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1,2,3-Triiodobenzene

Igor Novak[a]* and Dongbo Li[b]

[a]Charles Sturt University, POB 883, Orange, New South Wales 2800, Australia, and [b]Institute of Chemical and Engineering Sciences, Singapore 138667, Singapore

Correspondence e-mail: inovak@csu.edu.au

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In the asymmetric unit of the title compound, $C_6H_3I_3$, there are two independent molecules. The molecules are stacked along the *a* axis. The molecular geometry shows evidence of I···I intramolecular steric repulsion.

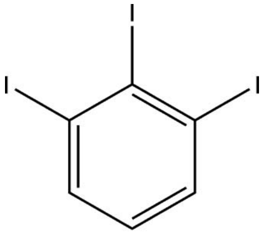
Key indicators

Single-crystal X-ray study
T = 223 K
Mean σ(C–C) = 0.007 Å
R factor = 0.034
wR factor = 0.086
Data-to-parameter ratio = 30.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Study of the electronic structure of polyiodobenzenes (Novak *et al.*, 2002) has suggested the existence of steric repulsion between vicinal iodines. In order to detect such repulsion, we compared the molecular structure of the title compound, (I), with the structures of iodobenzene (Merz, 2006), 1,3,5-triiodobenzene (Margraf & Bats 2006) and hexaiodobenzene (Steer *et al.*, 1970). The key molecular parameters are given in Table 1. The data show that relief of intramolecular steric crowding between iodine substituents occurs *via* the reduction of endocyclic angles, rather than *via* C—I bond elongation. The values in Table 1 also suggest that the iodine atoms can tolerate internuclear distances much smaller than the sum of van der Waals radii (4.3 Å) without significant bond length or angle deformation.



(I)

In the asymmetric unit of (I) there are two crystallographically distinct molecules (Fig. 1). The molecules are planar with the exception of a single iodine atom (I2) which deviates from the molecular plane by 7°. The shortest, non-bonding intramolecular I···I separation in (I) is 3.60 (2)Å which is well below the sum of van der Waals radii for iodine (4.3Å). Similar short intramolecular I···I distances were observed in other molecules where steric compression of iodines can be expected *e.g.* hexaiodobenzene (Table 1) or 1,8-diiodonaphthalene (Bock *et al.* 1998). In these molecules, the intramolecular I···I distances are also well below the sum of van der Waals radii and in 1,8-diiodonaphthalene, in particular, the iodine atoms are severely twisted out of the aromatic plane. The short, intramolecular I···I distances thus indicate steric compression and spatial repulsion, as shown in the example of 1,8-diiodonaphthalene. Furthermore, in 1,2,4,5-tetraiodobenzene (Novak *et al.*, 2006), where steric

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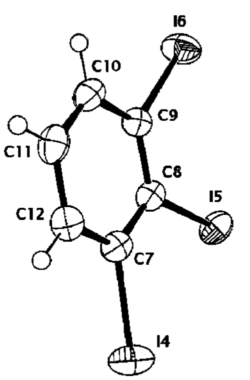

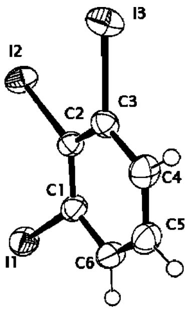

Figure 1

The asymmetric unit of (I) with displacement parameters drawn at the 50% probability level.

repulsion is lower than in (I), the intramolecular I···I distance is 3.67 (2) Å compared to 3.60 (2) Å in (I). We therefore interpret the small value of the intramolecular I···I separation in (I) as the consequence of the large currently accepted value for the van der Waals radius of iodine rather than attractive halogen–halogen interactions.

The crystal packing of (I) comprises stacks of molecules along the *a* axis (Fig. 2). The short intermolecular I···I contacts have the value of 3.802 (8) Å while the interplanar distance within the stack is 3.605 Å. These contacts represent weak van der Waals interactions holding the stacks together.

Experimental

The synthesis of 1,2,3-triodobenzene was performed according to the procedure reported previously by Mattern & Chen (1991). Single crystals were collected from the sublimate.

Crystal data

$C_6H_3I_3$
M_r = 455.78
Triclinic, $P\bar{1}$
a = 7.2439 (5) Å
b = 10.4665 (7) Å
c = 11.7952 (8) Å
α = 90.45 (5)°
β = 96.869 (5)°
γ = 90.84 (5)°
V = 887.74 (10) Å^3
Z = 4
D_x = 3.410 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 10.48 mm^{-1}
T = 223 (2) K
Block, colorless
0.30 × 0.18 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.120, T_{max} = 0.349
13551 measured reflections
5119 independent reflections
4554 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 30.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.086
S = 1.06
5119 reflections
167 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.5033P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.10 e Å^{-3}
$\Delta\rho_{min}$ = −1.13 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00151 (17)

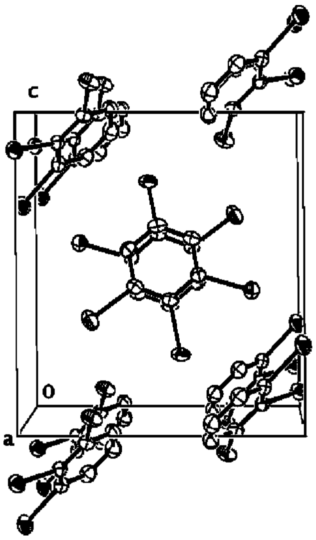

Figure 2

A packing diagram of (I), viewed down the *a* axis. H atoms have been omitted.

Table 1

Average molecular geometries (Å, °) of some iodobenzenes.

Molecule	C—I	C—C—C	I···I
Iodobenzene	2.09 (1)	121 (1)	none
1,3,5-Triiodobenzene	2.095 (5)	121.7 (6)	none
1,2,3-Triiodobenzene	2.09 (1)	118.0 (4)	3.60 (2)
Hexaiodobenzene	2.09 (4)	119.8 (8)	3.51 (1)

Note: C—C—C and I···I correspond to the endocyclic angles at carbons with vicinal iodines and non-bonding intramolecular distances, respectively.

H atoms were positioned geometrically (C—H = 0.94 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C). The highest peak is located 0.78 Å from atom I3 and the deepest hole is located 0.73 Å from atom I4.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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References

Bock, H., Sievert, M. & Havlas, Z. (1998). *Chem. Eur. J.* **4**, 677–685.
Bruker (1997). *SMART* (Version 5.631) and *SAINT* (Version 6.63). Bruker AXS Inc., Wisconsin, Madison, USA.
Margraf, D. & Bats, J. W. (2006). *Acta Cryst. E***62**, o502-o504..
Mattern, D. W. & Chen, X. (1991). *J. Org. Chem.* **56**, 5903–5907.
Merz, K. (2006). *Cryst. Growth Des.* **6**, 1615–1619.
Novak, I. & Li, D. B. (2006). *Acta Cryst.* E**62**, o5736–o5737.
Novak, I., Li, D. B. & Kovac, B. (2002). *J. Phys. Chem. A*, **106**, 2850–2854.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Steer, R. J., Watkins, S. F. & Woodward, P. (1970). *J. Chem. Soc. C*, pp. 403–408.