Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

1,3,5-Triiodo-2,4,6-trimethylbenzene at 293 K

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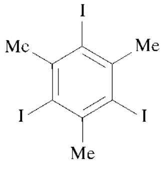
Received 20 February 2001
Accepted 19 June 2001

In the structure of triiodomesitylene (1,3,5-triiodo-2,4,6-trimethylbenzene), $C_9H_9I_3$, at 293 K, the benzene ring is found to be significantly distorted from ideal D_{6h} symmetry; the average endocyclic angles facing the I atoms and the methyl groups are 123.8 (3) and 116.2 (3)°, respectively. The angle between the normal to the molecular plane and the normal to the (100) plane is 5.1°. No disorder was detected at 293 K. The thermal motion was investigated by a rigid-body motion tensor analysis. Intra- and intermolecular contacts are described and topological differences compared with the isomorphous compounds trichloromesitylene and tribromomesitylene are discussed.

Comment

At room temperature, almost all hexasubstituted halogenomethylbenzenes with different substituents crystallize in the monoclinic system, with two molecules per unit cell located on a centre of symmetry, even if the isolated molecules are asymmetric. This apparent contradiction is understood if one takes into account the occurrence of dynamical orientational disorder, whereby molecules jump by 60° around their centre of gravity in the ring plane [see Tazi *et al.* (1995) for a comprehensive review]. In some cases, when the isolated molecule displays a threefold symmetry axis, other molecular stacking modes are encountered, *e.g.* the hexagonal system, space group *P*63/*m*, for 1,3,5-trichloro-2,4,6-trifluorobenzene (Chaplot *et al.*, 1981), and the triclinic system, space group $P\overline{1}$, for 1,3,5-trichloro-2,4,6-trimethylbenzene (trichloromesitylene, TCM; Tazi *et al.*, 1995) and 1,3,5-tribromo-2,4,6-trimethylbenzene (tribromomesitylene, TBM; Meinnel *et al.*, 2000). Even though no disorder is observed in TCM and TBM at 293 K, the molecules nonetheless jump in their plane by 120° in equivalent positions (Eveno & Meinnel, 1966). Furthermore, TCM and TBM can be considered as prototype systems for studying the rotational tunnelling behaviour (Prager & Heidemann, 1997) of methyl groups. Indeed, the three methyl groups of each molecule display different tunnelling excitations, reflecting different hindering potentials (Meinnel *et al.*, 1992). As the tunnelling behaviour of 1,3,5-triiodo-2,4,6-trimethylbenzene (triiodomesitylene, TIM) is similar to that of TBM but with one methyl group being still less hindered, high quality structural data concerning TIM are required. We report herein a structural study of TIM, (I), at 293 K, in order to complete and enlighten the previously published work concerning the two aforementioned isomorphous compounds, *i.e.* TCM (Tazi *et al.*, 1995) and TBM (Meinnel *et al.*, 2000).



(I)

The conformation of the molecule of (I) (Fig. 1) is characterized mainly by a significant distortion of the endocyclic angles of the benzene ring from ideal D_{6h} symmetry; 123.8 (3)° on average for atoms facing the I atoms *versus* 116.2 (3)° on average for atoms facing the methyl groups. The widest angle is found for the most electronegative substituent, corroborating the general trends established by Domenicano *et al.* (1975). It is also for the same reason that the difference between the mean endocyclic angle for atoms facing the halogens and that for atoms facing the methyl groups decreases progressively from TCM [124.4 (2) and 115.6 (2)°, respectively] to TBM [124.1 (1) and 115.9 (1)°, respectively] and then to (I). The average intramolecular bond lengths [$C_{ar}-I$ 2.117 (3), $C_{ar}-C_{ar}$ 1.403 (5) and $C_{ar}-C_{Me}$ 1.506 (5) Å] are in agreement with the distances reported in the literature.

We have computed the least-squares best plane (unit weights) through all the non-H atoms using the *MOLAX* routine in *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1999). The angle between the normal to this molecular plane and the normal to the (100) plane is found to be 5.1°. While deviations from this plane are negligible for C atoms belonging to the ring [between 0.003 (4) and 0.010 (4) Å in absolute values], it appears that atom I5 is significantly more out of the plane than atoms I1 and I3 [−0.052 (1) Å *versus* 0.013 (1) and 0.016 (1) Å, respectively]; the same conclusion can be drawn for atom C21 of the methyl group facing I5 [−0.046 (5) Å *versus* 0.023 (5) and 0.031 (5) Å for C41 and C61, respectively]. The refinement of the occupancies of the substituted groups, *i.e.* I atoms and methyl groups, reveals no deviation (within the s.u.'s) from the site-symmetry multiplicity. We can thus conclude that no disorder can be detected in (I) at 293 K.

In compound (I), eight molecules are located on the four unit-cell edges parallel to the *a* axis and they are related to each other by an inversion centre at ($\frac{1}{2}$, 0, 0), leading to $Z = 2$ (Fig. 2). This description has been chosen in order to make it easier to compare the structure with that of the isomorphous compound TCM (Tazi *et al.*, 1995).

The structure of (I) can be described as a stacking of molecular layers (at $x/a \simeq \frac{1}{4}$ and $\frac{3}{4}$) along the *a* axis forming antiferroelectric columns along this axis, *i.e.* an I atom is more or less directly below (*a*-projected shift $\simeq$ 1.04 Å) the methyl groups of the two molecules generated by an inversion centre and belonging to adjacent layers. This shift between molecules when looking along the *a* axis (Fig. 2) is explained by the fact that the centre of gravity of the molecules of (I) is not located on the unit-cell edge parallel to the *a* axis, but at $\simeq$ 0.5236 Å in the (100) plane. Within each layer, one molecule of (I) is surrounded by six neighbours in such a way that each I atom or methyl group is opposite another, with two of the I atoms or methyl groups belonging to nearby molecules, the three corresponding contact distances being very similar. The shortest intermolecular distances are I$\cdots$I 3.8875 (4), $C_{Me}\cdots$I 4.095 (4) and $C_{Me}\cdots C_{Me}$ 4.740 (6) Å. The shortest intramolecular distances are 6.0479 (4), 3.229 (4) and 5.077 (5) Å, respectively. For molecules in different layers, it turns out that the minimum intermolecular distances, compared with those between molecules within the same layer, are significantly shortened for the $C_{Me}\cdots C_{Me}$ contacts [4.000 (7) Å], almost unchanged for the $C_{Me}\cdots$I contacts [4.007 (5) Å] and significantly increased for the I$\cdots$I contacts [4.2843 (6) Å].

The C atoms of the ring display U_{eq} parameters significantly lower (mean 0.0324 Å^2) than those of the substituted atoms (means of 0.0477 and 0.0479 Å^2 for the I and methyl-C atoms, respectively). In order to clarify this point, we performed a conventional **TLS** analysis using the *CRYSTALS* program (Watkin, Prout, Carruthers & Betteridge, 1999). The overall rigid-body motion tensors **T**, **L** and **S** (Schomaker & Trueblood, 1968) were least-squares fitted to the individual anisotropic displacement parameters. Considering the whole molecule of (I), with the exception of the H atoms, as a rigid-body group leads to an overall *R* factor for U_{ij} of 0.064, indicating that the latter assumption is reasonably relevant. Nevertheless, once the methyl groups or the I atoms are removed from the above-mentioned set of atoms used for the **TLS** calculation, the *R* factor for U_{ij} decreases to 0.036 or to 0.035, respectively, while the main **TLS** features remain unchanged. The diagonal values of the translational **T** and screw **S** thermal tensors, with respect to the principal axes of the librational **L** tensor, are negligible, while those of the **L** tensor are $L_{11} = 5.4$, $L_{22} = 10.3$ and $L_{33} = 14.3°^2$. The centre of libration is close to the centre of gravity of the molecule. Axis 2 is roughly parallel to the C6—C61 bond, axis 1 is almost perpendicular to the molecular plane and axis 3 bisects the C2—C21 and axis 1 directions.

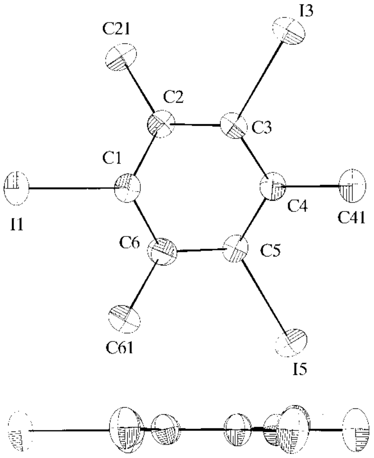


Figure 1
The molecular view of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

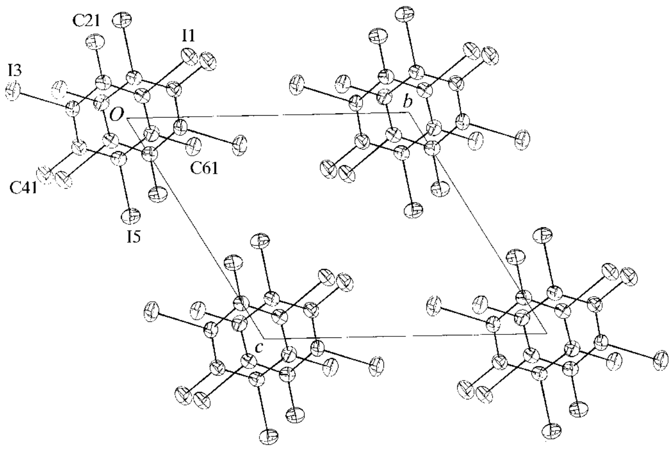


Figure 2
The packing diagram for (I) along the *a* axis, with labels shown for the substituted atoms of one molecule.

Let us compare the main crystallographic features of (I), TCM (Tazi *et al.*, 1995) and TBM (Meinnel *et al.*, 2000). In the latter two compounds, the molecular layers are also antiferroelectrically stacked along the *a* axis at $x/a \simeq \frac{1}{4}$ and $\frac{3}{4}$, but in TCM, the centre of gravity of one given molecule is located at (0.7494, −0.0016, −0.0007), *i.e.* almost exactly on the unit-cell edge parallel to the *a* axis. Consequently, and with respect to the [100] direction, a Cl atom is directly below and perfectly aligned with the methyl groups of the two molecules generated by an inversion centre and belonging to adjacent layers. On the contrary, following the example of (I), the centre of gravity of the TBM molecules is not located on the unit-cell edge parallel to the *a* axis, but at $\simeq$ 0.4256 Å in the (100) plane, leading to a zigzag antiferroelectric stacking of the molecules along the latter axis. On the other hand, the minimum intermolecular $C_{Me}\cdots C_{Me}$ contact distance within one layer is drastically lower for TCM and TBM (3.887 and 4.168 Å, respectively) than for (I) and increases slightly between layers (4.037 and 4.070 Å, respectively). We note that in (I), as well as in TCM, the largest bond lengths, C_{ar}—I(Cl) or C_{ar}—C_{Me}, coincide with the largest endocyclic angles. Lastly, it turns out that at room temperature and for the three isomorphous compounds under discussion, the two extracyclic angles on both sides of each substituted group are very similar.

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Experimental

Compound (I) was synthesized at 343 K as follows: a solution containing nitric acid (22 ml) and sulfuric acid (18 ml) diluted in acetic acid (400 ml) was introduced drop by drop into a balloon flask containing mesitylene (14 ml), pulverized iodine (36 g) and acetic acid (200 ml). After 5 h of reaction, periodically monitored by gas chromatography, the mixture was cooled by adding distilled water. Compound (I) precipitated with the excess of iodine and the crude material was vacuum filtered under a flux of dimethyl ether in order to eliminate the residual iodine. A subsequent recrystallization by sublimation yielded pure colourless crystals of (I) suitable for X-ray analysis.

Crystal data

$C_9H_9I_3$
$M_r = 497.88$
Triclinic, $P\bar{1}$
$a = 8.0486$ (1) Å
$b = 9.6105$ (1) Å
$c = 9.6204$ (1) Å
$\alpha = 60.1766$ (6)°
$\beta = 66.7586$ (7)°
$\gamma = 85.3542$ (7)°
$V = 586.97$ (2) Å^3
$Z = 2$
$D_x = 2.818$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 6527 reflections
$\theta = 1.0$–40.3°
$\mu = 7.94$ mm^{-1}
$T = 293$ (1) K
Prism, colourless
0.26 × 0.18 × 0.16 mm

Data collection

Nonius KappaCCD diffractometer
CCD scans
Absorption correction: multi-scan from symmetry-related measurements (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.365$, $T_{\max} = 0.577$
31 221 measured reflections
6822 independent reflections
3123 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.069$
$\theta_{\max} = 40.3$°
$h = -13 \rightarrow 13$
$k = -17 \rightarrow 17$
$l = -17 \rightarrow 17$

Refinement

Refinement on F
$R = 0.030$
$wR = 0.030$
$S = 1.12$
3123 reflections
140 parameters
All H-atom parameters refined
Weighting scheme: Chebychev polynomial with 5 parameters (Carruthers & Watkin, 1979) 3.59, −1.92, 4.50, −0.767, 1.48
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 1.29$ e Å^{-3}
$\Delta\rho_{\min} = -1.26$ e Å^{-3}
Extinction correction: equation 22 in Larson (1970)
Extinction coefficient: 77 (3)

The H atoms of the methyl groups were generated geometrically and their positions were further refined along with the other atoms using geometric (distance, angle and planarity) soft restraints [C—H = 1.04 (3)–1.05 (3) Å]. The isotropic displacement parameters of the H atoms of a given methyl group were set to a single least-squares parameter.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997); program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1999); molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1999); software used to prepare material for publication: *CRYSTALS*.

Table 1
Selected geometric parameters (Å, °).

I1—C1	2.117 (3)	C2—C21	1.507 (5)
I3—C3	2.120 (3)	C4—C41	1.515 (5)
I5—C5	2.115 (3)	C6—C61	1.496 (5)
C1—C2	1.404 (5)	I1—C21	3.229 (4)
C1—C6	1.402 (5)	I1—C61	3.262 (4)
C2—C3	1.400 (5)	I3—C21	3.270 (4)
C3—C4	1.400 (5)	I3—C41	3.240 (4)
C4—C5	1.401 (5)	I5—C41	3.259 (4)
C5—C6	1.410 (5)	I5—C61	3.240 (4)
I1—C1—C2	117.6 (2)	C3—C4—C5	116.6 (3)
I1—C1—C6	118.4 (2)	C3—C4—C41	121.9 (3)
C2—C1—C6	124.1 (3)	C5—C4—C41	121.5 (3)
C1—C2—C3	116.2 (3)	I5—C5—C4	118.8 (2)
C1—C2—C21	121.7 (3)	I5—C5—C6	117.7 (2)
C3—C2—C21	122.2 (3)	C4—C5—C6	123.5 (3)
I3—C3—C2	118.6 (2)	C1—C6—C5	115.9 (3)
I3—C3—C4	117.7 (2)	C1—C6—C61	122.3 (3)
C2—C3—C4	123.7 (3)	C5—C6—C61	121.8 (3)

We would like to thank the Centre de Diffractométrie de l'Université de Rennes 1 for the opportunity to collect data on the Nonius KappaCCD X-ray diffractometer. In particular, the useful advice of Dr T. Roisnel is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1075). Services for accessing these data are described at the back of the journal.

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