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Crystal structure and DFT study of (*E*)-2-chloro-4-{[2-(2,4-dinitrophenyl)hydrazin-1-ylidene]methyl}phenol acetonitrile hemisolvate

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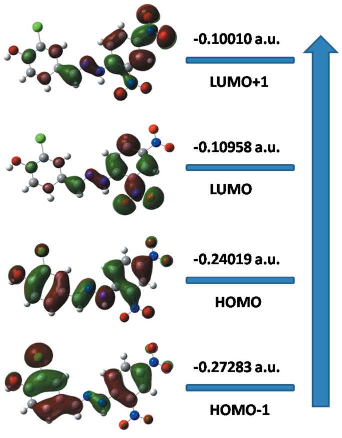
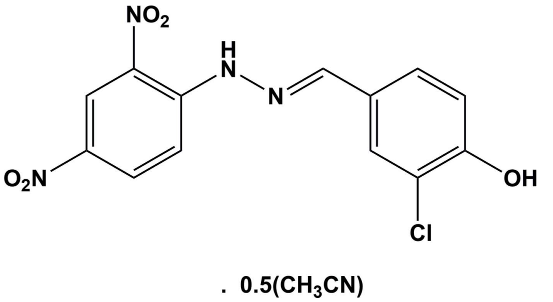
The title Schiff base compound, $C_{13}H_9ClN_4O_5 \cdot 0.5CH_3CN$, crystallizes as an acetonitrile hemisolvate; the solvent molecule being located on a twofold rotation axis. The molecule is nearly planar, with a dihedral angle between the two benzene rings of 3.7 (2)°. The configuration about the C═N bond is *E*, and there is an intramolecular $N—H\cdots O_{nitro}$ hydrogen bond present forming an *S*(6) ring motif. In the crystal, molecules are linked by $O—H\cdots O$ and $N—H\cdots O$ hydrogen bonds, forming layers lying parallel to $(10\overline{1})$. The layers are linked by $C—H\cdots Cl$ hydrogen bonds, forming a supramolecular framework. Within the framework there are offset π–π stacking interactions [intercentroid distance = 3.833 (2) Å] present involving inversion-related molecules. The DFT study shows that the HOMO and LUMO are localized in the plane extending from the phenol ring to the 2,4-dinitrobenzene ring, and the HOMO–LUMO gap is found to be 0.13061 a.u.



1. Chemical context

Over the past 25 years, extensive research has surrounded the synthesis and use of Schiff base compounds in organic and inorganic chemistry, as they have important medicinal and pharmaceutical applications. These compounds show biological activities including antibacterial, antifungal, anticancer and herbicidal activities (Desai *et al.*, 2001; Singh & Dash, 1988; Karia & Parsania, 1999). Schiff bases are also becoming increasingly important in the dye and plastics industries as well as for liquid-crystal technology and the mechanistic investigation of drugs used in pharmacology, biochemistry and physiology (Sheikhshoaie & Sharif, 2006). 2,4-Dinitrophenylhydrazine is frequently used as a reagent for the characterization of aldehydes and ketones (Furniss *et al.*, 1999). Its derivatives are widely used as dyes (Guillaumont & Nakamura, 2000). They are also found to have versatile coordinating abilities towards different metal ions (Raj & Kurup, 2007). The present work is a part of an ongoing structural study of Schiff bases and their utilization in the synthesis of quinoxaline derivatives (Faizi *et al.*, 2016*a*), fluorescence sensors (Faizi *et al.*, 2016*b*) and coordination compounds (Faizi & Prisyazhnaya, 2015). We report herein on the synthesis, crystal structure and DFT computational calculations of the title new Schiff base compound. The results of calculations by density functional theory (DFT) carried out at the B3LYP/6–311 G(d,p) level are compared with the experimentally determined molecular structure in the solid state.



2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The configuration about the C7═N1 bond is *E*, and there is intramolecular N—H$\cdots$O$_{\rm nitro}$ hydrogen bond that generates an *S*(6) ring motif (Fig. 1 and Table 1). The N1—N2 bond length is 1.380 (3) Å and the N1═C7 bond length is 1.275 (4) Å. These bond lengths are comparable with those of some closely related compounds (Fun *et al.*, 2013; Faizi *et al.*, 2017; Ghosh *et al.*, 2016). The C8—C9 and C8—C13 bonds [1.411 (5) and 1.414 (4) Å, respectively], which are adjacent to the imino N2 atom, are significantly longer than the average distance of 1.375 (3) Å for the other C—C bonds in the same benzene ring. This same pattern of bond lengths has been observed previously in some 2,4-dinitrophenylhydrazone derivatives (Ohba, 1996; Borwick *et al.*, 1997). The title molecule is almost planar with the dihedral angle between the benzene rings being 3.70 (17)°. The nitro groups of the 2,4-dinitrophenyl unit are twisted slightly with respect to the C8–C13 benzene ring to which they are attached: nitro group N2/O4/O5 is inclined to the benzene ring by 2.1 (4)°, while nitro group N3/O2/O3 is inclined to it by 6.5 (5)°.

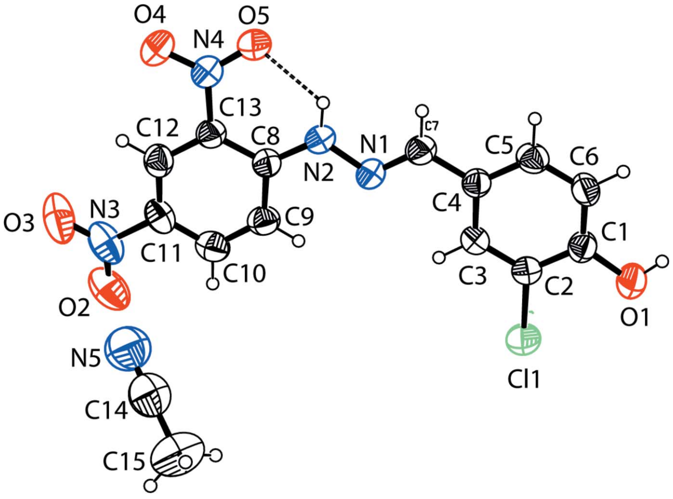


Figure 1
The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 40% probability level. The intramolecular N—H$\cdots$O hydrogen bond (see Table 1), forming an *S*(6) ring motif, is shown as a dashed line.

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
N2—H2$\cdots$O5	0.86	2.01	2.619 (4)	127
O1—H1$\cdots$O2$^{\rm i}$	0.82	2.37	3.114 (4)	152
O1—H1$\cdots$O3$^{\rm i}$	0.82	2.25	2.998 (4)	152
N2—H2$\cdots$O5$^{\rm ii}$	0.86	2.58	3.362 (4)	152
C9—H9$\cdots$Cl1$^{\rm iii}$	0.93	2.72	3.485 (4)	140

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

3. Supramolecular features

In the crystal, molecules are linked by O—H$\cdots$O and N—H$\cdots$O hydrogen bonds (Table 1), forming layers lying parallel

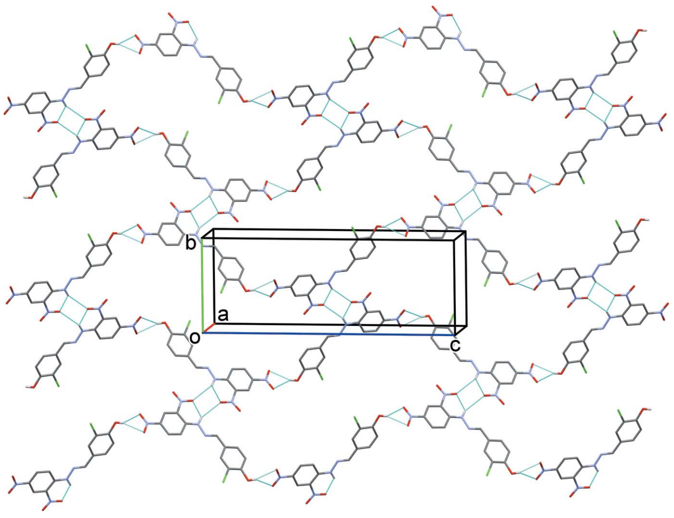


Figure 2
A view along the *a* axis of the crystal packing of the title compound. Hydrogen bonds (see Table 1) are shown as dashed lines. For clarity, the acetonitrile solvent molecules have been omitted and only hydrogen atoms H1 and H2 have been included.

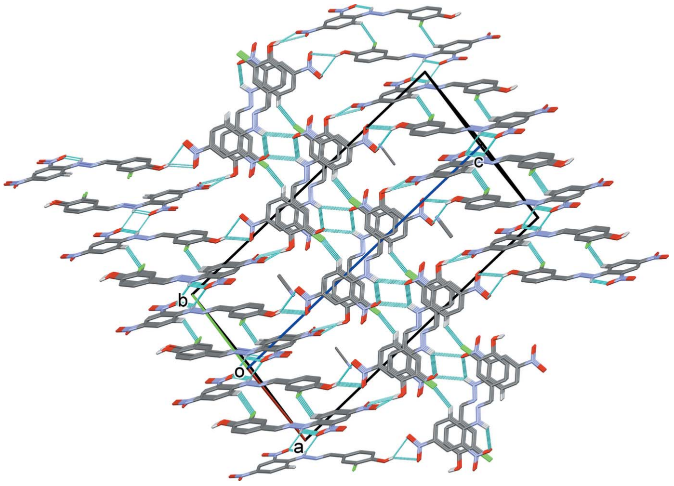


Figure 3
A view normal to plane (110) of the crystal packing of the title compound. Hydrogen bonds (see Table 1) are shown as dashed lines, and, for clarity, only hydrogen atoms H1, H2 and H9 have been included.

to (10$\bar{1}$), as shown in Fig. 2. The layers are linked by C—H$\cdots$Cl hydrogen bonds, forming a supramolecular framework (Fig. 3 and Table 1). Within the framework, inversion-related molecules are linked by offset π–π stacking interactions (Fig. 3); $Cg1\cdots Cg2^{i}$ = 3.833 (2) Å, where $Cg1$ and $Cg2$ are the centroids of rings C1–C6 and C8–C13, respectively, α = 3.70 (17)°, β = 27.9°, γ = 24.5°, interplanar distances are 3.489 (2) and 3.388 (2) Å, offset = 1.791 Å; symmetry code: (i) $-x + 1, -y + 1, -z + 1$. There are no other significant intermolecular contacts present in the crystal.

4. DFT study

The DFT quantum-chemical calculations were performed at the B3LYP/6-311 G(d,p) level (Becke, 1993) as implemented in *GAUSSIAN09* (Frisch *et al.*, 2009). The DFT structure optimization of the title compound was performed starting from the X-ray geometry, with experimental values of bond lengths and bond angles matching with theoretical values. The 6-311 G(d,p) basis set is well suited in its approach to the experimental data. The DFT study shows that the HOMO and LUMO are localized in the plane extending from the whole phenol ring to the 2,4-dinitrobenzene ring. The electron distribution of the HOMO-1, HOMO, LUMO and the LUMO+1 energy levels are shown in Fig. 4. The HOMO molecular orbital exhibits both σ and π character, whereas HOMO-1 is dominated by π-orbital density. The LUMO is mainly composed of π-density while LUMO+1 has both σ and π electronic density. The HOMO–LUMO gap was found to be 0.13061 a.u. and the frontier molecular orbital energies, $E_{\rm HOMO}$ and $E_{\rm LUMO}$ are −0.24019 and −0.10958 a.u., respectively.

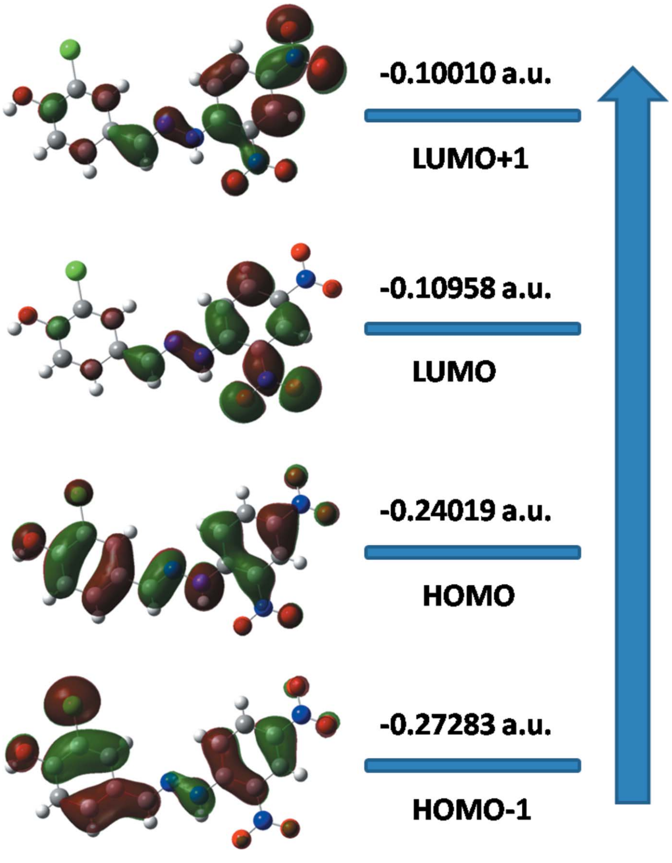


Figure 4
Electron distribution of the HOMO-1, HOMO, LUMO and the LUMO+1 energy levels for the title compound.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_9ClN_4O_5\cdot0.5C_2H_3N$
M_r	357.22
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	296
a, b, c (Å)	12.0614 (11), 9.6960 (6), 26.688 (2)
β (°)	99.619 (7)
V (Å^3)	3077.2 (4)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.29
Crystal size (mm)	0.49 × 0.28 × 0.04
Data collection	
Diffractometer	Stoe IPDS 2
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\rm min}$, $T_{\rm max}$	0.908, 0.989
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8928, 3027, 1416
$R_{\rm int}$	0.056
$(\sin \theta/\lambda)_{\rm max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.137, 0.93
No. of reflections	3027
No. of parameters	224
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.30, −0.26

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2002), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

5. Database survey

A search of the Cambridge Structural Database (CSD, version 5.40, update February 2019; Groom *et al.*, 2016) for the 1-benzylidene-2-(2,4-dinitrophenyl)hydrazine skeleton gave 71 hits (see supporting information). 18 of these structures involve a halide substituent and 23 involve a hydroxyl substituent. Only one compound involves both a halide and an hydroxyl substituent and closely resembles the title compound, *viz*. 4-chloro-2-{[(2,4-dinitrophenyl)hydrazono]-methyl}phenol (CSD refcode HUTHOV; Ghosh *et al.*, 2016). Here the benzene rings are inclined to each other by 3.40 (9)°, compared to 3.70 (17)° in the title compound, and again there is an intramolecular N—H$\cdots$O$_{\rm nitro}$ hydrogen bond present forming an *S*(6) ring motif. In fact, in all 71 structures (see supporting information) there is an intramolecular N—H$\cdots$O$_{\rm nitro}$ hydrogen bond present forming an *S*(6) ring motif, and in the majority of the compounds the two benzene rings are almost coplanar with the dihedral angle varying between *ca* 0 to 8°, with a few exceptions.

6. Synthesis and crystallization

The title compound was prepared by refluxing a mixture of 4-chloro-3-hydroxybenzaldehyde (39.1 mg, 0.25 mmol) in ethanol (15 ml) and 2,4-dinitrophenylhydrazine (49.5 mg, 0.25 mmol) in ethanol (15 ml). The reaction mixture was stirred for 5 h under reflux. Orange plate-like crystals of the title compound were obtained by slow evaporation of a solution in ethanol (yield 68%, m.p. 542–544K).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The OH and NH hydrogen atoms and the C-bound H atoms were included in calculated positions and allowed to ride on the parent atoms: O—H = 0.82 Å, N—H = 0.86 Å, C—H = 0.93–0.96 Å with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O-hydroxyl, C-methyl) and 1.2$U_{\rm eq}$(N,C) for other H atoms.

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supporting information

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Crystal structure and DFT study of (*E*)-2-chloro-4-{[2-(2,4-dinitrophenyl)hydrazin-1-ylidene]methyl}phenol acetonitrile hemisolvate

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015b), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

(*E*)-2-Chloro-4-{[2-(2,4-dinitrophenyl)hydrazin-1-ylidene]methyl}phenol acetonitrile hemisolvate

Crystal data

$C_{13}H_9ClN_4O_5\cdot0.5C_2H_3N$
$M_r = 357.22$
Monoclinic, $C2/c$
$a = 12.0614$ (11) Å
$b = 9.6960$ (6) Å
$c = 26.688$ (2) Å
$\beta = 99.619$ (7)°
$V = 3077.2$ (4) Å^3
$Z = 8$

$F(000) = 1464$
$D_x = 1.542$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8879 reflections
$\theta = 1.6$–27.9°
$\mu = 0.28$ mm^{-1}
$T = 296$ K
Plate, orange
0.49 × 0.28 × 0.04 mm

Data collection

Stoe IPDS 2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Plane graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)

$T_{\min} = 0.908$, $T_{\max} = 0.989$
8928 measured reflections
3027 independent reflections
1416 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 26.0°$, $\theta_{\min} = 1.6°$
$h = -14\rightarrow14$
$k = -11\rightarrow11$
$l = -32\rightarrow32$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.137$
$S = 0.93$
3027 reflections
224 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.52434 (10)	1.07475 (11)	0.57323 (4)	0.0964 (4)	
O1	0.6912 (2)	1.0735 (3)	0.66391 (9)	0.0832 (8)	
H1	0.733227	1.065785	0.691276	0.125*	
N1	0.6314 (2)	0.5959 (3)	0.49923 (11)	0.0606 (7)	
N2	0.6383 (2)	0.4785 (3)	0.47069 (11)	0.0633 (8)	
H2	0.684398	0.413575	0.481954	0.076*	
O4	0.6517 (2)	0.1472 (3)	0.37327 (11)	0.0926 (9)	
N4	0.6512 (3)	0.2398 (3)	0.40402 (13)	0.0736 (9)	
O5	0.7122 (3)	0.2383 (3)	0.44573 (11)	0.0972 (9)	
O2	0.2825 (3)	0.5344 (4)	0.27290 (12)	0.1162 (12)	
N3	0.3566 (3)	0.4469 (5)	0.28233 (14)	0.0906 (11)	
C4	0.6977 (3)	0.7239 (3)	0.57388 (12)	0.0547 (8)	
O3	0.3675 (3)	0.3539 (4)	0.25304 (12)	0.1189 (12)	
C8	0.5723 (3)	0.4668 (3)	0.42510 (13)	0.0572 (9)	
C7	0.6998 (3)	0.6042 (3)	0.54105 (14)	0.0620 (9)	
H7	0.751146	0.533624	0.550646	0.074*	
C1	0.6946 (3)	0.9554 (3)	0.63640 (13)	0.0622 (9)	
C3	0.6217 (3)	0.8310 (3)	0.55996 (12)	0.0600 (9)	
H3	0.571249	0.825918	0.529585	0.072*	
C2	0.6210 (3)	0.9437 (3)	0.59087 (13)	0.0618 (9)	
C13	0.5754 (3)	0.3556 (3)	0.39104 (13)	0.0582 (9)	
C9	0.4926 (3)	0.5706 (4)	0.40833 (14)	0.0666 (9)	
H9	0.486539	0.645038	0.429653	0.080*	
C5	0.7703 (3)	0.7353 (4)	0.61968 (13)	0.0653 (10)	
H5	0.820955	0.664350	0.629757	0.078*	
C12	0.5062 (3)	0.3507 (4)	0.34458 (13)	0.0664 (10)	
H12	0.510551	0.276937	0.322720	0.080*	
C11	0.4313 (3)	0.4545 (4)	0.33077 (13)	0.0683 (10)	
C6	0.7698 (3)	0.8491 (4)	0.65093 (13)	0.0658 (10)	
H6	0.819628	0.854208	0.681488	0.079*	
C10	0.4249 (3)	0.5663 (4)	0.36269 (15)	0.0724 (10)	
H10	0.374492	0.637587	0.352688	0.087*	
C14	0.500000	0.8470 (10)	0.250000	0.108 (2)	
N5	0.500000	0.7307 (8)	0.250000	0.129 (2)	
C15	0.500000	0.9945 (8)	0.250000	0.133 (3)	
H15A	0.477479	1.027514	0.280695	0.200*	0.5

H15B	0.448298	1.027514	0.221207	0.200*	0.5
H15C	0.574223	1.027514	0.248098	0.200*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1112 (8)	0.0726 (7)	0.0951 (8)	0.0330 (6)	−0.0125 (6)	−0.0092 (6)
O1	0.096 (2)	0.0762 (17)	0.0716 (18)	0.0121 (15)	−0.0028 (15)	−0.0197 (14)
N1	0.0692 (19)	0.0535 (17)	0.0591 (18)	0.0024 (14)	0.0106 (17)	−0.0066 (14)
N2	0.074 (2)	0.0512 (17)	0.0631 (19)	0.0102 (14)	0.0082 (17)	−0.0038 (14)
O4	0.116 (2)	0.0702 (17)	0.0891 (19)	0.0191 (16)	0.0082 (18)	−0.0220 (16)
N4	0.089 (2)	0.063 (2)	0.068 (2)	0.0086 (18)	0.009 (2)	−0.0067 (18)
O5	0.123 (2)	0.0750 (19)	0.0822 (19)	0.0406 (17)	−0.0170 (18)	−0.0116 (15)
O2	0.086 (2)	0.166 (3)	0.089 (2)	0.016 (2)	−0.0102 (19)	0.023 (2)
N3	0.067 (2)	0.142 (4)	0.063 (2)	−0.009 (3)	0.010 (2)	0.012 (2)
C4	0.058 (2)	0.0523 (19)	0.054 (2)	−0.0033 (17)	0.0103 (18)	0.0007 (17)
O3	0.102 (2)	0.181 (4)	0.068 (2)	0.004 (2)	−0.0016 (18)	−0.029 (2)
C8	0.065 (2)	0.052 (2)	0.054 (2)	−0.0015 (17)	0.0092 (19)	0.0003 (17)
C7	0.067 (2)	0.057 (2)	0.063 (2)	0.0063 (17)	0.013 (2)	−0.0013 (18)
C1	0.067 (2)	0.061 (2)	0.059 (2)	0.0006 (19)	0.0101 (19)	−0.0087 (18)
C3	0.065 (2)	0.058 (2)	0.054 (2)	0.0043 (18)	0.0010 (18)	0.0017 (17)
C2	0.068 (2)	0.055 (2)	0.061 (2)	0.0074 (18)	0.006 (2)	0.0002 (18)
C13	0.060 (2)	0.056 (2)	0.059 (2)	0.0045 (17)	0.0111 (19)	0.0004 (17)
C9	0.070 (2)	0.060 (2)	0.071 (3)	0.009 (2)	0.015 (2)	0.0028 (19)
C5	0.060 (2)	0.071 (2)	0.064 (2)	0.0143 (19)	0.009 (2)	0.003 (2)
C12	0.075 (3)	0.071 (2)	0.055 (2)	−0.005 (2)	0.016 (2)	−0.0022 (19)
C11	0.065 (2)	0.089 (3)	0.051 (2)	−0.007 (2)	0.010 (2)	0.007 (2)
C6	0.064 (2)	0.076 (2)	0.053 (2)	0.003 (2)	−0.0012 (18)	−0.0052 (19)
C10	0.071 (3)	0.075 (2)	0.072 (3)	0.010 (2)	0.013 (2)	0.011 (2)
C14	0.090 (5)	0.123 (7)	0.110 (6)	0.000	0.012 (4)	0.000
N5	0.121 (5)	0.120 (5)	0.137 (5)	0.000	−0.001 (4)	0.000
C15	0.103 (6)	0.103 (6)	0.196 (9)	0.000	0.029 (6)	0.000

Geometric parameters (Å, º)

Cl1—C2	1.736 (3)	C3—C2	1.370 (4)
O1—C1	1.364 (4)	C3—H3	0.9300
O1—H1	0.8200	C13—C12	1.375 (5)
N1—C7	1.275 (4)	C9—C10	1.349 (5)
N1—N2	1.380 (3)	C9—H9	0.9300
N2—C8	1.343 (4)	C5—C6	1.384 (4)
N2—H2	0.8600	C5—H5	0.9300
O4—N4	1.217 (3)	C12—C11	1.362 (5)
N4—O5	1.228 (4)	C12—H12	0.9300
N4—C13	1.452 (4)	C11—C10	1.388 (5)
O2—N3	1.228 (5)	C6—H6	0.9300
N3—O3	1.215 (4)	C10—H10	0.9300
N3—C11	1.449 (5)	C14—N5	1.128 (9)

C4—C5	1.384 (4)	C14—C15	1.430 (10)
C4—C3	1.394 (4)	C15—H15A	0.9600
C4—C7	1.457 (4)	C15—H15B	0.9600
C8—C9	1.411 (5)	C15—H15C	0.9600
C8—C13	1.414 (4)	C15—H15A^{i}	0.9600
C7—H7	0.9300	C15—H15B^{i}	0.9600
C1—C2	1.384 (5)	C15—H15C^{i}	0.9600
C1—C6	1.385 (5)		

C1—O1—H1	109.5	C4—C5—H5	119.0
C7—N1—N2	116.5 (3)	C6—C5—H5	119.0
C8—N2—N1	119.2 (3)	C11—C12—C13	119.6 (3)
C8—N2—H2	120.4	C11—C12—H12	120.2
N1—N2—H2	120.4	C13—C12—H12	120.2
O4—N4—O5	122.1 (3)	C12—C11—C10	120.9 (4)
O4—N4—C13	118.9 (3)	C12—C11—N3	119.3 (4)
O5—N4—C13	118.9 (3)	C10—C11—N3	119.8 (4)
O3—N3—O2	122.3 (4)	C5—C6—C1	119.5 (3)
O3—N3—C11	119.6 (4)	C5—C6—H6	120.2
O2—N3—C11	118.1 (4)	C1—C6—H6	120.2
C5—C4—C3	117.8 (3)	C9—C10—C11	119.4 (4)
C5—C4—C7	121.5 (3)	C9—C10—H10	120.3
C3—C4—C7	120.6 (3)	C11—C10—H10	120.3
N2—C8—C9	119.8 (3)	N5—C14—C15	180.0
N2—C8—C13	124.8 (3)	C14—C15—H15A	109.5
C9—C8—C13	115.4 (3)	C14—C15—H15B	109.5
N1—C7—C4	120.2 (3)	H15A—C15—H15B	109.5
N1—C7—H7	119.9	C14—C15—H15C	109.5
C4—C7—H7	119.9	H15A—C15—H15C	109.5
O1—C1—C2	117.9 (3)	H15B—C15—H15C	109.5
O1—C1—C6	123.4 (3)	C14—C15—H15A^{i}	109.471 (2)
C2—C1—C6	118.6 (3)	H15A—C15—H15A^{i}	141.1
C2—C3—C4	120.2 (3)	H15B—C15—H15A^{i}	56.3
C2—C3—H3	119.9	H15C—C15—H15A^{i}	56.2
C4—C3—H3	119.9	C14—C15—H15B^{i}	109.470 (3)
C3—C2—C1	121.8 (3)	H15A—C15—H15B^{i}	56.3
C3—C2—Cl1	119.5 (3)	H15B—C15—H15B^{i}	141.1
C1—C2—Cl1	118.8 (3)	H15C—C15—H15B^{i}	56.3
C12—C13—C8	121.9 (3)	H15A^{i}—C15—H15B^{i}	109.5
C12—C13—N4	116.8 (3)	C14—C15—H15C^{i}	109.470 (5)
C8—C13—N4	121.3 (3)	H15A—C15—H15C^{i}	56.3
C10—C9—C8	122.8 (4)	H15B—C15—H15C^{i}	56.2
C10—C9—H9	118.6	H15C—C15—H15C^{i}	141.1
C8—C9—H9	118.6	H15A^{i}—C15—H15C^{i}	109.5
C4—C5—C6	122.0 (3)	H15B^{i}—C15—H15C^{i}	109.5

C7—N1—N2—C8	−176.8 (3)	O4—N4—C13—C8	−179.3 (3)
N1—N2—C8—C9	−3.5 (4)	O5—N4—C13—C8	1.0 (5)

N1—N2—C8—C13	176.4 (3)	N2—C8—C9—C10	178.9 (3)
N2—N1—C7—C4	−179.4 (3)	C13—C8—C9—C10	−1.0 (5)
C5—C4—C7—N1	179.5 (3)	C3—C4—C5—C6	−0.8 (5)
C3—C4—C7—N1	−0.4 (5)	C7—C4—C5—C6	179.4 (3)
C5—C4—C3—C2	0.7 (5)	C8—C13—C12—C11	−0.7 (5)
C7—C4—C3—C2	−179.4 (3)	N4—C13—C12—C11	178.3 (3)
C4—C3—C2—C1	0.0 (5)	C13—C12—C11—C10	0.9 (5)
C4—C3—C2—Cl1	−179.1 (2)	C13—C12—C11—N3	−178.4 (3)
O1—C1—C2—C3	177.5 (3)	O3—N3—C11—C12	−5.6 (5)
C6—C1—C2—C3	−0.6 (5)	O2—N3—C11—C12	172.9 (3)
O1—C1—C2—Cl1	−3.4 (4)	O3—N3—C11—C10	175.1 (4)
C6—C1—C2—Cl1	178.5 (3)	O2—N3—C11—C10	−6.4 (5)
N2—C8—C13—C12	−179.2 (3)	C4—C5—C6—C1	0.1 (5)
C9—C8—C13—C12	0.7 (5)	O1—C1—C6—C5	−177.5 (3)
N2—C8—C13—N4	1.8 (5)	C2—C1—C6—C5	0.6 (5)
C9—C8—C13—N4	−178.3 (3)	C8—C9—C10—C11	1.3 (5)
O4—N4—C13—C12	1.7 (5)	C12—C11—C10—C9	−1.2 (5)
O5—N4—C13—C12	−178.0 (3)	N3—C11—C10—C9	178.1 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O5	0.86	2.01	2.619 (4)	127
O1—H1···O2^{ii}	0.82	2.37	3.114 (4)	152
O1—H1···O3^{ii}	0.82	2.25	2.998 (4)	152
N2—H2···O5^{iii}	0.86	2.58	3.362 (4)	152
C9—H9···Cl1^{iv}	0.93	2.72	3.485 (4)	140

Symmetry codes: (ii) *x*+1/2, −*y*+3/2, *z*+1/2; (iii) −*x*+3/2, −*y*+1/2, −*z*+1; (iv) −*x*+1, −*y*+2, −*z*+1.