

Rotationally disordered phase of 1,3-dibromo-5-iodo-2,4,6-trimethyl- benzene at 293 K

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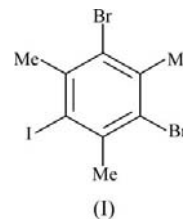
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In the crystal state at room temperature, the molecule of dibromiodomesitylene (1,3-dibromo-5-iodo-2,4,6-trimethylbenzene), $C_9H_9Br_2I$, is prone to strong disorder, apparently involving only the three halogen sites (occupied identically by 66.7% Br and 33.3% I). This disorder, of the rotational type according to previously published NMR measurements, corresponds to fast $2\pi/3$ stochastic in-plane reorientations of the whole molecule between three discernable locations. This kind of rotational disorder can be revealed for the first time by diffractometry thanks to the C_{2v} idealized molecular symmetry of the title compound, although it has been indirectly suspected at room temperature in other trihalogenomesitylenes of similar crystal packing but of D_{3h} molecular symmetry. The average endocyclic angles facing the Br/I sites and the methyl groups are 124.14 (6) and 115.85 (2)°, respectively. The angle between the normal to the aromatic ring and the normal to the (100) plane is 4.1°. TLS analysis indicates that only the aromatic ring and the methyl groups behave as a rigid body with respect to the thermal librations.

Comment

Most benzene compounds hexasubstituted by halogens, methyl groups or other small radicals crystallize at room temperature in the monoclinic space group $P2_1/n$ ($Z = 2$), according to the hexachlorobenzene structure type (Brown & Strydom, 1974; Reddy *et al.*, 2006). Partial compilations of previous contributions can be found in Kitaigorodsky (1973), Tazi *et al.* (1995), Brock & Fu (1997) and Reddy *et al.* (2006). The packing of these compounds is dominated by intermolecular π – π interactions and the molecules are arranged in

stacks (at distances typically ranging from 3.8 to 4.3 Å) parallel to the unique monoclinic axis. In addition, they form corrugated (110) molecular planes, with the halogen–halogen interactions within these planes turning out to be weaker than the π – π inter-stack forces. Another crystal packing is observed, too, at room temperature, especially if the molecules display a threefold axis of symmetry: they are stacked into a triclinic unit cell, space group $P\bar{1}$ ($Z = 2$), derived from the hexamethylbenzene structure type (Hamilton *et al.*, 1969; Le Maguères *et al.*, 2001). This is the case for the trihalogenomesitylene series (1,3,5-trihalogeno-2,4,6-trimethylbenzene; Table 1), of which only trichloromesitylene (TCM) (Tazi *et al.*, 1995; Hernandez *et al.*, 2006), tribromomesitylene (TBM) (Meinnel *et al.*, 2000; Bosch & Barnes, 2002) and triiodomesitylene (TIM) (Boudjada *et al.*, 2001, 2002; Bosch & Barnes, 2002) have been characterized so far. The methyl groups in these compounds experience relatively small hindering potentials and interesting tunnelling properties have been reported (Meinnel *et al.*, 1992, 1995, 2000; Boudjada *et al.*, 2002). What happens if one of the halogen atoms is replaced by another atom, breaking the idealized D_{3h} molecular symmetry of these molecules? If it is an H atom, as encountered for dibromomesitylene (DBM) (Hernandez *et al.*, 2003), the ordered low-temperature phase (the phase is disordered above ~ 297 K) is monoclinic, space group $P2_1/n$ ($Z = 4$). Unexpectedly, however, the methyl group located between the two Br atoms is a quasi-free rotor with H atoms highly delocalized in a sixfold potential, whereas the rotation of the other two methyl groups is quasi-forbidden (Meinnel *et al.*, 1995; Plazanet *et al.*, 2002). In order to establish for the trihalogenomesitylene series the impact of small changes on the molecular symmetry, we report here the crystal structure of 1,3-dibromo-5-iodo-2,4,6-trimethylbenzene (dibromiodomesitylene, DBIM), (I), obtained by single-crystal X-ray diffraction at 293 K. This compound can indeed be viewed as a TBM with one Br atom substituted by I, or alternatively as a TIM with two I atoms substituted by Br, the idealized symmetry of the isolated molecule (ignoring H atoms) decreasing in both cases from D_{3h} ($\bar{6}m2$) to C_{2v} ($mm2$).



The best refinement with 54 geometric soft restraints (see *Refinement*) led to the molecular structure shown in Fig. 1. The crystallographically inequivalent halogen sites are identically constituted by 67% Br and 33% I (see *Refinement*), the other atoms apparently not being affected by any kind of disorder. NMR measurements at room temperature showed a long time ago that in this family of compounds – at least for the hydrogenated materials – there is evidence for a dynamic reorientation of the molecules by jumps of $2n\pi/6$ within their plane (n is an integer), at a frequency in the MHz range

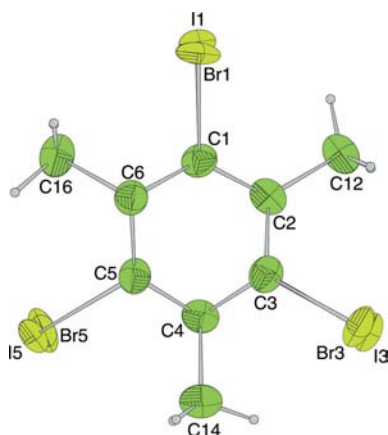


Figure 1

A view of the molecule of DBIM, (I), at 293 K, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

(Eveno & Meinel, 1966). The disorder in (I) therefore corresponds to fast $2\pi/3$ stochastic in-plane reorientations of the whole molecule between three discernable locations, inducing the apparent overlap of Br and I atoms, according to a $\frac{2}{3}:\frac{1}{3}$ ratio. This novel feature has been characterized by diffractometry thanks to the idealized (instantaneous) C_{2v} molecular symmetry of the isolated molecule (ignoring H atoms), which is time-averaged towards an apparent idealized D_{3h} symmetry by means of the diffraction probe. The same kind of rotational disorder, although suspected at room temperature in TCM (Tazi *et al.*, 1995; Hernandez *et al.*, 2006), TBM and TIM, has not been directly proved so far, due to the ternary symmetry of these latter molecules.

In (I), significant deformation of the angles of the benzene ring from a regular D_{6h} ($6/mmm$) hexagon is observed. The average endocyclic angle is $124.14(6)^\circ$ around the C atoms linked to Br/I sites, and an average value of $115.85(2)^\circ$ is observed for the C atoms bonded to the methyl groups, making the aromatic ring a distorted hexagon fulfilling approximately D_{3h} symmetry. This deformation is close to that found in TCM, TBM and TIM compounds at the same temperature and is in agreement with systematic trends establishing that the endocyclic angle facing the C atom bearing the most electronegative substituent is enlarged (Domenicano *et al.*, 1975). After the restrained refinement, the mean values for the $C_{ar}-Br$ and $C_{ar}-I$ distances are $1.907(9)$ and $2.106(6)$ Å, respectively.

The crystal packing of (I) can be described as a stacking of (100) molecular layers at $x/a \sim \frac{1}{4}$ and $\frac{3}{4}$, forming zigzag molecular columns propagating along the a axis (Figs. 2 and 3). The angle between the normal to the aromatic plane and the normal to the (100) plane is 4.1° . Within each column, the arrangement is approximately 'antiferroelectric': a given molecule is sandwiched between two molecules at ~ 4.06 Å generated by inversion centres and belonging to adjacent layers. A Br/I site is more or less directly below the methyl groups and *vice versa*. The symmetry centres are located on the a axis, but the centres of mass of the molecules are shifted

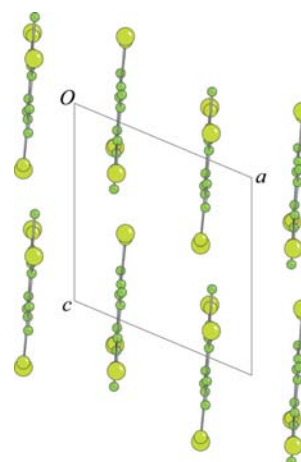


Figure 2

The crystal packing of (I) at 293 K, along the b axis. H atoms have been omitted for clarity.

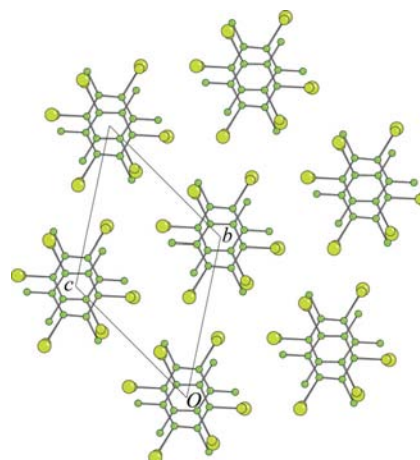


Figure 3

The crystal packing of (I) at 293 K, along the a axis. H atoms have been omitted for clarity. Notice within the (100) planes the pseudo-hexagonal environment around a given molecule.

away from the latter axis by 0.46 Å (Fig. 3), which explains the slightly zigzag shape of the molecular rows. Within each (100) layer, one probe molecule is surrounded by six neighbours in such a way that characteristic triangular halogen–halogen and Me–Me intermolecular contacts are formed, the three corresponding contact distances being very similar (*e.g.* mean value of 3.61 Å for $I \cdots I$). For molecules in different layers, the shortest intermolecular contact distances, compared with those between molecules within the same layer, are significantly shortened for $C_{Me} \cdots C_{Me}$ contacts, almost unchanged for $C_{Me} \cdots$ halogen contacts and significantly increased for halogen–halogen contacts. The same structural topology is encountered at room temperature in TBM (Meinel *et al.*, 2000) and TIM (Boudjada *et al.*, 2001), and also in TCM below 160 K (lowest temperature phase, or phase IV; Hernandez *et al.*, 2006).

The C atoms of the ring display U_{eq} displacement parameters significantly lower (mean 0.039 Å²) than those of the substituted atoms (mean values of 0.057 , 0.048 and 0.059 Å² for Br, I and C_{Me} , respectively). In order to clarify this point, we performed a conventional TLS analysis using the *CRYSTALS*

TALS program (Betteridge *et al.*, 2003). The overall rigid-body motion tensors **T**, **L** and **S** (Schomaker & Trueblood, 1968) were least-squares fitted to the individual anisotropic displacement parameters. At first, we included only the C atoms in the rigid-body treatment, and the reliability factor for the *U* values was *R* = 0.054, revealing the rigid character of the body constituted by the aromatic ring and the methyl groups. Clearly, the translation and screw tensors are negligible, the thermal motion of the aforementioned rigid body being essentially of librational origin. The eigenvalues of the libration tensor are $L_{11} = 9^{\circ 2}$ (in-plane libration), and $L_{22} = 19^{\circ 2}$ and $L_{33} = 22^{\circ 2}$ (both corresponding to off-plane librations). In the second step of the **TLS** analysis, we added the Br and I atoms, *i.e.* we took into account all the non-H atoms. The reliability factor for the *U* values increased substantially to *R* = 0.131, indicating that, relative to the aromatic ring and methyl groups, the halogen substituents do not behave rigidly.

Experimental

Compound (I) was synthesized at 353 K by adding dropwise a mixture of sulfuric acid (20 ml), nitric acid (30 ml) and acetic acid (150 ml) to a balloon flask containing dibromomesitylene (0.07 mol), iodine (0.04 mol) and acetic acid (200 ml). After 1 h of reaction, a powder of dibromiodomesitylene was obtained. Subsequent recrystallization of a saturated solution in chloroform yielded pure colourless crystals of (I) suitable for X-ray analysis. High-resolution mass spectrometry (electron energy 70 eV, temperature source 418 K) indicated $m/z = 401.8114$ versus a theoretical value of 401.81157. NMR decoupled spectra for protons were recorded for solutions of (I) and reveal that only one material is present. Solid-state ^{13}C NMR spectra carried out with a rotation at the magic angle (speed 6000 Hz) demonstrate that there is only one component at each molecular site within the entire crystal.

Crystal data

$\text{C}_9\text{H}_9\text{Br}_2\text{I}$	$\gamma = 95.100$ (10) $^\circ$
$M_r = 403.84$	$V = 545.33$ (13) \AA^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.8950$ (10) \AA	Mo $K\alpha$ radiation
$b = 9.3180$ (9) \AA	$\mu = 10.21$ mm^{-1}
$c = 9.3130$ (11) \AA	$T = 293$ K
$\alpha = 60.187$ (8) $^\circ$	$0.29 \times 0.28 \times 0.18$ mm
$\beta = 72.998$ (9) $^\circ$	

Data collection

Nonius KappaCCD area-detector diffractometer	5479 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2995 independent reflections
$T_{\min} = 0.06$, $T_{\max} = 0.16$	1629 reflections with $I > 3\sigma(I)$
	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	54 restraints
$wR(F^2) = 0.044$	H-atom parameters constrained
$S = 1.18$	$\Delta\rho_{\text{max}} = 1.21$ e \AA^{-3}
1629 reflections	$\Delta\rho_{\text{min}} = -1.01$ e \AA^{-3}
138 parameters	

The triclinic unit-cell setting, although not conventional, was chosen for the sake of comparison with the previously published isomorphous compounds TCM, TBM and TIM (Table 1). For the sake of stability, the refinement was undertaken by initially fixing the

Table 1

Published unit-cell parameters for the room-temperature phases of the trihalogenomesitylene compounds (1,3,5-trihalogeno-2,4,6-trimethylbenzene) discussed in the *Comment*.

Formula	$\text{C}_9\text{Cl}_3\text{H}_9$	$\text{C}_9\text{Br}_3\text{H}_9$	$\text{C}_9\text{I}_3\text{H}_9$
Chemical name	1,3,5-Trichloro-2,4,6-trimethylbenzene	1,3,5-Tribromo-2,4,6-trimethylbenzene	1,3,5-Triiodo-2,4,6-trimethylbenzene
Common name	Trichloromesitylene	Tribromomesitylene	Triiodomesitylene
Usual shortened name	TCM	TBM	TIM
Reference	Tazi <i>et al.</i> (1995)	Meinzel <i>et al.</i> (2000)	Boudjada <i>et al.</i> (2001)
IUCr CIF code	pa0298b		av1075
<i>T</i> (K)	297	295	293
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>Z</i>	2	2	2
<i>a</i> (\AA)	7.738 (6)	7.808 (4)	8.0486 (1)
<i>b</i> (\AA)	8.842 (4)	9.123 (4)	9.6105 (1)
<i>c</i> (\AA)	8.880 (3)	9.143 (4)	9.6204 (1)
α ($^\circ$)	59.74 (3)	59.77 (3)	60.1766 (6)
β ($^\circ$)	66.51 (5)	67.97 (4)	66.7586 (7)
γ ($^\circ$)	73.06 (4)	73.18 (4)	85.3542 (7)
<i>V</i> (\AA^3)	478.1	517.5	586.97 (2)

occupancies of the Br and I atoms to 0.667 and 0.333, respectively. These values are in agreement with the compound stoichiometry and with the above-mentioned dynamic disorder, and they were checked once convergence was reached (see below). Due to the disorder, 54 geometric soft restraints were applied in order to maintain a chemically reasonable molecule, according to the distances and angles calculated for the isolated molecule by means of density functional theory quantum chemistry calculations (MPW1PW91 function, LanL2DZ basis set; GAUSSIAN98; Frisch *et al.*, 1998): $\text{C}_r\text{—Br} = 1.920$ (5) \AA , $\text{C}_r\text{—I} = 2.120$ (5) \AA , $\text{C}_r\text{—C}_r = 1.40$ (1) \AA , $\text{C}_r\text{—C}_{\text{Me}} = 1.50$ (1) \AA , $\text{C}_r\text{—C}_r\text{—Br(I)} = 117.0$ (3) $^\circ$, $\text{C}_r\text{—C}_r\text{—C}_r = 124.0$ (1) or 116.0 (1) $^\circ$ in front of a halogen site or methyl group, respectively, and $\text{C}_r\text{—C}_r\text{—C}_{\text{Me}} = 122.0$ (4) $^\circ$, with planarity = 0.02 \AA for all non-H atoms. The final refinement cycles included the atomic coordinates and the anisotropic displacement parameters for all non-H atoms. Methyl H atoms, not detectable in the difference Fourier map, were generated geometrically, with their positions riding on their parent C atoms and their isotropic displacement parameters set to one least-squares parameter. Starting from the final structure model, refinement of the Br and I occupancies for each halogen site (plus the scale factor) led to the following values: 0.671 (3)/0.3351 (16), 0.663 (3)/0.3309 (17) and 0.666 (3)/0.3327 (16) for sites 1, 3 and 5, respectively, without changing the agreement factors (*i.e.* not significantly different from the reported model with $\frac{2}{3}, \frac{1}{3}$ disorder).

Data collection: COLLECT (Nonius, 2001); cell refinement: DIRAX (Duisenberg *et al.*, 2003); data reduction: EVALCCD (Duisenberg *et al.*, 2003); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: CRYSTALS.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3100). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
- Bosch, E. & Barnes, C. L. (2002). *Cryst. Growth Des.* **2**, 299–302.
- Boudjada, A., Hernandez, O., Meinnel, J., Mani, M. & Paulus, W. (2001). *Acta Cryst.* **C57**, 1106–1108.
- Boudjada, A., Meinnel, J. J., Boucekkine, A., Hernandez, O. J. & Fernandez-Diaz, M. T. (2002). *J. Chem. Phys.* **117**, 10173–10183.
- Brock, C. P. & Fu, Y. (1997). *Acta Cryst.* **B53**, 613–619.
- Brown, G. M. & Strydom, O. A. W. (1974). *Acta Cryst.* **B30**, 801–804.
- Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* **B31**, 221–234.
- Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
- Eveno, M. & Meinnel, J. (1966). *J. Chim. Phys.* **63**, 108–113.
- Frisch, M. J., *et al.* (1998). *GAUSSIAN98*. Revision A.5. Gaussian Inc., Pittsburgh, PA, USA.
- Hamilton, W. C., Edmonds, J. W., Tippe, A. & Rush, J. J. (1969). *Discuss. Faraday Soc.* **48**, 192–204.
- Hernandez, O., Cousson, A., Plazanet, M., Nierlich, M. & Meinnel, J. (2003). *Acta Cryst.* **C59**, o445–o450.
- Hernandez, O., Knight, K. S., Van Beek, W., Boucekkine, A., Boudjada, A., Paulus, W. & Meinnel, J. (2006). *J. Mol. Struct.* **791**, 41–52.
- Kitaigorodsky, A. I. (1973). *Molecular Crystals and Molecules*, p. 89. New York: Academic Press.
- Le Maguères, P., Lindeman, S. V. & Kochi, J. K. (2001). *Organometallics*, **20**, 115–125.
- Meinnel, J., Häusler, W., Mani, M., Tazi, M., Nusimovici, M., Sanquer, M., Wyncke, B., Heidemann, A., Carlile, C. J., Tomkinson, J. & Hennion, B. (1992). *Physica B*, **180/181**, 711–713.
- Meinnel, J., Hennion, B., Mani, M., Wyncke, B. & Carlile, C. J. (1995). *Physica B*, **213/214**, 649–651.
- Meinnel, J., Mani, M., Cousson, A., Boudjada, F., Paulus, W. & Johnson, M. (2000). *Chem. Phys.* **261**, 165–187.
- Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Plazanet, M., Johnson, M. R., Cousson, A., Meinnel, J. & Trommsdorff, H. P. (2002). *Chem. Phys.* **285**, 299–308.
- Reddy, C. M., Kirchner, M. T., Gundakaram, R. C., Padmanabhan, K. A. & Desiraju, G. R. (2006). *Chem. Eur. J.* **12**, 2222–2234.
- Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Tazi, M., Meinnel, J., Sanquer, M., Nusimovici, M., Tonnard, F. & Carrie, R. (1995). *Acta Cryst.* **B51**, 838–847.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.