

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Methyl (2Z)-2-bromomethyl-3-(2,4-dichlorophenyl)prop-2-enoate

K. Swaminathan,^a K. Sethusankar,^{a*} Anthonisamy Devaraj^b and Manickam Bakthadoss^b^aDepartment of Physics, RKM Vivekananda College (Autonomous), Chennai 600 004, India, and ^bDepartment of Organic Chemistry, University of Madras, Maraimalai Campus, Chennai 600 025, India

Correspondence e-mail: ksethusankar@yahoo.co.in

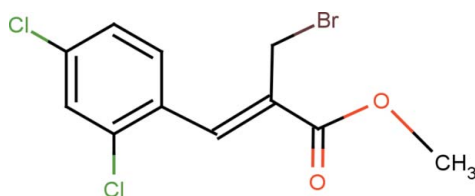
Received 27 February 2013; accepted 18 March 2013

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.037; wR factor = 0.102; data-to-parameter ratio = 25.7.

In the title compound $\text{C}_{11}\text{H}_9\text{BrCl}_2\text{O}_2$, which represents the *Z* isomer, the methylacrylate moiety is essentially planar within 0.039 (2) Å and has an extended *trans* configuration. The benzene ring makes a dihedral angle of 28.3 (1)° with the mean plane of the methylacrylate moiety. The crystal packing is characterized by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding and halogen-halogen interactions [$\text{Cl}\cdots\text{Cl} = 3.486$ (3) Å], resulting in the formation of $R_2^2(11)$ ring motifs and connecting the molecules into chains propagating along the *b* axis.

Related literature

For the uses of cinnamic acid and its derivatives, see: Xiao *et al.* (2008); De Fraine & Martin (1991). For the extended conformation of acrylate, see: Schweizer & Dunitz (1982). For a related structure, see: Karthikeyan *et al.* (2012). For graph-set notation, see: Bernstein *et al.* (1995). For type I halogen interactions, see: Johnson & Lemmerer (2012); Schmidt *et al.* (2011).



Experimental

Crystal data

 $\text{C}_{11}\text{H}_9\text{BrCl}_2\text{O}_2$
 $M_r = 323.99$
 Triclinic, $P\bar{1}$
 $a = 7.9174$ (3) Å
 $b = 8.8032$ (3) Å
 $c = 9.3585$ (3) Å

 $\alpha = 78.374$ (2)°
 $\beta = 86.599$ (2)°
 $\gamma = 73.528$ (2)°
 $V = 612.67$ (4) Å³
 $Z = 2$

 Mo $K\alpha$ radiation
 $\mu = 3.77$ mm⁻¹
 $T = 293$ K
 $0.25 \times 0.25 \times 0.20$ mm

Data collection

 Bruker Kappa APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.405$, $T_{\max} = 0.470$

 16418 measured reflections
 3748 independent reflections
 2262 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.102$
 $S = 1.00$
 3748 reflections

 146 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.59$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{C2}-\text{H2}\cdots\text{O1}^1$ | 0.93 | 2.33 | 3.238 (3) | 167 |

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

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

The authors thank Dr Babu Varghese, Senior Scientific Officer, SAIF, IIT, Chennai, India, for the data collection. KS thanks the University Grant Commission (UGC), India, for a Minor Research Project.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LD2096).

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2008). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- De Fraine, P. J. & Martin, A. (1991). US Patent No. 5 055 471.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Johnson, M. & Lemmerer, A. (2012). *Acta Cryst.* **E68**, o385.
- Karthikeyan, S., Sethusankar, K., Devaraj, A. & Bakthadoss, M. (2012). *Acta Cryst.* **E68**, o1273.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Schmidt, N., Schwarzer, A. & Weber, E. (2011). *Acta Cryst.* **E67**, o794.
- Schweizer, W. B. & Dunitz, J. D. (1982). *Helv. Chim. Acta*, **65**, 1547–1554.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Xiao, Z.-P., Fang, R.-Q., Li, H.-Q., Xue, J.-Y., Zheng, Y. & Zhu, H.-L. (2008). *Eur. J. Med. Chem.* **43**, 1828–1836.

supplementary materials

Acta Cryst. (2013). E69, o572 [doi:10.1107/S1600536813007368]

Methyl (2Z)-2-bromomethyl-3-(2,4-dichlorophenyl)prop-2-enoate

K. Swaminathan, K. Sethusankar, Anthonisamy Devaraj and Manickam Bakthadoss

Comment

Cinnamic acid and its derivatives are important compounds because of their agrochemical and medical applications (De Fraire & Martin, 1991). Also they possess significant antibacterial activities against *Staphylococcus aureus* (Xiao *et al.* 2008).

X-ray analysis established the molecular structure and atom connectivity of the title compound, as illustrated in Fig. 1. Its methylacrylate part is essentially planar with a maximum deviation of 0.0390 (24) Å for atom C8 and forms dihedral angle of 28.25 (9) ° with the phenyl ring C1–C6. The methylacrylate moiety adopts an extended conformation as evident from the torsion angle values [C7–C8–C9–O1 = 4.7 (4), C7–C8–C9–O2 = 175.2 (2), C8–C9–O2–C10 = -178.8 (2) and O1–C9–O2–C10 = 1.3 (4) °]. The reasons for the extended conformation were discussed earlier (Schweizer and Dunitz, 1982).

The phenyl ring (C1–C6) and the carbonyl group of the acrylate are (+)syn-periplanar to each other with the torsion angle of C7–C8–C9–O1 = 4.7 (4) °. The carbonyl group of the acrylate and the methyl bromide group are (-)anti-periplanar to each other with the torsion angle of C11–C8–C9–O1 = -171.8 (2) °. The least square plane of methyl bromide group forms dihedral angles of 81.44 (17) and 82.48 (15) ° with the phenyl ring and the acrylate group, respectively, being almost orthogonal to both. The chlorine atom C11 is slightly deviating from the phenyl ring plane (C1–C6) – by -0.033 (1) Å. The title compound exhibits structural similarities with an earlier reported related structure (Karthikeyan *et al.* 2012).

The crystal packing is stabilized by intermolecular C2—H2ⁱ⋯O1ⁱ hydrogen bond and halogen interaction of type I mode represented by C11ⁱ⋯C12ⁱ contact [d = 3.486 (3) Å, θ = 151.68 (6) °] which form $R_2^2(11)$ ring motifs which in turn, connect the molecules to form bands parallel to [0 1 0] (Schmidt *et al.* 2011, Johnson & Lemmerer, 2012). The symmetry code: (i) $x, -1 + y, z$. The packing view of the title compound is shown in Fig.2.

Experimental

To a stirred solution of methyl 2-((2,4-dichlorophenyl)(hydroxy)methyl) acrylate (4 mmol) in CH₂Cl₂ (15 ml), 48% aqueous HBr (0.68 ml) was added at room temperature. The reaction mixture was cooled to 273 K and then catalytic amount of concentrated H₂SO₄ was added dropwise. The reaction mixture was stirred well at room temperature for about 24 hrs. After the completion of the reaction (confirmed by TLC analysis), the reaction mixture was poured into water and the aqueous layer was extracted with ethyl acetate (3 x 10 ml). The combined organic layer was washed with brine (10 ml) and concentrated. The crude product thus obtained was purified by column chromatography (EtOAc/Hexane, 2–6%) to provide (Methyl (2Z)-2-(bromomethyl)-3-(2,4-dichlorophenyl) prop-2-enoate) in 93% yield, as a yellow crystalline solid.

Refinement

Hydrogen atoms were placed in calculated positions with C—H = 0.93 - 0.97 Å and refined in riding model with fixed isotropic displacement parameters: $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for aromatic and methylene groups $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$ for methyl group. The rotation angles for methyl group were optimized by least squares.

Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *S SAINT* (Bruker, 2008); data reduction: *S SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

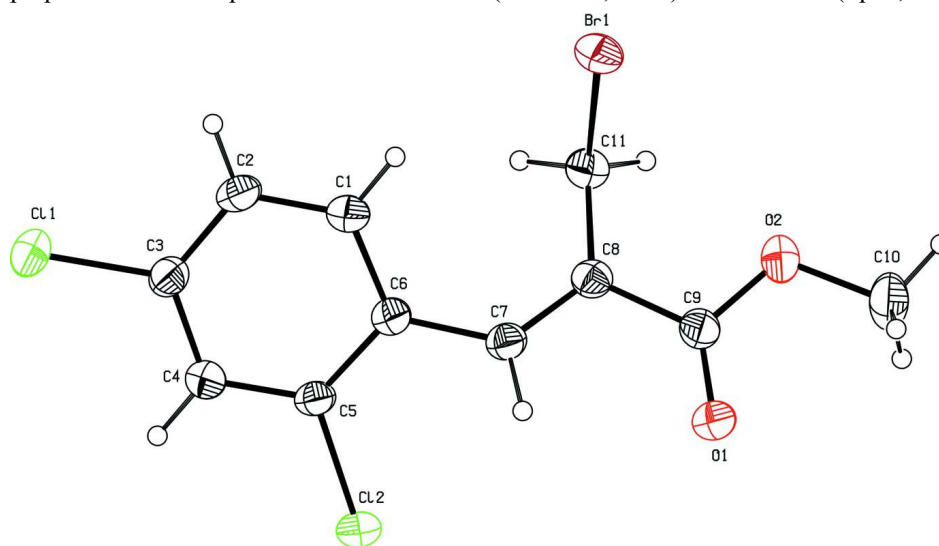


Figure 1

The molecular structure of the title compound with the atom numbering scheme. The displacement ellipsoids are drawn at 30% probability level. H atoms are presented as small spheres of arbitrary radius.

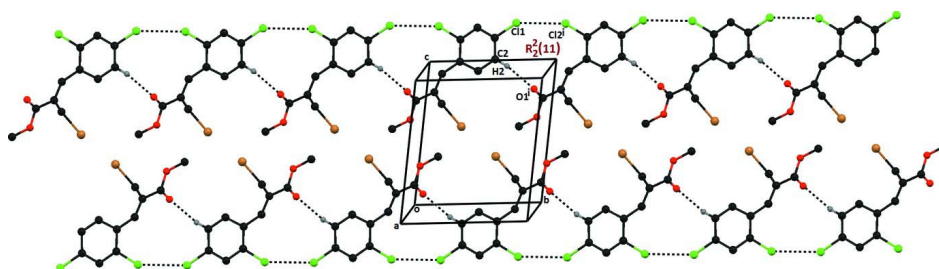


Figure 2

Crystal structure of the title compound, showing the formation of $R_2^2(11)$ ring motifs. Hydrogen bonds are shown as dotted lines. The hydrogen atoms not involved in bonding have been omitted for the sake of clarity.

Methyl (2Z)-2-bromomethyl-3-(2,4-dichlorophenyl)prop-2-enoate

Crystal data

$\text{C}_{11}\text{H}_9\text{BrCl}_2\text{O}_2$
 $M_r = 323.99$

Triclinic, $P\bar{1}$
Hall symbol: $-P 1$

$a = 7.9174$ (3) Å
 $b = 8.8032$ (3) Å
 $c = 9.3585$ (3) Å
 $\alpha = 78.374$ (2)°
 $\beta = 86.599$ (2)°
 $\gamma = 73.528$ (2)°
 $V = 612.67$ (4) Å³
 $Z = 2$
 $F(000) = 320$

$D_x = 1.756$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3748 reflections
 $\theta = 2.2$ – 30.6 °
 $\mu = 3.77$ mm⁻¹
 $T = 293$ K
 Block, yellow
 $0.25 \times 0.25 \times 0.20$ mm

Data collection

Bruker Kappa APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω and φ scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2008)
 $T_{\min} = 0.405$, $T_{\max} = 0.470$

16418 measured reflections
 3748 independent reflections
 2262 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\max} = 30.6$ °, $\theta_{\min} = 2.2$ °
 $h = -11 \rightarrow 11$
 $k = -12 \rightarrow 12$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.102$
 $S = 1.00$
 3748 reflections
 146 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
 $w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.0238P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.005$
 $\Delta\rho_{\max} = 0.59$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³

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 (Å²)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|------------|------------|-------------|----------------------------------|
| C1 | 0.2787 (3) | 0.5411 (3) | -0.0226 (3) | 0.0472 (6) |
| H1 | 0.2484 | 0.5224 | 0.0756 | 0.057* |
| C2 | 0.3057 (3) | 0.4177 (3) | -0.0979 (3) | 0.0485 (6) |
| H2 | 0.2935 | 0.3175 | -0.0513 | 0.058* |
| C3 | 0.3509 (3) | 0.4437 (3) | -0.2424 (3) | 0.0456 (6) |
| C4 | 0.3696 (3) | 0.5905 (3) | -0.3132 (3) | 0.0449 (5) |
| H4 | 0.4001 | 0.6071 | -0.4115 | 0.054* |
| C5 | 0.3424 (3) | 0.7123 (3) | -0.2360 (2) | 0.0409 (5) |
| C6 | 0.2948 (3) | 0.6937 (3) | -0.0878 (2) | 0.0402 (5) |

| | | | | |
|------|--------------|-------------|--------------|--------------|
| C7 | 0.2786 (3) | 0.8231 (3) | -0.0076 (2) | 0.0424 (5) |
| H7 | 0.3505 | 0.8903 | -0.0403 | 0.051* |
| C8 | 0.1750 (3) | 0.8592 (3) | 0.1064 (2) | 0.0416 (5) |
| C9 | 0.1931 (3) | 0.9985 (3) | 0.1650 (3) | 0.0457 (6) |
| C10 | 0.1030 (4) | 1.1546 (4) | 0.3480 (3) | 0.0701 (9) |
| H10A | 0.2227 | 1.1438 | 0.3718 | 0.105* |
| H10B | 0.0324 | 1.1564 | 0.4349 | 0.105* |
| H10C | 0.0585 | 1.2534 | 0.2792 | 0.105* |
| C11 | 0.0395 (3) | 0.7785 (3) | 0.1709 (3) | 0.0468 (6) |
| H11A | 0.0034 | 0.7295 | 0.0983 | 0.056* |
| H11B | -0.0630 | 0.8590 | 0.1971 | 0.056* |
| O1 | 0.2835 (3) | 1.0836 (2) | 0.1128 (2) | 0.0692 (6) |
| O2 | 0.0964 (3) | 1.0191 (2) | 0.2845 (2) | 0.0595 (5) |
| Cl1 | 0.38993 (11) | 0.28780 (9) | -0.33786 (9) | 0.0670 (2) |
| Cl2 | 0.36663 (10) | 0.89643 (7) | -0.32891 (7) | 0.05947 (19) |
| Br1 | 0.12451 (4) | 0.61222 (3) | 0.34428 (3) | 0.06038 (13) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|--------------|---------------|--------------|---------------|
| C1 | 0.0551 (14) | 0.0448 (14) | 0.0415 (13) | -0.0184 (12) | 0.0036 (11) | -0.0025 (11) |
| C2 | 0.0534 (14) | 0.0381 (12) | 0.0556 (15) | -0.0199 (11) | 0.0025 (11) | -0.0029 (11) |
| C3 | 0.0462 (13) | 0.0407 (13) | 0.0532 (14) | -0.0157 (11) | 0.0046 (11) | -0.0124 (11) |
| C4 | 0.0493 (13) | 0.0464 (14) | 0.0414 (12) | -0.0179 (11) | 0.0048 (10) | -0.0085 (11) |
| C5 | 0.0454 (12) | 0.0358 (12) | 0.0416 (12) | -0.0158 (10) | 0.0019 (10) | -0.0019 (10) |
| C6 | 0.0416 (12) | 0.0376 (12) | 0.0413 (12) | -0.0122 (10) | 0.0002 (9) | -0.0059 (10) |
| C7 | 0.0494 (13) | 0.0381 (12) | 0.0404 (12) | -0.0159 (10) | -0.0009 (10) | -0.0036 (10) |
| C8 | 0.0465 (12) | 0.0391 (12) | 0.0363 (12) | -0.0106 (10) | -0.0047 (10) | -0.0009 (10) |
| C9 | 0.0576 (14) | 0.0415 (13) | 0.0359 (12) | -0.0124 (11) | -0.0025 (10) | -0.0038 (10) |
| C10 | 0.079 (2) | 0.0678 (19) | 0.072 (2) | -0.0185 (16) | 0.0056 (16) | -0.0375 (17) |
| C11 | 0.0469 (13) | 0.0488 (14) | 0.0442 (13) | -0.0151 (11) | -0.0003 (10) | -0.0054 (11) |
| O1 | 0.1119 (17) | 0.0591 (12) | 0.0510 (11) | -0.0479 (12) | 0.0175 (11) | -0.0140 (9) |
| O2 | 0.0707 (12) | 0.0581 (12) | 0.0577 (12) | -0.0226 (10) | 0.0141 (9) | -0.0268 (10) |
| Cl1 | 0.0846 (5) | 0.0527 (4) | 0.0762 (5) | -0.0307 (4) | 0.0176 (4) | -0.0297 (4) |
| Cl2 | 0.0858 (5) | 0.0439 (3) | 0.0512 (4) | -0.0290 (3) | 0.0154 (3) | -0.0039 (3) |
| Br1 | 0.0792 (2) | 0.0610 (2) | 0.04088 (16) | -0.02708 (15) | 0.00521 (12) | -0.00037 (12) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|-----------|----------|-----------|
| C1—C2 | 1.371 (4) | C7—H7 | 0.9300 |
| C1—C6 | 1.397 (3) | C8—C11 | 1.484 (3) |
| C1—H1 | 0.9300 | C8—C9 | 1.485 (3) |
| C2—C3 | 1.369 (4) | C9—O1 | 1.195 (3) |
| C2—H2 | 0.9300 | C9—O2 | 1.331 (3) |
| C3—C4 | 1.372 (3) | C10—O2 | 1.451 (3) |
| C3—C11 | 1.731 (3) | C10—H10A | 0.9600 |
| C4—C5 | 1.372 (3) | C10—H10B | 0.9600 |
| C4—H4 | 0.9300 | C10—H10C | 0.9600 |
| C5—C6 | 1.404 (3) | C11—Br1 | 1.961 (2) |
| C5—Cl2 | 1.735 (2) | C11—H11A | 0.9700 |

| | | | |
|--------------|--------------|---------------|-------------|
| C6—C7 | 1.459 (3) | C11—H11B | 0.9700 |
| C7—C8 | 1.340 (3) | | |
| C2—C1—C6 | 122.5 (2) | C6—C7—H7 | 115.3 |
| C2—C1—H1 | 118.7 | C7—C8—C11 | 125.5 (2) |
| C6—C1—H1 | 118.7 | C7—C8—C9 | 115.8 (2) |
| C3—C2—C1 | 119.2 (2) | C11—C8—C9 | 118.6 (2) |
| C3—C2—H2 | 120.4 | O1—C9—O2 | 122.9 (2) |
| C1—C2—H2 | 120.4 | O1—C9—C8 | 124.8 (2) |
| C2—C3—C4 | 121.3 (2) | O2—C9—C8 | 112.3 (2) |
| C2—C3—C11 | 119.7 (2) | O2—C10—H10A | 109.5 |
| C4—C3—C11 | 118.97 (19) | O2—C10—H10B | 109.5 |
| C5—C4—C3 | 118.6 (2) | H10A—C10—H10B | 109.5 |
| C5—C4—H4 | 120.7 | O2—C10—H10C | 109.5 |
| C3—C4—H4 | 120.7 | H10A—C10—H10C | 109.5 |
| C4—C5—C6 | 122.9 (2) | H10B—C10—H10C | 109.5 |
| C4—C5—C12 | 117.39 (18) | C8—C11—Br1 | 112.60 (15) |
| C6—C5—C12 | 119.75 (18) | C8—C11—H11A | 109.1 |
| C1—C6—C5 | 115.5 (2) | Br1—C11—H11A | 109.1 |
| C1—C6—C7 | 123.4 (2) | C8—C11—H11B | 109.1 |
| C5—C6—C7 | 120.9 (2) | Br1—C11—H11B | 109.1 |
| C8—C7—C6 | 129.4 (2) | H11A—C11—H11B | 107.8 |
| C8—C7—H7 | 115.3 | C9—O2—C10 | 116.2 (2) |
| C6—C1—C2—C3 | 0.2 (4) | C1—C6—C7—C8 | -34.5 (4) |
| C1—C2—C3—C4 | 0.0 (4) | C5—C6—C7—C8 | 150.7 (2) |
| C1—C2—C3—C11 | 178.65 (19) | C6—C7—C8—C11 | -5.0 (4) |
| C2—C3—C4—C5 | 0.1 (4) | C6—C7—C8—C9 | 178.8 (2) |
| C11—C3—C4—C5 | -178.53 (18) | C7—C8—C9—O1 | 4.7 (4) |
| C3—C4—C5—C6 | -0.5 (4) | C11—C8—C9—O1 | -171.8 (2) |
| C3—C4—C5—C12 | -179.85 (18) | C7—C8—C9—O2 | -175.2 (2) |
| C2—C1—C6—C5 | -0.5 (4) | C11—C8—C9—O2 | 8.4 (3) |
| C2—C1—C6—C7 | -175.6 (2) | C7—C8—C11—Br1 | 98.2 (2) |
| C4—C5—C6—C1 | 0.7 (3) | C9—C8—C11—Br1 | -85.7 (2) |
| C12—C5—C6—C1 | -179.97 (18) | O1—C9—O2—C10 | 1.3 (4) |
| C4—C5—C6—C7 | 175.9 (2) | C8—C9—O2—C10 | -178.8 (2) |
| C12—C5—C6—C7 | -4.7 (3) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------|-------------|---------------|-----------------------|-------------------------|
| C2—H2...O1 ⁱ | 0.93 | 2.33 | 3.238 (3) | 167 |

Symmetry code: (i) *x*, *y*-1, *z*.