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2,4-Diiodoaniline

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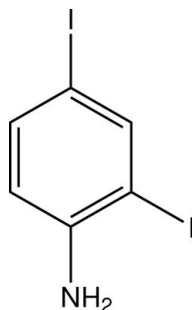
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å;
 R factor = 0.018; wR factor = 0.038; data-to-parameter ratio = 20.8.

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) |
| $\text{N1}-\text{H12}\cdots\text{N1}^i$ | 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*.

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

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supplementary materials

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2,4-Diiodoaniline

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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 C₆H₆I₂N (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—H1ⁱ⋯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 2₁ 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⋯I interactions [N1⋯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).

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).

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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

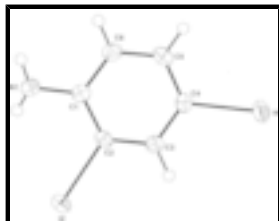


Fig. 1. Molecular configuration and atom naming scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

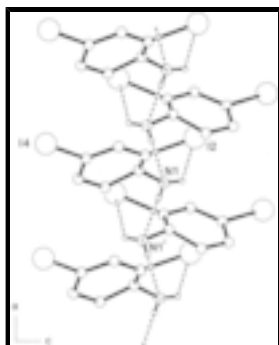


Fig. 2. The one-dimensional hydrogen-bonded chain structure of (I) extending down the *a* axial direction of the unit cell, showing hydrogen-bonding associations as dashed lines. Non-interactive H atoms are omitted. [Symmetry code (i): $x - 1/2, -y + 3/2, -z + 2$].

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

$\theta = 3.0$ – 32.2°

$\mu = 7.62$ mm⁻¹

$T = 200$ K

Needle, colourless

$0.30 \times 0.18 \times 0.18$ mm

Data collection

Oxford Diffraction Gemini-S Ultra CCD-detector diffractometer

Radiation source: Enhance (Mo) X-ray tube

Monochromator: graphite

$T = 200$ K

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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 27.5^\circ$

$\theta_{\text{min}} = 3.0^\circ$

$h = -5 \rightarrow 5$

$k = -13 \rightarrow 14$

$l = -22 \rightarrow 18$

Refinement

| | |
|--|---|
| Refinement on F^2 | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.018$ | $w = 1/[\sigma^2(F_o^2) + (0.0207P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.038$ | $(\Delta/\sigma)_{\max} = 0.003$ |
| $S = 1.05$ | $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$ |
| 1873 reflections | $\Delta\rho_{\min} = -0.47 \text{ e } \text{\AA}^{-3}$ |
| 90 parameters | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | Absolute structure: Flack (1983), 737 Friedel pairs |
| Secondary atom site location: difference Fourier map | Flack 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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|--------------|----------------------------------|
| 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)* |

supplementary materials

Atomic displacement parameters (\AA^2)

| | 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 (\AA , $^\circ$)

| | | | |
|-------------|------------|-------------|------------|
| 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 (\AA , $^\circ$)

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

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

Fig. 1

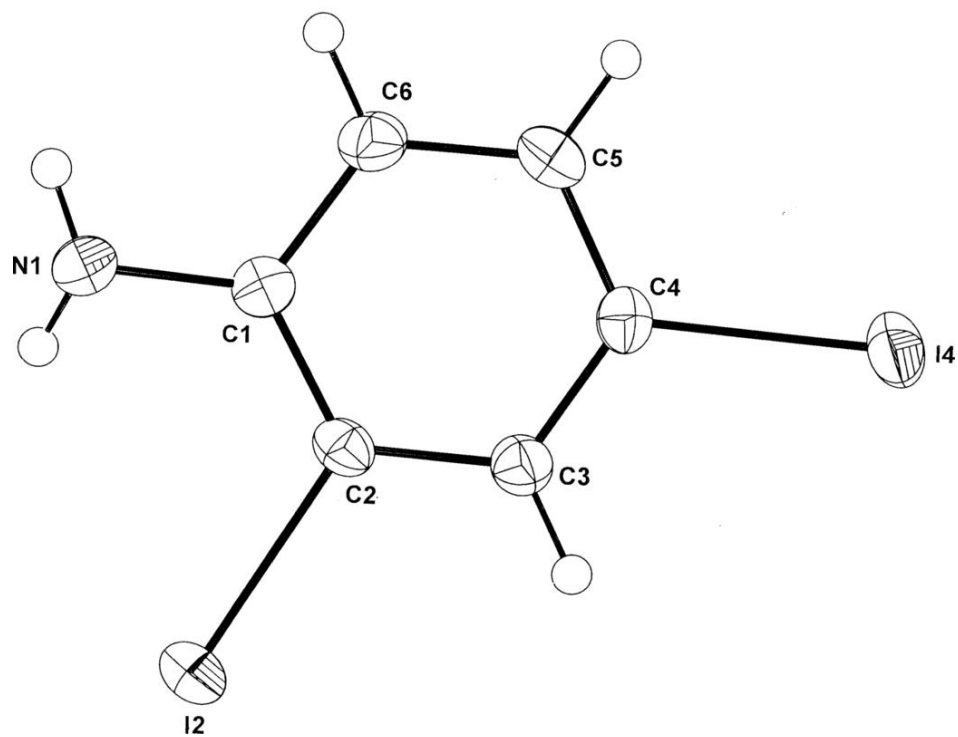


Fig. 2

