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# 1-(1-Hydroxyethyl)-7,8-dihydroindolo-[2,3-*a*]pyridine[3,4-*g*]quinolizin-5(13*H*)-one (angustoline) monohydrate from *Nauclea subdita* (Rubiaceae)

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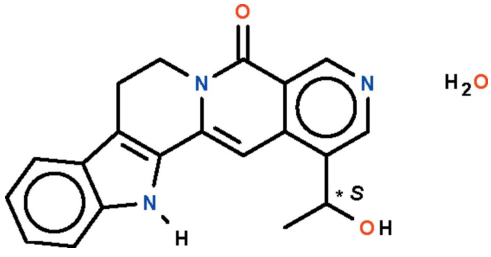
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.036; $wR$ factor = 0.098; data-to-parameter ratio = 13.0.

The title compound (trivial name: angustoline monohydrate), $C_{20}H_{17}N_3O_2{\cdot}H_2O$, features a fused-ring system formed by one five- and four six-membered rings. The nearly planar benzimidazole portion (r.m.s. deviation = 0.008 Å) and the nearly planar 2,7-naphthyridin-1-one portion (r.m.s. deviation = 0.022 Å) of the fused-ring system are slightly twisted, with a dihedral angle of 9.47 (8)°, owing to the tetrahedral nature of the two methylene linkages in the central six-membered ring. The secondary N atom acts as a hydrogen-bond donor to the water molecule of crystallization. In the crystal, the amino and hydroxy groups, and the water molecule are engaged in hydrogen bonding, generating a three-dimensional network.

## Related literature

For the isolation of the title compound from other plants, see: Abreu & Pereira (1998, 2001); Au *et al.* (1973); Carte *et al.* (1990); Erdelmeier *et al.* (1992); Fan *et al.* (2010); Hotellier *et al.* (1975); Kakuguchi *et al.* (2009); Lin *et al.* (1988); Sun *et al.* (2008); Xuan *et al.* (2007); Zeches *et al.* (1985).




## Experimental

### Crystal data

$C_{20}H_{17}N_3O_2{\cdot}H_2O$
$M_r$ = 349.38
Monoclinic, $P2_1$
$a$ = 8.8350 (3) Å
$b$ = 6.7002 (2) Å
$c$ = 14.7347 (4) Å
$\beta$ = 103.117 (3)°
$V$ = 849.48 (4) Å$^3$
$Z$ = 2
Cu $K\alpha$ radiation
$\mu$ = 0.76 mm$^{-1}$
$T$ = 100 K
0.30 × 0.03 × 0.03 mm

### Data collection

Agilent SuperNova Dual with an Atlas detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)
$T_{min}$ = 0.803, $T_{max}$ = 0.978
6453 measured reflections
3252 independent reflections
3015 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.027

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.098
$S$ = 1.02
3252 reflections
251 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$
Absolute structure: Flack (1983), 1395 Friedel pairs
Flack parameter: 0.1 (2)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2···N3$^{i}$ | 0.97 (4) | 1.77 (4) | 2.732 (2) | 171 (3) |
| O1w—H11···O1$^{ii}$ | 0.85 (4) | 2.08 (4) | 2.928 (2) | 169 (3) |
| O1w—H12···O2$^{iii}$ | 0.83 (4) | 1.95 (4) | 2.762 (2) | 167 (3) |
| N1—H1···O1w | 0.85 (3) | 2.02 (3) | 2.861 (2) | 177 (2) |

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

Data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5242).

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# supplementary materials

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# 1-(1-Hydroxyethyl)-7,8-dihydroindolo[2,3-*a*]pyridine[3,4-*g*]quinolizin-5(13*H*)-one (angustoline) monohydrate from *Nauclea subdita* (Rubiaceae)

**S. Y. Liew, M. R. Mukhtar, K. Awang, M. R. Mustafa and S. W. Ng**

## Comment

The alkaloid angustoline has been isolated from a number of plants: *Camptotheca acuminata* (Carte *et al.*, 1990; Lin *et al.*, 1988), *Nauclea latifolia* (Kakuguchi *et al.*, 2009; Hotellier *et al.*, 1975), *Nauclea officinalis* (Fan *et al.*, 2010; Sun *et al.*, 2008; Xuan *et al.*, 2007), *Nauclea orientalis* (Erdelmeier *et al.*, 1992), *Nauclea pobeguinii* (Zeches *et al.*, 1985), *Sarcocephalus latifolius* (Abreu & Pereira, 1998; 2001) and *Strychnos angustiflora* (Au *et al.*, 1973).

The alkaloid is isolated in the crystalline form as a monohydrate (Scheme I). The planar benzimidazole portion and the planar 2,7-naphthyridin-1-one portion of the fused-ring system are slightly twisted [dihedral angle 9.47 (8)°] owing to the tetrahedral nature of the two methylene linkages (Fig. 1). The secondary N atom is hydrogen-bond donor to the water molecule. The amino and hydroxy groups, and the lattice water molecule are engaged in hydrogen bonding to furnish a three-dimensional network (Table 1).

## Experimental

*Nauclea subdita* (Rubiaceae) was collected from Bukit Kinta forest reserve, Chemor, Perak, Malaysia, and specimens were deposited at the Herbarium, Department of Chemistry, University of Malaya.

Dried and ground bark of *Nauclea subdita* (1.7 kg) was extracted with hexane (17 *L*) for 3 days. The hexane extract was concentrated under reduced pressure. The dried plant material was soaked in ammonium hydroxide for 2 h. It was further extracted with dichloromethane (17 *L*) for 3 days. The dichloromethane extract was concentrated under reduced pressure to give a crude alkaloid (7.1 g). A portion (6.0 g) was subjected to column chromatography on silica gel 60 $GF_{254}$ by using a step gradient of dichloromethane and methanol. One of the fractions when further purified by using dichloromethane/methanol (95:5) afforded the pure compound, whose formulation was established by NMR spectroscopic analysis.

## Refinement

Carbon-bound H-atoms were placed in calculated positions [C—H 0.95 to 0.99 Å, $U_{iso}$(H) 1.2 to 1.5$U_{eq}$(C)] and were included in the refinement in the riding model approximation.

The nitrogen and oxygen bound H-atoms were located in a difference Fourier map, and were freely refined.

The Flack parameter was determined from 1395 Friedel pairs.

## Figures

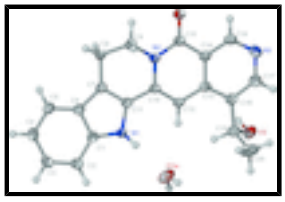


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $C_{20}H_{17}N_3O_2 \cdot H_2O$ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

## 1-(1-Hydroxyethyl)-7,8-dihydroindolo[2,3-*a*]pyridine[3,4- *g*]quinolizin-5(13*H*)-one monohydrate

### *Crystal data*

| | |
|---|---|
| $C_{20}H_{17}N_3O_2 \cdot H_2O$ | $F(000) = 368$ |
| $M_r = 349.38$ | $D_x = 1.366$ Mg m$^{-3}$ |
| Monoclinic, $P2_1$ | Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å |
| Hall symbol: P 2yb | Cell parameters from 3352 reflections |
| $a = 8.8350$ (3) Å | $\theta = 3.1$–$74.0°$ |
| $b = 6.7002$ (2) Å | $\mu = 0.76$ mm$^{-1}$ |
| $c = 14.7347$ (4) Å | $T = 100$ K |
| $\beta = 103.117$ (3)° | Prism, yellow |
| $V = 849.48$ (4) Å$^3$ | 0.30 × 0.03 × 0.03 mm |
| $Z = 2$ | |

### *Data collection*

| | |
|---|---|
| Agilent SuperNova Dual with an Atlas detector diffractometer | 3252 independent reflections |
| Radiation source: SuperNova (Cu) X-ray Source | 3015 reflections with $I > 2\sigma(I)$ |
| Mirror | $R_{int} = 0.027$ |
| Detector resolution: 10.4041 pixels mm$^{-1}$ | $\theta_{max} = 74.2°$, $\theta_{min} = 3.1°$ |
| ω scans | $h = -11 \rightarrow 9$ |
| Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010) | $k = -7 \rightarrow 8$ |
| $T_{min} = 0.803$, $T_{max} = 0.978$ | $l = -17 \rightarrow 18$ |
| 6453 measured reflections | |

### *Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.098$ | $w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 0.0395P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.02$ | $(\Delta/\sigma)_{max} = 0.001$ |

| | |
|---|---|
| 3252 reflections | $\Delta\rho_{max}$ = 0.29 e Å$^{-3}$ |
| 251 parameters | $\Delta\rho_{min}$ = −0.23 e Å$^{-3}$ |
| 1 restraint | Absolute structure: Flack (1983), 1395 Friedel pairs |
| Primary atom site location: structure-invariant direct methods | Flack parameter: 0.1 (2) |

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.33730 (17) | 0.5046 (2) | 0.78985 (11) | 0.0309 (3) |
| O2 | 0.76411 (17) | 0.6678 (2) | 0.44802 (9) | 0.0280 (3) |
| H2 | 0.677 (4) | 0.578 (5) | 0.429 (2) | 0.061 (9)* |
| O1W | 1.0970 (2) | 0.2216 (3) | 0.70030 (13) | 0.0384 (4) |
| H11 | 1.157 (4) | 0.316 (6) | 0.725 (2) | 0.060 (10)* |
| H12 | 1.125 (4) | 0.196 (6) | 0.652 (2) | 0.063 (10)* |
| N1 | 0.89459 (18) | 0.0009 (2) | 0.78964 (11) | 0.0210 (3) |
| H1 | 0.953 (3) | 0.071 (4) | 0.7637 (15) | 0.022 (6)* |
| N2 | 0.54310 (19) | 0.2982 (2) | 0.79266 (12) | 0.0234 (3) |
| N3 | 0.4603 (2) | 0.8811 (3) | 0.59777 (12) | 0.0280 (4) |
| C1 | 0.9248 (2) | −0.1772 (3) | 0.83570 (12) | 0.0212 (4) |
| C2 | 1.0553 (2) | −0.3025 (3) | 0.84619 (13) | 0.0238 (4) |
| H2A | 1.1403 | −0.2694 | 0.8195 | 0.029* |
| C3 | 1.0547 (2) | −0.4757 (3) | 0.89683 (12) | 0.0245 (4) |
| H3 | 1.1405 | −0.5644 | 0.9040 | 0.029* |
| C4 | 0.9304 (2) | −0.5250 (3) | 0.93830 (12) | 0.0256 (4) |
| H4 | 0.9340 | −0.6452 | 0.9729 | 0.031* |
| C5 | 0.8035 (2) | −0.3999 (3) | 0.92892 (12) | 0.0236 (4) |
| H5 | 0.7204 | −0.4328 | 0.9574 | 0.028* |
| C6 | 0.7989 (2) | −0.2238 (3) | 0.87687 (12) | 0.0214 (4) |
| C7 | 0.6920 (2) | −0.0637 (3) | 0.85452 (13) | 0.0218 (4) |
| C8 | 0.5381 (2) | −0.0264 (3) | 0.87749 (14) | 0.0250 (4) |
| H8A | 0.5377 | −0.0813 | 0.9398 | 0.030* |
| H8B | 0.4545 | −0.0924 | 0.8311 | 0.030* |
| C9 | 0.5108 (2) | 0.1974 (3) | 0.87643 (14) | 0.0280 (4) |
| H9A | 0.4015 | 0.2229 | 0.8789 | 0.034* |
| H9B | 0.5781 | 0.2566 | 0.9330 | 0.034* |
| C10 | 0.6769 (2) | 0.2496 (3) | 0.76131 (13) | 0.0209 (4) |
| C11 | 0.7537 (2) | 0.0699 (3) | 0.80190 (12) | 0.0214 (4) |
| C12 | 0.7238 (2) | 0.3627 (3) | 0.69551 (13) | 0.0205 (4) |
| H12A | 0.8131 | 0.3245 | 0.6740 | 0.025* |
| C13 | 0.6401 (2) | 0.5366 (3) | 0.65911 (12) | 0.0207 (4) |
| C14 | 0.5043 (2) | 0.5833 (3) | 0.69001 (13) | 0.0224 (4) |
| C15 | 0.4529 (2) | 0.4620 (3) | 0.75959 (13) | 0.0238 (4) |
| C16 | 0.4187 (2) | 0.7539 (3) | 0.65684 (13) | 0.0250 (4) |
| H16 | 0.3263 | 0.7802 | 0.6775 | 0.030* |
| C17 | 0.5887 (2) | 0.8336 (3) | 0.56645 (13) | 0.0274 (4) |
| H17 | 0.6179 | 0.9220 | 0.5230 | 0.033* |
| C18 | 0.6799 (2) | 0.6681 (3) | 0.59251 (12) | 0.0230 (4) |

| | | | | |
|---|---|---|---|---|
| C19 | 0.8136 (2) | 0.6270 (3) | 0.54537 (13) | 0.0260 (4) |
| H19 | 0.8421 | 0.4826 | 0.5537 | 0.031* |
| C20 | 0.9565 (3) | 0.7508 (4) | 0.58426 (16) | 0.0396 (5) |
| H20A | 1.0380 | 0.7178 | 0.5514 | 0.059* |
| H20B | 0.9938 | 0.7220 | 0.6508 | 0.059* |
| H20C | 0.9306 | 0.8928 | 0.5758 | 0.059* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0278 (7) | 0.0272 (7) | 0.0445 (8) | 0.0050 (6) | 0.0228 (6) | 0.0025 (6) |
| O2 | 0.0305 (7) | 0.0321 (7) | 0.0238 (7) | −0.0063 (6) | 0.0114 (6) | 0.0003 (6) |
| O1W | 0.0409 (9) | 0.0419 (10) | 0.0405 (9) | −0.0122 (7) | 0.0261 (7) | −0.0102 (7) |
| N1 | 0.0210 (7) | 0.0209 (8) | 0.0245 (7) | 0.0005 (6) | 0.0125 (6) | 0.0017 (6) |
| N2 | 0.0229 (8) | 0.0223 (8) | 0.0300 (8) | 0.0018 (6) | 0.0161 (6) | 0.0006 (6) |
| N3 | 0.0267 (9) | 0.0310 (10) | 0.0272 (8) | 0.0079 (7) | 0.0081 (7) | 0.0055 (7) |
| C1 | 0.0232 (9) | 0.0216 (9) | 0.0197 (8) | −0.0019 (7) | 0.0068 (7) | −0.0023 (7) |
| C2 | 0.0233 (9) | 0.0278 (10) | 0.0222 (8) | 0.0038 (7) | 0.0089 (7) | −0.0024 (7) |
| C3 | 0.0263 (9) | 0.0255 (10) | 0.0218 (8) | 0.0061 (7) | 0.0057 (7) | −0.0009 (7) |
| C4 | 0.0324 (10) | 0.0217 (10) | 0.0234 (9) | 0.0005 (8) | 0.0080 (8) | 0.0014 (7) |
| C5 | 0.0268 (9) | 0.0231 (9) | 0.0233 (8) | −0.0033 (8) | 0.0107 (7) | −0.0011 (7) |
| C6 | 0.0215 (8) | 0.0225 (9) | 0.0218 (8) | −0.0013 (7) | 0.0081 (7) | −0.0036 (7) |
| C7 | 0.0232 (9) | 0.0207 (9) | 0.0243 (8) | −0.0015 (7) | 0.0109 (7) | −0.0025 (7) |
| C8 | 0.0239 (9) | 0.0218 (10) | 0.0337 (10) | 0.0013 (7) | 0.0161 (7) | 0.0023 (8) |
| C9 | 0.0323 (10) | 0.0241 (10) | 0.0344 (10) | 0.0022 (8) | 0.0222 (9) | 0.0029 (8) |
| C10 | 0.0206 (8) | 0.0194 (9) | 0.0255 (9) | 0.0002 (7) | 0.0114 (7) | −0.0032 (7) |
| C11 | 0.0218 (8) | 0.0205 (9) | 0.0248 (8) | 0.0004 (7) | 0.0112 (7) | −0.0049 (7) |
| C12 | 0.0189 (8) | 0.0222 (10) | 0.0232 (8) | 0.0002 (7) | 0.0105 (7) | −0.0024 (7) |
| C13 | 0.0188 (8) | 0.0248 (10) | 0.0198 (8) | −0.0010 (7) | 0.0070 (7) | −0.0036 (6) |
| C14 | 0.0204 (8) | 0.0242 (9) | 0.0240 (8) | −0.0003 (7) | 0.0082 (7) | −0.0011 (7) |
| C15 | 0.0224 (9) | 0.0214 (10) | 0.0305 (9) | 0.0003 (7) | 0.0122 (7) | −0.0026 (7) |
| C16 | 0.0218 (9) | 0.0287 (10) | 0.0266 (9) | 0.0021 (7) | 0.0101 (7) | −0.0002 (8) |
| C17 | 0.0273 (10) | 0.0328 (11) | 0.0233 (9) | 0.0028 (8) | 0.0086 (8) | 0.0062 (7) |
| C18 | 0.0223 (9) | 0.0277 (10) | 0.0201 (8) | −0.0006 (7) | 0.0073 (7) | −0.0015 (8) |
| C19 | 0.0251 (9) | 0.0320 (11) | 0.0235 (8) | 0.0017 (7) | 0.0107 (7) | 0.0020 (7) |
| C20 | 0.0277 (10) | 0.0625 (15) | 0.0319 (11) | −0.0070 (10) | 0.0134 (8) | −0.0115 (10) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C15 | 1.237 (2) | C7—C11 | 1.375 (3) |
| O2—C19 | 1.428 (2) | C7—C8 | 1.495 (2) |
| O2—H2 | 0.97 (4) | C8—C9 | 1.518 (3) |
| O1W—H11 | 0.85 (4) | C8—H8A | 0.9900 |
| O1W—H12 | 0.83 (4) | C8—H8B | 0.9900 |
| N1—C1 | 1.369 (2) | C9—H9A | 0.9900 |
| N1—C11 | 1.378 (2) | C9—H9B | 0.9900 |
| N1—H1 | 0.85 (3) | C10—C12 | 1.366 (2) |
| N2—C15 | 1.379 (3) | C10—C11 | 1.443 (3) |
| N2—C10 | 1.402 (2) | C12—C13 | 1.419 (3) |

| | | | |
|---|---|---|---|
| N2—C9 | 1.490 (2) | C12—H12A | 0.9500 |
| N3—C16 | 1.328 (3) | C13—C14 | 1.412 (2) |
| N3—C17 | 1.356 (3) | C13—C18 | 1.421 (3) |
| C1—C2 | 1.406 (3) | C14—C16 | 1.396 (3) |
| C1—C6 | 1.418 (2) | C14—C15 | 1.459 (3) |
| C2—C3 | 1.380 (3) | C16—H16 | 0.9500 |
| C2—H2A | 0.9500 | C17—C18 | 1.373 (3) |
| C3—C4 | 1.412 (3) | C17—H17 | 0.9500 |
| C3—H3 | 0.9500 | C18—C19 | 1.525 (2) |
| C4—C5 | 1.381 (3) | C19—C20 | 1.511 (3) |
| C4—H4 | 0.9500 | C19—H19 | 1.0000 |
| C5—C6 | 1.403 (3) | C20—H20A | 0.9800 |
| C5—H5 | 0.9500 | C20—H20B | 0.9800 |
| C6—C7 | 1.418 (3) | C20—H20C | 0.9800 |
| C19—O2—H2 | 102.3 (19) | H9A—C9—H9B | 107.7 |
| H11—O1W—H12 | 104 (3) | C12—C10—N2 | 121.26 (17) |
| C1—N1—C11 | 107.94 (15) | C12—C10—C11 | 124.55 (16) |
| C1—N1—H1 | 129.4 (16) | N2—C10—C11 | 114.15 (15) |
| C11—N1—H1 | 122.2 (16) | C7—C11—N1 | 109.94 (17) |
| C15—N2—C10 | 122.12 (15) | C7—C11—C10 | 124.60 (16) |
| C15—N2—C9 | 116.72 (15) | N1—C11—C10 | 125.37 (16) |
| C10—N2—C9 | 120.11 (16) | C10—C12—C13 | 120.54 (16) |
| C16—N3—C17 | 116.71 (17) | C10—C12—H12A | 119.7 |
| N1—C1—C2 | 129.66 (17) | C13—C12—H12A | 119.7 |
| N1—C1—C6 | 108.67 (16) | C14—C13—C12 | 117.92 (16) |
| C2—C1—C6 | 121.66 (17) | C14—C13—C18 | 116.52 (17) |
| C3—C2—C1 | 117.27 (17) | C12—C13—C18 | 125.56 (16) |
| C3—C2—H2A | 121.4 | C16—C14—C13 | 120.08 (16) |
| C1—C2—H2A | 121.4 | C16—C14—C15 | 118.13 (16) |
| C2—C3—C4 | 121.95 (17) | C13—C14—C15 | 121.74 (17) |
| C2—C3—H3 | 119.0 | O1—C15—N2 | 120.96 (17) |
| C4—C3—H3 | 119.0 | O1—C15—C14 | 122.63 (18) |
| C5—C4—C3 | 120.55 (18) | N2—C15—C14 | 116.38 (16) |
| C5—C4—H4 | 119.7 | N3—C16—C14 | 123.12 (16) |
| C3—C4—H4 | 119.7 | N3—C16—H16 | 118.4 |
| C4—C5—C6 | 119.14 (17) | C14—C16—H16 | 118.4 |
| C4—C5—H5 | 120.4 | N3—C17—C18 | 125.27 (19) |
| C6—C5—H5 | 120.4 | N3—C17—H17 | 117.4 |
| C5—C6—C1 | 119.41 (17) | C18—C17—H17 | 117.4 |
| C5—C6—C7 | 134.32 (17) | C17—C18—C13 | 118.21 (17) |
| C1—C6—C7 | 106.26 (16) | C17—C18—C19 | 118.98 (17) |
| C11—C7—C6 | 107.19 (16) | C13—C18—C19 | 122.73 (17) |
| C11—C7—C8 | 121.06 (17) | O2—C19—C20 | 108.34 (17) |
| C6—C7—C8 | 131.75 (17) | O2—C19—C18 | 109.32 (16) |
| C7—C8—C9 | 108.24 (15) | C20—C19—C18 | 113.28 (16) |
| C7—C8—H8A | 110.1 | O2—C19—H19 | 108.6 |
| C9—C8—H8A | 110.1 | C20—C19—H19 | 108.6 |
| C7—C8—H8B | 110.1 | C18—C19—H19 | 108.6 |
| C9—C8—H8B | 110.1 | C19—C20—H20A | 109.5 |

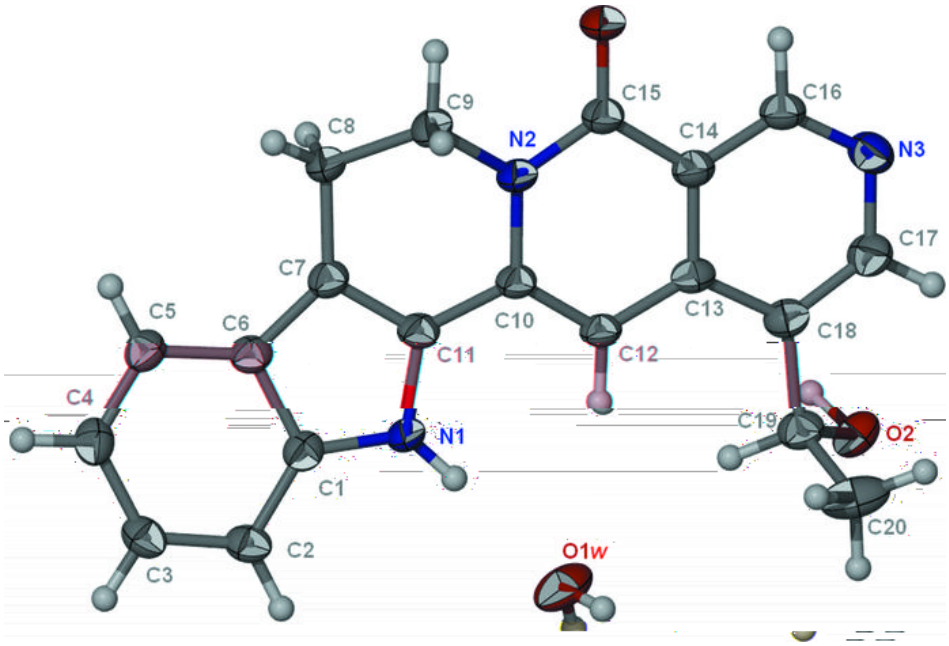
| | | | |
|---|---|---|---|
| H8A—C8—H8B | 108.4 | C19—C20—H20B | 109.5 |
| N2—C9—C8 | 113.37 (16) | H20A—C20—H20B | 109.5 |
| N2—C9—H9A | 108.9 | C19—C20—H20C | 109.5 |
| C8—C9—H9A | 108.9 | H20A—C20—H20C | 109.5 |
| N2—C9—H9B | 108.9 | H20B—C20—H20C | 109.5 |
| C8—C9—H9B | 108.9 | | |
| C11—N1—C1—C2 | −177.98 (19) | N2—C10—C11—C7 | 10.4 (3) |
| C11—N1—C1—C6 | 0.94 (19) | C12—C10—C11—N1 | 8.9 (3) |
| N1—C1—C2—C3 | −179.93 (17) | N2—C10—C11—N1 | −173.35 (17) |
| C6—C1—C2—C3 | 1.3 (3) | N2—C10—C12—C13 | 1.9 (3) |
| C1—C2—C3—C4 | −1.2 (3) | C11—C10—C12—C13 | 179.54 (17) |
| C2—C3—C4—C5 | 0.3 (3) | C10—C12—C13—C14 | −2.7 (3) |
| C3—C4—C5—C6 | 0.6 (3) | C10—C12—C13—C18 | 178.32 (18) |
| C4—C5—C6—C1 | −0.5 (3) | C12—C13—C14—C16 | 179.44 (17) |
| C4—C5—C6—C7 | −178.7 (2) | C18—C13—C14—C16 | −1.5 (3) |
| N1—C1—C6—C5 | −179.48 (16) | C12—C13—C14—C15 | 2.1 (3) |
| C2—C1—C6—C5 | −0.5 (3) | C18—C13—C14—C15 | −178.81 (17) |
| N1—C1—C6—C7 | −0.8 (2) | C10—N2—C15—O1 | −178.32 (18) |
| C2—C1—C6—C7 | 178.23 (17) | C9—N2—C15—O1 | −10.0 (3) |
| C5—C6—C7—C11 | 178.7 (2) | C10—N2—C15—C14 | −0.1 (3) |
| C1—C6—C7—C11 | 0.3 (2) | C9—N2—C15—C14 | 168.16 (17) |
| C5—C6—C7—C8 | −1.8 (4) | C16—C14—C15—O1 | 0.0 (3) |
| C1—C6—C7—C8 | 179.82 (19) | C13—C14—C15—O1 | 177.41 (18) |
| C11—C7—C8—C9 | −26.5 (3) | C16—C14—C15—N2 | −178.11 (18) |
| C6—C7—C8—C9 | 154.1 (2) | C13—C14—C15—N2 | −0.7 (3) |
| C15—N2—C9—C8 | 147.19 (18) | C17—N3—C16—C14 | 3.0 (3) |
| C10—N2—C9—C8 | −44.3 (3) | C13—C14—C16—N3 | −1.6 (3) |
| C7—C8—C9—N2 | 47.4 (2) | C15—C14—C16—N3 | 175.87 (18) |
| C15—N2—C10—C12 | −0.5 (3) | C16—N3—C17—C18 | −1.5 (3) |
| C9—N2—C10—C12 | −168.38 (18) | N3—C17—C18—C13 | −1.4 (3) |
| C15—N2—C10—C11 | −178.32 (17) | N3—C17—C18—C19 | 175.34 (19) |
| C9—N2—C10—C11 | 13.8 (2) | C14—C13—C18—C17 | 2.8 (3) |
| C6—C7—C11—N1 | 0.2 (2) | C12—C13—C18—C17 | −178.17 (18) |
| C8—C7—C11—N1 | −179.32 (17) | C14—C13—C18—C19 | −173.81 (17) |
| C6—C7—C11—C10 | 176.94 (17) | C12—C13—C18—C19 | 5.2 (3) |
| C8—C7—C11—C10 | −2.6 (3) | C17—C18—C19—O2 | −41.1 (2) |
| C1—N1—C11—C7 | −0.7 (2) | C13—C18—C19—O2 | 135.53 (18) |
| C1—N1—C11—C10 | −177.41 (17) | C17—C18—C19—C20 | 79.8 (2) |
| C12—C10—C11—C7 | −167.33 (19) | C13—C18—C19—C20 | −103.6 (2) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2···N3$^{i}$ | 0.97 (4) | 1.77 (4) | 2.732 (2) | 171 (3) |
| O1w—H11···O1$^{ii}$ | 0.85 (4) | 2.08 (4) | 2.928 (2) | 169 (3) |
| O1w—H12···O2$^{iii}$ | 0.83 (4) | 1.95 (4) | 2.762 (2) | 167 (3) |
| N1—H1···O1w | 0.85 (3) | 2.02 (3) | 2.861 (2) | 177 (2) |

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

**Fig. 1**


C9
C15
C16
C8
N2
C14
N3
C17
C7
C5
C6
C10
C13
C18
C11
C12
C4
C19
O2
N1
C1
C20
C2
O1w
C3