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2,3,6,7-Tetrakis(bromomethyl)-naphthalene

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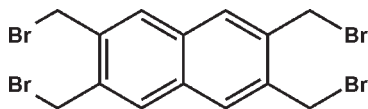
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.016; wR factor = 0.034; data-to-parameter ratio = 25.9.

The title compound, $\text{C}_{14}\text{H}_{12}\text{Br}_4$, crystallizes with imposed inversion symmetry. In the crystal, the molecules pack in layers parallel to $(10\bar{1})$. The layers involve two $\text{Br}\cdots\text{Br}$ and one $\text{H}\cdots\text{Br}$ contact. Between the layers, one contact each of types $\text{Br}\cdots\text{Br}$, $\text{H}\cdots\text{Br}$ and $\text{Br}\cdots\pi$ is observed.

Related literature

For the use of 2,3,6,7-tetrakis(bromomethyl)naphthalene in the preparation of cyclophanes, see: Otsubo *et al.* (1983, 1989); Yano *et al.* (1999); Skibiński *et al.* (2009). For its applications in the synthesis of hydrogen-bonded molecular capsules, see: Valdes *et al.* (1995); Rivera *et al.* (2001). For reviews on halogen–halogen contacts and ‘weak’ hydrogen bonding, see: Desiraju & Steiner (1999); Metrangolo & Resnati (2001); Metrangolo *et al.* (2008); Rissanen (2008). For the X-ray structures of the full series of ten isomeric bis(bromomethyl)naphthalenes, see: Jones & Kuś (2010). For the X-ray structures of two isomeric tetrakis(bromomethyl)benzene derivatives, see: Jones & Kuś (2007).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{12}\text{Br}_4$ $\gamma = 64.555$ (3) $^\circ$
 $M_r = 499.88$ $V = 368.32$ (2) Å³
 Triclinic, $P\bar{1}$ $Z = 1$
 $a = 6.6144$ (2) Å Mo $K\alpha$ radiation
 $b = 7.1770$ (2) Å $\mu = 10.91$ mm⁻¹
 $c = 8.7761$ (3) Å $T = 100$ K
 $\alpha = 84.744$ (3) $^\circ$ $0.20 \times 0.06 \times 0.04$ mm
 $\beta = 78.251$ (3) $^\circ$

Data collection

Oxford Diffraction Xcalibur Eos diffractometer 17701 measured reflections
 Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009) 2122 independent reflections
 $T_{\min} = 0.356$, $T_{\max} = 1.000$ 1716 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$ 82 parameters
 $wR(F^2) = 0.034$ H-atom parameters constrained
 $S = 0.92$ $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 2122 reflections $\Delta\rho_{\text{min}} = -0.49$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{C6}-\text{H6A}\cdots\text{Br2}^{\text{i}}$ | 0.99 | 2.96 | 3.7967 (17) | 143 |
| $\text{C6}-\text{H6A}\cdots\text{Br2}^{\text{ii}}$ | 0.99 | 2.98 | 3.7359 (16) | 134 |
| $\text{C5}-\text{H5}\cdots\text{Br1}^{\text{iii}}$ | 0.95 | 3.11 | 3.9399 (16) | 147 |

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

Table 2

Bromine–bromine and related contacts and angles (Å, $^\circ$).Cg is the centroid of the C1–C5, C1(– $x, 1 - y, -z$) ring.

| System C–Br \cdots Br–C or C–Br \cdots Cg | Br \cdots Br or Br \cdots Cg | C–Br \cdots Br (or C–Br \cdots Cg), Br \cdots Br–C | Operator |
|--|----------------------------------|--|-----------------------|
| $\text{C6}-\text{Br1}\cdots\text{Br2}-\text{C7}$ | 3.8972 (3) | 76.45 (5), 134.79 (5) | $1 - x, 1 - y, 1 - z$ |
| $\text{C7}-\text{Br2}\cdots\text{Br2}-\text{C7}$ | 3.8873 (4) | 134.93 (5) $\times 2$ | $-x, 2 - y, 1 - z$ |
| $\text{C7}-\text{Br2}\cdots\text{Br2}-\text{C7}$ | 3.8913 (4) | 76.72 (5) $\times 2$ | $1 - x, 1 - y, 1 - z$ |
| $\text{C6}-\text{Br1}\cdots\text{Cg}$ | 3.89 | 158 | $1 + x, -1 + y, z$ |

Data collection: CrysAlis PRO (Oxford Diffraction, 2009); cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; 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.

We are grateful to Dr P. Kuś, Silesian University, Katowice, Poland, for crystallizing the title compound.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FK2020).

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supporting information

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2,3,6,7-Tetrakis(bromomethyl)naphthalene

Maciej Skibiński, Vladimir A. Azov and Peter G. Jones

S1. Comment

The title compound is a symmetric rigid molecule with four bromomethyl groups. The bromine atoms can be easily substituted by other nucleophiles, which offers the opportunity of employing the compound as a building block for construction of various functional architectures. The title compound was prepared to serve as a spacer between two tetra-thiafulvalene (TTF) groups in TTF-containing molecular tweezers (Skibiński *et al.*, 2009). It was first employed as an intermediate in the preparation of triple-layered [2.2]naphthalenophane (Otsubo *et al.*, 1983), and several other triple-layered cyclophanes (Otsubo *et al.*, 1983; Yano *et al.*, 1999). It was also used as an intermediate in the synthesis of H-bonded molecular capsules (Valdes *et al.*, 1995; Rivera *et al.*, 2001).

The molecule of the title compound is shown in Fig. 1. It displays crystallographic inversion symmetry (operator #1 - x , 1 - y , 1 - z); for this reason, the crystallographic numbering does not correspond to the IUPAC numbering scheme. Bond lengths and angles may be considered normal; the bromine atoms are directed to opposite sides of the ring system, with C(2)—C(3)—C(6)—Br(1) 92.22 (16), C(3)—C(4)—C(7)—Br(2) 79.86 (17)°, which leads to a +/-/-/+ pattern of Br atoms about the ring plane for the IUPAC-numbered C2,3,6,7; this contrasts with the -/-/+ pattern in 1,2,4,5-tetrakis-(bromomethyl)benzene (Jones & Kuś, 2007), which is also inversion-symmetric.

Details of the packing interactions are given in the Tables. The molecules pack in layers parallel to (10 $\bar{1}$). Within the layers, the contacts Br1...Br2, the longer Br2...Br2 and the shorter H6A...Br2 are observed. These combine to form columns of interactions parallel to the b axis; chains of molecules parallel to [101] (horizontal in Fig. 2) are also formed. The contacts Br2...Br2 (the shorter), H6A...Br2 (the longer) and Br1...Cg (Cg = centre of gravity of the ring C1–5 and C1#1) link the layers (Fig. 3). H5...Br1 3.11 Å between the layers is a borderline interaction. The Br...Cg interaction could alternatively be interpreted as Br...C5, which at 3.450 (2) Å is by far the shortest of the six Br...C contacts; it is often unclear which is the better interpretation in such systems (Jones & Kuś, 2010). Despite the presence of the naphthalene ring systems, there are no significant Cg...Cg interactions. The shortest H...Cg contact is H7A...Cg (1 - x , 1 - y , - z) 3.10 Å between layers, but this is both long and has a narrow angle (124°). We can conclude that the crystal packing of the title compound is dominated by the contacts involving bromomethylene groups.

S2. Experimental

The title compound was prepared as described by Rivera *et al.* (2001) by treatment of a solution of 2,3-bis[[(1,1-dimethylethyl)dimethylsilyl]oxy]methyl]-6,7-bis[(phenylmethoxy)methyl]-naphthalene in chloroform with gaseous HBr. The compound was obtained as a colourless microcrystalline solid. Yield: 87%. Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution in EtOH/hexane/CH₂Cl₂. *M.p.* (decomp.) 230–231° C (lit. 230° C). ¹H NMR (CDCl₃): δ = 7.83 (s, 4H), 4.84 (s, 8H) p.p.m..

The title compound is poorly soluble (< 1 g/L) in most organic solvents at room temperature, but is much more soluble in aromatic solvents, such as toluene or chlorobenzene, upon reflux.

S3. Refinement

Hydrogen atoms were included at calculated positions using a riding model with aromatic C—H 0.95, methylene C—H 0.99 Å. The $U(H)$ values were fixed at $1.2 \times U_{eq}(C)$ of the parent C atom.

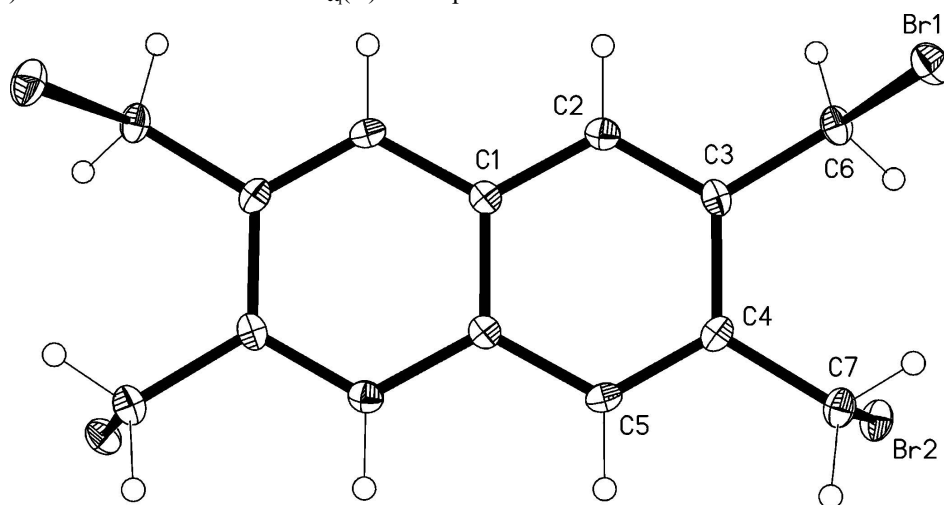


Figure 1

Structure of the title compound in the crystal. Ellipsoids represent 50% probability levels. Only the asymmetric unit is numbered.

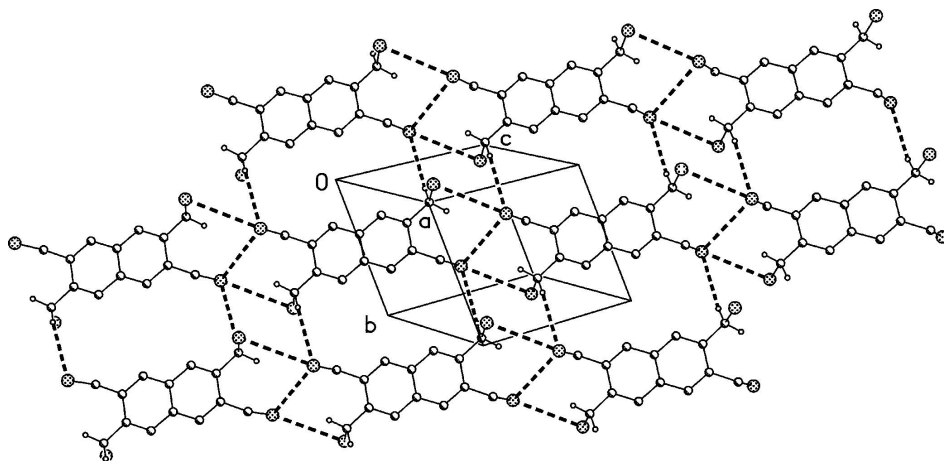


Figure 2

Molecular packing of the title compound as a layer parallel to $(10\bar{1})$. Br...Br and H...Br contacts are shown as thick dashed bonds.

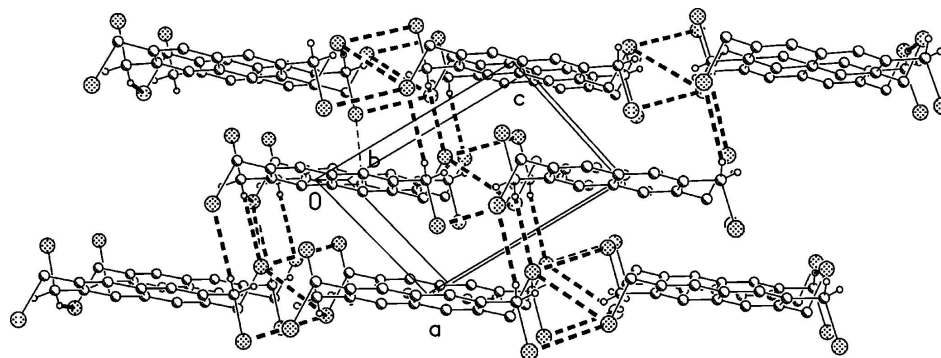


Figure 3

Linking between the layers of the title compound. Br...Br and H...Br contacts are shown as thick dashed bonds. One representative Br...Cg contact is shown as a thin dashed bond (top left).

2,3,6,7-Tetrakis(bromomethyl)naphthalene

Crystal data

$C_{14}H_{12}Br_4$
 $M_r = 499.88$
 Triclinic, $P\bar{1}$
 Hall symbol: $-P\ 1$
 $a = 6.6144$ (2) Å
 $b = 7.1770$ (2) Å
 $c = 8.7761$ (3) Å
 $\alpha = 84.744$ (3)°
 $\beta = 78.251$ (3)°
 $\gamma = 64.555$ (3)°
 $V = 368.32$ (2) Å³

$Z = 1$
 $F(000) = 236$
 $D_x = 2.254$ Mg m⁻³
 Melting point: 503 K
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9533 reflections
 $\theta = 2.4$ – 30.7 °
 $\mu = 10.91$ mm⁻¹
 $T = 100$ K
 Prism, colourless
 $0.20 \times 0.06 \times 0.04$ mm

Data collection

Oxford Diffraction Xcalibur Eos
 diffractometer
 Radiation source: Enhance (Mo) X-ray Source
 Graphite monochromator
 Detector resolution: 16.1419 pixels mm⁻¹
 ω -scan
 Absorption correction: multi-scan
 (*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.356$, $T_{\max} = 1.000$

17701 measured reflections
 2122 independent reflections
 1716 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\max} = 30.0$ °, $\theta_{\min} = 2.4$ °
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -11 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.016$
 $wR(F^2) = 0.034$
 $S = 0.92$
 2122 reflections
 82 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
 $w = 1/[\sigma^2(F_o^2) + (0.0181P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.50$ e Å⁻³
 $\Delta\rho_{\min} = -0.49$ 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|--------------|--------------|----------------------------------|
| Br1 | 0.64988 (3) | −0.00387 (3) | 0.24985 (2) | 0.01628 (5) |
| Br2 | 0.23208 (3) | 0.72525 (3) | 0.44061 (2) | 0.01672 (5) |
| C1 | −0.0170 (3) | 0.4100 (3) | 0.02483 (19) | 0.0108 (3) |
| C2 | 0.0922 (3) | 0.2877 (3) | 0.14549 (19) | 0.0122 (3) |
| H2 | 0.0699 | 0.1672 | 0.1791 | 0.015* |
| C3 | 0.2297 (3) | 0.3393 (3) | 0.21518 (19) | 0.0111 (3) |
| C4 | 0.2621 (3) | 0.5223 (3) | 0.16547 (19) | 0.0110 (3) |
| C5 | 0.1575 (3) | 0.6419 (3) | 0.04994 (19) | 0.0112 (3) |
| H5 | 0.1791 | 0.7633 | 0.0185 | 0.013* |
| C6 | 0.3431 (3) | 0.2029 (3) | 0.34014 (19) | 0.0136 (3) |
| H6A | 0.2495 | 0.1316 | 0.3945 | 0.016* |
| H6B | 0.3563 | 0.2876 | 0.4173 | 0.016* |
| C7 | 0.4062 (3) | 0.5854 (3) | 0.24055 (18) | 0.0135 (3) |
| H7A | 0.4559 | 0.6799 | 0.1704 | 0.016* |
| H7B | 0.5437 | 0.4620 | 0.2592 | 0.016* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| Br1 | 0.01360 (10) | 0.01494 (10) | 0.01724 (10) | −0.00349 (8) | −0.00312 (7) | 0.00232 (7) |
| Br2 | 0.01615 (10) | 0.01865 (11) | 0.01468 (9) | −0.00544 (8) | −0.00321 (7) | −0.00581 (7) |
| C1 | 0.0099 (8) | 0.0112 (9) | 0.0093 (8) | −0.0031 (7) | 0.0001 (6) | −0.0012 (6) |
| C2 | 0.0130 (8) | 0.0120 (9) | 0.0105 (8) | −0.0053 (7) | 0.0000 (7) | −0.0003 (6) |
| C3 | 0.0085 (8) | 0.0127 (9) | 0.0087 (8) | −0.0016 (7) | −0.0006 (6) | −0.0008 (6) |
| C4 | 0.0092 (8) | 0.0139 (9) | 0.0097 (8) | −0.0050 (7) | 0.0011 (6) | −0.0040 (6) |
| C5 | 0.0111 (8) | 0.0104 (8) | 0.0120 (8) | −0.0055 (7) | 0.0012 (6) | −0.0020 (6) |
| C6 | 0.0111 (8) | 0.0156 (9) | 0.0115 (8) | −0.0033 (7) | −0.0017 (7) | 0.0003 (7) |
| C7 | 0.0128 (8) | 0.0177 (9) | 0.0101 (8) | −0.0064 (7) | −0.0017 (7) | −0.0023 (7) |

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

| | | | |
|--------------------|-------------|--------------------|-----------|
| Br1—C6 | 1.9801 (16) | C4—C7 | 1.493 (2) |
| Br2—C7 | 1.9806 (16) | C5—C1 ⁱ | 1.422 (2) |
| C1—C2 | 1.418 (2) | C2—H2 | 0.9500 |
| C1—C1 ⁱ | 1.420 (3) | C5—H5 | 0.9500 |
| C1—C5 ⁱ | 1.422 (2) | C6—H6A | 0.9900 |

| | | | |
|-------------------------------------|--------------|--------------------------|--------------|
| C2—C3 | 1.377 (2) | C6—H6B | 0.9900 |
| C3—C4 | 1.436 (2) | C7—H7A | 0.9900 |
| C3—C6 | 1.494 (2) | C7—H7B | 0.9900 |
| C4—C5 | 1.363 (2) | | |
| C2—C1—C1 ⁱ | 118.85 (18) | C1—C2—H2 | 119.2 |
| C2—C1—C5 ⁱ | 122.57 (15) | C4—C5—H5 | 119.0 |
| C1 ⁱ —C1—C5 ⁱ | 118.58 (19) | C1 ⁱ —C5—H5 | 119.0 |
| C3—C2—C1 | 121.68 (15) | C3—C6—H6A | 109.6 |
| C2—C3—C4 | 119.29 (15) | Br1—C6—H6A | 109.6 |
| C2—C3—C6 | 119.30 (15) | C3—C6—H6B | 109.6 |
| C4—C3—C6 | 121.41 (15) | Br1—C6—H6B | 109.6 |
| C5—C4—C3 | 119.70 (15) | H6A—C6—H6B | 108.1 |
| C5—C4—C7 | 119.52 (15) | C4—C7—H7A | 109.6 |
| C3—C4—C7 | 120.77 (15) | Br2—C7—H7A | 109.6 |
| C4—C5—C1 ⁱ | 121.90 (15) | C4—C7—H7B | 109.6 |
| C3—C6—Br1 | 110.35 (11) | Br2—C7—H7B | 109.6 |
| C4—C7—Br2 | 110.18 (11) | H7A—C7—H7B | 108.1 |
| C3—C2—H2 | 119.2 | | |
| C1 ⁱ —C1—C2—C3 | 0.0 (3) | C6—C3—C4—C7 | -1.7 (2) |
| C5 ⁱ —C1—C2—C3 | 179.24 (16) | C3—C4—C5—C1 ⁱ | -0.5 (2) |
| C1—C2—C3—C4 | 0.5 (2) | C7—C4—C5—C1 ⁱ | -179.53 (15) |
| C1—C2—C3—C6 | -179.09 (15) | C2—C3—C6—Br1 | 92.22 (16) |
| C2—C3—C4—C5 | -0.2 (2) | C4—C3—C6—Br1 | -87.36 (16) |
| C6—C3—C4—C5 | 179.34 (15) | C5—C4—C7—Br2 | 99.15 (16) |
| C2—C3—C4—C7 | 178.76 (15) | C3—C4—C7—Br2 | -79.86 (17) |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|-------|-------------|-------------|---------------|
| C6—H6A \cdots Br2 ⁱⁱ | 0.99 | 2.96 | 3.7967 (17) | 143 |
| C6—H6A \cdots Br2 ⁱⁱⁱ | 0.99 | 2.98 | 3.7359 (16) | 134 |
| C5—H5 \cdots Br1 ^{iv} | 0.95 | 3.11 | 3.9399 (16) | 147 |

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