Crystal structures of anhydrous and hydrated
N-benzylcinchonidinium bromide

Daron E. Janzen, a,⁎ Maya S. Butler a and Eric W. Reinheimer b

⁎Dept. of Chemistry & Biochemistry, St. Catherine University, 2004 Randolph Avenue, St. Paul, MN 55105, USA, and bRigaku Americas Corporation, 9009 New Trails Drive, The Woodlands, TX 77381, USA. *Correspondence e-mail: dejanzen@stkate.edu

N-benzylcinchonidinium bromide, C26H29N2O+-Br−, with the systematic name (R)-[(2S,4S,5R)-1-benzyl-5-ethenyl-1-azoniabicyclo[2.2.2]octan-2-yl](quinolin-4-yl)methanol bromide, is a quaternary ammonium salt of the cinchona alkaloid cinchonidine. This salt is widely used as a chiral phase-transfer catalyst and chiral resolution agent. Both classical and non-classical hydrogen-bonding interactions, as well as anion effects have been shown to play key mechanistic roles in the catalysis of cinchona alkaloids. In an effort to understand the effects of water on these intermolecular interactions, the structures of anhydrous N-benzylcinchonidinium bromide, (I), and the sesquihydrate, C26H29N2O+-Br−·1.5H2O, (II), were determined.

1. Chemical context

Cinchona-derived enantioselective phase-transfer catalysts have been used in a variety of applications including [2,3]-Wittig rearrangements (Denmark & Cullen, 2015), synthesis of unnatural α-amino acids (O’Donnell et al., 1989), and even industrial-scale synthesis of pharmaceuticals (Moccia et al., 2015). As this class of phase-transfer catalysts are easy to prepare from the parent natural product alkaloids, and demonstrate aspects of green and sustainable chemistry, they are attractive organocatalysts for further development. Mechanistic studies of N-benzylcinchonidinium bromide and substrates in solution provide evidence for the importance of quaternary ammonium benzylic C–H hydrogen-bond donor interactions as well as the classical OH donor (Bencivenni et al., 2021). Anion effects also demonstrate differences in the binding mode of substrates with mechanistic implications and potential enantioselectivity.
While structures are reported for analogs of this cation, that of the commercially available bromide salt is unpublished. We report here the structures of N-benzylcinchonidinium bromide (I) and the sesquihydrate (II).

2. Structural commentary

The anhydrous compound (I) (Fig. 1) crystallizes in the monoclinic space group $P2_1$. The asymmetric unit of (I) consists of one molecular cation and one bromide anion. The sesquihydrate (II) (Fig. 2) crystallizes in the tetragonal space group $P4_12_12$. The asymmetric unit of (II) consists of one molecular cation, one bromide anion, and one water on a general position and one half water, as O3 lies on a twofold axis at $z = 0.5$. For (I) and (II), the absolute configuration of chiral atoms N1, C2, C3, C7, and C8 are determined as $S$, $R$, $S$, $S$, and $R$, respectively, by anomalous dispersion and are consistent with previous structures of cinchonidine.

Most analogous bond lengths in (I) and (II) show only minor differences, with two exceptions (Tables 1 and 2). The largest differences in bond lengths occur for C6–C7 [1.510 (4) Å (I), 1.553 (8) Å (II)] and N2–C11 [1.282 (6) Å (I), 1.319 (9) Å (II)]. The quinuclidine intramolecular N1···C3 distances show small expansion of this bicyclic ring system from (I) [2.534 (5) Å] to (II) [2.591 (8) Å]. Overlap of the N-benzylcinchonidinium cation atom coordinates of (I) and (II) (Fig. 3) shows significant conformational differences. While the quinuclidine, benzyl, and vinyl functionalities adopt very similar conformations for (I) and (II), larger changes are observed in the alcohol and quinoline groups. Torsion angles that highlight the largest conformational changes include C7–C8–C13–C12 [107.9 (3)° (I); 101.3 (7)° (II)], C8–C7–N1–C20 [–39.0 (3)° (I); –53.6 (7)° (II)], and O1–C8–C13–C12 [–11.7 (4)° (I); –19.2 (8)° (II)]. These torsion-angle differences result in large changes in the relative angles between least-squares planes of the phenyl and quinoline groups in (I) [14.8 (2)°] and (II) [41.8 (3)°]. Intramolecular C–H···O contacts C5–H5A···O1 are found in both (I) and (II), but (I) shows an additional benzylic C20–H20B···O1 contact (Tables 3 and 4, Figs. 4 and 5).

Table 1

| Bond | Length (Å) | Ref. | Angle (°) | Ref. |
|------|-----------|------|-----------|------|
| C20–N1–C7–C8 | –39.0 (3) | (II) | | |

Table 2

| Bond | Length (Å) | Ref. | Angle (°) | Ref. |
|------|-----------|------|-----------|------|
| O1–C8–C13–C12 | –19.2 (8) | (II) | | |

Figure 1

Molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level.

Figure 2

Molecular structure of (II) with displacement ellipsoids drawn at the 50% probability level.

Figure 3

Overlap of quinuclidine non-H atom coordinates (C1–C7, N1) of the N-benzylcinchonidinium cation of (I) (red) and (II) (green).
3. Supramolecular features

The extended structure of (I) displays a simple isolated charge-assisted hydrogen bond with the alcohol donor O1 and Br1 anion acceptor (Table 3, Fig. 4). The quinoline N2 acceptor does not participate in any hydrogen-bonding interactions. Each bromide also has four short C—H···Br contacts with the same cation (phenyl, benzyl, quinoline, and vinyl) as well as an additional quinuclidine methine C—H.

The sesquihydrate (II) shows very different hydrogen-bonding interactions (Table 4, Fig. 5). The alcohol group O1 acts as a donor with a water acceptor, O2. Water O2 hydrogen bonds as donor with Br1 and quinoline N2, while water O3 acts a donor to two bromide acceptors. This pattern of hydrogen bonds forms a chain with terminal O1 donors and water and bromide links, with the water O2 relating the two halves of the chain. Quinoline N2 acceptors of O2 hydrogen-bond donors link the chains forming an extended network. Each bromide also has four short C—H···Br contacts with the same cation (benzyl, vinyl, and two quinuclidine) as well as two additional quinuclidine contacts with a neighboring molecular cation (Figs. 5 and 6).

Table 3
Hydrogen-bond geometry (Å, °) for (I).

| D—H · · ·A   | D—H | H · · ·A | D—A   | D—H · · ·A |
|-------------|------|---------|--------|-----------|
| O1—H1—Br1   | 0.73 (5) | 2.45 (5) | 3.149 (3) | 162 (5) |
| C15—H15—Br1* | 0.93 | 2.90 | 3.644 (4) | 137 |
| C12—H12—O1  | 0.93 | 2.39 | 2.739 (5) | 102 |
| C6—H6A—O1   | 0.97 | 2.58 | 2.967 (4) | 104 |
| C2—H2—Br1   | 0.98 | 2.83 | 3.779 (3) | 164 |
| C26—H26—Br1* | 0.93 | 2.87 | 3.738 (4) | 155 |
| C5—H5—O1    | 0.97 | 2.36 | 3.024 (4) | 125 |
| C20—H20A—Br1* | 0.97 | 2.91 | 3.800 (3) | 153 |
| C20—H20B—O1  | 0.97 | 2.64 | 3.198 (4) | 117 |
| C10—H10A—Br1* | 0.93 | 3.02 | 3.943 (4) | 172 |

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

Table 4
Hydrogen-bond geometry (Å, °) for (II).

| D—H · · ·A   | D—H | H · · ·A | D—A   | D—H · · ·A |
|-------------|------|---------|--------|-----------|
| O1—H1—O2   | 0.89 (8) | 1.75 (8) | 2.629 (7) | 168 (8) |
| O2—H2A—N2a | 0.88 (10) | 1.97 (10) | 2.824 (8) | 161 (9) |
| O2—H2B—Br1  | 0.75 (9) | 2.48 (9) | 3.202 (5) | 160 (10) |
| C7—H7—Br1   | 1.00 | 2.99 | 3.894 (6) | 151 |
| C12—H12—O1  | 0.95 | 2.44 | 2.771 (8) | 101 |
| C2—H2—Br1m  | 1.00 | 2.98 | 3.811 (7) | 142 |
| C1—H1B—Br1  | 0.99 | 2.88 | 3.779 (7) | 152 |
| C5—H5A—O1   | 0.99 | 2.29 | 2.836 (8) | 114 |
| C5—H5B—O3   | 0.99 | 2.56 | 3.464 (6) | 151 |
| C17—H17—O1  | 0.95 | 2.61 | 3.500 (8) | 157 |
| C6—H6A—O1   | 0.99 | 2.70 | 3.016 (8) | 99 |
| O4—H4A—Br1m | 0.99 | 2.94 | 3.785 (7) | 144 |
| C20—H20A—Br1 | 0.99 | 2.89 | 3.794 (7) | 152 |
| C10—H10A—Br1 | 0.95 | 3.01 | 3.960 (8) | 176 |
| C23—H23—O2  | 0.95 | 2.71 | 3.518 (11) | 143 |
| O3—H3A—Br1  | 0.90 (10) | 2.61 (10) | 3.499 (6) | 170 (11) |

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

4. Database survey

A search of the Cambridge Structural Database (ConQuest version 2022.1.0; Groom et al., 2016) yields several related analogs of both N-benzylcinchonidinium salts as well as the pseudo-enantiomer N-benzylcinchoninium. The 2-fluorobenzyl bromide sesquihydrate analog XUNQIG (Jew et al., 2002) is isostructural with (II) though additional C—H···F intra- and intermolecular interactions are present. Introduction of the aromatic 2-fluoro substituent yielded enhanced enantioselectivity in catalytic phase-transfer alkylation reactions, with possible origins related to more conformational or dipole changes to enhance substrate binding. Other closely
related N-benzylcinchonidinium chloride salts have been employed in co-crystal resolution of a chiral spirocyclic diol (GAJBOJ01; Zhang et al., 2005), atropisomeric chiral diols (HADSIS; Walsh et al., 2021 and JAPGIR; Sweetman et al., 2005) and a related mixed chiral amine/alcohol (GOSWIU; Ding et al., 1999). Even in the presence of multiple additional hydrogen-bond donors in these co-crystals, short benzyl C—H···Cl contacts are retained in GAJBOJ01 and JAPGIR, though not in HADSIS or GOSWIU. The N-benzylcinchonidinium cation has also been employed in resolution of chiral halogenated phosphates (GARJUF, GAWSUT; Frantz et al., 2005). Short benzyl C—H···O contacts are found in these chiral phosphate salts.

Closely related cinchoninium anhydrous bromide structures with phenyl substituents [2-bromobenzyl, QEDZAC (Skór ska-Stania et al., 2012) and 3,5-bistrifluoromethyl, UHINU V (Kawai et al., 2009)] show similar O—H···Br hydrogen bonding to (I). However, the C—H···Br interactions differ. In QEDZAC, each bromide has quinuclidine, quinoline, and benzyl C—H···Br contacts with the same cation. In UHINU V, quinoline, benzyl, and phenyl C—H···Br contacts with the same cation are found. The N-benzylcinchoninium chloride salt has also been employed in a co-crystal resolution of BINOL (WOMQUK01; Walsh et al., 2021).

5. Synthesis and crystallization

N-benzylcinchonidinium bromide was purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Crystals of the anhydrous form (I) were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of N-benzylcinchonidinium bromide.
Crystals of the sesquihydrate (II) were obtained by slow evaporation of an ethanol solution of N-benzylcinchonidinium bromide.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. The O—H hydrogen positions were assigned from residual electron-density peaks and positions were refined. All remaining hydrogen atoms were placed in calculated positions and refined in the riding-model approximation with distances of C—H = 0.93, 0.93, 0.93, 0.97, and 0.98 Å for the aromatic C—H, terminal vinyl CH₂, vinyl C9—H9, methylene C—H, and methine C—H, respectively, and with \( U_{iso}(H) = k \cdot U_{eq}(C) \), \( k = 1.2 \) for all C—H and 1.5 for the hydroxyl H1.

Funding information

Funding for this research was provided by: National Science Foundation, Major Research Instrumentation Program (award No. 1125975 to St. Catherine University); St. Catherine University, Collaborative Undergraduate Research Program, Summer Scholars (grant to D. Janzen, M. Butler).

References

Bencivenni, G., Illera, D. S., Moccia, M., Houk, K. N., Izzo, J. A., Novacek, J., Grieco, P., Vetticatt, M. J., Waser, M. & Adamo, M. F. A. (2021). *Chem. Eur. J.* 27, 11352–11366.

Denmark, S. E. & Cullen, L. R. (2015). *J. Org. Chem.* 80, 11818–11848.

Ding, K., Wang, Y., Yun, H., Liu, J., Wu, Y., Terada, M., Okubo, Y. & Mikami, K. (1999). *Chem. Eur. J.* 5, 1734–1737.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* 42, 339–341.

Frantz, R., Pinto, A., Constant, S., Bernardino, G. & Lacour, J. (2005). *Angew. Chem. Int. Ed.* 44, 5060–5064.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B72, 171–179.

Jew, S.-S., Yoo, M.-S., Jeong, B.-S., Park, Y. & Park, H.-G. (2002). *Org. Lett.* 4, 4245–4248.

Kawai, H., Kusuda, A., Nakamura, S., Shiro, M. & Shibata, N. (2009). *Angew. Chem. Int. Ed.* 48, 6324–6327.

Moccia, M., Cortigiani, M., Monasterolo, C., Torri, F., Del Fiandra, C., Fuller, G., Kelly, B. & Adamo, M. F. A. (2015). *Org. Process Res. Dev.* 19, 1274–1281.

O’Donnell, M. J., Bennett, W. D. & Wu, S. (1989). *J. Am. Chem. Soc.* 111, 2353–2355.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B69, 249–259.

Rigaku OD (2020). *CrysAlis PRO*. Rigaku Oxford Diffraction, Tokyo, Japan.

Sheldrick, G. M. (2015a). *Acta Cryst.* A71, 3–8.

Sheldrick, G. M. (2015b). *Acta Cryst.* C71, 3–8.

Skórski-Stania, A., Jezierska-Zięba, M., Kałol, B., Fedoryni, M. & Oleksyn, B. J. (2012). *Acta Cryst.* E68, o2803–o2804.

Sweetman, B. A., Müller-Bunz, H. & Guiry, P. J. (2005). *Tetrahedron* Lett. 46, 4643–4646.

Walsh, M. P., Phelps, J. M., Lennon, M. E., Yufit, D. S. & Kitching, M. O. (2021). *Nature*, 597, 70–76.

Zhang, W., Wu, S., Zhang, Z., Yennawar, H. & Zhang, X. (2006). *Org. Biomol. Chem.* 4, 4474–4477.
**Crystal structures of anhydrous and hydrated N-benzylcinchonidinium bromide**

Daron E. Janzen, Maya S. Butler and Eric W. Reinheimer

**Computing details**

For both structures, data collection: CrysAlis PRO (Rigaku OD, 2020); cell refinement: CrysAlis PRO (Rigaku OD, 2020); data reduction: CrysAlis PRO (Rigaku OD, 2020). Program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a) for (I); SHELXT2014/5 (Sheldrick, 2015a) for (II). For both structures, program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

**(R)-[(2S,4S,5R)-1-Benzyl-5-ethenyl-1-azoniabicyclo[2.2.2]octan-2-yl](quinolin-4-yl)methanol bromide (I)**

**Crystal data**

| Parameter | Value |
|-----------|-------|
| C26H29N2O+·Br− | |
| Mr | 465.42 |
| Monoclinic, P2₁ | |
| a | 11.2574 (7) Å |
| b | 8.8445 (5) Å |
| c | 11.9039 (9) Å |
| β | 110.126 (8)° |
| V | 1112.85 (14) Å³ |
| Z | 2 |
| F(000) | 484 |
| Dₓ | 1.389 Mg m⁻³ |
| Mo Kα radiation, λ = 0.71073 Å |
| Cell parameters from 8428 reflections |
| θ | 2.2–32.9° |
| μ | 1.87 mm⁻¹ |
| T | 173 K |
| Block, colourless |
| 0.61 × 0.25 × 0.15 mm |

**Data collection**

XtaLABmini
diffraction
termini
Radiation source: fine-focus sealed X-ray tube,
Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scans
(CrysAlisPro; Rigaku OD, 2020)
Tₘᵢₙ = 0.610, Tₘₐₓ = 1.000
15118 measured reflections
7531 independent reflections
5890 reflections with I > 2σ(I)
Rₑₑₘ = 0.030
θₑₑₑₑ = 32.9°, θₑₑₑᵣ = 1.8°
h = −16→16
k = −12→13
l = −18→17

**Refinement**

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.041
wR(F²) = 0.084
S = 1.01
7531 reflections
274 parameters
1 restraint
Primary atom site location: dual

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(Fc) + (0.0383P)² + 0.0838P]
where P = (Fc² + 2Fc)³/3
(Δ/σ)max = 0.001
Δρₑₑₑₑ = 0.54 e Å⁻³
Δρₑₑₑᵣ = −0.29 e Å⁻³
Absolute structure: Flack $x$ determined using 2185 quotients $([I^+]-[I^-])/([I^+]+[I^-])$ (Parsons et al., 2013)
Absolute structure parameter: $-0.011 (5)$

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 ($\AA^2$)

|    | x       | y       | z       | $U_{eq}$/$U_{eq}$ |
|----|---------|---------|---------|------------------|
| Br1| 0.75057 (3) | 0.27380 (4) | 0.57880 (3) | 0.03605 (9) |
| O1 | 0.5115 (2)  | 0.2121 (3)  | 0.6521 (3)  | 0.0362 (6)  |
| H1 | 0.572 (5)   | 0.209 (5)   | 0.642 (4)   | 0.054*     |
| N1 | 0.2489 (2)  | 0.3098 (2)  | 0.5310 (2)  | 0.0221 (5) |
| C15| 0.4907 (4)  | 0.6939 (4)  | 0.7102 (3)  | 0.0306 (8) |
| H15| 0.445324    | 0.659535    | 0.633537    | 0.037*     |
| C14| 0.5537 (3)  | 0.5893 (4)  | 0.7985 (3)  | 0.0284 (6) |
| C19| 0.6229 (4)  | 0.6432 (5)  | 0.9122 (3)  | 0.0403 (8) |
| N2 | 0.6882 (3)  | 0.5531 (4)  | 1.0046 (3)  | 0.0514 (9) |
| C12| 0.6235 (3)  | 0.3448 (4)  | 0.8711 (3)  | 0.0412 (8) |
| H12| 0.628646    | 0.241104    | 0.860850    | 0.049*     |
| C6 | 0.3120 (3)  | 0.3024 (4)  | 0.7490 (3)  | 0.0296 (7) |
| H6A| 0.369452    | 0.219011    | 0.781731    | 0.035*     |
| H6B| 0.323150    | 0.376529    | 0.811878    | 0.035*     |
| C2 | 0.0924 (3)  | 0.3675 (4)  | 0.6283 (3)  | 0.0352 (7) |
| H2 | 0.005740    | 0.328351    | 0.603565    | 0.042*     |
| C3 | 0.1782 (3)  | 0.2461 (4)  | 0.7058 (3)  | 0.0336 (9) |
| H3 | 0.151610    | 0.221515    | 0.773899    | 0.040*     |
| C1 | 0.1254 (3)  | 0.3847 (4)  | 0.5157 (3)  | 0.0270 (6) |
| H1A| 0.059424    | 0.339538    | 0.448607    | 0.032*     |
| H1B| 0.130621    | 0.491206    | 0.498492    | 0.032*     |
| C21| 0.1927 (3)  | 0.3134 (3)  | 0.3070 (3)  | 0.0299 (7) |
| C13| 0.5546 (3)  | 0.4325 (3)  | 0.7787 (3)  | 0.0280 (6) |
| C26| 0.1140 (3)  | 0.4260 (4)  | 0.2454 (3)  | 0.0372 (7) |
| H26| 0.120294    | 0.522060    | 0.278633    | 0.045*     |
| C22| 0.1858 (3)  | 0.1739 (4)  | 0.2559 (3)  | 0.0347 (7) |
| H22| 0.240605    | 0.097563    | 0.296478    | 0.042*     |
| C5 | 0.2326 (3)  | 0.1423 (4)  | 0.5392 (3)  | 0.0306 (6) |
| H5A| 0.314362    | 0.092895    | 0.561339    | 0.037*     |
| H5B| 0.179902    | 0.103515    | 0.461868    | 0.037*     |
| C25| 0.0260 (4)  | 0.3983 (5)  | 0.1352 (3)  | 0.0470 (9) |
| H25| −0.029164   | 0.474416    | 0.094748    | 0.056*     |
| C4 | 0.1721 (3)  | 0.1082 (4)  | 0.6311 (3)  | 0.0386 (8) |
| H4A| 0.084569    | 0.078650    | 0.591521    | 0.046*     |
| H4B| 0.216071    | 0.025160    | 0.681528    | 0.046*     |
### Atomic displacement parameters (Å$^2$)

|      | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|------|-----------|-----------|-----------|-----------|-----------|-----------|
| Br   | 0.03099 (14) | 0.02947 (13) | 0.05035 (18) | −0.00130 (17) | 0.01742 (12) | −0.00135 (18) |
| O1   | 0.0240 (12) | 0.0280 (11) | 0.0565 (16) | 0.0028 (10) | 0.0135 (12) | −0.0032 (10) |
| N1   | 0.0179 (10) | 0.0253 (15) | 0.0227 (11) | −0.0007 (8) | 0.0066 (8) | 0.0006 (8) |
| C15  | 0.0284 (18) | 0.031 (2) | 0.0341 (17) | −0.0009 (14) | 0.0123 (14) | 0.0020 (14) |
| C14  | 0.0234 (15) | 0.0352 (17) | 0.0298 (15) | −0.0040 (12) | 0.0132 (12) | −0.0003 (12) |
| C19  | 0.044 (2) | 0.048 (2) | 0.0326 (18) | −0.0106 (17) | 0.0173 (16) | −0.0027 (16) |
| N2   | 0.053 (2) | 0.064 (2) | 0.0288 (15) | −0.0178 (17) | 0.0041 (14) | 0.0011 (15) |
| C12  | 0.0271 (16) | 0.0372 (17) | 0.049 (2) | −0.0009 (13) | −0.0001 (15) | 0.0110 (15) |
| C6   | 0.0229 (12) | 0.039 (2) | 0.0255 (13) | −0.0011 (12) | 0.0070 (10) | 0.0034 (12) |
| C2   | 0.0208 (14) | 0.054 (2) | 0.0326 (16) | −0.0013 (14) | 0.0121 (13) | 0.0024 (15) |
| C3   | 0.0282 (14) | 0.048 (3) | 0.0263 (14) | −0.0076 (14) | 0.0113 (11) | 0.0053 (13) |
| C1   | 0.0177 (13) | 0.0355 (16) | 0.0262 (14) | 0.0008 (11) | 0.0055 (11) | 0.0019 (12) |
| C21  | 0.0299 (14) | 0.038 (2) | 0.0239 (14) | −0.0055 (12) | 0.0118 (12) | −0.0017 (11) |
| C13  | 0.0181 (13) | 0.0314 (15) | 0.0339 (16) | −0.0016 (11) | 0.0080 (12) | 0.0022 (12) |
| C26  | 0.0406 (19) | 0.0417 (19) | 0.0284 (16) | −0.0056 (15) | 0.0108 (14) | 0.0032 (14) |
| C22  | 0.0297 (17) | 0.045 (2) | 0.0332 (17) | −0.0022 (14) | 0.0159 (14) | −0.0032 (14) |
| C5   | 0.0283 (16) | 0.0277 (16) | 0.0336 (16) | −0.0049 (12) | 0.0076 (13) | −0.0008 (12) |
| C25  | 0.042 (2) | 0.064 (3) | 0.0294 (18) | −0.0018 (19) | 0.0049 (16) | 0.0106 (17) |
| C4   | 0.0350 (18) | 0.0391 (17) | 0.0407 (18) | −0.0134 (14) | 0.0118 (15) | 0.0053 (14) |
| C24  | 0.0456 (18) | 0.075 (3) | 0.0235 (14) | −0.015 (2) | 0.0069 (13) | −0.004 (2) |
supporting information

| C20  | 0.0255 (14) | 0.0305 (15) | 0.0243 (14) | −0.0024 (11) | 0.0105 (11) | 0.0001 (11) |
|------|-------------|-------------|-------------|--------------|-------------|-------------|
| C23  | 0.049 (2)   | 0.055 (2)   | 0.0354 (19) | −0.0148 (19) | 0.0204 (18) | −0.0161 (17) |
| C9   | 0.0385 (19) | 0.067 (3)   | 0.0357 (19) | 0.0168 (19)  | 0.0185 (15) | 0.0017 (17)  |
| C10  | 0.044 (2)   | 0.057 (2)   | 0.040 (2)   | 0.0177 (19)  | 0.0119 (17) | −0.0095 (17) |
| C11  | 0.037 (2)   | 0.062 (3)   | 0.038 (2)   | −0.0084 (18) | −0.0051 (16)| 0.0168 (18)  |
| C7   | 0.0172 (12) | 0.0271 (14) | 0.0218 (13) | −0.0016 (10) | 0.0047 (10) | −0.0019 (11) |
| C18  | 0.086 (3)   | 0.056 (3)   | 0.0393 (19) | −0.021 (2)   | 0.026 (2)   | −0.023 (2)   |
| C16  | 0.055 (3)   | 0.034 (2)   | 0.056 (3)   | 0.0037 (19)  | 0.026 (2)   | 0.0030 (19)  |
| C8   | 0.0188 (15) | 0.0255 (16) | 0.0340 (16) | −0.0011 (11)| 0.0088 (12) | 0.0008 (12)  |
| C17  | 0.104 (4)   | 0.036 (2)   | 0.067 (3)   | −0.012 (3)   | 0.040 (3)   | −0.019 (2)   |

Geometric parameters (Å, º)

| O1—H1 | 0.73 (5) | C21—C20 | 1.500 (4) |
|-------|---------|---------|-----------|
| O1—C8 | 1.392 (4)| C13—C8  | 1.501 (4) |
| N1—C1 | 1.494 (4)| C26—H26 | 0.9300    |
| N1—C5 | 1.500 (4)| C26—C25 | 1.366 (5) |
| N1—C20| 1.506 (4)| C22—H22 | 0.9300    |
| N1—C7 | 1.517 (3)| C22—C23 | 1.369 (5) |
| C15—H15| 0.9300  | C5—H5A  | 0.9700    |
| C15—C14| 1.397 (5)| C5—H5B  | 0.9700    |
| C15—C16| 1.353 (5)| C5—C4   | 1.505 (5) |
| C14—C19| 1.393 (5)| C25—H25 | 0.9300    |
| C14—C13| 1.407 (4)| C25—C24 | 1.368 (7) |
| C19—N2 | 1.352 (5)| C4—H4A  | 0.9700    |
| C19—C18| 1.401 (6)| C4—H4B  | 0.9700    |
| N2—C11 | 1.282 (6)| C24—H24 | 0.9300    |
| C12—H12| 0.9300  | C24—C23 | 1.360 (6) |
| C12—C13| 1.351 (4)| C20—H20A| 0.9700    |
| C12—C11| 1.397 (5)| C20—H20B| 0.9700    |
| C6—C3 | 1.499 (4)| C9—H9   | 0.9300    |
| C6—C7 | 1.510 (4)| C9—C10  | 1.299 (6) |
| C2—H2 | 0.9800  | C10—H10A| 0.9300    |
| C2—C3 | 1.524 (5)| C10—H10B| 0.9300    |
| C2—C1 | 1.517 (4)| C11—H11 | 0.9300    |
| C2—C9 | 1.485 (5)| C7—H7   | 0.9800    |
| C3—H3 | 0.9800  | C18—H18 | 0.9300    |
| C3—C4 | 1.497 (5)| C18—C17 | 1.332 (7) |
| C1—H1A| 0.9700  | C16—H16 | 0.9300    |
| C1—H1B| 0.9700  | C16—C17 | 1.383 (7) |
| C21—C26| 1.366 (5)| C8—H8   | 0.9800    |
| C21—C22| 1.366 (5)| C17—H17 | 0.9300    |
| C8—O1—H1 | 108 (4) | N1—C5—H5B | 109.7 |
| C1—N1—C5 | 108.4 (2) | N1—C5—C4 | 110.0 (3) |
| C1—N1—C20| 110.0 (2)| H5A—C5—H5B| 108.2 |

Acta Cryst. (2022). E78, 594-598

sup-4
C1—N1—C7  105.5 (2)  C4—C5—H5A  109.7
C5—N1—C20  110.4 (2)  C4—C5—H5B  109.7
C5—N1—C7  111.6 (2)  C26—C25—H25  120.1
C20—N1—C7  110.7 (2)  C26—C25—C24  119.7 (4)
C14—C15—H15  119.2  C24—C25—H25  120.1
C16—C15—H15  119.2  C3—C4—C5  109.2 (3)
C16—C15—C14  121.6 (4)  C3—C4—H4A  109.8
C15—C14—C13  123.9 (3)  C3—C4—H4B  109.8
C19—C14—C15  118.3 (3)  C5—C4—H4A  109.8
C19—C14—C13  117.8 (3)  C5—C4—H4B  109.8
C14—C19—C18  118.8 (4)  H4A—C4—H4B  108.3
N2—C19—C14  123.6 (4)  C25—C24—H24  120.0
N2—C19—C18  117.5 (3)  C23—C24—C25  120.0 (3)
C11—N2—C19  116.3 (3)  C23—C24—H24  120.0
C13—C12—H12  120.3  N1—C20—H20A  108.8
C13—C12—C11  119.5 (4)  N1—C20—H20B  108.8
C11—C12—H12  120.3  C21—C20—N1  113.9 (2)
H6A—C6—H6B  108.2  C21—C20—H20A  108.8
C3—C6—H6A  109.7  C21—C20—H20B  108.8
C3—C6—H6B  109.7  C22—C23—H23  119.9
C3—C6—C7  109.6 (2)  C24—C23—C22  120.1 (4)
C7—C6—H6A  109.7  C24—C23—H23  119.9
C7—C6—H6B  109.7  C3—C2—H2  106.9
C3—C2—H2  106.9  C2—C9—H9  115.2
C1—C2—C3  108.0 (3)  C2—C9—C10  129.5 (4)
C9—C2—H2  106.9  C10—C9—C11  115.2
C9—C2—C3  111.4 (3)  C9—C10—H10A  120.0
C9—C2—C1  116.3 (3)  C9—C10—H10B  120.0
C6—C3—C2  109.0 (3)  H10A—C10—H10B  120.0
C6—C3—H3  110.3  C2—C9—C10  125.1 (3)
C2—C3—H3  110.3  N1—C11—C12  117.5
C4—C3—C6  108.1 (3)  C12—C11—H11  117.5
C4—C3—C2  108.9 (3)  C14—C13—C8  106.4
C4—C3—H3  110.3  C6—C7—C8  116.0 (2)
N1—C1—C2  110.4 (2)  C6—C7—N1  107.8 (2)
N1—C1—H1A  109.6  C6—C7—H7  106.4
N1—C1—H1B  109.6  C6—C7—C8  113.2 (2)
C2—C1—H1A  109.6  C8—C7—H7  106.4
C2—C1—H1B  109.6  C19—C18—H18  119.5
H1A—C1—H1B  108.1  C17—C18—C19  121.0 (4)
C26—C21—C20  119.6 (3)  C17—C18—H18  119.5
C22—C21—C26  119.5 (3)  C15—C16—H16  120.4
C22—C21—C20  120.8 (3)  C15—C16—C17  119.2 (5)
C14—C13—C8  121.8 (3)  C17—C16—H16  120.4
C12—C13—C14  117.6 (3)  O1—C8—C13  112.7 (3)
C12—C13—C8  120.5 (3)  O1—C8—C7  108.8 (3)
C21—C26—H26  119.8  O1—C8—H8  109.4
C13—C8—C7  107.2 (3)
C25—C26—C21 120.5 (4) C13—C8—H8 109.4
C25—C26—H26 119.8 C7—C8—H8 109.4
C21—C22—H22 119.9 C18—C17—C16 121.0 (4)
C21—C22—C23 120.1 (4) C18—C17—H17 119.5
C23—C22—H22 119.9 C16—C17—H17 119.5
N1—C5—C15 109.7
C25—C26—C21—C22 −2.0 (6) C13—C12—C11—N2 −1.8 (6)
N1—C5—C15—C16 1.0 (8) C13—C12—C11—C8 −71.2 (4)
C4—C3—C2—C1 −14.5 (4) C12—C13—C8—O1 −55.1 (3)
C6—C3—C2—C1 67.9 (3) C3—C6—C7—N1 −21.9 (3)
C3—C6—C7—C8 151.6 (3) C3—C6—C7—N1 −21.9 (3)
C3—C2—C1—N1 −14.5 (4) C3—C2—C1—N1 −14.5 (4)
C3—C2—C9—C10 119.5 (4) C1—N1—C5—C4 0.93 2.90 3.644 (4) 137
C1—N1—C5—C4 0.93 2.90 3.644 (4) 137
C1—N1—C7—C6 73.9 (3) C7—C6—C3—C2 −45.7 (3)
C1—N1—C7—C6 73.9 (3) C7—C6—C3—C2 −45.7 (3)
C1—N1—C7—C8 −158.0 (2) C18—C19—N2—C11 −177.5 (4)
C1—C2—C3—C6 66.9 (3) C16—C15—C14—C19 −1.1 (6)
C1—C2—C3—C4 −50.8 (3) C16—C15—C14—C19 −179.1 (4)
C1—C2—C9—C10 −4.8 (6)

Hydrogen-bond geometry (Å, °)

|          | D—H—A        | D—H  | H···A  | D···A  | D—H···A |
|----------|--------------|------|-------|-------|---------|
| O1—H1···Br1 | 0.73 (5) 2.45 (5) 3.149 (3) 162 (5) |
| C15—H15···Br1 | 0.93 2.90 3.644 (4) 137 |
sup-7

Acta Cryst. (2022). E78, 594-598

C12—H12···O1 0.93 2.39 2.739 (5) 102
C6—H6d···O1 0.97 2.58 2.967 (4) 104
C2—H2···Br1i 0.98 2.83 3.779 (3) 164
C26—H26···Br1i 0.93 2.87 3.738 (4) 155
C5—H5a···O1 0.97 2.36 3.024 (4) 125
C20—H20a···Br1i 0.97 2.91 3.800 (3) 153
C20—H20b···O1 0.97 2.64 3.198 (4) 117
C10—H10a···Br1i 0.93 3.02 3.943 (4) 172

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

(R)-[(2S,4S,5R)-1-Benzyl-5-ethenyl-1-azoniabicyclo[2.2.2]octan-2-yl](quinolin-4-yl)methanol bromide sesquihydrate (II)

Crystal data

\[2\text{C}_{26}\text{H}_{29}\text{N}_{2}\text{O}^+\cdot\text{2Br}^-\cdot\text{3H}_2\text{O}\]
\[M_r = 984.89\]

Tetragonal, \(P\bar{4}_1212\)

\(a = 9.9254 (2) \, \text{Å}\)
\(c = 47.1267 (14) \, \text{Å}\)

\(V = 4642.6 (2) \, \text{Å}^3\)

\(Z = 4\)

\(F(000) = 2056\)

Data collection

XtaLABmini diffractometer

\(\omega\) scans

Absorption correction: multi-scan
(CrystalisPro; Rigaku OD, 2020)

\(T_{\text{min}} = 0.281, T_{\text{max}} = 1.000\)

36339 measured reflections

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.051\)
\(wR(F^2) = 0.111\)
\(S = 1.05\)

4154 independent reflections
297 parameters
0 restraints

H atoms treated by a mixture of independent and constrained refinement

\(\Delta\sigma/\sigma\) max < 0.001

\(\Delta p_{\text{max}} = 0.35 \, \text{e Å}^{-3}\)
\(\Delta p_{\text{min}} = -0.40 \, \text{e Å}^{-3}\)

Absolute structure: Flack determined using 1347 quotients \([I^+]-[I^-]/[I^+]+[I^-]\) (Parsons et al., 2013)

Absolute structure parameter: 0.005 (7)

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)

| Atom | x          | y          | z          | Uiso*/Ueq |
|------|------------|------------|------------|-----------|
| Br1  | 0.35481 (9) | 0.04938 (9) | 0.45637 (2) | 0.0479 (2) |
| O1   | 0.7691 (5)  | 0.4108 (5)  | 0.40753 (10) | 0.0320 (12) |
| H1   | 0.771 (8)   | 0.440 (8)   | 0.3897 (17)  | 0.048*     |
| O2   | 0.2790 (7)  | −0.0285 (6) | 0.39240 (11) | 0.0490 (16) |
| H2A  | 0.291 (10)  | −0.117 (10) | 0.3911 (19)  | 0.074*     |
| H2B  | 0.314 (10)  | −0.004 (10) | 0.406 (2)    | 0.074*     |
| N1   | 0.7332 (6)  | 0.2070 (5)  | 0.45114 (11) | 0.0252 (12) |
| N2   | 0.3561 (6)  | 0.6995 (5)  | 0.39911 (11) | 0.0303 (13) |
| C14  | 0.3953 (6)  | 0.4566 (7)  | 0.40458 (12) | 0.0235 (14) |
| C19  | 0.3097 (7)  | 0.5689 (7)  | 0.39967 (13) | 0.0264 (15) |
| C15  | 0.3366 (7)  | 0.3281 (6)  | 0.40504 (12) | 0.0255 (14) |
| H15  | 0.392546    | 0.251558    | 0.407842    | 0.031*     |
| C21  | 0.7978 (7)  | −0.0296 (7) | 0.43689 (13) | 0.0272 (15) |
| C8   | 0.6369 (6)  | 0.3692 (7)  | 0.41379 (12) | 0.0243 (14) |
| H8   | 0.612513    | 0.292345    | 0.401081    | 0.029*     |
| C18  | 0.1705 (7)  | 0.5476 (8)  | 0.39555 (13) | 0.0344 (16) |
| H18  | 0.113163    | 0.622347    | 0.392030    | 0.041*     |
| C13  | 0.5362 (7)  | 0.4828 (6)  | 0.40935 (12) | 0.0238 (14) |
| C7   | 0.6324 (7)  | 0.3211 (6)  | 0.44467 (11) | 0.0222 (13) |
| H7   | 0.540122    | 0.283909    | 0.448028    | 0.027*     |
| C26  | 0.7495 (7)  | −0.1293 (7) | 0.45498 (14) | 0.0327 (15) |
| H26  | 0.660524    | −0.123764   | 0.462339    | 0.039*     |
| C12  | 0.5777 (7)  | 0.6140 (7)  | 0.40851 (13) | 0.0276 (15) |
| H12  | 0.670326    | 0.634744    | 0.411066    | 0.033*     |
| C3   | 0.7655 (7)  | 0.4006 (7)  | 0.48738 (13) | 0.0293 (16) |
| H3   | 0.778720    | 0.475896    | 0.501210    | 0.035*     |
| C2   | 0.7276 (7)  | 0.2713 (7)  | 0.50314 (13) | 0.0293 (16) |
| H2   | 0.808128    | 0.242861    | 0.514409    | 0.035*     |
| C1   | 0.6996 (7)  | 0.1598 (7)  | 0.48123 (12) | 0.0271 (15) |
| H1A  | 0.754331    | 0.079421    | 0.485869    | 0.033*     |
| H1B  | 0.603387    | 0.133791    | 0.482176    | 0.033*     |
| C16  | 0.2012 (7)  | 0.3101 (7)  | 0.40157 (14) | 0.0307 (16) |
| H16  | 0.163499    | 0.222222    | 0.402525    | 0.037*     |
| C11  | 0.4857 (8)  | 0.7178 (7)  | 0.40396 (14) | 0.0325 (17) |
| H11  | 0.518450    | 0.807669    | 0.404381    | 0.039*     |
| C5   | 0.8787 (7)  | 0.2519 (7)  | 0.45190 (14) | 0.0301 (15) |
| H5A  | 0.909847    | 0.271857    | 0.432393    | 0.036*     |
| H5B  | 0.935407    | 0.178419    | 0.459612    | 0.036*     |
| C17  | 0.1177 (7)  | 0.4223 (8)  | 0.39656 (14) | 0.0347 (17) |
| H17  | 0.023662    | 0.409823    | 0.393869    | 0.042*     |
| C6   | 0.6538 (8)  | 0.4363 (7)  | 0.46649 (13) | 0.0304 (15) |
| H6A  | 0.677762    | 0.520318    | 0.456348    | 0.036*     |
| H6B  | 0.568948    | 0.452397    | 0.476995    | 0.036*     |
| C4   | 0.8939 (7)  | 0.3778 (7)  | 0.47045 (14) | 0.0340 (17) |
| H4A  | 0.970945    | 0.366248    | 0.483558    | 0.041*     |
supporting information

| Atomic displacement parameters (Å²) |
|-------------------------------------|
|  | \(U^11\)  | \(U^22\)  | \(U^33\)  | \(U^{12}\)  | \(U^{13}\)  | \(U^{23}\)  |
| Br1 | 0.0629 (6) | 0.0556 (5) | 0.0251 (3) | −0.0257 (4) | −0.0098 (4) | 0.0106 (4) |
| O1  | 0.024 (2)   | 0.046 (3)   | 0.026 (2)   | 0.002 (2)   | −0.001 (2)   | 0.012 (2)   |
| O2  | 0.089 (5)   | 0.029 (3)   | 0.029 (3)   | 0.007 (3)   | −0.015 (3)   | 0.005 (2)   |
| N1  | 0.032 (3)   | 0.023 (3)   | 0.021 (3)   | −0.001 (2)  | −0.003 (2)   | 0.000 (2)   |
| N2  | 0.042 (4)   | 0.026 (3)   | 0.022 (3)   | 0.006 (3)   | −0.004 (3)   | 0.005 (2)   |
| C14 | 0.031 (4)   | 0.030 (4)   | 0.010 (3)   | 0.004 (3)   | −0.002 (2)   | 0.000 (3)   |
| C19 | 0.034 (4)   | 0.028 (4)   | 0.017 (3)   | 0.006 (3)   | −0.003 (3)   | 0.001 (3)   |
| C15 | 0.033 (4)   | 0.027 (4)   | 0.016 (3)   | 0.002 (3)   | −0.001 (3)   | 0.000 (3)   |
| C21 | 0.037 (4)   | 0.029 (4)   | 0.015 (3)   | 0.005 (3)   | −0.001 (3)   | 0.000 (3)   |
| C8  | 0.026 (3)   | 0.031 (4)   | 0.015 (3)   | 0.001 (3)   | 0.000 (3)    | 0.005 (3)   |
| C18 | 0.032 (4)   | 0.041 (4)   | 0.030 (3)   | 0.015 (4)   | −0.002 (3)   | 0.001 (3)   |
| C13 | 0.031 (4)   | 0.026 (4)   | 0.014 (3)   | −0.001 (3)  | −0.001 (3)   | 0.001 (2)   |
| C7  | 0.029 (4)   | 0.028 (4)   | 0.010 (3)   | 0.002 (3)   | 0.000 (3)    | 0.001 (2)   |
| C26 | 0.041 (4)   | 0.028 (4)   | 0.030 (3)   | −0.004 (3)  | 0.001 (3)    | −0.001 (3)  |
| C12 | 0.033 (4)   | 0.029 (4)   | 0.020 (3)   | −0.002 (3)  | 0.001 (3)    | 0.004 (3)   |
| C3  | 0.041 (4)   | 0.026 (4)   | 0.021 (3)   | −0.003 (3)  | −0.009 (3)   | 0.000 (3)   |
| C2  | 0.043 (4)   | 0.026 (4)   | 0.019 (3)   | −0.002 (3)  | −0.010 (3)   | 0.000 (3)   |
| C1  | 0.041 (4)   | 0.027 (4)   | 0.014 (3)   | 0.001 (3)   | −0.003 (3)   | 0.002 (3)   |
| C16 | 0.034 (4)   | 0.035 (4)   | 0.023 (3)   | −0.004 (3)  | 0.001 (3)    | 0.002 (3)   |
| C11 | 0.049 (5)   | 0.025 (4)   | 0.024 (3)   | −0.003 (3)  | 0.003 (3)    | 0.007 (3)   |
| C5  | 0.027 (4)   | 0.034 (4)   | 0.028 (3)   | 0.001 (3)   | −0.004 (3)   | 0.006 (3)   |
| C17 | 0.027 (4)   | 0.046 (5)   | 0.031 (4)   | 0.004 (3)   | −0.006 (3)   | 0.000 (3)   |
| C6  | 0.045 (4)   | 0.026 (3)   | 0.021 (3)   | 0.002 (3)   | −0.004 (3)   | −0.001 (3)  |
| C4  | 0.039 (4)   | 0.032 (4)   | 0.031 (4)   | −0.007 (3)  | −0.006 (3)   | 0.009 (3)   |
| C9  | 0.060 (6)   | 0.033 (4)   | 0.022 (3)   | −0.003 (4)  | 0.001 (3)    | −0.008 (3)  |

Acta Cryst. (2022). E78, 594-598

sup-9
### Geometric parameters (Å, °)

|                  | Distance (Å) | Angle (°) |
|------------------|--------------|-----------|
| O1—H1            | 0.89 (8)     |           |
| O1—C8            | 1.406 (8)    |           |
| O2—H2A           | 0.88 (10)    |           |
| O2—H2B           | 0.75 (9)     |           |
| N1—C7            | 1.541 (8)    |           |
| N1—C1            | 1.530 (8)    |           |
| N1—C5            | 1.512 (8)    |           |
| N1—C20           | 1.514 (8)    |           |
| N2—C19           | 1.376 (9)    |           |
| N2—C11           | 1.319 (9)    |           |
| C14—C19          | 1.421 (9)    |           |
| C14—C13          | 1.440 (9)    |           |
| C19—C18          | 1.411 (10)   |           |
| C15—H15          | 0.9500       |           |
| C15—C16          | 1.366 (10)   |           |
| C21—C26          | 1.391 (9)    |           |
| C21—C20          | 1.496 (9)    |           |
| C21—C22          | 1.390 (10)   |           |
| C8—H8            | 1.0000       |           |
| C8—C13           | 1.521 (9)    |           |
| C8—C7            | 1.532 (7)    |           |
| C18—H18          | 0.9500       |           |
| C18—C17          | 1.350 (11)   |           |
| C13—C12          | 1.367 (9)    |           |
| C7—H7            | 1.0000       |           |
| C7—C6            | 1.553 (8)    |           |
| C26—H26          | 0.9500       |           |
| C26—C25          | 1.388 (10)   |           |
| C12—H12          | 0.9500       |           |
| C12—C11          | 1.393 (9)    |           |
| C3—H3            | 1.0000       |           |
| C3—C2            | 1.530 (9)    |           |
| C8—O1—H1         | 109 (5)      |           |
| H2A—O2—H2B       | 108 (9)      |           |
| N1—C1—H1A        |             | 109.4     |
| N1—C1—H1B        |             | 109.4     |
| C2—C1—H1A        |             | 109.4     |
| C2—C1—H1B        |             | 109.4     |
| C20—O1—H1        | 109 (5)      |           |
| H2A—O2—H2B       | 108 (9)      |           |
| C1—N1—C7         | 105.5 (5)    |           |
| C5—N1—C7         | 114.1 (5)    |           |
C5—N1—C1 106.0 (5)
C5—N1—C20 110.9 (5)
C20—N1—C7 110.2 (5)
C20—N1—C1 109.8 (5)
N2—C19—C14 122.8 (6)
N2—C19—C18 117.8 (6)
C18—C19—C14 119.4 (6)
C14—C15—H15 119.1
O1—C8—H8 108.9
O1—C8—C13 111.5 (5)
C13—C8—C19 108.9
C13—C8—C7 110.0 (5)
C7—C8—H8 108.9
C19—C18—H18 119.5
C17—C18—C19 120.9 (7)
N1—C7—H7 107.0
N1—C7—C6 108.7 (5)
C8—C7—N1 113.5 (5)
C8—C7—H7 107.0
C8—C7—C6 113.3 (5)
C6—C7—H7 107.0
C21—C26—H26 120.2
C25—C26—C21 119.6 (7)
C25—C26—H26 120.2
C13—C12—H12 119.6
C13—C12—C11 120.8 (7)
C11—C12—H12 119.6
C2—C3—H3 110.1
C6—C3—H3 110.1
C6—C3—C2 109.3 (6)
C4—C3—H3 110.1
C4—C3—C2 109.6 (6)
C4—C3—C6 107.8 (5)
C3—C2—H2 107.4
| Bond | Length (Å) | Bond | Length (Å) |
|------|------------|------|------------|
| C3—C2—C1 | 108.8 (5) | H10A—C10—H10B | 120.0 |
| C1—C2—H2 | 107.4 | C24—C23—C22 | 119.4 (8) |
| C9—C2—C3 | 111.1 (6) | C24—C23—H23 | 120.3 |
| C9—C2—H2 | 107.4 | C22—C23—H23 | 120.3 |
| C9—C2—C1 | 114.5 (6) | H3A—O3—H3A | 110 (10) |
| N1—C1—C2 | 111.2 (5) |

| Bond | Symmetry Code | Length (Å) |
|------|---------------|------------|
| O1—C8—C13—C14 | (i) y+1, x−1, −z+1 | 157.9 (5) |
| O1—C8—C13—C12 | (i) y+1, x−1, −z+1 | −19.2 (8) |
| O1—C8—C7—N1 | (i) y+1, x−1, −z+1 | −56.9 (7) |
| O1—C8—C7—C6 | (i) y+1, x−1, −z+1 | 67.7 (7) |
| N1—C7—C6—C3 | (i) y+1, x−1, −z+1 | −0.5 (7) |
| N1—C5—C4—C3 | (i) y+1, x−1, −z+1 | 12.3 (7) |
| N2—C19—C18—C17 | (i) y+1, x−1, −z+1 | −178.3 (6) |
| C14—C19—C18—C17 | (i) y+1, x−1, −z+1 | 0.8 (10) |
| C14—C15—C16—C17 | (i) y+1, x−1, −z+1 | 1.9 (10) |
| C14—C13—C12—C11 | (i) y+1, x−1, −z+1 | 1.7 (9) |
| C19—N2—C11—C12 | (i) y+1, x−1, −z+1 | 2.4 (10) |
| C19—C14—C15—C16 | (i) y+1, x−1, −z+1 | −1.5 (9) |
| C19—C14—C13—C8 | (i) y+1, x−1, −z+1 | −177.9 (5) |
| C19—C14—C13—C12 | (i) y+1, x−1, −z+1 | −0.7 (8) |
| C19—C18—C17—C16 | (i) y+1, x−1, −z+1 | −0.4 (10) |
| C15—C14—C19—N2 | (i) y+1, x−1, −z+1 | 179.2 (6) |
| C15—C14—C19—C18 | (i) y+1, x−1, −z+1 | 0.2 (9) |
| C15—C14—C13—C8 | (i) y+1, x−1, −z+1 | 3.5 (9) |
| C15—C14—C13—C12 | (i) y+1, x−1, −z+1 | −179.3 (6) |
| C15—C16—C17—C18 | (i) y+1, x−1, −z+1 | −0.9 (10) |
| C21—C26—C25—C24 | (i) y+1, x−1, −z+1 | −2.6 (11) |
| C21—C22—C23—C24 | (i) y+1, x−1, −z+1 | 1.6 (13) |
| C8—C13—C12—C11 | (i) y+1, x−1, −z+1 | 178.9 (6) |
| C8—C7—C6—C3 | (i) y+1, x−1, −z+1 | −127.6 (6) |
| C13—C14—C19—N2 | (i) y+1, x−1, −z+1 | 0.5 (9) |
| C13—C14—C19—C18 | (i) y+1, x−1, −z+1 | −178.6 (6) |
| C13—C14—C15—C16 | (i) y+1, x−1, −z+1 | 177.1 (6) |
| C13—C8—C7—N1 | (i) y+1, x−1, −z+1 | −179.2 (5) |
| C13—C8—C7—C6 | (i) y+1, x−1, −z+1 | −54.6 (7) |
| C13—C12—C11—N2 | (i) y+1, x−1, −z+1 | −2.7 (10) |
| C7—N1—C1—C2 | (i) y+1, x−1, −z+1 | −65.4 (6) |
| C7—N1—C5—C4 | (i) y+1, x−1, −z+1 | 48.7 (7) |
| C7—N1—C20—C21 | (i) y+1, x−1, −z+1 | −173.9 (5) |
| C7—C8—C13—C14 | (i) y+1, x−1, −z+1 | −81.6 (7) |
| C7—C8—C13—C12 | (i) y+1, x−1, −z+1 | 101.3 (7) |

Symmetry code: (i) y+1, x−1, −z+1.

**Hydrogen-bond geometry (Å, †)**

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| O1—H1—O2ii | 0.89 (8) | 1.75 (8) | 2.629 (7) | 168 (8) |

---

*Acta Cryst. (2022), E78, 594-598*
O2—H2···N2\textsuperscript{iii} & 0.88 (10) & 1.97 (10) & 2.824 (8) & 161 (9) \\
O2—H2B···Br1 & 0.75 (9) & 2.48 (9) & 3.202 (5) & 160 (10) \\
C15—H15···Br1 & 0.95 & 3.07 & 3.679 (6) & 124 \\
C15—H15···O2 & 0.95 & 3.09 & 3.634 (9) & 118 \\
C7—H7···Br1 & 1.00 & 2.99 & 3.894 (6) & 151 \\
C12—H12···O1 & 0.95 & 2.44 & 2.771 (8) & 101 \\
C12—H12···O2\textsuperscript{iv} & 0.95 & 2.94 & 3.236 (9) & 100 \\
C3—H3···Br1\textsuperscript{iv} & 1.00 & 3.56 & 3.895 (6) & 102 \\
C2—H2···Br1\textsuperscript{iv} & 1.00 & 2.98 & 3.811 (7) & 142 \\
C2—H2···O3 & 1.00 & 3.19 & 3.946 (8) & 134 \\
C1—H14···O3 & 0.99 & 3.21 & 3.888 (9) & 127 \\
C1—H18···Br1 & 0.99 & 2.88 & 3.779 (7) & 152 \\
C16—H16···O1\textsuperscript{v} & 0.95 & 3.29 & 3.608 (9) & 102 \\
C16—H16···O2 & 0.95 & 2.78 & 3.475 (9) & 131 \\
C11—H11···O2\textsuperscript{vi} & 0.95 & 2.93 & 3.293 (9) & 104 \\
C5—H5···O1 & 0.99 & 2.29 & 2.836 (8) & 114 \\
C5—H5···O3 & 0.99 & 2.56 & 3.464 (6) & 151 \\
C17—H17···O1\textsuperscript{vii} & 0.95 & 2.61 & 3.500 (8) & 157 \\
C17—H17···O2\textsuperscript{v} & 0.95 & 3.19 & 3.973 (10) & 140 \\
C6—H6···O1 & 0.99 & 2.70 & 3.016 (8) & 99 \\
C4—H4···Br1\textsuperscript{iv} & 0.99 & 2.94 & 3.785 (7) & 144 \\
C4—H4···O3 & 0.99 & 3.19 & 3.784 (8) & 120 \\
C4—H4···O1 & 0.99 & 2.82 & 3.230 (8) & 106 \\
C9—H9···N2\textsuperscript{iii} & 0.95 & 2.91 & 3.780 (9) & 153 \\
C20—H20···Br1 & 0.99 & 2.89 & 3.794 (7) & 152 \\
C20—H20···O1 & 0.99 & 2.87 & 3.387 (8) & 114 \\
C22—H22···O2\textsuperscript{iv} & 0.95 & 3.36 & 3.837 (11) & 114 \\
C10—H10···Br1 & 0.95 & 3.01 & 3.960 (8) & 176 \\
C23—H23···O2\textsuperscript{iv} & 0.95 & 2.71 & 3.518 (11) & 143 \\
O3—H3···Br1\textsuperscript{iv} & 0.90 (10) & 2.61 (10) & 3.499 (6) & 170 (11) \\

Symmetry codes: (ii) x+1/2, −y+1/2, −z+3/4; (iii) x, y−1, z; (iv) y+1, x, −z+1; (v) x−1/2, −y+1/2, −z+3/4; (vi) x, y+1, z; (vii) x−1, y, z; (viii) y, x, −z+1; (ix) x+1, y, z.