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## Structure Reports

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3-Iodo-1*H*-pyrazolo[3,4-*b*]pyridinePing-Hsin Huang,<sup>a\*</sup> Yuh-Sheng Wen<sup>b</sup> and Jiun-Yi Shen<sup>c</sup>

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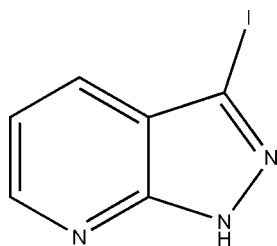
Received 6 March 2014; accepted 4 May 2014

Key indicators: single-crystal X-ray study;  $T = 150$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.017;  $wR$  factor = 0.040; data-to-parameter ratio = 16.2.

The title compound,  $\text{C}_6\text{H}_4\text{IN}_3$ , is essentially planar, with a dihedral angle of  $0.82$  (3)° between the planes of the pyridine and pyrazole rings. In the crystal, pairs of molecules are connected into inversion dimers through  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds.  $\text{C}-\text{I}\cdots\text{N}$  halogen bonds link the dimers into zigzag chains parallel to the  $b$ -axis direction. The packing also features  $\pi-\pi$  stacking interactions along (110) with interplanar distances of 3.292 (1) and 3.343 (1) Å, and centroid-centroid distances of 3.308 (1) and 3.430 (1) Å.

## Related literature

For the production of antitumor agents, see: Huang *et al.* (2007); Ye *et al.* (2009). For a related structure, see: Huang *et al.* (2013).



## Experimental

## Crystal data

$\text{C}_6\text{H}_4\text{IN}_3$   
 $M_r = 245.02$

Monoclinic,  $C2/c$   
 $a = 10.7999$  (13) Å

$b = 7.7939$  (9) Å  
 $c = 17.406$  (2) Å  
 $\beta = 101.748$  (2)°  
 $V = 1434.5$  (3) Å<sup>3</sup>  
 $Z = 8$

Mo  $K\alpha$  radiation  
 $\mu = 4.38$  mm<sup>-1</sup>  
 $T = 150$  K  
 $0.35 \times 0.32 \times 0.25$  mm

## Data collection

Bruker SMART APEX CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 1996)  
 $T_{\min} = 0.309$ ,  $T_{\max} = 0.407$

5315 measured reflections  
1470 independent reflections  
1423 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$   
 $wR(F^2) = 0.040$   
 $S = 1.13$   
1470 reflections  
91 parameters

26 restraints  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.46$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2A}\cdots\text{N1}^i$	0.88	2.09	2.926 (3)	159
$\text{C6}-\text{I1}\cdots\text{N3}^{ii}$	2.076 (2)	3.013 (2)	5.056 (3)	166.72 (7)

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT (Bruker, 2001; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: WinGX (Farrugia, 2012).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: ZL2581).

## References

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## supporting information

*Acta Cryst.* (2014). E70, o650 [doi:10.1107/S1600536814010009]

## 3-Iodo-1*H*-pyrazolo[3,4-*b*]pyridine

Ping-Hsin Huang, Yuh-Sheng Wen and Jiun-Yi Shen

### S1. Comment

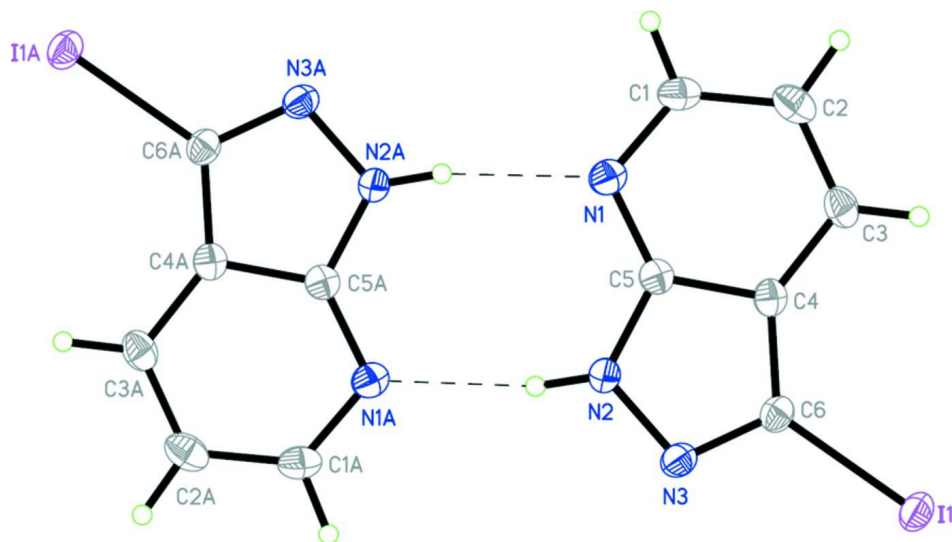
The title compound has been shown to be a precursor for the production of anticancer drugs (Huang *et al.*, 2007; Ye *et al.*, 2009). The molecular structure is shown in Figure 1. The dihedral angle between the pyridine and the pyrazole rings is 0.82 (3)°. (Huang *et al.*, 2013) As shown in Fig.1, N—H···N H-bonds connect molecules into centrosymmetric dimers. The molecules connected the H-bonds are arranged in a parallel but non-coplanar fashion, with the planes of the two molecules being about 0.67 Å apart. C—I···N halogen bonds create zig zag chains parallel to the *b* axis direction, Fig. 2. Packing is also facilitated through  $\pi\cdots\pi$  stacking interactions along (1 1 0) with interplanar distances of 3.292 (1) and 3.343 (1) Å, and centroid to centroid distances of 3.308 (1) and 3.430 (1) Å (Fig 3.). Molecules in the crystal structure are thus connected through N—H···N hydrogen bonding interactions, through a C—I···N halogen bond as well as  $\pi\cdots\pi$  stacking interactions that help to stabilize the crystal structure.

### S2. Experimental

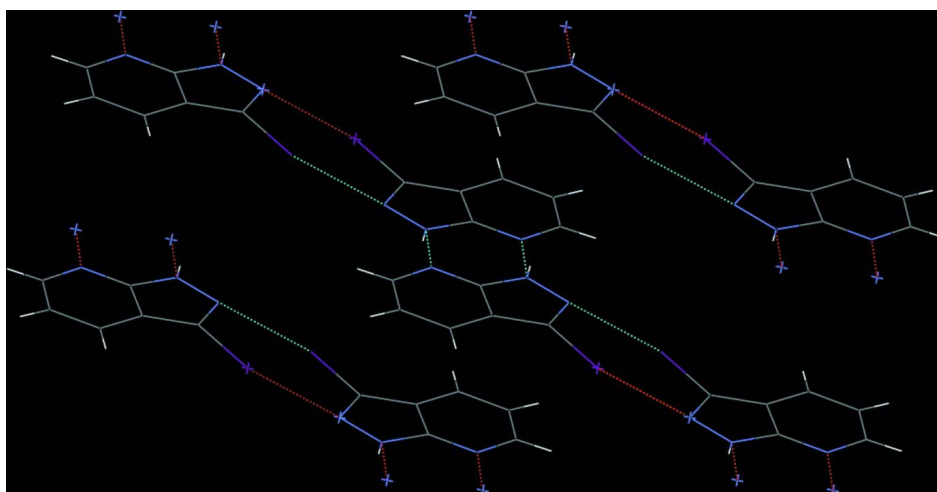
The compound was synthesized by the following procedure (Ye *et al.*, 2009). Iodine (18.7 g, 73.6 mmol) was added to a solution of 1*H*-pyrazolo[3,4-*b*]pyridine (3.5 g, 29.4 mmol) in DMF (50 ml), followed by KOH (6.6 g, 118.0 mmol). The mixture was stirred at room temperature for 2 h. After that, it was poured into brine and extracted with ethyl acetate and the organic extract was washed with brine and aqueous Na<sub>2</sub>SO<sub>4</sub>, dried and concentrated in vacuum. The residue was purified by recrystallization in CH<sub>2</sub>Cl<sub>2</sub> and hexane to give a white solid (6.3 g, 87.5%). Crystals suitable for X-ray diffraction were grown from a CH<sub>2</sub>Cl<sub>2</sub> solution layered with hexane at room temperature. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 13.18 (br, 1 H), 8.64 (dd, 1 H, *J* = 4.8, 1.6 Hz), 7.89 (dd, 1 H, *J* = 8.4, 1.6 Hz), 7.25–7.22 (m, 1H). Mass spectrum: *m/e*245 (*M*<sup>+</sup>), calcd. (245.02).

### S3. Refinement

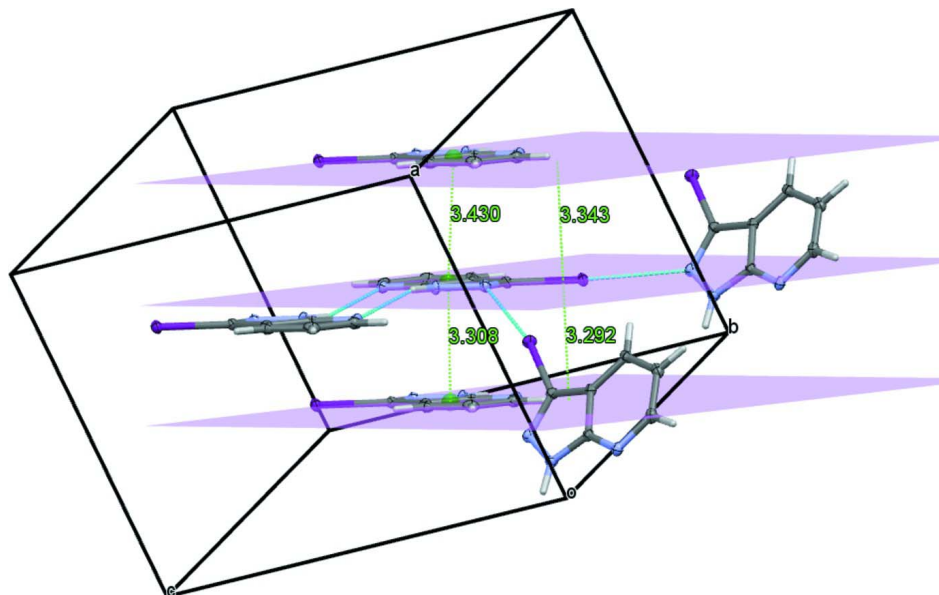
H atoms were located in difference map but were positioned with idealized geometry and refined isotropic with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

**Figure 1**

The centrosymmetric dimer molecular structures of the title compound with labeling and displacement ellipsoids drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii.

**Figure 2**

Packing diagram for title compound, viewed along the *b* axis. H atoms have been omitted for clarity.



**Figure 3**

In the crystal, there are significant  $\pi\cdots\pi$  stacking interactions between molecules.

### 3-Iodo-1*H*-pyrazolo[3,4-*b*]pyridine

#### Crystal data

$C_6H_4IN_3$

$M_r = 245.02$

Monoclinic,  $C2/c$

$a = 10.7999$  (13) Å

$b = 7.7939$  (9) Å

$c = 17.406$  (2) Å

$\beta = 101.748$  (2)°

$V = 1434.5$  (3) Å<sup>3</sup>

$Z = 8$

$F(000) = 912$

$D_x = 2.269$  Mg m<sup>-3</sup>

$D_m = 2.269$  Mg m<sup>-3</sup>

$D_m$  measured by not measured

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4550 reflections

$\theta = 2.4$ – $27.5$ °

$\mu = 4.38$  mm<sup>-1</sup>

$T = 150$  K

Block, colorless

$0.35 \times 0.32 \times 0.25$  mm

#### Data collection

Bruker SMART APEX CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 1996)

$T_{\min} = 0.309$ ,  $T_{\max} = 0.407$

5315 measured reflections

1470 independent reflections

1423 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 26.4$ °,  $\theta_{\min} = 2.4$ °

$h = -14 \rightarrow 13$

$k = -10 \rightarrow 9$

$l = -22 \rightarrow 22$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.017$

$wR(F^2) = 0.040$

$S = 1.13$

1470 reflections

91 parameters

26 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0156P)^2 + 1.9173P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$   
 $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.23044 (2)	1.04283 (2)	0.29263 (2)	0.02252 (7)
N1	0.46725 (18)	0.6969 (3)	0.56007 (11)	0.0202 (4)
N2	0.44327 (18)	0.6579 (3)	0.42063 (11)	0.0196 (4)
H2A	0.4869	0.5622	0.4219	0.023*
N3	0.38503 (19)	0.7396 (3)	0.35341 (11)	0.0201 (4)
C1	0.4368 (2)	0.8083 (3)	0.61183 (13)	0.0226 (5)
H1	0.4641	0.7822	0.6660	0.027*
C2	0.3682 (2)	0.9594 (3)	0.59272 (15)	0.0249 (5)
H2	0.3517	1.0325	0.6332	0.030*
C3	0.3242 (2)	1.0027 (3)	0.51533 (15)	0.0223 (5)
H3	0.2758	1.1038	0.5010	0.027*
C4	0.3539 (2)	0.8915 (3)	0.45868 (13)	0.0177 (4)
C5	0.4249 (2)	0.7441 (3)	0.48502 (13)	0.0178 (4)
C6	0.3326 (2)	0.8785 (3)	0.37596 (13)	0.0189 (4)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
I1	0.02567 (11)	0.01896 (10)	0.02189 (10)	0.00157 (6)	0.00242 (7)	0.00504 (6)
N1	0.0215 (10)	0.0196 (10)	0.0186 (9)	-0.0028 (8)	0.0020 (8)	0.0012 (8)
N2	0.0222 (10)	0.0173 (10)	0.0184 (9)	0.0042 (8)	0.0020 (8)	0.0004 (7)
N3	0.0229 (10)	0.0192 (10)	0.0174 (9)	-0.0007 (8)	0.0022 (8)	0.0019 (8)
C1	0.0264 (13)	0.0240 (12)	0.0174 (10)	-0.0075 (10)	0.0043 (9)	-0.0015 (9)
C2	0.0281 (14)	0.0234 (13)	0.0252 (12)	-0.0062 (10)	0.0105 (10)	-0.0064 (10)
C3	0.0241 (13)	0.0159 (11)	0.0287 (12)	-0.0020 (10)	0.0097 (10)	-0.0022 (9)
C4	0.0181 (11)	0.0138 (11)	0.0218 (11)	-0.0036 (9)	0.0051 (9)	0.0011 (9)
C5	0.0171 (11)	0.0160 (11)	0.0200 (11)	-0.0037 (9)	0.0031 (8)	-0.0009 (8)
C6	0.0187 (11)	0.0168 (11)	0.0205 (11)	-0.0006 (9)	0.0023 (9)	0.0026 (9)

Geometric parameters (Å, °)

I1—C6	2.076 (2)	C1—H1	0.9500
N1—C1	1.339 (3)	C2—C3	1.376 (4)
N1—C5	1.345 (3)	C2—H2	0.9500
N2—C5	1.356 (3)	C3—C4	1.398 (3)
N2—N3	1.368 (3)	C3—H3	0.9500
N2—H2A	0.8800	C4—C5	1.405 (3)
N3—C6	1.318 (3)	C4—C6	1.415 (3)
C1—C2	1.396 (4)		
C1—N1—C5	113.2 (2)	C2—C3—H3	121.5
C5—N2—N3	110.93 (18)	C4—C3—H3	121.5
C5—N2—H2A	124.5	C3—C4—C5	117.7 (2)
N3—N2—H2A	124.5	C3—C4—C6	138.5 (2)
C6—N3—N2	106.15 (18)	C5—C4—C6	103.79 (19)
N1—C1—C2	125.3 (2)	N1—C5—N2	126.1 (2)
N1—C1—H1	117.4	N1—C5—C4	126.6 (2)
C2—C1—H1	117.4	N2—C5—C4	107.31 (19)
C3—C2—C1	120.1 (2)	N3—C6—C4	111.8 (2)
C3—C2—H2	120.0	N3—C6—I1	119.88 (16)
C1—C2—H2	120.0	C4—C6—I1	128.30 (17)
C2—C3—C4	117.1 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N2—H2A $\cdots$ N1 <sup>i</sup>	0.88	2.09	2.926 (3)	159
C6—I1 $\cdots$ N3 <sup>ii</sup>	2.08 (1)	3.01 (1)	5.056 (3)	167 (1)

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $-x+1/2, y+1/2, -z+1/2$ .