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1,3,5-Tris(bromomethyl)benzene

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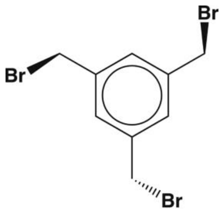
The asymmetric unit of the title compound, $C_9H_9Br_3$, is composed of a single molecule. Two bromo substituents are located on one side of the plane of the aromatic ring and the third is on the opposite side, with the molecular unit exhibiting an approximate noncrystallographic C_s point group. The crystal structure is rich in Br···Br, CH_2···Br and CH···π weak intermolecular contacts which mediate the crystal packing of individual molecules. These interactions promote a red-shift of a handful of vibrational modes (associated with the pendant –CH_2Br groups) compared with values from theoretical density functional theory (DFT) calculations.

Comment

The title compound, (I), is an important starting material for the synthesis of branched ligands (Reger *et al.*, 2010; Podyachev *et al.*, 2006; Spiccia *et al.*, 1997) or dendrimeric molecules (Newkome *et al.*, 1986; Berl *et al.*, 2002) which have a mesitylene unit at their core. Given the synthetic possibilities of this molecule, our research group is now using it for the preparation of new ligands which may be employed in the self-assembly of coordination polymers (Rocha *et al.*, 2011; Klinowski *et al.*, 2011; Shi *et al.*, 2008; Cunha-Silva *et al.*, 2007). We note a recent publication focused on similar molecules, such as 2,4,6-tris(bromomethyl)mesitylene, which explores the various types of Br···Br, CH_2···Br and CH_3···Br interactions present in the crystal structures (Mazik *et al.*, 2010). Because we are also interested in the study of weak hydrogen bonds of the C—H···*X* type and their effect on vibrational spectra (Vaz *et al.*, 2010; Nolasco & Ribeiro-Claro, 2005), we decided to isolate crystals of (I) and study in detail the relationship between the crystal structure and its FT–IR spectroscopic features.

The asymmetric unit of (I) comprises a whole molecule of 1,3,5-tris(bromomethyl)benzene (Fig. 1). The three average planes defined by the peripheral C—C—Br bonds bisect the average plane of the aromatic ring at angles varying from 82.6 (2) to 85.1 (2)°. Conversely, the C—Br bonds subtend angles in the range 66.43 (12)–68.02 (12)° with the average plane of the aromatic ring. Despite these similarities concerning the local geometries, atoms Br1 and Br3 are situated on the opposite side of the plane of the aromatic ring from atom Br2.



(I)

The Br atoms participate in several short C—H···Br interactions, among which C7—H7*A*···Br1^{ii} is considered to be a weak hydrogen bond (see Table 1 for details). As in the crystal structures reported by Mazik *et al.* (2010), Br···Br interactions are present in the crystal structure of (I). This kind of interaction has been divided into two different classes (Pedireddi *et al.*, 1994), defined by the angles subtended by the C—*X*···*X*—C bonds (where *X* is a halogen). In type I, the two C—*X*···*X* angles are similar, and in type II one is near 90° and the other 180°. Based on this classification, the Br2···Br2^{iv} interaction of (I) is a clear example of a type I interaction, while the Br1···Br3^{iii} interaction cannot be unequivocally defined because the angles are neither similar to each other nor close to 90 and 180° (for details, including symmetry codes, see Table 1). Finally, a short C—H···π interaction is also present, establishing a connection between a methylene group and an adjacent aromatic ring (Table 1). These weak interactions, along with the need to avoid empty space, contribute to the formation of a close-packed crystalline structure (Fig. 2).

For a full description of the vibrational modes of (I), the theoretical IR spectrum was calculated by density functional theory (DFT) methods using *GAUSSIAN03W* (Frisch *et al.*, 2003) at the B3LYP/LanL2DZ calculation level. There is a reasonable match between the calculated and experimental spectra, which allows the assignments detailed in Table 2. The most significant differences arise for two sets of normal modes, which were calculated to have very close wavenumbers in the

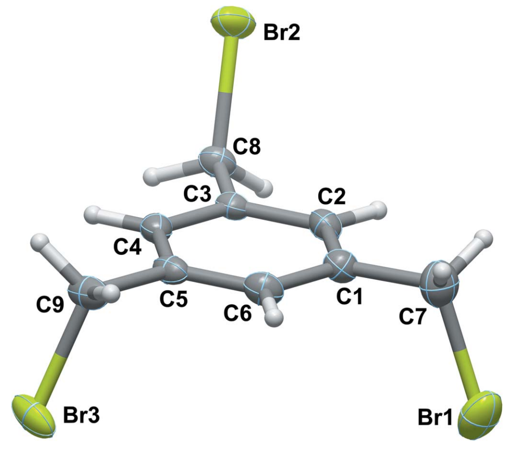


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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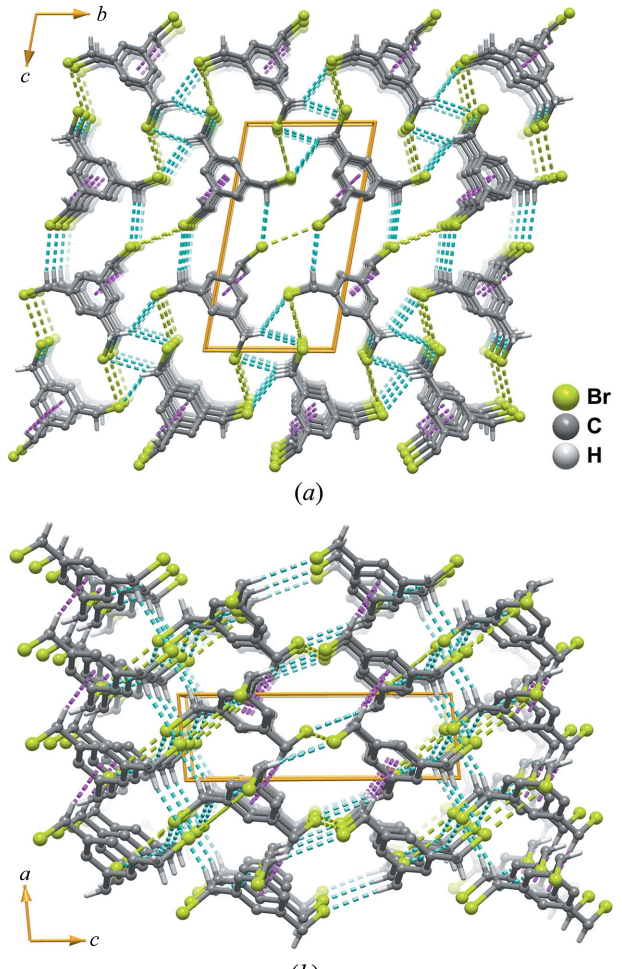

Figure 2
The crystal packing of (I), viewed in perspective along (*a*) the [100] direction and (*b*) the [010] direction of the unit cell. C—H$\cdots\pi$, H$\cdots$Br and Br$\cdots$Br interactions are represented as dashed lines (coloured pink, blue and green, respectively, in the electronic version of the paper).

regions of 1450 and 540 cm^{-1}. However, in the experimental spectrum some of these modes are red-shifted and observed at much wider intervals [see modes associated with footnotes (*a*) and (*b*) in Table 2]. This effect is attributed to the crystal packing, in particular to the weak interactions discussed above (which are not described in a single-molecule calculation). For instance, the four bands observed between 1455 and 1385 cm^{-1} include normal modes involving the motion of C—H bonds engaged in C—H$\cdots$Br and C—H$\cdots\pi$ interactions (see Table 2 for details).

Experimental

The title compound was purchased from Sigma–Aldrich (97%) and recrystallized from CHCl$_3$. ^{1}H and ^{13}C NMR spectra were measured in CDCl$_3$ solution using a Bruker CXP 300 spectrometer. Chemical shifts are quoted in parts per million and referenced by the residual protons of the solvent. The FT–IR spectrum was obtained from KBr pellets using a Bruker Tensor 27 spectrometer. DFT calculations were performed on a personal computer using the *GAUSSIAN03W* package (Frisch *et al.*, 2003) at the B3LYP/LanL2DZ level. The calculated wavenumbers were corrected for anharmonicity by an empirical scaling factor of 0.967. Please refer to the CIF file in the online *Supplementary Material* for optimized atomic coordinates and experimental DFT details. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 4.46 (*s*, 6H, CH$_2$) and 7.36 (*s*, 3H, CH); ^{13}C NMR (75.47 MHz, CDCl$_3$): δ 32.2 (CH$_2$), 129.6 (Ar—H), 139.0 (Ar—C).

Crystal data

$C_9H_9Br_3$
$M_r = 356.89$
Triclinic, $P\overline{1}$
$a = 4.6061$ (2) Å
$b = 8.2473$ (2) Å
$c = 14.7545$ (4) Å
$\alpha = 99.756$ (2)°
$\beta = 93.909$ (2)°
$\gamma = 96.506$ (2)°
$V = 546.64$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 11.02$ mm^{-1}
$T = 150$ K
0.12 × 0.04 × 0.03 mm

Data collection

Bruker X8 KappaCCD APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
$T_{\min} = 0.352$, $T_{\max} = 0.734$
13782 measured reflections
4130 independent reflections
2866 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.077$
$S = 1.01$
4130 reflections
109 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.48$ e Å^{-3}
$\Delta\rho_{\min} = -1.13$ e Å^{-3}

H atoms were placed at their idealized positions and included in the final structural model in a riding-motion approximation, with C—H = 0.95 (aromatic) or 0.99 Å (aliphatic –CH$_2$–), and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT-Plus* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Branden-

Table 1
Selected short interactions (Å, °).

Cg is the centroid of the C6–C6 ring

$A—B\cdots C$	$A—B$	$B\cdots C$	$A\cdots C$	$A—B\cdots C$	Type of interaction
C8—H8*B*$\cdots$*Cg*$^{\rm i}$	0.99	2.84	3.493 (3)	124	C—H$\cdots\pi$†
C7—H7*A*$\cdots$Br1$^{\rm ii}$	0.99	2.91	3.878 (3)	166	Weak hydrogen bond
C7—H7*B*$\cdots$Br1$^{\rm iii}$	0.99	3.00	3.896 (3)	152	Short distance
C7—H7*B*$\cdots$Br3$^{\rm iv}$	0.99	3.05	3.754 (3)	129	Short distance
C9—H9*A*$\cdots$Br2$^{\rm v}$	0.99	2.99	3.971 (3)	171	Short distance
C7—Br1$\cdots$Br3$^{\rm vi}$	1.954 (3)	3.8520 (5)		148.14 (10)	Undefined Br$\cdots$Br
C9—Br3$\cdots$Br1$^{\rm vi}$	1.965 (3)	3.8520 (5)		109.04 (8)	Undefined Br$\cdots$Br
C8—Br2$\cdots$Br2$^{\rm vii}$	1.970 (2)	3.7813 (5)		144.99 (8)	Type I Br$\cdots$Br

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 1, -z + 2$; (iv) $x, y + 1, z$; (v) $-x, -y, -z + 1$; (vi) $-x + 1, -y, -z + 2$; (vii) $-x + 1, 1y + 1, -z + 1$. † The C—H$\cdots$(ring plane) angle is 36°.

burg, 2009); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TP3001). Services for accessing these data are described at the back of the journal.

Table 2
Vibrational spectrum and assignment.

Wavenumber (cm^{-1})	Intensity	Assignment	Wavenumber (cm^{-1})	Intensity	Assignment
3024	*w*	$\nu_{as}(CH_2)$	980	*w*	$\delta(Ph)$
2972	*w*	$\nu(CH)$	894	*m*	$\gamma(CH)$
2856	*w*	$\nu_{sym}(CH_2)$	857	*m*	$\rho(CH)$
1605	*m*	$\nu(Ph)$	704	*s*	$\gamma(CH)$
1455	*m*	(*a*)	663	*m*	$\gamma(CH)$
1435	*m*	(*a*)	634	*m*	$\gamma(CH)$
1401	*m*	(*a*)	582	*s*	$\delta(Ph)$
1385	*s*	(*a*)	554	*m*	(*b*)
1213	*m*	$\omega(CH_2)$	530	*m*	(*b*)
1167	*m*	$\delta(CH)$	477	*w*	$\gamma(Ph-C)$
1120	*m*	$\tau(CH_2)$			

Notes: (*a*) $\delta(CH_2)$ or $[\rho(CH_2) + \nu(Ph)]$ (four very close theoretical vibrational modes); (*b*) $\delta(Ph-C)$ and $\gamma(Ph-C)$ [two very close theoretical vibrational modes below $\delta(Ph)$].

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