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Crystal structure and Hirshfeld surface analysis of methyl 4′-amino-3′,5′-dicyano-2,2″-dioxodispiro-[indoline-3,1′-cyclopentane-2′,3″-indolin]-3′-ene-5′-carboximidate with an unknown solvent

Farid N. Naghiyev,[a] Victor N. Khrustalev,[b,c] Elena A. Fortalnova,[b] Mehmet Akkurt,[d] Ali N. Khalilov,[a,e] Ajaya Bhattarai[f]* and İbrahim G. Mamedov[a]

[a]Department of Chemistry, Baku State University, Z. Khalilov str. 23, Az, 1148 Baku, Azerbaijan, [b]Peoples' Friendship University of Russia (RUDN University), Miklukho-Maklay St. 6, Moscow, 117198, Russian Federation, [c]N. D. Zelinsky Institute of Organic Chemistry RAS, Leninsky Prosp. 47, Moscow, 119991, Russian Federation, [d]Department of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey, [e]"Composite Materials" Scientific Research Center, Azerbaijan State Economic University (UNEC), H. Aliyev str. 135, Az 1063, Baku, Azerbaijan, and [f]Department of Chemistry, M.M.A.M.C (Tribhuvan University) Biratnagar, Nepal. *Correspondence e-mail: ajaya.bhattarai@mmamc.tu.edu.np2173900

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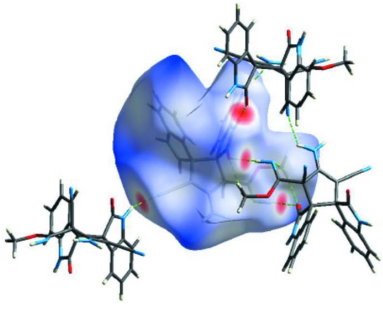
Supporting information: this article has supporting information at journals.iucr.org/e

In the title compound, $C_{23}H_{16}N_6O_3$, the central five-membered cyclopentene ring adopts an envelope conformation while the five-membered spiro 2,3-dihydro-1*H*-pyrrole rings exhibit twisted envelope and envelope conformations. One of the 1,3-dihydro-2*H*-indol-2-one units is in an axial position and the other is in a bisectional position. The methyl methanimidate unit is in an equatorial position. The crystal structure of the title compound is consolidated by intermolecular N—H···N, N—H···O and C—H···O hydrogen bonds, forming a three dimensional network.

1. Chemical context

Functionalized carbo- and heterocycles are of great interest in the fields of organic synthesis, catalysis, material science and medicinal chemistry (Zubkov *et al.*, 2018; Shikhaliyev *et al.*, 2019; Viswanathan *et al.*, 2019; Gurbanov *et al.*, 2020). Cyclization of carbo- and heterocycles with the participation of malononitrile to obtain spiro compounds has been reported in the literature. (Zhu *et al.*, 2016; Tan *et al.*, 2020). In addition, it is known that the reaction of Hantzsch ester with two molecules of 2-(2-oxoindolin-3-ylidene)malononitrile, **1**, leads to the formation of dispiro[cyclopent-3-ene]bisoxindoles, **2** (Shanthi & Perumal, 2008). We found that one of the nitrile groups of dispiro[cyclopent-3-ene]bisoxindole tricarbonitrile **2** reacted with the methanol (solvent) gave rise to compound **3** (Fig. 1).

Thus, in the framework of ongoing structural studies (Safavora *et al.*, 2019; Aliyeva *et al.*, 2011; Mamedov *et al.*, 2022), we report the crystal structure and Hirshfeld surface analysis of the title compound, methyl 4′-amino-3′,5′-dicyano-



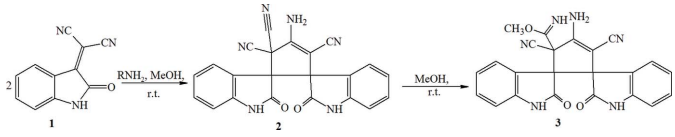


Figure 1
The formation of **3**.

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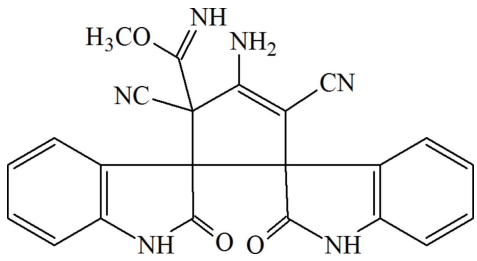
2,2′′-dioxodispiro[indoline-3,1′-cyclopentane-2′,3′′-indolin]-3′-ene-5′-carbimidate, which has an unknown solvent.



2. Structural commentary

The title compound (Fig.2) crystallizes in the monoclinic space group $P2_1/c$ with Z = 4. The N1/O2/C2/C3/C3*A*/C4–C7/C7*A* 1,3-dihydro-2*H*-indol-2-one unit, which is attached to C3, makes a dihedral angle of 1.71 (6)° with the mean plane of the central five-membered cyclopentene ring (C3/C10/C15–C17). The N8/C9/C10/C10*A*/C14*A* 1,3-dihydro-2*H*-indol-2-one unit, which is attached to C10, forms a dihedral angle of 57.50 (4)° with the other 1,3-dihydro-2*H*-indol-2-one unit. The methyl methanimidate unit, which is attached to C17, is in an equatorial position. The conformation of the title molecule, (Fig. 2), is fixed because of the weak intramolecular N16—H16*A*···N19 [2.079 (19) Å, 132.5 (16)°] and C11—H11···O2 [2.53 Å, 123°] hydrogen bonds, which close the six- and seven-membered rings with graph-set notations *S*(6) and *S*(7), respectively (Bernstein *et al.*, 1995; Table 1).

The central five-membered cyclopentene ring (C3/C10/C15–C17) adopts an envelope conformation with the flap atom, C3, lying 0.181 (1) Å out of the plane defined by the remaining atoms. The puckering parameters (Cremer & Pople, 1975) are $Q(2)$ = 0.2915 (14) Å, $\varphi(2)$ = 175.0 (3)°. The five-membered spiro 2,3-dihydro-1*H*-pyrrole rings (N1/C2/C3/C3*A*/C7*A* and N8/C9/C10/C10*A*/C14*A*) exhibit a twisted envelope conformation on bond C2–C3 and an envelope conformation with atom C10 as a flap, respectively. Their puckering parameters are $Q(2)$ = 0.0864 (13) Å, $\varphi(2)$ = 62.5 (9)° and $Q(2)$ = 0.0810 (14) Å, $\varphi(2)$ = 64.7 (10)°, respectively.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O9^{i}	0.860 (19)	1.963 (18)	2.8145 (14)	170.0 (16)
N8—H8···N18^{ii}	0.866 (19)	2.110 (18)	2.9270 (19)	157.1 (17)
N16—H16*A*···N19	0.883 (19)	2.079 (19)	2.7531 (17)	132.5 (16)
N16—H16*A*···N21^{iii}	0.883 (19)	2.684 (19)	3.1854 (17)	117.1 (14)
N19—H19···O2^{iv}	0.894 (19)	2.130 (19)	2.9912 (15)	161.6 (17)
C11—H11···O2	0.95	2.53	3.1499 (18)	123
C20—H20*C*···O2^{iv}	0.98	2.56	3.1938 (16)	123

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

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, pairs of molecules are linked by intermolecular N19—-H19···O2($-x+1, -y+1, -z+1$) hydrogen bonds into inversion dimers with an $R_2^2(14)$ ring motif (Bernstein *et al.*, 1995). Weak intermolecular C20—-H20*C*···O2($-x+1, -y+1,$

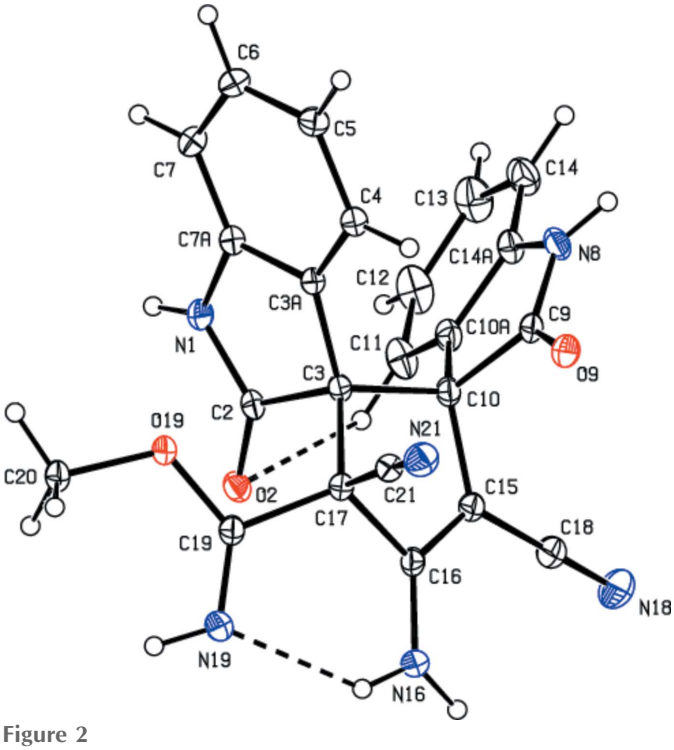


Figure 2
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

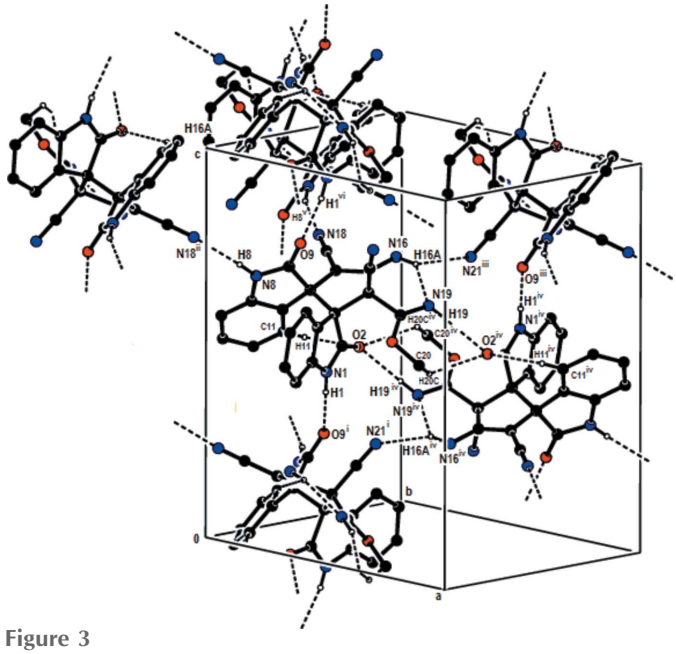


Figure 3
A general view of the packing and N—H···N, N—H···O and C—H···O hydrogen bonding of the title compound in the unit cell. The hydrogen atoms not involved in the hydrogen bonds have been omitted for clarity. Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+1, -y+1, -z+1$; (v) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vi) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

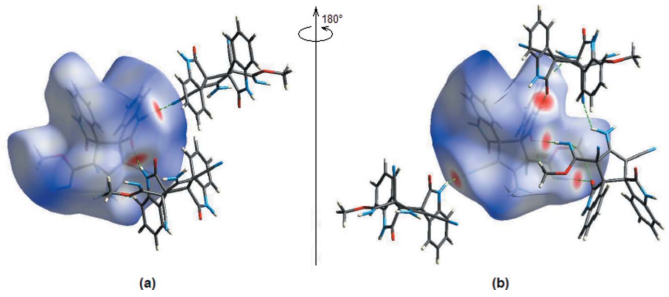


Figure 4
The three-dimensional Hirshfeld surface of the title compound plotted over d_{norm} in the range −0.6120 to 2.8879 a.u. The N—H···N and N—H···O hydrogen bonds are shown.

$-z + 1$) and intramolecular N16—H16*A*···N19 (x, y, z) hydrogen bonds also form an $S(6)R_1^2(6)R_2^2(14)R_1^2(6)S(6)$ ring motif system between these dimer molecules. Futhermore, these dimers are linked by N8—H8···N18($-x$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$) hydrogen bonds in the directions of both base diagonals of the *ab* plane of the unit cell, forming sheets parallel to the (001) plane. These layers are also connected along the *c*-axis direction by N1—H1···O9 (x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$) and N16—H16*A*···N21 ($-x + 1$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$) hydrogen bonds (Table 1, Fig. 3). The three-dimensional hydrogen-bonded network thus formed keeps the crystal structure stable.

Hirshfeld surface analysis can be used to qualitatively visualize the main interactions between molecules (Spackman & Jayatilaka, 2009). *CrystalExplorer17.5* (Turner *et al.*, 2017) was used to map the normalized contact distance (d_{norm}). On the Hirshfeld surfaces, the most notable interactions (short contact areas) are represented in red, whereas long contacts are displayed in blue. Fig. 4 depicts the three-dimensional Hirshfeld surface overlaid over d_{norm} in the range −0.6120 (red) to +2.8879 (blue) a.u.

Fingerprint plots were created to indicate intermolecular surface bond distances, with regions highlighted for N···H/H···N and O···H/H···O interactions (Table 1, Fig. 5). Such connections contribute 30.3% and 14.6%, respectively, of the surface area. The very low number of C···H/H···C connections (14.9%) shows that these interactions play a minor role in crystal-packing consolidation. The contribution to the surface area for H···H contacts is 38.3%. Other weak contacts contribute only 1.0% (C···C), 0.5% (N···C/C···N), 0.2% (O···O), 0.1% (N···N) and 0.1% (O···C/C···O) to the Hirshfeld surface.

4. Database survey

The compound most closely related to the 2,8-diazadispiro-[4.0.4^6.3^5]trideca-3,9,11-triene unit of the title compound was found to be 4′-amino-2,2″-dioxo-1,1″,2,2″-tetrahydro-3′*H*-dispiro[indole-3,1′-cyclopent[4]ene-2′,3″-indole]-3′,3′-dicarbonitrile dihydrate (GITGUM; Gayathri *et al.*, 2008), which crystallizes in the orthorhombic space group, $Pna2_1$. The cyclopentene ring adopts an envelope conformation, with the spiro C atom bonded to the dicyano-substituted C atom deviating by 0.437 (2) Å from the plane of the remaining four atoms in the ring. The dihedral angle between the two indole groups is 60.1 (1)°. The structure contains intermolecular N—H···O hydrogen bonds involving the indole groups and O—H···O and O—H···N hydrogen bonds involving the water molecules.

5. Synthesis and crystallization

A solution of 2-(2-oxoindolin-3-ylidene)malononitrile (0.99 g; 5.1 mmol) and furfurylamine (0.5 g; 5.2 mmol) in methanol (25 mL) was stirred for 10 minutes and was kept in room temperature for 96 h. Then 15 mL of methanol were removed from the reaction mixture, which was left overnight. The precipitated crystals were separated by filtration and recrystallized from ethanol/water (1:1) solution (yield 46%; m.p. 574–575 K).

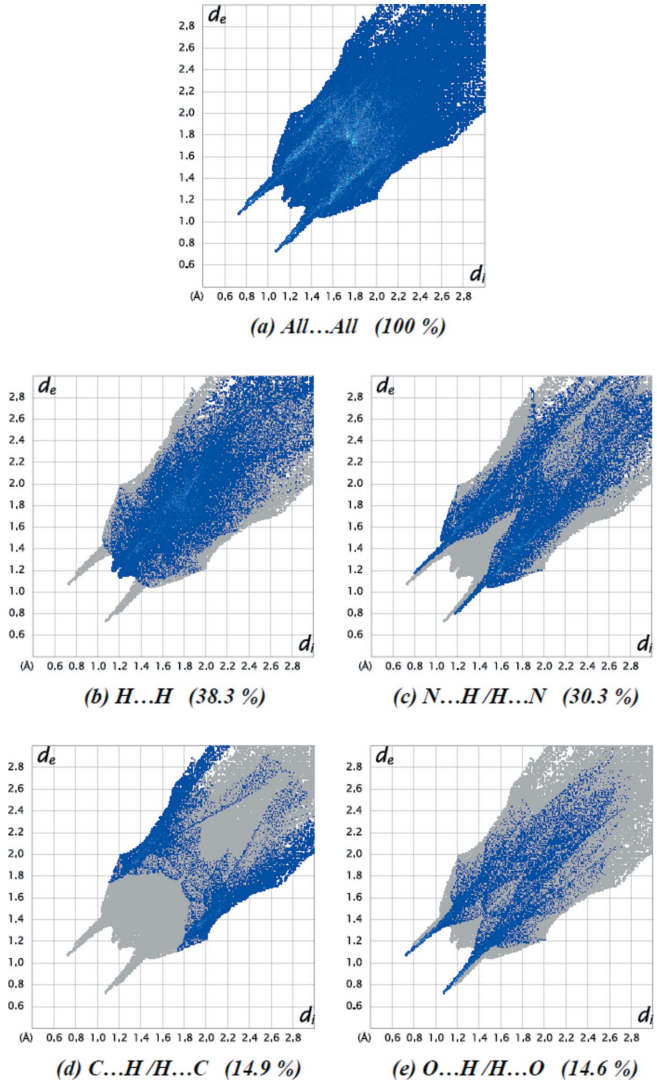


Figure 5
The two-dimensional fingerprint plots for the title compound, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) N···H/H···N, (*d*) C···H/H···C and (*e*) O···H/H···O interactions [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{23}H_{16}N_6O_3$
M_r	424.42
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	12.0085 (1), 12.4719 (1), 15.4909 (1)
β (°)	94.489 (1)
V (Å^3)	2312.94 (3)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.70
Crystal size (mm)	0.15 × 0.12 × 0.10
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2021)
T_{min}, T_{max}	0.891, 0.927
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31502, 5011, 4771
R_{int}	0.038
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.128, 1.04
No. of reflections	5011
No. of parameters	305
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.25

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

^{1}H NMR (300 MHz, DMSO-d_6, p.p.m.): 3.78 (*s*, 3H, CH_3); 6.62–7.26 (*m*, 8H, 8$CH_{arom.}$); 7.69 (*s*, 2H, NH_2); 8.87 (*s*, 1H, NH); 10.56 (*s*, 1H, NH), 10.62 (*s*, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): 53.66 (OCH_3), 54.56 ($C_{quat.}$), 56.63 ($C_{quat.}$), 75.06 (=C_{quat}), 76.72 (=C_{quat}), 109.96 ($CH_{arom.}$), 110.18 ($CH_{arom.}$), 116.32 (CN), 116.83 (CN), 122.08 ($CH_{arom.}$), 122.63 ($CH_{arom.}$), 124.17 ($C_{arom.}$), 124.41 ($C_{arom.}$), 126.07 ($CH_{arom.}$), 126.62 ($CH_{arom.}$), 130.27 ($CH_{arom.}$), 130.65 ($CH_{arom.}$), 143.14 ($C_{arom.}$), 143.31 ($C_{arom.}$), 159.57 (=$C_{quat.}$), 160.18 (=$C_{quat.}$), 175.07 (O=C−NH), 177.32 (O=C−NH).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were positioned geometrically (C—H = 0.95–0.98 Å) and included as riding contributions with isotropic displacement parameters fixed at 1.2U_{eq}(C) (1.5 for methyl groups). The N-bound H atoms were found in difference-Fourier maps and their coordinates refined with U_{iso}(H)=1.2U_{eq}(N). The residual electron density was difficult to model and therefore the SQUEEZE routine (Spek, 2015) in *PLATON* (Spek, 2020) was used to remove the contribution of the electron density in the solvent region from the intensity data and the solvent-free model was employed for the final refinement. The solvent formula mass and unit-cell characteristics were not taken into account during refinement. The cavity of volume *ca* 404.2 Å^3 (*ca* 17.5% of the unit-cell volume) contains approximately 101 electrons. A suitable solvent with this electron number may be about four ethanol molecules per unit cell.

Acknowledgements

Authors' contributions are as follows. Conceptualization, ANK and IGM; methodology, ANK and IGM; investigation, ANK, MA and EAF; writing (original draft), MA and ANK; writing (review and editing of the manuscript), MA and ANK; visualization, MA, ANK and IGM; funding acquisition, VNK, FNN and ANK; resources, AB, VNK and FNN; supervision, ANK and MA.

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supporting information

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Crystal structure and Hirshfeld surface analysis of methyl 4′-amino-3′,5′-dicyano-2,2′′-dioxodispiro[indoline-3,1′-cyclopentane-2′,3′′-indolin]-3′-ene-5′-carboximidate with an unknown solvent

Farid N. Naghiyev, Victor N. Khrustalev, Elena A. Fortalnova, Mehmet Akkurt, Ali N. Khalilov, Ajaya Bhattarai and İbrahim G. Mamedov

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* (Rigaku OD, 2021); data reduction: *CrysAlis PRO* (Rigaku OD, 2021); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

Methyl 4′-amino-3′,5′-dicyano-2,2′′-dioxodispiro[indoline-3,1′-cyclopentane-2′,3′′-indolin]-3′-ene-5′-carboximidate

Crystal data

$C_{23}H_{16}N_6O_3$
M_r = 424.42
Monoclinic, $P2_1/c$
a = 12.0085 (1) Å
b = 12.4719 (1) Å
c = 15.4909 (1) Å
β = 94.489 (1)°
V = 2312.94 (3) Å^3
Z = 4
$F(000)$ = 880
D_x = 1.219 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 22193 reflections
θ = 3.7–79.3°
μ = 0.70 mm^{-1}
T = 100 K
Prism, colourless
0.15 × 0.12 × 0.10 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube
φ and ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2021)
T_{min} = 0.891, T_{max} = 0.927
31502 measured reflections
5011 independent reflections
4771 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 79.7°, θ_{min} = 3.7°
h = −15→14
k = −15→15
l = −16→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.128
S = 1.04
5011 reflections
305 parameters
0 restraints
Primary atom site location: difference Fourier map

Secondary atom site location: difference Fourier map	$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 1.0231P]$ where $P = (F_o^2 + 2F_c^2)/3$
Hydrogen site location: mixed	$(\Delta/\sigma)_{max} < 0.001$
H atoms treated by a mixture of independent and constrained refinement	$\Delta\rho_{max} = 0.35$ e Å^{-3}
	$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Experimental. CrysAlisPro 1.171.41.117a (Rigaku OD, 2021) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.29981 (9)	0.24967 (9)	0.44133 (7)	0.0245 (2)
H1	0.2870 (14)	0.2626 (14)	0.3869 (12)	0.029*
C2	0.30095 (10)	0.32803 (10)	0.50096 (8)	0.0217 (2)
O2	0.29321 (8)	0.42469 (7)	0.48817 (6)	0.0257 (2)
C3	0.31293 (10)	0.27464 (10)	0.59181 (8)	0.0203 (2)
C3A	0.33681 (10)	0.15908 (10)	0.56953 (8)	0.0207 (2)
C4	0.36295 (10)	0.06941 (10)	0.61983 (8)	0.0241 (3)
H4	0.3722	0.0747	0.6811	0.029*
C5	0.37540 (12)	−0.02910 (10)	0.57855 (9)	0.0278 (3)
H5	0.3942	−0.0911	0.6122	0.033*
C6	0.36067 (12)	−0.03723 (11)	0.48910 (9)	0.0305 (3)
H6	0.3694	−0.1049	0.4623	0.037*
C7	0.33332 (12)	0.05214 (11)	0.43778 (9)	0.0288 (3)
H7	0.3224	0.0465	0.3765	0.035*
C7A	0.32274 (10)	0.14916 (10)	0.47930 (8)	0.0231 (3)
N8	0.09577 (10)	0.13898 (10)	0.67133 (7)	0.0275 (2)
H8	0.0674 (15)	0.0887 (15)	0.7013 (12)	0.033*
C9	0.18227 (10)	0.20090 (10)	0.70137 (8)	0.0232 (3)
O9	0.23955 (8)	0.18888 (8)	0.76917 (6)	0.0284 (2)
C10	0.19781 (10)	0.29116 (10)	0.63396 (8)	0.0227 (3)
C10A	0.09505 (11)	0.27542 (11)	0.57198 (8)	0.0257 (3)
C11	0.04983 (12)	0.33584 (13)	0.50258 (10)	0.0346 (3)
H11	0.0839	0.4011	0.4872	0.041*
C12	−0.04637 (13)	0.29896 (16)	0.45597 (11)	0.0437 (4)
H12	−0.0784	0.3396	0.4084	0.052*
C13	−0.09603 (13)	0.20330 (16)	0.47827 (11)	0.0440 (4)
H13	−0.1604	0.1785	0.4446	0.053*
C14	−0.05321 (12)	0.14320 (14)	0.54893 (10)	0.0368 (3)
H14	−0.0876	0.0782	0.5647	0.044*
C14A	0.04124 (11)	0.18180 (11)	0.59521 (9)	0.0276 (3)
C15	0.21617 (11)	0.39881 (10)	0.67678 (8)	0.0256 (3)
C16	0.32451 (11)	0.43111 (10)	0.68444 (8)	0.0233 (3)

N16	0.36972 (11)	0.51996 (9)	0.72048 (7)	0.0281 (2)
H16A	0.4391 (16)	0.5352 (15)	0.7097 (12)	0.034*
H16B	0.3234 (15)	0.5750 (15)	0.7399 (11)	0.034*
C17	0.39908 (10)	0.34282 (10)	0.64964 (8)	0.0217 (2)
C18	0.12832 (12)	0.45803 (11)	0.70963 (10)	0.0315 (3)
N18	0.05723 (12)	0.50576 (12)	0.73688 (10)	0.0455 (3)
C19	0.49892 (10)	0.38414 (10)	0.60184 (8)	0.0233 (3)
O19	0.52472 (7)	0.31043 (7)	0.54332 (6)	0.0246 (2)
N19	0.54541 (10)	0.47131 (10)	0.62336 (8)	0.0305 (3)
H19	0.6035 (16)	0.4899 (15)	0.5939 (12)	0.037*
C20	0.61787 (12)	0.33447 (11)	0.49283 (9)	0.0285 (3)
H20A	0.6255	0.2776	0.4501	0.043*
H20B	0.6865	0.3390	0.5312	0.043*
H20C	0.6047	0.4031	0.4630	0.043*
C21	0.45228 (11)	0.28321 (10)	0.72483 (8)	0.0239 (3)
N21	0.50020 (10)	0.24235 (10)	0.78254 (8)	0.0322 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0290 (5)	0.0262 (5)	0.0187 (5)	−0.0010 (4)	0.0053 (4)	0.0020 (4)
C2	0.0198 (5)	0.0246 (6)	0.0215 (6)	−0.0013 (4)	0.0063 (4)	0.0026 (4)
O2	0.0279 (5)	0.0229 (4)	0.0272 (5)	−0.0006 (3)	0.0074 (4)	0.0046 (3)
C3	0.0211 (5)	0.0201 (6)	0.0203 (5)	−0.0008 (4)	0.0064 (4)	0.0014 (4)
C3A	0.0200 (5)	0.0207 (6)	0.0222 (6)	−0.0017 (4)	0.0066 (4)	−0.0012 (4)
C4	0.0253 (6)	0.0236 (6)	0.0241 (6)	−0.0009 (5)	0.0058 (5)	0.0004 (5)
C5	0.0324 (7)	0.0212 (6)	0.0305 (7)	0.0006 (5)	0.0066 (5)	0.0013 (5)
C6	0.0361 (7)	0.0235 (6)	0.0329 (7)	−0.0010 (5)	0.0094 (6)	−0.0066 (5)
C7	0.0344 (7)	0.0293 (7)	0.0236 (6)	−0.0031 (5)	0.0074 (5)	−0.0057 (5)
C7A	0.0235 (6)	0.0244 (6)	0.0222 (6)	−0.0018 (5)	0.0059 (4)	−0.0001 (5)
N8	0.0279 (6)	0.0293 (6)	0.0263 (5)	−0.0066 (4)	0.0076 (4)	0.0047 (4)
C9	0.0247 (6)	0.0240 (6)	0.0223 (6)	0.0003 (5)	0.0098 (5)	−0.0009 (4)
O9	0.0339 (5)	0.0312 (5)	0.0206 (4)	−0.0012 (4)	0.0051 (4)	0.0002 (4)
C10	0.0227 (6)	0.0229 (6)	0.0237 (6)	0.0007 (4)	0.0083 (5)	0.0016 (5)
C10A	0.0222 (6)	0.0287 (6)	0.0271 (6)	0.0010 (5)	0.0074 (5)	0.0019 (5)
C11	0.0258 (6)	0.0418 (8)	0.0366 (7)	0.0021 (6)	0.0058 (6)	0.0119 (6)
C12	0.0295 (7)	0.0611 (11)	0.0398 (8)	0.0025 (7)	−0.0008 (6)	0.0153 (7)
C13	0.0255 (7)	0.0643 (11)	0.0414 (8)	−0.0069 (7)	−0.0033 (6)	0.0034 (8)
C14	0.0280 (7)	0.0443 (8)	0.0386 (8)	−0.0090 (6)	0.0053 (6)	0.0016 (6)
C14A	0.0238 (6)	0.0324 (7)	0.0273 (6)	−0.0019 (5)	0.0076 (5)	0.0018 (5)
C15	0.0292 (6)	0.0216 (6)	0.0273 (6)	0.0009 (5)	0.0113 (5)	−0.0003 (5)
C16	0.0296 (6)	0.0208 (6)	0.0210 (5)	0.0010 (5)	0.0100 (5)	0.0017 (4)
N16	0.0337 (6)	0.0211 (5)	0.0308 (6)	−0.0033 (4)	0.0120 (5)	−0.0041 (4)
C17	0.0243 (6)	0.0206 (6)	0.0208 (5)	−0.0004 (4)	0.0064 (4)	−0.0004 (4)
C18	0.0325 (7)	0.0273 (7)	0.0361 (7)	0.0007 (5)	0.0121 (6)	−0.0021 (5)
N18	0.0412 (7)	0.0417 (8)	0.0561 (8)	0.0086 (6)	0.0195 (6)	−0.0100 (6)
C19	0.0238 (6)	0.0243 (6)	0.0226 (6)	0.0004 (5)	0.0068 (4)	0.0003 (5)
O19	0.0257 (4)	0.0238 (4)	0.0256 (4)	−0.0020 (3)	0.0107 (3)	−0.0018 (3)

N19	0.0286 (6)	0.0289 (6)	0.0356 (6)	−0.0073 (5)	0.0127 (5)	−0.0051 (5)
C20	0.0298 (6)	0.0271 (6)	0.0306 (6)	−0.0017 (5)	0.0154 (5)	−0.0011 (5)
C21	0.0253 (6)	0.0227 (6)	0.0244 (6)	−0.0022 (5)	0.0059 (5)	−0.0029 (5)
N21	0.0343 (6)	0.0323 (6)	0.0296 (6)	0.0016 (5)	0.0006 (5)	−0.0005 (5)

Geometric parameters (Å, º)

N1—C2	1.3442 (17)	C10A—C14A	1.3953 (19)
N1—C7A	1.4028 (17)	C11—C12	1.392 (2)
N1—H1	0.860 (18)	C11—H11	0.9500
C2—O2	1.2240 (16)	C12—C13	1.389 (3)
C2—C3	1.5534 (16)	C12—H12	0.9500
C3—C3A	1.5147 (16)	C13—C14	1.392 (2)
C3—C17	1.5655 (17)	C13—H13	0.9500
C3—C10	1.5878 (16)	C14—C14A	1.380 (2)
C3A—C4	1.3849 (17)	C14—H14	0.9500
C3A—C7A	1.4003 (17)	C15—C16	1.3582 (19)
C4—C5	1.3984 (18)	C15—C18	1.4148 (18)
C4—H4	0.9500	C16—N16	1.3368 (17)
C5—C6	1.3868 (19)	C16—C17	1.5429 (17)
C5—H5	0.9500	N16—H16A	0.88 (2)
C6—C7	1.393 (2)	N16—H16B	0.947 (19)
C6—H6	0.9500	C17—C21	1.4835 (17)
C7—C7A	1.3809 (18)	C17—C19	1.5461 (16)
C7—H7	0.9500	C18—N18	1.148 (2)
N8—C9	1.3477 (17)	C19—N19	1.2553 (18)
N8—C14A	1.4083 (18)	C19—O19	1.3441 (15)
N8—H8	0.87 (2)	O19—C20	1.4457 (15)
C9—O9	1.2188 (16)	N19—H19	0.89 (2)
C9—C10	1.5566 (17)	C20—H20A	0.9800
C10—C15	1.5060 (18)	C20—H20B	0.9800
C10—C10A	1.5158 (18)	C20—H20C	0.9800
C10A—C11	1.3882 (19)	C21—N21	1.1443 (18)
C2—N1—C7A	111.74 (11)	C14A—C10A—C10	108.39 (11)
C2—N1—H1	121.9 (12)	C10A—C11—C12	118.74 (14)
C7A—N1—H1	126.4 (12)	C10A—C11—H11	120.6
O2—C2—N1	127.46 (12)	C12—C11—H11	120.6
O2—C2—C3	124.71 (11)	C13—C12—C11	120.65 (15)
N1—C2—C3	107.83 (10)	C13—C12—H12	119.7
C3A—C3—C2	101.96 (9)	C11—C12—H12	119.7
C3A—C3—C17	121.25 (10)	C12—C13—C14	121.24 (15)
C2—C3—C17	107.21 (9)	C12—C13—H13	119.4
C3A—C3—C10	113.81 (10)	C14—C13—H13	119.4
C2—C3—C10	107.16 (9)	C14A—C14—C13	117.31 (15)
C17—C3—C10	104.59 (9)	C14A—C14—H14	121.3
C4—C3A—C7A	119.64 (11)	C13—C14—H14	121.3
C4—C3A—C3	132.76 (11)	C14—C14A—C10A	122.43 (13)

C7A—C3A—C3	107.53 (10)	C14—C14A—N8	127.74 (13)
C3A—C4—C5	118.67 (12)	C10A—C14A—N8	109.81 (12)
C3A—C4—H4	120.7	C16—C15—C18	123.36 (12)
C5—C4—H4	120.7	C16—C15—C10	114.15 (11)
C6—C5—C4	120.75 (12)	C18—C15—C10	122.43 (12)
C6—C5—H5	119.6	N16—C16—C15	129.59 (12)
C4—C5—H5	119.6	N16—C16—C17	120.64 (12)
C5—C6—C7	121.16 (12)	C15—C16—C17	109.63 (11)
C5—C6—H6	119.4	C16—N16—H16A	117.3 (12)
C7—C6—H6	119.4	C16—N16—H16B	120.3 (11)
C7A—C7—C6	117.48 (12)	H16A—N16—H16B	119.3 (16)
C7A—C7—H7	121.3	C21—C17—C16	108.02 (10)
C6—C7—H7	121.3	C21—C17—C19	103.92 (10)
C7—C7A—C3A	122.28 (12)	C16—C17—C19	114.99 (10)
C7—C7A—N1	127.58 (12)	C21—C17—C3	113.69 (10)
C3A—C7A—N1	110.12 (11)	C16—C17—C3	102.24 (10)
C9—N8—C14A	111.54 (11)	C19—C17—C3	114.17 (10)
C9—N8—H8	123.7 (12)	N18—C18—C15	179.49 (18)
C14A—N8—H8	123.1 (12)	N19—C19—O19	130.56 (12)
O9—C9—N8	126.50 (12)	N19—C19—C17	120.46 (11)
O9—C9—C10	125.30 (12)	O19—C19—C17	108.87 (10)
N8—C9—C10	108.20 (11)	C19—O19—C20	116.87 (10)
C15—C10—C10A	118.58 (11)	C19—N19—H19	116.0 (12)
C15—C10—C9	111.74 (10)	O19—C20—H20A	109.5
C10A—C10—C9	101.35 (10)	O19—C20—H20B	109.5
C15—C10—C3	101.22 (10)	H20A—C20—H20B	109.5
C10A—C10—C3	114.49 (10)	O19—C20—H20C	109.5
C9—C10—C3	109.63 (10)	H20A—C20—H20C	109.5
C11—C10A—C14A	119.54 (13)	H20B—C20—H20C	109.5
C11—C10A—C10	132.06 (13)	N21—C21—C17	174.75 (14)

C7A—N1—C2—O2	173.52 (12)	C9—C10—C10A—C14A	−7.41 (13)
C7A—N1—C2—C3	−7.02 (14)	C3—C10—C10A—C14A	110.49 (12)
O2—C2—C3—C3A	−171.59 (12)	C14A—C10A—C11—C12	−2.3 (2)
N1—C2—C3—C3A	8.93 (12)	C10—C10A—C11—C12	178.83 (14)
O2—C2—C3—C17	−43.22 (15)	C10A—C11—C12—C13	−0.2 (3)
N1—C2—C3—C17	137.30 (10)	C11—C12—C13—C14	1.8 (3)
O2—C2—C3—C10	68.59 (15)	C12—C13—C14—C14A	−0.8 (3)
N1—C2—C3—C10	−110.89 (11)	C13—C14—C14A—C10A	−1.8 (2)
C2—C3—C3A—C4	175.38 (13)	C13—C14—C14A—N8	176.05 (15)
C17—C3—C3A—C4	56.55 (18)	C11—C10A—C14A—C14	3.4 (2)
C10—C3—C3A—C4	−69.58 (17)	C10—C10A—C14A—C14	−177.49 (13)
C2—C3—C3A—C7A	−7.73 (12)	C11—C10A—C14A—N8	−174.82 (12)
C17—C3—C3A—C7A	−126.56 (11)	C10—C10A—C14A—N8	4.31 (15)
C10—C3—C3A—C7A	107.30 (11)	C9—N8—C14A—C14	−176.69 (14)
C7A—C3A—C4—C5	0.46 (18)	C9—N8—C14A—C10A	1.39 (16)
C3—C3A—C4—C5	177.04 (12)	C10A—C10—C15—C16	−141.23 (12)
C3A—C4—C5—C6	−0.7 (2)	C9—C10—C15—C16	101.48 (13)

C4—C5—C6—C7	0.1 (2)	C3—C10—C15—C16	−15.12 (14)
C5—C6—C7—C7A	0.7 (2)	C10A—C10—C15—C18	41.63 (17)
C6—C7—C7A—C3A	−1.0 (2)	C9—C10—C15—C18	−75.66 (16)
C6—C7—C7A—N1	177.60 (12)	C3—C10—C15—C18	167.73 (12)
C4—C3A—C7A—C7	0.41 (19)	C18—C15—C16—N16	−1.2 (2)
C3—C3A—C7A—C7	−176.96 (12)	C10—C15—C16—N16	−178.31 (12)
C4—C3A—C7A—N1	−178.41 (11)	C18—C15—C16—C17	174.49 (12)
C3—C3A—C7A—N1	4.22 (13)	C10—C15—C16—C17	−2.62 (15)
C2—N1—C7A—C7	−176.84 (13)	N16—C16—C17—C21	75.41 (14)
C2—N1—C7A—C3A	1.90 (15)	C15—C16—C17—C21	−100.73 (12)
C14A—N8—C9—O9	174.09 (12)	N16—C16—C17—C19	−40.11 (16)
C14A—N8—C9—C10	−6.31 (14)	C15—C16—C17—C19	143.75 (11)
O9—C9—C10—C15	−44.88 (17)	N16—C16—C17—C3	−164.39 (11)
N8—C9—C10—C15	135.52 (11)	C15—C16—C17—C3	19.47 (13)
O9—C9—C10—C10A	−172.13 (12)	C3A—C3—C17—C21	−41.76 (15)
N8—C9—C10—C10A	8.26 (13)	C2—C3—C17—C21	−157.97 (10)
O9—C9—C10—C3	66.51 (15)	C10—C3—C17—C21	88.47 (12)
N8—C9—C10—C3	−113.10 (11)	C3A—C3—C17—C16	−157.92 (10)
C3A—C3—C10—C15	160.56 (10)	C2—C3—C17—C16	85.87 (11)
C2—C3—C10—C15	−87.52 (11)	C10—C3—C17—C16	−27.69 (11)
C17—C3—C10—C15	26.07 (12)	C3A—C3—C17—C19	77.25 (14)
C3A—C3—C10—C10A	−70.67 (13)	C2—C3—C17—C19	−38.96 (13)
C2—C3—C10—C10A	41.26 (14)	C10—C3—C17—C19	−152.52 (10)
C17—C3—C10—C10A	154.85 (10)	C21—C17—C19—N19	−86.46 (15)
C3A—C3—C10—C9	42.42 (14)	C16—C17—C19—N19	31.40 (17)
C2—C3—C10—C9	154.34 (10)	C3—C17—C19—N19	149.14 (12)
C17—C3—C10—C9	−92.07 (11)	C21—C17—C19—O19	90.07 (11)
C15—C10—C10A—C11	48.9 (2)	C16—C17—C19—O19	−152.07 (11)
C9—C10—C10A—C11	171.58 (14)	C3—C17—C19—O19	−34.33 (14)
C3—C10—C10A—C11	−70.52 (18)	N19—C19—O19—C20	−3.0 (2)
C15—C10—C10A—C14A	−130.06 (12)	C17—C19—O19—C20	−179.10 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O9^{i}	0.860 (19)	1.963 (18)	2.8145 (14)	170.0 (16)
N8—H8···N18^{ii}	0.866 (19)	2.110 (18)	2.9270 (19)	157.1 (17)
N16—H16*A*···N19	0.883 (19)	2.079 (19)	2.7531 (17)	132.5 (16)
N16—H16*A*···N21^{iii}	0.883 (19)	2.684 (19)	3.1854 (17)	117.1 (14)
N19—H19···O2^{iv}	0.894 (19)	2.130 (19)	2.9912 (15)	161.6 (17)
C11—H11···O2	0.95	2.53	3.1499 (18)	123
C20—H20*C*···O2^{iv}	0.98	2.56	3.1938 (16)	123

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