

# X-Ray Structure Determinations of Bromo- and/or Bromomethyl-substituted Benzenes: C–H···Br, C–Br···Br, and C–Br··· $\pi$ Interactions

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The structures of seven benzene derivatives [1,2,3-tri(bromomethyl)benzene, (**1**); 3,5-di(bromomethyl)bromobenzene, (**2**); 2,5-di(bromomethyl)bromobenzene, (**3**); 4-(bromomethyl)-2,5-dibromotoluene, (**4**); 4-(bromomethyl)bromobenzene, (**5**); 2,3-di(bromomethyl)bromobenzene, (**6**) and (bromomethyl)-*p*-dibromobenzene, (**7**)] with bromo and bromomethyl (and in one case methyl) substituents are presented and analysed in terms of Br···Br interactions up to 4.0 Å, supported by hydrogen bonds H···Br. Some interactions of the type Br··· $\pi$  and  $\pi$ ··· $\pi$  are encountered and play a subordinate role in the packing. Despite the close chemical similarity of the compounds, some of which are isomers with permuted substituent positions, the packing motifs are highly variable. Compounds **2–5** are based on layer structures with Br<sub>*n*</sub> (*n* = 3, 4) and/or mixed Br/C rings. Compounds **1**, **6** and **7** display three-dimensional packings of differing complexity, but with interpretable substructures; **1** can be analysed in terms of ribbons of linked Br<sub>3</sub> and Br<sub>4</sub> rings; **6** displays chains of linked Br<sub>3</sub> triangles; **7** consists of ribbons of linked Br<sub>4</sub> quadrilaterals.

*Key words:* Halogen Bonds, “Weak” Hydrogen Bonds, Secondary Interactions

## Introduction

We are interested in intermolecular secondary interactions between bromine atoms in organic compounds. One previous report concerned five doubly or quadruply bromomethyl-substituted benzene derivatives based on *o*-, *m*- and *p*-xylene, durene and isodurene [1]. Other papers have discussed the structures of all di(bromomethyl)naphthalene isomers [2], 1,6,7-tris(bromomethyl)naphthalene [3], 1,5-dibromo-2,6-dimethylnaphthalene [4], 2,5-bis(bromomethyl)-biphenyl [5], 2,2''-bis(bromomethyl)-*p*-terphenyl [6], mesitylene and dimesitylene compounds bearing bromomethyl units [7], a new polymorph of 1,4-dibromo-2,5-dimethylbenzene [8] and two polymorphs of 1,4-bis(tribromomethyl)benzene [9]. Other authors have reported the structure of 1,3,5-tris(bromomethyl)benzene [10].

In general we have found that the packing diagrams are dominated by Br···Br contacts and “weak” C–H···Br hydrogen bonds. To a lesser extent, H··· $\pi$ ,  $\pi$ ··· $\pi$  and Br··· $\pi$  contacts may also be observed. The Br···Br contacts tend to provide a more easily assimilated view of the packing, because they often form clearly recognisable, simple aggregates of bromine atoms (such as chains or simple polygons).

Halogen···halogen contacts are seen as a special case of “halogen bonding” [11–13]. The model involves a positive area in the extension of the C–Hal bond, with which a second C–Hal <sup>$\delta^-$</sup>  group may then interact *via* its negative region cylindrically surrounding the halogen atom. Correspondingly, one C–Hal···Hal angle should be *ca.* 180° and the other *ca.* 90°, corresponding to a “type II interaction” as described by Desiraju and coworkers [14]; “type I” contacts, thought to represent less significant “packing ef-

fects” with at best a weak interaction, have approximately equal angles and are often formed across symmetry elements.

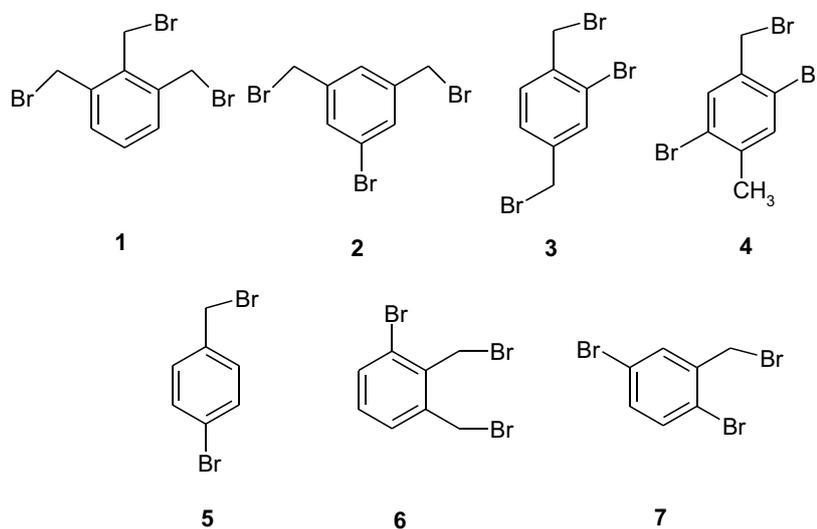
In this report we continue the theme of bromomethyl-substituted benzenes [1], but have extended the scope of our studies to include some structures with additional bromine and (in one case) methyl substituents directly bonded to the ring. Structures of the following seven benzene derivatives are presented: 1,2,3-tri(bromomethyl)benzene, (**1**); 3,5-di(bromomethyl)bromobenzene, (**2**); 2,5-di(bromomethyl)bromobenzene, (**3**); 4-(bromomethyl)-2,5-dibromotoluene, (**4**); 4-(bromomethyl)bromobenzene, (**5**); 2,3-di(bromomethyl)bromobenzene, (**6**) and (bromomethyl)-*p*-dibromobenzene, (**7**) (Scheme 1). The structure of 2,6-di(bromomethyl)bromobenzene was investigated but proved to be severely disordered.

## Discussion

The molecular structures of compounds **1–7** are presented in Figs. 1a–7a. All compounds crystallize with no imposed symmetry and with one molecule in the asymmetric unit. All the aromatic ring systems are planar (max. mean deviation 0.005 Å) and no directly bonded substituent atom lies markedly out of the ring plane. Bond lengths and angles may be regarded as normal (Table 1). The ring angles at carbon atoms directly bonded to bromine are consistently slightly larger than 120°. Similarly to the naphthalene

derivatives [2], the absolute torsion angles C–C–Br all lie in the range 77–94°, so that the planes of the C–C–Br units are approximately perpendicular to the ring planes; in compounds with more than one bromomethyl group, the Br atoms may in principle lie on the same or on opposite sides of the ring plane. For compounds **2**, **3** and **6**, the “*trans*” form (bromines on opposite sides of the ring) is observed; for compound **1**, Br2 is “*trans*” to Br1 and Br3. For substituents at neighbouring ring positions, such contacts necessarily lead to short intramolecular C–H···Br contacts (typically with distances H···Br around 3 Å and C–H···Br angles of *ca.* 135°), which however will neither be tabulated nor discussed.

There are no short (H··· $\pi$  < 2.9 Å) C–H··· $\pi$  contacts. The C–H···Br contacts for all compounds are summarised in Table 2, with Br···Br contacts in Table 3. Again as for the naphthalene derivatives [2], few of the intermolecular C–H···Br contacts are very short (*cf.* sum of van der Waals’ radii for H···Br 3.05 Å). The nominal limit for Br···Br distances based on van der Waals’ radii would be *ca.* 3.7 Å, and we tend to call contacts below this value “short”, but some slightly longer contacts up to a limit of *ca.* 4.0 Å have been included because of apparent structural relevance. We have previously noted for systems involving I···I interactions that the sum of several borderline interactions, which we have loosely termed “tertiary interactions”, may represent a significant contribution to a stable packing pattern [15]; a more generalised form of this



Scheme 1.

Comp.	C–Br <sup>b</sup>	C–CH <sub>2</sub> –Br <sup>b</sup>	C–C–CH <sub>2</sub> –Br <sup>b,c</sup>	Angle at <i>ipso</i> -C	Disposition of bromomethyl groups <sup>c</sup>
<b>1</b>	1.978(2)	110.12(12)	89.8(2)		C2 <i>trans</i> to C1 and C3
	1.979(2)	112.12(12)	–92.3(2)		
	1.981(2)	112.16(12)	82.5(2)		
<b>2</b>	1.898(2)			122.3(2)	<i>trans</i>
	1.975(3)	111.2(2)	77.4(3)		
	1.977(3)	110.3(2)	–74.8(3)		
<b>3</b>	1.906(5)			123.2(5)	<i>trans</i>
	1.981(5)	110.6(4)	–84.3(6)		
	1.971(5)	110.7(4)	86.3(5)		
<b>4</b>	1.900(3)			122.0(3)	
	1.895(3)			121.0(3)	
	1.969(3)	110.2(2)	89.9(3)		
<b>5</b>	1.902(4)			121.7(3)	
	1.968(4)	110.9(3)	93.5(4)		
<b>6</b>	1.901(2)			122.5(2)	<i>trans</i>
	1.981(2)	109.59(14)	–93.9(2)		
	1.969(2)	112.43(15)	82.0(2)		
<b>7</b>	1.894(2)			121.5(2)	
	1.895(2)			121.6(2)	
	1.977(2)	111.08(13)	–88.1(2)		

Table 1. Selected details of molecular geometry (Å and deg)<sup>a</sup>.

<sup>a</sup> Involving all bromine atoms (ring substituents and methyl substituents); <sup>b</sup> beginning with the lowest-numbered bromine; <sup>c</sup> *cis/trans* = both bromine atoms on same/different sides of ring system. The first two carbon atoms are chosen clockwise in the ring system, starting from C1 at top right. Does not apply if only one bromomethyl group is present.

Comp.	D–H...A	C–H	H...Br	CH...Br	Operator
<b>1</b>	C9–H9A...Br1	0.99	3.10	136	$x - 1/2, -y + 3/2, z - 1/2$
	C9–H9B...Br2	0.99	2.90	168	$-x + 1/2, y - 1/2, -z + 1/2$
	C7–H7A...Br3	0.99	3.09	138	$x + 1/2, -y + 3/2, z + 1/2$
	C8–H8B...Br3	0.99	2.99	148	$-x + 3/2, y + 1/2, -z + 1/2$
<b>2</b>	C8–H8B...Br1	0.99	2.96	147	$-x + 1, -y + 1, -z + 1$
	C4–H4...Br2	0.95	3.01	175	$-x + 1, -y, -z + 1$
	C7–H7A...Br3	0.99	3.02	149	$x, y, z - 1$
<b>3</b>	C3–H3...Br1	0.95	2.93	128	$-x + 1, -y + 2, z + 1/2$
	C3–H3...Br3	0.95	3.06	131	$x + 1/2, -y + 1, z$
	C8–H8B...Br1	0.99	3.13	159	$x - 1/2, -y + 1, z$
<b>4</b>	C3–H3...Br3	0.95	3.07	155	$-x, -y + 1, -z + 1$
	C8–H8A...Br3	0.99	3.00	146	$-x, -y + 1, -z + 1$
<b>5</b>	C2–H2...Br1	0.95	3.14	135	$-x, -y + 2, z + 1/2$
	C6–H6...Br1	0.95	3.13	131	$x - 1/2, -y + 3/2, z$
<b>6</b>	C5–H5...Br1	0.95	3.05	135	$-x + 2, y - 1/2, -z + 1/2$
	C5–H5...Br2	0.95	3.00	140	$-x + 2, y - 1/2, -z + 1/2$
	C4–H4...Br3	0.95	3.04	138	$x + 1, y, z$
	C4–H4...Br3	0.95	3.14	138	$x + 1/2, -y + 1/2, -z + 1$
<b>7</b>	C8–H8B...Br3	0.99	3.04	159	$x + 1, y, z$
	C5–H5...Br1	0.95	3.15	154	$-x + 3/2, y + 1/2, -z + 1/2$
	C3–H3...Br3	0.95	2.97	161	$-x, -y + 1, -z$

Table 2. Intermolecular C–H...Br hydrogen bonds (Å and deg).

principle had already been presented by Dance [16]. It is also appropriate to repeat our caveat from the naphthalene systems [2]: in view of the large number of potential interactions, the choice of a hierarchy of interactions (in our case: the preference for basing discussion on Br...Br contacts) may to some extent be subjective.

Compound **1** displays a complex three-dimensional packing pattern, but the main features (Fig. 1b) can be recognised in terms of ribbons of molecules parallel to the *b* axis (which are then linked in the third dimension). The ribbons consist of linked triangles and quadrilaterals and are built up from of a total of five

Comp.	C–Br...Br–C	Br...Br	C–Br...Br	Br...Br–C	Operator	Table 3. Br...Br contacts (Å and deg).
<b>1</b>	C7–Br1...Br3–C9	3.7593(4)	84.53(6)	139.56(5)	$-x + 3/2, y + 1/2, -z + 1/2$	
	C8–Br2...Br3–C9	3.8322(3)	154.28(5)	157.71(5)	$x, y + 1, z$	
	C7–Br1...Br2–C8	3.9102(3)	133.98(6)	87.49(5)	$x + 1/2, -y + 3/2, z + 1/2$	
	C7–Br1...Br2–C8	3.9355(3)	103.99(5)	147.30(5)	$-x + 3/2, y - 1/2, -z + 1/2$	
<b>2</b>	C7–Br1...Br3–C9	3.9720(3)	72.93(5)	72.76(5)	$x + 1/2, -y + 3/2, z + 1/2$	
	C1–Br1...Br3–C8	3.5291(5)	167.03(8)	114.52(8)	$x, y + 1, z - 1$	
	C7–Br2...Br3–C8	3.5360(5)	149.84(7)	161.86(7)	$x + 1, y, z - 1$	
<b>3</b>	C8–Br3...Br3–C8	3.8359(7)	75.58(9)	75.58(9) <sup>a</sup>	$-x, -y + 1, -z + 2$	
	C1–Br1...Br3–C8	3.6111(7)	113.5(2)	178.7(2)	$-x + 1/2, y, z - 1/2$	
	C7–Br2...Br3–C8	3.7204(8)	162.8(2)	82.4(2)	$-x + 1, -y + 1, z - 1/2$	
	C1–Br1...Br3–C8	3.9211(7)	139.1(2)	110.5(2)	$-x + 1/2, y + 1, z - 1/2$	
<b>4</b>	C1–Br1...Br2–C7	4.0374(8)	88.5(2)	132.8(2)	$x - 1/2, -y + 2, z$	
	C7–Br2...Br3–C8	4.0511(8)	109.5(2)	115.5(2)	$-x + 1, -y + 2, z - 1/2$	
	C2–Br1...Br2–C5	3.9784(6)	104.32(9)	153.74(9)	$-x + 1/2, y - 1/2, -z + 1/2$	
	C2–Br1...Br2–C5	3.7119(6)	168.37(9)	84.74(9)	$x + 1/2, -y + 1/2, z + 1/2$	
<b>5</b>	C2–Br1...Br3–C8	3.8562(6)	77.97(9)	163.21(8)	$-x + 1, -y + 1, -z + 1$	
	C1–Br1...Br2–C7	3.6065(5)	164.53(9)	110.79(12)	$x - 1, y, z - 1$	
	C1–Br1...Br2–C7	3.8989(5)	106.19(11)	158.48(12)	$x - 1, y, z$	
<b>6</b>	C8–Br3...Br3–C8 <sup>b</sup>	3.7487(3)	81.48(7)	157.71(7)	$x + 1/2, -y + 1/2, -z + 1$	
	C1–Br1...Br3–C8	3.9662(3)	137.58(6)	140.32(7)	$-x + 1/2, -y + 1, z - 1/2$	
	C1–Br1...Br3–C8	3.9760(3)	143.39(7)	90.40(7)	$-x + 1, y + 1/2, -z + 1/2$	
<b>7</b>	C1–Br1...Br2–C4	3.5717(3)	108.71(5)	167.31(6)	$x - 1/2, -y + 3/2, z + 1/2$	
	C1–Br1...Br2–C4	3.7924(3)	156.44(6)	82.57(6)	$-x + 1/2, y - 1/2, -z + 1/2$	
	C1–Br1...Br2–C4	3.8345(3)	133.73(6)	97.34(6)	$-x + 3/2, y - 1/2, -z + 1/2$	
	C4–Br2...Br3–C7	3.7743(3)	84.99(6)	157.40(6)	$-x + 1, -y + 1, -z$	

<sup>a</sup> Angles equal by symmetry; <sup>b</sup> a symmetry-equivalent interaction is observed at  $x - 1/2, -y + 1/2, -z + 1$ .

independent Br...Br contacts ranging in length from 3.76 to 3.97 Å; there are no other such contacts shorter than 4.2 Å. Two of the contacts are clearly type I; the others have an intermediate form, with one angle approximately 90° and the other *ca.* 130–140°. It may be that the geometric constraints of forming a condensed system of contact triangles does not allow type II contacts with ideal 180° angles. The hydrogen bonds H7A...Br3 and H8B...Br3, not shown explicitly in the Figure, support the two interactions from Br1 to the Br3 atoms (they are formed between the same pairs of molecules). The shortest  $\pi\cdots\pi$  contact is 4.03 Å (operator  $1 - x, 1 - y, 1 - z$ ) and is probably of marginal significance.

The packing of compound **2** is in marked contrast to that of **1**; it involves only three Br...Br contacts, but they are appreciably shorter (although only one of them approximates to a type II contact and the others are clearly type I). The two shortest, both *ca.* 3.53 Å, involve only translational symmetry; they combine to form highly corrugated layers consisting of 20-membered rings, seven atoms of which are bromine atoms (Fig. 2b). As an *ad hoc* notation related to the familiar graph sets for hydrogen bonds [17], we shall

label these rings as  $R(20,7)$  and other rings accordingly. The layers, parallel to (111), are linked in pairs (Fig. 2c) by the third and longest Br...Br contact; the rings form an infinite stack parallel to the *a* axis *via* symmetry operators  $-x, 1 - y, 1 - z$  and  $1 - x, 1 - y, 1 - z$  (referred to the molecule of the asymmetric unit) with two independent  $\pi\cdots\pi$  distances of 3.7 Å. Only the shortest hydrogen bond H8B...Br1 is observed within a given double layer; it supports the stacking interaction.

Compound **3** is an isomer of **2**, whereby the substituents are permuted; its packing is, at least in two dimensions, closely related to that of **2**. Again, the two shortest Br...Br contacts are Br1...Br3 and Br2...Br3 (both in this case corresponding reasonably well to type II); they again combine to form highly corrugated layers parallel to the *ac* plane, consisting of  $R(20,7)$  rings (Fig. 3b). The equivalent molecules are generated by a *c* glide plane and a  $2_1$  screw axis. The other three, appreciably longer, Br...Br contacts are formed to neighbouring layers but the corresponding diagrams are highly complex. The main hydrogen bond is a symmetric three-centre interaction, one component of which, H3...Br1, lies within the layer.

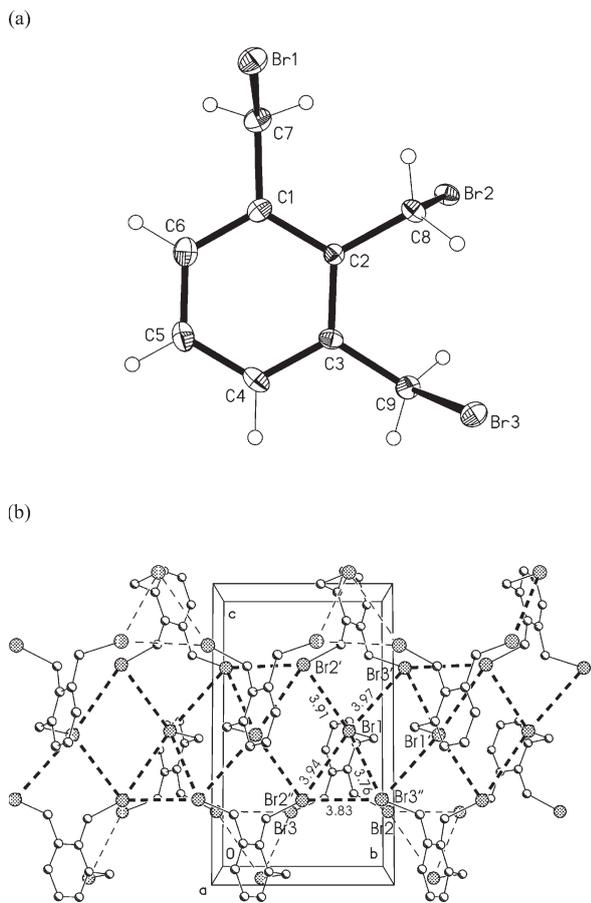


Fig. 1. (a) Molecular structure of compound **1** in the crystal. (b) Packing diagram of compound **1** viewed parallel to the  $a$  axis in the region  $x \approx 0$ . Br...Br contacts are shown as dashed bonds (the thicker bonds correspond to the central ribbon, thinner bonds form parts of neighbouring, linked ribbons). Approximate distances are given in Å; Table 3 should be consulted for exact values and symmetry operators. The “missing” contacts Br2'...Br3' (intramolecular) and Br1...Br1' are too long (at 4.90 and 4.27 Å respectively) to be considered as structurally relevant.

Compound **4** again forms a layer structure, this time parallel to  $(10\bar{1})$ . All three Br...Br contacts, which are all quite long but correspond satisfactorily to type II, combine to form Br<sub>4</sub> rhombuses and two types of mixed rings,  $R(12,4)$  in the centre of the cell surrounded by  $R(12,5)$  (Fig. 4b). All three contacts involve Br1; the equivalent molecules are here generated by an  $n$  glide plane, a  $2_1$  screw axis and an inversion centre. The two hydrogen bonds form a bifurcated system across an inversion centre, and link neighbouring layers.

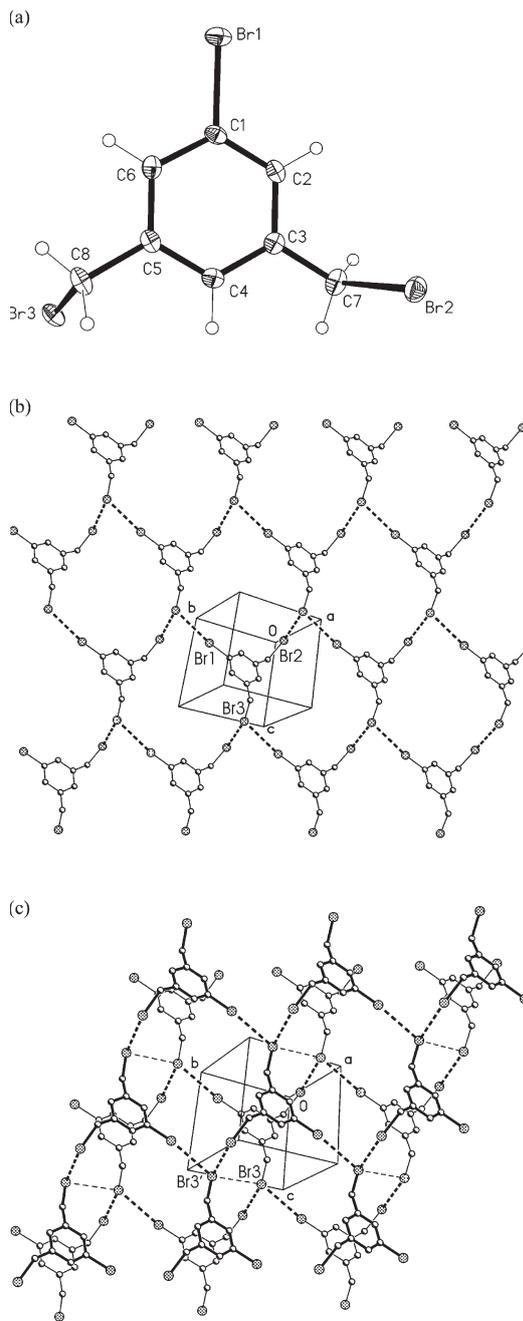


Fig. 2. (a) Molecular structure of compound **2** in the crystal. (b) Packing diagram of compound **2** viewed perpendicular to  $(111)$ . The atoms Br1, 2, 3 correspond to the asymmetric unit. Br...Br contacts are shown as dashed bonds. (c) Packing of compound **2**; depth-cued double layers (thinner bonds at rear of diagram) showing the interconnecting Br3...Br3' contacts (thin dashed bonds) and the incipient stacking in the  $a$  direction. The origin is at the rear of the diagram.

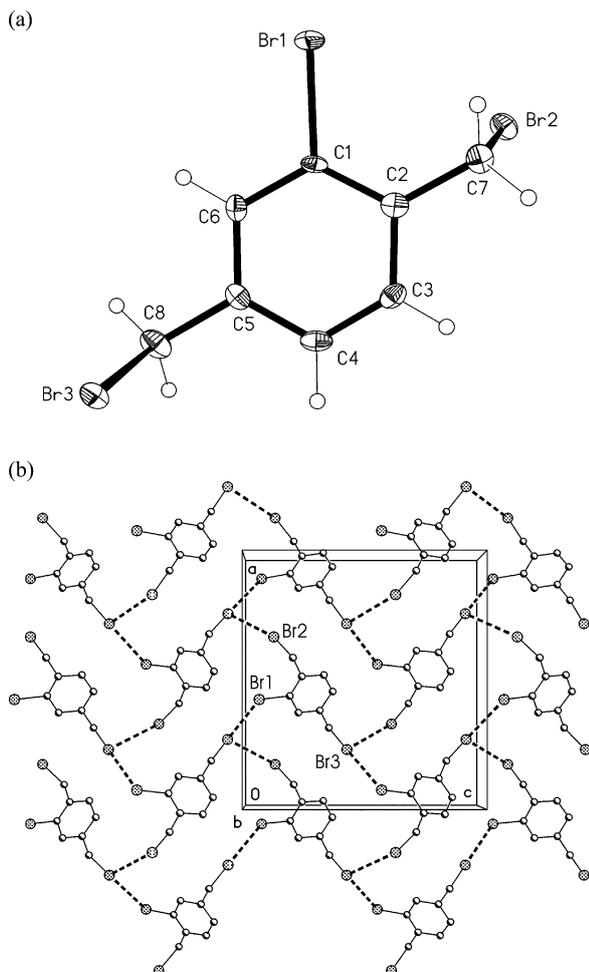


Fig. 3. (a) Molecular structure of compound **3** in the crystal. (b) Packing diagram of compound **3** viewed along the short *b* axis.

Compound **5** also forms a layer structure, parallel to the *ac* plane. The two Br1...Br2 contacts, which correspond adequately to type II, combine to form zigzag chains parallel to the short and polar *c* axis. The operators are purely translational. The molecular frames of **5** link the bromine chains to form  $R(16,6)$  rings (Fig. 5b). Contacts of the form C1–Br1... $\pi$  are observed within the layer, with Br1... $\pi$  3.79 Å and an angle of 77°, and might be considered as part of stacking interactions between ring systems extended by the bromine atom. The two hydrogen bonds connect neighbouring layers (and indeed form layers in their own right parallel to the *ab* plane).

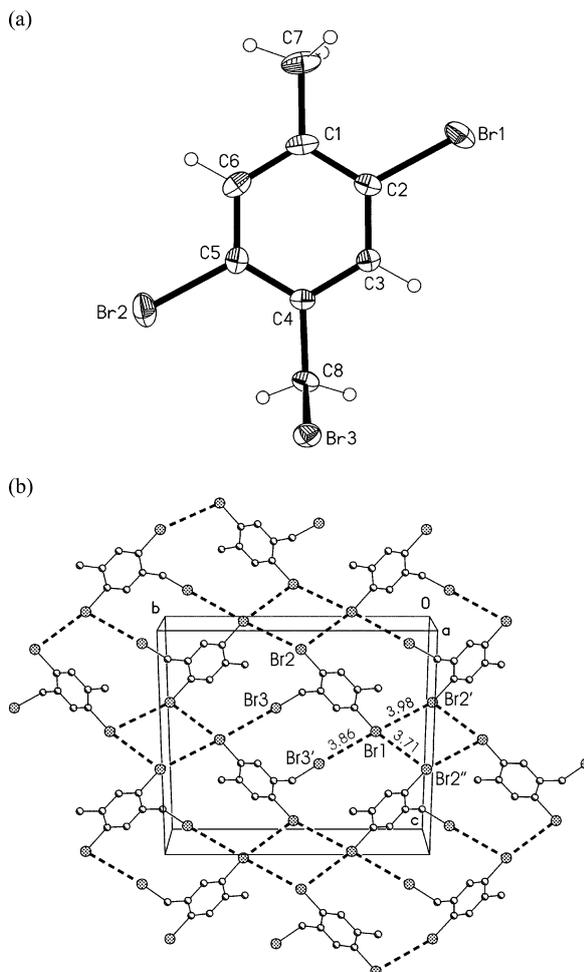


Fig. 4. (a) Molecular structure of compound **4** in the crystal. (b) Packing diagram of compound **4** viewed perpendicular to (10 $\bar{1}$ ).

Compound **6** is another isomer of **2** and **3** and might therefore be expected to show a similarly simple layer pattern. In fact the opposite is the case; the packing (in space group  $P2_12_12_1$ , which seldom leads to simple packing diagrams) is three-dimensional and involves a variety of interactions. The simplest substructure (Fig. 6b) is a chain of linked Br<sub>3</sub> triangles parallel to the short *a* axis; the main linear chain involves the shortest interactions Br3...Br3 (type II). The chain is supported by all five H...Br hydrogen bonds (including two three-centre systems) and a contact C1–Br1... $\pi$ , with Br1... $\pi$  3.70 Å and an angle of 136°. It is surprising that the atom Br2 is involved in just one hydro-

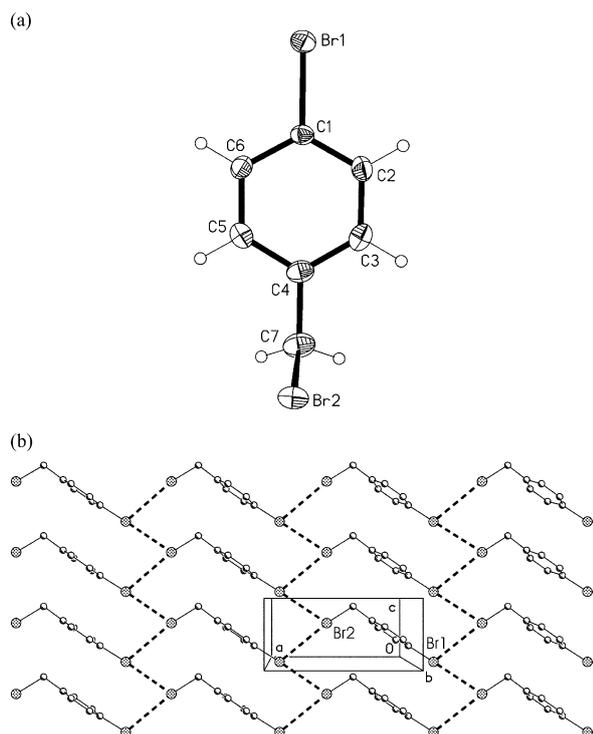


Fig. 5. (a) Molecular structure of compound **5** in the crystal. (b) Packing diagram of compound **5** viewed parallel to the *b* axis in the region  $y \approx 7/8$ .

gen bond, whereas Br3 participates in three hydrogen bonds and all three Br...Br contacts.

The packing of compound **7** is also three-dimensional, but can be easily analysed in terms of a double chain or “staircase” pattern of three independent Br1...Br2 interactions, one of which is especially short, parallel to the short *a* axis (Fig. 7b). The chain is propagated *via* the  $2_1$  screw axis and the “rungs” *via* the *n* glide plane. The interplanar angle between successive Br<sub>4</sub> planes is  $63.5^\circ$  (or  $116.5^\circ$ ). A fourth interaction Br2...Br3, formed over an inversion centre, connects the chains in the third dimension, supported by the two H...Br hydrogen bonds (Fig. 7c). Three of the four contacts are a good (and the fourth a reasonable) approximation to type II geometry.

### Experimental Section

All compounds were obtained from commercially available hydrocarbons and bromohydrocarbons: 1,2,3-trimethylbenzene (for **1**), 3,5-dimethylbromobenzene (for **2**), 2,5-dimethylbromobenzene (for **3**), 2,5-dibromo-*p*-xylene

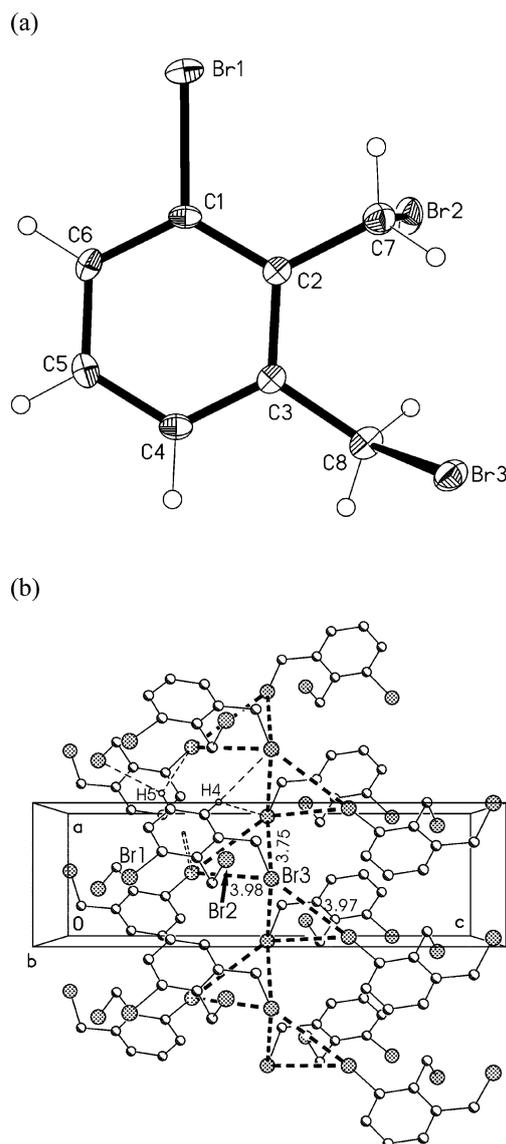


Fig. 6. (a) Molecular structure of compound **6** in the crystal. (b) Packing diagram of compound **6** viewed parallel to the *b* axis in the region  $y \approx 1/4$ . For reasons of clarity, symmetry-equivalent Br atoms are not labelled. Thin dashed lines indicate either hydrogen bonds or the Br... $\pi$  interaction; only one each of these interactions is shown. The hydrogen bond H8B...Br3 is omitted because it eclipses a Br...Br contact.

(for **4**), 4-bromotoluene (for **5**), 2,3-dimethylbromobenzene (for **6**), and 2,5-dibromotoluene (for **7**) by radical bromination with *N*-bromosuccinimide in carbon tetrachloride. Spectroscopic data for compounds **1** [18], **2** [19], **3** [20], **4** [21], **5** [22, 23], **6** [24, 25], and **7** [26] agree with those reported in

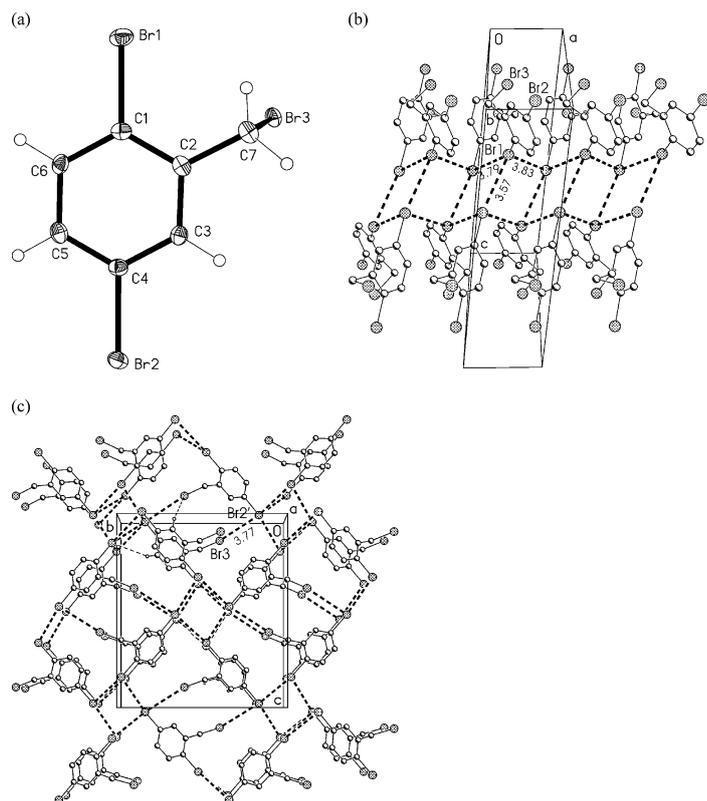


Fig. 7. (a) Molecular structure of compound **7** in the crystal. (b) Packing diagram of compound **7** in the crystal; view direction approximately perpendicular to (011). For reasons of clarity, symmetry-equivalent Br atoms are not labelled. (c) Packing diagram of compound **7** in the crystal; view direction parallel to the short *a* axis; one of the Br...Br contacts that connect the double chains (seen here end-on as rhombuses) is labelled explicitly. Two representative H...Br hydrogen bonds are shown in the upper left corner of the cell.

Table 4. Crystallographic data for compounds **1–7**.

Compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
Formula	C <sub>9</sub> H <sub>9</sub> Br <sub>3</sub>	C <sub>8</sub> H <sub>7</sub> Br <sub>3</sub>	C <sub>8</sub> H <sub>7</sub> Br <sub>3</sub>	C <sub>8</sub> H <sub>7</sub> Br <sub>3</sub>	C <sub>7</sub> H <sub>6</sub> Br <sub>2</sub>	C <sub>8</sub> H <sub>7</sub> Br <sub>3</sub>	C <sub>7</sub> H <sub>5</sub> Br <sub>3</sub>
<i>M<sub>r</sub></i>	356.89	342.87	342.87	342.87	249.94	342.87	328.84
Crystal size, mm <sup>3</sup>	0.20 × 0.08 × 0.08	0.22 × 0.13 × 0.08	0.24 × 0.14 × 0.08	0.25 × 0.05 × 0.05	0.18 × 0.18 × 0.06	0.15 × 0.12 × 0.08	0.22 × 0.10 × 0.08
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>Pca</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	8.7466(6)	7.3062(7)	15.2421(6)	4.5278(6)	9.6283(8)	5.2694(3)	4.2600(2)
<i>b</i> , Å	8.3835(6)	8.8368(9)	4.3633(3)	15.6051(18)	18.1165(15)	10.5073(3)	13.2354(3)
<i>c</i> , Å	14.1337(11)	8.9401(10)	14.2695(6)	13.6899(16)	4.4279(4)	17.1833(6)	15.1444(4)
$\alpha$ , deg	90	66.972(6)	90	90	90	90	90
$\beta$ , deg	94.420(4)	69.440(6)	90	93.185(8)	90	90	95.506(2)
$\gamma$ , deg	90	71.419(6)	90	90	90	90	90
<i>V</i> , Å <sup>3</sup>	1033.30(13)	486.24(9)	949.01(9)	965.8(2)	772.36(11)	951.39(7)	849.94(5)
<i>Z</i>	4	2	4	4	4	4	4
<i>D<sub>x</sub></i> , Mg m <sup>-3</sup>	2.29	2.34	2.40	2.36	2.15	2.39	2.57
$\mu$ , mm <sup>-1</sup>	11.7	12.4	12.7	12.5	10.4	12.7	14.2
<i>F</i> (000), e	672	320	640	640	472	640	608
<i>T</i> , K	100(2)	100(2)	100(2)	100(2)	133(2)	103(2)	100(2)
2 $\theta$ <sub>max</sub> , deg	66.7	65.5	57.4	60	57.4	62	64
Measured/indep. refl./ <i>R</i> <sub>int</sub>	4086/4086/	4431/4431/	13 993/2429/	25 218/2829/	13 198/1974/	29 282/302/	19 601/2880/
Ref. parameters	110	101	100	101	82	100	91
Restraints	0	18	1	18	58	0	0
Flack parameter <i>x</i>	–	–	–0.01(2)	–	0.02(2)	0.003(10)	–
<i>wR</i> ( <i>F</i> <sup>2</sup> , all refl.)	0.042	0.070	0.067	0.067	0.057	0.030	0.041
<i>R</i> [ <i>F</i> > 4 $\sigma$ ( <i>F</i> )]	0.020	0.028	0.035	0.028	0.026	0.018	0.020
<i>S</i>	1.04	1.05	1.07	1.03	1.07	0.95	0.99
Max. $\Delta\rho$ , e Å <sup>-3</sup>	0.62	0.86	0.92	0.92	0.69	0.51	0.75

the literature. Single crystals used in crystallographic studies were obtained by slow evaporation of solutions: from ethanol (**1**, **3** and **7**), hexanes (**2** and **6**), CCl<sub>4</sub> (**5**), and CH<sub>2</sub>Cl<sub>2</sub>-hexanes-ethanol (**4**).

#### X-Ray structure determinations

Crystal data are summarised in Table 4. Data were registered on various diffractometers (Bruker SMART 1000 CCD, Bruker APEX-2, Oxford Diffraction Xcalibur) using MoK $\alpha$  radiation at low temperature. Absorption corrections were applied using the multi-scan method. Structures were refined using the program SHELXL-97 [27, 28]. Hydrogen atoms were included using a riding model (for **4** the methyl group was included as an idealized rigid group allowed to rotate but not tip). Compounds **1** and **2** were non-merohedrally twinned by 180° rotation about **c** and **b**\*, respectively; the untwin-

ning routines merge all equivalent reflections, so that no  $R_{\text{int}}$  value can be given, and the number of reflections is not well-defined because of overlap.

Molecular structures are presented in the figures with thermal ellipsoids at the 50% level. The following comments apply to all packing diagrams unless otherwise stated: Hydrogen atoms are omitted. The atoms labelled Br1, 2, 3 (without primes) correspond to the asymmetric unit. Br...Br contacts are shown as dashed bonds, usually drawn thick (less important or significantly longer contacts may be drawn with thin lines). Primes indicate symmetry-equivalent atoms; the corresponding operators are given explicitly in the tables.

CCDC 896170–896176 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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