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# Ethyl 4-(5-bromo-2-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

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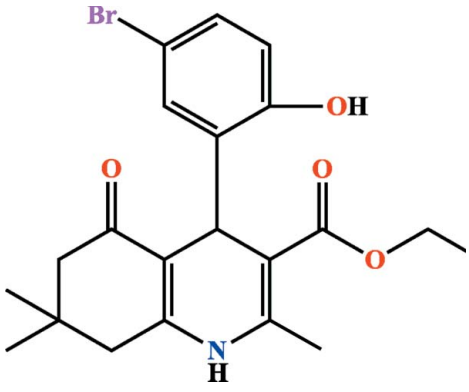
Key indicators: single-crystal X-ray study; $T$ = 294 K; mean $\sigma$(C–C) = 0.004 Å; disorder in main residue; $R$ factor = 0.050; $wR$ factor = 0.136; data-to-parameter ratio = 18.8.

In the title compound, $C_{21}H_{24}BrNO_4$, the dihedral angle between the heterocyclic ring and the pendant aromatic ring is 80.20 (13)°. The hexahydroquinone [*i.e.* the one with the C=O group] ring adopts a sofa conformation. An intramolecular O—H···O hydrogen bond generates an $S$(6) ring motif. The ethyl group is disordered over two sets of sites with a refined site occupancy ratio of 0.633 (10):0.366 (10). In the crystal, molecules are linked by N—H···O interactions, forming chains parallel to [101]. There are no significant C—H···$\pi$ or $\pi$–$\pi$ interactions in the crystal structure.

## Related literature

For standard bond lengths, see: Allen *et al.* (1987). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For background to hexahydroquinoline compounds and their applications, see: Sausins & Duburs (1988); Nakayama & Kasoaka (1996); Klusa (1995). For the synthesis of related compounds, see: Kumar *et al.* (2008); Song *et al.* (2012).




## Experimental

### Crystal data

$C_{21}H_{24}BrNO_4$
$M_r$ = 434.32
Monoclinic, $P2_1/n$
$a$ = 9.5969 (3) Å
$b$ = 19.0805 (5) Å
$c$ = 11.0678 (3) Å
$\beta$ = 97.387 (1)°
$V$ = 2009.84 (10) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.07 mm$^{-1}$
$T$ = 294 K
0.24 × 0.22 × 0.18 mm

### Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min}$ = 0.636, $T_{max}$ = 0.707
23241 measured reflections
5008 independent reflections
3604 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.022

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.136
$S$ = 1.05
5008 reflections
266 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.10 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.02 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O4—H4···O1 | 0.88 | 1.75 | 2.625 (3) | 171 |
| N1—H1···O2$^{i}$ | 0.86 | 2.05 | 2.866 (3) | 158 |

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

The authors thank the Chemistry Department, Baku State University, for providing the X-ray diffraction facility.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ5051).

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# supporting information

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# Ethyl 4-(5-bromo-2-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

**Malahat M. Kurbanova, Elnur Z. Huseynov, Atash V. Gurbanov, Abel M. Maharramov and Reza Kia**

## S1. Comment

Hexahydroquinoline derivatives possess a variety of biological activities, such as vasodilatory, bronchodilatory, antiatherosclerotic, hepatoprotective, and antidiabetic activity (Sausins *et al.*, 1988), and some of them have been used as calcium channel modulators and curatives for cardiovascular diseases (Nakayama *et al.*, 1996). In past years, their uses as neuroprotectants, platelet anti-aggregatory agents, and cerebral anti-ischemic agents in the treatment of Alzheimer's disease and as chemosensitizers in tumor therapy have been also reported (Klusa, 1995).

The asymmetric unit of the title compound, Fig. 1, comprises a substituted hexahydroquinoline compound. Both six-membered rings of the hexahydroquinoline ring system adopt a half-boat conformation. Bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. An intramolecular O—H···O hydrogen bond generates an *S(6)* ring motif (Bernstein *et al.*, 1995). In the crystal structure, molecules are linked together by intermolecular N—H···O hydrogen interactions (Table 1, Fig. 2) forming chains parallel to the [101] direction. The ethyl group is disordered over two sets of sites with a refined site occupancy ratio of 0.633 (10):0.366 (10). The compound contains one chiral center but the space group is centrosymmetric, so the molecule exists as a racemate.

## S2. Experimental

5-Bromsalicylaldehyde (0.201 g, 1 mmol), ethyl acetoacetate (0.25 ml, 1 mmol), dimedone (0.14 g, 1 mmol), ammonium acetate (0.116 g, 1.5 mmol) and ethanol (15 ml) were charged in a round bottom flask. Then the reaction mixture was stirred at room temperature for 12 hours, then the product was separated by filtration. Recrystallization was effected by using ethanol as solvent. Yield 86%. M. p. 520 K.

## S3. Refinement

The O- and N-bound H atoms were located in a difference Fourier map and constrained to ride on their parent atoms with O–H = 0.88 Å, N–H = 0.86 Å and $U_{iso}$ (H) = 1.5 $U_{eq}$(O, N). The C-bound H-atoms were included in calculated positions and treated as riding atoms with C–H = 0.93–0.98 Å and $U_{iso}$(H) = 1.2 $U_{eq}$(C) or 1.5 $U_{eq}$(C) for methyl H atoms. Distance restraints were applied to the components of the disordered ethyl group.

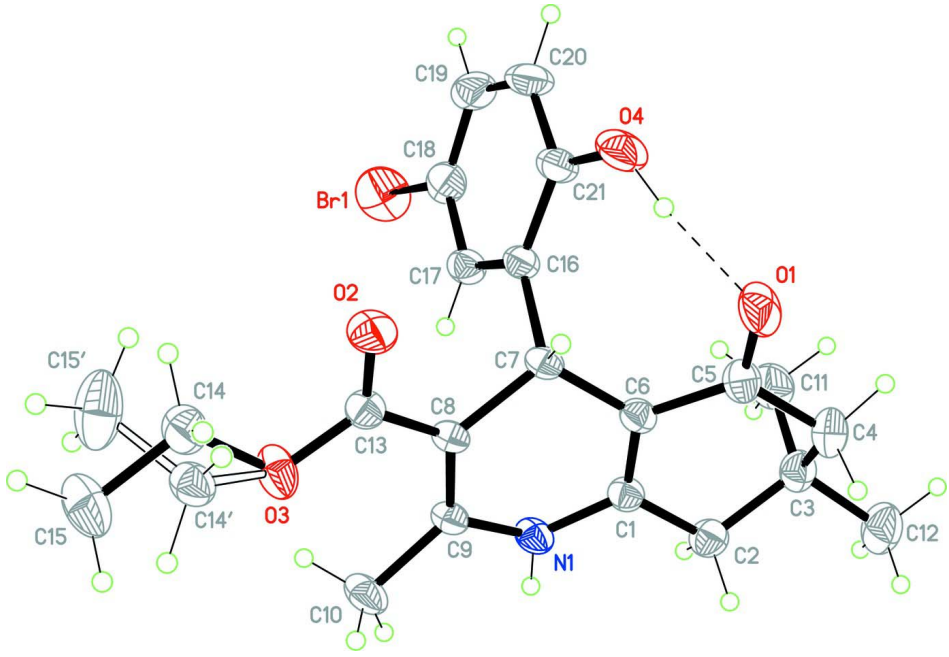


**Figure 1**

The molecular structure of the title compound, showing 40% probability displacement ellipsoids.

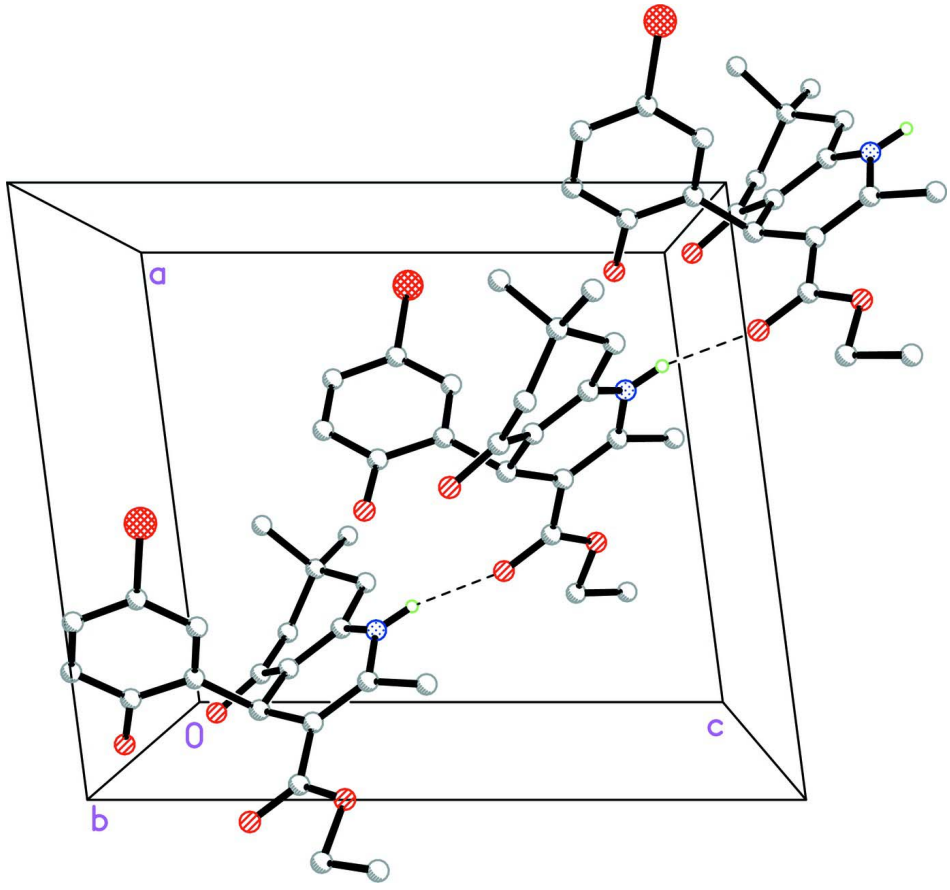


**Figure 2**

Packing diagram of the title compound viewed down the *b* axis, showing the linkage of molecules through N—H···O hydrogen interactions (dashed lines). Only H atoms involved in hydrogen bonding are shown.

**Ethyl 4-(5-bromo-2-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate**

*Crystal data*

$C_{21}H_{24}BrNO_4$
$M_r = 434.32$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 9.5969$ (3) Å
$b = 19.0805$ (5) Å
$c = 11.0678$ (3) Å
$\beta = 97.387$ (1)°
$V = 2009.84$ (10) Å$^3$
$Z = 4$
$F(000) = 896$
$D_x = 1.435$ Mg m$^{-3}$
Melting point: 520 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2045 reflections
$\theta = 3.3$–27.5°
$\mu = 2.07$ mm$^{-1}$
$T = 294$ K
Block, colourless
0.24 × 0.22 × 0.18 mm

*Data collection*

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.636$, $T_{max} = 0.707$
23241 measured reflections
5008 independent reflections
3604 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.022
$\theta_{max}$ = 28.3°, $\theta_{min}$ = 2.1°
$h$ = −12→12
$k$ = −25→25
$l$ = −14→14

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.136
$S$ = 1.05
5008 reflections
266 parameters
3 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
$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 1.4854P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.10 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.02 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.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Br1 | 0.91668 (4) | 0.11235 (2) | 0.50601 (4) | 0.09330 (19) | |
| O1 | 0.4895 (3) | 0.41833 (11) | 0.5435 (2) | 0.0719 (6) | |
| O2 | 0.3062 (2) | 0.18500 (11) | 0.61555 (16) | 0.0577 (5) | |
| O3 | 0.3634 (2) | 0.13165 (11) | 0.79229 (19) | 0.0597 (5) | |
| O4 | 0.4398 (2) | 0.31539 (12) | 0.38649 (17) | 0.0657 (6) | |
| H4 | 0.4496 | 0.3478 | 0.4434 | 0.099* | |
| N1 | 0.6847 (2) | 0.28211 (11) | 0.87199 (18) | 0.0436 (5) | |
| H1 | 0.7348 | 0.2820 | 0.9422 | 0.052* | |
| C1 | 0.6826 (2) | 0.34138 (12) | 0.8040 (2) | 0.0392 (5) | |
| C2 | 0.7744 (3) | 0.40011 (14) | 0.8550 (2) | 0.0487 (6) | |
| H2A | 0.8640 | 0.3812 | 0.8910 | 0.058* | |
| H2B | 0.7312 | 0.4228 | 0.9193 | 0.058* | |
| C3 | 0.8001 (3) | 0.45464 (14) | 0.7599 (3) | 0.0507 (6) | |
| C4 | 0.6576 (3) | 0.47395 (14) | 0.6893 (3) | 0.0584 (7) | |
| H4A | 0.6025 | 0.4986 | 0.7434 | 0.070* | |
| H4B | 0.6726 | 0.5057 | 0.6238 | 0.070* | |
| C5 | 0.5754 (3) | 0.41168 (14) | 0.6362 (3) | 0.0494 (6) | |
| C6 | 0.5958 (2) | 0.34543 (12) | 0.6974 (2) | 0.0385 (5) | |
| C7 | 0.5182 (2) | 0.28168 (12) | 0.64397 (19) | 0.0372 (5) | |
| H7A | 0.4239 | 0.2969 | 0.6095 | 0.045* | |
| C8 | 0.5009 (2) | 0.22835 (12) | 0.74306 (19) | 0.0350 (5) | |
| C9 | 0.5861 (2) | 0.22942 (13) | 0.85029 (19) | 0.0379 (5) | |

| | | | | | |
|---|---|---|---|---|---|
| C10 | 0.5868 (3) | 0.17973 (17) | 0.9557 (2) | 0.0576 (7) | |
| H10A | 0.5907 | 0.1324 | 0.9270 | 0.086* | |
| H10B | 0.5028 | 0.1862 | 0.9930 | 0.086* | |
| H10C | 0.6674 | 0.1889 | 1.0144 | 0.086* | |
| C11 | 0.8970 (3) | 0.42483 (18) | 0.6729 (3) | 0.0673 (8) | |
| H11A | 0.8543 | 0.3841 | 0.6329 | 0.101* | |
| H11B | 0.9855 | 0.4121 | 0.7182 | 0.101* | |
| H11C | 0.9120 | 0.4596 | 0.6132 | 0.101* | |
| C12 | 0.8689 (4) | 0.51939 (17) | 0.8232 (4) | 0.0734 (9) | |
| H12A | 0.8085 | 0.5383 | 0.8779 | 0.110* | |
| H12B | 0.8840 | 0.5540 | 0.7633 | 0.110* | |
| H12C | 0.9574 | 0.5065 | 0.8684 | 0.110* | |
| C13 | 0.3830 (2) | 0.18055 (13) | 0.7107 (2) | 0.0407 (5) | |
| C14 | 0.2502 (7) | 0.0825 (4) | 0.7444 (6) | 0.0617 (18) | 0.633 (10) |
| H14A | 0.2704 | 0.0612 | 0.6690 | 0.074* | 0.633 (10) |
| H14B | 0.1606 | 0.1066 | 0.7295 | 0.074* | 0.633 (10) |
| C15 | 0.2477 (6) | 0.0278 (4) | 0.8428 (7) | 0.080 (2) | 0.633 (10) |
| H15A | 0.1797 | −0.0076 | 0.8157 | 0.120* | 0.633 (10) |
| H15B | 0.2229 | 0.0495 | 0.9154 | 0.120* | 0.633 (10) |
| H15C | 0.3389 | 0.0067 | 0.8599 | 0.120* | 0.633 (10) |
| C14′ | 0.2263 (8) | 0.0963 (5) | 0.7967 (10) | 0.051 (3) | 0.367 (10) |
| H14C | 0.1501 | 0.1219 | 0.7502 | 0.061* | 0.367 (10) |
| H14D | 0.2062 | 0.0910 | 0.8799 | 0.061* | 0.367 (10) |
| C15′ | 0.2497 (11) | 0.0255 (6) | 0.7387 (15) | 0.094 (5) | 0.367 (10) |
| H15D | 0.1635 | −0.0007 | 0.7296 | 0.141* | 0.367 (10) |
| H15E | 0.3205 | −0.0001 | 0.7899 | 0.141* | 0.367 (10) |
| H15F | 0.2798 | 0.0326 | 0.6602 | 0.141* | 0.367 (10) |
| C16 | 0.5888 (3) | 0.25025 (13) | 0.5398 (2) | 0.0407 (5) | |
| C17 | 0.6996 (3) | 0.20358 (14) | 0.5642 (2) | 0.0459 (6) | |
| H17A | 0.7331 | 0.1922 | 0.6444 | 0.055* | |
| C18 | 0.7603 (3) | 0.17389 (15) | 0.4702 (3) | 0.0561 (7) | |
| C19 | 0.7115 (4) | 0.18797 (18) | 0.3507 (3) | 0.0662 (9) | |
| H19A | 0.7507 | 0.1661 | 0.2881 | 0.079* | |
| C20 | 0.6038 (4) | 0.23495 (18) | 0.3256 (2) | 0.0643 (9) | |
| H20A | 0.5706 | 0.2451 | 0.2448 | 0.077* | |
| C21 | 0.5431 (3) | 0.26783 (15) | 0.4182 (2) | 0.0499 (6) | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0748 (3) | 0.1056 (3) | 0.1086 (4) | 0.0222 (2) | 0.0469 (2) | 0.0037 (2) |
| O1 | 0.0849 (15) | 0.0519 (12) | 0.0703 (14) | 0.0074 (11) | −0.0226 (12) | 0.0177 (10) |
| O2 | 0.0550 (11) | 0.0705 (13) | 0.0419 (10) | −0.0123 (9) | −0.0152 (8) | 0.0044 (9) |
| O3 | 0.0498 (11) | 0.0594 (11) | 0.0645 (12) | −0.0181 (9) | −0.0140 (9) | 0.0208 (10) |
| O4 | 0.0744 (14) | 0.0777 (14) | 0.0404 (10) | −0.0011 (11) | −0.0102 (9) | 0.0150 (10) |
| N1 | 0.0421 (10) | 0.0523 (12) | 0.0332 (9) | −0.0084 (9) | −0.0066 (8) | 0.0074 (9) |
| C1 | 0.0378 (11) | 0.0429 (12) | 0.0373 (11) | −0.0015 (9) | 0.0062 (9) | 0.0009 (10) |
| C2 | 0.0483 (14) | 0.0512 (15) | 0.0459 (14) | −0.0081 (11) | 0.0028 (11) | −0.0035 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C3 | 0.0509 (14) | 0.0430 (14) | 0.0595 (16) | −0.0037 (11) | 0.0123 (12) | −0.0006 (12) |
| C4 | 0.0626 (17) | 0.0386 (14) | 0.0738 (19) | 0.0055 (12) | 0.0078 (14) | 0.0038 (13) |
| C5 | 0.0514 (15) | 0.0432 (14) | 0.0526 (15) | 0.0085 (11) | 0.0036 (12) | 0.0053 (11) |
| C6 | 0.0399 (12) | 0.0405 (12) | 0.0349 (11) | 0.0032 (9) | 0.0040 (9) | 0.0039 (9) |
| C7 | 0.0373 (11) | 0.0447 (13) | 0.0280 (10) | 0.0021 (9) | −0.0024 (8) | 0.0054 (9) |
| C8 | 0.0337 (10) | 0.0426 (12) | 0.0284 (10) | 0.0016 (9) | 0.0032 (8) | 0.0042 (9) |
| C9 | 0.0373 (11) | 0.0463 (13) | 0.0298 (10) | −0.0021 (10) | 0.0031 (8) | 0.0047 (9) |
| C10 | 0.0631 (17) | 0.0708 (18) | 0.0352 (12) | −0.0208 (14) | −0.0084 (11) | 0.0165 (12) |
| C11 | 0.0628 (18) | 0.070 (2) | 0.074 (2) | −0.0017 (15) | 0.0281 (16) | 0.0055 (16) |
| C12 | 0.075 (2) | 0.0544 (18) | 0.092 (2) | −0.0175 (16) | 0.0133 (18) | −0.0061 (17) |
| C13 | 0.0382 (11) | 0.0438 (13) | 0.0388 (12) | 0.0019 (10) | 0.0002 (9) | 0.0021 (10) |
| C14 | 0.061 (3) | 0.065 (4) | 0.055 (4) | −0.022 (3) | −0.004 (3) | 0.005 (3) |
| C15 | 0.065 (3) | 0.084 (4) | 0.093 (5) | −0.018 (3) | 0.012 (3) | 0.028 (4) |
| C14′ | 0.047 (4) | 0.062 (6) | 0.044 (6) | −0.012 (4) | 0.003 (4) | 0.006 (4) |
| C15′ | 0.053 (5) | 0.064 (7) | 0.169 (16) | −0.009 (5) | 0.025 (7) | −0.002 (8) |
| C16 | 0.0462 (13) | 0.0448 (13) | 0.0311 (11) | −0.0106 (10) | 0.0046 (9) | 0.0024 (10) |
| C17 | 0.0461 (13) | 0.0529 (14) | 0.0398 (12) | −0.0080 (11) | 0.0102 (10) | 0.0020 (11) |
| C18 | 0.0559 (15) | 0.0575 (16) | 0.0594 (17) | −0.0096 (13) | 0.0248 (13) | −0.0029 (13) |
| C19 | 0.081 (2) | 0.073 (2) | 0.0509 (16) | −0.0240 (18) | 0.0309 (15) | −0.0138 (15) |
| C20 | 0.081 (2) | 0.083 (2) | 0.0298 (12) | −0.0262 (18) | 0.0102 (13) | −0.0010 (13) |
| C21 | 0.0578 (15) | 0.0581 (16) | 0.0328 (12) | −0.0163 (13) | 0.0022 (10) | 0.0049 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C18 | 1.907 (3) | C10—H10A | 0.9600 |
| O1—C5 | 1.238 (3) | C10—H10B | 0.9600 |
| O2—C13 | 1.208 (3) | C10—H10C | 0.9600 |
| O3—C13 | 1.329 (3) | C11—H11A | 0.9600 |
| O3—C14 | 1.481 (5) | C11—H11B | 0.9600 |
| O3—C14′ | 1.485 (7) | C11—H11C | 0.9600 |
| O4—C21 | 1.357 (4) | C12—H12A | 0.9600 |
| O4—H4 | 0.8798 | C12—H12B | 0.9600 |
| N1—C1 | 1.357 (3) | C12—H12C | 0.9600 |
| N1—C9 | 1.381 (3) | C14—C15 | 1.512 (4) |
| N1—H1 | 0.8600 | C14—H14A | 0.9700 |
| C1—C6 | 1.356 (3) | C14—H14B | 0.9700 |
| C1—C2 | 1.491 (3) | C15—H15A | 0.9600 |
| C2—C3 | 1.523 (4) | C15—H15B | 0.9600 |
| C2—H2A | 0.9700 | C15—H15C | 0.9600 |
| C2—H2B | 0.9700 | C14′—C15′ | 1.526 (5) |
| C3—C12 | 1.528 (4) | C14′—H14C | 0.9700 |
| C3—C4 | 1.530 (4) | C14′—H14D | 0.9700 |
| C3—C11 | 1.531 (4) | C15′—H15D | 0.9600 |
| C4—C5 | 1.503 (4) | C15′—H15E | 0.9600 |
| C4—H4A | 0.9700 | C15′—H15F | 0.9600 |
| C4—H4B | 0.9700 | C16—C17 | 1.386 (4) |
| C5—C6 | 1.436 (3) | C16—C21 | 1.402 (3) |
| C6—C7 | 1.507 (3) | C17—C18 | 1.378 (4) |

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| C7—C8 | 1.521 (3) | C17—H17A | 0.9300 |
| C7—C16 | 1.532 (3) | C18—C19 | 1.371 (4) |
| C7—H7A | 0.9800 | C19—C20 | 1.369 (5) |
| C8—C9 | 1.352 (3) | C19—H19A | 0.9300 |
| C8—C13 | 1.461 (3) | C20—C21 | 1.392 (4) |
| C9—C10 | 1.503 (3) | C20—H20A | 0.9300 |
| | | | |
| C13—O3—C14 | 111.3 (3) | C3—C11—H11A | 109.5 |
| C13—O3—C14′ | 123.0 (5) | C3—C11—H11B | 109.5 |
| C21—O4—H4 | 106.1 | H11A—C11—H11B | 109.5 |
| C1—N1—C9 | 123.33 (19) | C3—C11—H11C | 109.5 |
| C1—N1—H1 | 118.0 | H11A—C11—H11C | 109.5 |
| C9—N1—H1 | 116.5 | H11B—C11—H11C | 109.5 |
| C6—C1—N1 | 119.6 (2) | C3—C12—H12A | 109.5 |
| C6—C1—C2 | 123.6 (2) | C3—C12—H12B | 109.5 |
| N1—C1—C2 | 116.8 (2) | H12A—C12—H12B | 109.5 |
| C1—C2—C3 | 113.1 (2) | C3—C12—H12C | 109.5 |
| C1—C2—H2A | 109.0 | H12A—C12—H12C | 109.5 |
| C3—C2—H2A | 109.0 | H12B—C12—H12C | 109.5 |
| C1—C2—H2B | 109.0 | O2—C13—O3 | 121.2 (2) |
| C3—C2—H2B | 109.0 | O2—C13—C8 | 122.4 (2) |
| H2A—C2—H2B | 107.8 | O3—C13—C8 | 116.37 (19) |
| C2—C3—C12 | 109.5 (2) | O3—C14—C15 | 105.0 (4) |
| C2—C3—C4 | 107.7 (2) | O3—C14—H14A | 110.8 |
| C12—C3—C4 | 110.2 (2) | C15—C14—H14A | 110.8 |
| C2—C3—C11 | 110.2 (2) | O3—C14—H14B | 110.8 |
| C12—C3—C11 | 109.1 (3) | C15—C14—H14B | 110.8 |
| C4—C3—C11 | 110.1 (3) | H14A—C14—H14B | 108.8 |
| C5—C4—C3 | 113.5 (2) | O3—C14′—C15′ | 102.1 (6) |
| C5—C4—H4A | 108.9 | O3—C14′—H14C | 111.4 |
| C3—C4—H4A | 108.9 | C15′—C14′—H14C | 111.4 |
| C5—C4—H4B | 108.9 | O3—C14′—H14D | 111.4 |
| C3—C4—H4B | 108.9 | C15′—C14′—H14D | 111.4 |
| H4A—C4—H4B | 107.7 | H14C—C14′—H14D | 109.2 |
| O1—C5—C6 | 121.2 (3) | C14′—C15′—H15D | 109.5 |
| O1—C5—C4 | 120.2 (2) | C14′—C15′—H15E | 109.5 |
| C6—C5—C4 | 118.6 (2) | H15D—C15′—H15E | 109.5 |
| C1—C6—C5 | 119.5 (2) | C14′—C15′—H15F | 109.5 |
| C1—C6—C7 | 120.9 (2) | H15D—C15′—H15F | 109.5 |
| C5—C6—C7 | 119.7 (2) | H15E—C15′—H15F | 109.5 |
| C6—C7—C8 | 110.56 (18) | C17—C16—C21 | 118.5 (2) |
| C6—C7—C16 | 111.54 (19) | C17—C16—C7 | 120.5 (2) |
| C8—C7—C16 | 112.36 (19) | C21—C16—C7 | 121.0 (2) |
| C6—C7—H7A | 107.4 | C18—C17—C16 | 120.4 (2) |
| C8—C7—H7A | 107.4 | C18—C17—H17A | 119.8 |
| C16—C7—H7A | 107.4 | C16—C17—H17A | 119.8 |
| C9—C8—C13 | 125.9 (2) | C19—C18—C17 | 121.5 (3) |
| C9—C8—C7 | 120.9 (2) | C19—C18—Br1 | 118.9 (2) |

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|---|---|---|---|
| C13—C8—C7 | 113.17 (18) | C17—C18—Br1 | 119.6 (2) |
| C8—C9—N1 | 119.2 (2) | C20—C19—C18 | 118.7 (3) |
| C8—C9—C10 | 127.9 (2) | C20—C19—H19A | 120.7 |
| N1—C9—C10 | 112.93 (19) | C18—C19—H19A | 120.7 |
| C9—C10—H10A | 109.5 | C19—C20—C21 | 121.5 (3) |
| C9—C10—H10B | 109.5 | C19—C20—H20A | 119.3 |
| H10A—C10—H10B | 109.5 | C21—C20—H20A | 119.3 |
| C9—C10—H10C | 109.5 | O4—C21—C20 | 118.2 (2) |
| H10A—C10—H10C | 109.5 | O4—C21—C16 | 122.4 (2) |
| H10B—C10—H10C | 109.5 | C20—C21—C16 | 119.4 (3) |
| | | | |
| C9—N1—C1—C6 | −11.6 (4) | C1—N1—C9—C8 | 14.5 (4) |
| C9—N1—C1—C2 | 166.2 (2) | C1—N1—C9—C10 | −164.2 (2) |
| C6—C1—C2—C3 | −19.6 (4) | C14—O3—C13—O2 | 6.0 (5) |
| N1—C1—C2—C3 | 162.7 (2) | C14′—O3—C13—O2 | −21.9 (6) |
| C1—C2—C3—C12 | 168.6 (2) | C14—O3—C13—C8 | −174.5 (4) |
| C1—C2—C3—C4 | 48.8 (3) | C14′—O3—C13—C8 | 157.6 (5) |
| C1—C2—C3—C11 | −71.4 (3) | C9—C8—C13—O2 | 175.8 (2) |
| C2—C3—C4—C5 | −53.9 (3) | C7—C8—C13—O2 | −1.8 (3) |
| C12—C3—C4—C5 | −173.3 (3) | C9—C8—C13—O3 | −3.7 (4) |
| C11—C3—C4—C5 | 66.4 (3) | C7—C8—C13—O3 | 178.8 (2) |
| C3—C4—C5—O1 | −152.6 (3) | C13—O3—C14—C15 | 176.1 (5) |
| C3—C4—C5—C6 | 29.2 (4) | C14′—O3—C14—C15 | −62.6 (10) |
| N1—C1—C6—C5 | 169.3 (2) | C13—O3—C14′—C15′ | 102.7 (10) |
| C2—C1—C6—C5 | −8.3 (4) | C14—O3—C14′—C15′ | 31.1 (9) |
| N1—C1—C6—C7 | −9.4 (3) | C6—C7—C16—C17 | 84.8 (3) |
| C2—C1—C6—C7 | 173.0 (2) | C8—C7—C16—C17 | −40.0 (3) |
| O1—C5—C6—C1 | −174.8 (3) | C6—C7—C16—C21 | −95.2 (3) |
| C4—C5—C6—C1 | 3.3 (4) | C8—C7—C16—C21 | 140.0 (2) |
| O1—C5—C6—C7 | 3.9 (4) | C21—C16—C17—C18 | −1.8 (4) |
| C4—C5—C6—C7 | −178.0 (2) | C7—C16—C17—C18 | 178.2 (2) |
| C1—C6—C7—C8 | 24.1 (3) | C16—C17—C18—C19 | −1.6 (4) |
| C5—C6—C7—C8 | −154.6 (2) | C16—C17—C18—Br1 | 177.85 (19) |
| C1—C6—C7—C16 | −101.7 (2) | C17—C18—C19—C20 | 2.8 (4) |
| C5—C6—C7—C16 | 79.6 (3) | Br1—C18—C19—C20 | −176.7 (2) |
| C6—C7—C8—C9 | −21.1 (3) | C18—C19—C20—C21 | −0.5 (5) |
| C16—C7—C8—C9 | 104.2 (2) | C19—C20—C21—O4 | 178.0 (3) |
| C6—C7—C8—C13 | 156.56 (19) | C19—C20—C21—C16 | −2.8 (4) |
| C16—C7—C8—C13 | −78.1 (2) | C17—C16—C21—O4 | −177.0 (2) |
| C13—C8—C9—N1 | −173.8 (2) | C7—C16—C21—O4 | 3.1 (4) |
| C7—C8—C9—N1 | 3.6 (3) | C17—C16—C21—C20 | 3.9 (4) |
| C13—C8—C9—C10 | 4.8 (4) | C7—C16—C21—C20 | −176.0 (2) |
| C7—C8—C9—C10 | −177.8 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O4—H4···O1 | 0.88 | 1.75 | 2.625 (3) | 171 |

| | | | | |
|---|---|---|---|---|
| N1—H1···O2$^{i}$ | 0.86 | 2.05 | 2.866 (3) | 158 |

Symmetry code: (i) $x+1/2, -y+1/2, z+1/2$.