



Crystal structure and Hirshfeld surface analysis of the hydrochloride salt of 8-{4-[(6-phenylpyridin-3-yl)methyl]piperazin-1-yl}-3,4-dihydroquinolin-2(1H)-one

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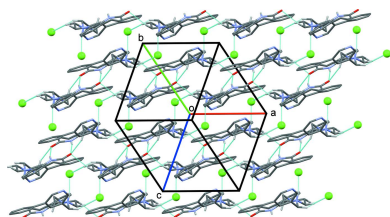
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The amine 8-{4-[(6-phenylpyridin-3-yl)methyl]piperazin-1-yl}-3,4-dihydroquinolin-2(1H)-one was crystallized as the hydrochloride salt, 4-(2-oxo-1,2,3,4-tetrahydroquinolin-8-yl)-1-[(6-phenylpyridin-3-yl)methyl]piperazin-1-ium chloride, C₂₅H₂₇N₄⁺·Cl⁻ (**I·HCl**). The conformation of the organic cation is half-moon in shape enclosing the chloride anion. The piperidine ring of the 3,4-dihydroquinolin-2(1H)-one moiety has a screw-boat conformation, while the piperazine ring has a chair conformation. In the biaryl group, the pyridine ring is inclined to the phenyl ring by 40.17 (7) and by 36.86 (8)° to the aromatic ring of the quinoline moiety. In the crystal, the cations are linked by pairwise N—H···O hydrogen bonds, forming inversion dimers enclosing an R₂²(8) ring motif. The Cl⁻ anion is linked to the cation by an N—H···Cl hydrogen bond. These units are linked by a series of C—H···O, C—H···N and C—H···Cl hydrogen bonds, forming layers lying parallel to the *ab* plane.

1. Chemical context

Schizophrenia is a psychiatric illness afflicting over 1% of the world's population. Adoprazine[®] and Bifeprunox[®] (Fig. 1) are two drugs that were developed for the treatment of Schizophrenia in the early 2000s. The main action of these two compounds is to combine dopamine D₂ receptor blockade with serotonin 5-HT_{1A} receptor activation rather than antagonism (Feenstra *et al.*, 2001, 2006). In continuing efforts in this field, Ullah and collaborators have synthesized a series of compounds that are structural analogues of Adoprazine[®] and Bifeprunox[®] (Ullah, 2012, 2014*a,b*; Ullah & Al-Shaheri, 2012). These include a number of 1-aryl-4-(biarylmethylene)piperazines (Ullah, 2012), such as 8-{4-[(6-phenylpyridin-3-yl)methyl]piperazin-1-yl}-3,4-dihydroquinolin-2(1H)-one (**I**), and 8-(4-[[6-(4-fluorophenyl)pyridin-3-yl]methyl]piperazin-1-yl)-3,4-dihydroquinolin-2(1H)-one (**II**) Ghani *et al.* (2014) have reported that the D₂ receptor binding affinity of compounds **I** and **II** are K_i = 28.4 nM for **I** and 42.0 nM for **II**. The 5-HT_{1A} receptor binding affinities were reported to be K_i = 4.30 nM for **I** and 52.5 nM for **II**. Hence, inserting a fluorine atom in the phenylpyridine unit in **II** did not improve its binding affinity compared to that of **I**. Full details concerning these assays are given in Ghani *et al.* (2014).

The crystal structure of the hydrochloride salt of **II** has been reported previously (Ullah & Altaf, 2014) and will be



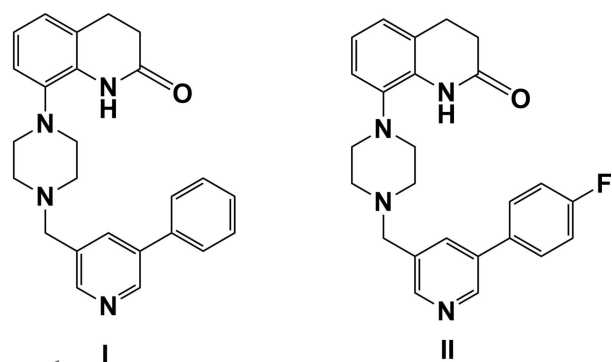
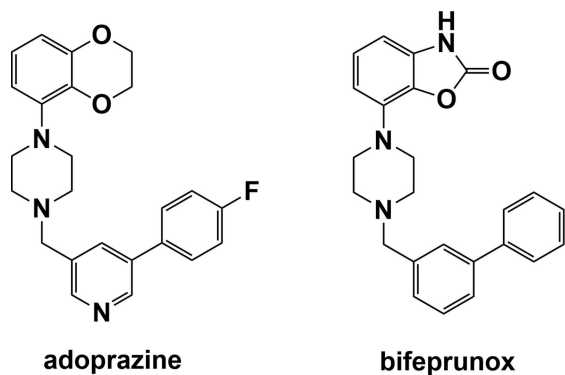


Figure 1
Chemical diagrams for adoprazine, bifeprunox and compounds **I** and **II**.

compared here to that of the hydrochloride salt of compound **I**.

2. Structural commentary

Due to the difficulty of forming suitable crystals for X-ray diffraction analysis compounds **I** and **II** were converted to their hydrochloride salts by treatment with HCl in MeOH.

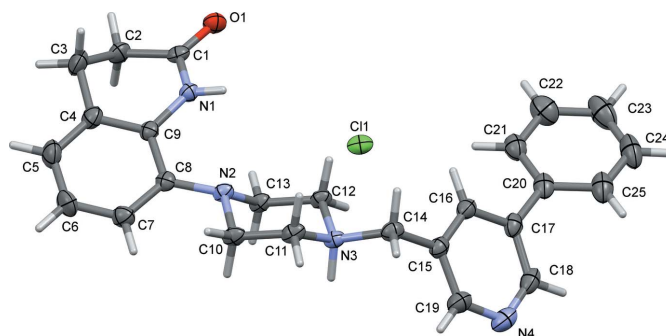
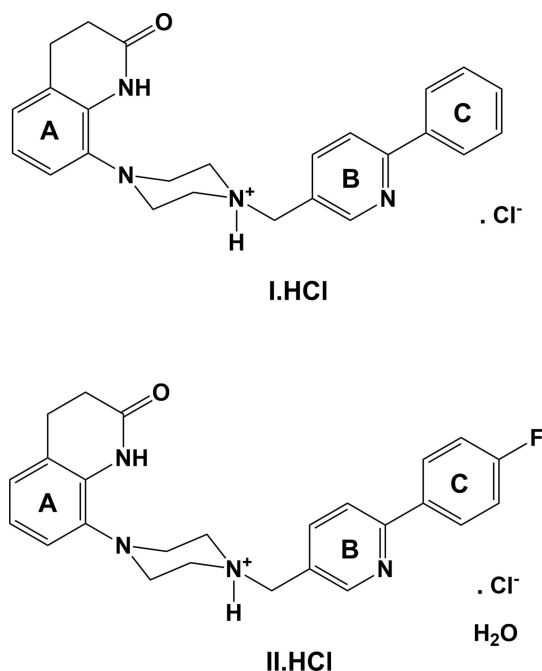


Figure 2
A view of the molecular structure of **I.HCl**, with atom labelling. The displacement ellipsoids are drawn at the 50% probability level.

The organic cation of **I.HCl** has a half-moon shape enclosing the chloride anion (Fig. 2). The molecular salt **II.HCl** crystallized as a monohydrate and here, while the cation also has a half-moon shape, it encloses the water molecule of crystallization (Ullah & Altaf, 2014; see Fig. S1 in the supporting information). The two cations differ essentially in the conformation of the biaryl group (rings *B* = N4/C15–C19 and *C* = C20–C25) and their orientation with respect to the aromatic ring (*A* = C4–C9) of the 3,4-dihydroquinolin-2(1*H*)-one moiety. This is illustrated by the view of their structural overlap, shown in Fig. 3. In **I.HCl**, pyridine ring *B* is inclined to phenyl ring *C* by 40.17 (8)° while in **II.HCl** the equivalent dihedral angle is 10.06 (11)°. In **I.HCl**, ring *A* is inclined to rings *B* and *C* by 36.86 (8) and 14.16 (8)°, respectively. These dihedral angles differ considerably from the dihedral angles in **II.HCl**, where ring *A* is inclined to rings *B* and *C* by 51.20 (9) and 41.40 (11)°, respectively. In both compounds, the piperidine ring (N1/C1–C4/C9) has a screw-boat conformation with the torsion angle C1–C2–C3–C4 being –56.17 (18)° in **I.HCl** and –55.6 (2)° in **II.HCl**. In both compounds, the piperazine ring (N2/N3/C10–C13) has a chair conformation.

3. Supramolecular features

In the crystal of **I.HCl**, the organic cations are linked by a pair of N–H···O hydrogen bonds, forming an inversion dimer enclosing an $R_2^2(8)$ ring motif (Fig. 4 and Table 1). The Cl[–] anion is linked to the cation by an N–H···Cl hydrogen bond

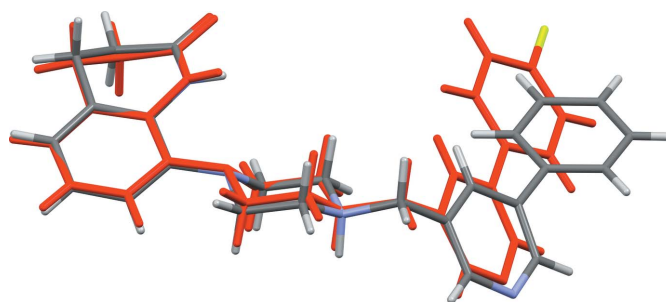


Figure 3
A view of the structural overlap of the cations of salts **I.HCl** and **II.HCl**; r.m.s. deviation 0.125 Å (Mercury; Macrae *et al.*, 2020). The structure of the **II.HCl** cation is given in red with the F atom in yellow (see also supplementary figure S1; Ullah & Altaf, 2014).

Table 1

Hydrogen-bond geometry (Å, °).

Cg is the centroid of the C4–C9 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots O1^i$	0.85 (2)	2.01 (2)	2.844 (2)	168 (2)
$N3-H3N\cdots Cl1^{ii}$	0.97 (2)	2.12 (2)	3.065 (1)	167 (2)
$C10-H10B\cdots O1^{iii}$	0.99	2.40	3.151 (2)	132
$C11-H11A\cdots Cl1^{iii}$	0.99	2.80	3.668 (2)	147
$C12-H12A\cdots Cl1$	0.99	2.81	3.520 (2)	129
$C12-H12B\cdots O1^i$	0.99	2.26	3.123 (2)	144
$C13-H13A\cdots N1$	0.99	2.53	3.138 (2)	120
$C14-H14A\cdots Cl1^{iii}$	0.99	2.71	3.585 (2)	147
$C21-H21\cdots Cl1$	0.95	2.83	3.757 (2)	165
$C18-H18\cdots Cg^{ii}$	0.95	2.83	3.487 (2)	127

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

(Fig. 4 and Table 1). The dimers are linked by a $C-H\cdots O$ hydrogen bond, forming ribbons propagating along the a -axis direction. The ribbons are then linked *via* $C-H\cdots Cl$ hydrogen bonds to form layers lying parallel to the ab plane (Fig. 5 and Table 1). There are $C-H\cdots \pi(C4-C9)$ contacts present within the layers (Table 1), but there are no significant contacts present between the layers.

In the crystal of **II·HCl** (Ullah & Altaf, 2014; see Figs. S2 and S3, and Table S1 in the supporting information), the cations are linked by the water molecules of crystallization *via* $N-H\cdots O_w$ and $O_w-H\cdots O$ hydrogen bonds to form dimers with $R_4^4(12)$ ring motifs. The dimers are in turn linked by the Cl^- anions, *via* $O_w-H\cdots Cl\cdots H-N$ hydrogen bonds, to form chains propagating along the b -axis direction. The chains are linked *via* $C-H\cdots Cl$ and $C-H\cdots O$ hydrogen bonds, forming layers parallel to the ab plane.

In both cases, hydrogen-bonded layers are formed stacking along the c -axis direction and lying parallel to the ab plane. There are no significant directional inter-layer contacts present in either crystal structure.

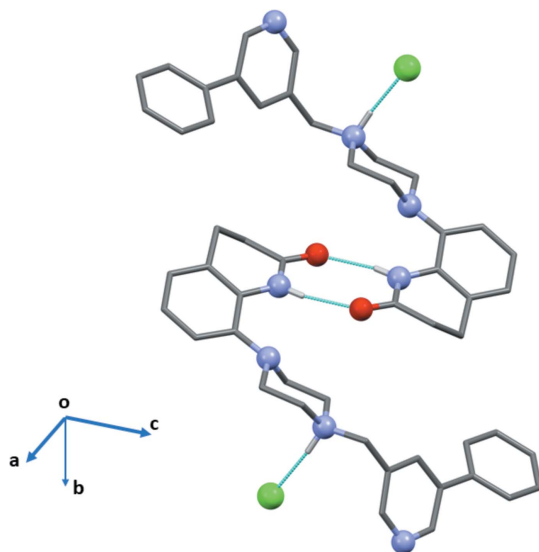


Figure 4

A view of the hydrogen bonded dimer formation in the crystal of salt **I·HCl**. Hydrogen bonds are shown as dashed lines (see Table 1).

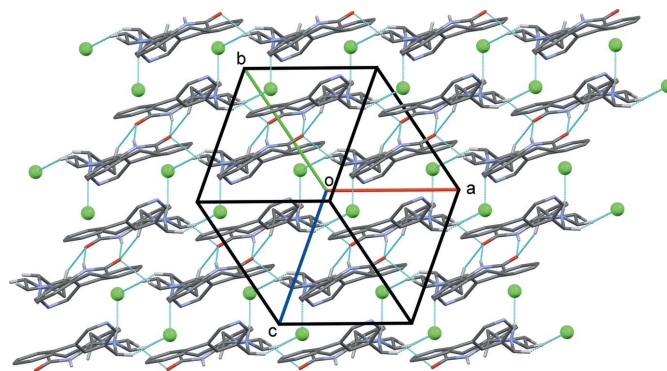


Figure 5

A view along the [111] direction of the crystal packing of salt **I·HCl**. Hydrogen bonds are shown as dashed lines (see Table 1).

4. Hirshfeld surface analysis and two-dimensional fingerprint plots

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed with *Crystal-Explorer17* (Turner *et al.*, 2017) following the protocol of Tiekink and collaborators (Tan *et al.*, 2019).

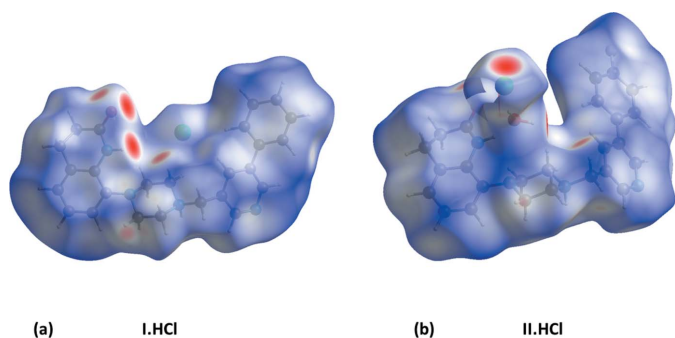
The Hirshfeld surfaces are colour-mapped with the normalized contact distance, d_{norm} , varying from red (distances shorter than the sum of the van der Waals radii) through white to blue (distances longer than the sum of the van der Waals radii). The Hirshfeld surfaces (HS) of **I·HCl** and **II·HCl** mapped over d_{norm} are given in Fig. 6. It is evident from Fig. 6a and 6b that there are important contacts present in the crystals of both compounds, the strong hydrogen bonds (Table 1 and Table S1) being indicated by the large red zones.

The percentage contributions of inter-atomic contacts to the HS for both compounds are compared in Table 2. The two-dimensional fingerprint plots for the title salt, **I·HCl**, and those for **II·HCl**, are compared in Figs. 7 and 8. They reveal, as expected, that the principal contributions to the overall HS surface involve $H\cdots H$ contacts at 51.5 and 42.1%, respectively. The difference is attributed to the presence of $F\cdots H/H\cdots F$ contacts in the crystal of **II·HCl**, amounting to 7.5%. The second most important contribution to the HS is from the $C\cdots H/H\cdots C$ contacts at 20.2 and 20.5%, for **I·HCl** and

Table 2

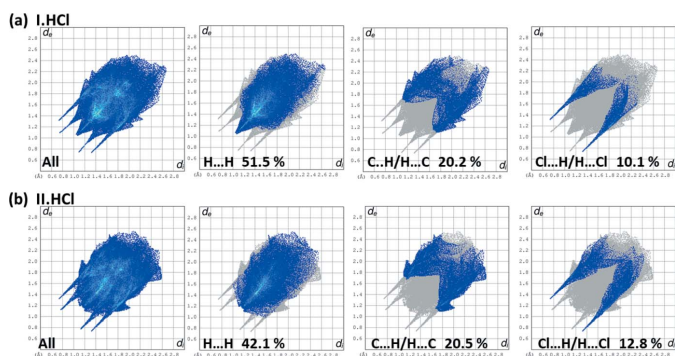
Principal percentage contributions of inter-atomic contacts to the Hirshfeld surfaces of **I·HCl** and **II·HCl**.

Contact	I·HCl % contribution	II·HCl % contribution
$H\cdots H$	51.5	42.1
$C\cdots H/H\cdots C$	20.2	20.5
$Cl\cdots H/H\cdots Cl$	10.1	12.8
$O\cdots H/H\cdots O$	7.4	8.7
$N\cdots H/H\cdots N$	6.5	5.3
$F\cdots H/H\cdots F$	–	7.5
$C\cdots F/F\cdots C$	–	1.4
$C\cdots C$	2.9	0.8

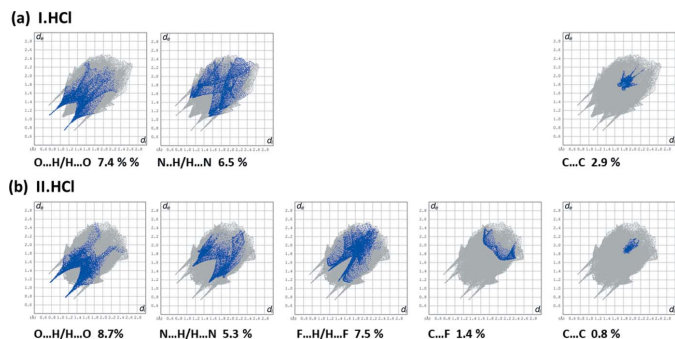

Figure 6

The Hirshfeld surfaces of compounds **I·HCl** and **II·HCl**, mapped over d_{norm} in the colour ranges of -0.5847 to 1.5642 au. and -0.5555 to 1.5111 au., respectively.

II·HCl, respectively. These are followed by the $\text{Cl}\cdots\text{H}\cdots\text{Cl}$ contacts at 10.1 and 12.8% for **I·HCl** and **II·HCl**, respectively, and $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ contacts at, respectively, 7.4 and 8.7%. The $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ contacts contribute, respectively, 6.5 and 5.3%. The $\text{C}\cdots\text{C}$ contacts in **I·HCl** contribute 2.9%, while the $\text{C}\cdots\text{F}$ contacts in **II·HCl** contribute 1.4%. All other atom \cdots atom contacts contribute <1% to the HS for both compounds.


Figure 7

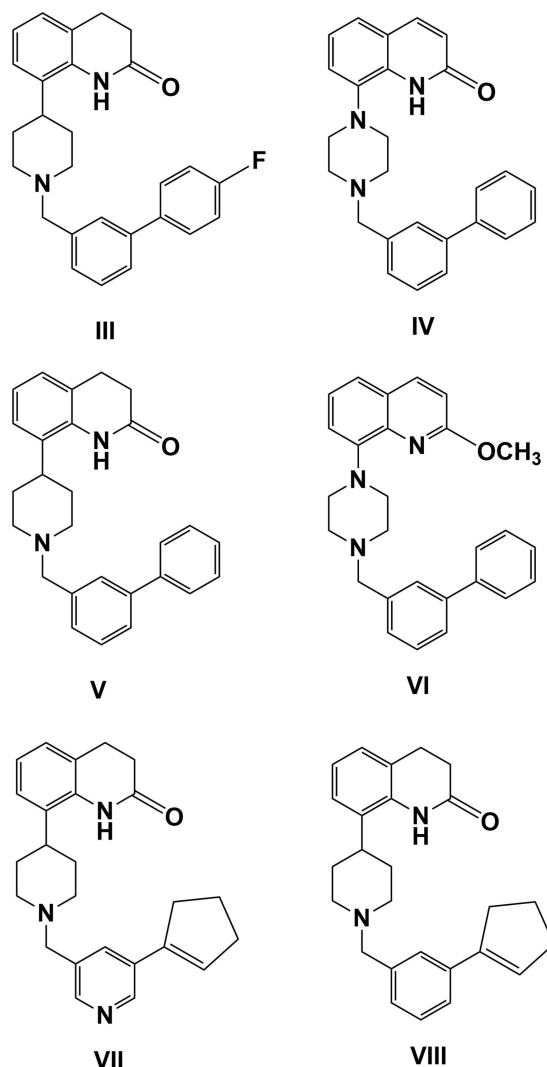
The two-dimensional fingerprint plots for compounds (a) **I·HCl** and (b) **II·HCl**, and those delineated into $\text{H}\cdots\text{H}$, $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$, and $\text{Cl}\cdots\text{H}/\text{H}\cdots\text{Cl}$ contacts.


Figure 8

The two-dimensional fingerprint plots for compounds (a) **I·HCl** delineated into $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$, $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ and $\text{C}\cdots\text{C}$, and (b) **II·HCl** delineated into $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$, $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$, $\text{F}\cdots\text{H}/\text{H}\cdots\text{F}$, $\text{C}\cdots\text{F}/\text{F}\cdots\text{C}$ and $\text{C}\cdots\text{C}$ contacts.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, last update November 2020; Groom *et al.*, 2016) for 8-(piperazin-1-yl)-3,4-dihydroquinolin-2(1*H*)-ones gave three hits for compounds 8-[1-[(4'-fluoro-[1,1'-biphenyl]-3-yl)methyl]piperidin-4-yl]-3,4-dihydroquinolin-2(1*H*)-one (**III**), that crystallized as a chloroform 0.25-solvate (CSD refcode FITSEI; Ullah & Stoeckli-Evans, 2014), 8-[4-([1,1'-biphenyl]-3-ylmethyl)piperazin-1-yl]quinolin-2(1*H*)-one (**IV**) (REYHIP; Ullah *et al.*, 2017) and 8-[1-([1,1'-biphenyl]-3-ylmethyl)piperidin-4-yl]-3,4-dihydroquinolin-2(1*H*)-one (**V**) (REYHEL; Ullah *et al.*, 2017). Their chemical structures are shown in Fig. 9, together with those for compounds 8-[4-([1,1'-biphenyl]-3-ylmethyl)piperazin-1-yl]-2-methoxyquinoline (**VI**) (AKUXIQ; Ullah & Altaf, 2014), 8-(1-[5-(cyclopent-1-en-1-yl)pyridin-3-yl]methyl)piperidin-4-yl]-3,4-dihydroquinolin-2(1*H*)-one (**VII**) (AKUWOV; Ullah *et al.*, 2015) and 8-[1-[3-(cyclopent-1-en-1-yl)benzyl]piperidin-4-yl]-3,4-dihydroquinolin-2(1*H*)-one (**VIII**) (AKUWUB; Ullah *et al.*, 2015).


Figure 9

Chemical diagrams of similar compounds deposited with the CSD (Groom *et al.*, 2016); see § 5 Database survey.

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₂₅ H ₂₇ N ₄ O ⁺ ·Cl ⁻
<i>M_r</i>	434.95
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.4791 (8), 10.4091 (10), 13.6862 (14)
α , β , γ (°)	90.138 (8), 94.833 (8), 113.745 (7)
<i>V</i> (Å ³)	1100.88 (19)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.20
Crystal size (mm)	0.45 × 0.33 × 0.18
Data collection	
Diffraction	Stoe <i>IPDS 2</i>
Absorption correction	Multi-scan (<i>MULABS</i> ; Spek, 2020)
<i>T</i> _{min} – <i>T</i> _{max}	0.379, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	13410, 4156, 2912
<i>R</i> _{int}	0.077
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.609
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.033, 0.071, 0.83
No. of reflections	4156
No. of parameters	289
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)	0.22, -0.22

Computer programs: *X-AREA* (Stoe & Cie, 2009), *X-RED32* (Stoe & Cie, 2009), *SHELXS97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2020), *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

The CIFs for compounds **II·HCl** (AKUXEM; Ullah & Altaf, 2014) and **VI–VIII** have been updated recently in the CSD.

Compounds **III** to **VIII** all have a similar conformation; a curved or half-moon shape, as shown for the cation of **I·HCl** in Fig. 2. The piperidine rings of the dihydroquinoline units in compounds **I·HCl**, **II·HCl**, **III**, **V**, **VII** and **VIII** have screw-boat conformations. The piperidine or piperazine rings in all eight compounds have chair conformations.

6. Synthesis and crystallization

The synthesis of compounds **I** and **II** has been reported (Ullah, 2012; compounds **5c** and **5d** in that paper). Colourless plate-like crystals of their hydrochloride salts were obtained by slow evaporation of solutions in dichloromethane and methanol; ratios (8:3) and (8.5:1.5), respectively.

7. Refinement

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

difference electron-density map and freely refined. The C-bound H atoms were included in calculated positions and refined as riding on the parent atom: C–H = 0.95–0.99 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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supporting information

Acta Cryst. (2021). E77, 208-212 [https://doi.org/10.1107/S2056989021000979]

Crystal structure and Hirshfeld surface analysis of the hydrochloride salt of 8-{4-[(6-phenylpyridin-3-yl)methyl]piperazin-1-yl}-3,4-dihydroquinolin-2(1H)-one

Nisar Ullah and Helen Stoeckli-Evans

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA* (Stoe & Cie, 2009); data reduction: *X-RED32* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

4-(2-Oxo-1,2,3,4-tetrahydroquinolin-8-yl)-1-[(6-phenylpyridin-3-yl)methyl]piperazin-1-ium chloride

Crystal data

$C_{25}H_{27}N_4O^+Cl^-$
 $M_r = 434.95$
 Triclinic, $P\bar{1}$
 $a = 8.4791$ (8) Å
 $b = 10.4091$ (10) Å
 $c = 13.6862$ (14) Å
 $\alpha = 90.138$ (8)°
 $\beta = 94.833$ (8)°
 $\gamma = 113.745$ (7)°
 $V = 1100.88$ (19) Å³

$Z = 2$
 $F(000) = 460$
 $D_x = 1.312$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9997 reflections
 $\theta = 1.5$ – 26.1 °
 $\mu = 0.20$ mm⁻¹
 $T = 173$ K
 Rod, colourless
 $0.45 \times 0.33 \times 0.18$ mm

Data collection

Stoe IPDS 2
 diffractometer
 Radiation source: fine-focus sealed tube
 Plane graphite monochromator
 $\varphi + \omega$ scans
 Absorption correction: multi-scan
 (MULABS; Spek, 2020)
 $T_{\min} = 0.379$, $T_{\max} = 1.000$

13410 measured reflections
 4156 independent reflections
 2912 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.077$
 $\theta_{\max} = 25.6$ °, $\theta_{\min} = 1.5$ °
 $h = -10 \rightarrow 9$
 $k = -12 \rightarrow 12$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.071$
 $S = 0.83$
 4156 reflections
 289 parameters

0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map
 Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0262P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$$

Extinction correction: (SHELXL-2018/3;

Sheldrick, 2015),

$$F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0061 (11)

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	-0.17052 (13)	0.47203 (11)	-0.07307 (8)	0.0288 (3)
N1	0.07882 (16)	0.49233 (13)	-0.13301 (10)	0.0234 (3)
H1N	0.122 (2)	0.5073 (18)	-0.0734 (13)	0.034 (5)*
N2	0.44879 (14)	0.63611 (12)	-0.11540 (9)	0.0220 (3)
N3	0.68062 (15)	0.82122 (13)	0.04180 (9)	0.0217 (3)
H3N	0.746 (2)	0.906 (2)	0.0090 (13)	0.052 (5)*
N4	0.94060 (18)	1.20937 (14)	0.25205 (11)	0.0399 (4)
C1	-0.09235 (18)	0.46487 (15)	-0.14318 (11)	0.0236 (3)
C2	-0.1799 (2)	0.42765 (18)	-0.24529 (12)	0.0329 (4)
H2A	-0.160759	0.514512	-0.280987	0.040*
H2B	-0.306002	0.375119	-0.242625	0.040*
C3	-0.1077 (2)	0.33797 (19)	-0.29954 (13)	0.0392 (4)
H3A	-0.135909	0.247286	-0.267359	0.047*
H3B	-0.160866	0.318222	-0.368136	0.047*
C4	0.0858 (2)	0.41520 (16)	-0.29844 (12)	0.0302 (4)
C5	0.1751 (2)	0.41199 (19)	-0.37763 (13)	0.0392 (4)
H5	0.114179	0.360241	-0.436140	0.047*
C6	0.3535 (2)	0.48412 (19)	-0.37196 (13)	0.0392 (4)
H6	0.414790	0.480812	-0.426264	0.047*
C7	0.4424 (2)	0.56092 (17)	-0.28716 (12)	0.0310 (4)
H7	0.564389	0.610806	-0.284514	0.037*
C8	0.35719 (18)	0.56693 (15)	-0.20549 (11)	0.0230 (3)
C9	0.17520 (18)	0.49231 (15)	-0.21240 (11)	0.0228 (3)
C10	0.63546 (18)	0.67238 (16)	-0.10867 (11)	0.0266 (4)
H10A	0.692624	0.755875	-0.147562	0.032*
H10B	0.656720	0.593449	-0.136332	0.032*
C11	0.71077 (19)	0.70267 (16)	-0.00407 (11)	0.0256 (4)
H11A	0.836721	0.727272	-0.001024	0.031*
H11B	0.657845	0.617257	0.033766	0.031*
C12	0.49249 (17)	0.79433 (16)	0.02658 (11)	0.0238 (3)
H12A	0.476973	0.878517	0.049257	0.029*
H12B	0.425884	0.715170	0.066760	0.029*
C13	0.42172 (18)	0.75986 (15)	-0.08004 (11)	0.0232 (3)

H13A	0.296647	0.739395	-0.086798	0.028*
H13B	0.481455	0.841377	-0.120110	0.028*
C14	0.74694 (19)	0.83801 (16)	0.14807 (11)	0.0271 (4)
H14A	0.863559	0.836905	0.153532	0.033*
H14B	0.670376	0.755999	0.182549	0.033*
C15	0.75825 (19)	0.96984 (16)	0.19971 (11)	0.0259 (4)
C16	0.6286 (2)	0.97397 (16)	0.25369 (11)	0.0276 (4)
H16	0.521948	0.894116	0.253316	0.033*
C17	0.6549 (2)	1.09519 (16)	0.30836 (11)	0.0289 (4)
C18	0.8145 (2)	1.20792 (17)	0.30499 (12)	0.0354 (4)
H18	0.835305	1.290278	0.343377	0.042*
C19	0.9109 (2)	1.09080 (17)	0.20072 (13)	0.0351 (4)
H19	0.998875	1.089041	0.162807	0.042*
C20	0.5209 (2)	1.10509 (17)	0.36734 (12)	0.0326 (4)
C21	0.3467 (2)	1.04802 (18)	0.33182 (13)	0.0366 (4)
H21	0.312714	1.001744	0.268836	0.044*
C22	0.2225 (3)	1.0581 (2)	0.38747 (14)	0.0480 (5)
H22	0.103978	1.017354	0.362924	0.058*
C23	0.2710 (3)	1.1276 (2)	0.47900 (15)	0.0557 (6)
H23	0.186196	1.135071	0.517087	0.067*
C24	0.4438 (3)	1.1856 (2)	0.51400 (14)	0.0515 (5)
H24	0.477753	1.233593	0.576400	0.062*
C25	0.5676 (3)	1.17463 (19)	0.45928 (13)	0.0436 (5)
H25	0.685829	1.214852	0.484499	0.052*
Cl1	0.16918 (5)	0.91117 (4)	0.07387 (3)	0.02965 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0214 (5)	0.0315 (6)	0.0325 (6)	0.0094 (5)	0.0034 (5)	0.0009 (5)
N1	0.0193 (6)	0.0251 (7)	0.0233 (8)	0.0067 (5)	0.0005 (6)	-0.0016 (6)
N2	0.0166 (6)	0.0211 (7)	0.0291 (7)	0.0082 (5)	0.0028 (5)	-0.0021 (5)
N3	0.0168 (6)	0.0190 (6)	0.0284 (7)	0.0063 (5)	0.0026 (5)	0.0015 (5)
N4	0.0338 (8)	0.0276 (8)	0.0486 (9)	0.0042 (6)	-0.0047 (7)	-0.0027 (7)
C1	0.0190 (7)	0.0168 (7)	0.0326 (9)	0.0045 (6)	0.0034 (7)	0.0017 (6)
C2	0.0223 (8)	0.0363 (10)	0.0332 (9)	0.0056 (7)	-0.0024 (7)	-0.0034 (8)
C3	0.0324 (9)	0.0379 (10)	0.0365 (10)	0.0046 (8)	-0.0038 (8)	-0.0151 (8)
C4	0.0314 (9)	0.0255 (9)	0.0318 (9)	0.0100 (7)	0.0002 (7)	-0.0055 (7)
C5	0.0440 (10)	0.0421 (11)	0.0304 (10)	0.0168 (8)	0.0004 (8)	-0.0131 (8)
C6	0.0448 (11)	0.0452 (11)	0.0306 (10)	0.0196 (9)	0.0129 (8)	-0.0062 (8)
C7	0.0277 (8)	0.0314 (9)	0.0346 (9)	0.0120 (7)	0.0074 (7)	-0.0004 (7)
C8	0.0253 (8)	0.0197 (8)	0.0259 (8)	0.0109 (6)	0.0035 (7)	0.0009 (6)
C9	0.0253 (8)	0.0182 (7)	0.0255 (8)	0.0089 (6)	0.0037 (7)	-0.0004 (6)
C10	0.0182 (7)	0.0260 (8)	0.0366 (9)	0.0093 (6)	0.0059 (7)	-0.0005 (7)
C11	0.0184 (7)	0.0223 (8)	0.0383 (10)	0.0105 (6)	0.0021 (7)	-0.0009 (7)
C12	0.0152 (7)	0.0248 (8)	0.0313 (9)	0.0079 (6)	0.0029 (6)	-0.0023 (6)
C13	0.0183 (7)	0.0217 (8)	0.0302 (9)	0.0091 (6)	0.0007 (6)	-0.0018 (6)
C14	0.0217 (8)	0.0273 (9)	0.0311 (9)	0.0092 (6)	-0.0006 (7)	0.0032 (7)

C15	0.0261 (8)	0.0246 (8)	0.0242 (8)	0.0085 (6)	-0.0037 (7)	0.0011 (6)
C16	0.0281 (8)	0.0232 (8)	0.0267 (9)	0.0063 (6)	-0.0019 (7)	0.0001 (7)
C17	0.0379 (9)	0.0271 (9)	0.0216 (9)	0.0144 (7)	-0.0041 (7)	-0.0001 (7)
C18	0.0448 (10)	0.0227 (9)	0.0325 (10)	0.0099 (7)	-0.0103 (8)	-0.0043 (7)
C19	0.0278 (9)	0.0305 (10)	0.0404 (10)	0.0057 (7)	-0.0010 (8)	-0.0003 (8)
C20	0.0492 (11)	0.0253 (9)	0.0252 (9)	0.0179 (8)	-0.0002 (8)	0.0013 (7)
C21	0.0497 (11)	0.0336 (10)	0.0296 (9)	0.0197 (8)	0.0049 (8)	0.0003 (7)
C22	0.0534 (12)	0.0526 (12)	0.0471 (12)	0.0299 (10)	0.0099 (10)	0.0062 (10)
C23	0.0860 (17)	0.0597 (14)	0.0428 (13)	0.0481 (13)	0.0242 (12)	0.0077 (10)
C24	0.0872 (17)	0.0492 (12)	0.0286 (11)	0.0380 (12)	0.0067 (11)	-0.0037 (9)
C25	0.0672 (13)	0.0374 (10)	0.0294 (10)	0.0259 (9)	-0.0023 (9)	-0.0025 (8)
C11	0.02283 (19)	0.0261 (2)	0.0381 (2)	0.00758 (15)	0.00489 (17)	0.00481 (17)

Geometric parameters (Å, °)

O1—C1	1.2298 (17)	C10—H10B	0.9900
N1—C1	1.3562 (19)	C11—H11A	0.9900
N1—C9	1.4136 (19)	C11—H11B	0.9900
N1—H1N	0.852 (17)	C12—C13	1.515 (2)
N2—C8	1.4233 (19)	C12—H12A	0.9900
N2—C10	1.4665 (18)	C12—H12B	0.9900
N2—C13	1.4832 (19)	C13—H13A	0.9900
N3—C14	1.4981 (19)	C13—H13B	0.9900
N3—C12	1.5002 (17)	C14—C15	1.507 (2)
N3—C11	1.5031 (19)	C14—H14A	0.9900
N3—H3N	0.967 (18)	C14—H14B	0.9900
N4—C18	1.336 (2)	C15—C16	1.390 (2)
N4—C19	1.340 (2)	C15—C19	1.395 (2)
C1—C2	1.498 (2)	C16—C17	1.394 (2)
C2—C3	1.527 (2)	C16—H16	0.9500
C2—H2A	0.9900	C17—C18	1.394 (2)
C2—H2B	0.9900	C17—C20	1.484 (2)
C3—C4	1.507 (2)	C18—H18	0.9500
C3—H3A	0.9900	C19—H19	0.9500
C3—H3B	0.9900	C20—C25	1.395 (2)
C4—C5	1.381 (2)	C20—C21	1.393 (2)
C4—C9	1.400 (2)	C21—C22	1.387 (2)
C5—C6	1.387 (2)	C21—H21	0.9500
C5—H5	0.9500	C22—C23	1.389 (3)
C6—C7	1.384 (2)	C22—H22	0.9500
C6—H6	0.9500	C23—C24	1.382 (3)
C7—C8	1.395 (2)	C23—H23	0.9500
C7—H7	0.9500	C24—C25	1.380 (3)
C8—C9	1.415 (2)	C24—H24	0.9500
C10—C11	1.496 (2)	C25—H25	0.9500
C10—H10A	0.9900		
C1—N1—C9	123.74 (14)	C10—C11—H11B	109.3

C1—N1—H1N	112.8 (11)	N3—C11—H11B	109.3
C9—N1—H1N	123.5 (11)	H11A—C11—H11B	107.9
C8—N2—C10	114.51 (12)	N3—C12—C13	112.12 (12)
C8—N2—C13	118.19 (12)	N3—C12—H12A	109.2
C10—N2—C13	108.27 (11)	C13—C12—H12A	109.2
C14—N3—C12	112.69 (12)	N3—C12—H12B	109.2
C14—N3—C11	108.66 (12)	C13—C12—H12B	109.2
C12—N3—C11	110.14 (11)	H12A—C12—H12B	107.9
C14—N3—H3N	109.2 (11)	N2—C13—C12	109.53 (12)
C12—N3—H3N	108.5 (11)	N2—C13—H13A	109.8
C11—N3—H3N	107.6 (11)	C12—C13—H13A	109.8
C18—N4—C19	116.51 (14)	N2—C13—H13B	109.8
O1—C1—N1	122.03 (14)	C12—C13—H13B	109.8
O1—C1—C2	121.99 (13)	H13A—C13—H13B	108.2
N1—C1—C2	115.97 (14)	N3—C14—C15	115.00 (13)
C1—C2—C3	110.04 (14)	N3—C14—H14A	108.5
C1—C2—H2A	109.7	C15—C14—H14A	108.5
C3—C2—H2A	109.7	N3—C14—H14B	108.5
C1—C2—H2B	109.7	C15—C14—H14B	108.5
C3—C2—H2B	109.7	H14A—C14—H14B	107.5
H2A—C2—H2B	108.2	C16—C15—C19	117.83 (15)
C4—C3—C2	109.40 (13)	C16—C15—C14	122.94 (13)
C4—C3—H3A	109.8	C19—C15—C14	119.00 (15)
C2—C3—H3A	109.8	C15—C16—C17	120.04 (14)
C4—C3—H3B	109.8	C15—C16—H16	120.0
C2—C3—H3B	109.8	C17—C16—H16	120.0
H3A—C3—H3B	108.2	C18—C17—C16	116.57 (15)
C5—C4—C9	119.99 (15)	C18—C17—C20	121.22 (15)
C5—C4—C3	122.79 (15)	C16—C17—C20	122.21 (14)
C9—C4—C3	117.22 (14)	N4—C18—C17	125.19 (16)
C4—C5—C6	120.19 (16)	N4—C18—H18	117.4
C4—C5—H5	119.9	C17—C18—H18	117.4
C6—C5—H5	119.9	N4—C19—C15	123.81 (17)
C7—C6—C5	119.99 (15)	N4—C19—H19	118.1
C7—C6—H6	120.0	C15—C19—H19	118.1
C5—C6—H6	120.0	C25—C20—C21	118.47 (17)
C6—C7—C8	121.68 (14)	C25—C20—C17	120.38 (17)
C6—C7—H7	119.2	C21—C20—C17	121.13 (15)
C8—C7—H7	119.2	C22—C21—C20	120.67 (18)
C7—C8—N2	121.99 (13)	C22—C21—H21	119.7
C7—C8—C9	117.59 (14)	C20—C21—H21	119.7
N2—C8—C9	120.26 (13)	C21—C22—C23	120.2 (2)
C4—C9—N1	118.14 (13)	C21—C22—H22	119.9
C4—C9—C8	120.56 (14)	C23—C22—H22	119.9
N1—C9—C8	121.30 (13)	C24—C23—C22	119.25 (19)
N2—C10—C11	110.45 (12)	C24—C23—H23	120.4
N2—C10—H10A	109.6	C22—C23—H23	120.4
C11—C10—H10A	109.6	C25—C24—C23	120.72 (19)

N2—C10—H10B	109.6	C25—C24—H24	119.6
C11—C10—H10B	109.6	C23—C24—H24	119.6
H10A—C10—H10B	108.1	C24—C25—C20	120.67 (19)
C10—C11—N3	111.72 (13)	C24—C25—H25	119.7
C10—C11—H11A	109.3	C20—C25—H25	119.7
N3—C11—H11A	109.3		
C9—N1—C1—O1	-176.62 (13)	C14—N3—C12—C13	-172.97 (12)
C9—N1—C1—C2	2.4 (2)	C11—N3—C12—C13	-51.46 (16)
O1—C1—C2—C3	-143.54 (15)	C8—N2—C13—C12	165.68 (11)
N1—C1—C2—C3	37.46 (18)	C10—N2—C13—C12	-62.04 (14)
C1—C2—C3—C4	-56.18 (18)	N3—C12—C13—N2	57.34 (15)
C2—C3—C4—C5	-141.79 (17)	C12—N3—C14—C15	-69.10 (16)
C2—C3—C4—C9	38.3 (2)	C11—N3—C14—C15	168.56 (12)
C9—C4—C5—C6	0.5 (3)	N3—C14—C15—C16	95.52 (17)
C3—C4—C5—C6	-179.36 (17)	N3—C14—C15—C19	-90.00 (17)
C4—C5—C6—C7	-0.7 (3)	C19—C15—C16—C17	-1.5 (2)
C5—C6—C7—C8	0.8 (3)	C14—C15—C16—C17	173.04 (14)
C6—C7—C8—N2	174.79 (15)	C15—C16—C17—C18	0.1 (2)
C6—C7—C8—C9	-0.5 (2)	C15—C16—C17—C20	-179.93 (14)
C10—N2—C8—C7	-12.7 (2)	C19—N4—C18—C17	-1.9 (3)
C13—N2—C8—C7	116.78 (16)	C16—C17—C18—N4	1.7 (2)
C10—N2—C8—C9	162.54 (13)	C20—C17—C18—N4	-178.24 (15)
C13—N2—C8—C9	-68.01 (17)	C18—N4—C19—C15	0.4 (3)
C5—C4—C9—N1	-179.77 (15)	C16—C15—C19—N4	1.3 (3)
C3—C4—C9—N1	0.1 (2)	C14—C15—C19—N4	-173.47 (16)
C5—C4—C9—C8	-0.3 (2)	C18—C17—C20—C25	-39.3 (2)
C3—C4—C9—C8	179.60 (15)	C16—C17—C20—C25	140.79 (17)
C1—N1—C9—C4	-23.1 (2)	C18—C17—C20—C21	139.46 (17)
C1—N1—C9—C8	157.43 (14)	C16—C17—C20—C21	-40.5 (2)
C7—C8—C9—C4	0.3 (2)	C25—C20—C21—C22	-1.1 (2)
N2—C8—C9—C4	-175.13 (14)	C17—C20—C21—C22	-179.88 (15)
C7—C8—C9—N1	179.77 (14)	C20—C21—C22—C23	1.1 (3)
N2—C8—C9—N1	4.4 (2)	C21—C22—C23—C24	-0.4 (3)
C8—N2—C10—C11	-162.59 (12)	C22—C23—C24—C25	-0.3 (3)
C13—N2—C10—C11	63.20 (15)	C23—C24—C25—C20	0.2 (3)
N2—C10—C11—N3	-58.73 (16)	C21—C20—C25—C24	0.5 (3)
C14—N3—C11—C10	175.64 (11)	C17—C20—C25—C24	179.25 (15)
C12—N3—C11—C10	51.76 (15)		

Hydrogen-bond geometry (\AA , $^\circ$)C_g is the centroid of the C4—C9 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1N \cdots O1 ⁱ	0.85 (2)	2.01 (2)	2.844 (2)	168 (2)
N3—H3N \cdots C11 ⁱⁱ	0.97 (2)	2.12 (2)	3.065 (1)	167 (2)
C10—H10B \cdots O1 ⁱⁱⁱ	0.99	2.40	3.151 (2)	132
C11—H11A \cdots C11 ⁱⁱⁱ	0.99	2.80	3.668 (2)	147

C12—H12 <i>A</i> ···C11	0.99	2.81	3.520 (2)	129
C12—H12 <i>B</i> ···O1 ⁱ	0.99	2.26	3.123 (2)	144
C13—H13 <i>A</i> ···N1	0.99	2.53	3.138 (2)	120
C14—H14 <i>A</i> ···C11 ⁱⁱⁱ	0.99	2.71	3.585 (2)	147
C21—H21···C11	0.95	2.83	3.757 (2)	165
C18—H18···C <i>g</i> ⁱⁱ	0.95	2.83	3.487 (2)	127

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