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Diiododurene: four centrosymmetric molecules in general positions

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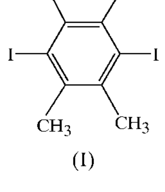
Diiododurene (1,4-diodo-2,3,5,6-tetramethylbenzene), $C_{10}H_{12}I_2$, packs with four molecules in the asymmetric unit. All four of these moleules violate Kitaigorodsky's suggestion that molecules with centers of symmetry will lie on crystallographic centers of symmetry. There is 5.6% disorder at one of the sites. Most of the I atoms are in contact with other I atoms, but only six of the I$\cdots$I contacts are shorter than 4.2 Å. Of these six contacts, one set of three contacts forms a triangular set in which all of the I$\cdots$I distances are less than 3.9 Å.

Comment

Following the determination of the structure of the complex p-$C_6(CH_3)_4I_2$/p-$C_6F_4(CN)_2$ (Britton & Gleason, 2002), we have determined the crystal structure of diiododurene, (I). There are four molecules in the asymmetric unit. In the notation of Zorky and co-workers (Zorky *et al.*, 1967; Belsky *et al.*, 1995; Zorky, 1996), the description of the unit cell would be $P\overline{1}$, $Z = 8(1^4)$. This is remarkable in that none of the four independent molecules lies on a center of symmetry. Kitaigorodsky (1961, 1973) went so far as to state that a molecular center of symmetry always coincides with a crystallographic center of symmetry, even though he described pyrene as an exception to this rule. Recently, the program *CSDSymmetry* (Yao *et al.*, 2002) has been used to re-examine this question and it was found that out of 18 008 molecules with approximate molecular symmetry $\overline{1}$, only 15 156 lie on the crystallographic inversion center.



(I)

Three of the four independent molecules of (I) are free of measurable disorder, but the fourth molecule shows a disorder with the minor component having an occupancy of 5.61 (6)%. Fig. 1 shows the labelling and the anisotropic displacement ellipsoids for the disordered pair; the numbering and ellipsoids for the remaining molecules are similar. To check the disorder, a second set of data was collected on a new crystal. The disorder from this refinement was 5.52 (7)%.

The bond lengths and angles are normal and agree within experimental error among the four molecules. The *Crystal Data* section of the *Experimental* reports the refinement with all four molecules independent of each other. To obtain the best possible estimates for the bond lengths and angles in an isolated molecule, the data were refined with all chemically equivalent bond lengths and angles constrained to be the same. The constraints only increased R from 0.027 to 0.028. The results are: C1$\cdots$I = 2.124 (2) Å, C1—C2 = 1.398 (1) Å, C2—C3 = 1.406 (2) Å, C2—CH_3 = 1.516 (2) Å, C2—C1—C2′ = 123.72 (13)° and C1—C2—C2′ = 118.14 (8)°. The angles can be compared with those found in two separate determinations of triiodomesitylene, *viz*. 123.8 (3) and 116.2 (3)° (Boudjada *et al.*, 2001), and 123.5 (6) and 116.5 (6)° (Bosch & Barnes, 2002). The results in both molecules agree with the trends described by Domenicano (1992).

Fig. 2 shows a view approximately along the a axis. The molecules pack in two kinds of stacks, with molecules 1 and 2 alternating in one stack (stack-12), and molecules 3 and 4 alternating in the other (stack-34). The stacks are aligned in a hexagonal array of parallel stacks, with each stack surrounded by two of one kind and four of the other kind. In stack-12, molecule 1 is tilted 23.1 (2)° away from the normal to the stack direction (a axis), while molecule 2 is tilted 24.1 (2)°. The perpendicular distances between the planes are both 3.75 (2) Å. In stack-34, the tilts are 25.2 (2) and 24.9 (2)° for molecules 3 and 4. The distances between the planes are alternately 3.69 (2) and 3.66 (2) Å.

In addition to the stacks involving π interactions, there are approximately planar ribbons of molecules at angles to the

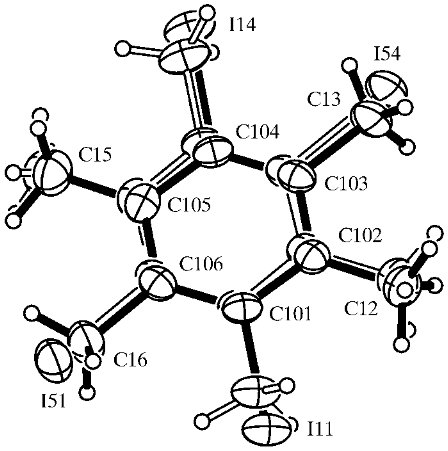


Figure 1
Molecule 1 of (I). Displacement ellipsoids are drawn at the 50% probability level. Molecule 5, the minor component of the disorder at molecule 1, is shown with open bonds. Only the I atoms in the minor component are labeled. Molecules 2, 3, and 4, all ordered, have very similar displacement ellipsoids to molecule 1.

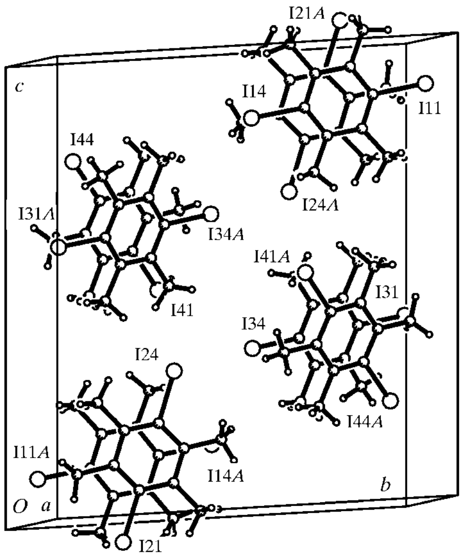


Figure 2
The unit cell, viewed normal to (100), showing stacks of molecules. There are two types of stacks, namely molecule 1 alternating with molecule 2, and molecule 3 alternating with molecule 4. These stacks are parallel to *a*. Atoms labeled with the suffix *A* are related to the unlabeled atoms by an inversion center at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$).

stacks. Fig. 3 shows two views of these ribbons. There are two types of ribbon, one involving molecules 1 and 2 (ribbon-12), the other molecules 3 and 4 (ribbon-34). In ribbon-12, the molecular order is –1–1–2–2–1–1–, while in ribbon-34, the order is –3–4–3–4–.

Before discussing the intermolecular σ contacts, we will look at some earlier I···I and $\mathrm{C_{Me}}$···$\mathrm{C_{Me}}$ contacts. It is well known (Bent, 1968) that the shortest X—I1···I2—Y intermolecular interactions involving small molecules usually occur with a nearly linear X—I1···I2 angle and a nearly tetrahedral I1···I2—Y angle. This is interpreted that I1 is a Lewis acid (electron acceptor) and I2 is a Lewis base (electron donor). In centrosymetric diiodides, this leads to linear chains of molecules. In triiodides with approximate threefold symmetry, such interactions can lead to cyclic I···I···I groups. Table 1 gives the distances and angles for some of these interactions. The linear interactions have distances slightly larger than 4.0 Å, while the I···I···I cylic arrangements have distances slightly less than 4.0 Å. This suggests that the I···I interactions in the cylic arrangement are stronger than those in the linear arrangement. Both the occurrence of this cyclic arrangement and the shortening of the distances were described by Anthony *et al.* (1998) for Cl and Br atoms in 2,4,6-tris(4-halophenoxy)-1,3,5-triazine.

It is also well known that similar cyclic C···C···C contacts occur in hexamethylbenzene (Lonsdale-Yardley, 1929). In the most recent determination of the structure of hexamethylbenzene (Le Maguèees *et al.*, 2001), the three C···C distances are 3.85, 3.94, and 3.95 Å.

Based on the distances quoted above, we report in Table 2 all of the I···I, I···$\mathrm{C_{Me}}$, and $\mathrm{C_{Me}}$···$\mathrm{C_{Me}}$ distances shorter than 4.20 Å and lying approximately in the plane of one or both of the molecules. The distances shorter than 4.20 Å that arise from the π contacts are not included. The arrangement is such that every entry has the C—Y···Z angle larger than the Y···Z—C angle, *i.e.* Y is the Lewis acid and Z the Lewis base.

There are five I···I contacts where the angles are consistent with a Lewis acid–base interaction and one where they are not. The first three I···I contacts in the list form a cyclic I···I···I group, with distances comparable to those in the I···I···I groups in hexaiodobenzene and triiodomesitylene. An arrangement of this sort would not be possible if there were only one-half or one molecule in the asymmetric unit; this may be the reason for the complexity of the structure.

There are three I···$\mathrm{C_{Me}}$ and three $\mathrm{C_{Me}}$···I contacts where the angles are consistent with a Lewis acid–base interaction, and three I···$\mathrm{C_{Me}}$ and two $\mathrm{C_{Me}}$···I contacts where they are not. If the angles do tell us something meaningful about the interactions, then the methyl and iodo groups appear to be roughly interchangeable with respect to these Lewis acid–base interactions.

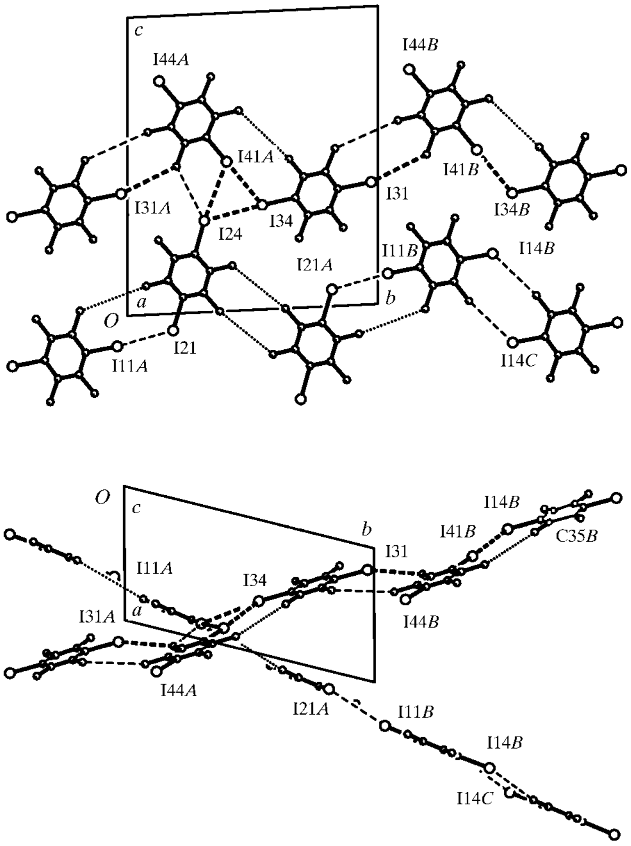


Figure 3
The molecular ribbons. Top: view along *a*. Bottom: view along *c*. Heavy dashed lines show I···I or I···$\mathrm{C_{Me}}$ contact distances of less than 4.00 Å, dashed lines show distances between 4.00 and 4.20 Å, and dotted lines show longer distances and are only present to define the ribbons. Molecule 1*A* is at (x, $y-1$, $z-1$) relative to the position in Fig. 2, 1*B* is at ($2-x$, $2-y$, $1-z$), 1*C* at ($1+x$, $1+y$, $z-1$), 2*A* at ($2-x$, $1-y$, $-z$), 3*A* at ($1+x$, $y-1$, z), 3*B* at ($x-1$, $1+y$, z), 4*A* at ($1+x$, y, z) and 4*B* at (x, $1+y$, z).

There are six $C_{Me}\cdots C_{Me}$ contacts where the angles are similar to those in the short I···I interactions. All have distances slightly longer than those in hexamethylbenzene, but none is involved in a cyclic arrangement. It is, however, difficult to regard these as Lewis acid–base interactions.

Although there are four crystallographically different molecules in the unit cell and the details of the packing as shown above are complex, there is also a certain simplicity about the packing. The coordinates of the molecular centers are, approximately: molecule 1 ($\frac{5}{8}, \frac{3}{4}, \frac{7}{8}$), molecule 2 ($\frac{7}{8}, \frac{1}{4}, \frac{1}{8}$), molecule 3 ($\frac{3}{8}, \frac{3}{4}, \frac{3}{8}$), and molecule 4 ($\frac{1}{8}, \frac{1}{4}, \frac{5}{8}$). If the molecules were spherical, which would require the *a* axis to be about twice as large, then the packing of the spheres would be roughly hexagonal close-packed with *b* the hexagonal axis.

Experimental

The title compound was prepared from durene according to the method of Suzuki *et al.* (1966). The crystal used for analysis was recrystallized from acetonitrile.

Crystal data

$C_{10}H_{12}I_2$
$M_r = 386.00$
Triclinic, $P\overline{1}$
$a = 8.152$ (2) Å
$b = 15.622$ (4) Å
$c = 18.080$ (5) Å
$\alpha = 86.60$ (1)°
$\beta = 86.93$ (1)°
$\gamma = 75.57$ (1)°
$V = 2224.1$ (10) Å^3
$Z = 8$
$D_x = 2.305$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3385 reflections
$\theta = 2.6$–27.2°
$\mu = 5.61$ mm^{-1}
$T = 174$ (2) K
Needle, colorless
0.50 × 0.10 × 0.05 mm

Data collection

Siemens SMART area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{min} = 0.55$, $T_{max} = 0.76$
26 644 measured reflections
10 118 independent reflections
7650 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -20 \rightarrow 20$
$l = -23 \rightarrow 23$

Table 1

Distances and angles (Å, °)^a in X—I···I—X contacts.

Molecule	X—I···I	I···I	I···I—X	Reference
I_2	171	3.63	104	*d*
p-$I_2C_6H_4$^{b}	160	4.13	97	*e*
p-$I_2C_6H_4$^{c}	164	4.11	98	*e*
p-$I_2C_6F_4$	161	4.06	99	*f*
C_6I_6	175	3.77	115	*g*
C_6I_6	177	3.78	124	*g*
C_6I_6	175	4.03	122	*g*
$C_6(CH_3)_3I_3$	173	3.89	120	*h*
$C_6(CH_3)_3I_3$	173	3.93	120	*h*
$C_6(CH_3)_3I_3$	165	3.97	119	*h*
$C_6(CH_3)_3I_3$	173	3.85	120	*i*
$C_6(CH_3)_3I_3$	174	3.90	119	*i*
$C_6(CH_3)_3I_3$	166	3.93	120	*i*

† Notes: (*a*) for purposes of comparison, the angles have been rounded to the nearest degree and the distances to the nearest 0.01 Å; the s.u. values have been omitted; (*b*) polymorph 1; (*c*) polymorph 2; (*d*) Wycoff (1963); (*e*) Boese & Miebach (1996); (*f*) Chaplot *et al.* (1981); (*g*) Steer *et al.* (1970); (*h*) Boudjada *et al.* (2001); (*i*) Bosch & Barnes (2002).

Table 2

Distances and angles (Å, °)^a in (I) for the C—Y···Z—C contacts, where X and Y are I or C_{Me}.

Y	Z	C—Y···Z	Y···Z	Y···Z—C
I41^{i}	I34	177	3.82	120
I34	I24	174	3.85	115
I24	I41^{i}	175	3.85	120
I44	I11^{ii}	163	4.07	104
C12^{iii}	I44	177	3.75	126
I11^{iv}	I21	169	4.20	121
I21	C36^{v}	172	3.90	133
I14	C35^{vi}	162	3.85	137
C13^{iii}	I14	165	4.09	130
I31	C46^{vii}	155	3.76	137
C16^{viii}	I31	169	3.99	109
C15	C33	171	4.17	132
C42^{i}	C15	174	4.15	119
C43	C22^{ix}	152	4.05	133
C23^{vi}	C43	166	4.03	131
C45	C32^{ii}	158	4.17	136
C25^{x}	C45	167	4.19	118
I31	I31^{xi}	118	4.18	118
C26^{x}	I44	137	4.06	129
C36^{viii}	I11	132	4.14	127
I21	C35^{v}	130	4.08	126
I24	C46^{i}	137	4.01	133
I41	C33^{xii}	131	4.05	131

† Notes: (*a*) for purposes of comparison, the angles have been rounded to the nearest degree and the distances to the nearest 0.01 Å; the s.u. values have been omitted. Each entry has been ordered so that the larger angle is given first.
Symmetry codes: (i) $1 + x, y, z$; (ii) $x, y - 1, z$; (iii) $1 - x, 1 - y, 2 - z$; (iv) $x, y - 1, z - 1$; (v) $1 - x, 1 - y, -z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $x, 1 + y, z$; (viii) $1 - x, 2 - y, 1 - z$; (ix) $x - 1, y, 1 + z$; (x) $1 - x, -y, 1 - z$; (xi) $-x, 2 - y, 1 - z$; (xii) $x - 1, y, z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.061$
$S = 1.00$
10 118 reflections
471 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 1.06P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.93$ e Å^{-3}
$\Delta\rho_{min} = -0.99$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 3.8 (4) × 10^{-4}

The structure was refined initially without considering disorder and converged with $R = 0.033$. The difference map suggested that molecule 1 might be disordered; there were peaks of 1.77 and 1.63 e Å^{-3} at the positions where I atoms bonded to C103 and C106 might be expected. The minor component of the disorder was constrained to have the same geometry as the major component with identical anisotropic displacement parameters for atoms in near coincidence. The refinement with disorder converged with $R = 0.027$ for 5.61 (6)% disorder. The minor component has been ignored in the discussion of the packing. The disorder leads to one unreasonably short I···I distance of 3.44 Å between I31 and I51($1 - x$, $2 - y$, $1 - z$). This is presumably a consequence of inaccuracy in the position of the minor component plus the failure to find the small amount of disorder in molecule 3 that must also be present.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1213). Services for accessing these data are described at the back of the journal.

References

Anthony, A., Desiraju, G. R., Jetti, R. K. R., Kuduva, N. N. L., Madhavi, A., Nangia, A., Thaimattam, R. & Thalladi, V. R. (1998). *Cryst. Eng.* **1**, 1–18.

Belsky, V. K., Zorkaya, O. N. & Zorky, P. M. (1995). *Acta Cryst.* A**51**, 473–481.

Bent, H. A. (1968). *Chem. Rev.* **68**, 587–648.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Boese, R. & Miebach, T. (1996). Refcodes ZZZPRO05 and ZZZPRO07. Private communications to the Cambridge Structural Database. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.

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.* C**57**, 1106–1108.

Britton, D. & Gleason, W. B. (2002). *Acta Cryst.* E**58**, o1375–o1377.

Chaplot, S. L., MacIntyre, G. J., Meirzejewski, A. & Pawley, G. S. (1981). *Acta Cryst.* B**37**, 2210–2214.

Domenicano, A. (1992). *Accurate Molecular Structures*, edited by A. Domenicano & I. Hargittai, pp. 437–468. Oxford University Press.

Kitaigorodsky, A. I. (1961). *Organic Chemical Crystallography*, pp. 172 and 429. New York: Consultants Bureau.

Kitaigorodsky, A. I. (1973). *Molecular Crystals and Molecules*, p. 35. New York: Academic Press.

Le Maguères, P., Lindeman, S. V. & Kochi, J. K. (2001). *Organometallics*, **20**, 115–215.

Lonsdale-Yardley, K. (1929). *Proc. R. Soc.* **123**, 494–515.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Steer, R. J., Watkins, S. F. & Woodward, P. (1970). *J. Chem. Soc. C*, pp. 403–408.

Suzuki, H., Nakamura, K. & Goto, R. (1966). *Bull. Chem. Soc. Jpn*, **39**, 128–131.

Wycoff, R. W. G. (1963). *Crystal Structures*, Vol. 1, 2nd ed., pp. 52–53. New York: Interscience Publishers.

Yao, J. W., Cole, J. C., Pidcock, E., Allen, F. H., Howard, J. A. K. & Motherwell, W. D. S. (2002). *Acta Cryst.* B**58**, 640–646.

Zorky, P. M. (1996). *J. Mol. Struct.* **374**, 9–28.

Zorky, P. M., Belsky, V. K., Lazareva, S. G. & Porai-Koshits, M. A. (1967). *J. Struct. Chem.* **8**, 267–270.