Crystal structure and Hirshfeld surface analysis of 4-bromo-2-[3-methyl-5-(2,4,6-trimethylbenzyl)oxazolidin-2-yl]phenol

Ali N. Khalilov, Victor N. Khrustalev, Elena A. Fortalnova, Mehmet Akkurt, Sema Öztürk Yıldırım, Ajaya Bhattarai and İbrahim G. Mamedov

The title compound, C_{20}H_{24}BrNO_2, is chiral at the carbon atoms on either side of the oxygen atom of the oxazolidine ring and crystallizes as a racemate. The 1,3-oxazolidine ring adopts an envelope conformation with the N atom in an endo position. The mean plane of the oxazolidine ring makes dihedral angles of 77.74 (10) and 45.50 (11)°, respectively, with the 4-bromophenol and 1,3,5-trimethylbenzene rings. In the crystal, adjacent molecules are connected via C—H···O hydrogen bonds and C—H···π interactions into layers parallel to the (001) plane. The packing is strengthened by van der Waals interactions between parallel molecular layers. A Hirshfeld surface analysis shows that H···H (58.2%), C···H/H···C (18.9%), and Br···H/H···Br (11.5%) interactions are the most abundant in the crystal packing.

1. Chemical context

Functionalization of amine and carbonyl compounds represents a cornerstone of organic synthesis, material science and medicinal chemistry (Zubkov et al., 2018; Shikhaliyev et al., 2019; Viswanathan et al., 2019; Gurbanov et al., 2020). In particular, the reaction of 1,2-amino alcohols with oxo compounds is an effective tool in the construction of a broad class of organic compounds such as amides, esters, enamino-nes, ureas, carbamates, aziridines, oxazolidines, oxazolines, oxazolidinones, oxazines, pyrroles, pyridones, morpholines, acridinones etc (Juhaš et al., 2011; Tamura et al., 2014; Sepideh et al., 2018; Khalilov, 2021).

In the context of our recent studies, herein we report the structural analysis of a 1,3-oxazolidine, synthesized on the base of racemic 1,2-amino alcohol. Theoretically, in the solid
state, this 1,3-oxazolidine can exist as eight optical isomers due to two CH and one N-chiral center. However, NMR analysis of the obtained product indicated the formation of a pair of diastereoisomers in a 1:1 ratio (Khalilov, 2021) and single-crystal X-ray analysis of the racemic mixture confirmed the 2R,3S,5R- and 2S,3R,5S-configuration of these isomers (Fig. 1).

Thus, in the framework of our ongoing structural studies (Naghiyev et al., 2020, 2021, 2022; Khalilov et al., 2022), we report the crystal structure and Hirshfeld surface analysis of the racemic title compound, 4-bromo-2-[3-methyl-5-(2,4,6-trimethylbenzyl)oxazolidin-2-yl]phenol.

### 2. Structural commentary

In the title compound, (Fig. 2), the 1,3-oxazolidine ring (O1/N3/C2/C4/C5) adopts an envelope conformation with the N atom in an endo position [the puckering parameters (Cremer & Pople, 1975) are $Q(2) = 0.413$ (2) Å, $\phi(2) = 256.7$ (3)°]. The mean plane of the oxazolidine ring makes dihedral angles of 77.74 (10) and 45.50 (11)° with the 4-bromo-phenol (C6–C11) and the 1,3,5-trimethylbenzene (C14–C19) rings. The molecular conformation is stabilized by intramolecular O11—H11/C1/N3 and C20—H20/C1/O1 hydrogen bonds (Table 1). There are two stereogenic centers in the racemic title compound and the chirality about the C2 and C5 atoms is $R$ in the chosen asymmetric unit. The geometric properties of the title compound are normal and consistent with those of related compounds listed in the Database survey section.

### 3. Supramolecular features and Hirshfeld surface analysis

In the crystal, adjacent molecules are connected via C—H···O hydrogen bonds and C—H···π interactions into layers parallel to the (200) plane (Table 1; Figs. 3 and 4). The packing

![Figure 1](image1.png)  
**Figure 1** Synthesis of the racemic mixture of 2R,3S,5R- and 2S,3R,5S-oxazolidines.

![Figure 2](image2.png)  
**Figure 2** The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

![Figure 3](image3.png)  
**Figure 3** A general view of the C—H···O hydrogen bonding and C—H···π interactions of the title compound. Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x, y + 1, z$; (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

### Table 1

Hydrogen-bond geometry (Å, °).

| D—H···A | H···A | D···A | D—H···A |
|---------|------|-------|--------|
| O11—H11···N3 | 0.81 (4) | 1.89 (4) | 2.644 (2) | 155 (3) |
| C4—H4A···O1’ | 0.99 | 2.58 | 3.564 (2) | 171 |
| C20—H20B···O11w | 0.98 | 2.57 | 3.548 (3) | 173 |
| C20—H20C···O1 | 0.98 | 2.55 | 3.332 (3) | 136 |
| C2—H2···Cg2’ | 1.00 | 2.91 | 3.908 (2) | 176 |
| C4—H4B···Cg3’ | 0.99 | 2.88 | 3.622 (2) | 132 |
| C21—H21C···Cg3iii | 0.98 | 2.93 | 3.723 (4) | 138 |

Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x, y + 1, z$; (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.
is strengthened by van der Waals interactions between parallel molecular layers.

A Hirshfeld surface analysis was performed and the associated two-dimensional fingerprint plots were obtained with CrystalExplorer17.5 (Turner et al., 2017). The overall two-dimensional fingerprint plot for the title compound is given in Fig. 5a, and those delineated into H⋯H (58.2%), C⋯H/ H⋯C (18.9%), and Br⋯H/H⋯Br (11.5%) contacts are shown in Fig. 5b–d, while numerical details of the different contacts are given in Table 2. The O⋯H/H⋯O (8.3%), C⋯C (1.4%), Br⋯C/Br (1.0%), Br⋯O/O⋯Br (0.5%) and Br⋯Br (0.3%) contacts have little directional influence on the molecular packing. A result, in the crystal packing, C–H⋯π (ring) and van der Waals interactions are dominant.

Table 2
Summary of short interatomic contacts (Å) in the title compound.

| Contact          | Distance | Symmetry operation |
|------------------|----------|--------------------|
| Br⋯H10           | 2.96     | 1 – x, 1+y, 1+z    |
| Br⋯C12           | 3.598    | 1 – x, 1+y, 1+z    |
| C9⋯C8            | 3.409    | 1 – x, 1+y, 1+z    |
| H9⋯H7            | 2.45     | x, 1/2 – y, 1/2 + z|
| H11⋯H20B         | 2.35     | x, 1+y, z          |
| C15⋯H21C         | 2.80     | x, 1/2 – y, 1/2 + z|
| H22B⋯C18         | 3.07     | –x, 1+y, 1+z       |
| H21B⋯H22B        | 2.51     | –x, 1+y, 1+z       |

4. Database survey
A search of the Cambridge Structural Database (CSD, Version 5.42, update of September 2021; Groom et al., 2016) for similar structures with a 1,3-oxazolidine ring showed that the five most closely related to the title compound are (S)-5-chloro-N-[(2-oxo-3-[4-(3-oxomorpholin-4-yl)phenyl]-oxazolidin-5-yl)methyl]-thiophene-2-carboxamide [(I): Shen et al., 2018], 2,2-dichloro-1-(2-phenyl-1,3-oxazolidin-3-yl)-ethanone [(II): Ye et al., 2010], (4-benzyl-2-oxo-1,3-oxazolidin-5-yl)-methyl methanesulfonate [(III): Cunico et al., 2010], 2-bromo-4-(3,4-dimethyl-1,3-oxazolidin-2-yl)-6-methoxyphenol [(IV): Hariono et al., 2012] and (R)-2-phenoxy-1-(4-phenyl-2-sulfanylidene-1,3-oxazolidin-3-yl)ethanone [(V): Caracelli et al., 2011].

In the crystal of (I), classical N–H⋯O hydrogen bonds and weak C–H⋯O hydrogen bonds link the molecules into a three-dimensional supramolecular architecture. In (II), molecules are linked by weak intermolecular C–H⋯O hydrogen bonds, forming one-dimensional chains. In the crystal of (III), N–H⋯O hydrogen bonds, involving one of the sulfur-bound oxo groups as acceptor, lead to the formation of supramolecular chains along the b-axis direction. These
chains are reinforced by C—H···O contacts, with the carbonyl O atom accepting three such interactions. In (IV), adjacent molecules are connected via O—H···O and C—H···O hydrogen bonds and C—H···π interactions into a zigzag chain along the b-axis direction. In (V), molecules are linked into supramolecular arrays two molecules thick in the bc plane through C—H···O, C—H···S and C—H···π interactions.

5. Synthesis and crystallization

The title compound was synthesized using our recently reported procedure (Khalilov, 2021), and colorless needle-like crystals were obtained upon recrystallization from an ethanol/water solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All C-bound H atoms were placed at calculated positions and refined using a riding model, with C—H = 0.95 to 1.00 Å, and with U(eq)(H) = 1.2 or 1.5U(eq)(C). The hydroxyl H atom was found in a difference-Fourier map and was refined freely.

Acknowledgements

Authors’ contributions are as follows. Conceptualization, ANK and IGM; methodology, ANK and IGM; investigation, ANK, MA and EAF; writing (original draft), MA and ANK; writing (review and editing of the manuscript), MA and ANK; visualization, MA, SOY, ANK and IGM; funding acquisition, VNK, AB and ANK; resources, AB, VNK and EAF; supervision, ANK and MA.

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Table 3

| Crystal data | Chemical formula | C₂₀H₂₄BrNO₂ |
|--------------|------------------|-------------|
| System       | M₀               | 390.30      |
| Space group  | Monoclinic, P2₁/c |             |
| Temperature  | (K)              | 100         |
| a, b, c (Å)  |                  | 21.1019 (3), 9.01359 (11) |
| β (°)        |                  | 96.1425 (11) |
| Volume (Å³)  |                  | 1898.66 (4)  |
| Z            |                  | 4           |
| Radiation type |                  | Cu Kα      |
| µ (mm⁻¹)     |                  | 3.03        |

Data collection

Diffractometer: XtaLAB Synergy, Dualflex, HyPix
Absorption correction: Multi-scan (CrysAlis PRO; Rigaku OD, 2021)

Refinement

Tₘᵢₙ, Tₘₐₓ | 0.424, 0.882 |
No of measured, independent and observed [F > 2σ(F)] | 4096 |
R(Fw) | 0.034 |
S | 1.07 |
No of parameters | 225 |
H-atom treatment: H atoms treated by a mixture of independent and constrained refinement |

Δρₘₐₓ | 0.58, −0.60 |
Δρₘᵦₜₜ (e Å⁻³) | |

Computor programs: CrysAlis PRO (Rigaku OD, 2021), SHELXT (Sheldrick, 2015a, b), SHELXL2018 (Sheldrick, 2015b), ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2020).

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Crystal structure and Hirshfeld surface analysis of 4-bromo-2-[3-methyl-5-(2,4,6-trimethylbenzyl)oxazolidin-2-yl]phenol

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Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2021); cell refinement: CrysAlis PRO (Rigaku OD, 2021); data reduction: CrysAlis PRO (Rigaku OD, 2021); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2020).

4-Bromo-2-[3-methyl-5-(2,4,6-trimethylbenzyl)oxazolidin-2-yl]phenol

Crystal data

C_{20}H_{24}BrNO_2

Mr = 390.30

Monoclinic, P2_{1}/c

a = 21.1019 (3) Å

b = 9.01359 (11) Å

C = 10.03985 (11) Å

β = 96.1425 (11)°

V = 1898.66 (4) Å³

Z = 4

F(000) = 808

D_x = 1.365 Mg m⁻³

Cu Kα radiation, λ = 1.54184 Å

Cell parameters from 13703 reflections

θ = 2.1–78.6°

μ = 3.03 mm⁻¹

T = 100 K

Needle, colourless

0.32 × 0.04 × 0.03 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer

Radiation source: micro-focus sealed X-ray tube

φ and ω scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2021)

T_{min} = 0.424, T_{max} = 0.882

21431 measured reflections

4096 independent reflections

3783 reflections with I > 2σ(I)

R_{int} = 0.043

θ_{max} = 79.6°, θ_{min} = 2.1°

h = −25→26

k = −11→11

l = −12→10

Refinement

Refinement on F^2

Least-squares matrix: full

R[F^2 > 2σ(F^2)] = 0.033

wR(F^2) = 0.096

S = 1.07

4096 reflections

225 parameters

0 restraints

Primary atom site location: difference Fourier map

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

Acta Cryst. (2022). E78, 695-698
\[ w = \frac{1}{\sigma^2(F^2_o) + (0.055P)^2 + 1.11P} \]
where \[ P = \frac{(F^2_o + 2F^2_c)}{3} \]
\[(\Delta/\sigma)_{\text{max}} = 0.001\]

**Special details**

**Experimental.** CrysAlisPro 1.171.41.117a (Rigaku OD, 2021) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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

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

|     | x      | y      | z      | Uiso */Ueq |
|-----|--------|--------|--------|-----------|
| Br1 | 0.54220 (2) | 0.31515 (2) | 0.43735 (2) | 0.02813 (9) |
| O1  | 0.27633 (7)  | 0.25150 (17) | 0.58702 (14) | 0.0298 (3)  |
| C2  | 0.32957 (9)  | 0.1726 (2)  | 0.65118 (19) | 0.0232 (4)  |
| H2  | 0.3517       | 0.2334      | 0.7256      | 0.028*      |
| N3  | 0.30119 (8)  | 0.03941 (18) | 0.70533 (15) | 0.0240 (3)  |
| C4  | 0.24396 (10) | 0.0998 (2)  | 0.7578 (2)  | 0.0286 (4)  |
| H4A | 0.2548       | 0.1518      | 0.8441      | 0.034*      |
| H4B | 0.2124       | 0.0210      | 0.7696      | 0.034*      |
| C5  | 0.21970 (10) | 0.2075 (2)  | 0.6467 (2)  | 0.0275 (4)  |
| H5  | 0.1901       | 0.1541      | 0.5785      | 0.033*      |
| C6  | 0.37483 (9)  | 0.1367 (2)  | 0.54907 (18) | 0.0226 (4)  |
| C7  | 0.42805 (9)  | 0.2251 (2)  | 0.53991 (18) | 0.0235 (4)  |
| H7  | 0.4364       | 0.3066      | 0.5991      | 0.028*      |
| C8  | 0.46904 (9)  | 0.1942 (2)  | 0.44404 (19) | 0.0229 (4)  |
| C9  | 0.45780 (9)  | 0.0753 (2)  | 0.35676 (18) | 0.0238 (4)  |
| H9  | 0.4865       | 0.0541      | 0.2925      | 0.029*      |
| C10 | 0.40439 (10) | −0.0118 (2) | 0.36452 (18) | 0.0255 (4)  |
| H10 | 0.3961       | −0.0925     | 0.3043      | 0.031*      |
| C11 | 0.36252 (9)  | 0.0175 (2)  | 0.45995 (18) | 0.0237 (4)  |
| O11 | 0.31123 (7)  | −0.07205 (17) | 0.46493 (15) | 0.0287 (3)  |
| H11 | 0.2980 (17)  | −0.053 (4)  | 0.536 (4)   | 0.050 (9)*  |
| C12 | 0.34457 (10) | −0.0365 (2) | 0.8069 (2)  | 0.0295 (4)  |
| H12A| 0.3823       | −0.0707     | 0.7665      | 0.044*      |
| H12B| 0.3228       | −0.1218     | 0.8418      | 0.044*      |
| H12C| 0.3577       | 0.0323      | 0.8803      | 0.044*      |
| C13 | 0.18595 (10) | 0.3429 (2)  | 0.6965 (2)  | 0.0293 (4)  |
| H13A| 0.1502       | 0.3093      | 0.7453      | 0.035*      |
| H13B| 0.2162       | 0.3982      | 0.7606      | 0.035*      |
| C14 | 0.16029 (10) | 0.4466 (2)  | 0.5851 (2)  | 0.0288 (4)  |
| C15 | 0.19383 (11) | 0.5761 (2)  | 0.5574 (2)  | 0.0301 (4)  |
| C16 | 0.16792 (12) | 0.6723 (3)  | 0.4563 (2)  | 0.0361 (5)  |
| H16 | 0.1904       | 0.7603      | 0.4389      | 0.043*      |
| C17 | 0.11055 (12) | 0.6426 (3)  | 0.3812 (3)  | 0.0430 (6)  |
| C18 | 0.07858 (11) | 0.5135 (4)  | 0.4079 (3)  | 0.0452 (6)  |
|   | U¹¹        | U¹²       | U¹³       | U¹²       | U¹³       | U¹³       |
|---|------------|-----------|-----------|-----------|-----------|-----------|
| Br1| 0.02612 (13)| 0.02966 (14)| 0.02922 (14)| −0.00322 (7)| 0.00584 (9)| 0.00477 (7)|
| O1 | 0.0269 (7)  | 0.0344 (8) | 0.0296 (7) | 0.0054 (6) | 0.0103 (6) | 0.0108 (6) |
| C2 | 0.0242 (9)  | 0.0241 (9) | 0.0216 (8) | −0.0010 (7)| 0.0035 (7) | 0.0011 (7) |
| N3 | 0.0258 (8)  | 0.0261 (8) | 0.0201 (7) | −0.0015 (6)| 0.0024 (6) | 0.0029 (6) |
| C4 | 0.0291 (9)  | 0.0332 (10)| 0.0245 (9) | −0.0019 (8)| 0.0076 (7) | 0.0037 (8) |
| C5 | 0.0270 (10) | 0.0315 (10)| 0.0249 (9) | −0.0003 (8)| 0.0068 (7) | 0.0021 (8) |
| C6 | 0.0254 (9)  | 0.0250 (9) | 0.0173 (8) | 0.0018 (7) | 0.0018 (6) | 0.0021 (7) |
| C7 | 0.0269 (9)  | 0.0231 (8) | 0.0201 (8) | 0.0005 (7) | 0.0007 (7) | 0.0015 (7) |
| C8 | 0.0223 (9)  | 0.0250 (9) | 0.0212 (9) | −0.0002 (7)| 0.0014 (7) | 0.0040 (7) |
| C9 | 0.0257 (9)  | 0.0273 (9) | 0.0183 (8) | 0.0048 (7) | 0.0018 (6) | 0.0014 (7) |
| C10| 0.0296 (9)  | 0.0266 (9) | 0.0197 (8) | 0.0039 (8) | 0.0005 (7) | −0.0025 (7)|
| C11| 0.0260 (9)  | 0.0238 (9) | 0.0209 (8) | −0.0015 (7)| 0.0002 (7) | 0.0039 (7) |
| O11| 0.0297 (7)  | 0.0317 (8) | 0.0249 (7) | −0.0075 (6)| 0.0040 (6) | −0.0043 (6)|
| C12| 0.0347 (10)| 0.0290 (10)| 0.0239 (9) | 0.0027 (8) | −0.0009 (8)| 0.0043 (8) |
| C13| 0.0312 (10)| 0.0322 (10)| 0.0260 (10)| 0.0005 (8) | 0.0093 (8) | 0.0018 (8) |
| C14| 0.0282 (9)  | 0.0335 (10)| 0.0264 (9) | 0.0076 (8) | 0.0109 (7) | 0.0004 (8) |
| C15| 0.0369 (11)| 0.0319 (10)| 0.0231 (9) | 0.0056 (8) | 0.0102 (8) | −0.0007 (8)|
| C16| 0.0421 (13)| 0.0376 (12)| 0.0314 (11)| 0.0092 (9) | 0.0167 (10)| 0.0062 (9) |
| C17| 0.0364 (12)| 0.0587 (15)| 0.0361 (12)| 0.0159 (11)| 0.0142 (10)| 0.0169 (11)|
| C18| 0.0252 (10)| 0.0668 (17)| 0.0435 (13)| 0.0095 (11)| 0.0032 (9) | 0.0111 (12)|
| C19| 0.0240 (9)  | 0.0471 (13)| 0.0392 (11)| 0.0059 (9) | 0.0072 (8) | 0.0041 (10)|
| C20| 0.0515 (14)| 0.0358 (12)| 0.0306 (11)| −0.0086 (10)| 0.0039 (10) | −0.0001 (9) |
| C21| 0.0446 (15)| 0.094 (3) | 0.0574 (17) | 0.0211 (17) | 0.0119 (13) | 0.0422 (19) |
| C22| 0.0265 (11)| 0.0609 (17)| 0.0689 (18) | −0.0046 (12)| 0.0016 (11) | 0.0095 (15)|

**Geometric parameters (Å, °)**

|   | C8       | H12B     | C12       | H12C     | C13       | C14       |
|---|---------|----------|-----------|----------|-----------|-----------|
| Br1—C8 | 1.9019 (19)|          | C12—H12B | 0.9800   |          |           |
| O1—C2  | 1.424 (2)  |          | C12—H12C | 0.9800   |          |           |
| O1—C5  | 1.448 (2)  |          | C13—C14  | 1.513 (3)|          |           |
| Bond       | Distance (Å) | Bond    | Distance (Å) |
|------------|--------------|---------|--------------|
| C2—N3      | 1.472 (2)    | C13—H13A| 0.9900       |
| C2—C6      | 1.509 (3)    | C13—H13B| 0.9900       |
| C2—H2      | 1.0000       | C14—C19 | 1.404 (3)    |
| N3—C12     | 1.465 (2)    | C14—C15 | 1.407 (3)    |
| N3—C4      | 1.472 (3)    | C15—C16 | 1.401 (3)    |
| C4—C5      | 1.525 (3)    | C15—C20 | 1.505 (3)    |
| C4—H4A     | 0.9900       | C16—C17 | 1.382 (4)    |
| C4—H4B     | 0.9900       | C16—H16 | 0.9500       |
| C5—C13     | 1.524 (3)    | C17—C18 | 1.385 (4)    |
| C5—H5      | 1.0000       | C17—C21 | 1.513 (4)    |
| C6—C7      | 1.388 (3)    | C18—C19 | 1.399 (4)    |
| C6—C11     | 1.404 (3)    | C18—H18 | 0.9500       |
| C7—C8      | 1.389 (3)    | C19—C22 | 1.510 (4)    |
| C7—H7      | 0.9500       | C20—H20A| 0.9800       |
| C8—C9      | 1.388 (3)    | C20—H20B| 0.9800       |
| C9—C10     | 1.383 (3)    | C20—H20C| 0.9800       |
| C9—H9      | 0.9500       | C21—H21A| 0.9800       |
| C10—C11    | 1.396 (3)    | C21—H21B| 0.9800       |
| C10—H10    | 0.9500       | C21—H21C| 0.9800       |
| C11—O11    | 1.356 (2)    | C22—H22A| 0.9800       |
| O11—H11    | 0.81 (4)     | C22—H22B| 0.9800       |
| C12—H12A   | 0.9800       | C22—H22C| 0.9800       |

C2—O1—C5  108.79 (14)  H12A—C12—H12C  109.5
O1—C2—N3  104.01 (15)  H12B—C12—H12C  109.5
O1—C2—C6  109.02 (15)  C14—C13—C5     113.25 (17)
N3—C2—C6  112.83 (16)  C14—C13—H13A  108.9
O1—C2—H2  110.3        C5—C13—H13A  108.9
N3—C2—H2  110.3        C14—C13—H13B 108.9
C6—C2—H2  110.3        C5—C13—H13B 108.9
C12—N3—C2 112.92 (16)  H13A—C13—H13B 107.7
C12—N3—C4 113.51 (15)  C19—C14—C15  119.3 (2)
C2—N3—C4  102.26 (15)  C19—C14—C13  120.0 (2)
N3—C4—C5  101.41 (15)  C15—C14—C13  120.7 (2)
N3—C4—H4A | 111.5        C16—C15—C20  118.9 (2)
C5—C4—H4A | 111.5        C14—C15—C20  121.7 (2)
N3—C4—H4B | 111.5        C17—C16—C15  121.8 (2)
C5—C4—H4B | 111.5        C17—C16—C15  121.8 (2)
H4A—C4—H4B| 109.3        C17—C16—H16  119.1
O1—C5—C13 | 110.61 (17)  C15—C16—H16  119.1
O1—C5—C4  | 104.45 (16)  C16—C17—C18  118.2 (2)
C13—C5—C4 | 113.71 (17)  C16—C17—C21  120.5 (3)
O1—C5—H5  | 109.3        C18—C17—C21  121.3 (3)
C13—C5—H5 | 109.3        C17—C18—C19  122.1 (2)
C4—C5—H5  | 109.3        C17—C18—H18  119.0
C7—C6—C11 | 119.50 (17)  C19—C18—H18  119.0
C7—C6—C2  | 119.82 (17)  C18—C19—C14  119.2 (2)
C11—C6—C2 | 120.64 (17)  C18—C19—C22  118.8 (2)
| Bond  | Angle (°) (E) | Bond  | Angle (°) (E) | Bond  | Angle (°) (E) |
|-------|--------------|-------|--------------|-------|--------------|
| C6—C7—C8 | 119.94 (18) | C14—C19—C22 | 122.0 (2) |
| C6—C7—H7 | 120.0 | C15—C20—H20A | 109.5 |
| C8—C7—H7 | 120.0 | C15—C20—H20B | 109.5 |
| C9—C8—C7 | 121.00 (18) | H20A—C20—H20B | 109.5 |
| C9—C8—Br1 | 119.54 (14) | C15—C20—H20C | 109.5 |
| C7—C8—Br1 | 119.46 (15) | H20A—C20—H20C | 109.5 |
| C10—C9—C8 | 119.20 (17) | H20B—C20—H20C | 109.5 |
| C10—C9—H9 | 120.4 | C17—C21—H21A | 109.5 |
| C8—C9—H9 | 120.4 | C17—C21—H21B | 109.5 |
| C9—C10—C11 | 120.70 (18) | H21A—C21—H21B | 109.5 |
| C9—C10—H10 | 119.7 | C17—C21—H21C | 109.5 |
| C11—C10—H10 | 119.7 | H21A—C21—H21C | 109.5 |
| O11—C11—C10 | 118.61 (18) | H21B—C21—H21C | 109.5 |
| O11—C11—C6 | 121.74 (17) | C19—C22—H22A | 109.5 |
| C10—C11—C6 | 119.65 (18) | C19—C22—H22B | 109.5 |
| C11—O11—H11 | 105 (2) | C19—C22—H22C | 109.5 |
| N3—C12—H12A | 109.5 | C19—C22—H22C | 109.5 |
| N3—C12—H12B | 109.5 | C19—C22—H22C | 109.5 |
| H12A—C12—H12B | 109.5 | C19—C22—H22C | 109.5 |
| N3—C12—H12C | 109.5 | C19—C22—H22C | 109.5 |

C5—O1—C2—N3 | 23.8 (2) | C7—C6—C11—O11 | 179.93 (17) |
| C5—O1—C2—C6 | 144.39 (16) | C2—C6—C11—O11 | −2.2 (3) |
| O1—C2—N3—C12 | −163.70 (15) | C7—C6—C11—C10 | 0.9 (3) |
| C6—C2—N3—C12 | 78.3 (2) | C2—C6—C11—C10 | 178.71 (17) |
| O1—C2—N3—C4 | −41.36 (18) | O1—C5—C13—C14 | 64.6 (2) |
| C6—C2—N3—C4 | −159.35 (16) | C4—C5—C13—C14 | −178.21 (18) |
| C12—N3—C4—C5 | 163.78 (17) | C5—C13—C14—C19 | 80.4 (2) |
| C2—N3—C4—C5 | 41.84 (18) | C5—C13—C14—C15 | −99.8 (2) |
| C2—O1—C5—C13 | 125.28 (18) | C19—C14—C15—C16 | 1.7 (3) |
| C2—O1—C5—C4 | 2.6 (2) | C13—C14—C15—C16 | −178.05 (18) |
| N3—C4—C5—O1 | −27.6 (2) | C19—C14—C15—C20 | −178.2 (2) |
| N3—C4—C5—C13 | −148.32 (17) | C13—C14—C15—C20 | 2.1 (3) |
| O1—C2—C6—C7 | 98.9 (2) | C14—C15—C16—C17 | −1.0 (3) |
| N3—C2—C6—C7 | −146.13 (17) | C20—C15—C16—C17 | 178.9 (2) |
| O1—C2—C6—C11 | −79.0 (2) | C15—C16—C17—C18 | −0.1 (4) |
| N3—C2—C6—C11 | 36.0 (2) | C15—C16—C17—C21 | 179.6 (2) |
| C11—C6—C7—C8 | −0.7 (3) | C16—C17—C18—C19 | 0.5 (4) |
| C2—C6—C7—C8 | −178.59 (17) | C21—C17—C18—C19 | −179.2 (3) |
| C6—C7—C8—C9 | −0.2 (3) | C17—C18—C19—C14 | 0.2 (4) |
| C6—C7—C8—Br1 | −179.44 (14) | C17—C18—C19—C22 | 179.8 (3) |
| C7—C8—C9—C10 | 1.0 (3) | C15—C14—C19—C18 | −1.3 (3) |
| Br1—C8—C9—C10 | −179.76 (14) | C13—C14—C19—C18 | 178.4 (2) |
| C8—C9—C10—C11 | −0.9 (3) | C15—C14—C19—C22 | 179.1 (2) |
| C9—C10—C11—O11 | −179.15 (17) | C13—C14—C19—C22 | −1.1 (3) |
| C9—C10—C11—C6 | −0.1 (3) | C13—C14—C19—C22 | −1.1 (3) |
Hydrogen-bond geometry (Å, °)

Cg2 and Cg3 are the centroids of the 4-bromophenol (C6–C11) and 1,3,5-trimethylbenzene (C14–C19) rings, respectively.

| D—H···A  | D—H  | H···A  | D···A  | D—H···A |
|----------|-------|--------|--------|---------|
| O11—H11···N3  | 0.81 (4) | 1.89 (4) | 2.644 (2) | 155 (3) |
| C4—H4A···O1i  | 0.99  | 2.58  | 3.564 (2) | 171 |
| C20—H20B···O11ii  | 0.98  | 2.57  | 3.548 (3) | 173 |
| C20—H20C···O1  | 0.98  | 2.55  | 3.332 (3) | 136 |
| C2—H2···Cg2i  | 1.00  | 2.91  | 3.908 (2) | 176 |
| C4—H4B···Cg3i  | 0.99  | 2.88  | 3.622 (2) | 132 |
| C21—H21C···Cg3iii | 0.98  | 2.93  | 3.723 (4) | 138 |

Symmetry codes: (i) x, −y+1/2, z+1/2; (ii) x, y+1, z; (iii) x, −y+3/2, z−1/2.