

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2-(1-Adamantyl)-4-bromoanisole at 123 K

Xiang-Wei Cheng

Zhejiang Police College Experience Center, Zhejiang Police College, Hangzhou 310053, People's Republic of China
Correspondence e-mail: zpccxw@126.com

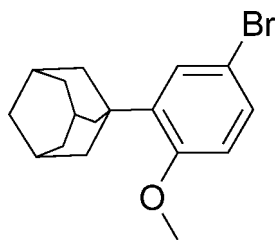
Received 26 May 2008; accepted 2 June 2008

Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.040; wR factor = 0.107; data-to-parameter ratio = 15.0.

In the title compound [systematic name: 2-(1-adamantyl)-4-bromo-1-methoxybenzene], $\text{C}_{17}\text{H}_{21}\text{BrO}$, two weak intramolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds influence the molecular conformation. The crystal packing exhibits $\text{C}-\text{H}\cdots\pi$ interactions, with a relatively short intermolecular $\text{C}\cdots\text{C}_g$ contact of 3.568 (5) Å, where C_g is the centroid of the benzene ring. The crystal studied exhibited inversion twinning.

Related literature

For related crystal structures, see: Nordman & Schmitkons (1965); Amoureux *et al.* (1980); Amoureux & Bee (1980); Pouwer *et al.* (2007). For general background, see: Chomienne *et al.* (1994). For synthesis, see: Antibes *et al.* (1988).



Experimental

Crystal data

$\text{C}_{17}\text{H}_{21}\text{BrO}$
 $M_r = 321.25$
Orthorhombic, $P2_12_12_1$
 $a = 7.3815$ (11) Å

$b = 13.2067$ (19) Å
 $c = 15.067$ (2) Å
 $V = 1468.8$ (4) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 2.79$ mm⁻¹

$T = 123$ (2) K
 $0.30 \times 0.26 \times 0.25$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.438$, $T_{\max} = 0.492$

12697 measured reflections
2580 independent reflections
2279 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.106$
 $S = 0.86$
2580 reflections
172 parameters
H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.51$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.59$ e Å⁻³
Absolute structure: Flack (1983), with 1072 Friedel pairs
Flack parameter: 0.340 (15)

Table 1

Hydrogen-bond geometry (Å, °).

 C_g is the centroid of the benzene ring.

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{C9}-\text{H9A}\cdots\text{O1}$ | 0.99 | 2.35 | 3.003 (5) | 123 |
| $\text{C17}-\text{H17B}\cdots\text{O1}$ | 0.99 | 2.35 | 3.004 (4) | 123 |
| $\text{C4}-\text{H4}\cdots\text{C}_g^i$ | 0.95 | 2.66 | 3.568 (5) | 161 |

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

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

The author acknowledges financial support from Zhejiang Police College, China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2416).

References

- Amoureux, J. P. & Bee, M. (1980). *Acta Cryst.* **B36**, 2636–2642.
Amoureux, J. P., Bee, M. & Damien, J. C. (1980). *Acta Cryst.* **B36**, 2633–2636.
Antibes, B. S., Grasse, J. E. & Nice, J. B. (1988). US Patent 4 717 720.
Bruker (2002). *SADABS*, *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chomienne, C., Ballerini, P., Balitrand, N., Amor, M., Bernard, J. F., Boivin, P., Daniel, M. T., Berger, R., Castaigne, S. & Degos, L. (1994). *Lancet ii*, **344**, 746–747.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Nordman, C. E. & Schmitkons, D. L. (1965). *Acta Cryst.* **18**, 764–767.
Pouwer, R. H., Harper, J. B., Vyakaranam, K., Michl, J., Williams, C. M., Jessen, C. H. & Bernhardt, P. V. (2007). *Eur. J. Org. Chem.* pp. 241–248.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

Acta Cryst. (2008). E64, o1212 [doi:10.1107/S1600536808016772]

2-(1-Adamantyl)-4-bromoanisole at 123 K**Xiang-Wei Cheng****S1. Comment**

The molecule of adamantane has high symmetry, Td, and adamantane crystallizes in the highest space group, Fm $\bar{3}$ m (Nordman & Schmitkons, 1965; Amoureux *et al.*, 1980; Amoureux & Bee, 1980). In view of the development of crystal structure systems and the design of organic crystals, it is of interest to study the effects of some simple functional substituents having hydrogen-bonding ability on the symmetry of the crystals of adamantane derivatives. The title compound is an important intermediate of adapalene, which is a new synthetic retinoid of the naphthoic acid series, and was developed for the topical treatment of *Acne vulgaris* and prevention of some forms of cancer, including the acute promyelocytic leukaemia (Chomienne *et al.*, 1994). Here we report the crystal structure of the title compound (Fig. 1).

In the title compound, the structural parameters of the adamantyl are closely comparable to those found in reported molecule (Pouwer *et al.*, 2007). The C atoms of the adamantine moiety have Csp³ hybridized orbitals, with C—C—C angles in the range 106.6 (4)–111.6 (4)°. The methoxy group and bromo group are coplanar with the benzene ring.

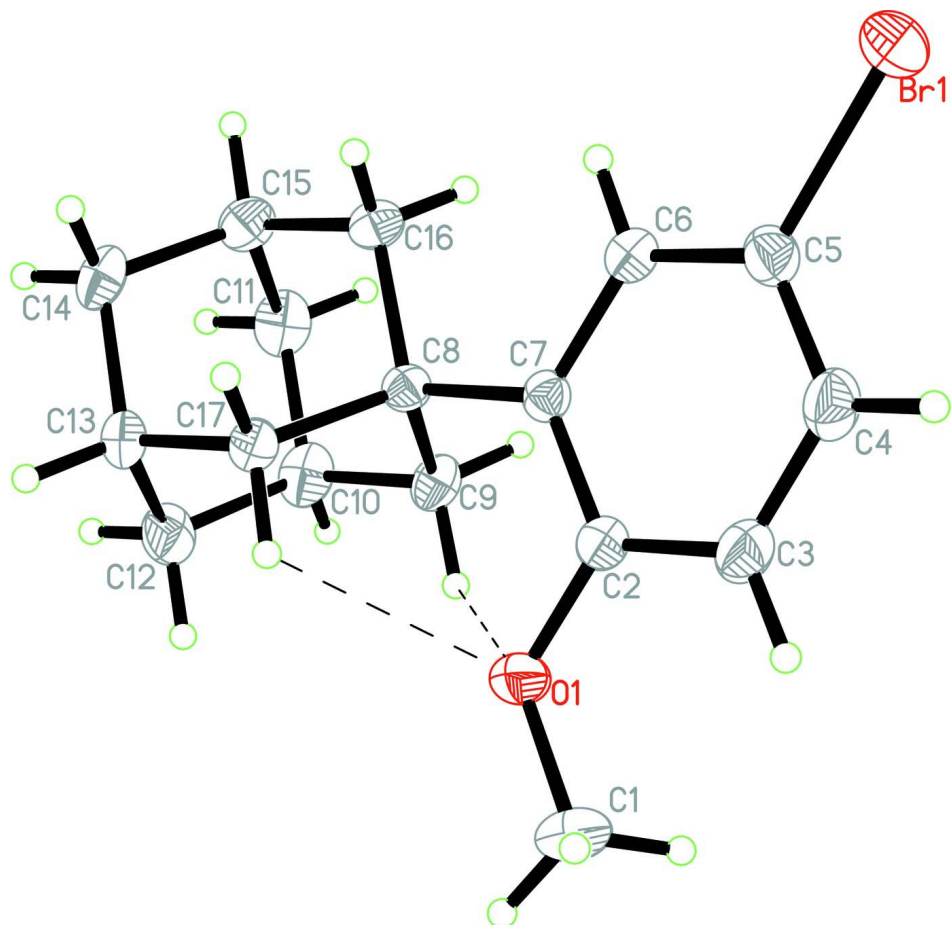
It is of note that the O atoms of the methoxy group participates in formation of two intramolecular C—H \cdots O interactions, and both intramolecular C—H \cdots O interactions are nearly the same (Table.1). Meanwhile, in the crystal structure, an intermolecular C—H \cdots π interaction involving the benzene ring (with the centroid Cg) is observed (Table 1).

S2. Experimental

The title compound was prepared according to the literature method (Antibes *et al.*, 1988). Crystals suitable for X-ray analysis were obtained by slow evaporation of an 2-propanol solution at 295 K.

S3. Refinement

H atoms were positioned geometrically (C—H = 0.95–0.99 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$.

**Figure 1**

Molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atomic numbering.

2-(1-adamantyl)-4-bromomethoxybenzene

Crystal data

$C_{17}H_{21}BrO$

$M_r = 321.25$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 7.3815$ (11) Å

$b = 13.2067$ (19) Å

$c = 15.067$ (2) Å

$V = 1468.8$ (4) Å³

$Z = 4$

$F(000) = 664$

$D_x = 1.453$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2580 reflections

$\theta = 2-25.0^\circ$

$\mu = 2.79$ mm⁻¹

$T = 123$ K

Block, colourless

$0.30 \times 0.26 \times 0.25$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2002)

$T_{\min} = 0.438$, $T_{\max} = 0.492$

12697 measured reflections

2580 independent reflections

2279 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$
 $\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.1^\circ$
 $h = -8 \rightarrow 8$

$k = -15 \rightarrow 14$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.106$
 $S = 0.86$
 2580 reflections
 172 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
 $w = 1/[\sigma^2(F_o^2) + (0.0694P)^2 + 1.9231P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.51 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.59 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), with 1072
 Friedel pairs
 Absolute structure parameter: 0.340 (15)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|-------------|--------------|----------------------------------|
| Br1 | 0.49661 (7) | 0.52137 (3) | 0.02595 (3) | 0.05940 (19) |
| O1 | 0.3914 (4) | 0.9390 (2) | 0.17914 (19) | 0.0495 (7) |
| C8 | 0.1674 (5) | 0.7808 (3) | 0.2493 (2) | 0.0306 (8) |
| C17 | 0.2606 (5) | 0.8175 (3) | 0.3350 (2) | 0.0334 (8) |
| H17A | 0.3496 | 0.7662 | 0.3548 | 0.040* |
| H17B | 0.3269 | 0.8812 | 0.3228 | 0.040* |
| C2 | 0.4172 (5) | 0.8448 (3) | 0.1434 (2) | 0.0363 (9) |
| C11 | -0.2109 (5) | 0.7762 (4) | 0.3180 (3) | 0.0512 (11) |
| H11A | -0.2768 | 0.7516 | 0.2650 | 0.061* |
| H11B | -0.2999 | 0.7871 | 0.3662 | 0.061* |
| C12 | -0.0155 (7) | 0.9143 (3) | 0.3787 (3) | 0.0495 (10) |
| H12A | 0.0472 | 0.9785 | 0.3646 | 0.059* |
| H12B | -0.1034 | 0.9275 | 0.4270 | 0.059* |
| C9 | 0.0205 (6) | 0.8587 (3) | 0.2208 (2) | 0.0403 (9) |
| H9A | 0.0790 | 0.9237 | 0.2052 | 0.048* |
| H9B | -0.0441 | 0.8333 | 0.1677 | 0.048* |
| C7 | 0.3094 (5) | 0.7656 (3) | 0.1763 (2) | 0.0307 (8) |
| C14 | 0.0274 (6) | 0.7365 (3) | 0.4301 (2) | 0.0439 (10) |
| H14A | -0.0610 | 0.7469 | 0.4786 | 0.053* |
| H14B | 0.1175 | 0.6858 | 0.4499 | 0.053* |

| | | | | |
|------|-------------|------------|------------|-------------|
| C16 | 0.0668 (5) | 0.6818 (3) | 0.2726 (3) | 0.0374 (9) |
| H16A | 0.0037 | 0.6562 | 0.2191 | 0.045* |
| H16B | 0.1559 | 0.6300 | 0.2913 | 0.045* |
| C6 | 0.3380 (5) | 0.6697 (3) | 0.1394 (2) | 0.0346 (8) |
| H6 | 0.2673 | 0.6141 | 0.1594 | 0.042* |
| C4 | 0.5731 (6) | 0.7319 (4) | 0.0433 (3) | 0.0469 (10) |
| H4 | 0.6633 | 0.7200 | -0.0005 | 0.056* |
| C1 | 0.4924 (7) | 1.0210 (3) | 0.1470 (3) | 0.0544 (10) |
| H1A | 0.4601 | 1.0823 | 0.1800 | 0.082* |
| H1B | 0.4660 | 1.0309 | 0.0839 | 0.082* |
| H1C | 0.6219 | 1.0070 | 0.1547 | 0.082* |
| C3 | 0.5459 (6) | 0.8275 (3) | 0.0770 (3) | 0.0472 (11) |
| H3 | 0.6155 | 0.8825 | 0.0549 | 0.057* |
| C15 | -0.0708 (5) | 0.6981 (3) | 0.3467 (3) | 0.0428 (9) |
| H15 | -0.1328 | 0.6326 | 0.3604 | 0.051* |
| C13 | 0.1216 (5) | 0.8356 (3) | 0.4087 (2) | 0.0380 (9) |
| H13 | 0.1854 | 0.8607 | 0.4629 | 0.046* |
| C10 | -0.1150 (6) | 0.8754 (4) | 0.2966 (3) | 0.0472 (11) |
| H10 | -0.2068 | 0.9267 | 0.2777 | 0.057* |
| C5 | 0.4671 (5) | 0.6541 (3) | 0.0743 (2) | 0.0400 (9) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|---------------|
| Br1 | 0.0757 (3) | 0.0442 (3) | 0.0583 (3) | 0.0164 (3) | 0.0146 (3) | -0.00538 (19) |
| O1 | 0.0647 (19) | 0.0356 (16) | 0.0483 (16) | -0.0131 (14) | 0.0155 (15) | -0.0039 (14) |
| C8 | 0.0306 (19) | 0.030 (2) | 0.0313 (19) | 0.0015 (15) | 0.0001 (14) | 0.0022 (15) |
| C17 | 0.0330 (18) | 0.038 (2) | 0.0294 (18) | -0.0019 (16) | -0.0002 (15) | 0.0021 (16) |
| C2 | 0.041 (2) | 0.037 (2) | 0.0314 (18) | -0.0044 (18) | 0.0016 (16) | 0.0021 (16) |
| C11 | 0.029 (2) | 0.071 (3) | 0.053 (3) | 0.001 (2) | 0.0018 (19) | 0.000 (2) |
| C12 | 0.056 (2) | 0.050 (3) | 0.043 (2) | 0.014 (2) | 0.009 (2) | -0.0064 (17) |
| C9 | 0.040 (2) | 0.045 (2) | 0.0352 (17) | 0.006 (2) | -0.0033 (17) | 0.0085 (15) |
| C7 | 0.0307 (17) | 0.034 (2) | 0.0274 (17) | -0.0012 (15) | -0.0032 (14) | 0.0003 (15) |
| C14 | 0.040 (2) | 0.057 (3) | 0.0337 (18) | 0.005 (2) | 0.0062 (17) | 0.0110 (17) |
| C16 | 0.036 (2) | 0.034 (2) | 0.043 (2) | -0.0045 (16) | 0.0017 (15) | 0.0047 (18) |
| C6 | 0.035 (2) | 0.037 (2) | 0.0327 (18) | -0.0003 (16) | 0.0008 (14) | 0.0045 (16) |
| C4 | 0.045 (2) | 0.057 (3) | 0.039 (2) | -0.002 (2) | 0.0116 (17) | -0.0006 (19) |
| C1 | 0.056 (2) | 0.040 (2) | 0.068 (3) | -0.010 (3) | 0.000 (2) | 0.0100 (19) |
| C3 | 0.050 (3) | 0.051 (3) | 0.040 (2) | -0.013 (2) | 0.0087 (18) | 0.0027 (19) |
| C15 | 0.037 (2) | 0.046 (2) | 0.046 (2) | -0.0059 (17) | 0.0053 (17) | 0.0051 (19) |
| C13 | 0.040 (2) | 0.046 (2) | 0.0274 (18) | 0.0017 (17) | 0.0017 (16) | -0.0017 (17) |
| C10 | 0.036 (2) | 0.060 (3) | 0.046 (2) | 0.018 (2) | -0.0030 (18) | 0.007 (2) |
| C5 | 0.045 (2) | 0.040 (2) | 0.0353 (18) | 0.0066 (18) | 0.0013 (17) | -0.0023 (16) |

Geometric parameters (Å, °)

| | | | |
|--------|-----------|--------|-----------|
| Br1—C5 | 1.911 (4) | C9—H9B | 0.9900 |
| O1—C2 | 1.369 (5) | C7—C6 | 1.399 (5) |

| | | | |
|---------------|-----------|---------------|-----------|
| O1—C1 | 1.400 (5) | C14—C13 | 1.516 (6) |
| C8—C7 | 1.533 (5) | C14—C15 | 1.536 (6) |
| C8—C17 | 1.541 (5) | C14—H14A | 0.9900 |
| C8—C16 | 1.544 (5) | C14—H14B | 0.9900 |
| C8—C9 | 1.555 (5) | C16—C15 | 1.525 (6) |
| C17—C13 | 1.531 (5) | C16—H16A | 0.9900 |
| C17—H17A | 0.9900 | C16—H16B | 0.9900 |
| C17—H17B | 0.9900 | C6—C5 | 1.383 (5) |
| C2—C3 | 1.398 (5) | C6—H6 | 0.9500 |
| C2—C7 | 1.405 (5) | C4—C5 | 1.373 (6) |
| C11—C10 | 1.523 (7) | C4—C3 | 1.375 (6) |
| C11—C15 | 1.524 (6) | C4—H4 | 0.9500 |
| C11—H11A | 0.9900 | C1—H1A | 0.9800 |
| C11—H11B | 0.9900 | C1—H1B | 0.9800 |
| C12—C13 | 1.519 (6) | C1—H1C | 0.9800 |
| C12—C10 | 1.528 (6) | C3—H3 | 0.9500 |
| C12—H12A | 0.9900 | C15—H15 | 1.0000 |
| C12—H12B | 0.9900 | C13—H13 | 1.0000 |
| C9—C10 | 1.535 (6) | C10—H10 | 1.0000 |
| C9—H9A | 0.9900 | | |
| | | | |
| C2—O1—C1 | 119.5 (3) | C15—C16—C8 | 111.5 (3) |
| C7—C8—C17 | 109.7 (3) | C15—C16—H16A | 109.3 |
| C7—C8—C16 | 112.4 (3) | C8—C16—H16A | 109.3 |
| C17—C8—C16 | 106.9 (3) | C15—C16—H16B | 109.3 |
| C7—C8—C9 | 111.4 (3) | C8—C16—H16B | 109.3 |
| C17—C8—C9 | 109.6 (3) | H16A—C16—H16B | 108.0 |
| C16—C8—C9 | 106.7 (3) | C5—C6—C7 | 121.4 (4) |
| C13—C17—C8 | 110.9 (3) | C5—C6—H6 | 119.3 |
| C13—C17—H17A | 109.4 | C7—C6—H6 | 119.3 |
| C8—C17—H17A | 109.4 | C5—C4—C3 | 118.5 (4) |
| C13—C17—H17B | 109.4 | C5—C4—H4 | 120.7 |
| C8—C17—H17B | 109.4 | C3—C4—H4 | 120.7 |
| H17A—C17—H17B | 108.0 | O1—C1—H1A | 109.5 |
| O1—C2—C3 | 121.6 (4) | O1—C1—H1B | 109.5 |
| O1—C2—C7 | 117.4 (3) | H1A—C1—H1B | 109.5 |
| C3—C2—C7 | 121.0 (4) | O1—C1—H1C | 109.5 |
| C10—C11—C15 | 109.1 (3) | H1A—C1—H1C | 109.5 |
| C10—C11—H11A | 109.9 | H1B—C1—H1C | 109.5 |
| C15—C11—H11A | 109.9 | C4—C3—C2 | 120.9 (4) |
| C10—C11—H11B | 109.9 | C4—C3—H3 | 119.6 |
| C15—C11—H11B | 109.9 | C2—C3—H3 | 119.6 |
| H11A—C11—H11B | 108.3 | C11—C15—C16 | 109.9 (3) |
| C13—C12—C10 | 109.3 (3) | C11—C15—C14 | 109.2 (4) |
| C13—C12—H12A | 109.8 | C16—C15—C14 | 109.4 (3) |
| C10—C12—H12A | 109.8 | C11—C15—H15 | 109.5 |
| C13—C12—H12B | 109.8 | C16—C15—H15 | 109.5 |
| C10—C12—H12B | 109.8 | C14—C15—H15 | 109.5 |

| | | | |
|---------------|-----------|-------------|-----------|
| H12A—C12—H12B | 108.3 | C14—C13—C12 | 110.3 (3) |
| C10—C9—C8 | 110.1 (3) | C14—C13—C17 | 109.1 (3) |
| C10—C9—H9A | 109.6 | C12—C13—C17 | 109.7 (3) |
| C8—C9—H9A | 109.6 | C14—C13—H13 | 109.2 |
| C10—C9—H9B | 109.6 | C12—C13—H13 | 109.2 |
| C8—C9—H9B | 109.6 | C17—C13—H13 | 109.2 |
| H9A—C9—H9B | 108.2 | C11—C10—C12 | 109.9 (4) |
| C6—C7—C2 | 116.7 (3) | C11—C10—C9 | 109.7 (4) |
| C6—C7—C8 | 120.5 (3) | C12—C10—C9 | 109.7 (3) |
| C2—C7—C8 | 122.8 (3) | C11—C10—H10 | 109.1 |
| C13—C14—C15 | 109.1 (3) | C12—C10—H10 | 109.1 |
| C13—C14—H14A | 109.9 | C9—C10—H10 | 109.1 |
| C15—C14—H14A | 109.9 | C4—C5—C6 | 121.5 (4) |
| C13—C14—H14B | 109.9 | C4—C5—Br1 | 119.5 (3) |
| C15—C14—H14B | 109.9 | C6—C5—Br1 | 119.0 (3) |
| H14A—C14—H14B | 108.3 | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|--------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C9—H9A \cdots O1 | 0.99 | 2.35 | 3.003 (5) | 123 |
| C17—H17B \cdots O1 | 0.99 | 2.35 | 3.004 (4) | 123 |
| C4—H4 \cdots Cg ⁱ | 0.95 | 2.66 | 3.568 (5) | 161 |

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