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5,5-Dichloro-6-hydroxydihydropyrimidine- 2,4(1*H*,3*H*)-dione: molecular and crystal structure, Hirshfeld surface analysis and the new route for synthesis with $\text{Mg}(\text{ReO}_4)_2$ as a new catalyst

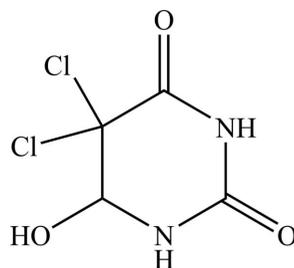
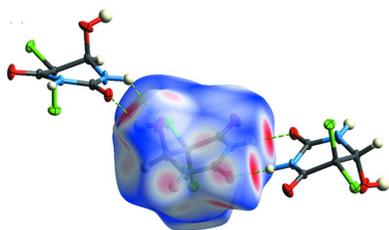
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The molecular and crystal structures of the title compound, $\text{C}_4\text{H}_4\text{Cl}_2\text{N}_2\text{O}_3$, were investigated by single-crystal X-ray diffraction and a Hirshfeld surface analysis. The title compound was synthesized by a new type of reaction using $\text{Mg}(\text{ReO}_4)_2$ as a new catalyst and a possible mechanism for this reaction is proposed. The six-membered ring adopts a half-chair conformation. In the crystal, hydrogen bonds connect the molecules into double layers, which are connected to each other by halogen bonds. The Hirshfeld surface analysis revealed that the most important contributions for the crystal packing are from $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ (35.8%), $\text{Cl}\cdots\text{Cl}$ (19.6%), $\text{Cl}\cdots\text{H}/\text{H}\cdots\text{Cl}$ (17.0%), $\text{H}\cdots\text{H}$ (8.3%), $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$ (4.3%), $\text{Cl}\cdots\text{O}/\text{O}\cdots\text{Cl}$ (4.2%) and $\text{O}\cdots\text{O}$ (4.1%) contacts.

1. Chemical context

Nitrogen heterocycles and pyrimidines are examples of the most important biologically active compounds and find a wide use in modern medicine (Pałasz *et al.*, 2015; Takeshita *et al.*, 2006; Henderson *et al.*, 2003). Uracil is widespread in nature as a pyrimidine derivative, and is found as a part of nucleic acids. Uracil derivatives are used for therapeutic purposes (Smith *et al.*, 2004; Kasradze *et al.*, 2012). Halogen derivatives of uracil serve as convenient intermediates for the preparation of compounds with various functional groups (Wamhoff *et al.*, 1992). Halogen–halogen bonding has recently attracted attention as it expands the possibilities of understanding the new properties of compounds containing halogens and their applications (Szell *et al.*, 2017). Pyrimidine derivatives are used as intermediates for the production of various complex organic molecules for the treatment of cancer and AIDS (Fawcett *et al.*, 1996). Several pyrimidine derivatives belong to the class of central nervous system depressants (Soayed *et al.*, 2015).



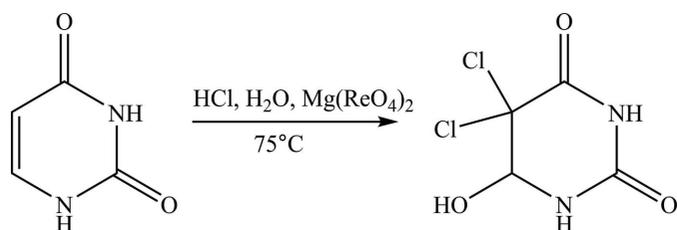


Figure 1
Synthesis scheme of **1**.

5,5-Dichloro-6-hydroxydihydropyrimidine-2,4(1*H*,3*H*)-dione (**1**) was earlier synthesized by two reaction schemes starting with uracil: (1) by addition of Cl₂ in H₂O (Johnson *et al.*, 1943) or (2) by addition of Na₂S₂O₈ and NaCl in acetic acid (Itahara *et al.*, 1986). We have found a new reaction for the synthesis of **1** by the reaction of uracil with hydrochloric acid and water in the presence of Mg(ReO₄)₂ as a catalyst. The reaction scheme is shown in Fig. 1.

2. Structural commentary

The title compound crystallizes in the space group *C2/c* with eight molecules in the unit cell. The asymmetric unit is illustrated in Fig. 2. A similar compound with a methyl group instead of an H atom at C5 (ZEQYIF; Kasradze *et al.*, 2012; ZEQYIF01; Sharutin, 2016) crystallizes in the space group *P1̄*. The six-membered ring adopts a half-chair conformation, as in ZEQYIF (Kasradze *et al.*, 2012). The largest angle at nitrogen atom, C6–N1–C2, is 126.69 (13)°. The angle involving the two chlorine atoms, Cl1–C5–Cl2, is 109.29 (8)°. The two C–N bonds at the N1 atom are similar in length while those at N3 differ because of the N3–C2 *sp*²-conjugation, the latter bond being only 1.344 (2) Å (Table 1). The six atoms N3, C2, O2, N1, C6 and O1 are almost planar (r.m.s. deviation of fitted atoms = 0.0462 Å) while the two other ring atoms of the ring

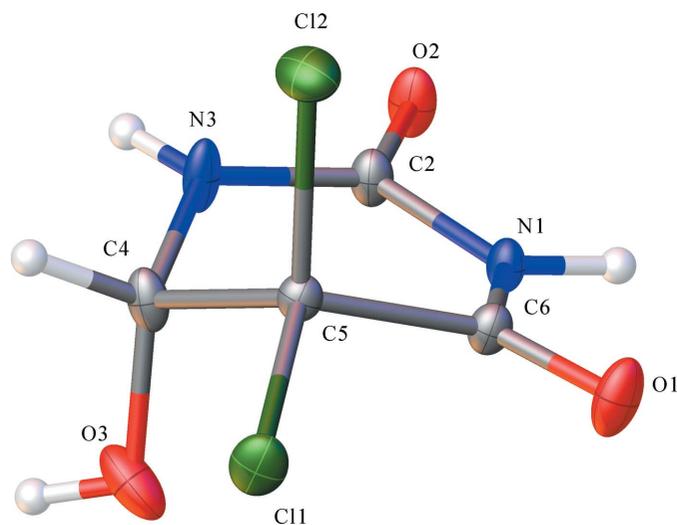


Figure 2
Molecular structure of the title compound, including atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Selected geometric parameters (Å, °).

N1–C6	1.3658 (19)	N3–C4	1.447 (2)
N1–C2	1.375 (2)	C4–C5	1.531 (2)
N3–C2	1.344 (2)	C5–C6	1.536 (2)
C6–N1–C2	126.69 (13)	Cl1–C5–Cl2	109.29 (8)

C4 and C5 are displaced from this plane by –0.275 (2) and 0.411 (3) Å, respectively, forming the above mentioned half-chair.

3. Supramolecular features

The hydrogen-bond system is shown in Fig. 3. In the structure, there are two bifurcated hydrogen bonds. O3–H3 forms a bifurcated hydrogen bond with the O1ⁱ and O2ⁱⁱ atoms [symmetry codes: (i) *x*, *y* + 1, *z*; (ii) *x*, –*y* + 2, *z* + ½] of different molecules. The C4–H4A···O1ⁱ hydrogen bond also involves O1ⁱ with a H4A···O1ⁱ distance of 3.058 (2) Å (Table 2). In the similar compound ZEQYIF (Kasradze *et al.*, 2012), the OH group participates as proton donor in a very strong hydrogen bond with the O atom of one of the CO groups of a neigh-

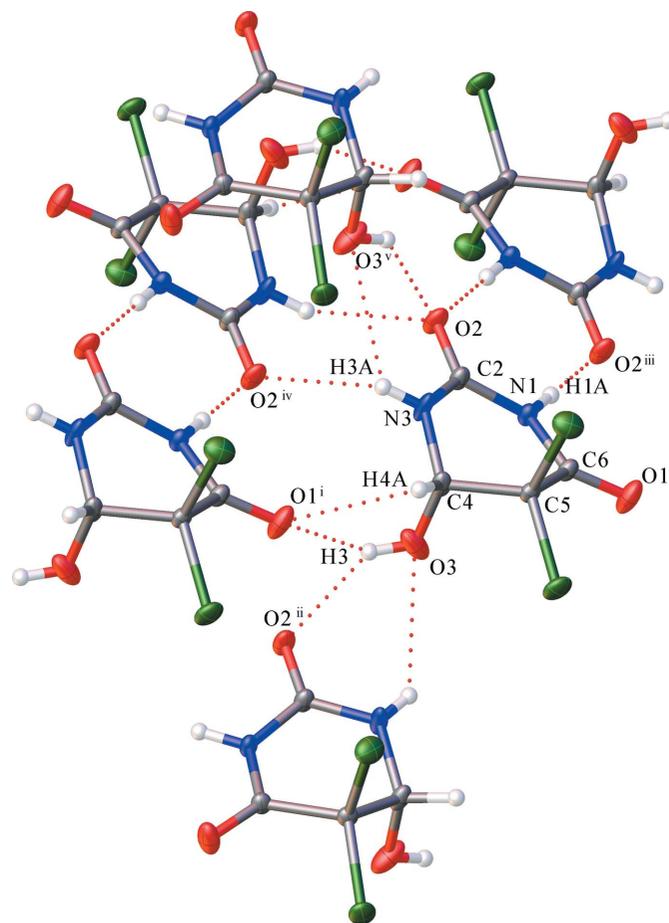


Figure 3
View showing the hydrogen bonds in **1**. [Symmetry codes: (i) *x*, *y* + 1, *z*; (ii) *x*, –*y* + 2, *z* + ½; (iii) –*x*, –*y* + 1, –*z* + 1; (iv) –*x*, –*y* + 2, –*z* + 1; (v) *x*, –*y* + 2, *z* – ½.]

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O3-H3\cdots O1^i$	0.81 (2)	2.41 (2)	3.045 (2)	136 (2)
$O3-H3\cdots O2^{ii}$	0.81 (2)	2.16 (2)	2.8076 (18)	138 (2)
$N1-H1A\cdots O2^{iii}$	0.89 (2)	1.91 (2)	2.7932 (17)	178 (2)
$N3-H3A\cdots O2^{iv}$	0.79 (2)	2.46 (2)	3.0978 (19)	138 (2)
$N3-H3A\cdots O3^v$	0.79 (2)	2.60 (2)	3.147 (2)	128 (2)
$C4-H4A\cdots O1^i$	1.00	2.45	3.058 (2)	119

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

bouring molecule. In our crystal structure, such strong hydrogen bonds are absent. $N3-H3A$ forms a bifurcated hydrogen bond weaker than $O3-H3$ with atoms $O2^{iv}$ and $O3^v$ [symmetry codes: (iv) $-x, -y + 2, -z + 1$; (v) $x, -y + 2, z - \frac{1}{2}$] of different molecules. The strongest hydrogen bond is $N1-H1A\cdots O2^{iii}$ [symmetry code: (iii) $-x, -y + 1, -z + 1$] with an $N1\cdots O2^{iii}$ distance of 2.793 (2) Å. The hydrogen bonds connect the molecules into double layers parallel to the (100) plane, as shown in Fig. 4. Halogen bonds $Cl1\cdots Cl1^{vi}$ [3.3670 (9) Å] and $Cl2\cdots Cl2^{vii}$ [3.3568 (8) Å; symmetry codes: (vi) $\frac{1}{2} - x, \frac{3}{2} - y, 2 - z$; (vii) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$] connect the layers, forming a three-dimensional framework.

4. Hirshfeld surface analysis

The *Crystal Explorer 17.5* (Turner *et al.*, 2017) program was used to analyse the interactions within the crystal. The donor-acceptor groups are visualized using a standard (high) surface resolution and d_{norm} surfaces are mapped over a fixed colour

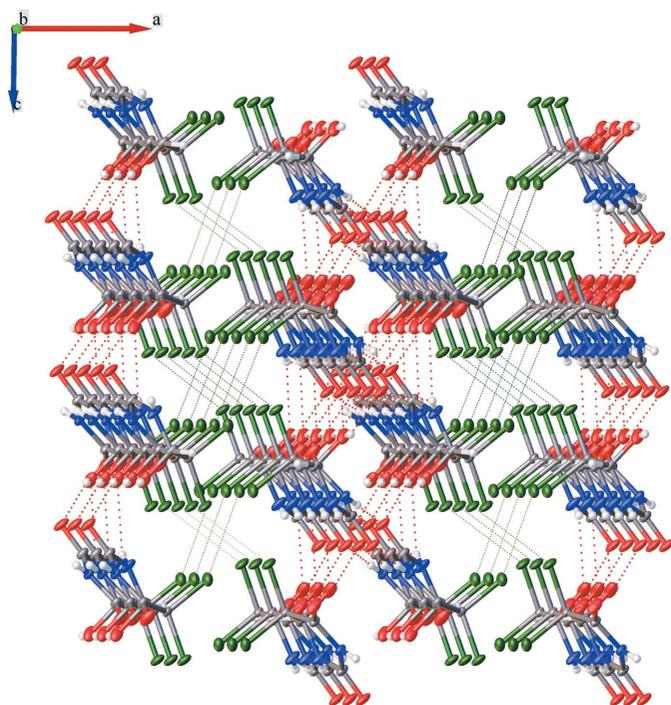


Figure 4
Crystal packing of **1** showing the double layers with halogen bonds between them.

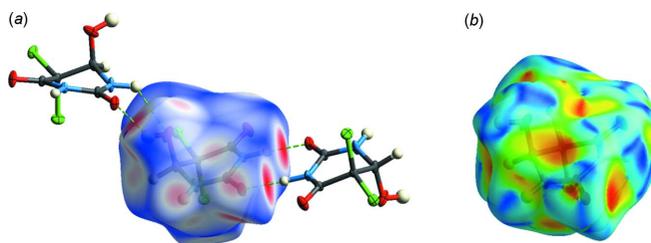


Figure 5
Hirshfeld surface mapper over (a) d_{norm} and (b) shape-index to visualize the interactions in the title compound.

scale of -0.640 (red) to 0.986 (blue) a.u., as illustrated in Fig. 5. Red spots on the surface of the d_{norm} plot indicate inter-

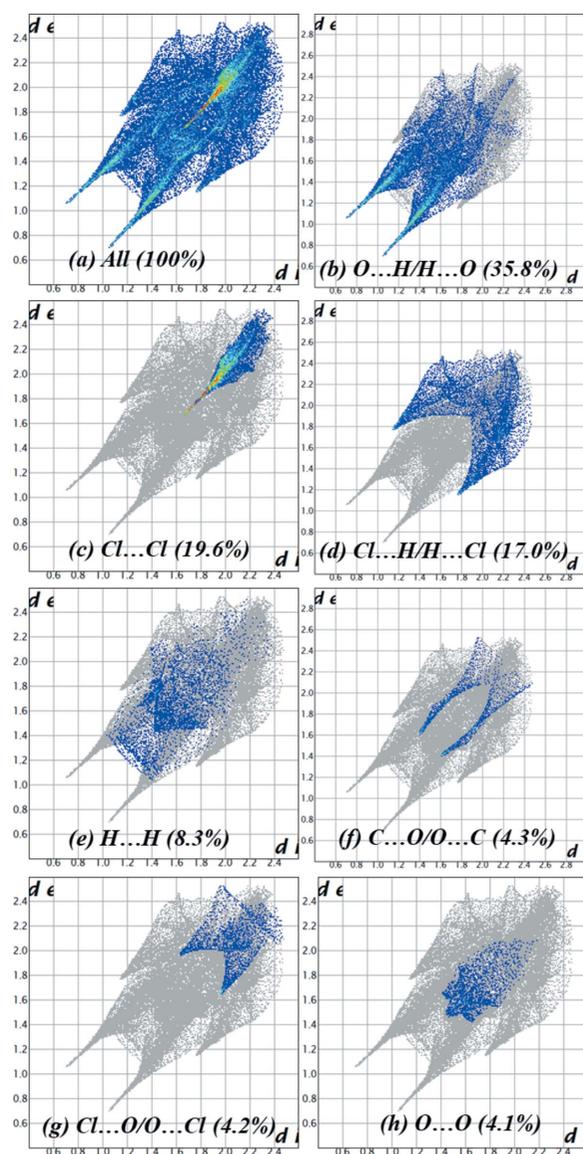


Figure 6
(a) A full two-dimensional fingerprint plot for the title compound, together with those delineated into (b) $O\cdots H/H\cdots O$, (c) $Cl\cdots Cl$, (d) $Cl\cdots H/H\cdots Cl$, (e) $H\cdots H$, (f) $C\cdots O/O\cdots C$, (g) $Cl\cdots O/O\cdots Cl$ and (h) $O\cdots O$ contacts.

molecular contacts involving the hydrogen and halogen bonds. The brightest red spots correspond to the strongest hydrogen bonds, N1—H1A···O2 and O3—H3···O2 (Table 2). There are no π – π interactions in the molecule, as can be seen from Fig. 5*b* by the absence of characteristic triangles. The fingerprint plots (Fig. 6) show that the O···H/H···O contacts (35.8%) make the largest contribution to the overall packing of the crystal, which is due to the fact that hydrogen bonds of the O—H···O and N—H···O types are predominantly formed in the crystal. Then, the Cl···Cl (19.6%) and Cl···H/H···Cl (17.0%) contacts make approximately the same contribution. H···H (8.3%) contacts make an insignificant contribution, similarly for the C···O/O···C (4.3%), Cl···O/O···Cl (4.2%) and O···O (4.1%) contacts, which make approximately the same contribution. Other contacts make weaker contributions to the packaging and are not shown in Fig. 6.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.41, update of November 2019; Groom *et al.*, 2016) for different possible substituents at C4 and C5 atoms gave only a few results. A similar compound was found with a methyl group instead of an H atom at C5 (ZEQYIF; Kasradze *et al.*, 2012; ZEQYIF01; Sharutin, 2016). In *cis*-thymine glycol (THYGLY10; Flippen, 1973), one of the chlorine atoms is replaced by an OH group, and the second chlorine atom is replaced by a methyl group. FUFDT (Flippen-Anderson, 1987) is the same as *cis*-thymine glycol, except that the H atom in the hydroxyl group is replaced by OH group and water of crystallization is present.

6. Synthesis and crystallization

The title compound was synthesized by adding 5 mg of uracil (Sigma Aldrich) to 1 ml of 1 mol l⁻¹ hydrochloric acid aqueous solution in the presence of magnesium perchlorate. This solution was heated in a water bath (at 348 K) until the components were completely dissolved. Crystallization occurred with isothermal evaporation of the resulting solution at room temperature for several weeks, giving colourless needle-shaped crystals, composition according to chemical analysis (obs./calc.): C, 24.12/24.14; H, 2.04/2.03; Cl, 35.64/35.63; N, 14.07/14.08; O, 24.13/24.12. Crystals suitable for a X-ray structural analysis were extracted manually from this batch.

We suggest a possible mechanism of the observed reaction. Typically, ReO₄⁻ does not react with HCl while TcO₄⁻ is actively reduced (German *et al.*, 2002). We found that in the presence of Mg²⁺, the ReO₄⁻ being distorted according to (Khrustalev, 2000; Ravi *et al.*, 2018) attacks the HCl, forming Cl₂ that is readily reacted with water to form HOCl. In the air and in low acidic HCl·H₂O solution, the Re is then oxidized back to Re^{VII}. Cl₂ is thus formed by the action of hydrochloric acid on the rhenium salt as a result of a redox reaction. The process of hypohalogenation is then likely to occur. Since the

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₄ H ₄ Cl ₂ N ₂ O ₃
<i>M_r</i>	198.99
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.9042 (10), 6.6243 (4), 10.5636 (7)
β (°)	90.819 (4)
<i>V</i> (Å ³)	1392.68 (14)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.89
Crystal size (mm)	0.50 × 0.10 × 0.02
Data collection	
Diffractometer	Bruker Kappa APEXII area-detector diffractometer
Absorption correction	Multi-scan (SADABS; Bruker, 2008)
<i>T_{min}</i> , <i>T_{max}</i>	0.802, 0.983
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	12430, 3046, 2128
<i>R_{int}</i>	0.045
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.807
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.042, 0.103, 1.02
No. of reflections	3046
No. of parameters	109
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.91, -0.55

Computer programs: APEX2 and SAINT-Plus (Bruker, 2012), SHELXS97 (Sheldrick, 2008) and SHELXL2018 (Sheldrick, 2015).

reaction takes place in an aqueous medium, the formation of hypohalogenic acid is possible by the reaction Cl₂ + H₂O = HOCl + HCl. Hypohalogenation is usually carried out with an aqueous solution of halogen. The addition to positions 5 and 6 is electrophilic, in accordance with the electron-density distribution. The partially positively charged halogen atom is directed towards carbon C5, which has a higher partial negative charge compared to the C6 atom, towards which the hydroxyl is directed. Then, at position C5, hydrogen is possibly replaced by Cl₂ by electrophilic (more likely in an aqueous medium) and possibly through radical substitution.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C-bound hydrogen atom was placed at a calculated position (C—H = 1.00 Å) and refined using a riding-atom model [*U*_{iso}(H) = 1.2*U*_{eq}(C)]. O- and N-bound H atoms were refined isotropically [*U*_{iso}(H) = 1.2*U*_{eq}(O, N)].

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5,5-Dichloro-6-hydroxydihydropyrimidine-2,4(1*H*,3*H*)-dione: molecular and crystal structure, Hirshfeld surface analysis and the new route for synthesis with $\text{Mg}(\text{ReO}_4)_2$ as a new catalyst

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Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT-Plus* (Bruker, 2012); data reduction: *SAINT-Plus* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015).

5,5-Dichloro-6-hydroxydihydropyrimidine-2,4(1*H*,3*H*)-dione

Crystal data

$\text{C}_4\text{H}_4\text{Cl}_2\text{N}_2\text{O}_3$	$F(000) = 800$
$M_r = 198.99$	$D_x = 1.898 \text{ Mg m}^{-3}$
Monoclinic, <i>C2/c</i>	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 19.9042 (10) \text{ \AA}$	Cell parameters from 3314 reflections
$b = 6.6243 (4) \text{ \AA}$	$\theta = 3.8\text{--}34.7^\circ$
$c = 10.5636 (7) \text{ \AA}$	$\mu = 0.89 \text{ mm}^{-1}$
$\beta = 90.819 (4)^\circ$	$T = 100 \text{ K}$
$V = 1392.68 (14) \text{ \AA}^3$	Needle, colourless
$Z = 8$	$0.50 \times 0.10 \times 0.02 \text{ mm}$

Data collection

Bruker Kappa APEXII area-detector diffractometer	3046 independent reflections
φ and ω scans	2128 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$R_{\text{int}} = 0.045$
$T_{\text{min}} = 0.802$, $T_{\text{max}} = 0.983$	$\theta_{\text{max}} = 35.0^\circ$, $\theta_{\text{min}} = 4.1^\circ$
12430 measured reflections	$h = -32 \rightarrow 31$
	$k = -9 \rightarrow 10$
	$l = -17 \rightarrow 16$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 0.922P]$
$wR(F^2) = 0.103$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3046 reflections	$\Delta\rho_{\text{max}} = 0.91 \text{ e \AA}^{-3}$
109 parameters	$\Delta\rho_{\text{min}} = -0.55 \text{ e \AA}^{-3}$
3 restraints	

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.18354 (2)	0.69299 (6)	0.90632 (4)	0.02208 (10)
C12	0.22188 (2)	0.68819 (7)	0.64394 (4)	0.02409 (11)
O1	0.11148 (7)	0.36996 (19)	0.76917 (14)	0.0270 (3)
O2	0.01449 (6)	0.75547 (19)	0.46558 (12)	0.0218 (3)
O3	0.07140 (7)	0.9344 (2)	0.82106 (14)	0.0296 (3)
H3	0.0619 (12)	1.052 (3)	0.828 (2)	0.036*
N1	0.05958 (6)	0.57272 (19)	0.62634 (13)	0.0142 (2)
H1A	0.0352 (10)	0.469 (3)	0.598 (2)	0.017*
N3	0.08836 (7)	0.9086 (2)	0.60091 (15)	0.0209 (3)
H3A	0.0803 (11)	1.010 (4)	0.564 (2)	0.025*
C2	0.05203 (8)	0.7500 (2)	0.55987 (15)	0.0160 (3)
C4	0.11860 (8)	0.9140 (2)	0.72628 (16)	0.0177 (3)
H4A	0.152164	1.026060	0.731982	0.021*
C5	0.15341 (7)	0.7110 (2)	0.74935 (15)	0.0135 (3)
C6	0.10627 (7)	0.5334 (2)	0.71907 (15)	0.0148 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.02396 (18)	0.0258 (2)	0.01618 (18)	−0.00256 (15)	−0.01093 (14)	0.00345 (15)
C12	0.01459 (16)	0.0329 (2)	0.0248 (2)	−0.00212 (15)	0.00148 (14)	−0.00355 (17)
O1	0.0290 (6)	0.0180 (6)	0.0334 (8)	−0.0055 (5)	−0.0147 (5)	0.0107 (5)
O2	0.0269 (6)	0.0176 (5)	0.0204 (6)	−0.0034 (4)	−0.0153 (5)	0.0025 (5)
O3	0.0226 (6)	0.0338 (7)	0.0323 (8)	0.0093 (5)	−0.0071 (5)	−0.0185 (6)
N1	0.0149 (5)	0.0114 (5)	0.0160 (6)	−0.0017 (4)	−0.0059 (4)	0.0003 (5)
N3	0.0280 (7)	0.0099 (6)	0.0242 (8)	−0.0025 (5)	−0.0163 (6)	0.0042 (5)
C2	0.0174 (6)	0.0133 (6)	0.0169 (7)	−0.0003 (5)	−0.0075 (5)	0.0008 (5)
C4	0.0195 (7)	0.0133 (6)	0.0200 (7)	0.0019 (5)	−0.0104 (6)	−0.0028 (6)
C5	0.0122 (5)	0.0149 (6)	0.0132 (6)	0.0001 (5)	−0.0038 (5)	0.0013 (5)
C6	0.0147 (6)	0.0143 (6)	0.0152 (7)	−0.0011 (5)	−0.0048 (5)	0.0025 (5)

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

C11—C5	1.7592 (15)	N1—H1A	0.89 (2)
C12—C5	1.7787 (16)	N3—C2	1.344 (2)
O1—C6	1.2086 (19)	N3—C4	1.447 (2)
O2—C2	1.2371 (18)	N3—H3A	0.79 (2)
O3—C4	1.389 (2)	C4—C5	1.531 (2)
O3—H3	0.805 (16)	C4—H4A	1.0000

N1—C6	1.3658 (19)	C5—C6	1.536 (2)
N1—C2	1.375 (2)		
C4—O3—H3	109.1 (19)	O3—C4—H4A	110.0
C6—N1—C2	126.69 (13)	N3—C4—H4A	110.0
C6—N1—H1A	117.2 (13)	C5—C4—H4A	110.0
C2—N1—H1A	115.5 (13)	C4—C5—C6	111.48 (12)
C2—N3—C4	121.97 (14)	C4—C5—C11	110.91 (11)
C2—N3—H3A	113.8 (17)	C6—C5—C11	110.09 (10)
C4—N3—H3A	120.2 (17)	C4—C5—C12	108.90 (11)
O2—C2—N3	123.56 (15)	C6—C5—C12	106.02 (11)
O2—C2—N1	119.77 (14)	C11—C5—C12	109.29 (8)
N3—C2—N1	116.65 (13)	O1—C6—N1	122.56 (14)
O3—C4—N3	112.65 (13)	O1—C6—C5	123.13 (13)
O3—C4—C5	106.26 (14)	N1—C6—C5	114.24 (13)
N3—C4—C5	107.77 (13)		
C4—N3—C2—O2	164.69 (16)	O3—C4—C5—C12	-172.67 (10)
C4—N3—C2—N1	-17.2 (2)	N3—C4—C5—C12	66.35 (14)
C6—N1—C2—O2	169.06 (16)	C2—N1—C6—O1	-176.62 (17)
C6—N1—C2—N3	-9.1 (3)	C2—N1—C6—C5	0.6 (2)
C2—N3—C4—O3	-70.5 (2)	C4—C5—C6—O1	-152.65 (17)
C2—N3—C4—C5	46.4 (2)	C11—C5—C6—O1	-29.1 (2)
O3—C4—C5—C6	70.70 (16)	C12—C5—C6—O1	88.98 (18)
N3—C4—C5—C6	-50.28 (18)	C4—C5—C6—N1	30.10 (19)
O3—C4—C5—C11	-52.36 (14)	C11—C5—C6—N1	153.63 (12)
N3—C4—C5—C11	-173.35 (11)	C12—C5—C6—N1	-88.27 (14)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 \cdots O1 ⁱ	0.81 (2)	2.41 (2)	3.045 (2)	136 (2)
O3—H3 \cdots O2 ⁱⁱ	0.81 (2)	2.16 (2)	2.8076 (18)	138 (2)
N1—H1A \cdots O2 ⁱⁱⁱ	0.89 (2)	1.91 (2)	2.7932 (17)	178 (2)
N3—H3A \cdots O2 ^{iv}	0.79 (2)	2.46 (2)	3.0978 (19)	138 (2)
N3—H3A \cdots O3 ^v	0.79 (2)	2.60 (2)	3.147 (2)	128 (2)
C4—H4A \cdots O1 ⁱ	1.00	2.45	3.058 (2)	119

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