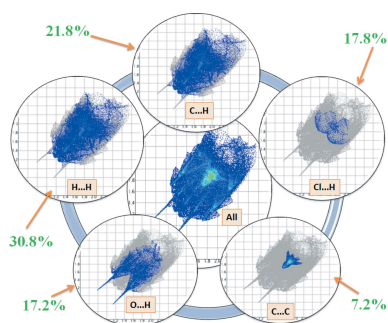


Table 1
Selected bond lengths (Å).

O2—C9	1.292 (4)	C8—C13	1.410 (5)
O3—C10	1.358 (4)	C9—C10	1.426 (4)
N1—C6	1.413 (4)	C10—C11	1.359 (5)
N1—C7	1.302 (4)	C11—C12	1.402 (5)
C7—C8	1.408 (4)	C12—C13	1.349 (4)
C8—C9	1.429 (4)		

2. Structural commentary

As shown in Fig. 1., the asymmetric unit of the title compound contains only one molecule, which adopts the keto–enamine tautomeric form: the H atom is located at N1, and the lengths of the N1—C7 and C8—C9 bonds indicate their single-bond character, whereas the O2—C9 and C7—C8 bonds are double (Table 1). Overall, the bond lengths in the title structure compare well with those of other keto–enamine tautomers known from the literature (see the *Database survey* section). The whole molecule is almost planar, with a dihedral angle of 5.34 (15)° between the benzene ring planes. The methoxy C14 atom deviates from the plane of the C1—C6 benzene ring by 0.038 (4) Å. The torsion angles C1—C6—N1—C7 and N1—C7—C8—C9 are 5.8 (5) and −0.6 (5)°, respectively. The planar molecular conformation is stabilized by the intramolecular N1—H2···O2 hydrogen bond (Table 2).

3. Supramolecular features

In the crystal, the molecules are connected *via* O—H···O hydrogen bonds into centrosymmetric pairs with an $R_2^2(10)$ graph-set motif (Table 2, Fig. 2). Molecules related by a [001] translation form stacks with an interplanar distance of 3.420 (3) Å and a shortest intercentroid separation of 3.6797 (17) Å. The molecular packing is further stabilized by C—H···O, C—H···Cl and C—H··· π interactions between the molecules of the neighbouring stacks (Fig. 3). Details of all these contacts are given in Table 2.

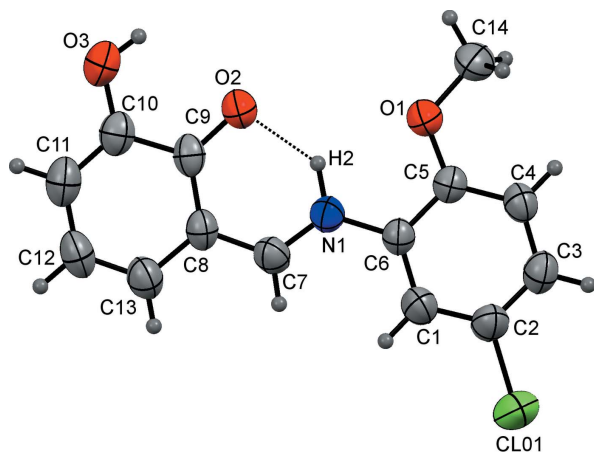


Figure 1
The molecular structure of the title compound with the displacement ellipsoids drawn at the 50% probability level. The intramolecular N—H···O hydrogen bond is shown as a dashed line.

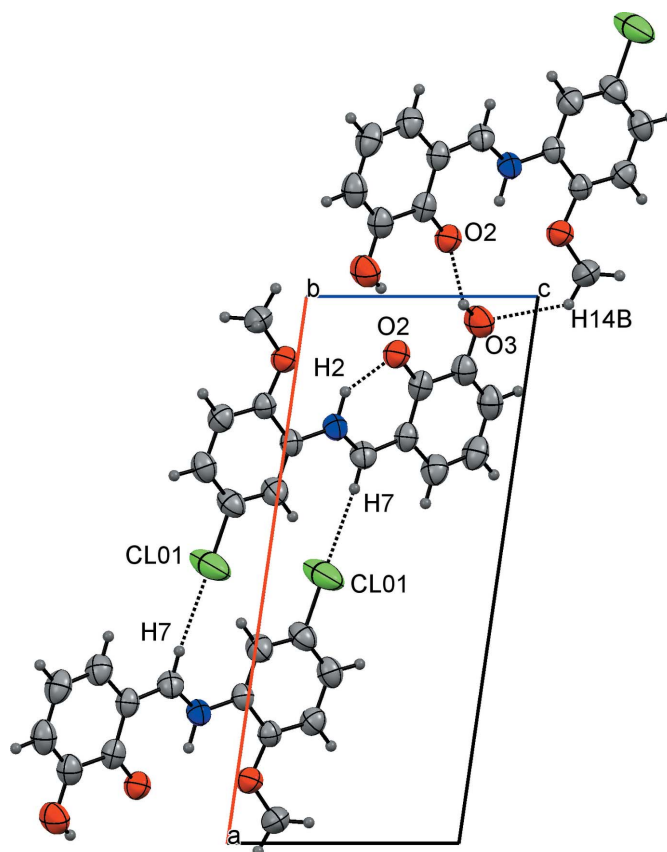


Figure 2
A view of the crystal packing of the title compound. Dashed lines denote the intra- and intermolecular hydrogen bonds.

4. Database survey

A search of the Cambridge Structural database (CSD, version 5.40, update November 2018; Groom *et al.*, 2016) for the 3-[(*E*)-(phenylimino)methyl]-benzene-1,2-diol fragment revealed eight hits where this fragment adopts the keto–enamine tautomeric form and 21 hits where it exists as the phenol–imine tautomer. Distinctive bond lengths (N1—C7,

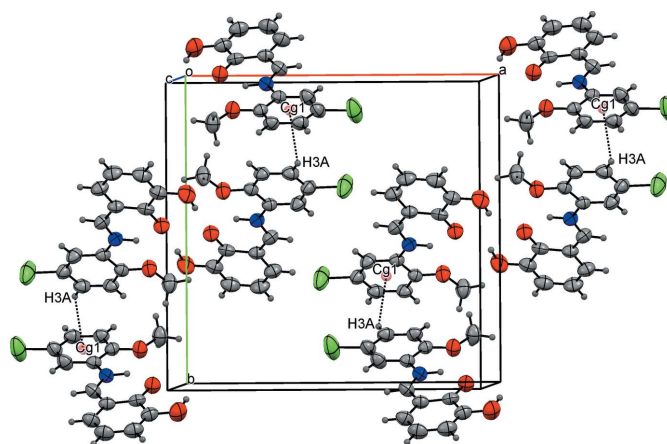


Figure 3
The packing diagram showing the stacking, C—H··· π and C—H···Cl interactions.

Table 2
Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 ring.

<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>
C7–H7...Cl01 ⁱ	0.93	2.88	3.737 (3)	154
C14–H14B...O3 ⁱⁱ	0.96	2.59	3.295 (4)	131
O3–H3...O2 ⁱⁱ	0.87 (4)	2.00 (4)	2.780 (4)	148 (4)
N1–H2...O2	0.97 (4)	1.82 (4)	2.598 (3)	136 (4)
C3–H3A...Cg1 ⁱⁱⁱ	0.93	2.73	3.463 (3)	136

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

C7=C8, C8–C9, C9=O2) in the title structure are the same within standard uncertainties as the corresponding bond lengths in the structures of 2-hydroxy-6-[(2-methoxyphenyl)aminomethylene]cyclohexa-2,4-dienone (FOCCOQ; Şahin *et al.*, 2005) and 6-[(4-chlorophenylamino)methylene]-2,3-dihydroxycyclohexa-2,4-dien-1-one (CIRTED; Karabiyik *et al.*, 2008). In the structures of typical phenol–imine tautomers, *viz.*, 3-[(3-bromophenyl)iminomethyl]benzene-1,2-diol (CUCZUW; Keleşoğlu *et al.*, 2009*b*), 3-[(2-bromophenyl)iminomethyl]benzene-1,2-diol (XEYSOK; Temel *et al.*, 2007) and 3-[(4-butylphenyl)iminomethyl]benzene-1,2-diol (XOZJUS; Keleşoğlu *et al.*, 2009*a*), the C9–O2 and C7–C8 bond lengths are distinctly longer, being in the ranges 1.324–1.355 Å and 1.427–1.447 Å, respectively. It is likely that the intermolecular O–H...O hydrogen bond, where the keto O atom acts as an hydrogen-bond acceptor, is an important prerequisite for the tautomeric shift toward the keto–enamine form. In fact, in all eight structures of the keto–enamine tautomers, hydrogen bonds of this type are observed. However, in 16 of 21 structures of phenol–imine tautomers, such hydrogen bonds are also present. This means that there is another unknown reason for the formation of keto–enamine tautomers.

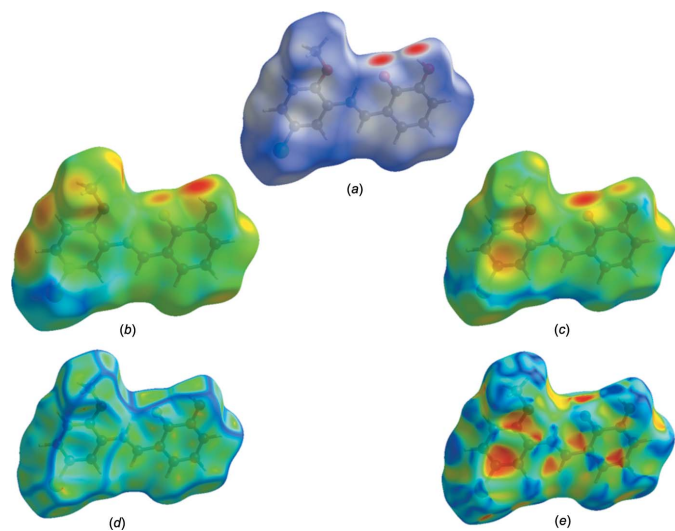


Figure 4
The Hirshfeld surface of the title compound mapped with (a) d_{norm} , (b) d_i , (c) d_e , (d) curvedness and (e) shape-index.

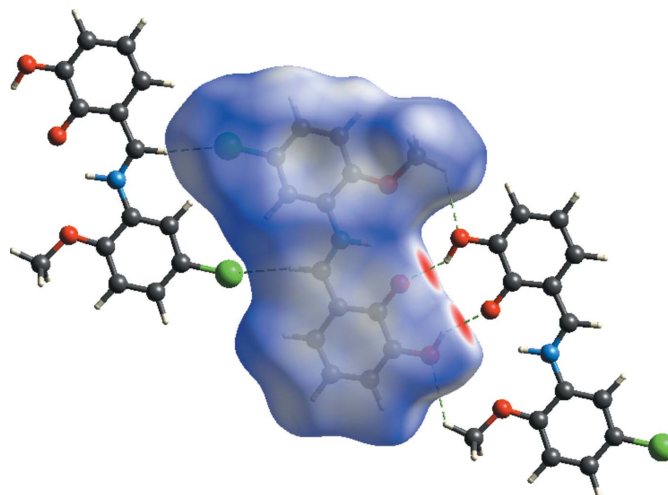


Figure 5
The d_{norm} -mapped Hirshfeld surface showing the intermolecular interactions in the title compound.

5. Hirshfeld surface analysis

The Hirshfeld surface analysis, together with the two-dimensional fingerprint plots, is a powerful tool for the visualization and interpretation of intermolecular contacts in molecular crystals, since it provides a concise description of all intermolecular interactions present in a crystal structure (Spackman & Jayatilaka, 2009; McKinnon *et al.*, 2007). All surfaces and 2D fingerprint plots were generated using *CrystalExplorer3.1* (Wolff *et al.*, 2012). The mappings of d_i , d_e , d_{norm} , shape-index and curvedness for the title structure are shown in Fig. 4. The Hirshfeld surface of a molecule in the crystal is presented in Fig. 5, with the prominent hydrogen-bonding interactions shown as intense red spots. The two-dimensional fingerprint plots provide information about the

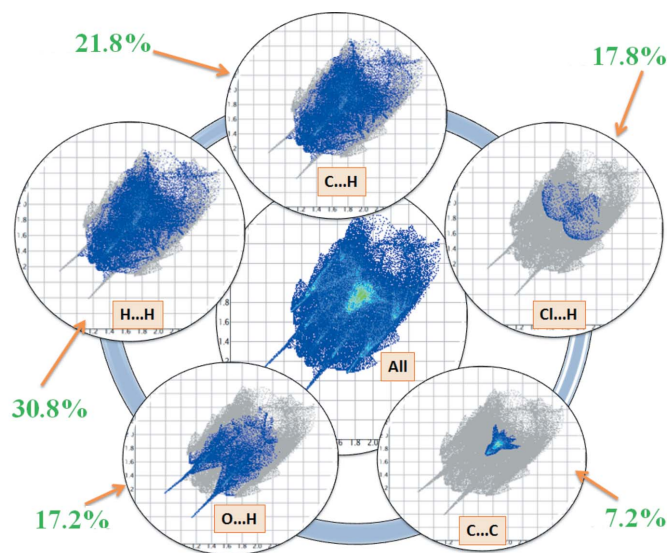


Figure 6
Two-dimensional fingerprint plots with d_{norm} views of all, the H...H, O...H/H...O, C...H/H...C and N...H/H...N contacts in the title compound.

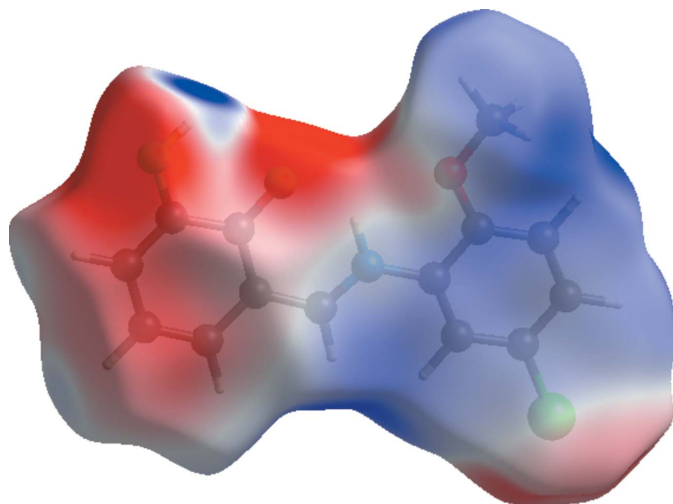


Figure 7
The view of the Hirshfeld surface of the title compound plotted over the electrostatic potential energy.

percentage contributions of the various interatomic contacts. As can be seen from these plots (Fig. 6), the most important are the H···H interactions, which contribute 30.8% to the total Hirshfeld surface. Other contributions are from O···C/ C···O (1.2%), O···H/H···O (17.2%), C···C (7.2%), O···O/ O···O (1.0%), Cl···H/H···Cl (17.8%) and C···H/H···C (21.8%). Analogous features were observed recently for some compounds of the same class (Kansız *et al.*, 2018; Özek Yıldırım *et al.*, 2018). The donor and acceptor centers of the hydrogen bonding are represented as blue (positive) and red (negative) regions on the Hirshfeld surface mapped over the electrostatic potential (Fig. 7). The electrostatic potential of the Cl01 atom is less negative as compared to those of atoms O2 and O3 of the hydroxy groups, as indicated by the lighter red color.

6. Synthesis and crystallization

The title compound was prepared by mixing solutions of 2,3-dihydroxybenzaldehyde (34.5 mg, 0.25 mmol) and 5-chloro-2-methoxyaniline (39.4 mg, 0.25 mmol), both in 15 mL of ethanol, with subsequent stirring for 5 h under reflux. Single crystals were obtained by slow evaporation of an ethanol solution (yield 65%; m.p. 442–444 K).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C-bound H atoms were geometrically positioned with C–H distances of 0.93–0.96 Å and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. The O- and N-bound H atoms were located in a difference map and freely refined.

Acknowledgements

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe

Table 3
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{14}\text{H}_{12}\text{ClNO}_3$
M_r	277.70
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	14.7251 (9), 14.4444 (9), 6.1698 (4)
β (°)	98.241 (5)
V (Å ³)	1298.74 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.30
Crystal size (mm)	0.23 × 0.16 × 0.09
Data collection	
Diffractometer	Stoe IPDS 2
Absorption correction	Integration (<i>X-RED32</i> ; Stoe & Cie, 2002)
$T_{\text{min}}, T_{\text{max}}$	0.948, 0.979
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13658, 2491, 1120
R_{int}	0.115
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.057, 0.100, 0.90
No. of reflections	2491
No. of parameters	181
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)	0.16, -0.24

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 2002), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

IPDS 2 diffractometer (purchased under grant F.279 of the University Research Fund).

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Crystal structure and Hirshfeld surface analysis of a Schiff base: (Z)-6-[(5-chloro-2-methoxyanilino)methylidene]-2-hydroxycyclohexa-2,4-dien-1-one

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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: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

(Z)-6-[(5-Chloro-2-methoxyanilino)methylidene]-2-hydroxycyclohexa-2,4-dien-1-one

Crystal data

$C_{14}H_{12}ClNO_3$

$M_r = 277.70$

Monoclinic, $P2_1/c$

$a = 14.7251$ (9) Å

$b = 14.4444$ (9) Å

$c = 6.1698$ (4) Å

$\beta = 98.241$ (5)°

$V = 1298.74$ (14) Å³

$Z = 4$

$F(000) = 576$

$D_x = 1.420$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8086 reflections

$\theta = 1.4$ – 27.1 °

$\mu = 0.30$ mm⁻¹

$T = 296$ K

Irregular specimen, red

$0.23 \times 0.16 \times 0.09$ 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)

$T_{\min} = 0.948$, $T_{\max} = 0.979$

13658 measured reflections

2491 independent reflections

1120 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.115$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 2.0$ °

$h = -18 \rightarrow 18$

$k = -17 \rightarrow 17$

$l = -7 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.100$

$S = 0.90$

2491 reflections

181 parameters

0 restraints

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
 $w = 1/[\sigma^2(F_o^2) + (0.0293P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl01	0.49115 (8)	0.36774 (9)	-0.2476 (2)	0.1172 (6)
O1	0.11503 (15)	0.37573 (16)	-0.0556 (4)	0.0611 (6)
O2	0.10563 (15)	0.50349 (16)	0.4247 (4)	0.0601 (7)
O3	0.0461 (2)	0.5981 (2)	0.7618 (4)	0.0782 (9)
N1	0.2392 (2)	0.46609 (18)	0.2056 (5)	0.0497 (8)
C1	0.3568 (2)	0.4173 (2)	-0.0160 (6)	0.0608 (10)
H1A	0.4026	0.4475	0.0774	0.073*
C2	0.3782 (2)	0.3706 (2)	-0.1958 (6)	0.0606 (10)
C3	0.3124 (2)	0.3262 (2)	-0.3362 (6)	0.0583 (10)
H3A	0.3277	0.2961	-0.4592	0.070*
C4	0.2231 (2)	0.3264 (2)	-0.2937 (6)	0.0540 (9)
H4	0.1780	0.2953	-0.3869	0.065*
C5	0.2002 (2)	0.3725 (2)	-0.1142 (5)	0.0459 (8)
C6	0.2675 (2)	0.4193 (2)	0.0256 (5)	0.0454 (8)
C7	0.2902 (2)	0.5189 (2)	0.3445 (6)	0.0546 (9)
H7	0.3515	0.5266	0.3277	0.066*
C8	0.2572 (2)	0.5648 (2)	0.5188 (5)	0.0495 (9)
C9	0.1632 (2)	0.5551 (2)	0.5481 (5)	0.0483 (9)
C10	0.1348 (3)	0.6045 (2)	0.7269 (6)	0.0577 (9)
C11	0.1941 (3)	0.6591 (2)	0.8593 (6)	0.0669 (11)
H11	0.1733	0.6919	0.9723	0.080*
C12	0.2862 (3)	0.6667 (2)	0.8274 (6)	0.0680 (11)
H12	0.3262	0.7037	0.9205	0.082*
C13	0.3171 (3)	0.6206 (2)	0.6623 (6)	0.0619 (10)
H13	0.3784	0.6257	0.6430	0.074*
C14	0.0424 (2)	0.3301 (3)	-0.1933 (6)	0.0698 (11)
H00F	0.0378	0.3546	-0.3392	0.105*
H14B	-0.0144	0.3402	-0.1375	0.105*
H14C	0.0548	0.2649	-0.1959	0.105*
H3	0.016 (3)	0.555 (3)	0.685 (8)	0.104 (18)*
H2	0.175 (3)	0.461 (3)	0.226 (8)	0.130 (17)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl01	0.0754 (8)	0.1458 (11)	0.1426 (12)	-0.0326 (7)	0.0573 (8)	-0.0628 (9)
O1	0.0504 (14)	0.0746 (16)	0.0578 (16)	-0.0021 (13)	0.0062 (12)	-0.0180 (13)
O2	0.0581 (15)	0.0667 (16)	0.0544 (17)	-0.0025 (13)	0.0051 (13)	-0.0148 (12)
O3	0.077 (2)	0.087 (2)	0.074 (2)	0.0025 (16)	0.0234 (17)	-0.0277 (16)
N1	0.0535 (19)	0.0501 (19)	0.047 (2)	-0.0040 (14)	0.0114 (17)	-0.0032 (14)
C1	0.063 (3)	0.060 (2)	0.061 (3)	-0.0134 (17)	0.014 (2)	-0.0135 (18)
C2	0.061 (2)	0.057 (2)	0.068 (3)	-0.011 (2)	0.025 (2)	-0.010 (2)
C3	0.073 (3)	0.050 (2)	0.056 (3)	0.001 (2)	0.019 (2)	-0.0059 (19)
C4	0.060 (3)	0.048 (2)	0.053 (2)	-0.0013 (17)	0.005 (2)	-0.0097 (17)
C5	0.051 (2)	0.043 (2)	0.044 (2)	0.0025 (17)	0.0085 (18)	0.0000 (17)
C6	0.055 (2)	0.041 (2)	0.041 (2)	-0.0018 (16)	0.0093 (19)	-0.0023 (15)
C7	0.059 (2)	0.052 (2)	0.053 (2)	-0.0125 (18)	0.010 (2)	-0.0031 (19)
C8	0.063 (2)	0.042 (2)	0.043 (2)	-0.0008 (16)	0.0073 (19)	-0.0044 (16)
C9	0.067 (2)	0.0347 (19)	0.042 (2)	0.0064 (17)	0.004 (2)	-0.0009 (16)
C10	0.072 (3)	0.050 (2)	0.052 (2)	0.007 (2)	0.011 (2)	-0.0005 (19)
C11	0.093 (3)	0.056 (3)	0.053 (3)	0.007 (2)	0.015 (2)	-0.0073 (19)
C12	0.088 (3)	0.058 (2)	0.055 (3)	-0.011 (2)	0.000 (2)	-0.015 (2)
C13	0.074 (2)	0.054 (2)	0.057 (3)	-0.010 (2)	0.008 (2)	-0.0087 (19)
C14	0.053 (2)	0.095 (3)	0.060 (3)	-0.002 (2)	0.002 (2)	-0.010 (2)

Geometric parameters (\AA , $^\circ$)

Cl01—C2	1.739 (3)	C4—H4	0.9300
O1—C5	1.354 (3)	C5—C6	1.393 (4)
O1—C14	1.429 (4)	C7—C8	1.408 (4)
O2—C9	1.292 (4)	C7—H7	0.9300
O3—C10	1.358 (4)	C8—C9	1.429 (4)
O3—H3	0.87 (4)	C8—C13	1.410 (5)
N1—C6	1.413 (4)	C9—C10	1.426 (4)
N1—C7	1.302 (4)	C10—C11	1.359 (5)
N1—H2	0.97 (4)	C11—C12	1.402 (5)
C1—C2	1.372 (4)	C11—H11	0.9300
C1—C6	1.376 (4)	C12—C13	1.349 (4)
C1—H1A	0.9300	C12—H12	0.9300
C2—C3	1.363 (5)	C13—H13	0.9300
C3—C4	1.379 (4)	C14—H00F	0.9600
C3—H3A	0.9300	C14—H14B	0.9600
C4—C5	1.375 (4)	C14—H14C	0.9600
C5—O1—C14	117.9 (3)	C8—C7—H7	118.3
C10—O3—H3	113 (3)	C7—C8—C13	119.7 (3)
C7—N1—C6	126.1 (3)	C7—C8—C9	119.8 (3)
C7—N1—H2	116 (3)	C13—C8—C9	120.4 (3)
C6—N1—H2	118 (3)	O2—C9—C10	120.3 (3)
C2—C1—C6	119.8 (3)	O2—C9—C8	123.2 (3)

C2—C1—H1A	120.1	C10—C9—C8	116.5 (3)
C6—C1—H1A	120.1	O3—C10—C11	119.6 (3)
C3—C2—C1	121.4 (3)	O3—C10—C9	118.9 (4)
C3—C2—C101	118.9 (3)	C11—C10—C9	121.4 (3)
C1—C2—C101	119.7 (3)	C10—C11—C12	120.8 (3)
C2—C3—C4	119.2 (3)	C10—C11—H11	119.6
C2—C3—H3A	120.4	C12—C11—H11	119.6
C4—C3—H3A	120.4	C13—C12—C11	120.3 (4)
C5—C4—C3	120.4 (3)	C13—C12—H12	119.8
C5—C4—H4	119.8	C11—C12—H12	119.8
C3—C4—H4	119.8	C12—C13—C8	120.5 (3)
O1—C5—C4	125.1 (3)	C12—C13—H13	119.7
O1—C5—C6	115.0 (3)	C8—C13—H13	119.7
C4—C5—C6	119.9 (3)	O1—C14—H00F	109.5
C1—C6—C5	119.3 (3)	O1—C14—H14B	109.5
C1—C6—N1	123.7 (3)	H00F—C14—H14B	109.5
C5—C6—N1	117.0 (3)	O1—C14—H14C	109.5
N1—C7—C8	123.3 (3)	H00F—C14—H14C	109.5
N1—C7—H7	118.3	H14B—C14—H14C	109.5
C6—C1—C2—C3	0.3 (6)	C6—N1—C7—C8	179.0 (3)
C6—C1—C2—C101	-179.7 (3)	N1—C7—C8—C13	179.9 (3)
C1—C2—C3—C4	-1.5 (6)	N1—C7—C8—C9	-0.6 (5)
C101—C2—C3—C4	178.6 (3)	C7—C8—C9—O2	2.0 (5)
C2—C3—C4—C5	1.3 (5)	C13—C8—C9—O2	-178.5 (3)
C14—O1—C5—C4	-1.8 (5)	C7—C8—C9—C10	-179.3 (3)
C14—O1—C5—C6	179.2 (3)	C13—C8—C9—C10	0.1 (5)
C3—C4—C5—O1	-178.8 (3)	O2—C9—C10—O3	-1.5 (5)
C3—C4—C5—C6	0.1 (5)	C8—C9—C10—O3	179.8 (3)
C2—C1—C6—C5	1.0 (5)	O2—C9—C10—C11	179.8 (3)
C2—C1—C6—N1	-179.5 (3)	C8—C9—C10—C11	1.2 (5)
O1—C5—C6—C1	177.8 (3)	O3—C10—C11—C12	179.7 (3)
C4—C5—C6—C1	-1.2 (5)	C9—C10—C11—C12	-1.7 (6)
O1—C5—C6—N1	-1.7 (4)	C10—C11—C12—C13	0.9 (6)
C4—C5—C6—N1	179.3 (3)	C11—C12—C13—C8	0.4 (6)
C7—N1—C6—C1	5.8 (5)	C7—C8—C13—C12	178.6 (3)
C7—N1—C6—C5	-174.7 (3)	C9—C8—C13—C12	-0.9 (5)

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C1—C6 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C7—H7 \cdots C101 ⁱ	0.93	2.88	3.737 (3)	154
C14—H14B \cdots O3 ⁱⁱ	0.96	2.59	3.295 (4)	131
O3—H3 \cdots O2 ⁱⁱ	0.87 (4)	2.00 (4)	2.780 (4)	148 (4)

N1—H2...O2	0.97 (4)	1.82 (4)	2.598 (3)	136 (4)
C3—H3A...Cg1 ⁱⁱⁱ	0.93	2.73	3.463 (3)	136

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