

2,6-Diiodopyridine

Brian T. Holmes, Clifford W. Padgett and William T. Pennington*

H. L. Hunter Research Laboratories, Chemistry Department, Clemson University, Clemson, SC 29634-0973, USA

Correspondence e-mail: billp@clemson.edu

Received 11 June 2002

Accepted 19 August 2002

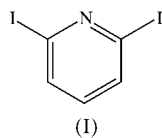
Online 21 September 2002

The title compound, $C_5H_3I_2N$, crystallizes in the polar space group *Fmm2*, with crystallographic *mm2* symmetry imposed on the molecule. Molecules are linked through C—H...N hydrogen bonding to form chains which are, in turn, joined through weak I...I halogen-bonding interactions to form layers. The pyridine ring lies parallel to the polar *z* axis and has the N atom pointing in the +*z* direction. The layers stack in a polar fashion normal to the *a* axis and the absolute structure has been determined.

Comment

Haloaromatic compounds are important for synthetic purposes, especially cross-coupling reactions with organometallic reagents (Li & Gribble, 2000; Finet, 1998). Iodoaromatics typically display increased reactivity compared with their bromo and chloro counterparts. Disubstituted iodo-heteroaromatic compounds are useful for the preparation of multifunctional ligands, but few are available due to the difficulty of their formation (Smith & Ho, 1990; Yang *et al.*, 1986).

This paper reports the preparation and crystal structure of 2,6-diiodopyridine, (I), which will be used as a more reactive base unit in an alternate synthesis of acetylene-expanded tridentate ligands (Holmes *et al.*, 2002). This appears to be only the second reported structure analysis of an iodopyridine, and the first of a diiodo derivative. Similar to the first reported example, 4-iodopyridine (Ahrens & Jones, 1999), (I) crystallizes in a polar space group, *viz.* *Fmm2* for (I) *versus* *Fdd2* for 4-iodopyridine.



The molecule of (I) lies on a crystallographic *mm2* site (Fig. 1), with the molecular plane coincident with one mirror and the molecule bisected by the other. Atoms N1 and C3 lie

on the twofold rotational axis at the intersection of the mirrors.

The geometric parameters for (I) (Table 1) are somewhat distorted relative to those found in both pyridine (Mootz & Wussow, 1981) and 4-iodopyridine, with expansion of the ring angle at atoms C1 and C3 and contraction at atoms N1 and C2. This could be due to steric and electronic factors associated with the large electron-dense substituents, but may also be the result of low precision in the positional parameters of the light atoms (which comprise only 27% of the scattering power of the unit cell).

The molecules of (I) form linear chains along the *c* axis through C—H...N hydrogen-bonding interactions (Table 2). These chains are linked through weak halogen bonding between I atoms (Walsh *et al.*, 2001; Bailey *et al.*, 2000; Bosch & Barnes, 2002) to form planar layers normal to the *a* axis (Fig. 2). The I...I distance (Table 1) is at the limit of the van der Waals contact distance, which has been estimated to be

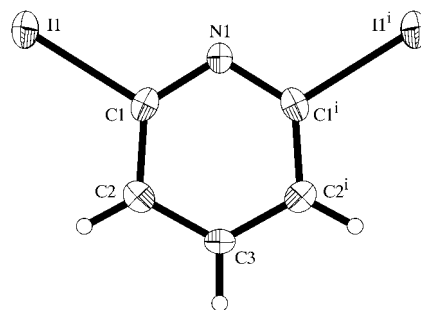


Figure 1

The molecular structure of (I). Displacement ellipsoids are at the 50% probability level and H atoms are of arbitrary radii. [Symmetry code: (i) $-x, 1 - y, z$.]

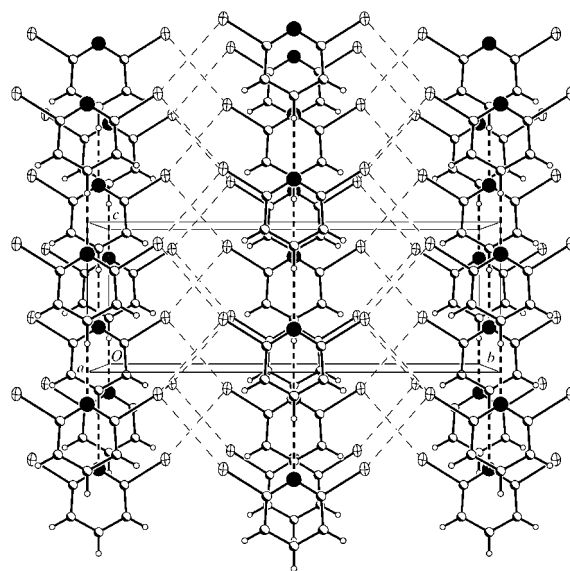


Figure 2

The molecular packing in (I), viewed down the *a* axis. Atoms are shown with arbitrary radii. Thick dashed lines represent C—H...N hydrogen bonds, while thin dashed lines represent I...I halogen-bonding contacts.

4.30 Å by Pauling (1960), 3.96 Å by Bondi (1964) and 4.00 Å by Rowland & Taylor (1996), but the angular orientation of the interactions fits the standard description of a type-II interaction quite well (Desiraju & Parthasarathy, 1989). Each I atom undergoes two close contacts with neighboring I atoms within the layer, with one being nearly linear with respect to the C1–I1 bond and the other being closer to a tetrahedral angle (Table 1). The layers are parallel to each other, with all of the N atoms aligned in the same absolute direction. Alternating layers are staggered by one half translation along the *c* axis. The absolute direction of the polar axis has been determined successfully.

Experimental

2,6-Diiodopyridine was synthesized by reacting commercially available 2,6-dibromopyridine with six equivalents of ethylmagnesium bromide in tetrahydrofuran. The resulting pyridyl dimagnesium bromide was quenched with iodine to afford the desired white solid in 42% yield following purification by chromatography on silica (hexane/dichloromethane) and recrystallization (hexane/chloroform). ¹H NMR (300 MHz, δ, CDCl₃, p.p.m.): 7.67 (*d*, *J* = 7.88 Hz, 2H), 6.93 (*t*, *J* = 7.75 Hz, 1H); ¹³C NMR (75 MHz, δ, CDCl₃, p.p.m.): 138.36 (CH), 134.19 (CH), 116.21. Diffraction-quality crystals of 2,6-diiodopyridine were obtained by slow evaporation of a xylene solution at room temperature.

Crystal data

C₅H₃I₂N
M_r = 330.88
 Orthorhombic, *Fmm*2
a = 6.8039 (14) Å
b = 17.011 (3) Å
c = 6.1959 (12) Å
V = 717.1 (2) Å³
Z = 4
D_x = 3.065 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 1322 reflections
 $\theta = 4.6\text{--}26.4^\circ$
 $\mu = 8.67\text{ mm}^{-1}$
T = 148 K
 Prism, colorless
 0.17 × 0.05 × 0.05 mm

Data collection

Mercury AFC-8S diffractometer
 ω scans
 Absorption correction: multi-scan (*REQAB*; Jacobson, 1998)
T_{min} = 0.300, *T_{max}* = 0.660
 1721 measured reflections
 406 independent reflections

405 reflections with *I* > 2σ(*I*)
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 26.3^\circ$
 $h = -8 \rightarrow 8$
 $k = -20 \rightarrow 20$
 $l = -7 \rightarrow 7$

Refinement

Refinement on *F*²
R(*F*) = 0.020
wR(*F*²) = 0.050
S = 1.11
 406 reflections
 27 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.67\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.58\text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 180 Friedel pairs
 Flack parameter = 0.00 (8)

Data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-*

Table 1

Selected geometric parameters (Å, °).

I1–C1	2.112 (5)	C1–C2	1.388 (8)
I1–I1 ⁱ	4.1038 (7)	C2–C3	1.383 (19)
N1–C1	1.319 (7)		
C1–I1–I1 ⁱ	98.84 (17)	N1–C1–I1	115.9 (4)
C1–I1–I1 ⁱⁱ	163.13 (18)	C2–C1–I1	118.5 (4)
I1 ⁱ –I1–I1 ⁱⁱ	98.03 (2)	C3–C2–C1	115.5 (14)
C1–N1–C1 ⁱⁱⁱ	116.1 (7)	C2 ⁱⁱⁱ –C3–C2	122 (3)
N1–C1–C2	125.7 (5)		

Symmetry codes: (i) $-x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $-x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $-x, 1 - y, z$.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C3–H3A···N1 ⁱ	0.93	2.51	3.44 (4)	180

Symmetry code: (i) *x*, *y*, *z* – 1.

Plus; software used to prepare material for publication: *SHELXTL-Plus*.

The financial support of the National Science Foundation for the purchase of the CCD-based X-ray system used in this study (CHE-9808165), and of the NASA/Space grant program (NCC5-575) provided by SC/EPSCoR is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1141). Services for accessing these data are described at the back of the journal.

References

- Ahrens, B. & Jones, P. G. (1999). *Acta Cryst.* **C55**, 1308–1310.
 Bailey, R. D., Hook, L. L., Watson, R. P., Hanks, T. W. & Pennington, W. T. (2000). *Cryst. Eng.* **3**, 155–171.
 Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 Bosch, E. & Barnes, C. L. (2002). *Cryst. Growth Des.* **3**, 299–302.
 Desiraju, G. R. & Parthasarathy, R. (1989). *J. Am. Chem. Soc.* **111**, 8725–8726.
 Finet, J.-P. (1998). In *Ligand Coupling Reactions with Heteroatomic Compounds*. Oxford: Elsevier Science Ltd.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Holmes, B. T., Pennington, W. T. & Hanks, T. W. (2002). *Molecules*, **7**, 447–455.
 Jacobson, R. A. (1998). *REQAB*. Version 1.1. Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Li, J. J. & Gribble, G. W. (2000). In *Palladium in Heterocyclic Chemistry*. Oxford: Elsevier Science Ltd.
 Mootz, D. & Wussow, H.-G. (1981). *J. Chem. Phys.* **75**, 1517–1522.
 Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell University Press.
 Rigaku/MSC (2001). *CrystalClear*. Version 1.3. Rigaku/Molecular Structure Corporation, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
 Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.
 Sheldrick, G. M. (2000). *SHELXTL-Plus*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Smith, W. B. & Ho, O. C. (1990). *J. Org. Chem.* **55**, 2543–2545.
 Walsh, R. B., Padgett, C. W., Metrangolo, P., Resnati, G., Hanks, T. W. & Pennington, W. T. (2001). *Cryst. Growth Des.* **1**, 165–175.
 Yang, S. H., Li, C. S. & Cheng, C. H. (1986). *J. Org. Chem.* **52**, 691–694.