

Crystal structure and Hirshfeld surface analysis of 1-[6-bromo-2-(3-bromophenyl)-1,2,3,4-tetrahydroquinolin-4-yl]pyrrolidin-2-one

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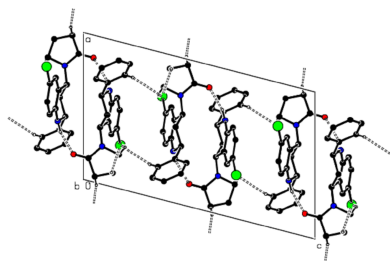
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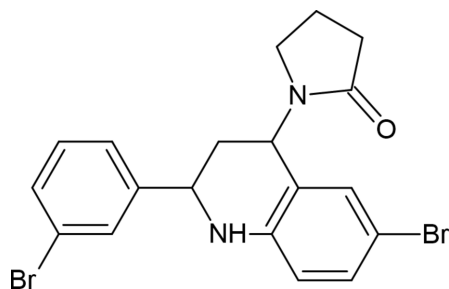
This study presents the synthesis, characterization and Hirshfeld surface analysis of 1-[6-bromo-2-(3-bromophenyl)-1,2,3,4-tetrahydroquinolin-4-yl]pyrrolidin-2-one, C₁₉H₁₈Br₂N₂O. In the title compound, the pyrrolidine ring adopts a distorted envelope configuration. In the crystal, molecules are linked by intermolecular N—H···O, C—H···O and C—H···Br hydrogen bonds, forming a three-dimensional network. In addition, pairs of molecules along the *c* axis are connected by C—H···π interactions. According to a Hirshfeld surface study, H···H (36.9%), Br···H/H···Br (28.2%) and C···H/H···C (24.3%) interactions are the most significant contributors to the crystal packing.

1. Chemical context

Currently, a large number of derivatives of known tetrahydroquinolines are promising candidates for testing against various types of biological activity. This class of *N*-heterocyclic compounds has attracted attention of biochemists for the past 50 years, as derivatives of the tetrahydroquinoline frame possess antibacterial, antitumor, and antiallergic properties. Some are already used as medicinal agents (Ghashghaei *et al.*, 2018).

In this regard, the synthesis and modification of the tetrahydroquinoline system to search for new drugs is an important task in organic chemistry. Over the years, several synthetic routes have been developed to obtain variously substituted tetrahydroquinolines (Sridharan *et al.*, 2011). However, the advantage remains with the Povarov reaction, due to the flexibility of this method, allowing the one-step synthesis of variously substituted 1,2,3,4-tetrahydroquinolines (Zubkov *et al.*, 2007, 2010; Kouznetsov, 2009; Varma *et al.*, 2010; Zaytsev *et al.*, 2013). Furthermore, the Povarov reaction is characterized by good yields and mild reaction conditions. Usually the reaction proceeds in two stages. The first stage is an aza-Diels–Alder reaction between *N*-arylimine and an electron-rich olefin in the presence of catalytic amounts of Lewis acid, which leads to the formation of a cycloadduct. The second stage involves a 1,3-H shift in the cycloadduct and results in the formation of the tetrahydroquinoline moiety.





In this work, the synthesis of the corresponding azomethine **3** was carried out using a condensation reaction between 4-bromoaniline (**1**) and 3-bromobenzaldehyde (**2**) to form product **3**, which was then introduced into the Povarov reaction. *N*-Vinylpyrrolidin-2-one was used as the alkene, and boron trifluoride etherate served as the Lewis acid (Fig. 1).

Thus, the Povarov method provides a convenient approach for the one-pot synthesis of substituted, partially hydrogenated quinolines and medicinal preparations based on the tetrahydroquinoline frame. Some stereochemical features of the resulting adduct **4** are discussed in this work. This work also discusses some stereochemical features of the resulting adduct **4**.

2. Structural commentary

In the title compound (Fig. 2), the 1,2,3,4-tetrahydropyridine ring (N1/C2–C4/C4A/C8A) of the 1,2,3,4-tetrahydroquinoline ring system (N1/C2–C4/C4A/C5–C8/C8A) adopts an envelope conformation [the puckering parameters (Cremer & Pople, 1975) are $Q_T = 0.523$ (2) Å, $\theta = 131.7$ (2)°, $\varphi = 300.9$ (3)°], while the benzene ring (C4A/C5–C8/C8A) is essentially planar (r.m.s. deviation = 0.002 Å). The plane (r.m.s. deviation = 0.002 Å) of the 1,2,3,4-tetrahydroquinoline ring system forms angles of 56.85 (9) and 83.05 (10)°, respectively, with the bromobenzene ring (C21–C26) and the pyrrolidine ring (N11/C12–C15; r.m.s. deviation = 0.002 Å), which has a distorted envelope conformation [the puckering parameters are $Q(2) = 0.225$ (2) Å, $\varphi(2) = 117.2$ (6)°]. The angle between the pyrro-

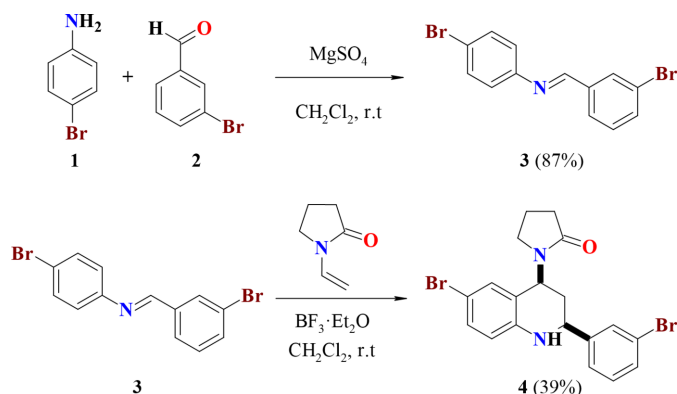


Figure 1
Synthesis of 1-[6-bromo-2-(3-bromophenyl)-1,2,3,4-tetrahydroquinolin-4-yl]pyrrolidin-2-one (**4**).

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

$Cg3$ is the centroid of the C4A/C5–C8/C8A benzene ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C13–H13A \cdots O1 ⁱ	0.99	2.46	3.431 (3)	169
C13–H13A \cdots Br2 ⁱⁱ	0.99	3.06	3.740 (3)	127
C14–H14A \cdots Br2 ⁱⁱ	0.99	3.12	3.664 (3)	116
C14–H14B \cdots Br1 ⁱⁱⁱ	0.99	3.02	3.786 (2)	135
C15–H15A \cdots Br1 ⁱⁱⁱ	0.99	3.00	3.748 (2)	133
C15–H15B \cdots Br2 ⁱⁱ	0.99	3.09	3.768 (2)	127
C22–H22 \cdots Br1 ^{iv}	0.95	2.94	3.820 (2)	155
C24–H24 \cdots Br2 ^v	0.95	3.04	3.932 (2)	158
N1–H1 \cdots O1 ^{vi}	0.86 (3)	2.30 (3)	3.115 (3)	159 (2)
C2–H2 \cdots Cg3 ^{vi}	1.00	2.66	3.655 (3)	173

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

lidine and bromobenzene rings is 84.92 (12)°. The geometric parameters in the molecule are normal and in good agreement with those in the compounds discussed in the *Database survey* (section 4).

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, molecules are linked by intermolecular N–H \cdots O, C–H \cdots O and C–H \cdots Br hydrogen bonds, forming a three-dimensional network (Table 1; Figs. 3, 4 and 5). In addition, pairs of molecules along the c axis are connected by C–H \cdots π interactions (Table 1; Figs. 6, 7 and 8). To quantify the intermolecular interactions in the crystal, the Hirshfeld surfaces of the title molecule and the two-dimensional fingerprints were generated with *CrystalExplorer17.5* (Spackman *et al.*, 2021). On the d_{norm} surfaces, bright-red spots show the locations of the N–H \cdots O, C–H \cdots O and C–H \cdots Br interactions (Table 1; Fig. 9*a,b*). The overall two-dimensional fingerprint plot for the title compound and those

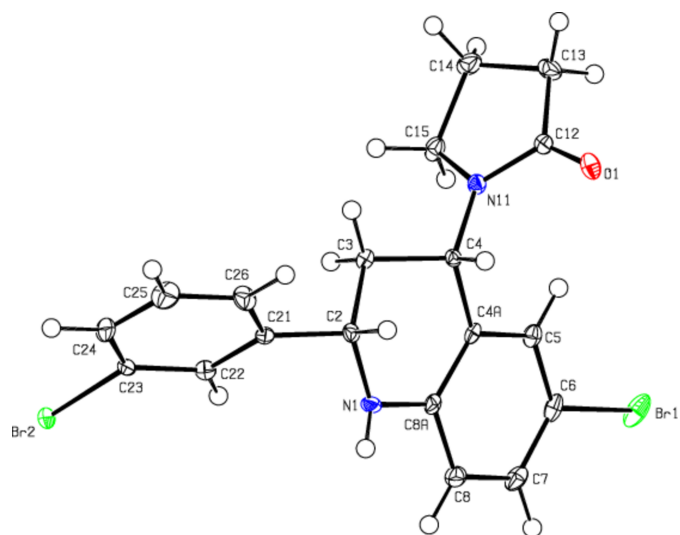
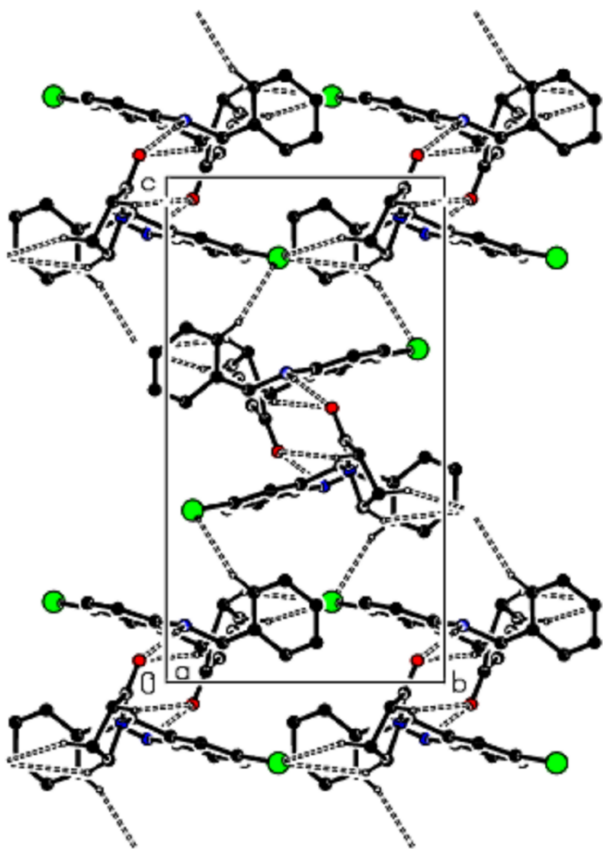
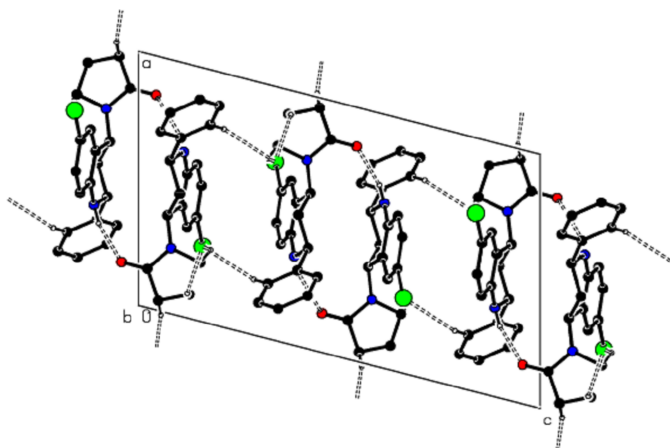


Figure 2
View of the title molecule. Displacement ellipsoids are drawn at the 50% probability level.

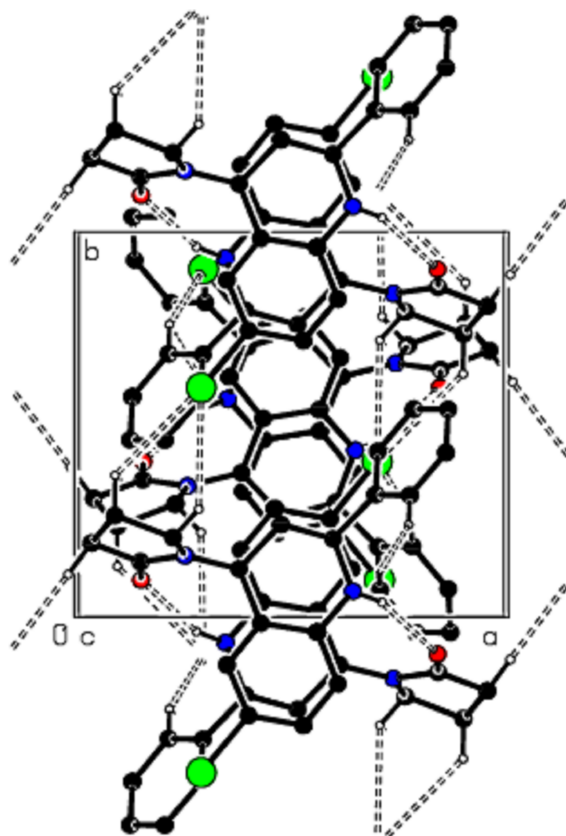

Figure 3

A view of the molecular packing along the *a* axis of the title compound, showing the N—H···O, C—H···O and C—H···Br hydrogen bonds as dashed lines.

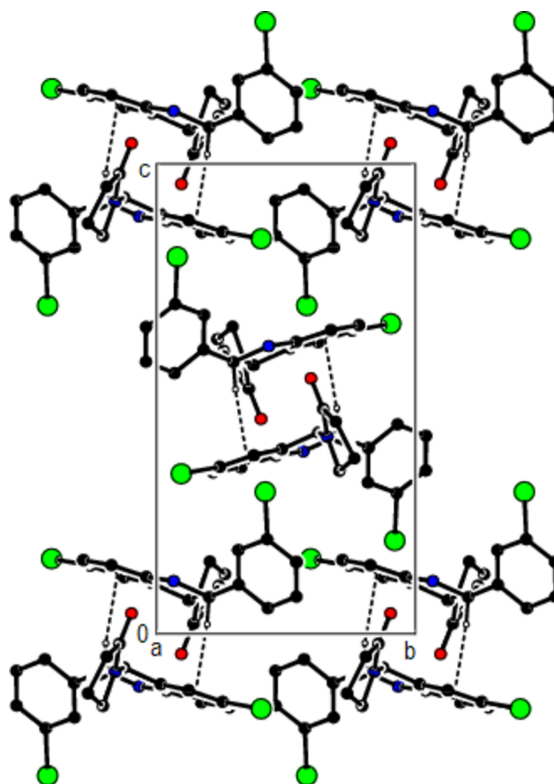
delineated into H···H (Fig. 10*b*; 36.9%), Br···H/H···Br (Fig. 10*c*; 28.2%) and C···H/H···C (Fig. 10*d*; 24.3%) contacts are shown in Fig. 10. O···H/H···O (7.1%), Br···O/O···Br (1.8%), Br···C/C···Br (0.9%), N···H/H···N (0.4%) and Br···N/N···Br (0.3%) contacts have little directional influence on the molecular packing.


Figure 4

A view of the molecular packing along the *b* axis of the title compound.


Figure 5

A view of the molecular packing along the *c* axis of the title compound.


Figure 6

A view of the molecular packing along the *a* axis of the title compound, showing the C—H··· π interactions.

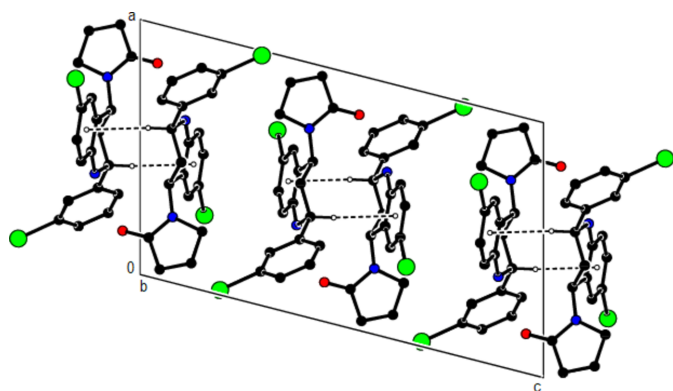


Figure 7
A view of the molecular packing along the *b* axis of the title compound.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, update of September 2021; Groom *et al.*, 2016) for similar structures with the 1,2,3,4-tetrahydroquinoline unit showed that the seven most closely related to the title compound are refcodes POSWAZ (Pronina *et al.*, 2024), EZOMIR (Çelik *et al.*, 2016), SUFDEE (Jeyaseelan, *et al.*, 2015c), NOVGAI (Jeyaseelan *et al.*, 2015a), WUFBEG (Jeyaseelan *et al.*, 2015b), WACWOO (Çelik *et al.*, 2010a) and CEDNUW (Çelik *et al.*, 2010b).

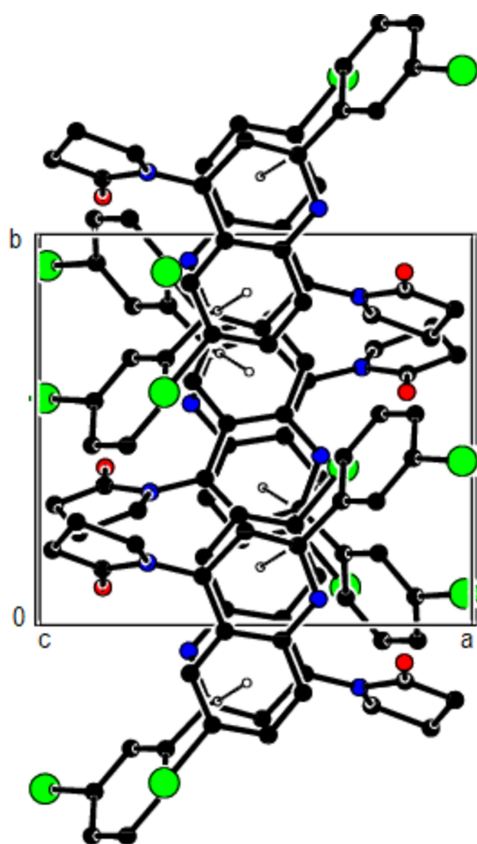


Figure 8
A view of the molecular packing along the *c* axis of the title compound.

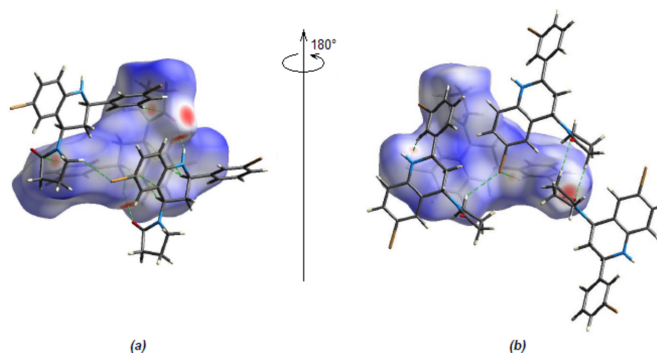


Figure 9
(*a*) Front and (*b*) back views of the three-dimensional Hirshfeld surface for the title compound. Some N–H···O, C–H···O and C–H···Br interactions are shown as dashed lines.

In the crystal of POSWAZ, molecules are linked by intermolecular N–H···O, C–H···O, C–H···F and C–H···Br hydrogen bonds, forming a three-dimensional network. In addition, C–H··· π interactions connect molecules into ribbons along the *b*-axis direction, consolidating the molecular packing. In the crystal of EZOMIR, inversion dimers linked by pairs of N–H···N hydrogen bonds generate $R_2^2(12)$ loops. In the crystal of SUFDEE, molecules are linked by weak C–H···O hydrogen bonds, generating C(8) and C(4) chains propagating along [100] and [010], respectively, which together

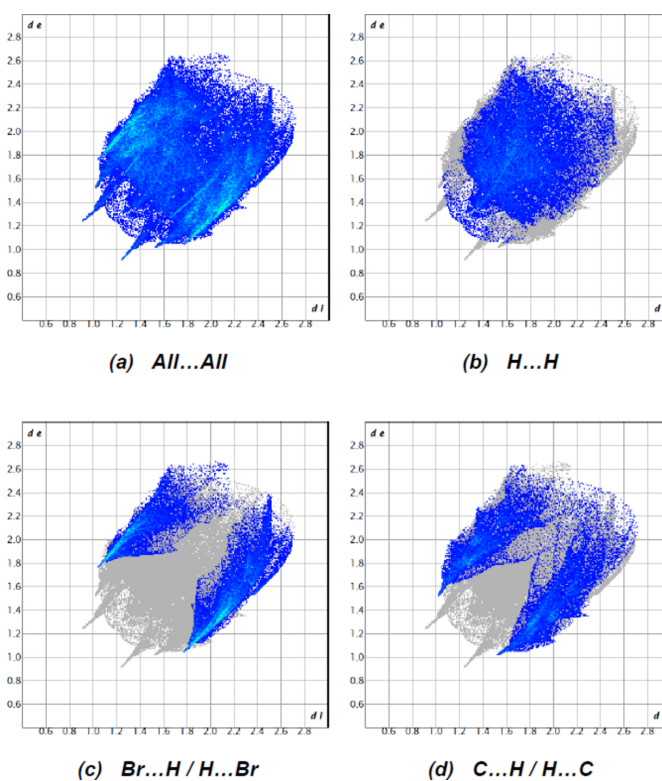


Figure 10
The two-dimensional fingerprint plots for the title compound showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) Br···H/H···Br and (*d*) C···H/H···C interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

generate (001) sheets. In the crystal of NOVGAI, inversion dimers linked by pairs of C—H...O hydrogen bonds generate $R_2^2(8)$ loops. In the crystal of WUFBEQ, inversion dimers linked by pairs of C—H...O hydrogen bonds generate $R_2^2(10)$ loops. Additional intermolecular C—H...O hydrogen bonds generate $C(7)$ chains along [100]. The crystal structure of WACWOO is stabilized by weak aromatic π – π interactions [centroid–centroid distance = 3.802 (4) Å] between the pyridine and benzene rings of the quinoline ring systems of adjacent molecules. In the crystal of CEDNUW, π – π stacking interactions are present between the pyridine and benzene rings of adjacent molecules [centroid–centroid distances = 3.634 (4) Å], and short Br...Br contacts [3.4443 (13) Å] occur.

5. Synthesis and crystallization

N-[(E)-(3-Bromophenyl)methylidene]-4-bromoaniline (3): A mixture of 4-bromoaniline (**1**) (2.00 g, 0.012 mol), 3-bromobenzaldehyde (**2**) (2.22 g, 0.012 mol) and anhydrous MgSO₄ (2.89 g, 0.024 mol) was stirred in CH₂Cl₂ (40 mL) for 24 h at room temperature. Then, the reaction mixture was passed through a silica gel layer (2 × 3 cm) (eluent CH₂Cl₂) and the solvent was evaporated under reduced pressure. Compound **3** was isolated as a yellow powder in 87% yield (3.54 g).

1-(6-Bromo-2-(3-bromophenyl)-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (4): Boron trifluoride ether (0.25 mL, 0.002 mol) and *N*-vinylpyrrolidin-2-one (1.18 mL, 0.011 mol) were added sequentially to a solution of the azomethine (**3**) (3.5 g, 0.010 mol) in freshly distilled CH₂Cl₂ (30 mL), under cooling (275–277 K) and constant stirring. The reaction was monitored by TLC (EtOAc/hexane, 1:2). After the reaction was complete (~24 h), the reaction mixture was treated with a small amount of water (0.2–0.3 mL) to decompose the catalyst. Then the resulting mixture was passed through a layer of silica gel (2 × 3 cm) and washed with dry CH₂Cl₂ (2 × 25 mL). The solvent was evaporated under reduced pressure. The obtained precipitate was recrystallized from a mixture of hexane/EtOAc. The desired product, **4**, was isolated as a white microcrystalline precipitate in 39% yield (1.76 g), m.p. 470.3–471.8 K. IR (KBr), ν (cm⁻¹): 3344 (NH), 2951 (Ph), 2889 (Ph), 1667 (N—C=O). ¹H NMR (700.2 MHz, CDCl₃, 298 K) (*J*, Hz): δ 2.01–2.10 (*m*, 4H, H-3 + H-4-pyrrole), 2.43–2.48 (*m*, 1H, H-3-pyrrole-A), 2.52–2.57 (*m*, 1H, H-3-pyrrole-B), 3.19–3.26 (*m*, 2H, H-5-pyrrole), 4.07 (*s*, 1H, NH), 4.54 (*dd*, *J* = 11.2, *J* = 2.9, 1H, H-2), 5.66 (*dd*, *J* = 11.7, *J* = 6.0 Hz, 1H, H-4), 6.49 (*d*, *J* = 8.6, 1H, H-8), 6.95 (*s*, 1H, H-5), 7.15 (*dd*, *J* = 8.6, *J* = 2.2, 1H, H-7), 7.24 (*t*, *J* = 7.9, 1H, H-5-C₆H₄-Br), 7.31 (*d*, *J* = 7.6, 1H, H-6-C₆H₄-Br), 7.45 (*d*, *J* = 7.9, 1H, H-4-C₆H₄-Br), 7.61 (*s*, 1H, H-2-C₆H₄-Br) ppm. ¹³C{¹H} NMR (176 MHz, CDCl₃, 298 K): δ 18.00, 31.00, 34.58, 42.03, 47.79, 55.60, 109.93, 116.48, 120.73, 122.71, 125.08, 128.93, 129.17, 130.20, 130.95, 131.00, 144.33, 144.69, 175.66 ppm.

Elemental analysis calculated (%) for C₁₉H₁₈Br₂N₂O: C, 50.69; H, 4.03; N, 6.22; found: C, 50.61; H, 3.94; N, 6.42.

Single crystals (splices of prisms) of compound **4** were grown from a mixture of hexane and ethyl acetate (~3:1).

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₉ H ₁₈ Br ₂ N ₂ O
<i>M_r</i>	450.17
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)	10.8691 (8), 9.4578 (7), 17.7217 (14)
β (°)	104.364 (3)
<i>V</i> (Å ³)	1764.8 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.60
Crystal size (mm)	0.36 × 0.32 × 0.26
Data collection	
Diffractometer	Bruker Kappa APEXII area-detector
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.714, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	25906, 4041, 3231
<i>R_{int}</i>	0.054
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.057, 1.02
No. of reflections	4041
No. of parameters	220
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)	0.47, -0.47

Computer programs: APEX3 and SAINT (Bruker, 2018), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2020).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were placed in calculated positions (0.95–1.00 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The N-bound H atom was located in a difference map and freely refined.

Acknowledgements

The authors' contributions are as follows. Conceptualization, MA and AB; synthesis, AAP and AGK; X-ray analysis, MSG, KIH and NDS; writing (review and editing of the manuscript) AAP, KIH and NDS; funding acquisition, AB and MA; supervision, MA and AB.

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Crystal structure and Hirshfeld surface analysis of 1-[6-bromo-2-(3-bromophenyl)-1,2,3,4-tetrahydroquinolin-4-yl]pyrrolidin-2-one

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Computing details

1-[6-Bromo-2-(3-bromophenyl)-1,2,3,4-tetrahydroquinolin-4-yl]pyrrolidin-2-one

Crystal data

$C_{19}H_{18}Br_2N_2O$

$M_r = 450.17$

Monoclinic, $P2_1/c$

$a = 10.8691$ (8) Å

$b = 9.4578$ (7) Å

$c = 17.7217$ (14) Å

$\beta = 104.364$ (3)°

$V = 1764.8$ (2) Å³

$Z = 4$

$F(000) = 896$

$D_x = 1.694$ Mg m⁻³

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

Cell parameters from 5029 reflections

$\theta = 2.9$ – 26.4 °

$\mu = 4.60$ mm⁻¹

$T = 100$ K

Bulk, colourless

$0.36 \times 0.32 \times 0.26$ mm

Data collection

Bruker Kappa APEXII area-detector diffractometer

φ and ω scans

Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.714$, $T_{\max} = 1.000$

25906 measured reflections

4041 independent reflections

3231 reflections with $I > 2\sigma(I)$

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

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 4.2$ °

$h = -13 \rightarrow 14$

$k = -11 \rightarrow 12$

$l = -23 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.057$

$S = 1.01$

4041 reflections

220 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0176P)^2 + 1.5651P]$

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

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

$\Delta\rho_{\max} = 0.47$ e Å⁻³

$\Delta\rho_{\min} = -0.47$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C2	0.3972 (2)	0.7031 (2)	0.42197 (14)	0.0095 (5)
H2	0.417106	0.695439	0.480026	0.011*
C3	0.5184 (2)	0.7407 (2)	0.39791 (14)	0.0103 (5)
H3A	0.551079	0.833284	0.420260	0.012*
H3B	0.500982	0.746994	0.340468	0.012*
C4	0.6161 (2)	0.6251 (2)	0.42821 (14)	0.0090 (5)
H4A	0.623691	0.617392	0.485461	0.011*
C4A	0.5649 (2)	0.4840 (2)	0.39280 (14)	0.0103 (5)
C5	0.6438 (2)	0.3756 (2)	0.37979 (14)	0.0116 (5)
H5A	0.732382	0.391768	0.387756	0.014*
C6	0.5933 (2)	0.2444 (2)	0.35526 (14)	0.0141 (5)
C7	0.4649 (2)	0.2184 (2)	0.34323 (14)	0.0153 (5)
H7A	0.431556	0.127113	0.327685	0.018*
C8	0.3852 (2)	0.3264 (2)	0.35403 (14)	0.0141 (5)
H8A	0.296550	0.309470	0.344583	0.017*
C8A	0.4337 (2)	0.4609 (2)	0.37876 (14)	0.0099 (5)
C12	0.8464 (2)	0.6433 (2)	0.47857 (15)	0.0108 (5)
C13	0.9605 (2)	0.6920 (2)	0.45130 (16)	0.0164 (6)
H13A	1.014249	0.610573	0.444761	0.020*
H13B	1.012448	0.759132	0.488933	0.020*
C14	0.9045 (2)	0.7642 (2)	0.37321 (16)	0.0183 (6)
H14A	0.954217	0.740510	0.335083	0.022*
H14B	0.903707	0.868151	0.379516	0.022*
C15	0.7689 (2)	0.7064 (2)	0.34649 (15)	0.0140 (5)
H15A	0.708860	0.781053	0.321194	0.017*
H15B	0.764491	0.626563	0.309794	0.017*
C21	0.2979 (2)	0.8177 (2)	0.39562 (14)	0.0098 (5)
C22	0.2170 (2)	0.8162 (2)	0.32186 (14)	0.0108 (5)
H22	0.219100	0.739884	0.287317	0.013*
C23	0.1327 (2)	0.9274 (2)	0.29887 (14)	0.0113 (5)
C24	0.1280 (2)	1.0400 (2)	0.34733 (16)	0.0176 (6)
H24	0.070147	1.115604	0.330570	0.021*
C25	0.2095 (3)	1.0404 (3)	0.42109 (17)	0.0207 (6)
H25	0.207518	1.117252	0.455296	0.025*
C26	0.2935 (2)	0.9304 (2)	0.44550 (15)	0.0157 (5)
H26	0.348384	0.931566	0.496389	0.019*
N1	0.35049 (19)	0.5666 (2)	0.38807 (12)	0.0121 (4)
H1	0.283 (3)	0.538 (3)	0.3999 (15)	0.014*
N11	0.74188 (18)	0.65967 (19)	0.41920 (12)	0.0105 (4)

O1	0.84580 (15)	0.59639 (17)	0.54316 (10)	0.0153 (4)
Br1	0.70318 (3)	0.09579 (2)	0.34029 (2)	0.02171 (8)
Br2	0.01897 (2)	0.91972 (2)	0.19816 (2)	0.01641 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0097 (12)	0.0106 (11)	0.0073 (13)	0.0004 (9)	0.0003 (9)	0.0003 (9)
C3	0.0121 (12)	0.0083 (10)	0.0106 (13)	0.0009 (9)	0.0031 (10)	0.0009 (9)
C4	0.0072 (11)	0.0102 (10)	0.0097 (13)	0.0008 (8)	0.0025 (9)	0.0018 (9)
C4A	0.0143 (13)	0.0078 (10)	0.0088 (13)	0.0014 (9)	0.0031 (10)	0.0028 (9)
C5	0.0144 (13)	0.0126 (11)	0.0092 (13)	0.0020 (9)	0.0052 (10)	0.0031 (9)
C6	0.0222 (14)	0.0103 (11)	0.0114 (13)	0.0063 (10)	0.0073 (11)	0.0023 (10)
C7	0.0257 (15)	0.0089 (11)	0.0098 (14)	-0.0016 (10)	0.0016 (11)	-0.0014 (9)
C8	0.0156 (13)	0.0135 (11)	0.0120 (14)	-0.0024 (10)	0.0011 (10)	0.0017 (10)
C8A	0.0132 (13)	0.0106 (10)	0.0059 (12)	0.0003 (9)	0.0021 (10)	0.0031 (9)
C12	0.0106 (12)	0.0065 (10)	0.0149 (14)	0.0024 (9)	0.0023 (10)	-0.0036 (9)
C13	0.0094 (13)	0.0146 (12)	0.0248 (16)	0.0010 (9)	0.0034 (11)	-0.0036 (10)
C14	0.0140 (13)	0.0136 (12)	0.0302 (17)	0.0008 (10)	0.0111 (12)	0.0043 (11)
C15	0.0152 (13)	0.0117 (11)	0.0170 (14)	0.0037 (9)	0.0074 (11)	0.0025 (10)
C21	0.0079 (12)	0.0109 (11)	0.0117 (13)	-0.0005 (9)	0.0047 (10)	0.0021 (9)
C22	0.0110 (12)	0.0115 (11)	0.0107 (13)	-0.0001 (9)	0.0044 (10)	-0.0009 (9)
C23	0.0081 (11)	0.0128 (11)	0.0117 (13)	-0.0021 (9)	0.0003 (9)	0.0032 (10)
C24	0.0131 (13)	0.0112 (11)	0.0283 (17)	0.0045 (9)	0.0047 (11)	0.0039 (10)
C25	0.0245 (15)	0.0128 (12)	0.0253 (16)	0.0015 (10)	0.0074 (12)	-0.0068 (11)
C26	0.0163 (13)	0.0188 (12)	0.0098 (13)	-0.0004 (10)	-0.0009 (10)	-0.0013 (10)
N1	0.0070 (10)	0.0101 (9)	0.0194 (12)	-0.0008 (8)	0.0036 (9)	-0.0001 (8)
N11	0.0100 (10)	0.0113 (9)	0.0106 (11)	0.0010 (8)	0.0030 (8)	0.0012 (8)
O1	0.0141 (9)	0.0190 (9)	0.0112 (9)	0.0034 (7)	0.0001 (7)	-0.0003 (7)
Br1	0.03536 (17)	0.01082 (12)	0.02535 (16)	0.00804 (11)	0.01967 (13)	0.00283 (11)
Br2	0.01226 (13)	0.01562 (12)	0.01764 (15)	-0.00140 (10)	-0.00331 (10)	0.00727 (10)

Geometric parameters (Å, °)

C2—N1	1.460 (3)	C12—C13	1.511 (3)
C2—C21	1.519 (3)	C13—C14	1.528 (4)
C2—C3	1.524 (3)	C13—H13A	0.9900
C2—H2	1.0000	C13—H13B	0.9900
C3—C4	1.526 (3)	C14—C15	1.532 (3)
C3—H3A	0.9900	C14—H14A	0.9900
C3—H3B	0.9900	C14—H14B	0.9900
C4—N11	1.453 (3)	C15—N11	1.459 (3)
C4—C4A	1.520 (3)	C15—H15A	0.9900
C4—H4A	1.0000	C15—H15B	0.9900
C4A—C5	1.392 (3)	C21—C22	1.383 (3)
C4A—C8A	1.402 (3)	C21—C26	1.393 (3)
C5—C6	1.383 (3)	C22—C23	1.389 (3)
C5—H5A	0.9500	C22—H22	0.9500

C6—C7	1.380 (4)	C23—C24	1.376 (3)
C6—Br1	1.905 (2)	C23—Br2	1.903 (2)
C7—C8	1.383 (3)	C24—C25	1.385 (4)
C7—H7A	0.9500	C24—H24	0.9500
C8—C8A	1.404 (3)	C25—C26	1.381 (3)
C8—H8A	0.9500	C25—H25	0.9500
C8A—N1	1.386 (3)	C26—H26	0.9500
C12—O1	1.229 (3)	N1—H1	0.86 (3)
C12—N11	1.352 (3)		
N1—C2—C21	110.84 (19)	C14—C13—H13A	110.8
N1—C2—C3	109.13 (19)	C12—C13—H13B	110.8
C21—C2—C3	110.18 (18)	C14—C13—H13B	110.8
N1—C2—H2	108.9	H13A—C13—H13B	108.9
C21—C2—H2	108.9	C13—C14—C15	104.92 (19)
C3—C2—H2	108.9	C13—C14—H14A	110.8
C2—C3—C4	107.97 (18)	C15—C14—H14A	110.8
C2—C3—H3A	110.1	C13—C14—H14B	110.8
C4—C3—H3A	110.1	C15—C14—H14B	110.8
C2—C3—H3B	110.1	H14A—C14—H14B	108.8
C4—C3—H3B	110.1	N11—C15—C14	102.9 (2)
H3A—C3—H3B	108.4	N11—C15—H15A	111.2
N11—C4—C4A	114.22 (19)	C14—C15—H15A	111.2
N11—C4—C3	113.07 (18)	N11—C15—H15B	111.2
C4A—C4—C3	109.42 (19)	C14—C15—H15B	111.2
N11—C4—H4A	106.5	H15A—C15—H15B	109.1
C4A—C4—H4A	106.5	C22—C21—C26	119.6 (2)
C3—C4—H4A	106.5	C22—C21—C2	121.3 (2)
C5—C4A—C8A	119.8 (2)	C26—C21—C2	119.0 (2)
C5—C4A—C4	122.5 (2)	C21—C22—C23	119.2 (2)
C8A—C4A—C4	117.5 (2)	C21—C22—H22	120.4
C6—C5—C4A	120.0 (2)	C23—C22—H22	120.4
C6—C5—H5A	120.0	C24—C23—C22	121.8 (2)
C4A—C5—H5A	120.0	C24—C23—Br2	119.92 (18)
C7—C6—C5	121.1 (2)	C22—C23—Br2	118.28 (18)
C7—C6—Br1	119.47 (17)	C23—C24—C25	118.5 (2)
C5—C6—Br1	119.45 (19)	C23—C24—H24	120.7
C6—C7—C8	119.4 (2)	C25—C24—H24	120.7
C6—C7—H7A	120.3	C26—C25—C24	120.8 (2)
C8—C7—H7A	120.3	C26—C25—H25	119.6
C7—C8—C8A	120.9 (2)	C24—C25—H25	119.6
C7—C8—H8A	119.6	C25—C26—C21	120.1 (2)
C8A—C8—H8A	119.6	C25—C26—H26	119.9
N1—C8A—C4A	122.1 (2)	C21—C26—H26	119.9
N1—C8A—C8	119.0 (2)	C8A—N1—C2	121.08 (19)
C4A—C8A—C8	118.9 (2)	C8A—N1—H1	115.4 (17)
O1—C12—N11	124.7 (2)	C2—N1—H1	114.1 (17)
O1—C12—C13	127.0 (2)	C12—N11—C4	121.4 (2)

N11—C12—C13	108.3 (2)	C12—N11—C15	114.0 (2)
C12—C13—C14	104.5 (2)	C4—N11—C15	124.49 (19)
C12—C13—H13A	110.8		
N1—C2—C3—C4	-60.0 (2)	N1—C2—C21—C26	149.1 (2)
C21—C2—C3—C4	178.05 (19)	C3—C2—C21—C26	-90.0 (3)
C2—C3—C4—N11	-171.22 (19)	C26—C21—C22—C23	0.0 (3)
C2—C3—C4—C4A	60.2 (2)	C2—C21—C22—C23	-176.4 (2)
N11—C4—C4A—C5	22.9 (3)	C21—C22—C23—C24	0.5 (4)
C3—C4—C4A—C5	150.8 (2)	C21—C22—C23—Br2	-178.16 (17)
N11—C4—C4A—C8A	-162.0 (2)	C22—C23—C24—C25	-0.5 (4)
C3—C4—C4A—C8A	-34.1 (3)	Br2—C23—C24—C25	178.1 (2)
C8A—C4A—C5—C6	-1.9 (4)	C23—C24—C25—C26	0.0 (4)
C4—C4A—C5—C6	173.1 (2)	C24—C25—C26—C21	0.5 (4)
C4A—C5—C6—C7	0.0 (4)	C22—C21—C26—C25	-0.5 (4)
C4A—C5—C6—Br1	-178.40 (18)	C2—C21—C26—C25	176.0 (2)
C5—C6—C7—C8	1.6 (4)	C4A—C8A—N1—C2	-7.4 (4)
Br1—C6—C7—C8	-179.91 (18)	C8—C8A—N1—C2	173.0 (2)
C6—C7—C8—C8A	-1.5 (4)	C21—C2—N1—C8A	155.7 (2)
C5—C4A—C8A—N1	-177.6 (2)	C3—C2—N1—C8A	34.2 (3)
C4—C4A—C8A—N1	7.2 (3)	O1—C12—N11—C4	1.7 (3)
C5—C4A—C8A—C8	2.0 (3)	C13—C12—N11—C4	-178.46 (19)
C4—C4A—C8A—C8	-173.2 (2)	O1—C12—N11—C15	-175.2 (2)
C7—C8—C8A—N1	179.3 (2)	C13—C12—N11—C15	4.7 (3)
C7—C8—C8A—C4A	-0.3 (4)	C4A—C4—N11—C12	-101.7 (2)
O1—C12—C13—C14	-169.8 (2)	C3—C4—N11—C12	132.3 (2)
N11—C12—C13—C14	10.3 (2)	C4A—C4—N11—C15	74.8 (3)
C12—C13—C14—C15	-20.3 (2)	C3—C4—N11—C15	-51.2 (3)
C13—C14—C15—N11	22.5 (2)	C14—C15—N11—C12	-17.5 (2)
N1—C2—C21—C22	-34.5 (3)	C14—C15—N11—C4	165.80 (19)
C3—C2—C21—C22	86.4 (3)		

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

Cg3 is the centroid of the C4A/C5—C8/C8A benzene ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C13—H13A \cdots O1 ⁱ	0.99	2.46	3.431 (3)	169
C13—H13A \cdots Br2 ⁱⁱ	0.99	3.06	3.740 (3)	127
C14—H14A \cdots Br2 ⁱⁱ	0.99	3.12	3.664 (3)	116
C14—H14B \cdots Br1 ⁱⁱⁱ	0.99	3.02	3.786 (2)	135
C15—H15A \cdots Br1 ⁱⁱⁱ	0.99	3.00	3.748 (2)	133
C15—H15B \cdots Br2 ⁱⁱ	0.99	3.09	3.768 (2)	127
C22—H22 \cdots Br1 ^{iv}	0.95	2.94	3.820 (2)	155
C24—H24 \cdots Br2 ^v	0.95	3.04	3.932 (2)	158
N1—H1 \cdots O1 ^{vi}	0.86 (3)	2.30 (3)	3.115 (3)	159 (2)
C2—H2 \cdots Cg3 ^{vi}	1.00	2.66	3.655 (3)	173

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