

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2,4-Diiodoaniline

Graham Smith* and Urs D. Wermuth

School of Physical and Chemical Sciences, Queensland University of Technology,
GPO Box 2434, Brisbane, Qld 4001, Australia
Correspondence e-mail: g.smith@qut.edu.au

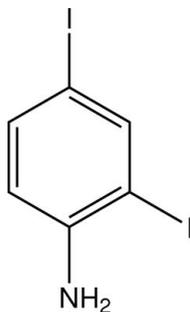
Received 14 July 2009; accepted 31 July 2009

Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å;
 R factor = 0.018; wR factor = 0.038; data-to-parameter ratio = 20.8.

The structure of the title compound, $\text{C}_6\text{H}_5\text{I}_2\text{N}$, shows a weak intermolecular amine–amine $\text{N}-\text{H}\cdots\text{N}$ hydrogen-bonding interaction, giving a helical chain which extends along the a axis. An intramolecular $\text{N}-\text{H}\cdots\text{I}$ hydrogen bond is also observed.

Related literature

For related structures, see: Garden *et al.* (2002). For the synthesis, see: Dains *et al.* (1935); Hodgson & Marsden (1937); O'Neil (2001). For graph-set analysis of hydrogen bonding, see: Etter *et al.* (1990).



Experimental

Crystal data

$\text{C}_6\text{H}_5\text{I}_2\text{N}$	$V = 816.51(3) \text{ \AA}^3$
$M_r = 344.91$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 4.3870(1) \text{ \AA}$	$\mu = 7.62 \text{ mm}^{-1}$
$b = 10.9626(3) \text{ \AA}$	$T = 200 \text{ K}$
$c = 16.9778(4) \text{ \AA}$	$0.30 \times 0.18 \times 0.18 \text{ mm}$

Data collection

Oxford Diffraction Gemini-S Ultra CCD-detector diffractometer	6739 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1873 independent reflections
$T_{\min} = 0.146$, $T_{\max} = 0.250$	1790 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$	$\Delta\rho_{\text{max}} = 0.38 \text{ e \AA}^{-3}$
$wR(F^2) = 0.038$	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$
$S = 1.05$	Absolute structure: Flack (1983), 737 Friedel pairs
1873 reflections	Flack parameter: $-0.03(4)$
90 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H11}\cdots\text{I2}$	0.77 (3)	2.81 (3)	3.283 (4)	122 (3)
$\text{N1}-\text{H12}\cdots\text{N1}^{\text{i}}$	0.80 (4)	2.30 (4)	3.106 (5)	180 (5)

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

The authors acknowledge financial support from the Australian Research Council and the School of Physical and Chemical Sciences, Queensland University of Technology.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2440).

References

- Dains, F. B., Brewster, R. Q. & Davis, J. A. (1935). *J. Am. Chem. Soc.* **57**, 2326–2327.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Garden, S. J., Fontes, S. P., Wardell, J. L., Skakle, J. M. S., Low, J. N. & Glidewell, C. (2002). *Acta Cryst.* **B58**, 701–709.
- Hodgson, H. H. & Marsden, E. (1937). *J. Chem. Soc.* pp. 1365–1366.
- O'Neil, M. J. (2001). Editor. *The Merck Index* 13th ed., p. 560. Whitehouse Station, NJ, USA: Merck & Co.
- Oxford Diffraction (2008). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
- Sheldrick, G. M. (1996). *SADABS*, University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

supporting information

Acta Cryst. (2009). E65, o2108 [doi:10.1107/S1600536809030438]

2,4-Diiodoaniline

Graham Smith and Urs D. Wermuth

S1. Comment

Although the crystal structures of a number of nitro-substituted iodoanilines including 3-nitro-2,4-diiodoaniline have been reported (Garden *et al.*, 2002), that of the title compound 2,4-diiodoaniline $C_6H_6I_2N$ (I) has not been determined and the structure is reported here. The compound was isolated as the major crystalline product in the attempted synthesis of an adduct of 4,5-dichlorophthalic acid with 4-iodoaniline in aqueous ethanol. This conversion of 4-iodoaniline to 2,4-diiodoaniline has been reported previously (Dains *et al.*, 1935), where solid 4-iodoaniline was observed to undergo a *ca* 25% conversion to the diiodo analogue in a sealed container over a period of three years. Hodgson & Marsden (1937) also reported the ready formation of the diiodo derivative along with 4-iodoaniline from the reaction of aniline with iodine.

In the structure of (I) (Fig. 1), single weak intermolecular hydrogen bonds are found [N1—H1 \cdots N1ⁱ, 3.106 (5) Å; symmetry code: (i) $x - 1/2, -y + 3/2, -z + 2$] [graph set S(4) (Etter *et al.*, 1990)], linking the amine groups of 2_1 screw-related molecules. These form one-dimensional chains which extend down the *a* cell direction in the unit cell (Fig. 2).

In this structure there are, not unexpectedly, short intramolecular N—H \cdots I interactions [N1 \cdots I2, 3.283 (4) Å], which are also present in the structure of 2,4-diiodo-3-nitroaniline [3.254 (7) Å (Garden *et al.*, 2002)]. However, unlike the nitro-derivative, no π – π stacking interactions are present in the structure of (I).

S2. Experimental

The title compound was formed in the attempted synthesis of a proton-transfer salt of 4,5-dichlorophthalic acid with 4-iodoaniline by heating together under reflux for 10 minutes 1 mmol quantities of the two reagents in 50 ml of 50% ethanol-water. After concentration to *ca* 30 ml, partial room temperature evaporation of the hot-filtered solution gave colourless needle prisms of 2,4-diiodoaniline [m.p. 368–389 K (O'Neil, 2001)] as the major product. This conversion of 4-iodoaniline to 2,4-diiodoaniline in the solid state has been reported previously (Dains *et al.*, 1935).

S3. Refinement

The hydrogen atoms of the amino group were located in a difference Fourier map and their positional and isotropic displacement parameters were refined freely. Other H-atoms were included in the refinement in calculated positions [C—H = 0.93 Å] and treated using a riding model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

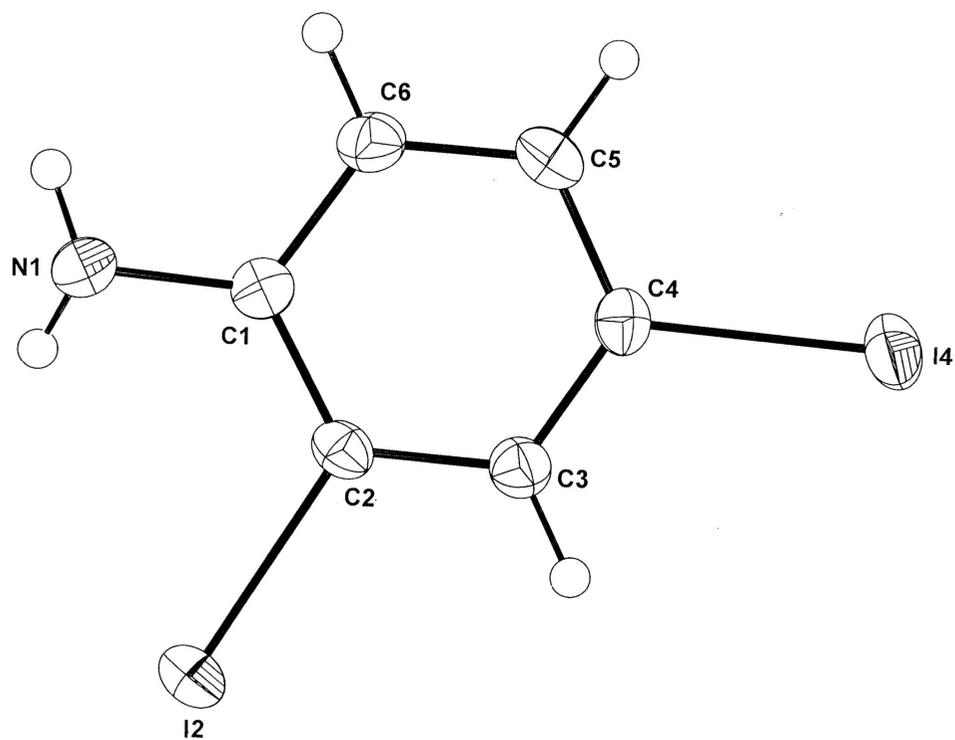


Figure 1

Molecular configuration and atom naming scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

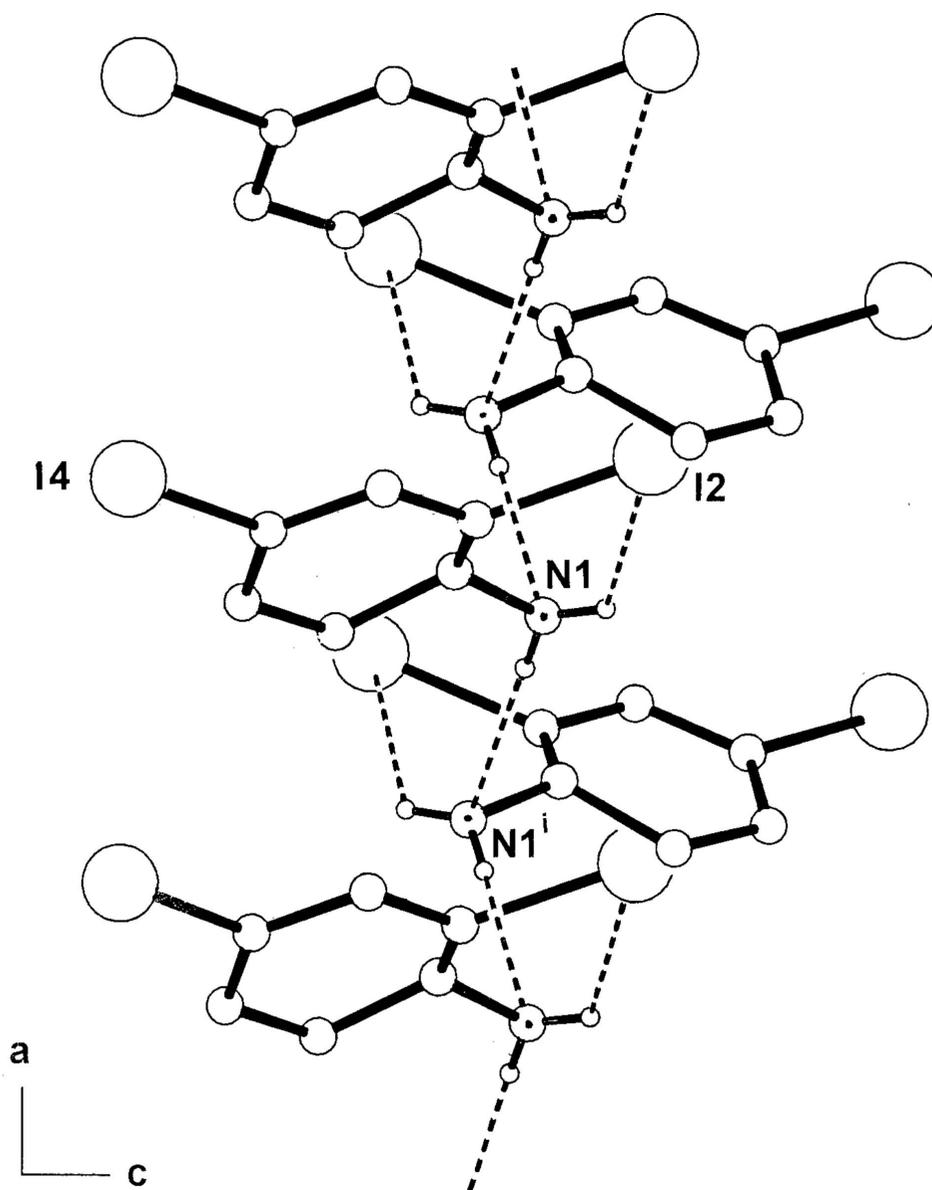


Figure 2

The one-dimensional hydrogen-bonded chain structure of (I) extending down the *a* axial direction of the unit cell, showing hydrogen-bonding associations as dashed lines. Non-interactive H atoms are omitted. [Symmetry code (i): $x - 1/2, -y + 3/2, -z + 2$].

2,4-Diiodoaniline

Crystal data

$C_6H_5I_2N$

$M_r = 344.91$

Orthorhombic, $P2_12_12_1$

Hall symbol: $P\ 2ac\ 2ab$

$a = 4.3870$ (1) Å

$b = 10.9626$ (3) Å

$c = 16.9778$ (4) Å

$V = 816.51$ (3) Å³

$Z = 4$

$F(000) = 616$

$D_x = 2.806$ Mg m⁻³

Melting point = 368–369 K

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

Cell parameters from 5620 reflections

$\theta = 3.0\text{--}32.2^\circ$
 $\mu = 7.62 \text{ mm}^{-1}$
 $T = 200 \text{ K}$

Needle, colourless
 $0.30 \times 0.18 \times 0.18 \text{ mm}$

Data collection

Oxford Diffraction Gemini-S Ultra CCD-
 detector
 diffractometer
 Radiation source: Enhance (Mo) X-ray tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.146$, $T_{\max} = 0.250$

6739 measured reflections
 1873 independent reflections
 1790 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$
 $h = -5 \rightarrow 5$
 $k = -13 \rightarrow 14$
 $l = -22 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.038$
 $S = 1.05$
 1873 reflections
 90 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0207P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.47 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), 737 Friedel
 pairs
 Absolute structure parameter: -0.03 (4)

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I2	0.57888 (5)	0.42657 (2)	1.08868 (1)	0.0293 (1)
I4	0.48489 (5)	0.28546 (2)	0.75021 (1)	0.0330 (1)
N1	0.1721 (9)	0.6552 (3)	1.0212 (2)	0.0291 (11)
C1	0.2299 (7)	0.5690 (3)	0.9630 (2)	0.0218 (9)
C2	0.4096 (8)	0.4658 (3)	0.97570 (19)	0.0221 (9)
C3	0.4807 (8)	0.3859 (3)	0.9156 (2)	0.0247 (9)
C4	0.3689 (8)	0.4074 (3)	0.8407 (2)	0.0235 (10)
C5	0.1876 (8)	0.5075 (3)	0.8256 (2)	0.0260 (11)
C6	0.1216 (9)	0.5877 (3)	0.8865 (2)	0.0278 (11)
H3	0.60280	0.31820	0.92530	0.0300*
H5	0.11070	0.52100	0.77530	0.0310*
H6	0.00190	0.65580	0.87610	0.0330*

H11	0.190 (8)	0.626 (3)	1.062 (2)	0.038 (9)*
H12	0.043 (8)	0.704 (4)	1.010 (2)	0.040 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I2	0.0335 (1)	0.0341 (1)	0.0202 (1)	0.0009 (1)	-0.0038 (1)	0.0021 (1)
I4	0.0383 (1)	0.0389 (1)	0.0219 (1)	0.0022 (1)	0.0017 (1)	-0.0069 (1)
N1	0.037 (2)	0.0222 (16)	0.028 (2)	0.0055 (15)	-0.0021 (16)	0.0013 (15)
C1	0.0214 (15)	0.0191 (16)	0.0248 (18)	-0.0039 (15)	0.0014 (14)	0.0021 (14)
C2	0.0251 (16)	0.0226 (16)	0.0186 (17)	-0.0034 (15)	-0.0009 (14)	0.0032 (11)
C3	0.0289 (18)	0.0218 (14)	0.0234 (17)	-0.0007 (11)	-0.0010 (16)	0.0015 (12)
C4	0.0252 (17)	0.0226 (18)	0.0228 (18)	-0.0031 (13)	0.0028 (14)	-0.0029 (13)
C5	0.027 (2)	0.0313 (19)	0.0197 (19)	-0.0028 (14)	-0.0018 (15)	0.0044 (14)
C6	0.0323 (19)	0.0236 (18)	0.0276 (19)	0.0028 (15)	0.0007 (15)	0.0051 (13)

Geometric parameters (Å, °)

I2—C2	2.101 (3)	C2—C3	1.381 (5)
I4—C4	2.099 (3)	C3—C4	1.383 (5)
N1—C1	1.391 (5)	C4—C5	1.379 (5)
N1—H12	0.80 (4)	C5—C6	1.388 (5)
N1—H11	0.77 (3)	C3—H3	0.9300
C1—C6	1.398 (5)	C5—H5	0.9300
C1—C2	1.396 (5)	C6—H6	0.9300
H11—N1—H12	124 (4)	I4—C4—C3	118.6 (2)
C1—N1—H11	110 (3)	C3—C4—C5	120.7 (3)
C1—N1—H12	114 (3)	C4—C5—C6	119.1 (3)
N1—C1—C6	119.9 (3)	C1—C6—C5	121.9 (3)
N1—C1—C2	123.0 (3)	C2—C3—H3	120.00
C2—C1—C6	117.0 (3)	C4—C3—H3	120.00
I2—C2—C1	120.4 (2)	C4—C5—H5	120.00
I2—C2—C3	117.7 (2)	C6—C5—H5	121.00
C1—C2—C3	121.9 (3)	C1—C6—H6	119.00
C2—C3—C4	119.4 (3)	C5—C6—H6	119.00
I4—C4—C5	120.7 (2)		
N1—C1—C2—I2	5.0 (5)	C1—C2—C3—C4	-0.7 (5)
N1—C1—C2—C3	-175.5 (3)	C2—C3—C4—I4	179.3 (3)
C6—C1—C2—I2	-178.9 (2)	C2—C3—C4—C5	0.0 (5)
C6—C1—C2—C3	0.6 (5)	I4—C4—C5—C6	-178.5 (3)
N1—C1—C6—C5	176.5 (3)	C3—C4—C5—C6	0.9 (5)
C2—C1—C6—C5	0.3 (5)	C4—C5—C6—C1	-1.0 (5)
I2—C2—C3—C4	178.8 (3)		

Hydrogen-bond 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>
N1—H11···I2	0.77 (3)	2.81 (3)	3.283 (4)	122 (3)
N1—H12···N1 ⁱ	0.80 (4)	2.30 (4)	3.106 (5)	180 (5)

Symmetry code: (i) $x-1/2, -y+3/2, -z+2$.