



This is an electronic reprint of the original article. This reprint *may differ* from the original in pagination and typographic detail.

Author(s): Tuikka, Matti; Haukka, Matti

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

Year: 2015

Version:

Please cite the original version:

Tuikka, M., & Haukka, M. (2015). Crystal structure of the pyridine–diiodine (1/1) adduct. Acta Crystallographica Section E : Crystallographic Communications, 71(7), o463. https://doi.org/10.1107/S2056989015010518

All material supplied via JYX is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.



CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

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

Matti Tuikka and Matti Haukka*

University of Jyvaskyla, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyvaskyla, Finland. *Correspondence e-mail: matti.o.haukka@jyu.fi

Received 17 April 2015; accepted 1 June 2015

Edited by C. Rizzoli, Universita degli Studi di Parma, Italy

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^{••}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
$\beta = 98.468 \ (3)^{\circ}$
V = 801.16 (8) Å ³
Z = 4
Mo $K\alpha$ radiation

 $\mu = 7.76 \text{ mm}^{-1}$ T = 120 K

OPEN access

2.2. Data collection

Bruker KAPPA APEX II CCD diffractometer Absorption correction: numerical (*SADABS*; Bruker,2012) *T*_{min} = 0.574, *T*_{max} = 0.902

2.3. Refinement $R[F^2 > 2\sigma(F^2)] = 0.049$ $wR(F^2) = 0.091$ S = 1.071853 reflections 6585 measured reflections 1853 independent reflections 1437 reflections with $I > 2\sigma(I)$ $R_{int} = 0.062$

 $0.09 \times 0.07 \times 0.02 \ \mathrm{mm}$

73 parameters H-atom parameters constrained $\Delta \rho_{max} = 1.11 \text{ e } \text{ Å}^{-3}$ $\Delta \rho_{min} = -1.26 \text{ e } \text{ Å}^{-3}$

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*.

Acknowledgements

Financial support provided by the Academy of Finland (project No. 129171) is gratefully acknowledged.

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

References

- Bondi, A. (1964). J. Phys. Chem. 68, 441-451.
- Bruker (2012). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Buontempo, U., DiCicco, A., Filipponi, A., Nardone, M. & Postorino, P. (1997). J. Chem. Phys. 107, 5720–5726.
- Dahl, T., Hassel, O. & Sky, K. (1967). Acta Chem. Scand. 21, 592-593.
- Desiraju, G. R., Ho, P. S., Kloo, L., Legon, A. C., Marquardt, R., Metrangolo, P., Politzer, P., Resnati, G. & Rissanen, K. (2013). Pure Appl. Chem. 85, 1711–1713.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
- Hassel, O. & Hope, H. (1961). Acta Chem. Scand. 15, 407-416.
- Nonius (2000). COLLECT. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Palatinus, L. & Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790.
- Palatinus, L., Prathapa, S. J. & van Smaalen, S. (2012). J. Appl. Cryst. 45, 575–580.
- Palatinus, L. & van der Lee, A. (2008). J. Appl. Cryst. 41, 975-984.
- Rømming, C. (1972). Acta Chem. Scand. 26, 1555-1560.
- Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

supporting information

Acta Cryst. (2015). E71, o463 [doi:10.1107/S2056989015010518]

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-I₂ 1:2 adduct (Hassel & Hope, 1961), the interaction eventually results in the heterolytic cleavage of I₂ and formaton of $[py_2I]^+$ I₃⁻ ion pairs. Although the crystal structures involving pyridine and interhalogens ICl and IBr are known (Rømming, 1972; Dahl *et al.*, 1967), the title pyI₂ 1:1 adduct has not been reported earlier. The N1—I1 distance in pyI₂ (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

 $C_{s}H_{s}N\cdot I_{2}$ $M_{r} = 332.90$ 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) Å³ *Z* = 4

Data collection

Bruker KAPPA APEX II CCD diffractometer Radiation source: fine-focus sealed tube Curved graphite crystal monochromator Detector resolution: 16 pixels mm⁻¹ φ scans and ω scans with κ offset Absorption correction: numerical (*SADABS*; Bruker,2012)

 $T_{\rm min} = 0.574, T_{\rm max} = 0.902$

Refinement

Refinement on F^2 Hydrogen site location: inferred from Least-squares matrix: full neighbouring sites $R[F^2 > 2\sigma(F^2)] = 0.049$ H-atom parameters constrained $wR(F^2) = 0.091$ $w = 1/[\sigma^2(F_o^2) + (0.0153P)^2 + 9.3396P]$ S = 1.07where $P = (F_0^2 + 2F_c^2)/3$ 1853 reflections $(\Delta/\sigma)_{\rm max} = 0.001$ 73 parameters $\Delta \rho_{\rm max} = 1.11 \text{ e Å}^{-3}$ 0 restraints $\Delta \rho_{\rm min} = -1.26 \text{ e} \text{ Å}^{-3}$ 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.

F(000) = 592

 $\theta = 1.0-27.5^{\circ}$

 $\mu = 7.76 \text{ mm}^{-1}$

T = 120 K

 $R_{\rm int} = 0.062$

 $h = -11 \rightarrow 11$

 $l = -26 \rightarrow 25$

 $k = -5 \rightarrow 5$

 $D_{\rm x} = 2.760 {\rm Mg} {\rm m}^{-3}$

Plate, clear light yellow

 $0.09 \times 0.07 \times 0.02 \text{ mm}$

6585 measured reflections

 $\theta_{\text{max}} = 27.6^{\circ}, \ \theta_{\text{min}} = 2.2^{\circ}$

1853 independent reflections 1437 reflections with $I > 2\sigma(I)$

Mo *K* α radiation, $\lambda = 0.71073$ Å

Cell parameters from 1865 reflections

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

	x	У	Ζ	$U_{ m iso}$ */ $U_{ m eq}$	
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*	

supporting information

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, °)

I1—I2	2.8043 (9)	C5—C4	1.388 (13)
I1—N1	2.425 (8)	C3—C2	1.397 (12)
N1C5	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)