



# Crystal structure and Hirshfeld surface analysis of (*E*)-6-(4-hydroxy-3-methoxystyryl)-4,5-dihydropyridazin-3(2*H*)-one

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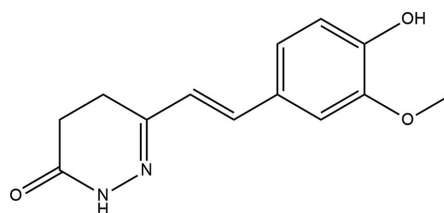
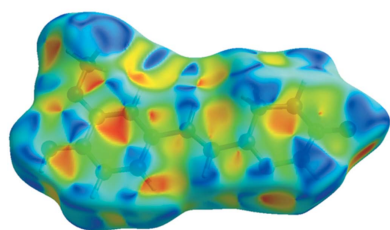
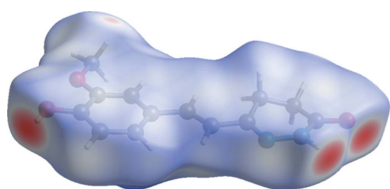
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In the title compound, C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>, the dihydropyridazine ring (r.m.s. deviation = 0.166 Å) has a screw-boat conformation. The dihedral angle between its mean plane and the benzene ring is 0.77 (12)°. In the crystal, intermolecular O—H···O hydrogen bonds generate C(5) chains and N—H···O hydrogen bonds produce R<sub>2</sub><sup>2</sup>(8) motifs. These types of interactions lead to the formation of layers parallel to (12 $\bar{1}$ ). The three-dimensional network is achieved by C—H···O interactions, including R<sub>2</sub><sup>4</sup>(8) motifs. Intermolecular interactions were additionally investigated using Hirshfeld surface analysis and two-dimensional fingerprint plots. The most significant contributions to the crystal packing are by H···H (43.3%), H···C/C···H (19.3%), H···O/H···O (22.6%), C···N/N···C (3.0%) and H···N/N···H (5.8%) contacts. C—H··· $\pi$  interactions and aromatic  $\pi$ – $\pi$  stacking interactions are not observed.

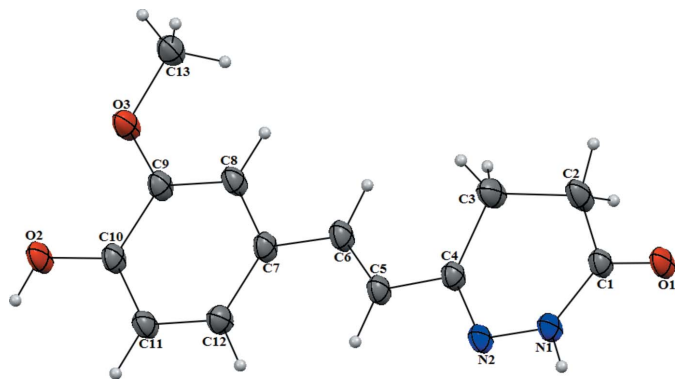
## 1. Chemical context

For decades the chemistry of pyridazinones has been an interesting field. This nitrogen heterocycle became a scaffold of choice for the development of potential drug candidates (Akhtar *et al.*, 2016; Dubey & Bhosle, 2015) because pyridazinone and its substituted derivatives are important pharmacophores possessing many different biological applications (Asif, 2014). Such compounds are used as anti-HIV (Livermore *et al.*, 1993), antimicrobial (Sönmez *et al.*, 2006), anti-convulsant (Partap *et al.*, 2018), antihypertensive (Siddiqui *et al.*, 2011), antidepressant (Boukharsa *et al.*, 2016), analgesic (Gökçe *et al.*, 2009), anti-inflammatory (Barberot *et al.*, 2018), antihistaminic (Tao *et al.*, 2012), cardiotoxic (Wang *et al.*, 2008) and herbicidal agents (Asif, 2013) or as glucan synthase inhibitors (Zhou *et al.*, 2011).

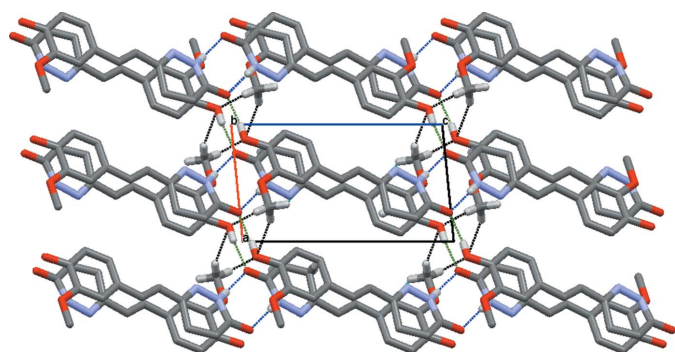


In continuation of our studies related to molecular structures and Hirshfeld surface analysis of new heterocyclic derivatives (Daoui *et al.*, 2019a,b; El Kalai *et al.*, 2019;





**Figure 1**  
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
The crystal packing of the title compound, with N–H...O, O–H...O and C–H...O interactions shown as blue, green and black dashed lines, respectively.

Karrouchi *et al.*, 2015), we report herein on the synthesis, molecular and crystal structures of (*E*)-6-(4-hydroxy-3-meth-

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

<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>
O2–H2...O1 <sup>i</sup>	0.82	1.86	2.671 (2)	168
N1–H1...O1 <sup>ii</sup>	0.86	2.02	2.875 (3)	170
C13–H13A...O2 <sup>iii</sup>	0.96	2.51	3.465 (3)	172
C13–H13C...O2 <sup>iv</sup>	0.96	2.57	3.489 (4)	159

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

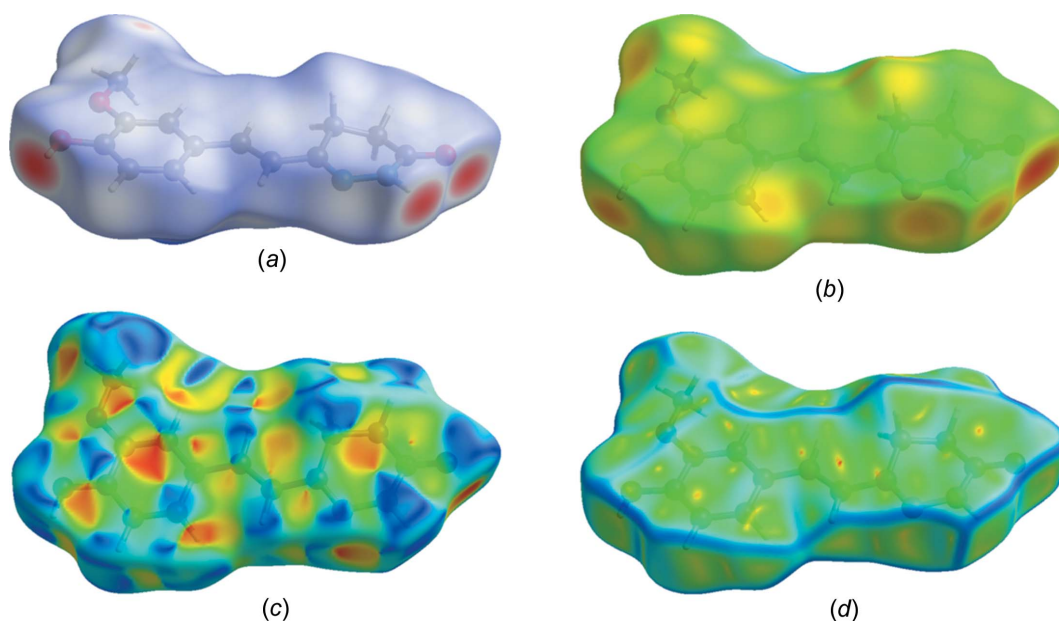
oxystyryl)-4,5-dihydropyridazin-3(2*H*)-one, as well as an analysis of the Hirshfeld surfaces.

## 2. Structural commentary

In the title molecule (Fig. 1), the configuration relative to the double bond at C5 and C6 is *E*. The dihydropyridazine ring has a screw-boat conformation, with an r.m.s. deviation of 0.166 Å for the ring atoms, with the maximum deviation from the ring being 0.178 (3) Å for the C3 atom; the C2 atom lies –0.177 (3) Å out of the plane in the opposite direction relative to the C3 atom. The dihedral angle between the dihydropyridazine ring mean plane and the benzene ring (C7–C12) is 0.77 (12)°, indicating an almost planar conformation of the molecule favouring delocalization over the C4–C5=C6–C7 bridge.

## 3. Supramolecular features

In the crystal, molecules are stacked in rows parallel to [100]. Notably, no significant C–H... $\pi$  or  $\pi$ – $\pi$  interactions are observed. O2–H2...O1<sup>i</sup> hydrogen bonds between the phenolic OH group and the carbonyl O atom of a neighbouring molecule generate *C*(5) chains extending parallel to

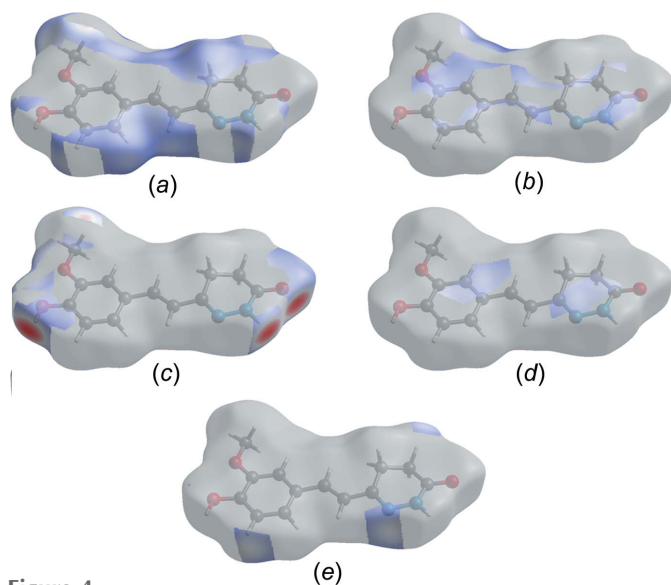


**Figure 3**  
(*a*)  $d_{\text{norm}}$  mapped on the Hirshfeld surface for visualizing the intermolecular interactions, (*b*)  $d_c$  mapped on the surface, (*c*) shape-index map of the title compound and (*d*) curvedness map of the title compound using a range from –4 to 4 Å.

[101]. Likewise,  $N1-H1 \cdots O1^{ii}$  hydrogen bonds between the N–H function of the dihydropyridazine ring and the carbonyl O atom generate centrosymmetric dimers with an  $R_2^2(8)$  motif. The two types of hydrogen bonding result in the formation of layers parallel to  $(12\bar{1})$ . A three-dimensional supramolecular network is eventually formed through intermolecular  $C13-H13A \cdots O2^{iii}$  and  $C13-H13C \cdots O2^{iv}$  hydrogen bonds with  $R_2^2(8)$  motifs (Fig. 2 and Table 1).

#### 4. Database survey

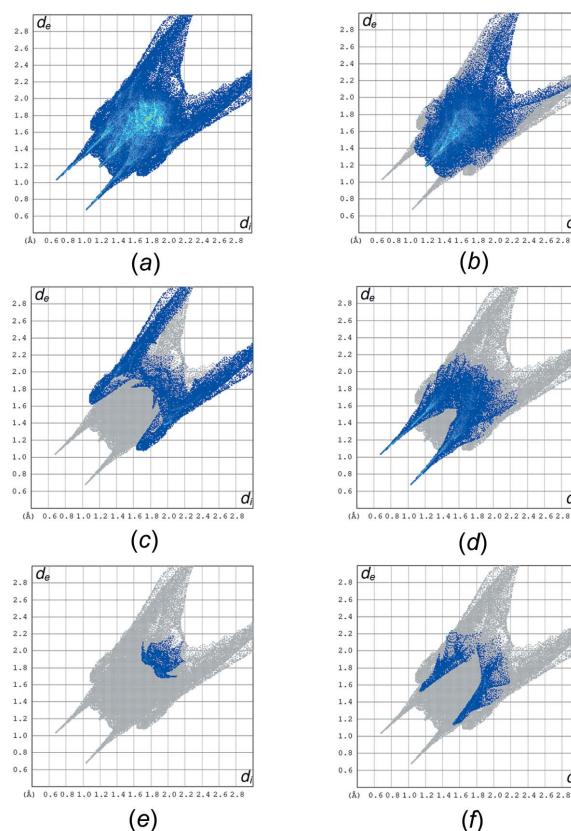
A search of the Cambridge Structural Database (CSD, Version 5.40, update November 2018; Groom *et al.*, 2016) revealed two structures containing a similar pyridazinone moiety as in the title structure but with different substituents, *viz.* 6-phenyl-4,5-dihydropyridazin-3(2*H*)-one (CSD refcode TADQUL; Abourichaa *et al.*, 2003) and (*R*)-(-)-6-(4-aminophenyl)-5-methyl-4,5-dihydropyridazin-3(2*H*)-one (ADIGOK; Zhang *et al.*, 2006). In the structure of TADQUL, the dihydropyridazine ring adopts a half-chair conformation, with atoms C1, N2, N3 and C4 in a common plane, with C5 0.222 (2) Å and C6 0.262 (2) Å on opposite sides of this plane. The plane is almost coplanar with the 4-aminophenyl ring, the dihedral angle between the two planes being 1.73 (9) Å. In the crystal, hydrogen-bonded centrosymmetric dimers are observed. The  $O1=C1$  bond length is 1.2316 (14) Å. The  $N3-C4$ ,  $N2-N3$  and  $N2-C1$  bond lengths are 1.3464 (15), 1.3877 (14) and 1.2830 (15) Å, respectively. In the structure of ADIGOK, the asymmetric unit consists of two molecules of the same enantiomer, and the crystal packing is stabilized by intermolecular  $N-H \cdots O$  hydrogen bonds.



**Figure 4**  
The Hirshfeld surface representations with the function  $d_{\text{norm}}$  plotted onto the surface for (a)  $H \cdots H$ , (b)  $H \cdots C/C \cdots H$ , (c)  $H \cdots O/O \cdots H$ , (d)  $C \cdots N/N \cdots C$  and (e)  $H \cdots N/N \cdots H$  interactions.

#### 5. Hirshfeld surface analysis

Hirshfeld surface analysis was used to quantify the intermolecular interactions of the title compound, using *Crystal-Explorer17.5* (Turner *et al.*, 2017). The Hirshfeld surface analysis was planned using a standard (high) surface resolution with the three-dimensional  $d_{\text{norm}}$  surfaces plotted over a fixed colour scale of  $-0.7021$  (red) to  $2.2382$  a.u. (blue). The surfaces mapped over relevant intermolecular contacts are illustrated in Fig. 3. The Hirshfeld surface representations with the function  $d_{\text{norm}}$  plotted onto the surface are shown for the  $H \cdots H$ ,  $H \cdots C/C \cdots H$ ,  $H \cdots O/O \cdots H$ ,  $C \cdots N/N \cdots C$  and  $H \cdots N/N \cdots H$  interactions in Figs. 4(a)–(e), respectively. The overall two-dimensional fingerprint plot and those delineated into  $H \cdots H$ ,  $H \cdots C/C \cdots H$ ,  $H \cdots O/O \cdots H$ ,  $C \cdots N/N \cdots C$  and  $H \cdots N/N \cdots H$  contacts are illustrated in Figs. 5(a)–(f), respectively. The largest interaction is that of  $H \cdots H$ , contributing 43.3% to the overall crystal packing.  $H \cdots C/C \cdots H$  contacts add a 19.3% contribution to the Hirshfeld surface, with the tips at  $d_e + d_i \sim 2.72$  Å.  $H \cdots O/O \cdots H$  contacts make a 22.6% contribution to the Hirshfeld surface and are represented by a pair of sharp spikes in the region  $d_e + d_i \sim 2.70$  Å in the fingerprint plot.  $H \cdots O/O \cdots H$  interactions arise from intermolecular  $O-H \cdots O$  hydrogen bonding and  $C-H \cdots O$



**Figure 5**  
The full two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and delineated into (b)  $H \cdots H$ , (c)  $H \cdots C/C \cdots H$ , (d)  $H \cdots O/O \cdots H$ , (e)  $C \cdots N/N \cdots C$  and (f)  $H \cdots N/N \cdots H$  interactions.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>
<i>M<sub>r</sub></i>	246.26
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.0828 (9), 9.4246 (13), 11.1724 (16)
$\alpha$ , $\beta$ , $\gamma$ (°)	75.838 (11), 83.099 (12), 84.059 (11)
<i>V</i> (Å <sup>3</sup> )	614.70 (16)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.10
Crystal size (mm)	0.72 × 0.39 × 0.16
Data collection	
Diffraction	Stoe IPDS 2
Absorption correction	Integration ( <i>X-RED32</i> ; Stoe & Cie, 2002)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.944, 0.989
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	6563, 2426, 1506
<i>R<sub>int</sub></i>	0.054
(sin $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.617
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> [ <i>F</i> <sup>2</sup> ], <i>S</i>	0.056, 0.147, 1.00
No. of reflections	2426
No. of parameters	165
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.17, -0.17

Computer programs: *X-AREA* (Stoe & Cie, 2002), *X-RED* (Stoe & Cie, 2002), *SHELXT2017* (Sheldrick, 2015a), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009), *WinGX* (Farrugia, 2012), *SHELXL2018* (Sheldrick, 2015b) and *publCIF* (Westrip, 2010).

contacts. The contributions of the other contacts to the Hirshfeld surface are negligible, *i.e.* C··N/N··C of 3.0% and H··N/N··H of 5.8%.

## 6. Synthesis and crystallization

To a solution of 6-(4-hydroxy-3-methoxyphenyl)-4-oxohex-5-enoic acid (0.25 g, 1 mmol) in 20 ml of ethanol, an equimolar amount of hydrazine hydrate was added. The mixture was maintained under reflux until thin-layer chromatography (TLC) indicated the end of the reaction. After cooling, the precipitate which formed was filtered off, washed with ethanol and recrystallized from ethanol. Slow evaporation at room temperature led to the formation of single crystals of the title compound.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms on C atoms were placed in idealized positions and refined as riding, with C—H = 0.93–0.97 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C) for methyl H atoms and 1.2*U*<sub>eq</sub>(C) otherwise. The NH and OH hydrogens were located in a difference Fourier map and were constrained with N—H = 0.86 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N), and O—H = 0.86 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O), using a riding model.

## Acknowledgements

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of (*E*)-6-(4-hydroxy-3-methoxystyryl)-4,5-dihydropyridazin-3(2*H*)-one

Said Daoui, Cemile Baydere, Fouad El Kalai, Rafik Saddik, Necmi Dege, Khalid Karrouchi and Nouredine Benchat

### 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: *SHELXT2017* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *SHELXL2018* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

### (*E*)-6-(4-Hydroxy-3-methoxystyryl)-4,5-dihydropyridazin-3(2*H*)-one

#### Crystal data

$C_{13}H_{14}N_2O_3$

$M_r = 246.26$

Triclinic,  $P\bar{1}$

$a = 6.0828$  (9) Å

$b = 9.4246$  (13) Å

$c = 11.1724$  (16) Å

$\alpha = 75.838$  (11)°

$\beta = 83.099$  (12)°

$\gamma = 84.059$  (11)°

$V = 614.70$  (16) Å<sup>3</sup>

$Z = 2$

$F(000) = 260$

$D_x = 1.330$  Mg m<sup>-3</sup>

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

Cell parameters from 13077 reflections

$\theta = 2.2\text{--}30.7^\circ$

$\mu = 0.10$  mm<sup>-1</sup>

$T = 293$  K

Prism, yellow

$0.72 \times 0.39 \times 0.16$  mm

#### Data collection

Stoe IPDS 2

diffractometer

Detector resolution: 6.67 pixels mm<sup>-1</sup>

rotation method scans

Absorption correction: integration

(*X-RED32*; Stoe & Cie, 2002)

$T_{\min} = 0.944$ ,  $T_{\max} = 0.989$

6563 measured reflections

2426 independent reflections

1506 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

$\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 2.2^\circ$

$h = -7 \rightarrow 7$

$k = -11 \rightarrow 11$

$l = -13 \rightarrow 13$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.147$

$S = 1.00$

2426 reflections

165 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$$

### 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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.7518 (3)	0.88682 (19)	0.99156 (15)	0.0601 (5)
O3	0.4960 (3)	0.58008 (19)	0.11563 (16)	0.0614 (5)
O2	0.1290 (3)	0.7317 (2)	0.05778 (16)	0.0636 (5)
H2	0.016474	0.786724	0.044599	0.095*
N1	0.4947 (3)	0.9323 (2)	0.85757 (17)	0.0525 (5)
H1	0.429651	0.995567	0.896673	0.063*
N2	0.3918 (3)	0.9139 (2)	0.75870 (17)	0.0519 (5)
C9	0.3982 (4)	0.6576 (2)	0.1986 (2)	0.0497 (6)
C5	0.3927 (4)	0.8291 (3)	0.5807 (2)	0.0506 (6)
H5	0.252921	0.878478	0.572201	0.061*
C1	0.6829 (4)	0.8631 (3)	0.8987 (2)	0.0492 (6)
C4	0.5043 (4)	0.8412 (2)	0.6851 (2)	0.0472 (6)
C8	0.4803 (4)	0.6645 (3)	0.3066 (2)	0.0521 (6)
H8	0.616062	0.614251	0.326018	0.062*
C11	0.0780 (4)	0.8118 (3)	0.2494 (2)	0.0538 (6)
H11	-0.059111	0.860442	0.230853	0.065*
C7	0.3664 (4)	0.7445 (2)	0.3875 (2)	0.0496 (6)
C10	0.1954 (4)	0.7364 (2)	0.1681 (2)	0.0487 (6)
C6	0.4707 (4)	0.7544 (3)	0.4962 (2)	0.0549 (6)
H6	0.607897	0.702171	0.507391	0.066*
C12	0.1607 (4)	0.8164 (3)	0.3580 (2)	0.0552 (6)
H12	0.078822	0.867751	0.411814	0.066*
C13	0.7007 (4)	0.4965 (3)	0.1419 (3)	0.0614 (7)
H13A	0.745228	0.441469	0.079994	0.092*
H13B	0.682204	0.430200	0.222071	0.092*
H13C	0.812721	0.561367	0.141331	0.092*
C2	0.7972 (5)	0.7565 (3)	0.8299 (3)	0.0694 (8)
H2A	0.761992	0.658432	0.875007	0.083*
H2B	0.956271	0.761159	0.827335	0.083*
C3	0.7375 (4)	0.7807 (3)	0.7002 (2)	0.0673 (8)
H3A	0.836608	0.847839	0.645178	0.081*
H3B	0.760060	0.688125	0.675416	0.081*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0632 (11)	0.0804 (12)	0.0479 (10)	0.0136 (8)	-0.0292 (8)	-0.0331 (8)
O3	0.0642 (11)	0.0739 (11)	0.0579 (10)	0.0218 (8)	-0.0273 (9)	-0.0392 (9)
O2	0.0633 (12)	0.0859 (13)	0.0537 (10)	0.0146 (9)	-0.0326 (9)	-0.0349 (9)
N1	0.0536 (12)	0.0686 (13)	0.0448 (11)	0.0094 (9)	-0.0204 (9)	-0.0299 (10)
N2	0.0510 (12)	0.0670 (13)	0.0450 (11)	0.0068 (9)	-0.0213 (9)	-0.0237 (10)
C9	0.0569 (14)	0.0515 (13)	0.0479 (13)	0.0029 (11)	-0.0190 (11)	-0.0217 (11)
C5	0.0550 (14)	0.0602 (14)	0.0422 (12)	0.0029 (11)	-0.0196 (11)	-0.0185 (11)
C1	0.0539 (14)	0.0552 (14)	0.0427 (12)	0.0056 (11)	-0.0182 (11)	-0.0172 (11)
C4	0.0524 (14)	0.0522 (13)	0.0416 (12)	0.0007 (10)	-0.0152 (11)	-0.0168 (10)
C8	0.0533 (14)	0.0584 (14)	0.0511 (14)	0.0074 (11)	-0.0248 (12)	-0.0207 (11)
C11	0.0495 (13)	0.0675 (15)	0.0506 (14)	0.0090 (11)	-0.0211 (11)	-0.0237 (12)
C7	0.0579 (14)	0.0565 (14)	0.0412 (12)	0.0011 (11)	-0.0181 (11)	-0.0204 (11)
C10	0.0540 (14)	0.0560 (14)	0.0432 (13)	-0.0004 (11)	-0.0192 (11)	-0.0202 (11)
C6	0.0601 (15)	0.0640 (15)	0.0467 (13)	0.0033 (12)	-0.0229 (12)	-0.0197 (12)
C12	0.0558 (15)	0.0681 (15)	0.0490 (14)	0.0056 (12)	-0.0149 (12)	-0.0274 (12)
C13	0.0656 (16)	0.0634 (15)	0.0600 (16)	0.0144 (12)	-0.0203 (13)	-0.0248 (13)
C2	0.0734 (18)	0.0867 (19)	0.0599 (16)	0.0316 (14)	-0.0365 (14)	-0.0406 (14)
C3	0.0576 (16)	0.098 (2)	0.0593 (16)	0.0136 (14)	-0.0231 (13)	-0.0423 (15)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C1	1.241 (3)	C8—H8	0.9300
O3—C9	1.362 (3)	C11—C10	1.377 (3)
O3—C13	1.424 (3)	C11—C12	1.379 (3)
O2—C10	1.355 (2)	C11—H11	0.9300
O2—H2	0.8200	C7—C12	1.396 (3)
N1—C1	1.331 (3)	C7—C6	1.462 (3)
N1—N2	1.387 (2)	C6—H6	0.9300
N1—H1	0.8600	C12—H12	0.9300
N2—C4	1.288 (3)	C13—H13A	0.9600
C9—C8	1.378 (3)	C13—H13B	0.9600
C9—C10	1.406 (3)	C13—H13C	0.9600
C5—C6	1.327 (3)	C2—C3	1.493 (3)
C5—C4	1.451 (3)	C2—H2A	0.9700
C5—H5	0.9300	C2—H2B	0.9700
C1—C2	1.480 (3)	C3—H3A	0.9700
C4—C3	1.486 (3)	C3—H3B	0.9700
C8—C7	1.394 (3)		
C9—O3—C13	117.98 (17)	O2—C10—C11	124.3 (2)
C10—O2—H2	109.5	O2—C10—C9	116.1 (2)
C1—N1—N2	127.3 (2)	C11—C10—C9	119.54 (19)
C1—N1—H1	116.4	C5—C6—C7	127.7 (2)
N2—N1—H1	116.4	C5—C6—H6	116.1
C4—N2—N1	117.42 (18)	C7—C6—H6	116.1

O3—C9—C8	126.0 (2)	C11—C12—C7	120.5 (2)
O3—C9—C10	115.23 (18)	C11—C12—H12	119.8
C8—C9—C10	118.8 (2)	C7—C12—H12	119.8
C6—C5—C4	126.4 (2)	O3—C13—H13A	109.5
C6—C5—H5	116.8	O3—C13—H13B	109.5
C4—C5—H5	116.8	H13A—C13—H13B	109.5
O1—C1—N1	120.4 (2)	O3—C13—H13C	109.5
O1—C1—C2	123.3 (2)	H13A—C13—H13C	109.5
N1—C1—C2	116.36 (19)	H13B—C13—H13C	109.5
N2—C4—C5	115.5 (2)	C1—C2—C3	114.4 (2)
N2—C4—C3	122.97 (19)	C1—C2—H2A	108.7
C5—C4—C3	121.5 (2)	C3—C2—H2A	108.7
C9—C8—C7	122.0 (2)	C1—C2—H2B	108.7
C9—C8—H8	119.0	C3—C2—H2B	108.7
C7—C8—H8	119.0	H2A—C2—H2B	107.6
C10—C11—C12	121.0 (2)	C4—C3—C2	113.3 (2)
C10—C11—H11	119.5	C4—C3—H3A	108.9
C12—C11—H11	119.5	C2—C3—H3A	108.9
C8—C7—C12	118.02 (19)	C4—C3—H3B	108.9
C8—C7—C6	118.9 (2)	C2—C3—H3B	108.9
C12—C7—C6	123.1 (2)	H3A—C3—H3B	107.7
C1—N1—N2—C4	-12.5 (4)	O3—C9—C10—O2	-3.3 (3)
C13—O3—C9—C8	0.8 (3)	C8—C9—C10—O2	176.6 (2)
C13—O3—C9—C10	-179.3 (2)	O3—C9—C10—C11	176.6 (2)
N2—N1—C1—O1	-177.3 (2)	C8—C9—C10—C11	-3.5 (4)
N2—N1—C1—C2	1.2 (4)	C4—C5—C6—C7	-177.5 (2)
N1—N2—C4—C5	-177.97 (19)	C8—C7—C6—C5	177.4 (3)
N1—N2—C4—C3	-1.5 (3)	C12—C7—C6—C5	0.0 (4)
C6—C5—C4—N2	-176.7 (3)	C10—C11—C12—C7	0.2 (4)
C6—C5—C4—C3	6.8 (4)	C8—C7—C12—C11	-2.2 (4)
O3—C9—C8—C7	-178.7 (2)	C6—C7—C12—C11	175.2 (2)
C10—C9—C8—C7	1.4 (4)	O1—C1—C2—C3	-159.6 (3)
C9—C8—C7—C12	1.4 (4)	N1—C1—C2—C3	21.9 (4)
C9—C8—C7—C6	-176.1 (2)	N2—C4—C3—C2	23.8 (4)
C12—C11—C10—O2	-177.4 (2)	C5—C4—C3—C2	-160.0 (2)
C12—C11—C10—C9	2.7 (4)	C1—C2—C3—C4	-32.7 (4)

Hydrogen-bond geometry (Å, °)

<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>
O2—H2 $\cdots$ O1 <sup>i</sup>	0.82	1.86	2.671 (2)	168
N1—H1 $\cdots$ O1 <sup>ii</sup>	0.86	2.02	2.875 (3)	170
C13—H13A $\cdots$ O2 <sup>iii</sup>	0.96	2.51	3.465 (3)	172
C13—H13C $\cdots$ O2 <sup>iv</sup>	0.96	2.57	3.489 (4)	159

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