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Synthesis and crystal structure of 2-(2,4-dioxo-6-methylpyran-3-ylidene)-4-(4-hydroxyphenyl)-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine

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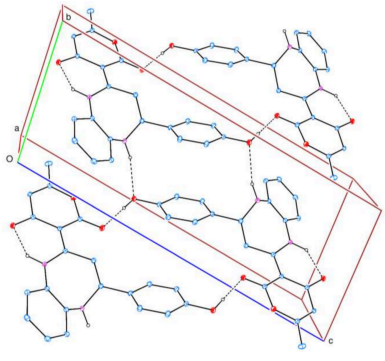
The title compound, $C_{21}H_{18}N_2O_4$, contains non-planar diazepine (in a boat–sofa conformation) and pyran (envelope) rings. In the crystal, O—H···O and N—H···O hydrogen bonds link the molecules, enclosing $R_2^2(16)$ and $R_2^2(24)$ ring motifs, to generate [110] chains. Very weak π–π stacking interactions between the phenyl rings of adjacent molecules with an inter-centroid distance of 4.0264 (9) Å help to consolidate a three-dimensional architecture. The Hirshfeld surface analysis of the crystal structure indicates that the most important contributions for the crystal packing are from H···H (45.1%), H···O/O···H (23.2%) and H···C/C···H (19.2%) interactions.

1. Chemical context

1,5-Benzodiazepine derivatives are known for their potent biological activities, being used as antitubercular agents (Singh *et al.*, 2017), anticonvulsants (Jyoti & Mithlesh, 2013), anti-cancer agents (Gawandi *et al.*, 2021), antimicrobials (An *et al.*, 2016), and antidepressants (Sharma *et al.*, 2017). This study continues our investigation into 1,5-benzodiazepine derivatives, as published by our team in earlier works (El Ghayati *et al.*, 2021; Essaghouani *et al.*, 2017). In this context, we synthesized the title compound, $C_{21}H_{18}N_2O_4$, (**I**), through the condensation reaction of the intermediate 3-[1-(2-amino-phenylimino)-ethyl]-4-hydroxy-6-methyl-pyran-2-one with 4-hydroxybenzaldehyde in ethanol. In this report, we present the synthesis, molecular and crystal structures and Hirshfeld surface analysis of (**I**).



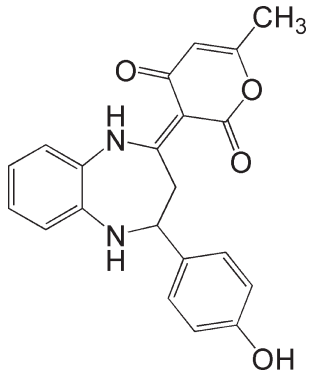


Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O3^{iii}	0.90 (3)	1.86 (3)	2.7597 (15)	178 (2)
N1—H1···O4^{iv}	0.92 (2)	2.21 (2)	3.1028 (16)	165.2 (17)
N2—H2···O1	0.93 (2)	1.80 (2)	2.5882 (15)	140.8 (18)

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

2. Structural commentary

Compound (**I**) contains a benzodiazepine ring system besides pyran and phenyl rings (Fig. 1). The benzene (*A*, C1–C6) and phenyl (*C*, C16–C21) rings are oriented at a dihedral angle of 42.68 (5)°, and atom O4 is displaced by 0.0246 (12) Å from the mean plane of the *C* ring. The seven-membered diazepine ring (*B*, N1/N2/C1/C6–C9) is in a boat–sofa conformation (Boessenkool & Boeyens, 1980) with puckering amplitudes Q_T = 0.9082 (14) Å, q_2 = 0.8845 (14) Å and q_3 = 0.2062 (14) Å: atoms N1, N2, C7 and C9 form the base, C8 the prow and C1 and C6 the stern. On the other hand, the pyran, (*D*, O2/C10–C14), ring is in a shallow envelope conformation with puckering parameters Q_T = 0.0661 (14) Å, θ = 53 (1)° and φ = 5 (2)°. Atom C11 at the flap position is displaced by 0.0802 (14) Å from the best least-squares plane of the other five atoms. An intramolecular N2—H2···O1 hydrogen bond (Table 1) between the diazepine and pyran rings completes an *S*(6) ring motif. Otherwise there are no unusual bond distances or interbond angles in the molecule.

3. Supramolecular features

In the crystal, O4—H4···O3 and N1—H1···O4 hydrogen bonds link the molecules (Fig. 2), enclosing $R_2^2(16)$ and $R_2^2(24)$ ring motifs (Etter *et al.*, 1990). A [110] infinite chain results. A very weak π–π stacking interaction between the *C* rings of adjacent molecules with an inter-centroid distance of 4.0264 (9) Å may help to consolidate the three-dimensional architecture. There are no identified C—H···π(ring) interactions.

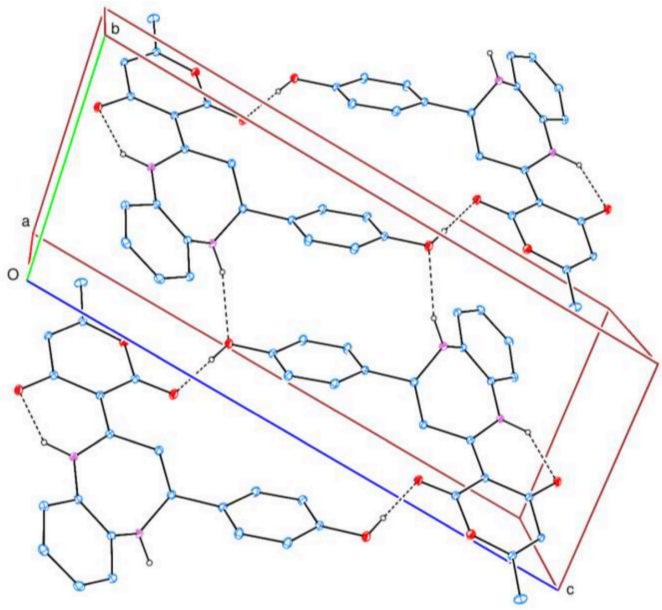


Figure 2
A partial packing diagram of (**I**) viewed down the *a*-axis direction. The intermolecular O—H···O and N—H···O and intramolecular N—H···O hydrogen bonds are shown as dashed lines. The other hydrogen atoms have been omitted for clarity.

4. Hirshfeld surface analysis

To visualize the intermolecular interactions in the crystal of (**I**), a Hirshfeld surface (HS) analysis was carried out using *Crystal Explorer 17.5* (Spackman *et al.*, 2021). Fig. 3 shows the

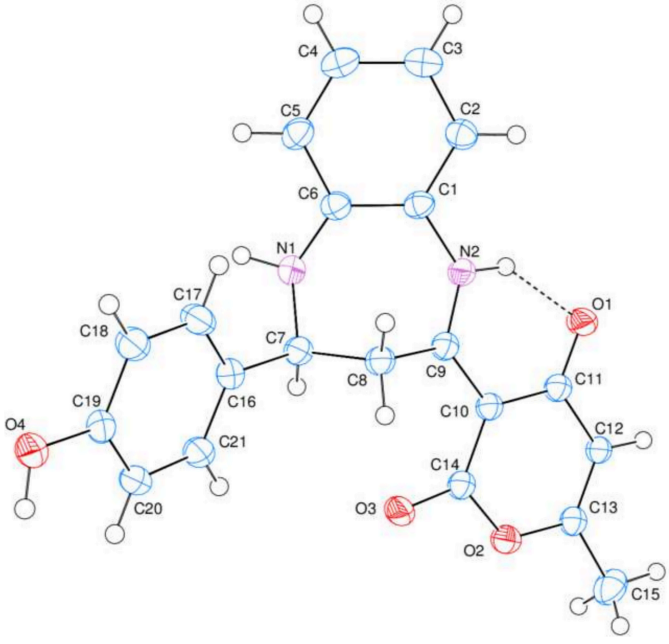


Figure 1
The molecular structure of (**I**) showing 50% probability ellipsoids.

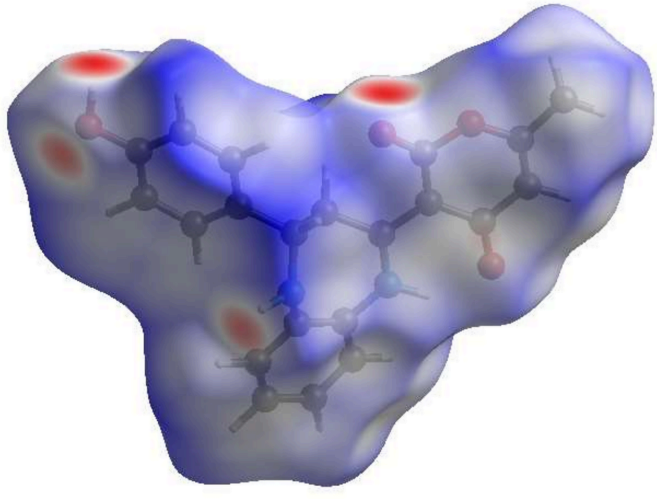


Figure 3
View of the three-dimensional Hirshfeld surface of (**I**) plotted over d_{norm}.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{18}N_2O_4$
M_r	362.37
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	160
a, b, c (Å)	6.3757 (1), 7.7506 (1), 17.9997 (4)
α, β, γ (°)	100.967 (2), 97.373 (2), 100.127 (2)
V (Å^3)	847.49 (3)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.82
Crystal size (mm)	0.10 × 0.03 × 0.02
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Analytical (*CrysAlis PRO*; Rigaku OD, 2024)
T_{min}, T_{max}	0.941, 0.988
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18745, 3608, 3159
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.115, 1.08
No. of reflections	3608
No. of parameters	258
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, −0.32

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

contact distances where the bright-red spots correspond to the respective donors and/or acceptors noted above. According to the two-dimensional fingerprint plots (McKinnon *et al.*, 2007), the H···H, H···O/O···H and H···C/C···H contacts make the most significant contributions to the HS, at 45.1%, 23.2% and 19.2%, respectively (Fig. 4).

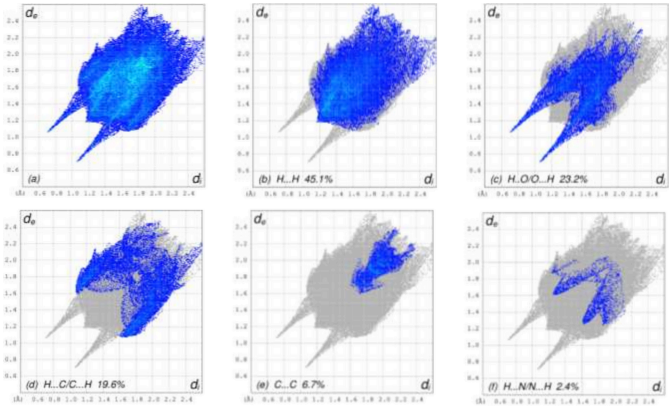
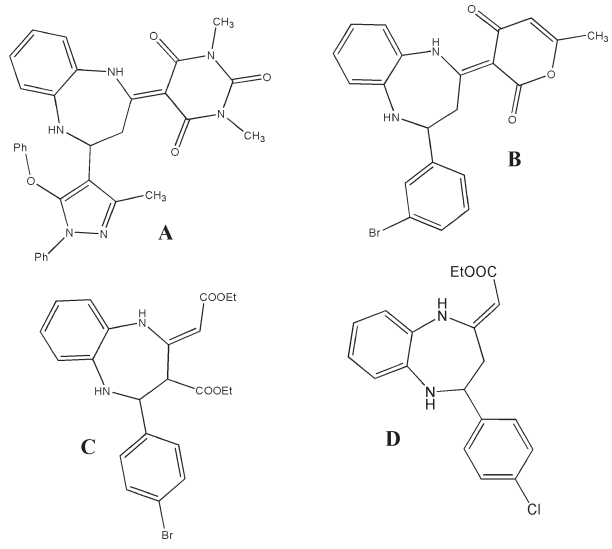


Figure 4
The two-dimensional fingerprint plots for (**I**), showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) H···O/O···H, (*d*) H···C/C···H, (*e*) C···C, (*f*) H···N/N···H interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

5. Database survey

A search of the Cambridge Structural Database (CSD updated to January 2025; Groom *et al.*, 2016) for 2,3,4,5-tetrahydro-1*H*-benzo[*b*][1,4]diazepines substituted at the 2- and 4-positions gave a substantial number of hits, with seven deemed closely similar to the title molecule. These are **A** (Siddiqui & Siddiqui, 2020), compound **B** with R = thiophene and 4-ClC_6H_4, and R' = 6-methyl-2*H*-pyran-2,4(3*H*)-dione, as well as R = 6-methyl-2*H*-pyran-2,4(3*H*)-dione and R' = 3-BrC_6H_4 (Faidallah *et al.*, 2015), and compounds **C** (Wu & Wang, 2020) and **D** (Lal *et al.*, 2013) (see scheme below). All have the tetrahydrodiazepine ring adopting a boat conformation, with total puckering amplitudes ranging from 0.702 (2) (for **A**) to 0.957 (2) Å (for **C**, R = thiophene). The dihedral angles between the mean plane of the benzo ring and those of the ring containing substituents on the seven-membered ring vary considerably, likely due to packing considerations, as the steric bulk of these groups differs markedly.



6. Synthesis and crystallization

A mixture of 3.87 mmol of 3-[1-(2-aminophenylimino)ethyl]-4-hydroxy-6-methyl-pyran-2-one in 40 ml of ethanol with 5.81 mmol of 4-hydroxybenzaldehyde, along with a catalytic amount of trifluoroacetic acid was made up. The reaction mixture was refluxed for 4 h. After cooling and filtration, the formed precipitate was recrystallized from ethanol solution to obtain the title compound (**I**).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The OH and NH hydrogen atoms were located in a difference-Fourier map and the positions were freely refined. The C-bound hydrogen-atom positions were calculated geometrically (C—H = 0.95–1.00 Å depending on hybridization) and refined using a riding model with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

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Synthesis and crystal structure of 2-(2,4-dioxo-6-methylpyran-3-ylidene)-4-(4-hydroxyphenyl)-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine

Imane Faraj, Lhoussaine El Ghayati, Olivier Blacque, Tuncer Hökelek, Ahmed Mazzah, El Mokhtar Essassi and Nada Kheira Sebbar

Computing details

4-(4-Hydroxyphenyl)-2-(6-methyl-2,4-dioxopyran-3-ylidene)-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine

Crystal data

$C_{21}H_{18}N_2O_4$
$M_r = 362.37$
Triclinic, $P\overline{1}$
$a = 6.3757$ (1) Å
$b = 7.7506$ (1) Å
$c = 17.9997$ (4) Å
$\alpha = 100.967$ (2)°
$\beta = 97.373$ (2)°
$\gamma = 100.127$ (2)°
$V = 847.49$ (3) Å^3
$Z = 2$
$F(000) = 380$
$D_x = 1.420$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 9714 reflections
$\theta = 2.5$–$79.1°$
$\mu = 0.82$ mm^{-1}
$T = 160$ K
Needle, yellow
0.10 × 0.03 × 0.02 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: analytical (CrysAlisPro; Rigaku OD, 2024)
$T_{min} = 0.941$, $T_{max} = 0.988$
18745 measured reflections
3608 independent reflections
3159 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 79.4°$, $\theta_{min} = 2.5°$
$h = -8\rightarrow8$
$k = -9\rightarrow7$
$l = -21\rightarrow22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.115$
$S = 1.08$
3608 reflections
258 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 0.3065P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Extinction correction: SHELXL (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0020 (5)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.65055 (17)	0.66657 (15)	0.03539 (6)	0.0334 (3)
O2	1.17867 (16)	0.94555 (14)	0.18839 (6)	0.0314 (2)
O3	1.03777 (17)	0.89041 (15)	0.28886 (6)	0.0352 (3)
O4	0.58361 (18)	0.87903 (15)	0.63441 (6)	0.0335 (3)
H4	0.709 (4)	0.952 (3)	0.6591 (14)	0.060 (7)*
N1	0.47933 (19)	0.44213 (16)	0.28508 (7)	0.0283 (3)
H1	0.462 (3)	0.363 (3)	0.3168 (11)	0.041 (5)*
N2	0.46259 (18)	0.58760 (16)	0.14729 (7)	0.0257 (3)
H2	0.478 (3)	0.574 (3)	0.0958 (12)	0.044 (5)*
C1	0.2753 (2)	0.49401 (18)	0.16861 (8)	0.0255 (3)
C2	0.0839 (2)	0.45358 (19)	0.11617 (8)	0.0289 (3)
H2A	0.081763	0.494087	0.069522	0.035*
C3	−0.1035 (2)	0.3553 (2)	0.13089 (9)	0.0330 (3)
H3	−0.232941	0.326686	0.094441	0.040*
C4	−0.0992 (2)	0.2990 (2)	0.19981 (9)	0.0337 (3)
H4A	−0.227750	0.234648	0.211340	0.040*
C5	0.0913 (2)	0.33631 (19)	0.25171 (8)	0.0306 (3)
H5	0.091044	0.296638	0.298496	0.037*
C6	0.2848 (2)	0.43108 (18)	0.23716 (8)	0.0257 (3)
C7	0.6316 (2)	0.61210 (19)	0.32150 (8)	0.0272 (3)
H7	0.781572	0.592843	0.318419	0.033*
C8	0.5909 (2)	0.75522 (18)	0.27661 (8)	0.0266 (3)
H8A	0.441204	0.773084	0.277664	0.032*
H8B	0.690582	0.870450	0.301855	0.032*
C9	0.6225 (2)	0.70452 (17)	0.19521 (7)	0.0246 (3)
C10	0.8083 (2)	0.78109 (18)	0.16665 (7)	0.0247 (3)
C11	0.8057 (2)	0.75700 (18)	0.08500 (8)	0.0265 (3)
C12	0.9941 (2)	0.84607 (18)	0.06080 (7)	0.0252 (3)
H12	0.994265	0.840831	0.007649	0.030*
C13	1.1697 (2)	0.93642 (18)	0.11166 (8)	0.0270 (3)
C14	1.0025 (2)	0.87205 (18)	0.21893 (8)	0.0266 (3)
C15	1.3704 (3)	1.0348 (2)	0.09359 (11)	0.0425 (4)
H15A	1.398618	1.160599	0.121192	0.064*
H15B	1.354219	1.028990	0.038227	0.064*
H15C	1.491521	0.980219	0.109353	0.064*
C16	0.6170 (2)	0.67727 (19)	0.40544 (8)	0.0281 (3)
C17	0.4208 (2)	0.6658 (2)	0.43198 (8)	0.0337 (3)
H17	0.290729	0.610431	0.397254	0.040*
C18	0.4116 (2)	0.7339 (2)	0.50830 (8)	0.0340 (3)

H18	0.276168	0.724100	0.525576	0.041*
C19	0.6007 (2)	0.81657 (19)	0.55939 (8)	0.0282 (3)
C20	0.7980 (2)	0.8286 (2)	0.53405 (8)	0.0336 (3)
H20	0.927986	0.884150	0.568830	0.040*
C21	0.8048 (2)	0.7590 (2)	0.45751 (8)	0.0328 (3)
H21	0.940413	0.767471	0.440438	0.039*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0320 (5)	0.0402 (6)	0.0219 (5)	−0.0044 (4)	0.0028 (4)	0.0037 (4)
O2	0.0288 (5)	0.0357 (5)	0.0268 (5)	0.0007 (4)	0.0040 (4)	0.0062 (4)
O3	0.0316 (5)	0.0468 (6)	0.0216 (5)	−0.0040 (4)	0.0018 (4)	0.0071 (4)
O4	0.0352 (6)	0.0388 (6)	0.0225 (5)	0.0007 (5)	0.0044 (4)	0.0037 (4)
N1	0.0298 (6)	0.0288 (6)	0.0258 (6)	0.0023 (5)	0.0034 (5)	0.0085 (5)
N2	0.0250 (6)	0.0293 (6)	0.0215 (6)	0.0012 (4)	0.0054 (4)	0.0051 (4)
C1	0.0242 (6)	0.0252 (6)	0.0258 (6)	0.0025 (5)	0.0069 (5)	0.0025 (5)
C2	0.0285 (7)	0.0291 (7)	0.0274 (7)	0.0052 (5)	0.0036 (5)	0.0034 (5)
C3	0.0251 (7)	0.0324 (7)	0.0368 (8)	0.0031 (6)	0.0024 (6)	0.0006 (6)
C4	0.0275 (7)	0.0308 (7)	0.0407 (8)	0.0011 (6)	0.0114 (6)	0.0035 (6)
C5	0.0322 (7)	0.0296 (7)	0.0294 (7)	0.0023 (6)	0.0105 (6)	0.0054 (5)
C6	0.0260 (6)	0.0243 (6)	0.0251 (6)	0.0032 (5)	0.0056 (5)	0.0022 (5)
C7	0.0253 (6)	0.0313 (7)	0.0241 (6)	0.0026 (5)	0.0055 (5)	0.0056 (5)
C8	0.0265 (6)	0.0284 (7)	0.0231 (6)	0.0016 (5)	0.0061 (5)	0.0034 (5)
C9	0.0257 (6)	0.0247 (6)	0.0233 (6)	0.0037 (5)	0.0047 (5)	0.0058 (5)
C10	0.0258 (7)	0.0257 (6)	0.0217 (6)	0.0024 (5)	0.0049 (5)	0.0048 (5)
C11	0.0276 (7)	0.0268 (6)	0.0237 (6)	0.0020 (5)	0.0048 (5)	0.0053 (5)
C12	0.0257 (6)	0.0303 (7)	0.0184 (6)	0.0006 (5)	0.0064 (5)	0.0056 (5)
C13	0.0284 (7)	0.0287 (7)	0.0244 (6)	0.0046 (5)	0.0064 (5)	0.0072 (5)
C14	0.0276 (7)	0.0278 (7)	0.0237 (6)	0.0025 (5)	0.0060 (5)	0.0061 (5)
C15	0.0309 (8)	0.0484 (9)	0.0552 (10)	0.0073 (7)	0.0146 (7)	0.0243 (8)
C16	0.0287 (7)	0.0316 (7)	0.0233 (6)	0.0034 (5)	0.0038 (5)	0.0076 (5)
C17	0.0258 (7)	0.0455 (8)	0.0252 (7)	0.0023 (6)	0.0010 (5)	0.0030 (6)
C18	0.0266 (7)	0.0464 (9)	0.0271 (7)	0.0037 (6)	0.0056 (5)	0.0066 (6)
C19	0.0326 (7)	0.0290 (7)	0.0219 (6)	0.0030 (5)	0.0037 (5)	0.0066 (5)
C20	0.0286 (7)	0.0413 (8)	0.0255 (7)	−0.0035 (6)	0.0004 (5)	0.0062 (6)
C21	0.0261 (7)	0.0427 (8)	0.0269 (7)	−0.0001 (6)	0.0047 (5)	0.0078 (6)

Geometric parameters (Å, º)

O1—C11	1.2484 (17)	C7—C16	1.5195 (18)
O2—C13	1.3626 (16)	C8—H8A	0.9900
O2—C14	1.3933 (16)	C8—H8B	0.9900
O3—C14	1.2260 (17)	C8—C9	1.4922 (18)
O4—H4	0.90 (3)	C9—C10	1.4300 (18)
O4—C19	1.3702 (17)	C10—C11	1.4434 (18)
N1—H1	0.92 (2)	C10—C14	1.4341 (19)
N1—C6	1.3963 (18)	C11—C12	1.4375 (18)

N1—C7	1.4717 (18)	C12—H12	0.9500
N2—H2	0.93 (2)	C12—C13	1.3414 (19)
N2—C1	1.4206 (17)	C13—C15	1.478 (2)
N2—C9	1.3254 (17)	C15—H15A	0.9800
C1—C2	1.3914 (19)	C15—H15B	0.9800
C1—C6	1.4086 (19)	C15—H15C	0.9800
C2—H2A	0.9500	C16—C17	1.390 (2)
C2—C3	1.384 (2)	C16—C21	1.390 (2)
C3—H3	0.9500	C17—H17	0.9500
C3—C4	1.390 (2)	C17—C18	1.387 (2)
C4—H4A	0.9500	C18—H18	0.9500
C4—C5	1.384 (2)	C18—C19	1.389 (2)
C5—H5	0.9500	C19—C20	1.386 (2)
C5—C6	1.4027 (19)	C20—H20	0.9500
C7—H7	1.0000	C20—C21	1.390 (2)
C7—C8	1.5295 (19)	C21—H21	0.9500

O1···N2	2.5882 (16)	C3···C10^{v}	3.400 (2)
O1···O1^{i}	2.8900 (16)	C1···H15A^{vi}	2.84
O2···C5^{ii}	3.1976 (18)	C1···H8A	2.59
O3···C8	2.8223 (17)	C2···H12^{i}	2.79
O3···O4^{iii}	2.7598 (16)	C6···H8A	2.59
O1···H2	1.80 (2)	C11···H2	2.36 (2)
O1···H2^{i}	2.65 (2)	C14···H8B	2.64
O2···H4^{iii}	2.67 (2)	C14···H4^{iii}	2.65 (2)
O3···H8B	2.24	C17···H1	2.90 (2)
O3···H4^{iii}	1.86 (3)	C19···H1^{iv}	2.88 (2)
O4···H1^{iv}	2.21 (2)	H1···H5	2.2962
N1···N2	2.9107 (17)	H2···H2A	2.45
N1···H17	2.72	H4···H20	2.32
C2···C11^{v}	3.272 (2)	H7···H21	2.35
C2···C10^{v}	3.3849 (19)		

C13—O2—C14	122.21 (11)	C10—C9—C8	123.66 (12)
C19—O4—H4	109.6 (16)	C9—C10—C11	120.11 (12)
C6—N1—H1	110.6 (12)	C9—C10—C14	120.03 (12)
C6—N1—C7	123.76 (12)	C14—C10—C11	119.74 (12)
C7—N1—H1	113.6 (12)	O1—C11—C10	124.06 (12)
C1—N2—H2	120.6 (13)	O1—C11—C12	119.13 (12)
C9—N2—H2	114.0 (13)	C12—C11—C10	116.80 (12)
C9—N2—C1	125.33 (11)	C11—C12—H12	119.3
C2—C1—N2	117.37 (12)	C13—C12—C11	121.42 (12)
C2—C1—C6	120.69 (12)	C13—C12—H12	119.3
C6—C1—N2	121.73 (12)	O2—C13—C15	112.37 (13)
C1—C2—H2A	119.5	C12—C13—O2	121.51 (12)
C3—C2—C1	121.03 (13)	C12—C13—C15	126.11 (13)
C3—C2—H2A	119.5	O2—C14—C10	117.90 (11)
C2—C3—H3	120.5	O3—C14—O2	114.04 (12)

C2—C3—C4	118.99 (14)	O3—C14—C10	128.03 (13)
C4—C3—H3	120.5	C13—C15—H15A	109.5
C3—C4—H4A	119.9	C13—C15—H15B	109.5
C5—C4—C3	120.29 (13)	C13—C15—H15C	109.5
C5—C4—H4A	119.9	H15A—C15—H15B	109.5
C4—C5—H5	119.1	H15A—C15—H15C	109.5
C4—C5—C6	121.83 (13)	H15B—C15—H15C	109.5
C6—C5—H5	119.1	C17—C16—C7	122.38 (12)
N1—C6—C1	122.60 (12)	C17—C16—C21	118.19 (13)
N1—C6—C5	119.93 (12)	C21—C16—C7	119.36 (12)
C5—C6—C1	117.06 (13)	C16—C17—H17	119.4
N1—C7—H7	108.1	C18—C17—C16	121.16 (13)
N1—C7—C8	109.11 (11)	C18—C17—H17	119.4
N1—C7—C16	113.14 (11)	C17—C18—H18	120.1
C8—C7—H7	108.1	C17—C18—C19	119.86 (14)
C16—C7—H7	108.1	C19—C18—H18	120.1
C16—C7—C8	110.02 (11)	O4—C19—C18	117.69 (13)
C7—C8—H8A	109.2	O4—C19—C20	122.47 (13)
C7—C8—H8B	109.2	C20—C19—C18	119.81 (13)
H8A—C8—H8B	107.9	C19—C20—H20	120.2
C9—C8—C7	112.11 (11)	C19—C20—C21	119.66 (13)
C9—C8—H8A	109.2	C21—C20—H20	120.2
C9—C8—H8B	109.2	C16—C21—H21	119.3
N2—C9—C8	116.72 (12)	C20—C21—C16	121.32 (14)
N2—C9—C10	119.55 (12)	C20—C21—H21	119.3

O1—C11—C12—C13	−176.20 (14)	C8—C7—C16—C21	−95.22 (15)
O4—C19—C20—C21	178.55 (14)	C8—C9—C10—C11	−165.74 (13)
N1—C7—C8—C9	−60.37 (14)	C8—C9—C10—C14	18.3 (2)
N1—C7—C16—C17	−40.57 (19)	C9—N2—C1—C2	147.66 (14)
N1—C7—C16—C21	142.47 (14)	C9—N2—C1—C6	−37.4 (2)
N2—C1—C2—C3	176.89 (12)	C9—C10—C11—O1	−2.4 (2)
N2—C1—C6—N1	−5.7 (2)	C9—C10—C11—C12	176.74 (12)
N2—C1—C6—C5	−178.41 (12)	C9—C10—C14—O2	−179.54 (12)
N2—C9—C10—C11	11.1 (2)	C9—C10—C14—O3	2.7 (2)
N2—C9—C10—C14	−164.86 (13)	C10—C11—C12—C13	4.6 (2)
C1—N2—C9—C8	−6.8 (2)	C11—C10—C14—O2	4.5 (2)
C1—N2—C9—C10	176.18 (12)	C11—C10—C14—O3	−173.28 (14)
C1—C2—C3—C4	1.0 (2)	C11—C12—C13—O2	1.0 (2)
C2—C1—C6—N1	169.01 (13)	C11—C12—C13—C15	−179.05 (14)
C2—C1—C6—C5	−3.7 (2)	C13—O2—C14—O3	179.40 (13)
C2—C3—C4—C5	−1.9 (2)	C13—O2—C14—C10	1.33 (19)
C3—C4—C5—C6	0.1 (2)	C14—O2—C13—C12	−4.2 (2)
C4—C5—C6—N1	−170.18 (13)	C14—O2—C13—C15	175.86 (12)
C4—C5—C6—C1	2.7 (2)	C14—C10—C11—O1	173.61 (13)
C6—N1—C7—C8	−21.39 (17)	C14—C10—C11—C12	−7.29 (19)
C6—N1—C7—C16	101.43 (15)	C16—C7—C8—C9	174.97 (11)
C6—C1—C2—C3	1.9 (2)	C16—C17—C18—C19	0.5 (2)

C7—N1—C6—C1	59.64 (19)	C17—C16—C21—C20	−0.3 (2)
C7—N1—C6—C5	−127.87 (14)	C17—C18—C19—O4	−178.94 (14)
C7—C8—C9—N2	78.98 (15)	C17—C18—C19—C20	−0.8 (2)
C7—C8—C9—C10	−104.10 (15)	C18—C19—C20—C21	0.5 (2)
C7—C16—C17—C18	−176.98 (14)	C19—C20—C21—C16	0.1 (2)
C7—C16—C21—C20	176.77 (14)	C21—C16—C17—C18	0.0 (2)
C8—C7—C16—C17	81.74 (17)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) *x*+1, *y*+1, *z*; (iii) −*x*+2, −*y*+2, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*+1; (v) *x*−1, *y*, *z*; (vi) *x*−1, *y*−1, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O3^{iii}	0.90 (3)	1.86 (3)	2.7597 (15)	178 (2)
N1—H1···O4^{iv}	0.92 (2)	2.21 (2)	3.1028 (16)	165.2 (17)
N2—H2···O1	0.93 (2)	1.80 (2)	2.5882 (15)	140.8 (18)

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