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Crystal structure and Hirshfeld surface analyses, intermolecular interaction energies and energy frameworks of methyl 6-amino-5-cyano-2-(2-methoxy-2-oxoethyl)-4-(4-nitrophenyl)-4*H*-pyran-3-carboxylate

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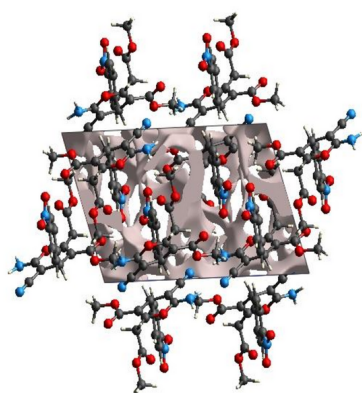
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The title compound, C₁₇H₁₅N₃O₇, contains pyran and phenyl rings, with the pyran ring exhibiting a flattened-boat conformation. In the crystal, intermolecular N—H...N hydrogen bonds link the molecules into centrosymmetric dimers, forming *R*₂²(12) ring motifs. These dimers are linked through N—H...O hydrogen bonds into a three-dimensional architecture. A Hirshfeld surface analysis indicates that the most important contributions for the crystal packing are from H...O/O...H (29.7%), H...H (28.7%), H...C/C...H (16.0%) and H...N/N...H (12.9%) interactions. In addition to van der Waals interactions and N—H...N and N—H...O hydrogen bonds, halogen bonds, tetrel bonds and pnictogen bonds also play an important role in the cohesion of the crystal structure.

1. Chemical context

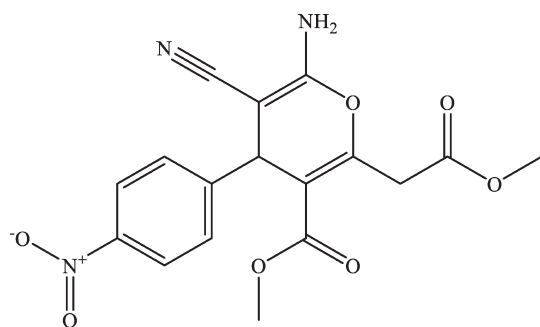
4*H*-Pyrans, a class of heterocyclic compounds containing multifunctional substituents such as nitro (–NO₂), cyano (–CN), amino (–NH₂) and ester (–COOR) groups have garnered significant interest due to their versatile chemical reactivities and wide range of applications (Akkurt *et al.*, 2018; Askerov *et al.*, 2020; Khalilov, 2021). The 4*H*-pyran fragment plays a critical role in pharmaceuticals, agrochemicals, material sciences and catalysis (Mahmoudi *et al.*, 2021; Gurbanov *et al.*, 2021). The unique combination of electron-withdrawing (*e.g.* nitro, cyano, ester) and electron-donating (*e.g.* amino) groups imparts remarkable chemical and biological properties, making these molecules indispensable in modern chemistry (Tas *et al.*, 2023; Khalilov *et al.*, 2024). Moreover, the structural characteristics of this class of compounds indicate their potential significance in coordination chemistry. The amino group, pyran ring and the biphenyl structure offer multiple coordination sites, enabling the formation of stable metal complexes (Khalilov *et al.*, 2018*a,b*; Naghiyev *et al.*, 2021*a,b*). Natural products containing 4*H*-pyran derivatives are widespread, forming the core structure of many bioactive compounds. Notable examples include flavonoids (*e.g.* cyanidin, delphinidin), which exhibit antioxidant, anti-inflammatory and photoreactive properties (Karimli *et al.*,



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2023; Rzaev & Khalilov, 2024). These compounds are found in plants, fruits and marine organisms, contributing to diverse biological activities such as antimicrobial, anticancer and cardiovascular benefits (Naghiyev *et al.*, 2022; Mamedov *et al.*, 2020). Herein, we report the synthesis, molecular and crystal structures and Hirshfeld surface analysis of methyl 6-amino-5-cyano-2-(2-methoxy-2-oxoethyl)-4-(4-nitrophenyl)-4*H*-pyran-3-carboxylate. The results provide comprehensive insights into its molecular geometry, hydrogen-bonding interactions and crystal packing, contributing valuable information to the growing database of functionalized carbo- and heterocyclic derivatives.



2. Structural commentary

The title compound contains pyran (*A*: O1/C2–C6) and phenyl (*B*: C8–C13), rings (Fig. 1). The pyran ring is in a flattened-

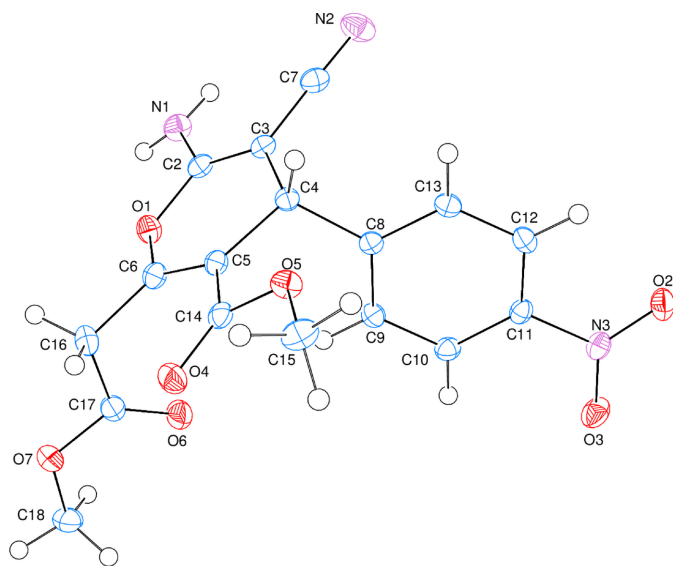


Figure 1

The title molecule with atom-numbering scheme and 50% probability ellipsoids.



Figure 2

Conformation of the pyran ring (O1/C2–C6).

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>
N1—H1 <i>A</i> ...O4 ⁱⁱ	0.887 (16)	2.112 (16)	2.9362 (12)	154.1 (13)
N1—H1 <i>B</i> ...N2 ^{iv}	0.892 (17)	2.152 (17)	3.0283 (14)	167.2 (14)

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

boat conformation with puckering parameters (Cremer & Pople, 1975) $Q_T = 0.1228$ (10) Å, $\theta = 110.83$ (47)° and $\varphi = 0.7$ (5)° (Fig. 2). Atom N3 is 0.0312 (9) Å away from the best mean plane of the phenyl ring. The nitro (N3/O2/O3) group is oriented at a dihedral angle of 12.06 (8)° with respect to the phenyl ring *B*. The O6—C17—O7 [124.87 (10)°] bond angle in the 2-methoxy-2-oxoethyl moiety is larger than the angle O4—C14—O5 [122.65 (9)°] in the carboxylate group. There are no unusual bond lengths or interbond angles in the molecule.

3. Supramolecular features

In the crystal, N—H...N hydrogen bonds (Table 1) link the molecules into centrosymmetric dimers, forming $R_2^2(12)$ ring motifs (Fig. 3). These dimers are linked through N—H...O hydrogen bonds into a three-dimensional architecture (Fig. 3). The distance between the N and O atoms may be slightly longer than the sum of the van der Waals radii of the atoms if the chemically involved atoms interact electrostatically. In addition, dispersion has an important role in every interaction. In this case, the nitro oxygen interacts above the plane of the —NH₂ group. These are N—(π hole)...O contacts under the category of pnictogen bonding (Varadwaj *et al.*, 2022). The O3...N1, O3...H1*B* and O2...H1*A* contacts are 3.1495 (13), 3.379 (13) and 2.618 (15) Å, respectively. Tetrel bonding (Varadwaj *et al.*, 2023) also occurs, involving the nucleophilic oxygen and electrophilic carbon of the carbonyl group

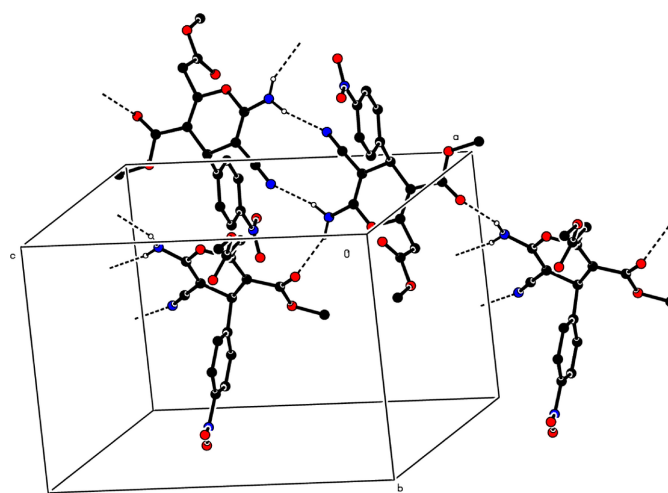


Figure 3

A partial packing diagram. Intermolecular N—H...O and N—H...N hydrogen bonds are shown as dashed lines. H atoms not involved in these interactions have been omitted for clarity.

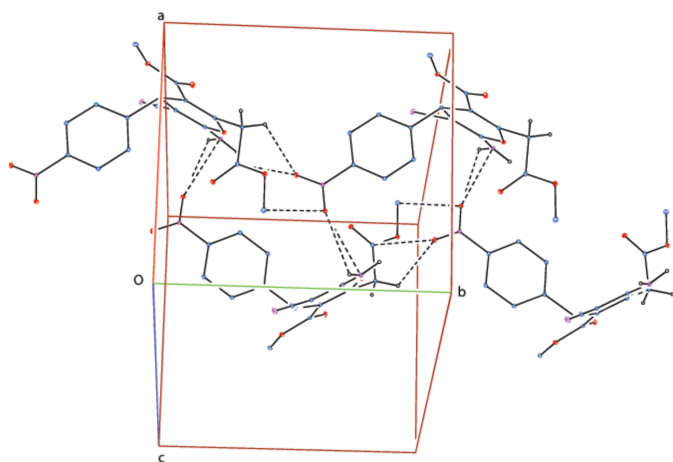


Figure 4

A partial packing diagram showing the halogen, tetrel and pnictogen bonds as dashed lines, where the O, N and C atoms are shown in red, light magenta and blue, respectively, while the H atoms are colourless. H atoms not involved in these interactions have been omitted for clarity.

[O2...C17 = 3.1242 (13), O3...C18 = 3.1325 (15) Å. These involve the Burgi–Dunitz trajectory wherein the angular approach of the nucleophile towards an electrophilic centre is probed (Rodríguez *et al.*, 2023). The Burgi–Dunitz angle herein is 111°. These interactions are depicted in Fig. 4. Thus, in addition to N–H...N and N–H...O hydrogen bonds, halogen bonds, tetrel bonds and pnictogen bonds also play an important role in the cohesion of the crystal structure. Neither π – π nor C–H... π (ring) interactions are observed.

4. Hirshfeld surface analysis

In order to visualize the intermolecular interactions in the title compound, a Hirshfeld surface (HS) analysis (Hirshfeld, 1977; Spackman & Jayatilaka, 2009) was carried out using *Crystal Explorer 17.5* (Spackman *et al.*, 2021). In the HS plotted over d_{norm} (Fig. 5), the white surface indicates contacts with

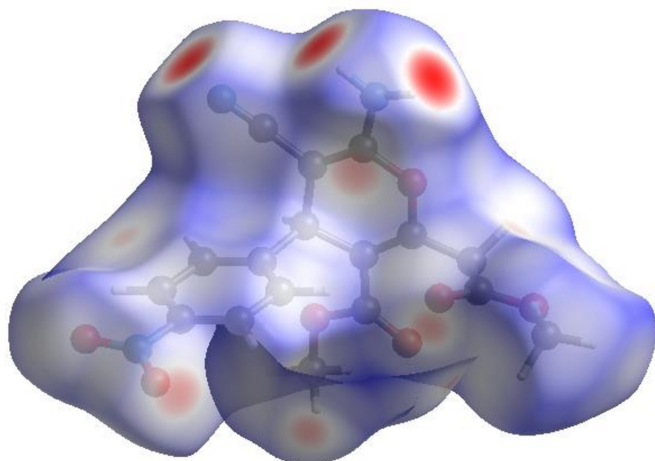


Figure 5

View of the three-dimensional Hirshfeld surface of the title compound plotted over d_{norm} .

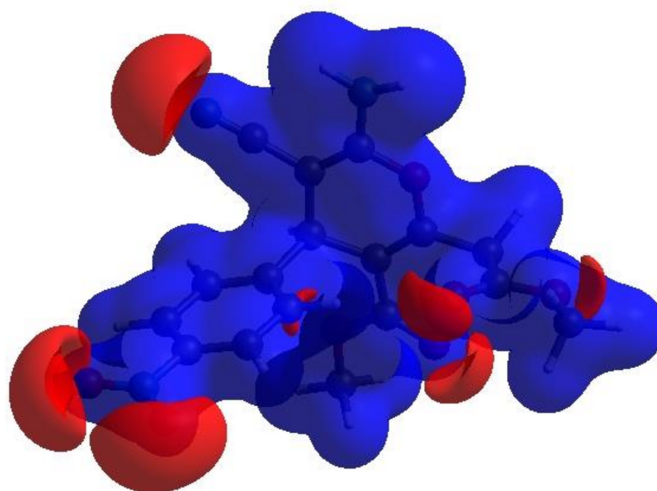


Figure 6

View of the three-dimensional Hirshfeld surface of the title compound plotted over electrostatic potential energy using the STO-3 G basis set at the Hartree–Fock level of theory. Hydrogen-bond donors and acceptors are shown as blue and red regions around the atoms corresponding to positive and negative potentials, respectively.

distances equal to the sum of van der Waals radii, and the red and blue colours indicate distances shorter (in close contact) or longer (distinct contact) than the van der Waals radii, respectively (Venkatesan *et al.*, 2016). The bright-red spots indicate their roles as the respective donors and/or acceptors; they also appear as blue and red regions corresponding to positive and negative potentials on the HS mapped over electrostatic potential (Spackman *et al.*, 2008; Jayatilaka *et al.*, 2005) as shown in Fig. 6. The blue regions indicate the positive electrostatic potential (hydrogen-bond donors), while the red regions indicate the negative electrostatic potential (hydrogen-bond acceptors). The shape-index surface can be used to identify characteristic packing modes, in particular, planar stacking arrangements and the presence of aromatic stacking interactions such as C–H... π and π – π interactions.

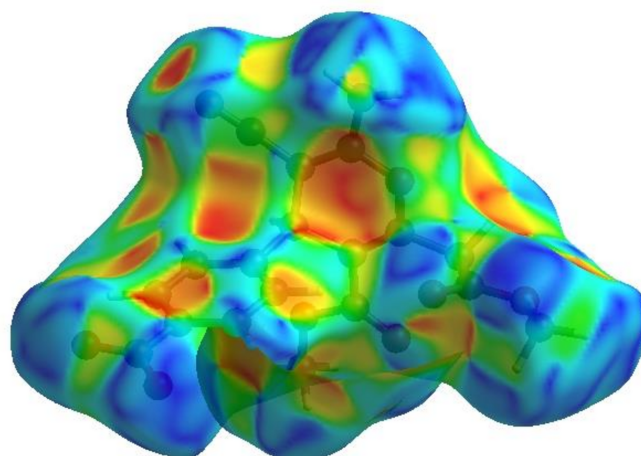


Figure 7

Hirshfeld surface of the title compound plotted over shape-index.

C—H $\cdots\pi$ interactions are seen as red p -holes, which are related to the electron ring interactions between the CH groups and the centroids of the aromatic rings of neighbouring molecules while π – π interactions are indicated by the presence of adjacent red and blue triangles. Fig. 7 clearly suggests that there are no C—H $\cdots\pi$ or π – π interactions present.

The overall two-dimensional fingerprint plot, Fig. 8a, and those delineated into H $\cdots$ O/O $\cdots$ H, H $\cdots$ H, H $\cdots$ C/C $\cdots$ H, H $\cdots$ N/N $\cdots$ H, O $\cdots$ O, C $\cdots$ O/O $\cdots$ C, N $\cdots$ O/O $\cdots$ N, C $\cdots$ C and C $\cdots$ C/N $\cdots$ C (McKinnon *et al.*, 2007) are illustrated in Fig. 8 b–j, respectively, together with their relative contributions to the Hirshfeld surface. The most important interaction is H $\cdots$ O/O $\cdots$ H (Table 2) contributing 29.7% to the overall crystal packing, which is shown in Fig. 8b with the pair of spikes at $d_e + d_i = 2.00$ Å. The H $\cdots$ H contacts, contributing 28.7% to the overall crystal packing, are represented in Fig. 8c as the widely scattered points of high density due to the large hydrogen content of the molecule with the tip at $d_e = d_i = 1.12$ Å. In the absence of C—H $\cdots\pi$ interactions, the characteristic wings of the H $\cdots$ C/C $\cdots$ H contacts, contributing 16.0% to the overall crystal packing, are shown in Fig. 8d with the tips at $d_e + d_i = 2.54$ Å. The symmetrical pair of spikes of

Table 2

Selected interatomic distances (Å).

C17 $\cdots$ O2 ⁱ	3.1242 (13)	O4 $\cdots$ H15C	2.64
C18 $\cdots$ O3 ⁱ	3.1325 (15)	O5 $\cdots$ H4	2.41
O4 $\cdots$ C16	2.8924 (13)	H15C $\cdots$ O6 ⁱⁱⁱ	2.47
N1 $\cdots$ O4 ⁱⁱ	2.9361 (13)	O6 $\cdots$ H18A	2.66
O5 $\cdots$ C8	2.9834 (12)	O6 $\cdots$ H18B	2.58
O2 $\cdots$ H12	2.44	N2 $\cdots$ N1 ^{iv}	3.0282 (14)
H16A $\cdots$ O2 ⁱ	2.62	H1B $\cdots$ N2 ^{iv}	2.152 (16)
O3 $\cdots$ H10	2.4456	C7 $\cdots$ C13	3.3501 (15)
H10 $\cdots$ O4 ⁱⁱⁱ	2.57	C5 $\cdots$ H9	2.67
O4 $\cdots$ H16B	2.20	C7 $\cdots$ H1B	2.616 (16)
H1A $\cdots$ O4 ⁱⁱ	2.112 (16)	C14 $\cdots$ H16B	2.70
O4 $\cdots$ H15A	2.54	H4 $\cdots$ H13	2.36

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

the H $\cdots$ N/N $\cdots$ H contacts (Fig. 8e; 12.9% contribution to the HS) have the tips at $d_e + d_i = 2.06$ Å. The O $\cdots$ O contacts (Fig. 8f) contribute 4.6% to the HS, and they are seen at $d_e = d_i = 1.54$ Å. The C $\cdots$ O/O $\cdots$ C (Fig. 8g) and N $\cdots$ O/O $\cdots$ N (Fig. 8h) contacts contribute 4.5% and 2.2%, respectively, to the HS with $d_e + d_i = 2.96$ Å and 3.16 Å, respectively. Finally, the C $\cdots$ C (Fig. 8i) and C $\cdots$ N/N $\cdots$ C (Fig. 8j) contacts with 0.6% and 0.4% contributions to the HS have very low density of points.

The nearest neighbour coordination environment of a molecule can be determined from the colour patches on the HS based on how close to other molecules they are. The Hirshfeld surface representations of contact patches plotted onto the surface are shown for the H $\cdots$ O/O $\cdots$ H, H $\cdots$ H, H $\cdots$ C/C $\cdots$ H and H $\cdots$ N/N $\cdots$ H interactions in Fig. 9a–c, respectively.

The Hirshfeld surface analysis confirms the importance of H-atom contacts in establishing the packing. The large number of H $\cdots$ O/O $\cdots$ H, H $\cdots$ H, H $\cdots$ C/C $\cdots$ H and H $\cdots$ N/N $\cdots$ H interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing (Hathwar *et al.*, 2015).

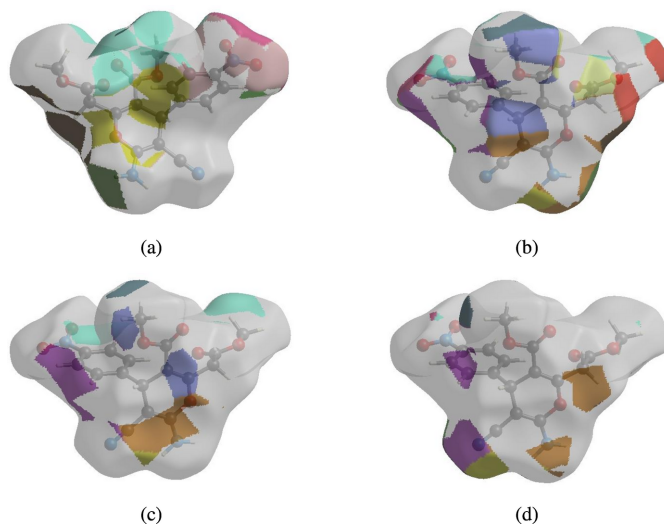


Figure 9

The Hirshfeld surface representations of contact patches plotted onto the surface for (a) H $\cdots$ O/O $\cdots$ H, (b) H $\cdots$ H, (c) H $\cdots$ C/C $\cdots$ H and (d) H $\cdots$ N/N $\cdots$ H interactions.

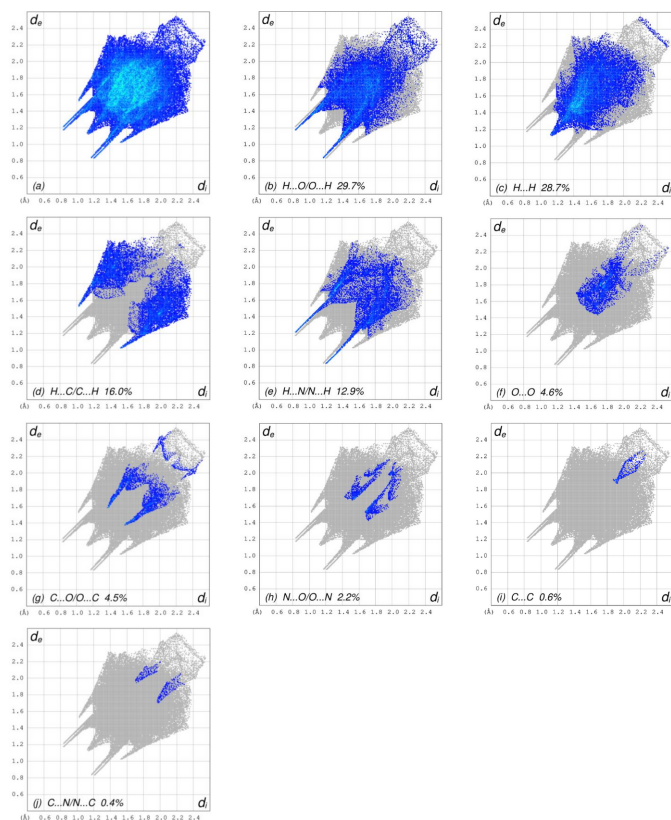


Figure 8

The full two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and those delineated into (b) H $\cdots$ O/O $\cdots$ H, (c) H $\cdots$ H, (d) H $\cdots$ C/C $\cdots$ H, (e) H $\cdots$ N/N $\cdots$ H, (f) O $\cdots$ O, (g) C $\cdots$ O/O $\cdots$ C, (h) N $\cdots$ O/O $\cdots$ N, (i) C $\cdots$ C and (j) C $\cdots$ C/N $\cdots$ C interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

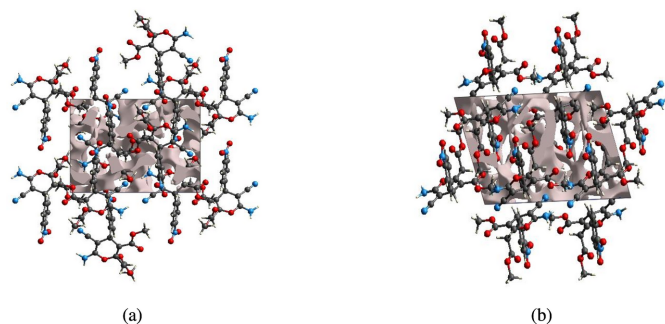


Figure 10
Graphical views of voids in the crystal packing of the title compound (a) along the *a*-axis and (b) along the *b*-axis directions.

5. Crystal voids

The strength of the crystal packing is important for determining the response to an applied mechanical force. If the crystal packing results in significant voids, then the molecules are not tightly packed and a small amount of applied external mechanical force may easily break the crystal. For checking the mechanical stability of the crystal, a void analysis was performed by adding up the electron densities of the spherically symmetric atoms contained in the asymmetric unit (Turner *et al.*, 2011). The void surface is defined as an isosurface of the procrystal electron density and is calculated for the whole unit cell where the void surface meets the boundary of the unit cell and capping faces are generated to create an enclosed volume. The volume of the crystal voids (Fig. 10*a,b*) and the percentage of free space in the unit cell are calculated as 170.52 Å³ and 10.20%, respectively. Thus, the crystal packing appears compact and the mechanical stability should be substantial.

6. Interaction energy calculations and energy frameworks

The intermolecular interaction energies were calculated using the CE-B3LYP/6-31G(d,p) energy model available in *Crystal Explorer 17.5* (Spackman *et al.*, 2021), where a cluster of molecules is generated by applying crystallographic symmetry operations with respect to a selected central molecule within the radius of 3.8 Å by default (Turner *et al.*, 2014). The total intermolecular energy (E_{tot}) is the sum of the electrostatic (E_{ele}), polarization (E_{pol}), dispersion (E_{dis}) and exchange-repulsion (E_{rep}) energies (Turner *et al.*, 2015) with scale factors of 1.057, 0.740, 0.871 and 0.618, respectively (Mackenzie *et al.*, 2017). Hydrogen-bonding interaction energies (in kJ mol⁻¹) were calculated to be -29.7 (E_{ele}), -7.0 (E_{pol}), -74.4 (E_{dis}), 55.0 (E_{rep}) and -67.3 (E_{tot}) for N1-H1A...O4 and -71.4 (E_{ele}), -15.8 (E_{pol}), -13.0 (E_{dis}), 58.0 (E_{rep}) and -62.6 (E_{tot}) for N1-H11B...N2. Energy frameworks combine the calculation of intermolecular interaction energies with a graphical representation of their magnitude (Turner *et al.*, 2015). Energies between molecular pairs are represented as cylinders joining the centroids of pairs of molecules with the cylinder

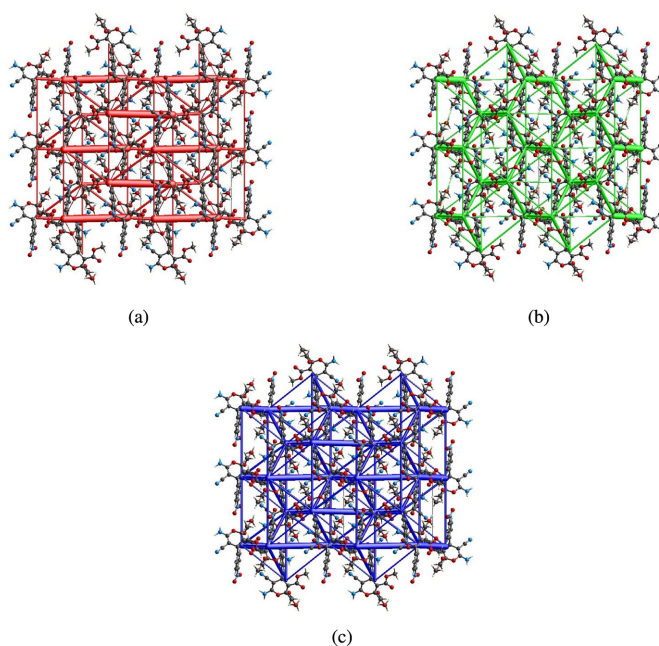


Figure 11
The energy frameworks for a cluster of molecules of the title compound viewed down the *a*-axis showing the (a) electrostatic energy, (b) dispersion energy and (c) total energy diagrams. The cylindrical radius is proportional to the relative strength of the corresponding energies and they were adjusted to the same scale factor of 80 with cut-off value of 5 kJ mol⁻¹ within 2×2×2 unit cells.

radius proportional to the relative strength of the corresponding interaction energy. Energy frameworks were constructed for E_{ele} (red cylinders), E_{dis} (green cylinders) and E_{tot} (blue cylinders) (Fig. 11*a,b,c*). The evaluation of the electrostatic, dispersion and total energy frameworks indicates that the stabilization is dominated by the electrostatic energy contributions in the crystal structure of the title compound.

7. Synthesis and crystallization

The title compound was synthesized following a reported procedure (Heber & Stoyanov, 2003). A mixture of 1.0 g (0.0051 mol) of *p*-nitrobenzylidenemalononitrile and 0.9 g (0.0052 mol) of dimethyl-1,3-acetonedicarboxylate was dissolved in 30 ml of methyl alcohol with stirring for 20 min, 3–4 drops of methylpiperazine were added and stirring was continued. The reaction mixture was kept for 48 h. After that, crystals precipitated as the solvent evaporated. Colorless crystals were obtained from an ethanol/water (3:1 v/v) solution after recrystallization. Yield 75.70%, m.p. 449–450 K. ¹H NMR (300 MHz, DMSO-*d*₆, δ). 3.48 (s, 3H, OCH₃), 3.69 (s, 3H, OCH₃), 3.74 (d, 1H, CH₂, J = 17.1 Hz), 3.96 (d, 1H, CH₂, J = 17.1 Hz), 4.52 (s, 1H, PhCH), 7.11 (s, 2H, NH₂), 7.47 (d, 2H, arom., J = 8.4 Hz), 8.21 (d, 2H, arom., J = 8.4 Hz).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The NH hydrogen atoms were

Table 3

Experimental details.

Crystal data	
Chemical formula	C ₁₇ H ₁₅ N ₃ O ₇
<i>M_r</i>	373.32
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.27958 (5), 11.18770 (6), 15.09983 (8)
β (°)	105.6759 (5)
<i>V</i> (Å ³)	1671.96 (2)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	1.00
Crystal size (mm)	0.21 × 0.15 × 0.13
Data collection	
Diffractometer	XtaLAB Synergy-i CCD diffractometer
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2022)
<i>T</i> _{min} , <i>T</i> _{max}	0.399, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	43458, 3550, 3505
<i>R</i> _{int}	0.024
(sin θ / λ) _{max} (Å ⁻¹)	0.634
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.082, 1.05
No. of reflections	3550
No. of parameters	254
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)	0.25, -0.26

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *SHELXTL* (Sheldrick, 2008).

located in a difference-Fourier map, and refined freely. The C-bound hydrogen-atom positions were calculated geometrically at distances of 1.00 Å (for methine CH), 0.95 Å (for aromatic CH), 0.99 Å (for CH₂) and 0.98 Å (for CH₃) and refined using a riding model by applying the constraint $U_{\text{iso}}(\text{H}) = k U_{\text{eq}}(\text{C})$, where $k = 1.5$ for methyl H atoms and $k = 1.2$ for all other C-bound H atoms.

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The authors contributions are as follows. Conceptualizations, IGM and TH; methodology, FNN and ANB; investigation, VNK and IGM; writing (original draft), TH, ANB and IGM; writing (review and editing of the manuscript), TH and IGM; visualization, TH and ANB; funding acquisition, VNK, TH and HMM; resources, TH, VNK and JA; supervision, FNN and TH.

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Crystal structure and Hirshfeld surface analyses, intermolecular interaction energies and energy frameworks of methyl 6-amino-5-cyano-2-(2-methoxy-2-oxoethyl)-4-(4-nitrophenyl)-4*H*-pyran-3-carboxylate

Farid N. Naghiyev, Tuncer Hökelek, Victor N. Khrustalev, Huseyn M. Mamedov, Alebel N. Belay, Jamshid Ashurov and Ibrahim G. Mamedov

Computing details

Methyl 6-amino-5-cyano-2-(2-methoxy-2-oxoethyl)-4-(4-nitrophenyl)-4*H*-pyran-3-carboxylate

Crystal data

$C_{17}H_{15}N_3O_7$

$M_r = 373.32$

Monoclinic, $P2_1/c$

$a = 10.27958$ (5) Å

$b = 11.18770$ (6) Å

$c = 15.09983$ (8) Å

$\beta = 105.6759$ (5)°

$V = 1671.96$ (2) Å³

$Z = 4$

$F(000) = 776$

$D_x = 1.483$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 36303 reflections

$\theta = 4.0\text{--}77.7^\circ$

$\mu = 1.00$ mm⁻¹

$T = 100$ K

Prism, colourless

$0.21 \times 0.15 \times 0.13$ mm

Data collection

XtaLAB Synergy-i CCD
diffractometer

Radiation source: micro-focus sealed X-ray tube

φ and ω scans

Absorption correction: gaussian
(CrysAlisPro; Rigaku OD, 2022)

$T_{\min} = 0.399$, $T_{\max} = 1.000$

43458 measured reflections

3550 independent reflections

3505 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 77.8^\circ$, $\theta_{\min} = 4.5^\circ$

$h = -13 \rightarrow 13$

$k = -14 \rightarrow 14$

$l = -19 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.082$

$S = 1.05$

3550 reflections

254 parameters

0 restraints

Primary atom site location: difference Fourier
map

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.66P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.25$ 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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.77251 (7)	0.28311 (6)	0.73783 (5)	0.01923 (16)
O2	0.60222 (8)	1.02372 (7)	0.72626 (6)	0.02412 (17)
O3	0.41912 (8)	0.92231 (7)	0.66787 (6)	0.02586 (18)
O4	0.72560 (8)	0.39316 (7)	0.45860 (5)	0.02369 (17)
O5	0.85282 (7)	0.55117 (7)	0.51861 (5)	0.01883 (16)
O6	0.47708 (8)	0.31475 (7)	0.61457 (6)	0.02503 (18)
O7	0.45768 (8)	0.13799 (7)	0.54080 (5)	0.02177 (17)
N1	0.86641 (9)	0.29814 (9)	0.88857 (7)	0.02135 (19)
H1A	0.8151 (15)	0.2350 (14)	0.8908 (10)	0.028 (4)*
H1B	0.9009 (16)	0.3401 (14)	0.9398 (11)	0.033 (4)*
N2	1.03545 (10)	0.58976 (9)	0.92255 (7)	0.0275 (2)
N3	0.54251 (9)	0.93095 (8)	0.69545 (6)	0.01857 (18)
C2	0.84714 (10)	0.35325 (9)	0.80715 (7)	0.0170 (2)
C3	0.89769 (10)	0.46004 (9)	0.78966 (7)	0.0160 (2)
C4	0.86693 (9)	0.51344 (9)	0.69395 (6)	0.01460 (19)
H4	0.9540	0.5385	0.6820	0.018*
C5	0.80138 (9)	0.42006 (9)	0.62345 (7)	0.0156 (2)
C6	0.75493 (10)	0.31621 (9)	0.64726 (7)	0.0170 (2)
C7	0.97348 (10)	0.52994 (10)	0.86393 (7)	0.0189 (2)
C8	0.77799 (9)	0.62376 (9)	0.68853 (6)	0.01387 (19)
C9	0.63820 (10)	0.61374 (9)	0.67295 (7)	0.0169 (2)
H9	0.5963	0.5375	0.6612	0.020*
C10	0.56015 (10)	0.71444 (9)	0.67456 (7)	0.0175 (2)
H10	0.4650	0.7082	0.6641	0.021*
C11	0.62397 (10)	0.82428 (9)	0.69179 (6)	0.01549 (19)
C12	0.76225 (10)	0.83757 (9)	0.70665 (7)	0.0172 (2)
H12	0.8035	0.9141	0.7179	0.021*
C13	0.83852 (10)	0.73601 (9)	0.70462 (7)	0.0169 (2)
H13	0.9335	0.7430	0.7143	0.020*
C14	0.78635 (10)	0.45024 (9)	0.52536 (7)	0.0164 (2)
C15	0.84512 (11)	0.58914 (11)	0.42552 (7)	0.0219 (2)
H15A	0.8778	0.5248	0.3931	0.033*
H15B	0.9012	0.6604	0.4274	0.033*
H15C	0.7511	0.6079	0.3932	0.033*
C16	0.67455 (11)	0.22033 (9)	0.58768 (7)	0.0198 (2)
H16A	0.7080	0.1409	0.6126	0.024*
H16B	0.6859	0.2267	0.5248	0.024*
C17	0.52626 (10)	0.23216 (9)	0.58392 (7)	0.0182 (2)
C18	0.31474 (11)	0.13772 (11)	0.53517 (8)	0.0258 (2)

H18A	0.2708	0.2054	0.4976	0.039*
H18B	0.3025	0.1447	0.5971	0.039*
H18C	0.2742	0.0629	0.5070	0.039*

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

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0228 (4)	0.0168 (3)	0.0193 (4)	−0.0020 (3)	0.0077 (3)	0.0004 (3)
O2	0.0298 (4)	0.0153 (4)	0.0275 (4)	0.0010 (3)	0.0082 (3)	−0.0020 (3)
O3	0.0180 (4)	0.0233 (4)	0.0373 (5)	0.0047 (3)	0.0092 (3)	0.0058 (3)
O4	0.0295 (4)	0.0212 (4)	0.0180 (4)	0.0001 (3)	0.0025 (3)	−0.0042 (3)
O5	0.0197 (4)	0.0225 (4)	0.0147 (3)	−0.0020 (3)	0.0053 (3)	0.0017 (3)
O6	0.0215 (4)	0.0221 (4)	0.0314 (4)	0.0010 (3)	0.0070 (3)	−0.0063 (3)
O7	0.0218 (4)	0.0199 (4)	0.0220 (4)	−0.0033 (3)	0.0032 (3)	−0.0035 (3)
N1	0.0228 (4)	0.0213 (5)	0.0201 (5)	−0.0002 (4)	0.0062 (4)	0.0054 (4)
N2	0.0292 (5)	0.0317 (5)	0.0189 (4)	−0.0087 (4)	0.0016 (4)	0.0029 (4)
N3	0.0213 (4)	0.0167 (4)	0.0188 (4)	0.0024 (3)	0.0074 (3)	0.0033 (3)
C2	0.0141 (4)	0.0191 (5)	0.0185 (5)	0.0036 (4)	0.0056 (4)	0.0012 (4)
C3	0.0141 (4)	0.0176 (5)	0.0160 (5)	0.0025 (4)	0.0036 (4)	0.0014 (4)
C4	0.0136 (4)	0.0154 (5)	0.0151 (4)	−0.0001 (3)	0.0046 (3)	0.0002 (3)
C5	0.0145 (4)	0.0158 (5)	0.0170 (5)	0.0023 (3)	0.0052 (4)	−0.0016 (4)
C6	0.0167 (4)	0.0172 (5)	0.0185 (5)	0.0026 (4)	0.0072 (4)	−0.0009 (4)
C7	0.0173 (5)	0.0225 (5)	0.0169 (5)	0.0005 (4)	0.0044 (4)	0.0056 (4)
C8	0.0155 (4)	0.0157 (5)	0.0105 (4)	0.0002 (3)	0.0036 (3)	0.0008 (3)
C9	0.0161 (5)	0.0155 (5)	0.0189 (5)	−0.0020 (4)	0.0041 (4)	0.0002 (4)
C10	0.0141 (4)	0.0189 (5)	0.0191 (5)	−0.0004 (4)	0.0037 (4)	0.0017 (4)
C11	0.0183 (5)	0.0151 (5)	0.0133 (4)	0.0026 (4)	0.0047 (3)	0.0016 (3)
C12	0.0194 (5)	0.0151 (5)	0.0171 (5)	−0.0034 (4)	0.0047 (4)	−0.0012 (4)
C13	0.0141 (4)	0.0188 (5)	0.0175 (5)	−0.0022 (4)	0.0041 (4)	−0.0006 (4)
C14	0.0154 (4)	0.0163 (5)	0.0179 (5)	0.0040 (4)	0.0055 (4)	−0.0009 (4)
C15	0.0216 (5)	0.0294 (6)	0.0159 (5)	0.0037 (4)	0.0068 (4)	0.0058 (4)
C16	0.0218 (5)	0.0159 (5)	0.0240 (5)	−0.0021 (4)	0.0098 (4)	−0.0038 (4)
C17	0.0218 (5)	0.0166 (5)	0.0156 (5)	−0.0010 (4)	0.0042 (4)	0.0007 (4)
C18	0.0197 (5)	0.0261 (6)	0.0274 (6)	−0.0027 (4)	−0.0006 (4)	−0.0002 (4)

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

O1—C2	1.3661 (13)	C5—C14	1.4860 (14)
O1—C6	1.3807 (12)	C6—C16	1.4970 (14)
O2—N3	1.2313 (12)	C8—C13	1.3934 (14)
O3—N3	1.2273 (12)	C8—C9	1.3965 (13)
O4—C14	1.2139 (13)	C9—C10	1.3870 (14)
O5—C14	1.3378 (13)	C9—H9	0.9500
O5—C15	1.4501 (12)	C10—C11	1.3842 (14)
O6—C17	1.2042 (13)	C10—H10	0.9500
O7—C17	1.3353 (12)	C11—C12	1.3858 (14)
O7—C18	1.4487 (13)	C12—C13	1.3855 (14)
N1—C2	1.3413 (14)	C12—H12	0.9500

N1—H1A	0.887 (16)	C13—H13	0.9500
N1—H1B	0.892 (17)	C15—H15A	0.9800
N2—C7	1.1543 (15)	C15—H15B	0.9800
N3—C11	1.4674 (13)	C15—H15C	0.9800
C2—C3	1.3570 (14)	C16—C17	1.5157 (14)
C3—C7	1.4156 (14)	C16—H16A	0.9900
C3—C4	1.5162 (13)	C16—H16B	0.9900
C4—C5	1.5137 (13)	C18—H18A	0.9800
C4—C8	1.5250 (13)	C18—H18B	0.9800
C4—H4	1.0000	C18—H18C	0.9800
C5—C6	1.3416 (14)		
C17…O2 ⁱ	3.1242 (13)	O4…H15C	2.64
C18…O3 ⁱ	3.1325 (15)	O5…H4	2.41
O4…C16	2.8924 (13)	H15C…O6 ⁱⁱⁱ	2.47
N1…O4 ⁱⁱ	2.9361 (13)	O6…H18A	2.66
O5…C8	2.9834 (12)	O6…H18B	2.58
O2…H12	2.44	N2…N1 ^{iv}	3.0282 (14)
H16A…O2 ⁱ	2.62	H1B…N2 ^{iv}	2.152 (16)
O3…H10	2.4456	C7…C13	3.3501 (15)
H10…O4 ⁱⁱⁱ	2.57	C5…H9	2.67
O4…H16B	2.20	C7…H1B	2.616 (16)
H1A…O4 ⁱⁱ	2.112 (16)	C14…H16B	2.70
O4…H15A	2.54	H4…H13	2.36
C2—O1—C6	120.07 (8)	C11—C10—H10	120.7
C14—O5—C15	115.20 (8)	C9—C10—H10	120.7
C17—O7—C18	115.07 (8)	C10—C11—C12	122.61 (9)
C2—N1—H1A	117.3 (10)	C10—C11—N3	118.87 (9)
C2—N1—H1B	118.5 (10)	C12—C11—N3	118.52 (9)
H1A—N1—H1B	119.2 (14)	C13—C12—C11	118.05 (9)
O3—N3—O2	123.95 (9)	C13—C12—H12	121.0
O3—N3—C11	118.11 (9)	C11—C12—H12	121.0
O2—N3—C11	117.94 (8)	C12—C13—C8	120.94 (9)
N1—C2—C3	127.86 (10)	C12—C13—H13	119.5
N1—C2—O1	110.58 (9)	C8—C13—H13	119.5
C3—C2—O1	121.46 (9)	O4—C14—O5	122.65 (9)
C2—C3—C7	119.33 (9)	O4—C14—C5	126.85 (10)
C2—C3—C4	122.70 (9)	O5—C14—C5	110.49 (8)
C7—C3—C4	117.77 (9)	O5—C15—H15A	109.5
C5—C4—C3	109.69 (8)	O5—C15—H15B	109.5
C5—C4—C8	111.99 (8)	H15A—C15—H15B	109.5
C3—C4—C8	109.73 (8)	O5—C15—H15C	109.5
C5—C4—H4	108.5	H15A—C15—H15C	109.5
C3—C4—H4	108.5	H15B—C15—H15C	109.5
C8—C4—H4	108.5	C6—C16—C17	110.25 (8)
C6—C5—C14	121.02 (9)	C6—C16—H16A	109.6
C6—C5—C4	122.16 (9)	C17—C16—H16A	109.6

C14—C5—C4	116.79 (9)	C6—C16—H16B	109.6
C5—C6—O1	122.47 (9)	C17—C16—H16B	109.6
C5—C6—C16	129.65 (9)	H16A—C16—H16B	108.1
O1—C6—C16	107.84 (8)	O6—C17—O7	124.87 (10)
N2—C7—C3	177.84 (11)	O6—C17—C16	125.10 (9)
C13—C8—C9	119.51 (9)	O7—C17—C16	110.03 (8)
C13—C8—C4	119.14 (8)	O7—C18—H18A	109.5
C9—C8—C4	121.25 (9)	O7—C18—H18B	109.5
C10—C9—C8	120.37 (9)	H18A—C18—H18B	109.5
C10—C9—H9	119.8	O7—C18—H18C	109.5
C8—C9—H9	119.8	H18A—C18—H18C	109.5
C11—C10—C9	118.51 (9)	H18B—C18—H18C	109.5
C6—O1—C2—N1	−172.01 (8)	C4—C8—C9—C10	175.54 (9)
C6—O1—C2—C3	4.55 (14)	C8—C9—C10—C11	0.07 (15)
N1—C2—C3—C7	−4.60 (16)	C9—C10—C11—C12	0.57 (15)
O1—C2—C3—C7	179.47 (9)	C9—C10—C11—N3	−178.79 (9)
N1—C2—C3—C4	−179.38 (9)	O3—N3—C11—C10	−12.19 (14)
O1—C2—C3—C4	4.70 (14)	O2—N3—C11—C10	167.63 (9)
C2—C3—C4—C5	−12.33 (13)	O3—N3—C11—C12	168.42 (9)
C7—C3—C4—C5	172.82 (8)	O2—N3—C11—C12	−11.75 (13)
C2—C3—C4—C8	111.09 (10)	C10—C11—C12—C13	−0.46 (15)
C7—C3—C4—C8	−63.76 (11)	N3—C11—C12—C13	178.90 (9)
C3—C4—C5—C6	12.41 (13)	C11—C12—C13—C8	−0.29 (15)
C8—C4—C5—C6	−109.67 (10)	C9—C8—C13—C12	0.91 (15)
C3—C4—C5—C14	−169.57 (8)	C4—C8—C13—C12	−175.50 (9)
C8—C4—C5—C14	68.34 (10)	C15—O5—C14—O4	1.14 (13)
C14—C5—C6—O1	177.07 (8)	C15—O5—C14—C5	179.93 (8)
C4—C5—C6—O1	−5.00 (15)	C6—C5—C14—O4	5.60 (16)
C14—C5—C6—C16	−5.52 (16)	C4—C5—C14—O4	−172.44 (9)
C4—C5—C6—C16	172.42 (9)	C6—C5—C14—O5	−173.13 (9)
C2—O1—C6—C5	−4.43 (14)	C4—C5—C14—O5	8.83 (12)
C2—O1—C6—C16	177.66 (8)	C5—C6—C16—C17	−99.61 (12)
C5—C4—C8—C13	−144.02 (9)	O1—C6—C16—C17	78.09 (10)
C3—C4—C8—C13	93.92 (10)	C18—O7—C17—O6	−2.19 (15)
C5—C4—C8—C9	39.64 (12)	C18—O7—C17—C16	178.38 (8)
C3—C4—C8—C9	−82.42 (11)	C6—C16—C17—O6	8.59 (15)
C13—C8—C9—C10	−0.79 (15)	C6—C16—C17—O7	−171.99 (8)

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

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

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N1—H1A $\cdots$ O4 ⁱⁱ	0.887 (16)	2.112 (16)	2.9362 (12)	154.1 (13)
N1—H1B $\cdots$ N2 ^{iv}	0.892 (17)	2.152 (17)	3.0283 (14)	167.2 (14)

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