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(Pyridin-2-yl)methyl 6-bromo-2-oxo-1-[(pyridin-2-yl)methyl]-1,2-dihydroquinoline-4-carboxylate

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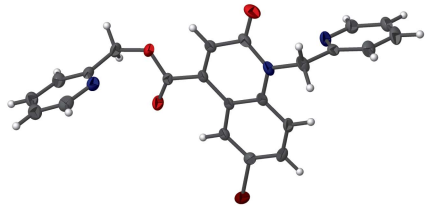
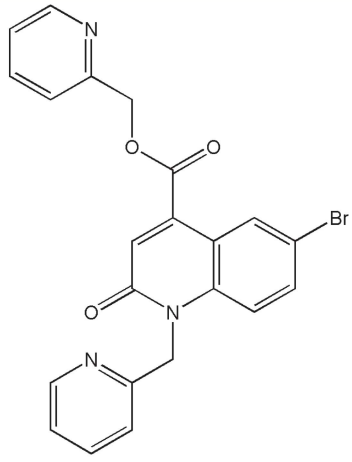
Structural data: full structural data are available from iucrdata.iucr.org

In the central dihydroquinoline unit of the title compound, $C_{22}H_{16}BrN_3O_3$, the dihydropyridinone and benzene rings are inclined to one another by 2.0 (1)°, while the outer pyridine rings are almost perpendicular to the plane of the dihydroquinoline ring system. The conformation of the molecule is partially determined by an intramolecular C—H···O hydrogen bond. In the crystal, molecules stack along the *b*-axis direction through a combination of C—H···N and C—H···O hydrogen bonds and π–π stacking interactions involving the dihydroquinoline units, with a centroid-to-centroid distance of 3.7648 (15) Å.

3D view



Chemical scheme



Structure description

The quinolone ring system is present in an important class of compounds that are not only of theoretical interest but that also display anti-fungal (Musiol *et al.*, 2006), anti-cancer (Elderfield *et al.*, 1960) and antimicrobial (Musiol *et al.*, 2010) properties. They also act as HIV-1 integrase inhibitors (Bénard *et al.*, 2004). Quinolone derivatives are also widely used as corrosion inhibitors for metals in acid environments (Eddy *et al.*, 2010). In recent years, research has focused on examining the pharmacological and biological effects of existing molecules and their modifications in order to reduce unwanted side effects. As a continuation of our work on the development of N-substituted quinolone derivatives and evaluating their potential pharmacological activities (Filali Baba *et al.*, 2016*a*,*b*), we have used the condensation reaction of 2-(bromomethyl)pyridine hydrobromide with 6-bromo-1,2-dihydro-2-oxoquinoline-4-carboxylic acid under phase-transfer catalysis conditions using tetra-*n*-butylammonium bromide (TBAB) as the

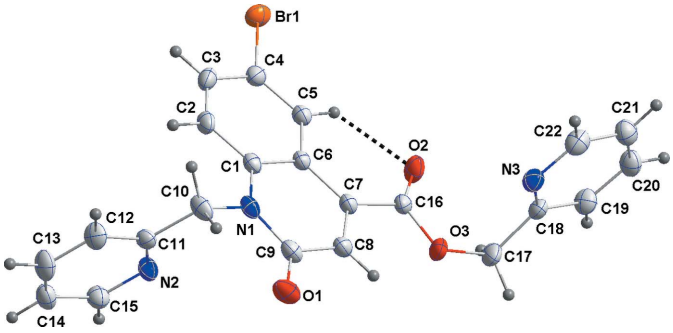


Figure 1
The title molecule with the labeling scheme and 50% probability ellipsoids. The intramolecular C—H···O hydrogen bond is shown as a dashed line.

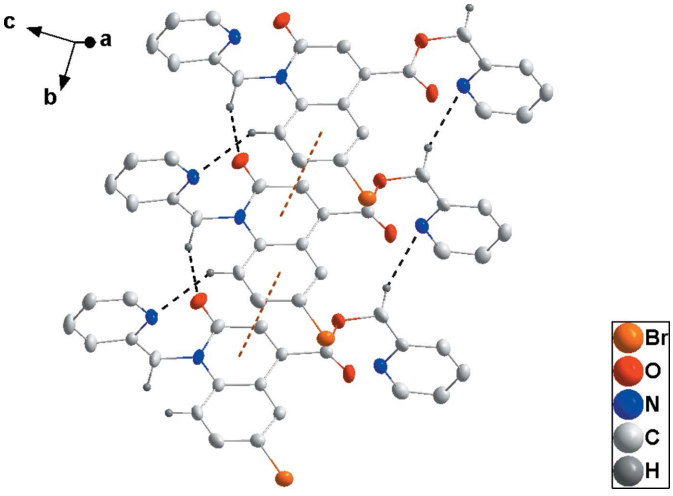


Figure 2
A portion of one stack of molecules showing the C—H···O and C—H···N hydrogen bonds as black dashed lines and the π–π stacking interactions as orange dashed lines.

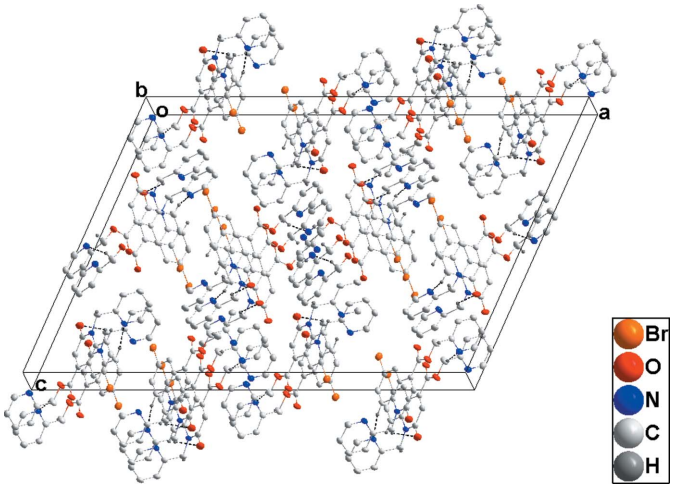


Figure 3
Packing projected along the *b*-axis direction with C—H···O and C—H···N hydrogen bonds shown as black dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···N2^{i}	0.95	2.49	3.294 (3)	143
C5—H5···O2	0.95	2.21	2.873 (3)	126
C10—H10A···O1^{i}	0.99	2.51	3.269 (3)	133
C17—H17B···N3^{ii}	0.99	2.52	3.482 (4)	163

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{16}BrN_3O_3$
M_r	450.29
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	150
a, *b*, *c* (Å)	34.0146 (11), 4.9522 (2), 23.4539 (7)
β (°)	111.578 (1)
V (Å^3)	3673.9 (2)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.31
Crystal size (mm)	0.17 × 0.09 × 0.03
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.74, 0.92
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13490, 3543, 2949
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.092, 1.03
No. of reflections	3543
No. of parameters	262
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, −0.54

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008).

catalyst and potassium carbonate as a base, to synthesize the title compound (Fig. 1) in good yield.

The dihydroquinoline unit deviates slightly from planarity, as indicated by the dihedral angle of 2.0 (1)° between the mean planes of its constituent rings. The N2 and N3 pyridyl rings make dihedral angles of 89.05 (7) and 84.07 (7)°, respectively, with the C1/C6–C9/N1 ring system. The conformation of the molecule is partially determined by an intramolecular C5—H5···O2 hydrogen bond (Table 1, Fig. 1).

In the crystal, molecules stack along the *b*-axis direction through a combination of C2—H2···N2^{i}, C10—H10A···O1^{i} and C17—H17B···N3^{ii} hydrogen bonds (Table 1) as well as π–π stacking interactions between the C1–C6 ring in one molecule and the C1/C6–C9/N1 ring in an adjacent molecule (Fig. 2). The dihedral angle between the two stacked rings is 1.95 (13)° and the distance between their centroids is 3.7648 (15) Å. The packing is shown in Fig. 3.

Synthesis and crystallization

A solution of 0.5 g (1.86 mmol) of 6-bromo-1,2-dihydro-2-oxoquinoline-4-carboxylic acid in 15 ml dimethylformamide (DMF) was mixed with 1.04 g (4.1 mmol) of 2-(bromomethyl)pyridine hydrobromide, 0.77 g (5.58 mmol) of K_2CO_3 and 0.12 g (0.37 mmol) of TBAB. The reaction mixture was stirred at room temperature for 6 h. After removal of salts by filtration, the DMF was evaporated under reduced pressure and the residue obtained was dissolved in dichloromethane. The organic phase was dried over Na_2SO_4 and then concentrated *in vacuo*. The resulting mixture was chromatographed on a silica-gel column (eluent: ethyl acetate–hexane 1:3 *v*/*v*). The product was obtained in 81% yield and was crystallized by slow evaporation from an ethanol solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Two reflections obscured by the nozzle of the low-temperature unit were omitted from the final refinement.

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References

Bénard, C., Zouhiri, F., Normand-Bayle, M., Danet, M., Desmaële, D., Leh, H., Mouscadet, J.-F., Mbemba, G., Thomas, C.-M., Bonnenfant, S., Le Bret, M. & d'Angelo, J. (2004). *Bioorg. Med. Chem. Lett.* **14**, 2473–2476.

Brandenburg, K. & Putz, H. (2012). *DIAMOND*, Crystal Impact GbR, Bonn, Germany.

Bruker (2016). *APEX3*, *SAINT* and *SADABS*. Bruker AXS, Inc., Madison, Wisconsin, USA.

Eddy, N. O., Stoyanov, S. R. & Ebenso, E. E. (2010). *Int. J. Electrochem. Sci.* **5**, 1127–1150.

Elderfield, R. C. & LeVon, E. F. (1960). *J. Org. Chem.* **25**, 1576–1583.

Filali Baba, Y., Elmsellem, H., Kandri Rodi, Y., Steli, H., Ad, C., Ouzidan, Y., Ouazzani Chahdi, F., Sebbar, N. K., Essassi, E. M. & Hammouti, B. (2016*a*). *Der Pharma Chem.* **8**, 159–169.

Filali Baba, Y., Mague, J. T., Kandri Rodi, Y., Ouzidan, Y., Essassi, E. M. & Zouihri, H. (2016*b*). *IUCrData*, **1**, x160997.

Musiol, R., Jampilek, J., Buchta, V., Silva, L., Niedbala, H., Podeszwa, B., Palka, A., Majerz-Maniecka, K., Oleksyn, B. & Polanski, J. (2006). *Bioorg. Med. Chem.* **14**, 3592–3598.

Musiol, R., Serda, M., Hensel-Bielowka, S. & Polanski, J. (2010). *Curr. Med. Chem.* **17**, 1960–1973.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

IUCrData (2018). **3**, x180288 [https://doi.org/10.1107/S2414314618002882]

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Crystal data

$C_{22}H_{16}BrN_3O_3$
M_r = 450.29
Monoclinic, $C2/c$
a = 34.0146 (11) Å
b = 4.9522 (2) Å
c = 23.4539 (7) Å
β = 111.578 (1)°
V = 3673.9 (2) Å^3
Z = 8
$F(000)$ = 1824
D_x = 1.628 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 8863 reflections
θ = 2.8–72.3°
μ = 3.31 mm^{-1}
T = 150 K
Plate, colourless
0.17 × 0.09 × 0.03 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro-focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.74, T_{max} = 0.92
13490 measured reflections
3543 independent reflections
2949 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 72.3°, θ_{min} = 4.0°
h = −38→40
k = −6→5
l = −27→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.092
S = 1.03
3543 reflections
262 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 7.2922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.76 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å) and included as riding contributions with isotropic displacement parameters 1.2 times those of the attached atoms. Two reflections obscured by the nozzle of the low temperature unit were omitted from the final refinement.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.26878 (2)	1.00524 (6)	0.40990 (2)	0.03283 (11)
O1	0.43219 (7)	0.1416 (4)	0.69327 (9)	0.0367 (5)
O2	0.37368 (6)	0.2748 (4)	0.42379 (8)	0.0331 (5)
O3	0.42042 (6)	−0.0110 (4)	0.48648 (9)	0.0324 (4)
N1	0.38551 (7)	0.4716 (4)	0.64422 (9)	0.0241 (5)
N2	0.32942 (7)	0.2559 (5)	0.69259 (10)	0.0280 (5)
N3	0.47417 (7)	0.2452 (5)	0.44118 (10)	0.0291 (5)
C1	0.35867 (8)	0.5925 (5)	0.58991 (11)	0.0213 (5)
C2	0.33081 (9)	0.7961 (5)	0.59189 (12)	0.0268 (6)
H2	0.3301	0.8510	0.6303	0.032*
C3	0.30433 (9)	0.9185 (5)	0.53902 (13)	0.0284 (6)
H3	0.2855	1.0571	0.5408	0.034*
C4	0.30551 (8)	0.8366 (5)	0.48302 (12)	0.0250 (5)
C5	0.33197 (8)	0.6358 (5)	0.47920 (11)	0.0222 (5)
H5	0.3318	0.5824	0.4402	0.027*
C6	0.35956 (8)	0.5069 (5)	0.53269 (10)	0.0199 (5)
C7	0.38849 (8)	0.2926 (5)	0.53266 (11)	0.0213 (5)
C8	0.41232 (8)	0.1745 (5)	0.58610 (11)	0.0243 (5)
H8	0.4308	0.0321	0.5852	0.029*
C9	0.41096 (8)	0.2554 (6)	0.64492 (11)	0.0258 (5)
C10	0.38727 (9)	0.5704 (6)	0.70401 (11)	0.0291 (6)
H10A	0.3847	0.7696	0.7022	0.035*
H10B	0.4153	0.5256	0.7351	0.035*
C11	0.35350 (8)	0.4564 (5)	0.72474 (11)	0.0226 (5)
C12	0.34918 (9)	0.5630 (6)	0.77699 (12)	0.0309 (6)
H12	0.3668	0.7071	0.7988	0.037*
C13	0.31882 (10)	0.4553 (7)	0.79662 (12)	0.0365 (7)
H13	0.3153	0.5244	0.8322	0.044*
C14	0.29378 (9)	0.2466 (6)	0.76399 (12)	0.0310 (6)
H14	0.2728	0.1686	0.7766	0.037*
C15	0.30006 (9)	0.1542 (6)	0.71265 (12)	0.0296 (6)
H15	0.2827	0.0108	0.6901	0.036*
C16	0.39263 (8)	0.1908 (5)	0.47460 (11)	0.0220 (5)

C17	0.42593 (10)	−0.1286 (6)	0.43340 (14)	0.0344 (7)
H17A	0.3977	−0.1616	0.4014	0.041*
H17B	0.4402	−0.3053	0.4451	0.041*
C18	0.45124 (8)	0.0457 (5)	0.40704 (12)	0.0250 (5)
C19	0.45091 (9)	−0.0180 (6)	0.34893 (12)	0.0297 (6)
H19	0.4336	−0.1600	0.3257	0.036*
C20	0.47612 (9)	0.1283 (6)	0.32571 (12)	0.0319 (6)
H20	0.4770	0.0862	0.2867	0.038*
C21	0.50000 (9)	0.3371 (6)	0.36028 (13)	0.0333 (6)
H21	0.5173	0.4437	0.3453	0.040*
C22	0.49820 (9)	0.3882 (6)	0.41741 (13)	0.0330 (6)
H22	0.5148	0.5318	0.4411	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02744 (17)	0.03222 (17)	0.03503 (17)	0.00629 (12)	0.00701 (11)	0.00512 (12)
O1	0.0401 (12)	0.0423 (12)	0.0248 (9)	0.0020 (9)	0.0085 (8)	0.0106 (9)
O2	0.0358 (11)	0.0439 (12)	0.0213 (9)	0.0123 (9)	0.0124 (8)	−0.0003 (8)
O3	0.0429 (12)	0.0309 (10)	0.0323 (10)	0.0138 (9)	0.0243 (9)	0.0037 (8)
N1	0.0286 (12)	0.0290 (12)	0.0174 (9)	−0.0060 (9)	0.0115 (8)	−0.0021 (8)
N2	0.0356 (13)	0.0273 (12)	0.0270 (11)	−0.0071 (10)	0.0185 (10)	−0.0070 (9)
N3	0.0336 (13)	0.0281 (12)	0.0273 (11)	0.0028 (10)	0.0131 (9)	−0.0033 (9)
C1	0.0234 (13)	0.0223 (12)	0.0206 (11)	−0.0059 (9)	0.0109 (10)	−0.0018 (9)
C2	0.0354 (15)	0.0246 (13)	0.0275 (13)	−0.0026 (11)	0.0198 (11)	−0.0060 (10)
C3	0.0265 (14)	0.0247 (13)	0.0394 (15)	0.0010 (10)	0.0185 (12)	−0.0042 (11)
C4	0.0237 (13)	0.0232 (13)	0.0298 (13)	−0.0009 (10)	0.0119 (10)	0.0010 (10)
C5	0.0247 (13)	0.0233 (13)	0.0207 (11)	−0.0031 (10)	0.0108 (10)	−0.0012 (10)
C6	0.0208 (12)	0.0216 (12)	0.0199 (11)	−0.0024 (10)	0.0104 (9)	−0.0002 (10)
C7	0.0227 (13)	0.0239 (12)	0.0202 (11)	−0.0015 (10)	0.0114 (10)	0.0006 (9)
C8	0.0248 (14)	0.0259 (13)	0.0247 (12)	0.0006 (10)	0.0121 (10)	0.0037 (10)
C9	0.0251 (14)	0.0315 (14)	0.0218 (12)	−0.0042 (11)	0.0097 (10)	0.0040 (11)
C10	0.0386 (16)	0.0330 (15)	0.0176 (11)	−0.0119 (11)	0.0127 (11)	−0.0057 (10)
C11	0.0273 (13)	0.0231 (13)	0.0177 (11)	0.0012 (10)	0.0086 (9)	0.0017 (9)
C12	0.0342 (15)	0.0385 (16)	0.0192 (12)	−0.0025 (12)	0.0087 (11)	−0.0064 (11)
C13	0.0383 (17)	0.053 (2)	0.0224 (12)	0.0001 (14)	0.0156 (11)	−0.0052 (12)
C14	0.0296 (15)	0.0411 (16)	0.0260 (13)	0.0024 (12)	0.0144 (11)	0.0042 (12)
C15	0.0329 (15)	0.0271 (14)	0.0314 (14)	−0.0039 (11)	0.0149 (12)	−0.0025 (11)
C16	0.0215 (13)	0.0223 (12)	0.0258 (12)	−0.0007 (9)	0.0130 (10)	0.0003 (10)
C17	0.0471 (18)	0.0241 (14)	0.0431 (16)	0.0024 (12)	0.0299 (14)	−0.0052 (12)
C18	0.0299 (14)	0.0209 (13)	0.0278 (12)	0.0050 (10)	0.0147 (11)	−0.0009 (10)
C19	0.0305 (15)	0.0317 (14)	0.0260 (12)	−0.0024 (11)	0.0092 (10)	−0.0073 (11)
C20	0.0310 (15)	0.0408 (16)	0.0245 (13)	0.0030 (12)	0.0111 (11)	−0.0003 (12)
C21	0.0285 (15)	0.0384 (16)	0.0355 (15)	−0.0010 (12)	0.0146 (12)	0.0009 (12)
C22	0.0278 (15)	0.0323 (15)	0.0369 (15)	−0.0012 (12)	0.0094 (12)	−0.0065 (12)

Geometric parameters (Å, º)

Br1—C4	1.904 (3)	C8—C9	1.454 (3)
O1—C9	1.234 (3)	C8—H8	0.9500
O2—C16	1.202 (3)	C10—C11	1.512 (4)
O3—C16	1.333 (3)	C10—H10A	0.9900
O3—C17	1.447 (3)	C10—H10B	0.9900
N1—C9	1.373 (3)	C11—C12	1.391 (3)
N1—C1	1.400 (3)	C12—C13	1.383 (4)
N1—C10	1.465 (3)	C12—H12	0.9500
N2—C11	1.331 (3)	C13—C14	1.379 (4)
N2—C15	1.348 (4)	C13—H13	0.9500
N3—C18	1.329 (3)	C14—C15	1.376 (4)
N3—C22	1.347 (4)	C14—H14	0.9500
C1—C2	1.396 (4)	C15—H15	0.9500
C1—C6	1.418 (3)	C17—C18	1.503 (4)
C2—C3	1.377 (4)	C17—H17A	0.9900
C2—H2	0.9500	C17—H17B	0.9900
C3—C4	1.389 (4)	C18—C19	1.395 (4)
C3—H3	0.9500	C19—C20	1.379 (4)
C4—C5	1.366 (4)	C19—H19	0.9500
C5—C6	1.413 (3)	C20—C21	1.379 (4)
C5—H5	0.9500	C20—H20	0.9500
C6—C7	1.448 (3)	C21—C22	1.387 (4)
C7—C8	1.350 (3)	C21—H21	0.9500
C7—C16	1.506 (3)	C22—H22	0.9500
C16—O3—C17	115.3 (2)	N2—C11—C12	122.7 (2)
C9—N1—C1	122.8 (2)	N2—C11—C10	118.6 (2)
C9—N1—C10	116.4 (2)	C12—C11—C10	118.7 (2)
C1—N1—C10	120.8 (2)	C13—C12—C11	118.7 (3)
C11—N2—C15	117.5 (2)	C13—C12—H12	120.6
C18—N3—C22	116.9 (2)	C11—C12—H12	120.6
C2—C1—N1	120.1 (2)	C14—C13—C12	119.3 (3)
C2—C1—C6	119.9 (2)	C14—C13—H13	120.4
N1—C1—C6	120.0 (2)	C12—C13—H13	120.4
C3—C2—C1	121.0 (2)	C15—C14—C13	118.2 (3)
C3—C2—H2	119.5	C15—C14—H14	120.9
C1—C2—H2	119.5	C13—C14—H14	120.9
C2—C3—C4	119.1 (2)	N2—C15—C14	123.7 (3)
C2—C3—H3	120.5	N2—C15—H15	118.2
C4—C3—H3	120.5	C14—C15—H15	118.2
C5—C4—C3	121.6 (2)	O2—C16—O3	123.2 (2)
C5—C4—Br1	119.36 (19)	O2—C16—C7	125.9 (2)
C3—C4—Br1	119.1 (2)	O3—C16—C7	110.9 (2)
C4—C5—C6	120.6 (2)	O3—C17—C18	113.4 (2)
C4—C5—H5	119.7	O3—C17—H17A	108.9
C6—C5—H5	119.7	C18—C17—H17A	108.9

C5—C6—C1	117.8 (2)	O3—C17—H17B	108.9
C5—C6—C7	124.1 (2)	C18—C17—H17B	108.9
C1—C6—C7	118.1 (2)	H17A—C17—H17B	107.7
C8—C7—C6	119.6 (2)	N3—C18—C19	123.3 (3)
C8—C7—C16	118.1 (2)	N3—C18—C17	118.5 (2)
C6—C7—C16	122.4 (2)	C19—C18—C17	118.2 (2)
C7—C8—C9	123.0 (2)	C20—C19—C18	119.0 (3)
C7—C8—H8	118.5	C20—C19—H19	120.5
C9—C8—H8	118.5	C18—C19—H19	120.5
O1—C9—N1	121.4 (2)	C19—C20—C21	118.6 (3)
O1—C9—C8	122.3 (3)	C19—C20—H20	120.7
N1—C9—C8	116.3 (2)	C21—C20—H20	120.7
N1—C10—C11	114.5 (2)	C20—C21—C22	118.6 (3)
N1—C10—H10A	108.6	C20—C21—H21	120.7
C11—C10—H10A	108.6	C22—C21—H21	120.7
N1—C10—H10B	108.6	N3—C22—C21	123.6 (3)
C11—C10—H10B	108.6	N3—C22—H22	118.2
H10A—C10—H10B	107.6	C21—C22—H22	118.2

C9—N1—C1—C2	174.3 (2)	C9—N1—C10—C11	−95.0 (3)
C10—N1—C1—C2	−4.9 (4)	C1—N1—C10—C11	84.3 (3)
C9—N1—C1—C6	−5.3 (4)	C15—N2—C11—C12	−0.5 (4)
C10—N1—C1—C6	175.5 (2)	C15—N2—C11—C10	178.8 (2)
N1—C1—C2—C3	179.6 (2)	N1—C10—C11—N2	8.8 (4)
C6—C1—C2—C3	−0.8 (4)	N1—C10—C11—C12	−172.0 (2)
C1—C2—C3—C4	0.1 (4)	N2—C11—C12—C13	0.4 (4)
C2—C3—C4—C5	0.7 (4)	C10—C11—C12—C13	−178.8 (3)
C2—C3—C4—Br1	179.8 (2)	C11—C12—C13—C14	−0.1 (4)
C3—C4—C5—C6	−0.9 (4)	C12—C13—C14—C15	−0.2 (4)
Br1—C4—C5—C6	−179.97 (19)	C11—N2—C15—C14	0.1 (4)
C4—C5—C6—C1	0.2 (4)	C13—C14—C15—N2	0.2 (4)
C4—C5—C6—C7	179.9 (2)	C17—O3—C16—O2	−1.1 (4)
C2—C1—C6—C5	0.6 (4)	C17—O3—C16—C7	178.4 (2)
N1—C1—C6—C5	−179.8 (2)	C8—C7—C16—O2	−180.0 (3)
C2—C1—C6—C7	−179.1 (2)	C6—C7—C16—O2	1.1 (4)
N1—C1—C6—C7	0.5 (3)	C8—C7—C16—O3	0.5 (3)
C5—C6—C7—C8	−177.2 (2)	C6—C7—C16—O3	−178.4 (2)
C1—C6—C7—C8	2.5 (4)	C16—O3—C17—C18	74.8 (3)
C5—C6—C7—C16	1.7 (4)	C22—N3—C18—C19	−0.5 (4)
C1—C6—C7—C16	−178.6 (2)	C22—N3—C18—C17	176.6 (3)
C6—C7—C8—C9	−1.0 (4)	O3—C17—C18—N3	16.3 (4)
C16—C7—C8—C9	−179.9 (2)	O3—C17—C18—C19	−166.5 (2)
C1—N1—C9—O1	−175.1 (2)	N3—C18—C19—C20	1.3 (4)
C10—N1—C9—O1	4.1 (4)	C17—C18—C19—C20	−175.7 (3)
C1—N1—C9—C8	6.6 (4)	C18—C19—C20—C21	−1.6 (4)
C10—N1—C9—C8	−174.2 (2)	C19—C20—C21—C22	1.1 (4)
C7—C8—C9—O1	178.3 (3)	C18—N3—C22—C21	−0.1 (4)
C7—C8—C9—N1	−3.5 (4)	C20—C21—C22—N3	−0.3 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···N2^{i}	0.95	2.49	3.294 (3)	143
C5—H5···O2	0.95	2.21	2.873 (3)	126
C10—H10*A*···O1^{i}	0.99	2.51	3.269 (3)	133
C17—H17*B*···N3^{ii}	0.99	2.52	3.482 (4)	163

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