Acta Cryst E STRUCTURE REPORTS

OPEN ACCESS

ISSN 1600-5368

# Crystal structure of (3,5-dibromo-2-hydroxyphenyl){1-[(naphthalen-1-yl)-carbonyl]-1*H*-pyrazol-4-yl}methanone

**Yoshinobu Ishikawa* and Yuya Motohashi**

School of Pharmaceutical Sciences, University of Shizuoka, 52-1 Yada, Suruga-ku, Shizuoka 422-8526 , Japan. *Correspondence e-mail: ishi206@u-shizuoka-ken.ac.jp

Received 14 August 2014; accepted 15 August 2014

Edited by E. R. T. Tiekink, University of Malaya, Malaysia

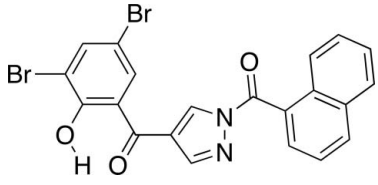
In the title compound, $C_{21}H_{12}Br_2N_2O_3$, a 1,4-diaroyl pyrazole derivative, the dihedral angles between the naphthalene ring system and the pyrazole ring, the pyrazole and benzene rings, and the naphthalene ring system and benzene ring are 50.0 (2), 51.1 (2) and 1.34 (16)°, respectively. The phenolic proton forms an intramolecular O—H···O hydrogen bond with the adjacent carbonyl O atom. In the crystal, molecules are linked by C—H···O hydrogen bonds, forming inversion dimers. The dimers are linked by C—H···Br hydrogen bonds, forming double stranded chains along [01$\bar{1}$]. The chains are linked by $\pi$–$\pi$ interactions between the pyrazole rings and between the naphthalene and benzene rings [centroid–centroid distances = 3.592 (4) and 3.632 (4) Å, respectively].

**Keywords:** crystal structure; diaroyl pyrazole; cyclization; stacking interaction; C—H···O hydrogen bonding.

**CCDC reference**: 1019490

## 1. Related literature

For the biological activity of related compounds, see: Khan *et al.* (2009); Tu *et al.* (2013). For related structures, see: Ishikawa (2014); Ishikawa & Watanabe (2014*a*,*b*,*c*,*d*).




## 2. Experimental

### 2.1. Crystal data

$C_{21}H_{12}Br_2N_2O_3$
$M_r$ = 500.15
Triclinic, $P\bar{1}$
$a$ = 7.390 (5) Å
$b$ = 8.919 (4) Å
$c$ = 14.955 (9) Å
$\alpha$ = 74.61 (4)°
$\beta$ = 76.71 (5)°
$\gamma$ = 71.03 (4)°
$V$ = 887.5 (9) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 4.61 mm$^{-1}$
$T$ = 100 K
0.40 × 0.18 × 0.08 mm

### 2.2. Data collection

Rigaku AFC7R diffractometer
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.448, $T_{max}$ = 0.692
5003 measured reflections
4088 independent reflections
3359 reflections with $F^2 > 2.0\sigma(F^2)$
$R_{int}$ = 0.062
3 standard reflections every 150 reflections
intensity decay: −0.6%

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.204
$S$ = 1.07
4088 reflections
254 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.15 e Å$^{-3}$
$\Delta\rho_{min}$ = −2.52 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H3···O2 | 0.84 | 1.85 | 2.565 (7) | 142 |
| C9—H4···O3$^{i}$ | 0.95 | 2.30 | 3.227 (8) | 165 |
| C16—H9···Br2$^{ii}$ | 0.95 | 2.88 | 3.613 (7) | 135 |

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

Data collection: *WinAFC* (Rigaku, 1999); cell refinement: *WinAFC*; data reduction: *WinAFC*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalStructure* (Rigaku, 2010); software used to prepare material for publication: *CrystalStructure*.

## Acknowledgements

We acknowledge the University of Shizuoka for instrumental support and Professor Kei Manabe (University of Shizuoka) for helpful discussions.

Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5338).

## References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Ishikawa, Y. (2014). *Acta Cryst.* E**70**, o439.
Ishikawa, Y. & Watanabe, K. (2014*a*). *Acta Cryst.* E**70**, o472.
Ishikawa, Y. & Watanabe, K. (2014*b*). *Acta Cryst.* E**70**, o565.
Ishikawa, Y. & Watanabe, K. (2014*c*). *Acta Cryst.* E**70**, o784.
Ishikawa, Y. & Watanabe, K. (2014*d*). *Acta Cryst.* E**70**, o832.
Khan, K. M., Ambreen, N., Hussain, S., Perveen, S. & Choudhary, M. I. (2009). *Bioorg. Med. Chem.* **17**, 2983–2988.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Rigaku (1999). *WinAFC*. Rigaku Corporation, Tokyo, Japan.
Rigaku (2010). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tu, Q. D., Li, D., Sun, Y., Han, X. Y., Yi, F., Sha, Y., Ren, Y. L., Ding, M. W., Feng, L. L. & Wan, J. (2013). *Bioorg. Med. Chem.* **21**, 2826–2831.

# supporting information

*Acta Cryst.* (2014). E**70**, o1033 [doi:10.1107/S1600536814018601]

# Crystal structure of (3,5-dibromo-2-hydroxyphenyl){1-[(naphthalen-1-yl)carbonyl]-1*H*-pyrazol-4-yl}methanone

**Yoshinobu Ishikawa and Yuya Motohashi**

## S1. Structural commentary

Schiff base derivatives of 3-formylchromones have attracted much attention due to their biological functions such as enzyme inhibition (Khan *et al.* 2009; Tu *et al.* 2013). We have recently reported the crystal structures of such compounds (Ishikawa & Watanabe, 2014*a*,*b*,*c*,*d*), which were prepared from condensation reaction of 3-formylchromones with aryl-hydrazides.

The reaction of 6,8-dibromo-3-formylchromone (Ishikawa, 2014) with 1-naphthoylhydrazide in ethanol gave white solids, and orange crystals were obtained from an acetonitrile/ethanol solution of the white solids (Fig. 1). The crystallographic analysis revealed that the structure of the orange crystals is a 1,4-diaroyl pyrazole, as shown in Fig. 2, which should be thermodynamically more stable than that of the white solids. The dihedral angles between the naphthalene and pyrazole rings, the pyrazole and benzene rings and the naphthalene and benzene rings are 50.0 (2), 51.1 (2) and 1.34 (16)°, respectively. The phenolic proton forms an intramolecular O—H···O hydrogen bond with the adjacent carbonyl O2 atom. In the crystal, the molecules are linked through stacking interactions between the pyrazole rings and the naphthalene and benzene rings [centroid–centroid distances = 3.553 (4) and 3.632 (4) Å, respectively, i: $-x+2$, $-y$, $-z+1$], and are further connected through intermolecular C–H···O hydrogen bonds, as shown in Fig. 3. A significant short contact around the bromine atoms is not observed.

The driving force of the intramolecular cyclization (Fig. 1) should be a resonance energy gain, resulting from the extension of the conjugated system across the entire molecule. The intramolecular cyclization is not observed for the chromone derivatives with electron-donating substituents (Ishikawa & Watanabe, 2014*a*,*b*,*c*,*d*), and thus the activation energy for the chromone derivative with the electron-withdrawing substituents should be lower than that for ones with electron-donating substituents.

## S2. Synthesis and crystallization

Preparation of the white precursor, (*E*)-*N*′-((6,8-dibromo-4-oxo-4*H*-chromen-3-yl)methylene)-1-naphthohydrazide, is as follows: 1-naphthohydrazide (1.1 mmol) and 6,8-dibromo-3-formylchromone (1.1 mmol) were dissolved in 50 ml of ethanol, and the mixture was refluxed with Dean-Stark apparatus for 15 min with stirring. After cooling, the white precipitates were collected, washed with *n*-hexane and dried *in vacuo* (yield 25%). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.60–7.64 (m, 4H), 7.77 (d, 1H, $J$ = 6.8 Hz), 8.02–8.05 (m, 1H), 8.11 (d, 1H, $J$ = 8.3 Hz), 8.17 (d, 1H, $J$ = 2.4 Hz), 8.21–8.23 (m, 1H), 8.45 (d, 1H, $J$ = 1.9 Hz), 8.47 (s, 1H), 12.16 (s, 1H). DART-MS (negative mode) calcd for [$C_{21}H_{12}Br_2N_2O_3$]: 499.919, found 498.920. The orange crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile/ethanol solution of the white precursor at room temperature.

## S3. Refinement

The O- and C($sp^2$)-bound hydrogen atoms were placed in their geometric positions [O—H = 0.84 Å and C—H 0.95 Å, $U_{iso}$(H) = 1.2$U_{eq}$(O,C)], and refined using a riding model. Three reflections, *i.e.* (4 6 7), (4 6 3) and (4 6 5) were omitted owing to poor agreement. The maximum and minimum residual electron density peaks of 2.15 and 2.52 eÅ$^{-3}$, respectively, were located 0.88 and 1.05 Å from the Br1 and Br2 atoms, respectively.

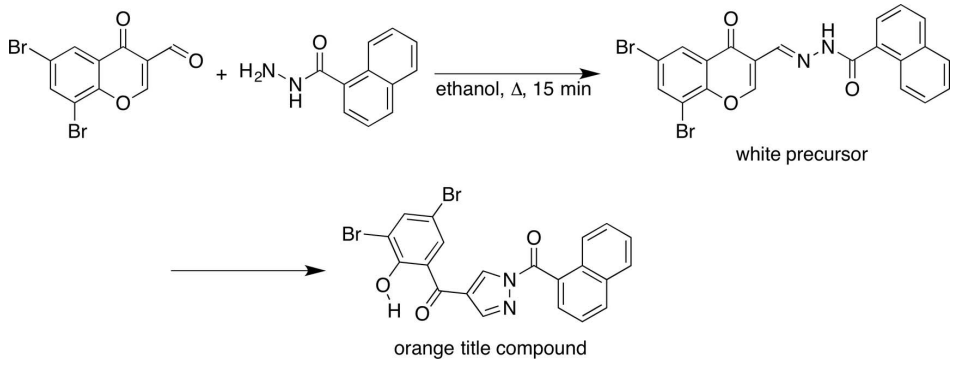



**Figure 1**

Reaction scheme for the title compound.

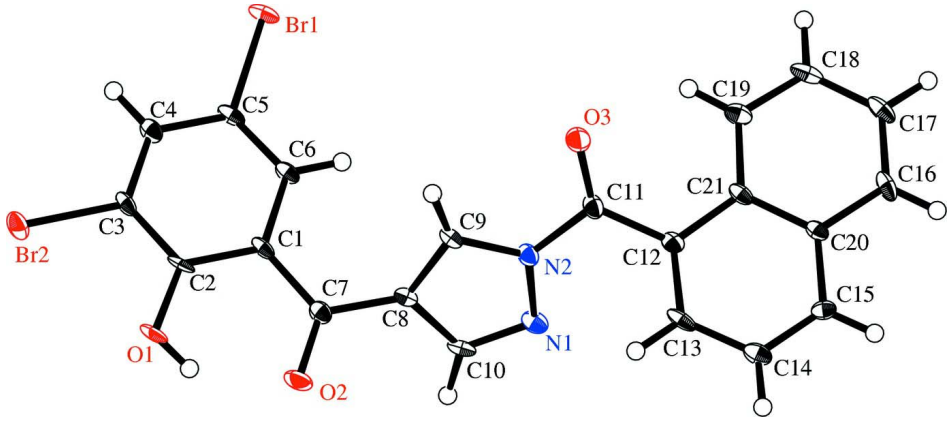



**Figure 2**

The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius.

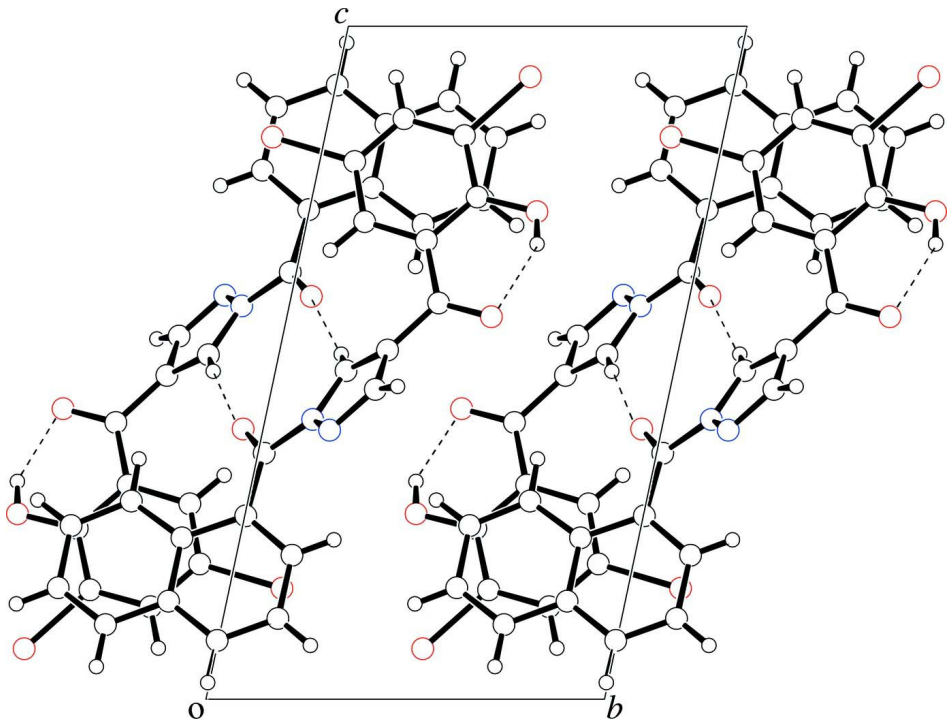



**Figure 3**

A crystal packing view of the title compound. Intramolecular O—H···O and intermolecular C–H···O hydrogen bonds are represented by dashed lines.

### (3,5-Dibromo-2-hydroxyphenyl){1-[(naphthalen-1-yl)carbonyl]-1*H*-pyrazol-4-yl}methanone

*Crystal data*

$C_{21}H_{12}Br_2N_2O_3$
$M_r$ = 500.15
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a$ = 7.390 (5) Å
$b$ = 8.919 (4) Å
$c$ = 14.955 (9) Å
$\alpha$ = 74.61 (4)°
$\beta$ = 76.71 (5)°
$\gamma$ = 71.03 (4)°
$V$ = 887.5 (9) Å$^3$
$Z$ = 2
$F(000)$ = 492.00
$D_x$ = 1.871 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71069 Å
Cell parameters from 25 reflections
$\theta$ = 15.1–17.5°
$\mu$ = 4.61 mm$^{-1}$
$T$ = 100 K
Plate, orange
0.40 × 0.18 × 0.08 mm

*Data collection*

Rigaku AFC7R diffractometer
$\omega$–2$\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.448, $T_{max}$ = 0.692
5003 measured reflections
4088 independent reflections
3359 reflections with $F^2 > 2.0\sigma(F^2)$
$R_{int}$ = 0.062
$\theta_{max}$ = 27.5°
$h$ = −5→9
$k$ = −10→11
$l$ = −18→19
3 standard reflections every 150 reflections
intensity decay: −0.6%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.204$
$S = 1.07$
4088 reflections
254 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
$w = 1/[\sigma^2(F_o^2) + (0.1444P)^2 + 3.2256P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.15$ e Å$^{-3}$
$\Delta\rho_{min} = -2.52$ e Å$^{-3}$

*Special details*

**Refinement**. Refinement was performed using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on $F^2$. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt).

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.50138 (8) | −0.13169 (6) | 0.83532 (4) | 0.0176 (2) |
| Br2 | 0.31452 (8) | 0.48290 (7) | 0.92499 (4) | 0.0201 (2) |
| O1 | 0.4963 (6) | 0.5714 (5) | 0.7244 (4) | 0.0187 (9) |
| O2 | 0.7063 (7) | 0.5130 (5) | 0.5684 (3) | 0.0202 (9) |
| O3 | 0.6724 (7) | −0.0505 (6) | 0.4014 (4) | 0.0240 (10) |
| N1 | 0.9928 (7) | 0.1676 (6) | 0.3998 (4) | 0.0160 (10) |
| N2 | 0.8285 (7) | 0.1192 (6) | 0.4157 (4) | 0.0139 (9) |
| C1 | 0.5910 (8) | 0.3094 (6) | 0.6818 (4) | 0.0127 (10) |
| C2 | 0.5037 (8) | 0.4138 (7) | 0.7463 (5) | 0.0145 (11) |
| C3 | 0.4201 (8) | 0.3493 (7) | 0.8375 (4) | 0.0139 (11) |
| C4 | 0.4218 (8) | 0.1885 (7) | 0.8626 (4) | 0.0146 (11) |
| C5 | 0.5058 (8) | 0.0873 (7) | 0.7989 (5) | 0.0142 (11) |
| C6 | 0.5922 (8) | 0.1444 (7) | 0.7097 (4) | 0.0132 (10) |
| C7 | 0.6900 (8) | 0.3729 (7) | 0.5888 (4) | 0.0139 (10) |
| C8 | 0.7757 (8) | 0.2698 (7) | 0.5188 (4) | 0.0134 (10) |
| C9 | 0.6977 (8) | 0.1766 (7) | 0.4881 (4) | 0.0147 (11) |
| C10 | 0.9595 (8) | 0.2605 (7) | 0.4605 (5) | 0.0160 (11) |
| C11 | 0.7991 (8) | 0.0156 (7) | 0.3655 (4) | 0.0152 (11) |
| C12 | 0.9184 (8) | 0.0025 (7) | 0.2726 (4) | 0.0132 (10) |
| C13 | 0.9601 (8) | 0.1394 (7) | 0.2138 (5) | 0.0157 (11) |
| C14 | 1.0545 (8) | 0.1378 (7) | 0.1201 (5) | 0.0165 (11) |
| C15 | 1.1092 (8) | −0.0030 (7) | 0.0873 (4) | 0.0135 (10) |
| C16 | 1.1317 (8) | −0.2919 (8) | 0.1108 (5) | 0.0186 (12) |
| C17 | 1.0949 (9) | −0.4298 (7) | 0.1657 (5) | 0.0187 (12) |
| C18 | 0.9958 (9) | −0.4307 (7) | 0.2580 (5) | 0.0202 (12) |
| C19 | 0.9346 (8) | −0.2926 (7) | 0.2944 (5) | 0.0161 (11) |
| C20 | 1.0704 (8) | −0.1464 (7) | 0.1456 (4) | 0.0130 (10) |
| C21 | 0.9702 (8) | −0.1460 (7) | 0.2399 (4) | 0.0135 (10) |
| H1 | 0.3650 | 0.1466 | 0.9241 | 0.0175* |
| H2 | 0.6521 | 0.0733 | 0.6672 | 0.0158* |

| | | | | |
|---|---|---|---|---|
| H3 | 0.5769 | 0.5890 | 0.6760 | 0.0225* |
| H4 | 0.5756 | 0.1558 | 0.5125 | 0.0176* |
| H5 | 1.0474 | 0.3148 | 0.4649 | 0.0192* |
| H6 | 0.9250 | 0.2364 | 0.2367 | 0.0189* |
| H7 | 1.0797 | 0.2336 | 0.0801 | 0.0198* |
| H8 | 1.1739 | −0.0043 | 0.0247 | 0.0162* |
| H9 | 1.1988 | −0.2924 | 0.0485 | 0.0223* |
| H10 | 1.1363 | −0.5261 | 0.1418 | 0.0224* |
| H11 | 0.9707 | −0.5279 | 0.2958 | 0.0243* |
| H12 | 0.8676 | −0.2959 | 0.3570 | 0.0193* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0169 (4) | 0.0074 (3) | 0.0300 (4) | −0.0043 (2) | −0.0080 (3) | −0.0017 (3) |
| Br2 | 0.0234 (4) | 0.0131 (4) | 0.0230 (4) | −0.0001 (3) | −0.0030 (3) | −0.0092 (3) |
| O1 | 0.022 (2) | 0.0063 (18) | 0.031 (3) | −0.0053 (15) | −0.0045 (17) | −0.0060 (16) |
| O2 | 0.025 (3) | 0.0088 (19) | 0.027 (3) | −0.0068 (16) | −0.0039 (18) | −0.0027 (17) |
| O3 | 0.020 (2) | 0.030 (3) | 0.029 (3) | −0.0151 (19) | 0.0060 (18) | −0.016 (2) |
| N1 | 0.013 (3) | 0.016 (3) | 0.022 (3) | −0.0056 (18) | −0.0070 (18) | −0.0047 (19) |
| N2 | 0.012 (2) | 0.013 (3) | 0.019 (3) | −0.0031 (17) | −0.0018 (18) | −0.0072 (18) |
| C1 | 0.010 (3) | 0.007 (3) | 0.023 (3) | 0.0008 (18) | −0.007 (2) | −0.006 (2) |
| C2 | 0.013 (3) | 0.007 (3) | 0.028 (3) | −0.0048 (19) | −0.008 (2) | −0.004 (2) |
| C3 | 0.010 (3) | 0.011 (3) | 0.023 (3) | 0.0010 (19) | −0.004 (2) | −0.010 (2) |
| C4 | 0.010 (3) | 0.012 (3) | 0.022 (3) | −0.000 (2) | −0.003 (2) | −0.008 (2) |
| C5 | 0.013 (3) | 0.006 (3) | 0.025 (3) | 0.0006 (18) | −0.011 (2) | −0.002 (2) |
| C6 | 0.012 (3) | 0.007 (3) | 0.021 (3) | −0.0001 (18) | −0.007 (2) | −0.004 (2) |
| C7 | 0.013 (3) | 0.010 (3) | 0.018 (3) | −0.0016 (19) | −0.004 (2) | −0.004 (2) |
| C8 | 0.015 (3) | 0.010 (3) | 0.016 (3) | −0.0046 (19) | −0.004 (2) | −0.002 (2) |
| C9 | 0.017 (3) | 0.010 (3) | 0.019 (3) | −0.005 (2) | −0.004 (2) | −0.005 (2) |
| C10 | 0.017 (3) | 0.009 (3) | 0.023 (3) | −0.007 (2) | −0.006 (3) | 0.000 (2) |
| C11 | 0.014 (3) | 0.015 (3) | 0.019 (3) | −0.003 (2) | −0.002 (2) | −0.009 (2) |
| C12 | 0.009 (3) | 0.015 (3) | 0.019 (3) | −0.0044 (19) | −0.0037 (19) | −0.005 (2) |
| C13 | 0.012 (3) | 0.008 (3) | 0.032 (4) | −0.0010 (19) | −0.012 (3) | −0.006 (3) |
| C14 | 0.016 (3) | 0.011 (3) | 0.023 (3) | −0.003 (2) | −0.009 (3) | −0.001 (2) |
| C15 | 0.010 (3) | 0.015 (3) | 0.017 (3) | −0.007 (2) | −0.0023 (19) | −0.002 (2) |
| C16 | 0.014 (3) | 0.017 (3) | 0.025 (3) | 0.003 (2) | −0.005 (3) | −0.014 (3) |
| C17 | 0.019 (3) | 0.009 (3) | 0.031 (4) | 0.001 (2) | −0.012 (3) | −0.008 (3) |
| C18 | 0.025 (3) | 0.011 (3) | 0.030 (4) | −0.008 (3) | −0.014 (3) | 0.001 (3) |
| C19 | 0.017 (3) | 0.013 (3) | 0.020 (3) | −0.005 (2) | −0.008 (2) | −0.001 (2) |
| C20 | 0.011 (3) | 0.011 (3) | 0.018 (3) | −0.0032 (19) | −0.004 (2) | −0.004 (2) |
| C21 | 0.012 (3) | 0.011 (3) | 0.021 (3) | −0.0029 (19) | −0.008 (2) | −0.005 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C5 | 1.893 (6) | C13—C14 | 1.417 (9) |
| Br2—C3 | 1.870 (7) | C14—C15 | 1.373 (9) |
| O1—C2 | 1.341 (7) | C15—C20 | 1.417 (8) |

| | | | |
|---|---|---|---|
| O2—C7 | 1.243 (8) | C16—C17 | 1.356 (9) |
| O3—C11 | 1.213 (8) | C16—C20 | 1.425 (10) |
| N1—N2 | 1.368 (8) | C17—C18 | 1.404 (9) |
| N1—C10 | 1.317 (9) | C18—C19 | 1.378 (10) |
| N2—C9 | 1.364 (7) | C19—C21 | 1.416 (8) |
| N2—C11 | 1.427 (10) | C20—C21 | 1.434 (8) |
| C1—C2 | 1.419 (9) | O1—H3 | 0.840 |
| C1—C6 | 1.417 (8) | C4—H1 | 0.950 |
| C1—C7 | 1.475 (8) | C6—H2 | 0.950 |
| C2—C3 | 1.415 (8) | C9—H4 | 0.950 |
| C3—C4 | 1.379 (8) | C10—H5 | 0.950 |
| C4—C5 | 1.389 (9) | C13—H6 | 0.950 |
| C5—C6 | 1.380 (8) | C14—H7 | 0.950 |
| C7—C8 | 1.473 (9) | C15—H8 | 0.950 |
| C8—C9 | 1.367 (11) | C16—H9 | 0.950 |
| C8—C10 | 1.426 (8) | C17—H10 | 0.950 |
| C11—C12 | 1.476 (8) | C18—H11 | 0.950 |
| C12—C13 | 1.382 (8) | C19—H12 | 0.950 |
| C12—C21 | 1.438 (9) | | |

| | | | |
|---|---|---|---|
| Br2···O1 | 3.001 (5) | H11···H12 | 2.3146 |
| O1···O2 | 2.565 (7) | Br1···H7$^{iii}$ | 3.3724 |
| O1···C7 | 2.867 (8) | Br1···H8$^{viii}$ | 3.4550 |
| O2···C2 | 2.807 (7) | Br1···H10$^{ix}$ | 3.3397 |
| O2···C9 | 3.538 (9) | Br2···H6$^{v}$ | 3.3350 |
| O2···C10 | 2.996 (8) | Br2···H7$^{viii}$ | 3.3550 |
| O3···N1 | 3.512 (9) | Br2···H7$^{v}$ | 3.1777 |
| O3···C9 | 2.751 (10) | Br2···H9$^{x}$ | 2.8779 |
| O3···C13 | 3.512 (8) | Br2···H9$^{iii}$ | 3.5074 |
| O3···C19 | 2.944 (8) | Br2···H10$^{x}$ | 3.1965 |
| O3···C21 | 2.972 (7) | Br2···H10$^{ii}$ | 3.5687 |
| N1···C12 | 2.930 (10) | O1···H6$^{v}$ | 3.0327 |
| N1···C13 | 2.928 (10) | O1···H10$^{iii}$ | 3.5909 |
| N2···C13 | 2.926 (8) | O2···H4$^{v}$ | 3.1289 |
| C1···C4 | 2.795 (8) | O2···H5$^{vi}$ | 2.6299 |
| C1···C9 | 3.252 (9) | O2···H11$^{iii}$ | 3.5241 |
| C2···C5 | 2.803 (8) | O2···H12$^{iv}$ | 3.3240 |
| C3···C6 | 2.800 (9) | O2···H12$^{iii}$ | 3.3782 |
| C6···C8 | 2.958 (8) | O3···H2$^{ii}$ | 2.8993 |
| C6···C9 | 3.181 (9) | O3···H4$^{ii}$ | 2.3008 |
| C8···C11 | 3.570 (10) | O3···H5$^{iii}$ | 3.1732 |
| C10···C11 | 3.507 (11) | N1···H2$^{iii}$ | 2.9620 |
| C11···C19 | 2.994 (9) | N1···H11$^{iv}$ | 2.7216 |
| C12···C15 | 2.810 (8) | N2···H3$^{v}$ | 3.5425 |
| C13···C20 | 2.802 (9) | N2···H11$^{iv}$ | 3.5371 |
| C14···C21 | 2.848 (8) | C2···H11$^{ii}$ | 3.4752 |
| C16···C19 | 2.797 (9) | C3···H9$^{iii}$ | 3.4520 |
| C17···C21 | 2.827 (10) | C3···H11$^{ii}$ | 3.5806 |

| | | | |
|---|---|---|---|
| C18···C20 | 2.789 (9) | C4···H8$^{viii}$ | 3.1593 |
| Br1···O1$^{i}$ | 3.492 (6) | C4···H8$^{iii}$ | 3.4809 |
| Br1···C12$^{ii}$ | 3.542 (7) | C6···H12$^{ii}$ | 3.4958 |
| Br1···C14$^{iii}$ | 3.477 (7) | C7···H12$^{iii}$ | 3.3582 |
| O1···Br1$^{iv}$ | 3.492 (6) | C8···H11$^{iv}$ | 3.5695 |
| O1···N2$^{v}$ | 3.564 (7) | C9···H3$^{v}$ | 3.3636 |
| O1···C17$^{iii}$ | 3.481 (9) | C10···H11$^{iv}$ | 2.6785 |
| O1···C18$^{iii}$ | 3.598 (8) | C10···H12$^{iii}$ | 3.3923 |
| O2···C9$^{v}$ | 3.440 (7) | C11···H4$^{ii}$ | 3.5045 |
| O2···C10$^{vi}$ | 3.558 (9) | C11···H5$^{iii}$ | 3.4029 |
| O2···C18$^{iii}$ | 3.563 (10) | C12···H2$^{iii}$ | 3.3072 |
| O2···C19$^{iii}$ | 3.476 (8) | C13···H2$^{iii}$ | 3.4633 |
| O3···O3$^{ii}$ | 3.530 (7) | C13···H10$^{iv}$ | 3.4537 |
| O3···C6$^{ii}$ | 3.253 (10) | C13···H11$^{iv}$ | 3.5269 |
| O3···C9$^{ii}$ | 3.227 (8) | C14···H1$^{xi}$ | 3.2807 |
| O3···C10$^{iii}$ | 3.520 (8) | C14···H9$^{vii}$ | 3.2254 |
| N1···N2$^{iii}$ | 3.411 (7) | C14···H10$^{iv}$ | 3.3528 |
| N1···C9$^{iii}$ | 3.455 (7) | C15···H1$^{xi}$ | 3.0172 |
| N2···O1$^{v}$ | 3.564 (7) | C15···H8$^{vii}$ | 2.9417 |
| N2···N1$^{iii}$ | 3.411 (7) | C15···H9$^{vii}$ | 3.4108 |
| N2···C10$^{iii}$ | 3.451 (7) | C16···H1$^{ii}$ | 3.5849 |
| C1···C19$^{iii}$ | 3.556 (9) | C16···H7$^{vii}$ | 3.4040 |
| C1···C21$^{iii}$ | 3.432 (8) | C16···H8$^{vii}$ | 3.4014 |
| C2···C16$^{iii}$ | 3.539 (10) | C17···H3$^{iii}$ | 3.4810 |
| C2···C17$^{iii}$ | 3.566 (11) | C17···H6$^{i}$ | 3.4220 |
| C3···C16$^{iii}$ | 3.421 (9) | C18···H3$^{iii}$ | 3.2763 |
| C3···C18$^{ii}$ | 3.468 (10) | C18···H5$^{i}$ | 3.3353 |
| C4···C15$^{iii}$ | 3.481 (8) | C18···H6$^{i}$ | 3.2839 |
| C5···C14$^{iii}$ | 3.513 (8) | C19···H5$^{iii}$ | 3.5826 |
| C5···C15$^{iii}$ | 3.422 (9) | C20···H8$^{vii}$ | 3.2058 |
| C5···C19$^{ii}$ | 3.570 (9) | H1···C14$^{viii}$ | 3.2807 |
| C5···C21$^{ii}$ | 3.544 (9) | H1···C15$^{viii}$ | 3.0172 |
| C6···O3$^{ii}$ | 3.253 (10) | H1···C16$^{ii}$ | 3.5849 |
| C6···C12$^{iii}$ | 3.470 (8) | H1···H1$^{xii}$ | 3.3932 |
| C6···C21$^{iii}$ | 3.491 (10) | H1···H7$^{viii}$ | 2.8501 |
| C7···C19$^{iii}$ | 3.395 (10) | H1···H8$^{viii}$ | 2.2922 |
| C9···O2$^{v}$ | 3.440 (7) | H1···H8$^{iii}$ | 3.4174 |
| C9···O3$^{ii}$ | 3.227 (8) | H2···O3$^{ii}$ | 2.8993 |
| C9···N1$^{iii}$ | 3.455 (7) | H2···N1$^{iii}$ | 2.9620 |
| C10···O2$^{vi}$ | 3.558 (9) | H2···C12$^{iii}$ | 3.3072 |
| C10···O3$^{iii}$ | 3.520 (8) | H2···C13$^{iii}$ | 3.4633 |
| C10···N2$^{iii}$ | 3.451 (7) | H3···N2$^{v}$ | 3.5425 |
| C10···C11$^{iii}$ | 3.448 (8) | H3···C9$^{v}$ | 3.3636 |
| C10···C18$^{iv}$ | 3.537 (8) | H3···C17$^{iii}$ | 3.4810 |
| C11···C10$^{iii}$ | 3.448 (8) | H3···C18$^{iii}$ | 3.2763 |
| C12···Br1$^{ii}$ | 3.542 (7) | H3···H4$^{v}$ | 3.2835 |
| C12···C6$^{iii}$ | 3.470 (8) | H3···H5$^{vi}$ | 3.2838 |
| C14···Br1$^{iii}$ | 3.477 (7) | H3···H11$^{iii}$ | 3.3159 |

| | | | |
|---|---|---|---|
| C14···C5$^{iii}$ | 3.513 (8) | H4···O2$^{v}$ | 3.1289 |
| C15···C4$^{iii}$ | 3.481 (8) | H4···O3$^{ii}$ | 2.3008 |
| C15···C5$^{iii}$ | 3.422 (9) | H4···C11$^{ii}$ | 3.5045 |
| C15···C15$^{vii}$ | 3.352 (10) | H4···H3$^{v}$ | 3.2835 |
| C16···C2$^{iii}$ | 3.539 (10) | H4···H4$^{ii}$ | 3.4472 |
| C16···C3$^{iii}$ | 3.421 (9) | H4···H12$^{ii}$ | 3.4341 |
| C17···O1$^{iii}$ | 3.481 (9) | H5···O2$^{vi}$ | 2.6299 |
| C17···C2$^{iii}$ | 3.566 (11) | H5···O3$^{iii}$ | 3.1732 |
| C18···O1$^{iii}$ | 3.598 (8) | H5···C11$^{iii}$ | 3.4029 |
| C18···O2$^{iii}$ | 3.563 (10) | H5···C18$^{iv}$ | 3.3353 |
| C18···C3$^{ii}$ | 3.468 (10) | H5···C19$^{iii}$ | 3.5826 |
| C18···C10$^{i}$ | 3.537 (8) | H5···H3$^{vi}$ | 3.2838 |
| C19···O2$^{iii}$ | 3.476 (8) | H5···H5$^{vi}$ | 3.5363 |
| C19···C1$^{iii}$ | 3.556 (9) | H5···H11$^{iv}$ | 2.6349 |
| C19···C5$^{ii}$ | 3.570 (9) | H5···H12$^{iv}$ | 3.3818 |
| C19···C7$^{iii}$ | 3.395 (10) | H5···H12$^{iii}$ | 2.8249 |
| C21···C1$^{iii}$ | 3.432 (8) | H6···Br2$^{v}$ | 3.3350 |
| C21···C5$^{ii}$ | 3.544 (9) | H6···O1$^{v}$ | 3.0327 |
| C21···C6$^{iii}$ | 3.491 (10) | H6···C17$^{iv}$ | 3.4220 |
| Br1···H1 | 2.9064 | H6···C18$^{iv}$ | 3.2839 |
| Br1···H2 | 2.9157 | H6···H10$^{iv}$ | 2.9117 |
| Br2···H1 | 2.9029 | H6···H11$^{iv}$ | 2.6271 |
| O2···H3 | 1.8478 | H7···Br1$^{iii}$ | 3.3724 |
| O2···H5 | 2.9382 | H7···Br2$^{xi}$ | 3.3550 |
| O3···H4 | 2.6228 | H7···Br2$^{v}$ | 3.1777 |
| O3···H12 | 2.3649 | H7···C16$^{vii}$ | 3.4040 |
| N1···H4 | 3.1758 | H7···H1$^{xi}$ | 2.8501 |
| N1···H6 | 2.4781 | H7···H9$^{vii}$ | 2.9645 |
| N2···H5 | 3.0438 | H7···H10$^{iv}$ | 2.7262 |
| N2···H6 | 2.6233 | H8···Br1$^{xi}$ | 3.4550 |
| C1···H3 | 2.4414 | H8···C4$^{xi}$ | 3.1593 |
| C1···H4 | 3.2200 | H8···C4$^{iii}$ | 3.4809 |
| C2···H1 | 3.2819 | H8···C15$^{vii}$ | 2.9417 |
| C2···H2 | 3.3118 | H8···C16$^{vii}$ | 3.4014 |
| C3···H3 | 3.0549 | H8···C20$^{vii}$ | 3.2058 |
| C4···H2 | 3.2658 | H8···H1$^{xi}$ | 2.2922 |
| C6···H1 | 3.2617 | H8···H1$^{iii}$ | 3.4174 |
| C6···H4 | 2.9521 | H8···H8$^{vii}$ | 2.8061 |
| C7···H2 | 2.6957 | H8···H9$^{vii}$ | 3.3014 |
| C7···H3 | 2.4287 | H9···Br2$^{xiii}$ | 2.8779 |
| C7···H4 | 2.9062 | H9···Br2$^{iii}$ | 3.5074 |
| C7···H5 | 2.8364 | H9···C3$^{iii}$ | 3.4520 |
| C8···H2 | 2.6214 | H9···C14$^{vii}$ | 3.2254 |
| C9···H2 | 2.5715 | H9···C15$^{vii}$ | 3.4108 |
| C9···H5 | 3.1225 | H9···H7$^{vii}$ | 2.9645 |
| C10···H4 | 3.1375 | H9···H8$^{vii}$ | 3.3014 |
| C10···H6 | 3.4812 | H10···Br1$^{ix}$ | 3.3397 |
| C11···H4 | 2.7515 | H10···Br2$^{xiii}$ | 3.1965 |

| | | | |
|---|---|---|---|
| C11···H6 | 2.6092 | H10···Br2$^{ii}$ | 3.5687 |
| C11···H12 | 2.6897 | H10···O1$^{iii}$ | 3.5909 |
| C12···H7 | 3.2902 | H10···C13$^{i}$ | 3.4537 |
| C12···H12 | 2.7322 | H10···C14$^{i}$ | 3.3528 |
| C13···H8 | 3.2701 | H10···H6$^{i}$ | 2.9117 |
| C15···H6 | 3.2629 | H10···H7$^{i}$ | 2.7262 |
| C15···H9 | 2.6357 | H11···O2$^{iii}$ | 3.5241 |
| C16···H8 | 2.6301 | H11···N1$^{i}$ | 2.7216 |
| C16···H11 | 3.2439 | H11···N2$^{i}$ | 3.5371 |
| C17···H12 | 3.2752 | H11···C2$^{ii}$ | 3.4752 |
| C18···H9 | 3.2522 | H11···C3$^{ii}$ | 3.5806 |
| C19···H10 | 3.2731 | H11···C8$^{i}$ | 3.5695 |
| C20···H7 | 3.2871 | H11···C10$^{i}$ | 2.6785 |
| C20···H10 | 3.2758 | H11···C13$^{i}$ | 3.5269 |
| C20···H12 | 3.3011 | H11···H3$^{iii}$ | 3.3159 |
| C21···H6 | 3.3053 | H11···H5$^{i}$ | 2.6349 |
| C21···H8 | 3.3269 | H11···H6$^{i}$ | 2.6271 |
| C21···H9 | 3.3286 | H12···O2$^{i}$ | 3.3240 |
| C21···H11 | 3.2836 | H12···O2$^{iii}$ | 3.3782 |
| H2···H4 | 2.3745 | H12···C6$^{ii}$ | 3.4958 |
| H6···H7 | 2.3618 | H12···C7$^{iii}$ | 3.3582 |
| H7···H8 | 2.3192 | H12···C10$^{iii}$ | 3.3923 |
| H8···H9 | 2.4494 | H12···H4$^{ii}$ | 3.4341 |
| H9···H10 | 2.3002 | H12···H5$^{i}$ | 3.3818 |
| H10···H11 | 2.3456 | H12···H5$^{iii}$ | 2.8249 |

| | | | |
|---|---|---|---|
| N2—N1—C10 | 104.6 (5) | C14—C15—C20 | 121.0 (5) |
| N1—N2—C9 | 111.9 (6) | C17—C16—C20 | 120.6 (6) |
| N1—N2—C11 | 124.5 (5) | C16—C17—C18 | 120.2 (6) |
| C9—N2—C11 | 123.5 (6) | C17—C18—C19 | 121.0 (6) |
| C2—C1—C6 | 119.7 (5) | C18—C19—C21 | 120.8 (6) |
| C2—C1—C7 | 118.9 (5) | C15—C20—C16 | 120.0 (5) |
| C6—C1—C7 | 121.2 (5) | C15—C20—C21 | 120.3 (6) |
| O1—C2—C1 | 122.9 (5) | C16—C20—C21 | 119.7 (5) |
| O1—C2—C3 | 118.5 (6) | C12—C21—C19 | 125.0 (5) |
| C1—C2—C3 | 118.6 (5) | C12—C21—C20 | 117.3 (5) |
| Br2—C3—C2 | 119.1 (5) | C19—C21—C20 | 117.7 (6) |
| Br2—C3—C4 | 120.3 (5) | C2—O1—H3 | 109.471 |
| C2—C3—C4 | 120.5 (6) | C3—C4—H1 | 119.719 |
| C3—C4—C5 | 120.6 (5) | C5—C4—H1 | 119.718 |
| Br1—C5—C4 | 119.3 (4) | C1—C6—H2 | 120.184 |
| Br1—C5—C6 | 119.8 (5) | C5—C6—H2 | 120.182 |
| C4—C5—C6 | 120.9 (6) | N2—C9—H4 | 126.528 |
| C1—C6—C5 | 119.6 (6) | C8—C9—H4 | 126.542 |
| O2—C7—C1 | 121.0 (6) | N1—C10—H5 | 124.031 |
| O2—C7—C8 | 118.7 (5) | C8—C10—H5 | 124.022 |
| C1—C7—C8 | 120.4 (5) | C12—C13—H6 | 119.423 |
| C7—C8—C9 | 130.1 (5) | C14—C13—H6 | 119.416 |

| | | | |
|---|---|---|---|
| C7—C8—C10 | 125.1 (7) | C13—C14—H7 | 120.217 |
| C9—C8—C10 | 104.6 (6) | C15—C14—H7 | 120.214 |
| N2—C9—C8 | 106.9 (6) | C14—C15—H8 | 119.513 |
| N1—C10—C8 | 111.9 (6) | C20—C15—H8 | 119.515 |
| O3—C11—N2 | 117.1 (6) | C17—C16—H9 | 119.699 |
| O3—C11—C12 | 125.0 (7) | C20—C16—H9 | 119.707 |
| N2—C11—C12 | 117.8 (6) | C16—C17—H10 | 119.889 |
| C11—C12—C13 | 119.0 (6) | C18—C17—H10 | 119.880 |
| C11—C12—C21 | 120.0 (5) | C17—C18—H11 | 119.506 |
| C13—C12—C21 | 120.6 (5) | C19—C18—H11 | 119.498 |
| C12—C13—C14 | 121.2 (6) | C18—C19—H12 | 119.584 |
| C13—C14—C15 | 119.6 (6) | C21—C19—H12 | 119.586 |

| | | | |
|---|---|---|---|
| H3—O1—C2—C1 | −17.0 | C9—C8—C10—H5 | 179.2 |
| H3—O1—C2—C3 | 163.3 | C10—C8—C9—N2 | −0.7 (5) |
| N2—N1—C10—C8 | 1.9 (6) | C10—C8—C9—H4 | 179.3 |
| N2—N1—C10—H5 | −178.1 | O3—C11—C12—C13 | 139.0 (6) |
| C10—N1—N2—C9 | −2.4 (5) | O3—C11—C12—C21 | −33.7 (8) |
| C10—N1—N2—C11 | −179.9 (4) | N2—C11—C12—C13 | −38.1 (7) |
| N1—N2—C9—C8 | 1.9 (6) | N2—C11—C12—C21 | 149.2 (5) |
| N1—N2—C9—H4 | −178.1 | C11—C12—C13—C14 | −172.6 (5) |
| N1—N2—C11—O3 | 161.6 (5) | C11—C12—C13—H6 | 7.4 |
| N1—N2—C11—C12 | −21.1 (7) | C11—C12—C21—C19 | −7.7 (9) |
| C9—N2—C11—O3 | −15.7 (7) | C11—C12—C21—C20 | 174.2 (5) |
| C9—N2—C11—C12 | 161.7 (4) | C13—C12—C21—C19 | 179.8 (5) |
| C11—N2—C9—C8 | 179.5 (4) | C13—C12—C21—C20 | 1.7 (8) |
| C11—N2—C9—H4 | −0.5 | C21—C12—C13—C14 | 0.1 (9) |
| C2—C1—C6—C5 | 1.0 (9) | C21—C12—C13—H6 | −179.9 |
| C2—C1—C6—H2 | −179.0 | C12—C13—C14—C15 | −1.4 (9) |
| C6—C1—C2—O1 | −179.6 (5) | C12—C13—C14—H7 | 178.6 |
| C6—C1—C2—C3 | 0.1 (9) | H6—C13—C14—C15 | 178.6 |
| C2—C1—C7—O2 | 3.7 (9) | H6—C13—C14—H7 | −1.4 |
| C2—C1—C7—C8 | −177.7 (5) | C13—C14—C15—C20 | 0.8 (9) |
| C7—C1—C2—O1 | 4.4 (9) | C13—C14—C15—H8 | −179.2 |
| C7—C1—C2—C3 | −175.9 (5) | H7—C14—C15—C20 | −179.2 |
| C6—C1—C7—O2 | −172.3 (5) | H7—C14—C15—H8 | 0.8 |
| C6—C1—C7—C8 | 6.4 (9) | C14—C15—C20—C16 | −178.9 (5) |
| C7—C1—C6—C5 | 176.9 (5) | C14—C15—C20—C21 | 1.0 (9) |
| C7—C1—C6—H2 | −3.1 | H8—C15—C20—C16 | 1.1 |
| O1—C2—C3—Br2 | −3.0 (8) | H8—C15—C20—C21 | −179.0 |
| O1—C2—C3—C4 | 179.0 (5) | C17—C16—C20—C15 | −179.8 (6) |
| C1—C2—C3—Br2 | 177.3 (5) | C17—C16—C20—C21 | 0.4 (9) |
| C1—C2—C3—C4 | −0.7 (9) | C20—C16—C17—C18 | −0.0 (10) |
| Br2—C3—C4—C5 | −177.8 (4) | C20—C16—C17—H10 | 180.0 |
| Br2—C3—C4—H1 | 2.2 | H9—C16—C17—C18 | 180.0 |
| C2—C3—C4—C5 | 0.1 (9) | H9—C16—C17—H10 | −0.0 |
| C2—C3—C4—H1 | −179.9 | H9—C16—C20—C15 | 0.2 |
| C3—C4—C5—Br1 | −178.9 (5) | H9—C16—C20—C21 | −179.6 |

| | | | |
|---|---|---|---|
| C3—C4—C5—C6 | 1.1 (9) | C16—C17—C18—C19 | −0.1 (10) |
| H1—C4—C5—Br1 | 1.1 | C16—C17—C18—H11 | 179.9 |
| H1—C4—C5—C6 | −178.9 | H10—C17—C18—C19 | 179.9 |
| Br1—C5—C6—C1 | 178.4 (4) | H10—C17—C18—H11 | −0.1 |
| Br1—C5—C6—H2 | −1.6 | C17—C18—C19—C21 | −0.1 (10) |
| C4—C5—C6—C1 | −1.6 (9) | C17—C18—C19—H12 | 179.9 |
| C4—C5—C6—H2 | 178.4 | H11—C18—C19—C21 | 179.9 |
| O2—C7—C8—C9 | −132.1 (6) | H11—C18—C19—H12 | −0.1 |
| O2—C7—C8—C10 | 41.0 (8) | C18—C19—C21—C12 | −177.6 (6) |
| C1—C7—C8—C9 | 49.2 (8) | C18—C19—C21—C20 | 0.5 (9) |
| C1—C7—C8—C10 | −137.7 (5) | H12—C19—C21—C12 | 2.4 |
| C7—C8—C9—N2 | 173.5 (5) | H12—C19—C21—C20 | −179.5 |
| C7—C8—C9—H4 | −6.5 | C15—C20—C21—C12 | −2.2 (8) |
| C7—C8—C10—N1 | −175.3 (5) | C15—C20—C21—C19 | 179.6 (5) |
| C7—C8—C10—H5 | 4.7 | C16—C20—C21—C12 | 177.6 (5) |
| C9—C8—C10—N1 | −0.8 (6) | C16—C20—C21—C19 | −0.6 (8) |

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+2, −*y*, −*z*+1; (iv) *x*, *y*+1, *z*; (v) −*x*+1, −*y*+1, −*z*+1; (vi) −*x*+2, −*y*+1, −*z*+1; (vii) −*x*+2, −*y*, −*z*; (viii) *x*−1, *y*, *z*+1; (ix) −*x*+2, −*y*−1, −*z*+1; (x) *x*−1, *y*+1, *z*+1; (xi) *x*+1, *y*, *z*−1; (xii) −*x*+1, −*y*, −*z*+2; (xiii) *x*+1, *y*−1, *z*−1.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H3···O2 | 0.84 | 1.85 | 2.565 (7) | 142 |
| C9—H4···O3$^{ii}$ | 0.95 | 2.30 | 3.227 (8) | 165 |
| C16—H9···Br2$^{xiii}$ | 0.95 | 2.88 | 3.613 (7) | 135 |

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