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A new polymorph of 1,4-dibromo-2,5-dimethylbenzene: H···Br and Br···π *versus* Br···Br interactions

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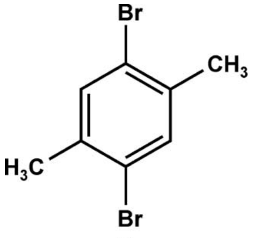
A new polymorph, (I*b*), of the title compound, $C_8H_8Br_2$, crystallizes in the space group $P2_1/n$, the same as the known polymorph (I*a*) but with $Z = 2$ (imposed inversion symmetry) rather than $Z = 4$. The molecular structures are closely similar because the molecule has no degrees of torsional freedom except for methyl groups, but the packing arrangements are completely different. Polymorph (I*a*) is characterized by linked trapezia of Br···Br interactions, whereas polymorph (I*b*) features H···Br and Br···π interactions.

Comment

We are interested in secondary interactions in brominated aromatic hydrocarbons [see, for example, our studies of all ten isomers of di(bromomethyl)naphthalenes; Jones & Kuś, 2010, and related references therein]. Such interactions may include 'weak' C—H···Br hydrogen bonds, Br···Br halogen bonds, π–π stacking, and H···π and Br···π contacts. We are currently preparing a study of several benzene derivatives multiply substituted with bromo, methyl and bromomethyl groups. The title compound, (I), is being published separately because it is a known compound and its structure, as crystallized from ethanol, has already been determined in the space group $P2_1/n$ with $Z = 4$ [Reiter *et al.* (2005), hereinafter polymorph (I*a*); refcode JAQJAN in the Cambridge Structural Database (Allen, 2002)]. However, in our hands the compound crystallized from acetone as a new polymorph in $P2_1/n$ with $Z = 2$ and thus with imposed inversion symmetry, hereafter polymorph (I*b*). We describe here the packing of both polymorphs, which are totally different from each other. The previous study described the packing of (I*a*) in only general terms, but clearly recognized the presence of Br···Br contacts; the compound was a starting material (for the synthesis of *p*-xylylene-1,4-diphosphines) and thus the structure was only of peripheral interest.

The molecule of polymorph (I*b*) is shown in Fig. 1. It has the same general features as the previous polymorph, (I*a*), such as coplanarity of all non-H atoms (r.m.s. deviation = 0.002 Å) and deviations of endocyclic angles from the ideal value of 120° (slightly wider at atom C1 and slightly narrower at C2; Table 1).



(I)

The molecular packing of polymorph (I*b*) is surprising. There are no interactions of the types H···π or π–π, and the shortest Br1···Br1 contact is 4.1761 (3) Å between the molecule at (x, y, z) and those at $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$ or $(x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2})$; this distance would usually be considered too long for any significant interaction. There is one weak intermolecular hydrogen bond of the type C—H···Br1 (Table 2) involving an aromatic H atom; the methyl H atoms play no significant role in the aggregation. The weakness of C—H···Br—C interactions has been commented on by Brammer *et al.* (2001). A search for contacts to the centre of gravity (*Cg*) of the ring reveals a Br1···*Cg* contact of 3.57 Å between the molecule at (x, y, z) and that at $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$, but closer inspection shows that the interaction is better represented by Br1···(mid-point of C1—C2), with a distance of 3.37 Å and an angle at Br1 to C1—Br1 of 167°. The interaction is almost perpendicular (80°) to the ring plane. The Br1···Br1 contact mentioned above is therefore best seen as a consequence of the Br1···π interaction; if this is short, then the two Br atoms related by the same symmetry operator must also approach each other.

The combination of these two contacts with the inversion symmetry of the molecule leads to a three-dimensional packing, but the general features are easily recognisable, especially when depth-cued (Fig. 2).

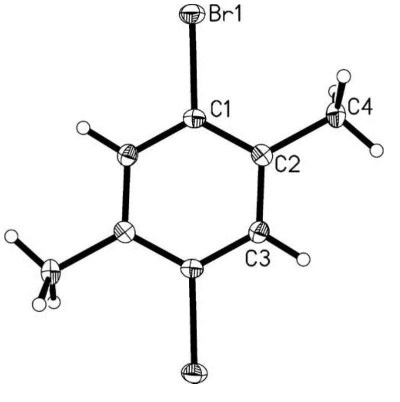


Figure 1
The molecule of polymorph (I*b*) in the crystal structure. Displacement ellipsoids are drawn at the 50% probability level. Only the asymmetric unit is numbered; unlabelled atoms are related by the symmetry operator $(-x + 1, -y + 1, -z)$.

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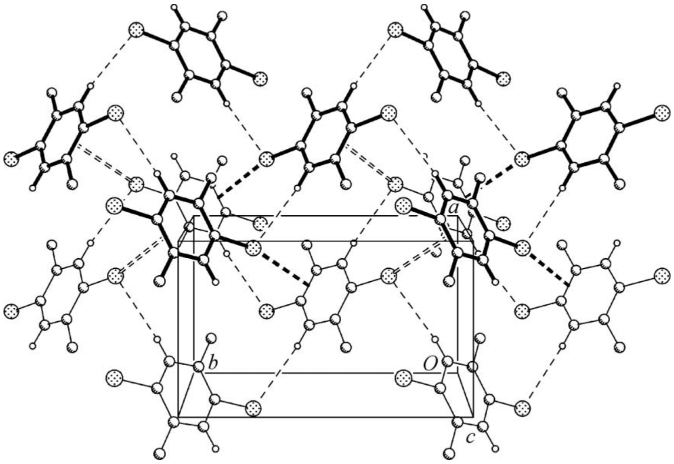

Figure 2
A packing diagram for polymorph (I*b*), viewed perpendicular to (001). The molecules are depth-cued; molecules with thicker bonds are nearer the viewer. C—H$\cdots$Br hydrogen bonds are represented by thin dashed lines and Br$\cdots\pi$ interactions by thick dashed lines. For the sake of clarity, methyl H atoms have been omitted.

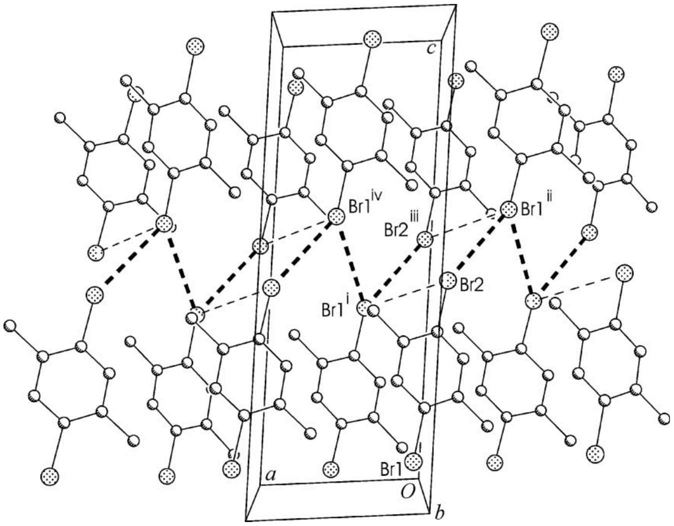

Figure 3
A packing diagram for polymorph (I*a*), viewed parallel to the *b* axis. Br$\cdots$Br interactions are indicated by dashed lines, while thin lines represent the longest contact. [Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x, -y+1, -z+1$; (iv) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.]

The packing of the previously known polymorph (I*a*) is conceptually much simpler. Apart from some rather nonlinear weak intermolecular hydrogen bonds (C—H$_{\rm methyl}\cdots$Br = 3.08 Å and angle = 136°; C—H$_{\rm ar}\cdots Cg$ = 2.92 Å and angle = 133°; C—H$_{\rm methyl}\cdots Cg$ = 2.88 Å and angle = 134°; distances are H$\cdots A$), the main features are Br$\cdots$Br interactions. The Br atoms occupy the regions $z \simeq 0, \frac{1}{2}, 1$, *etc.*, and the contacts link the molecules *via* chains of inversion-symmetric Br1$_2$Br2$_2$ trapezia parallel to the *a* axis, themselves connected by Br1$\cdots$Br1 contacts (Fig. 3 and Table 3). The classification of Pedireddi *et al.* (1994) suggests that the two shorter contacts are type I in nature (approximately equal C—Br$\cdots$Br angles), whereas the longest contact does not fit either of the two main types (type II, usually considered to represent stronger interactions, has one angle *ca* 90° and one *ca* 180°).

We have previously commented (Jones & Kuś, 2010) that it is difficult to predict or rationalize which type(s) of contacts will appear in the packing of any given brominated aromatic hydrocarbon. Our findings here lend weight to this view. The packing of the previously known polymorph (I*a*) of compound (I) was largely determined by Br$\cdots$Br interactions (as one might expect), but the new polymorph (I*b*) features H$\cdots$Br and Br$\cdots\pi$ contacts. The packing efficiency as judged by the density is slightly greater for polymorph (I*b*) [2.100 Mg m^{-3} at 133 K, compared with 2.087 Mg m^{-3} at 143 K for polymorph (I*a*)].

Experimental

The title compound was synthesized by bromination of *p*-xylene and was recrystallized by slow evaporation from acetone.

Polymorph (I*b*)

Crystal data

$C_8H_8Br_2$	V = 417.53 (7) Å^3
M_r = 263.96	Z = 2
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 6.2597 (6) Å	μ = 9.63 mm^{-1}
b = 10.4820 (11) Å	T = 133 K
c = 6.4281 (6) Å	0.20 × 0.15 × 0.12 mm
β = 98.134 (4)°	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	7909 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	1269 independent reflections
$T_{\rm min}$ = 0.292, $T_{\rm max}$ = 0.391	1214 reflections with $I > 2\sigma(I)$
	$R_{\rm int}$ = 0.021

Table 1
Selected bond angles (°) in polymorph (I*b*).

C3^{i}—C1—C2	122.68 (15)	C1^{i}—C3—C2	121.05 (15)
C1—C2—C3	116.27 (14)		

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

Table 2
Hydrogen-bond geometry (Å, °) in polymorph (I*b*).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$\cdots$Br1^{ii}	0.95	3.06	3.9829 (16)	165

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

Table 3
Br$\cdots$Br contacts (Å, °) in polymorph (I*a*).

C—Br$\cdots$Br—C system	Br$\cdots$Br (Å)	C—Br$\cdots$Br angles (°)	Symmetry code
C1—Br1$\cdots$Br1—C1	3.719	151 and 151	$-x, -y+2, -z$
C4—Br2$\cdots$Br1—C1	3.939	74 and 124	$-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$
C4—Br2$\cdots$Br1—C1	3.672	151 and 136	$x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$	47 parameters
$wR(F^2) = 0.051$	H-atom parameters constrained
$S = 1.13$	$\Delta\rho_{\max} = 0.63$ e Å^{-3}
1269 reflections	$\Delta\rho_{\min} = -0.46$ e Å^{-3}

Methyl H atoms were identified in difference syntheses and idealized (C—H = 0.98 Å and H—C—H = 109.5°). The methyl group was refined as a rigid group allowed to rotate but not tip. Aromatic H atoms were introduced at calculated positions and refined using a riding model, with C—H = 0.95 Å. The $U_{\rm iso}$(H) values were set equal to $mU_{\rm eq}$(C), with $m = 1.2$ for aromatic and 1.5 for methyl H atoms.

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 for this paper are available from the IUCr electronic archives (Reference: GD3380). Services for accessing these data are described at the back of the journal.

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