

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2,5-Bis(bromomethyl)biphenyl

 Piotr Kuś,^a Aleksander Zemanek^a and Peter G. Jones^{b*}

^aDepartment of Chemistry, University of Silesia, 9 Szkolna Street, 40-006 Katowice, Poland, and ^bInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany
Correspondence e-mail: p.jones@tu-bs.de

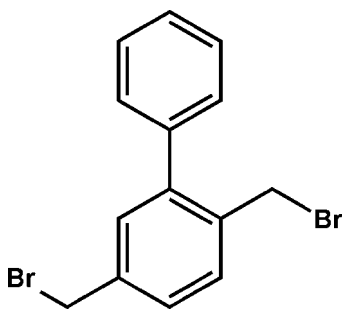
Received 12 May 2009; accepted 13 May 2009

Key indicators: single-crystal X-ray study; $T = 133$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.031; wR factor = 0.085; data-to-parameter ratio = 21.5.

In the title compound, $\text{C}_{14}\text{H}_{12}\text{Br}_2$, the Br atoms lie on opposite sides of their ring plane. The biphenyl interplanar angle is 53.52 (8)°. The packing is characterized by several $\text{H}\cdots\text{Br}$ contacts to each Br atom, but at long distances of 3.07–3.43 Å.

Related literature

For the structures of bromomethyl-substituted aromatic ring systems, see: Jones & Kuś (2005, 2007); Jones *et al.* (2007). For the synthesis, see: Czuchajowski & Zemanek (1990); For a related structure with a similar conformation, see: Obrey *et al.* (2002). For the phenomenon of tertiary contacts, see: Du Mont *et al.* (2008);



Experimental

Crystal data

$\text{C}_{14}\text{H}_{12}\text{Br}_2$
 $M_r = 340.06$
 Monoclinic, $C2/c$
 $a = 33.084$ (4) Å
 $b = 4.3354$ (6) Å
 $c = 18.017$ (2) Å
 $\beta = 103.702$ (4)°
 $V = 2510.7$ (5) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 6.43$ mm⁻¹
 $T = 133$ K
 $0.25 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
 $T_{\min} = 0.316$, $T_{\max} = 0.566$
 (expected range = 0.294–0.526)
 18269 measured reflections
 3120 independent reflections
 2518 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.085$
 $S = 1.05$
 3120 reflections
 145 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.00$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.00$ e Å⁻³

Table 1

H⋯Br contacts (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>
C7—H7B⋯Br1 ⁱ	0.99	3.23	3.773 (3)	116
C12—H12⋯Br1 ⁱⁱ	0.95	3.07	3.782 (3)	133
C13—H13⋯Br1 ⁱⁱ	0.95	3.37	3.931 (3)	120
C13—H13⋯Br1 ⁱⁱⁱ	0.95	3.24	3.634 (3)	107
C14—H14⋯Br1 ^{iv}	0.95	3.37	3.971 (3)	123
C14—H14⋯Br1 ^v	0.95	3.43	4.326 (3)	157
C4—H4⋯Br2 ^{vi}	0.95	3.37	4.260 (3)	156
C4—H4⋯Br2 ^{vii}	0.95	3.26	3.845 (3)	122
C6—H6⋯Br2 ^{viii}	0.95	3.20	4.124 (3)	166
C8—H8B⋯Br2 ^{ix}	0.99	3.29	3.746 (3)	110
C8—H8A⋯Br2 ^{ix}	0.99	3.43	3.746 (3)	101
C15—H15⋯Br2 ^x	0.95	3.27	3.913 (3)	127
C16—H16⋯Br2 ^{viii}	0.95	3.41	3.918 (3)	116
C16—H16⋯Br2 ^x	0.95	3.24	3.898 (3)	128

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x, -y + 1, z + \frac{1}{2}$; (v) $x, -y + 2, z + \frac{1}{2}$; (vi) $-x, -y, -z$; (vii) $-x, -y + 1, -z$; (viii) $-x, y, -z + \frac{1}{2}$; (ix) $x, y - 1, z$; (x) $-x, y + 1, -z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2951).

References

- Bruker (1998). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Czuchajowski, L. & Zemanek, A. (1990). *Pol. J. Chem.* **64**, 499–504.
 Du Mont, W.-W., Bätcher, M., Daniliuc, C., Devillanova, F. A., Druckenbrodt, C., Jeske, J., Jones, P. G., Lippolis, V., Ruthe, F. & Seppälä, E. (2008). *Eur. J. Inorg. Chem.* pp. 4562–4577.
 Jones, P. G. & Kuś, P. (2005). *Acta Cryst.* **E61**, o2947–o2948.
 Jones, P. G. & Kuś, P. (2007). *Z. Naturforsch. Teil B*, **62**, 725–731.
 Jones, P. G., Zemanek, A. & Kuś, P. (2007). *Acta Cryst.* **C63**, o73–o76.
 Obrey, S. J., Bott, S. G. & Barron, A. R. (2002). *J. Chem. Crystallogr.* **32**, 205–207.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Siemens (1994). *XP*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

supporting information

Acta Cryst. (2009). E65, o1327 [doi:10.1107/S1600536809018066]

2,5-Bis(bromomethyl)biphenyl

Piotr Kuś, Aleksander Zemanek and Peter G. Jones

S1. Comment

We are interested in the structures of bromomethyl-substituted aromatic ring systems, compounds that are often used as synthetic intermediates; *e.g.* various bromomethylbenzenes (Jones & Kuś, 2007), 2,2''- and 2',5'- bis(bromomethyl)-*p*-terphenyl (Jones & Kuś, 2005; Jones *et al.*, 2007). The packing patterns are often characterized by secondary interactions such as C—H \cdots Br, Br \cdots Br and C—H \cdots π .

As a part of the synthesis of phenyl derivatives of [2.2]paracyclophane (Czuchajowski & Zemanek 1990), 2,5-di(bromomethyl)biphenyl (1) was obtained by bromination of 2,5-dimethylbiphenyl. Here we present its structure (Fig. 1).

Bond lengths and angles may be regarded as normal (*e.g.* the single bond between the rings is 1.486 (4) Å; ring angles at the substituted atoms C1, C2, C5 are all about 1° less than the ideal 120°). The interplanar angle is 53.52 (8)°. The bromomethyl groups adopt an *anti*-conformation whereby Br1 and Br2 lie out of their ring plane by 1.680 (4) and -1.736 (4) Å; associated torsion angles are C3—C2—C7—Br1 - 77.2 (3) and C4—C5—C8—Br2 - 87.9 (3)°. A similar conformation was observed in 2,6-di(bromomethyl)biphenyl (Obrey *et al.*, 2002), whereas 2',5'-di(bromomethyl)-*p*-terphenyl adopts a *syn*-conformation (Jones *et al.* 2007).

The packing (Fig. 2) appears at first sight to be characterized by an almost total lack of secondary contacts. The shortest H \cdots Br contact is H12 \cdots Br1 3.07 Å (operator 0.5 - *x*, -1/2 + *y*, 0.5 - *z*) and there are no other H \cdots Br < 3.19 Å; there are no Br \cdots Br contacts < 4.2 Å and no H \cdots π contacts < 2.95 Å (and these with very narrow angles). Both bromine atoms however are situated in a pocket surrounded by several H atoms; Br1 by six H at distances of 3.07–3.43, Br2 by eight H from 3.20–3.43 Å. This corresponds to the phenomenon of *tertiary contacts* as postulated by Du Mont *et al.* (2008).

S2. Experimental

The title compound was obtained from 2,5-dimethylbiphenyl according to the method of Czuchajowski & Zemanek (1990). The analytical and spectroscopic data are consistent with the literature. Single crystals were grown by slow evaporation of a hexane solution. NMR data for (1): ¹H NMR (CDCl₃, 400 MHz): δ 7.52 (d, 1H), 7.50–7.39 (m, 6H), 7.29 (d, 1H), 4.50 (s, 2H), 4.44(s, 2H); ¹³C NMR (100 MHz): δ 142.54, 139.57, 138.07, 135.46, 131.53, 131.03, 128.94, 128.61, 128.44, 127.77, 32.75, 31.58.

S3. Refinement

H atoms were included at calculated positions and refined using a riding model, with fixed C—H bond lengths of 0.95 Å (CH, aromatic) or 0.99 Å (CH₂) Å; *U*_{iso}(H) values were fixed at 1.2*U*_{eq} of the parent C atom. Largest difference peaks of ± 1.0 e Å⁻³ near the bromine atoms may be attributed to residual absorption errors.

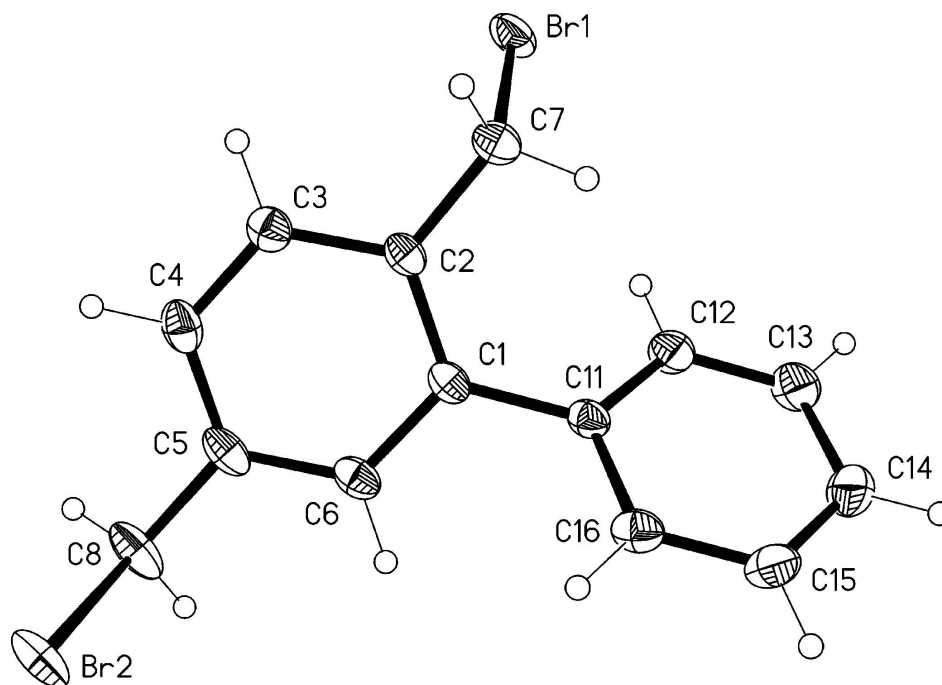


Figure 1

The title compound in the crystal. Displacement ellipsoids represent 50% probability levels.

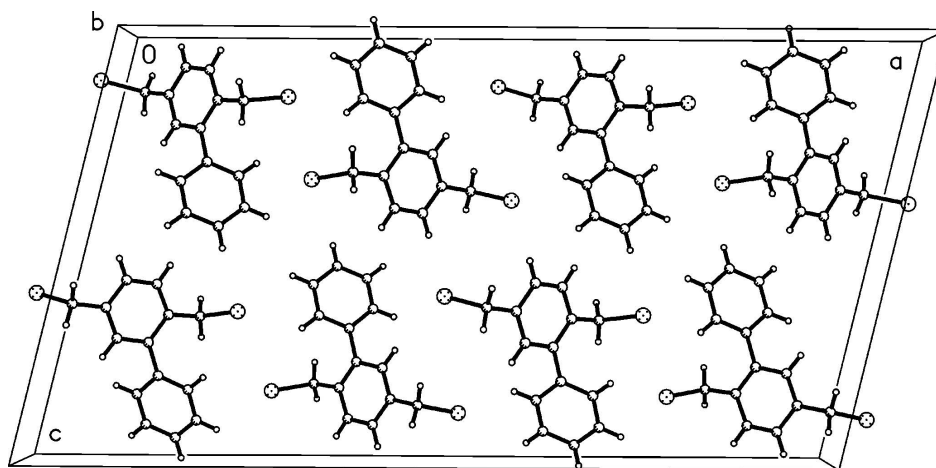


Figure 2

Packing diagram of the title compound viewed parallel to the short **b** axis.

2,5-Bis(bromomethyl)biphenyl

Crystal data

$C_{14}H_{12}Br_2$

$M_r = 340.06$

Monoclinic, $C2/c$

$a = 33.084 (4) \text{ \AA}$

$b = 4.3354 (6) \text{ \AA}$

$c = 18.017 (2) \text{ \AA}$

$\beta = 103.702 (4)^\circ$

$V = 2510.7 (5) \text{ \AA}^3$

$Z = 8$

$F(000) = 1328$

$D_x = 1.799 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 6730 reflections

$\theta = 2.3\text{--}28.8^\circ$

$\mu = 6.43 \text{ mm}^{-1}$
 $T = 133 \text{ K}$

Prism, colourless
 $0.25 \times 0.10 \times 0.10 \text{ mm}$

Data collection

Bruker SMART 1000 CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: $8.192 \text{ pixels mm}^{-1}$
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 1998)
 $T_{\min} = 0.316$, $T_{\max} = 0.566$

18269 measured reflections
 3120 independent reflections
 2518 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 1.3^\circ$
 $h = -44 \rightarrow 44$
 $k = -5 \rightarrow 5$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.085$
 $S = 1.05$
 3120 reflections
 145 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
 $w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 1.9201P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.00 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.00 \text{ e \AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.219743 (8)	0.60712 (7)	0.152339 (16)	0.02600 (10)
Br2	-0.025878 (8)	0.25836 (8)	0.108852 (19)	0.03229 (11)
C1	0.11964 (8)	0.5306 (6)	0.22477 (14)	0.0176 (5)
C2	0.13425 (8)	0.6193 (6)	0.16080 (15)	0.0179 (5)
C3	0.11266 (8)	0.5205 (7)	0.08827 (15)	0.0209 (5)
H3	0.1219	0.5856	0.0447	0.025*
C4	0.07831 (9)	0.3310 (7)	0.07839 (17)	0.0244 (6)
H4	0.0647	0.2621	0.0287	0.029*
C5	0.06355 (8)	0.2407 (6)	0.14127 (17)	0.0222 (6)
C6	0.08387 (8)	0.3445 (7)	0.21324 (16)	0.0209 (6)
H6	0.0733	0.2883	0.2560	0.025*
C7	0.17006 (8)	0.8325 (7)	0.16619 (16)	0.0211 (6)
H7A	0.1765	0.9347	0.2168	0.025*

H7B	0.1625	0.9942	0.1265	0.025*
C8	0.02710 (8)	0.0280 (7)	0.13151 (19)	0.0304 (7)
H8A	0.0294	-0.0937	0.1788	0.037*
H8B	0.0273	-0.1176	0.0893	0.037*
C11	0.14006 (8)	0.6257 (7)	0.30405 (14)	0.0187 (5)
C12	0.18247 (9)	0.5758 (7)	0.33539 (16)	0.0247 (6)
H12	0.1989	0.4783	0.3056	0.030*
C13	0.20058 (9)	0.6669 (8)	0.40922 (17)	0.0300 (7)
H13	0.2293	0.6288	0.4300	0.036*
C14	0.17707 (10)	0.8145 (8)	0.45354 (17)	0.0306 (7)
H14	0.1898	0.8822	0.5038	0.037*
C15	0.13489 (9)	0.8614 (8)	0.42342 (16)	0.0279 (7)
H15	0.1186	0.9615	0.4532	0.033*
C16	0.11642 (9)	0.7626 (7)	0.34998 (16)	0.0225 (6)
H16	0.0873	0.7883	0.3306	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01373 (14)	0.03068 (18)	0.03439 (16)	-0.00368 (11)	0.00730 (10)	-0.00446 (13)
Br2	0.01203 (15)	0.0309 (2)	0.0514 (2)	-0.00186 (11)	0.00244 (12)	0.00305 (14)
C1	0.0114 (11)	0.0171 (13)	0.0231 (12)	0.0036 (10)	0.0018 (9)	0.0018 (11)
C2	0.0130 (11)	0.0162 (13)	0.0236 (12)	0.0016 (10)	0.0027 (9)	0.0000 (11)
C3	0.0177 (12)	0.0208 (14)	0.0234 (12)	0.0028 (11)	0.0036 (10)	0.0026 (11)
C4	0.0165 (13)	0.0260 (15)	0.0273 (14)	0.0032 (11)	-0.0013 (10)	-0.0023 (12)
C5	0.0120 (12)	0.0158 (14)	0.0371 (15)	0.0029 (10)	0.0025 (11)	-0.0001 (12)
C6	0.0135 (12)	0.0208 (14)	0.0278 (13)	0.0025 (10)	0.0033 (10)	0.0051 (11)
C7	0.0174 (13)	0.0201 (14)	0.0264 (13)	0.0016 (11)	0.0064 (10)	0.0013 (11)
C8	0.0137 (13)	0.0213 (15)	0.0528 (19)	0.0011 (12)	0.0009 (12)	0.0013 (14)
C11	0.0139 (12)	0.0221 (14)	0.0194 (12)	0.0007 (10)	0.0027 (9)	0.0045 (11)
C12	0.0162 (13)	0.0326 (17)	0.0252 (13)	0.0037 (12)	0.0049 (10)	-0.0003 (12)
C13	0.0156 (13)	0.045 (2)	0.0266 (14)	0.0033 (13)	-0.0003 (11)	0.0033 (14)
C14	0.0276 (16)	0.0415 (19)	0.0209 (13)	-0.0006 (14)	0.0018 (11)	0.0002 (13)
C15	0.0260 (15)	0.0366 (18)	0.0233 (13)	0.0043 (13)	0.0104 (11)	0.0026 (13)
C16	0.0174 (13)	0.0252 (16)	0.0254 (13)	0.0055 (11)	0.0059 (10)	0.0057 (12)

Geometric parameters (Å, °)

Br1—C7	1.978 (3)	C14—C15	1.387 (4)
Br2—C8	1.974 (3)	C15—C16	1.387 (4)
C1—C2	1.405 (4)	C3—H3	0.9500
C1—C6	1.407 (4)	C4—H4	0.9500
C1—C11	1.486 (4)	C6—H6	0.9500
C2—C3	1.400 (4)	C7—H7A	0.9900
C2—C7	1.487 (4)	C7—H7B	0.9900
C3—C4	1.379 (4)	C8—H8A	0.9900
C4—C5	1.392 (4)	C8—H8B	0.9900
C5—C6	1.387 (4)	C12—H12	0.9500

C5—C8	1.495 (4)	C13—H13	0.9500
C11—C16	1.398 (4)	C14—H14	0.9500
C11—C12	1.400 (4)	C15—H15	0.9500
C12—C13	1.381 (4)	C16—H16	0.9500
C13—C14	1.395 (4)		
C2—C1—C6	118.5 (2)	C3—C4—H4	120.0
C2—C1—C11	123.1 (2)	C5—C4—H4	120.0
C6—C1—C11	118.4 (2)	C5—C6—H6	119.0
C3—C2—C1	118.9 (2)	C1—C6—H6	119.0
C3—C2—C7	118.3 (2)	C2—C7—H7A	109.4
C1—C2—C7	122.7 (2)	Br1—C7—H7A	109.4
C4—C3—C2	121.7 (3)	C2—C7—H7B	109.4
C3—C4—C5	120.0 (3)	Br1—C7—H7B	109.4
C6—C5—C4	119.0 (3)	H7A—C7—H7B	108.0
C6—C5—C8	120.6 (3)	C5—C8—H8A	109.4
C4—C5—C8	120.4 (3)	Br2—C8—H8A	109.4
C5—C6—C1	121.9 (3)	C5—C8—H8B	109.4
C2—C7—Br1	111.0 (2)	Br2—C8—H8B	109.4
C5—C8—Br2	111.4 (2)	H8A—C8—H8B	108.0
C16—C11—C12	118.3 (3)	C13—C12—H12	119.7
C16—C11—C1	119.7 (2)	C11—C12—H12	119.7
C12—C11—C1	121.9 (2)	C12—C13—H13	119.7
C13—C12—C11	120.6 (3)	C14—C13—H13	119.7
C12—C13—C14	120.6 (3)	C15—C14—H14	120.4
C15—C14—C13	119.3 (3)	C13—C14—H14	120.4
C14—C15—C16	120.2 (3)	C14—C15—H15	119.9
C15—C16—C11	120.9 (3)	C16—C15—H15	119.9
C4—C3—H3	119.1	C15—C16—H16	119.5
C2—C3—H3	119.1	C11—C16—H16	119.5
C6—C1—C2—C3	0.2 (4)	C6—C5—C8—Br2	93.8 (3)
C11—C1—C2—C3	-179.4 (3)	C4—C5—C8—Br2	-87.9 (3)
C6—C1—C2—C7	175.8 (3)	C2—C1—C11—C16	128.0 (3)
C11—C1—C2—C7	-3.8 (4)	C6—C1—C11—C16	-51.6 (4)
C1—C2—C3—C4	-2.1 (4)	C2—C1—C11—C12	-53.6 (4)
C7—C2—C3—C4	-177.8 (3)	C6—C1—C11—C12	126.8 (3)
C2—C3—C4—C5	1.9 (4)	C16—C11—C12—C13	-1.6 (4)
C3—C4—C5—C6	0.1 (4)	C1—C11—C12—C13	179.9 (3)
C3—C4—C5—C8	-178.2 (3)	C11—C12—C13—C14	-1.0 (5)
C4—C5—C6—C1	-1.9 (4)	C12—C13—C14—C15	1.8 (5)
C8—C5—C6—C1	176.3 (3)	C13—C14—C15—C16	-0.1 (5)
C2—C1—C6—C5	1.8 (4)	C14—C15—C16—C11	-2.5 (5)
C11—C1—C6—C5	-178.6 (3)	C12—C11—C16—C15	3.3 (4)
C3—C2—C7—Br1	-77.2 (3)	C1—C11—C16—C15	-178.2 (3)
C1—C2—C7—Br1	107.2 (3)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7—H7B \cdots Br1 ⁱ	0.99	3.23	3.773 (3)	116
C12—H12 \cdots Br1 ⁱⁱ	0.95	3.07	3.782 (3)	133
C13—H13 \cdots Br1 ⁱⁱ	0.95	3.37	3.931 (3)	120
C13—H13 \cdots Br1 ⁱⁱⁱ	0.95	3.24	3.634 (3)	107
C14—H14 \cdots Br1 ^{iv}	0.95	3.37	3.971 (3)	123
C14—H14 \cdots Br1 ^v	0.95	3.43	4.326 (3)	157
C4—H4 \cdots Br2 ^{vi}	0.95	3.37	4.260 (3)	156
C4—H4 \cdots Br2 ^{vii}	0.95	3.26	3.845 (3)	122
C6—H6 \cdots Br2 ^{viii}	0.95	3.20	4.124 (3)	166
C8—H8B \cdots Br2 ^{ix}	0.99	3.29	3.746 (3)	110
C8—H8A \cdots Br2 ^{ix}	0.99	3.43	3.746 (3)	101
C15—H15 \cdots Br2 ^x	0.95	3.27	3.913 (3)	127
C16—H16 \cdots Br2 ^{viii}	0.95	3.41	3.918 (3)	116
C16—H16 \cdots Br2 ^x	0.95	3.24	3.898 (3)	128

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1/2, y-1/2, -z+1/2$; (iii) $-x+1/2, y+1/2, -z+1/2$; (iv) $x, -y+1, z+1/2$; (v) $x, -y+2, z+1/2$; (vi) $-x, -y, -z$; (vii) $-x, -y+1, -z$; (viii) $-x, y, -z+1/2$; (ix) $x, y-1, z$; (x) $-x, y+1, -z+1/2$.