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Crystal structure of the pyridine–diiodine (1/1) adduct

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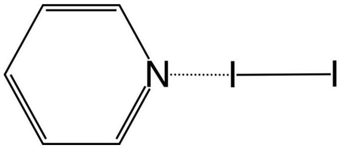
In the title adduct, $C_5H_5N{\cdot}I_2$, the N—I distance [2.424 (8) Å] is remarkably shorter than the sum of the van der Waals radii. The line through the I atoms forms an angle of 78.39 (16)° with the normal to the pyridine ring.

Keywords: pyridine; diiodine; halogen bonding; crystal structure.

CCDC reference: 1404151

1. Related literature

For the structure of the pyridine–I_2 1:2 adduct, see: Hassel & Hope (1961). For the crystal structures of pyridine with ICl and IBr, see: Rømming (1972); Dahl *et al.* (1967). For van der Walls radii, see: Bondi (1964). For the I—I distance of iodine, see: Buontempo *et al.* (1997). For I—I$\cdots$N angles in halogen bonding, see: Desiraju *et al.* (2013).



2. Experimental

2.1. Crystal data

$C_5H_5N{\cdot}I_2$
M_r = 332.90
Monoclinic, $P2/c$
a = 9.2432 (6) Å
b = 4.3392 (2) Å
c = 20.1953 (13) Å
β = 98.468 (3)°
V = 801.16 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 7.76 mm^{-1}
T = 120 K
0.09 × 0.07 × 0.02 mm

2.2. Data collection

Bruker KAPPA APEX II CCD diffractometer
Absorption correction: numerical (*SADABS*; Bruker,2012)
$T_{\min}$ = 0.574, $T_{\max}$ = 0.902
6585 measured reflections
1853 independent reflections
1437 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.062

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.091
S = 1.07
1853 reflections
73 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 1.11 e Å^{-3}
$\Delta\rho_{\min}$ = −1.26 e Å^{-3}

Data collection: Collect (Nonius, 2000); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007; Palatinus & van der Lee, 2008; Palatinus *et al.*, 2012); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: RZ5157).

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Crystal structure of the pyridine–diiodine (1/1) adduct

Matti Tuikka and Matti Haukka

S1. Comment

Diiodine is capable to act as halogen bond donor and form stable halogen bonds with Lewis bases, such as pyridine, due to the strong charge transfer. In the case of the pyridine-I_2 1:2 adduct (Hassel & Hope, 1961), the interaction eventually results in the heterolytic cleavage of I_2 and formaton of $[py_2I]^+$ I_3^- ion pairs. Although the crystal structures involving pyridine and interhalogens ICl and IBr are known (Rømming, 1972; Dahl *et al.*, 1967), the title pyI_2 1:1 adduct has not been reported earlier. The N1—I1 distance in pyI_2 (2.425 (8) Å) is remarkably shorter than the sum of the van der Walls radii of iodine and nitrogen (3.53 Å; Bondi, 1964). The I—I distance (2.8043 (9) Å) is significantly longer than that observed in free diiodine in solid state (2.715 Å; Buontempo *et al.*, 1997). The I—I···N angle is approximately linear (176.44 (18)°) as expected in halogen bonds (Desiraju *et al.*, 2013).

S2. Experimental

The title compound was synthesized by dissolving iodine (200 mg) in ethanol (5 ml) and adding pyridine (1 ml) into this solution. The solution was left to evaporate unde ambient conditions and after a couple of days light yellow crystals were formed.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model with C—H = 0.95 Å and with $U_{iso}(H) = 1.2 U_{eq}(C)$.

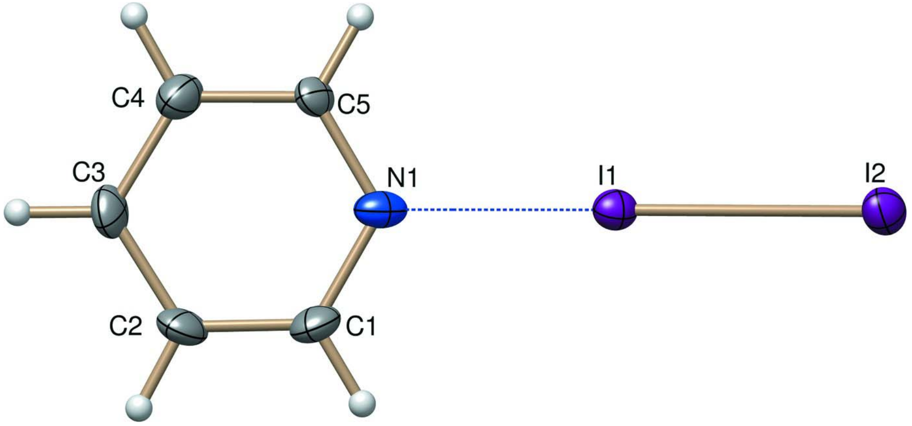

Figure 1

The molecular structure of the title compound, with 50% probability displacement ellipsoids for non-H atoms.

Pyridine–diiodine (1/1)

Crystal data

$C_5H_5N{\cdot}I_2$	$F(000) = 592$
$M_r = 332.90$	$D_x = 2.760$ Mg m^{-3}
Monoclinic, $P2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.2432$ (6) Å	Cell parameters from 1865 reflections
$b = 4.3392$ (2) Å	$\theta = 1.0$–$27.5°$
$c = 20.1953$ (13) Å	$\mu = 7.76$ mm^{-1}
$\beta = 98.468$ (3)°	$T = 120$ K
$V = 801.16$ (8) Å^3	Plate, clear light yellow
$Z = 4$	0.09 × 0.07 × 0.02 mm

Data collection

Bruker KAPPA APEX II CCD diffractometer	6585 measured reflections
Radiation source: fine-focus sealed tube	1853 independent reflections
Curved graphite crystal monochromator	1437 reflections with $I > 2\sigma(I)$
Detector resolution: 16 pixels mm^{-1}	$R_{\text{int}} = 0.062$
φ scans and ω scans with κ offset	$\theta_{\max} = 27.6°$, $\theta_{\min} = 2.2°$
Absorption correction: numerical (*SADABS*; Bruker,2012)	$h = -11 \rightarrow 11$
$T_{\min} = 0.574$, $T_{\max} = 0.902$	$k = -5 \rightarrow 5$
	$l = -26 \rightarrow 25$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0153P)^2 + 9.3396P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.091$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.07$	$\Delta\rho_{\max} = 1.11$ e Å^{-3}
1853 reflections	$\Delta\rho_{\min} = -1.26$ e Å^{-3}
73 parameters	
0 restraints	
Primary atom site location: iterative	

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
I1	0.27234 (6)	0.59684 (13)	0.54587 (3)	0.02083 (16)
I2	0.32645 (6)	0.35101 (14)	0.67558 (3)	0.02480 (18)
N1	0.2243 (7)	0.8407 (18)	0.4368 (4)	0.0243 (18)
C5	0.3349 (9)	0.933 (2)	0.4053 (4)	0.0207 (19)
H5	0.4323	0.8743	0.4223	0.025*
C3	0.1668 (10)	1.198 (2)	0.3214 (5)	0.028 (2)
H3	0.1471	1.3178	0.2818	0.033*
C1	0.0849 (10)	0.921 (2)	0.4121 (5)	0.030 (2)
H1	0.0069	0.8529	0.4342	0.035*

C2	0.0549 (10)	1.098 (2)	0.3558 (5)	0.030 (2)
H2	−0.0434	1.1533	0.3399	0.036*
C4	0.3076 (10)	1.112 (2)	0.3480 (5)	0.030 (2)
H4	0.3872	1.1783	0.3266	0.036*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0189 (3)	0.0224 (3)	0.0212 (3)	−0.0010 (2)	0.0027 (2)	−0.0016 (3)
I2	0.0253 (3)	0.0267 (3)	0.0222 (4)	0.0029 (2)	0.0031 (3)	0.0011 (3)
N1	0.016 (4)	0.032 (4)	0.024 (4)	−0.003 (3)	0.004 (3)	−0.007 (4)
C5	0.017 (4)	0.031 (5)	0.013 (5)	−0.001 (4)	−0.001 (3)	0.000 (4)
C3	0.031 (5)	0.035 (6)	0.014 (5)	−0.002 (4)	−0.003 (4)	0.004 (4)
C1	0.019 (5)	0.039 (6)	0.031 (6)	−0.009 (4)	0.007 (4)	0.005 (5)
C2	0.014 (4)	0.049 (7)	0.026 (6)	−0.002 (4)	−0.003 (4)	0.002 (5)
C4	0.025 (5)	0.042 (6)	0.022 (6)	−0.006 (4)	0.005 (4)	0.003 (5)

Geometric parameters (Å, º)

I1—I2	2.8043 (9)	C5—C4	1.388 (13)
I1—N1	2.425 (8)	C3—C2	1.397 (12)
N1—C5	1.342 (10)	C3—C4	1.383 (13)
N1—C1	1.357 (12)	C1—C2	1.364 (14)
N1—I1—I2	176.44 (18)	C4—C3—C2	116.6 (9)
C5—N1—I1	120.7 (6)	N1—C1—C2	121.1 (8)
C5—N1—C1	119.8 (8)	C1—C2—C3	120.9 (9)
C1—N1—I1	118.9 (6)	C3—C4—C5	121.2 (8)
N1—C5—C4	120.3 (8)		
I1—N1—C5—C4	−170.3 (7)	C5—N1—C1—C2	−0.8 (15)
I1—N1—C1—C2	170.4 (8)	C1—N1—C5—C4	0.8 (14)
N1—C5—C4—C3	−0.9 (15)	C2—C3—C4—C5	1.0 (15)
N1—C1—C2—C3	1.0 (16)	C4—C3—C2—C1	−1.0 (15)