Synthesis and structure of clozapine N-oxide hemi(hydrochloride): an infinite hydrogen-bonded poly[n]catenane

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The structure of the title compound, $2\text{C}_{18}\text{H}_{19}\text{ClN}_{4}\text{O} \cdot \text{HCl}$ or $(\text{CNO})_2\cdot\text{HCl}$ ($\text{C}_{36}\text{H}_{39}\text{Cl}_3\text{N}_8\text{O}_2$), at 100 K has tetragonal ($I\bar{4}m$) symmetry. The dihedral angle between the benzene rings of the fused ring system of the CNO molecule is $40.08 (6)^\circ$ and the equivalent angle between the seven-membered ring and its pendant N-oxide ring is $31.14 (7)^\circ$. The structure contains a very strong, symmetrical O–H···O hydrogen bond [O···O = 2.434 (2) Å] between two equivalent $R_3^2\text{N}^+–\text{O}^-$ moieties, which share a proton lying on a crystallographic twofold rotation axis. These units then form a $(\text{CNO})_4\cdot(\text{HCl})_2$ ring by way of two equivalent N–H···Cl hydrogen bonds (Cl{-} site symmetry $m$). These rings are catenated into infinite chains propagating along the c-axis direction by way of shape complementarity and directional C–H···N and C–H···π interactions.

1. Chemical context

Coordination-driven self-assembly of supramolecular structures is a major focus area of materials science. However, hydrogen-bond-driven self-assembly has been less well studied, most likely as a consequence of the weakness of hydrogen bonding relative to coordinate bonding. Nevertheless, the directionality of hydrogen bonding can lend it to the controllable formation of supramolecular networks (González-Rodríguez & Schenning, 2011; Steiner, 2002; Prins et al., 2001). The simplest infinite interlocking systems are the one-dimensional polycatenanes (poly[n]catenanes). Such systems have been described involving interpenetrating metallacycles of silver/bis(2-methylimidazolyl) (Jin et al., 2006, 2008, 2018) and mercury/1,2-bis(pyridin-4-ylthio)methyl]benzene (Xue et al., 2015). However, the lack of many examples beyond these suggests that the self-assembly of this interesting topological architecture is not easily achieved. Here, we report the serendipitous discovery of an infinite one-dimensional polycatenane architecture templated by a chloride anion that forms upon the attempted recrystallization of clozapine N-oxide ($\text{C}_{18}\text{H}_{19}\text{ClN}_{4}\text{O}$; hereafter CNO) mono-hydrochloride, an inactive metabolite of clozapine that is utilized as an actuator of engineered muscarinic acetylcholine receptors (Armbruster et al., 2007; Urban & Roth, 2015; Dong et al., 2010; Gomez et al., 2017).

As part of efforts to develop a water-soluble salt form of CNO (van der Peet et al., 2018) we synthesized CNO–HBr and CNO–HCl by formation of the salt in methanol (Scheme 1).
The latter compound has been reported previously (Allen et al., 2019), but its preparation was not described. Elemental analysis of the precipitated CNO-HCl was consistent with the proposed structure in Scheme 1. Although crystals suitable for single crystal X-ray analysis were not obtained from the crude precipitate, powder X-ray diffraction of the precipitate suggested the material was substantially crystalline. To obtain structural verification and to locate the site of protonation, we attempted to grow single crystals of CNO-HCl for single crystal X-ray analysis. Slow evaporation of a solution of CNO-HCl from a variety of solvents, or by diffusion of diethyl ether into a variety of solvents consistently yielded small orange block-shaped crystals of the title hemihydrochloride, which were found to be no longer soluble in water or other solvents (Scheme 2).

2. Structural commentary

Single-crystal X-ray diffraction analysis of the orange crystals revealed that the CNO-HCl salt implied by the analysis for the initially formed salt (above) had lost half an equivalent of HCl upon crystallization and crystallized as a hemihydrochloride, (CNO)_2·HCl, in the tetragonal space group I4/m (Scheme 2 and Fig. 1). In this structure, two molecules of CNO, which are related by a crystallographic twofold axis, share a proton, which is located on the rotation axis and forms a strong, essentially linear and apparently symmetric O—H⋯O/ O⋯H—O hydrogen bond between the two molecules via the N-oxide moieties [O1⋯O1' = 2.434 (2) Å; symmetry code (i) −x, 1 − y, z]. Within the structure, the chloride counter-ion (Cl2) is located on a crystallographic mirror plane and accepts equivalent N—H⋯Cl hydrogen bonds [N1⋯Cl2 = 3.3259 (14) Å] to two mirror-related (CNO)2H+ moieties resulting in the formation of a cyclic structure templated by the Cl− counter-ions (Fig. 2). The diazepine ring core in (CNO)2·HCl adopts a boat conformation (Table 1) in which the N1(H) group is at the bow and the C7=N2 imine group is the stern. A consequence of the boat conformation is the mean planes of the two fused benzene rings lie at an angle

Table 1

| Torsion angle (°) | C8—N1—C1—C2 | C7—N2—C9—C8 | C1—N1—C8—C9 | C3—N3—C4—C5 |
|------------------|---------------|---------------|---------------|----------------|
|                  | 55.7 (2)      | 33.5 (2)      | 54.0 (2)      | 4.9 (2)        |
|                  | −352.2 (2)    | −54.0 (2)     | −9.4 (2)      | 35.2 (2)       |

Figure 1

The molecular structure of (CNO)2·HCl showing 50% displacement ellipsoids with C-bound H atoms omitted for clarity. The unlabelled atoms are generated by the symmetry operation −x, 1 − y, z.

Figure 2

The cyclic tetramer (CNO)(HCl)2 templated by N—H⋯Cl hydrogen-bonding interactions.
40.08 (6)° to one another; this represents a less puckered ring to that observed in the (CNO)\textsubscript{2}·MeOH solvate in which the aromatic rings are at an angle of 56.2° (van der Peet et al., 2018) demonstrating the flexibility of this ring system. The equivalent angle between the seven-membered diazepine ring and its pendant N-oxide ring is 31.14 (7)°

### 3. Supramolecular features

The tetrameric cyclic structures are catenated and form infinite chains extending along the \( z \)-direction (Figs. 3 and 4) in which adjacent links in the chain are related by a \( 4_2 \) screw axis. The catenated rings form both as a result of general complementarity in the shapes of the internal cavities of the interacting (CNO)\textsubscript{2} dimers related by the symmetry operation \( (\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z) \), and further stabilized by four equivalent non-classical hydrogen-bonding interactions involving the polarized C—H bond adjacent to the N-oxide moiety; (C15—H15A···O1, Table 2) in addition to four equivalent C—H···π interactions [H15A···C8 = 2.706 (2) \( \text{Å} \)] (Fig. 5). Solvent voids, which account for approximately 17% of the unit-cell volume, lie between the catenated chains: the disordered solvent was accounted for using the Squeeze procedure in PLATON (Spek, 2015). To establish the relationship between the original material and that obtained after crystallization, powder X-ray diffraction data were obtained for the orange crystals and compared to that for the original material (Fig. 6). The two powder diffraction patterns are substantially different, which is consistent with the combustion analysis of the original material that analysed as (CNO)\textsubscript{2}HCl, whereas the crystallized material is (CNO)\textsubscript{2}HCl. Application of the same approach to CNO-HBr did not lead to an equivalent polymeric material.

### 4. Database survey

The formation of strong hydrogen bonds is predicted to occur when the \( pK_a \) value for the donor acid matches that for the...
acceptor’s conjugate acid form (Gilli et al., 2009). In this structure, a strong hydrogen bond between a protonated tertiary amine N-oxide and its conjugate base is predicted. A search of the Cambridge Structural Database (2022.2.0, September 2022; Groom et al., 2016) for structures containing the R,N—OH···O—NR₂ moiety with constraints on the R factor to 5% or less and only organic structures surveyed gave eight good-quality structures (CSD refcodes: RAJDAL (Bettencourt et al., 2021), AJESEQ (Włazłak et al., 2018), AREREW (Moore et al., 2016), BAYDEK (Jaskólski et al., 1982), EPSPOX (Maluszynśka & Okaya, 1977), FUBMAS (Moore et al., 2015), NUCDUK (Krzywda et al., 1996) and OBECUV (Bohmer et al., 2011): these structures are characterized by O···O distances ranging from 2.426–2.445 Å, which is comparable to the O···O distance of 2.434 (2) Å in this structure, thus all can be classified as strong O···H···O hydrogen bonds as predicted.

5. Synthesis and crystallization

Preparation of clozapine N-oxide hydrochloride (CNO·HCl)

A 250 ml round-bottom flask was charged with clozapine N-oxide (5.00 g, 0.015 mol) and methanol (50 ml) and stirred under N₂. Initially, the solid dissolved but then precipitated as a presumed CNO-methanolate adduct. A solution of HCl in ethyl acetate (2.8 M, 6 ml, 0.017 mol, 1.1 eq) was added slowly to the suspension. After 10 min the solid dissolved, and then precipitated as a yellow solid. The suspension was stirred for 1 h, then the solid was collected by filtration, and washed precipitated as a presumed CNO·HCl as small orange blocks. Degradation point: 483–493 K (corrected); ¹H NMR (400 MHz, CD₂OD) δ 3.68 (s, 3 H), 3.87 (br d, J 11.6 Hz, 2 H), 3.9–4.2 (m, 6 H), 7.01 (d, J 8.6 Hz, 1 H), 7.13–7.23 (m, 3 H), 7.27 (br s, 1 H), 7.53–7.60 (m, 2 H); ¹³C NMR (100 MHz, CD₂OD) δ 44.7, 57.8, 57.9, 64.6, 64.7, 122.6, 124.9, 125.0, 126.7, 126.8, 128.4, 130.0, 133.1, 136.5, 145.9, 156.4.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Regions of the unit cell occupied by disordered solvent (1409 Å³; ≈ 18.1% of the unit-cell volume) were processed with the Squeeze algorithm in PLATON (Spek, 2015); the stated composition, density, etc. do not take account of the solvent.

Acknowledgements

The Australian Synchrotron Collaborative Access Program is thanked for beamtime on MX1.

Table 3

| Crystal data | Chemical formula | 2C₁₃H₁₉Cl₂N₂O·HCl |
|--------------|------------------|--------------------|
| M₀           |                   | 722.10             |
| Temperature (K) |                   | 100               |
| a (Å)       |                   | 17.305 (2)         |
| c (Å)       |                   | 26.040 (5)         |
| V (Å³)      |                   | 7798 (3)           |
| μ (mm⁻¹)    |                   | 0.28               |
| Crystal size (mm) |             | 0.06 × 0.05 × 0.04 |

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Acta Cryst. (2022). E78, 1056–1060
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Computing details
Data collection: AS QEGUI; cell refinement: XDS (Kabsch, 1993); data reduction: XDS (Kabsch, 1993); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2016/6 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: WinGX (Farrugia, 2012).

8-Chloro-11-(4-methyl-1-piperazinyl)-5H-dibenzo[b,e][1,4]diazepine N-oxide hemi(hydrochloride)

Crystal data
2C\textsubscript{18}H\textsubscript{19}ClN\textsubscript{4}O·HCl

\(D_\text{calc} = 1.230 \text{ Mg m}^{-3}\)

Synchrotron radiation, \(\lambda = 0.710757 \text{ Å}\)

Cell parameters from 5908 reflections

\(\theta = 1.4-31.8^\circ\)

\(\mu = 0.28 \text{ mm}^{-1}\)

\(T = 100 \text{ K}\)

Block, yellow

0.06 × 0.05 × 0.04 mm

Data collection
ADSC Quantum 210r
diffractometer
Radiation source: MX1 Beamline Australian Synchrotron
Silicon Double Crystal monochromator
\(\omega\) Scan scans
66433 measured reflections

5901 independent reflections
5096 reflections with \(I > 2\sigma(I)\)

\(R_{int} = 0.049\)

\(\theta_{\max} = 31.8^\circ, \theta_{\min} = 1.4^\circ\)

\(h = -25 \rightarrow 25\)

\(k = -25 \rightarrow 25\)

\(l = -36 \rightarrow 36\)

Refinement
Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.049\)
\(wR(F^2) = 0.138\)

\(S = 1.03\)

5901 reflections

231 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

\(w = 1/[\sigma^2(F^2) + (0.0661P)^2 + 11.4576P]\)

where \(P = (F^2 + 2F_c^2)/3\)

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

\(\Delta\rho_{\max} = 0.81 \text{ e Å}^{-3}\)

\(\Delta\rho_{\min} = -0.49 \text{ e Å}^{-3}\)

Extinction correction: SHELXL2016/6 (Sheldrick 2015b),
\(Fc^2 = kFc[1+0.001xFc^2\lambda^2/\sin(2\theta)]^{1/4}\)

Extinction coefficient: 0.0069 (5)
Special details

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

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|      | x         | y         | z         | Uiso*/Ueq |
|------|-----------|-----------|-----------|-----------|
| Cl1  | 0.13932 (3)| 0.04426 (2)| 0.37292 (2)| 0.03680 (13) |
| Cl2  | 0.16534 (4)| 0.44691 (3)| 0.500000  | 0.03563 (15) |
| O1   | 0.02559 (6)| 0.43450 (7)| 0.13599 (5)| 0.0285 (2)   |
| N3   | 0.17304 (7)| 0.39022 (7)| 0.21729 (5)| 0.0225 (2)   |
| N2   | 0.15846 (7)| 0.30145 (7)| 0.28157 (5)| 0.0228 (2)   |
| N1   | 0.18161 (8)| 0.38441 (8)| 0.37970 (5)| 0.0261 (3)   |
| N4   | 0.10378 (8)| 0.43810 (8)| 0.12165 (5)| 0.0248 (3)   |
| C1   | 0.23713 (9)| 0.42470 (8)| 0.35074 (6)| 0.0242 (3)   |
| C7   | 0.18814 (8)| 0.36630 (8)| 0.26780 (5)| 0.0216 (3)   |
| C2   | 0.24220 (8)| 0.41696 (8)| 0.29712 (6)| 0.0228 (3)   |
| C10  | 0.15645 (9)| 0.18517 (9)| 0.32919 (6)| 0.0252 (3)   |
| H10  | 0.150809   | 0.159189   | 0.298148   | 0.030*       |
| C14  | 0.14157 (9)| 0.46872 (8)| 0.21112 (6)| 0.0239 (3)   |
| H14A | 0.170572   | 0.504443   | 0.232387   | 0.029*       |
| H14B | 0.088144   | 0.469610   | 0.222369   | 0.029*       |
| C9   | 0.16811 (8)| 0.26540 (8)| 0.32932 (6)| 0.0228 (3)   |
| C16  | 0.13708 (9)| 0.35868 (9)| 0.12884 (6)| 0.0254 (3)   |
| H16A | 0.190585   | 0.358444   | 0.117741   | 0.030*       |
| H16B | 0.108830   | 0.322118   | 0.107741   | 0.030*       |
| C15  | 0.14617 (9)| 0.49399 (8)| 0.15559 (6)| 0.0245 (3)   |
| H15A | 0.123725   | 0.545067   | 0.152003   | 0.029*       |
| H15B | 0.199875   | 0.496810   | 0.145089   | 0.029*       |
| C3   | 0.29823 (9)| 0.46033 (9)| 0.27067 (6)| 0.0256 (3)   |
| H3   | 0.302804   | 0.454729   | 0.235282   | 0.031*       |
| C11  | 0.15328 (9)| 0.14442 (9)| 0.37477 (6)| 0.0291 (3)   |
| C5   | 0.33991 (10)| 0.52005 (10)| 0.34901 (7)| 0.0317 (3)   |
| H5   | 0.371497   | 0.554918   | 0.366272   | 0.038*       |
| C8   | 0.17647 (9)| 0.30343 (9)| 0.37683 (6)| 0.0253 (3)   |
| C17  | 0.13260 (9)| 0.33933 (8)| 0.18470 (5)| 0.0237 (3)   |
| H17A | 0.078931   | 0.330314   | 0.195175   | 0.028*       |
| H17B | 0.156037   | 0.283374   | 0.188721   | 0.028*       |
| C6   | 0.28604 (9)| 0.47695 (10)| 0.37606 (6)| 0.0291 (3)   |
| H6   | 0.282259   | 0.482756   | 0.411475   | 0.035*       |
| C4   | 0.34685 (9)| 0.51128 (9)| 0.29616 (7)| 0.0294 (3)   |
| H4   | 0.383731   | 0.539293   | 0.278039   | 0.035*       |
| C13  | 0.17144 (12)| 0.26047 (10)| 0.42216 (6)| 0.0352 (4)   |
| H13  | 0.176053   | 0.285737   | 0.453531   | 0.042*       |
| C12  | 0.15973 (11)| 0.18114 (10)| 0.42162 (7)| 0.0361 (4)   |
| H12  | 0.156323   | 0.153376   | 0.452117   | 0.043*       |

Acta Cryst. (2022), E78, 1056-1060
**Atomic displacement parameters (Å²)**

|     | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|
| Cl1 | 0.0421 (2)| 0.02417 (19)| 0.0442 (2)| 0.00136 (15)| 0.01026 (17)| 0.00663 (15) |
| Cl2 | 0.0513 (4)| 0.0331 (3) | 0.0224 (2) | 0.0004 (2) | 0.0000 | 0.000 |
| O1  | 0.0225 (5)| 0.0313 (6) | 0.0318 (6) | -0.0003 (4) | -0.0012 (4) | 0.0007 (4) |
| N3  | 0.0265 (6)| 0.0200 (5) | 0.0210 (5) | -0.0002 (4) | -0.0015 (4) | -0.0017 (4) |
| N2  | 0.0234 (6)| 0.0225 (5) | 0.0224 (5) | 0.0017 (4) | 0.0001 (4) | -0.0013 (4) |
| N1  | 0.0321 (7)| 0.0252 (6) | 0.0211 (6) | 0.0006 (5) | 0.0007 (5) | -0.0034 (4) |
| N4  | 0.0263 (6)| 0.0271 (6) | 0.0210 (6) | -0.0012 (5) | 0.0007 (4) | -0.0003 (4) |
| C1  | 0.0234 (6)| 0.0237 (6) | 0.0256 (7) | 0.0024 (5) | -0.0024 (5) | -0.0013 (5) |
| C7  | 0.0216 (6)| 0.0219 (6) | 0.0214 (6) | 0.0025 (5) | 0.0000 (5) | -0.0024 (5) |
| C2  | 0.0219 (6)| 0.0214 (6) | 0.0249 (6) | 0.0018 (5) | -0.0018 (5) | -0.0015 (5) |
| C10 | 0.0234 (6)| 0.0241 (7) | 0.0282 (7) | 0.0020 (5) | 0.0025 (5) | 0.0007 (5) |
| C14 | 0.0272 (7)| 0.0211 (6) | 0.0233 (6) | 0.0015 (5) | -0.0014 (5) | -0.0014 (5) |
| C9  | 0.0203 (6)| 0.0236 (6) | 0.0246 (6) | 0.0021 (5) | 0.0006 (5) | 0.0006 (5) |
| C16 | 0.0286 (7)| 0.0256 (7) | 0.0220 (6) | -0.0001 (6) | 0.0009 (5) | -0.0028 (5) |
| C15 | 0.0264 (7)| 0.0228 (6) | 0.0241 (6) | -0.0020 (5) | -0.0011 (5) | 0.0003 (5) |
| C3  | 0.0239 (6)| 0.0236 (6) | 0.0293 (7) | 0.0010 (5) | 0.0000 (5) | -0.0010 (5) |
| C11 | 0.0286 (7)| 0.0238 (7) | 0.0349 (8) | 0.0030 (6) | 0.0051 (6) | 0.0046 (6) |
| C5  | 0.0275 (7)| 0.0284 (7) | 0.0392 (9) | -0.0019 (6) | -0.0071 (6) | -0.0053 (6) |
| C8  | 0.0258 (7)| 0.0257 (7) | 0.0245 (7) | 0.0022 (5) | -0.0009 (5) | 0.0001 (5) |
| C17 | 0.0275 (7)| 0.0230 (6) | 0.0205 (6) | -0.0010 (5) | -0.0005 (5) | -0.0027 (5) |
| C6  | 0.0294 (7)| 0.0304 (7) | 0.0274 (7) | 0.0016 (6) | -0.0056 (6) | -0.0055 (6) |
| C4  | 0.0233 (7)| 0.0262 (7) | 0.0387 (8) | -0.0019 (5) | -0.0006 (6) | -0.0014 (6) |
| C13 | 0.0494 (10) | 0.0340 (8) | 0.0224 (7) | 0.0029 (7) | -0.0001 (7) | 0.0013 (6) |
| C12 | 0.0477 (10) | 0.0327 (8) | 0.0279 (8) | 0.0034 (7) | 0.0032 (7) | 0.0070 (6) |
| C18 | 0.0464 (9) | 0.0368 (8) | 0.0203 (7) | -0.0016 (7) | 0.0000 (6) | 0.0033 (6) |

**Geometric parameters (Å, °)**

|     | C11—C11 | C9—C8 | C16—C17 | C15—H15A | C15—H15B | C3—C4 | C3—H3 | C11—C12 | C5—C6 |
|-----|---------|-------|----------|-----------|-----------|-------|-------|----------|-------|
| C11| 1.7506 (17) | 1.409 (2) | 1.518 (2) | 0.9700 | 0.9700 | 1.388 (2) | 0.9300 | 1.380 (2) | 1.386 (2) |
N1—H1 0.86 (2)  C5—C4 1.390 (2)
N4—C18 1.494 (2)  C5—H5 0.9300
N4—C15 1.5016 (19)  C8—C13 1.398 (2)
N4—C16 1.502 (2)  C17—H17A 0.9700
C1—C6 1.403 (2)  C17—H17B 0.9700
C1—C2 1.405 (2)  C6—H6 0.9300
C7—C2 1.492 (2)  C4—H4 0.9300
C2—C3 1.406 (2)  C13—C12 1.388 (3)
C10—C11 1.382 (2)  C13—H13 0.9300
C10—C9 1.403 (2)  C12—H12 0.9300
C10—H10 0.9300  C18—H18A 0.9600
C14—C15 1.513 (2)  C18—H18B 0.9600
C14—H14A 0.9700  C18—H18C 0.9600
C14—H14B 0.9700

N4—O1—H1A 107.9 (6)  N4—C15—H15A 109.5
C7—N3—C17 115.75 (12)  C14—C15—H15A 109.5
C7—N3—C14 116.31 (11)  C14—C15—H15B 109.5
C17—N3—C14 111.87 (11)  C14—C15—H15B 109.5
C7—N2—C9 126.07 (13)  H15A—C15—H15B 108.1
C1—N1—C8 120.58 (13)  C4—C3—C2 121.53 (15)
C1—N1—H1 114.0 (15)  C4—C3—H3 119.2
C8—N1—H1 109.5 (15)  C2—C3—H3 119.2
O1—N4—C18 109.17 (12)  C12—C11—C10 121.41 (15)
O1—N4—C15 110.03 (11)  C12—C11—Cl1 119.43 (13)
C18—N4—C15 110.59 (12)  C10—C11—Cl1 119.16 (13)
O1—N4—C16 107.20 (11)  C6—C5—C4 120.17 (15)
C18—N4—C16 110.61 (12)  C6—C5—H5 119.9
C15—N4—C16 110.18 (12)  C4—C5—H5 119.9
C6—C1—C2 119.37 (14)  C13—C8—N1 119.28 (14)
C6—C1—N1 118.67 (14)  C13—C8—C9 119.13 (15)
C2—C1—N1 121.88 (13)  N1—C8—C9 121.24 (13)
N2—C7—N3 116.40 (13)  N3—C17—C16 110.00 (12)
N2—C7—C2 128.37 (13)  N3—C17—H17A 109.7
N3—C7—C2 115.03 (12)  C16—C17—H17A 109.7
C1—C2—C3 118.60 (14)  N3—C17—H17B 109.7
C1—C2—C7 121.68 (13)  C16—C17—H17B 109.7
C3—C2—C7 119.68 (13)  H17A—C17—H17B 108.2
C11—C10—C9 120.58 (14)  C5—C6—C1 120.92 (15)
C11—C10—H10 119.7  C5—C6—H6 119.5
C9—C10—H10 119.7  C1—C6—H6 119.5
N3—C14—C15 110.58 (12)  C3—C4—C5 119.38 (15)
N3—C14—H14A 109.5  C3—C4—H4 120.3
C15—C14—H14A 109.5  C5—C4—H4 120.3
N3—C14—H14B 109.5  C12—C13—C18 121.79 (16)
C15—C14—H14B 109.5  C12—C13—H13 119.1
H14A—C14—H14B 108.1  C8—C13—H13 119.1
N2—C9—C10 114.92 (13)  C11—C12—C13 118.44 (15)
N2—C9—C8 125.70 (13) C11—C12—H12 120.8
C10—C9—C8 118.63 (13) C13—C12—H12 120.8
N4—C16—C17 110.97 (12) N4—C18—H18A 109.5
N4—C16—H16A 109.4 N4—C18—H18B 109.5
C17—C16—H16A 109.4 H18A—C18—H18B 109.5
C17—C16—H16B 109.4 H18A—C18—H18C 109.5
H16A—C16—H16B 108.0 H18B—C18—H18C 109.5
N4—C15—C14 110.53 (12)

C8—N1—C1—C6 −127.64 (15) C18—N4—C15—C14 −179.16 (13)
C8—N1—C1—C2 55.7 (2) C16—N4—C15—C14 −57.23 (15)
C9—N2—C7—N3 177.72 (13) N3—C14—C15—N4 57.38 (16)
C9—N2—C7—C2 −175.82 (13) N2—C9—C8—N1 −4.9 (2)
C9—N2—C7—C3 3.2 (2) N2—C9—C8—N1 −174.45 (14)
C11—C10—C9—N2 −170.69 (14) C15—C10—C9—C8 0.2 (3)
C11—C10—C9—C8 0.0 (2) O1—N4—C15—C14 175.84 (14)
O1—N4—C15—C14 175.84 (14)

N3—C7—C2—C1 168.54 (12) C7—N3—C17—C16 −166.50 (12)
N3—C7—C2—C3 −6.69 (19) C14—N3—C17—C16 57.13 (16)
N3—C7—C2—C3 −175.78 (13) C17—N3—C14—C15 −166.35 (12)
N3—C7—C2—C3 −168.54 (12) C7—N3—C14—C15 57.55 (16)

C15—H15 A···O1i 0.97 2.64 3.2598 (19) 122
C15—H15 A···N1ii 0.97 2.51 3.416 (2) 156
C15—H15B···Cl1iii 0.97 2.91 3.8431 (17) 162

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

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|------|-------|---------|
| O1···H14···O1i | 1.22 (1) | 1.22 (1) | 2.434 (2) | 179 (4) |
| N1···H11···Cl2 | 0.86 (2) | 2.46 (2) | 3.3259 (14) | 176 (2) |
| C15···H15A···O1i | 0.97 | 2.64 | 3.2598 (19) | 122 |
| C15···H15A···N1ii | 0.97 | 2.51 | 3.416 (2) | 156 |
| C15···H15B···Cl1iii | 0.97 | 2.91 | 3.8431 (17) | 162 |

Acta Cryst. (2022). E78, 1056-1060

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