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3-Methylbenzene-1,2-diamine

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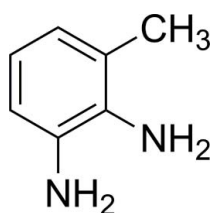
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.045; wR factor = 0.124; data-to-parameter ratio = 11.8.

The title compound, $\text{C}_7\text{H}_{10}\text{N}_2$, was synthesized from 2-methyl-6-nitroaniline by a reduction reaction. In the crystal, molecules are linked via $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, forming two-dimensional networks lying parallel to (100). These networks are stabilized by $\text{C}-\text{H}\cdots\pi$ and $\text{N}-\text{H}\cdots\pi$ interactions.

Related literature

The title compound is an important organic synthesis intermediate. For background to its applications, see: Wen *et al.* (2009). For the synthetic procedure, see: Li *et al.* (2011). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_7\text{H}_{10}\text{N}_2$
 $M_r = 122.17$
 Monoclinic, $P2_1/c$
 $a = 11.836$ (2) Å
 $b = 7.7160$ (15) Å
 $c = 7.7430$ (15) Å
 $\beta = 90.72$ (3)°

$V = 707.1$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.07$ mm⁻¹
 $T = 291$ K
 $0.3 \times 0.2 \times 0.1$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.979$, $T_{\max} = 0.993$
 2693 measured reflections

1300 independent reflections
 962 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$
 3 standard reflections every 200 reflections
 intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.124$
 $S = 1.00$
 1300 reflections
 110 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.13$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.12$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of C1–C6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{N2}^{\text{i}}$	0.91 (2)	2.36 (2)	3.237 (2)	163.5 (16)
$\text{N2}-\text{H2A}\cdots\text{N1}^{\text{ii}}$	0.84 (2)	2.48 (2)	3.248 (2)	152.2 (19)
$\text{C2}-\text{H2}\cdots\text{Cg1}^{\text{iii}}$	0.93	2.85	3.6713 (18)	148
$\text{N2}-\text{H2B}\cdots\text{Cg1}^{\text{iv}}$	0.90 (2)	2.776 (18)	3.5192 (17)	141.2 (16)

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z+1$; (iii) $x, -y+\frac{1}{2}, z-\frac{3}{2}$; (iv) $x, -y-\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2378).

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supporting information

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3-Methylbenzene-1,2-diamine

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S1. Comment

Aromatic amines are important organic intermediates and widely used in chemical, pharmaceutical, agricultural and photographic chemicals. Aromatic amines are mainly synthesized by the reduction of aromatic nitro compounds. Compared with other reduction methods, catalytic transfer hydrogenation (CTH) is environmentally friendly, high yield and good selectivity (Wen *et al.*, 2009), in which hydrogen gas is replaced by a hydrogen donor such as hydrazine hydrate. Here, the title compound, (I), was synthesized by the CTH of 2-methyl-6-nitroaniline, and we report the crystal structure of (I).

In the molecule of (I), (Fig.1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. In the crystal, there are two C—H \cdots Cg1 and N—H \cdots Cg1 interactions (Cg1 is the centroid of C1-C6 ring). The molecules are linked each other by the two intermolecular N—H \cdots N hydrogen bonds to form a three-dimensional network, which seem to be very effective in the stabilization of the crystal structure (Fig. 2.).

S2. Experimental

The title compound, (I) was prepared by the literature method (Li *et al.*, 2011). Crystals suitable for X-ray analysis were obtained by dissolving (I) (0.5 g) in ethyl acetate (20 ml) and evaporating the solvent slowly at room temperature for about 7 d.

S3. Refinement

H atoms were positioned geometrically, with C—H = 0.93 Å for aromatic H, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C/N})$, where $x = 1.2$ for aromatic H.

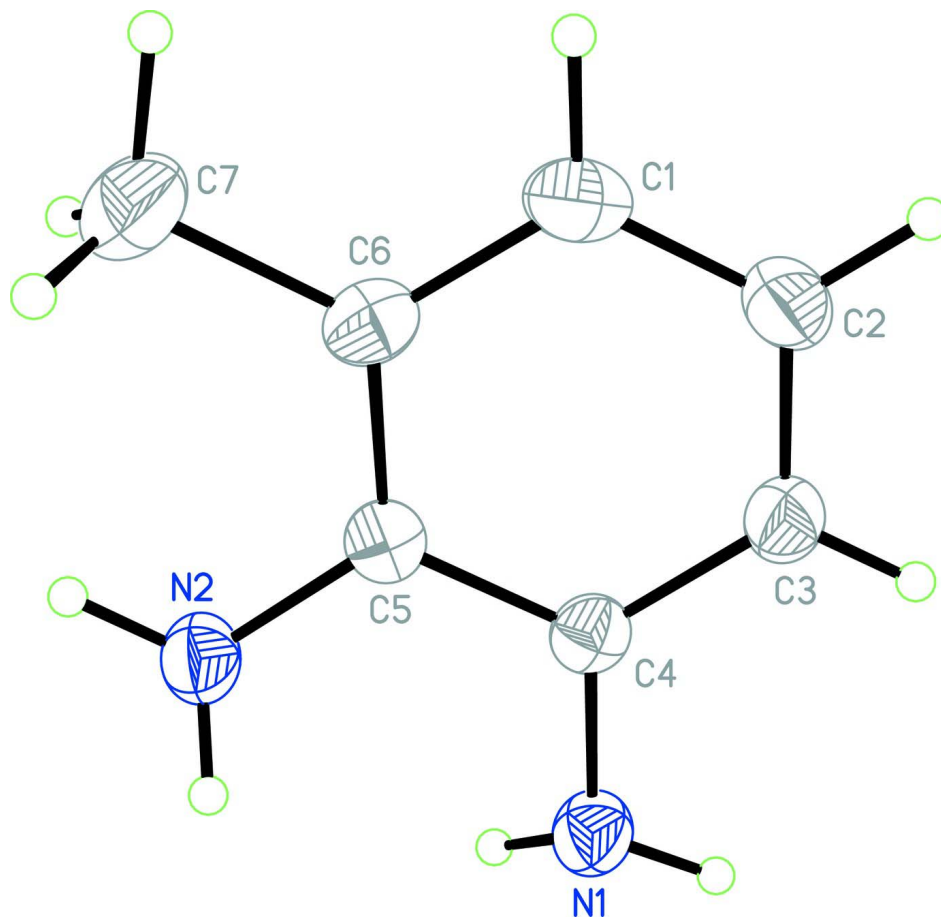
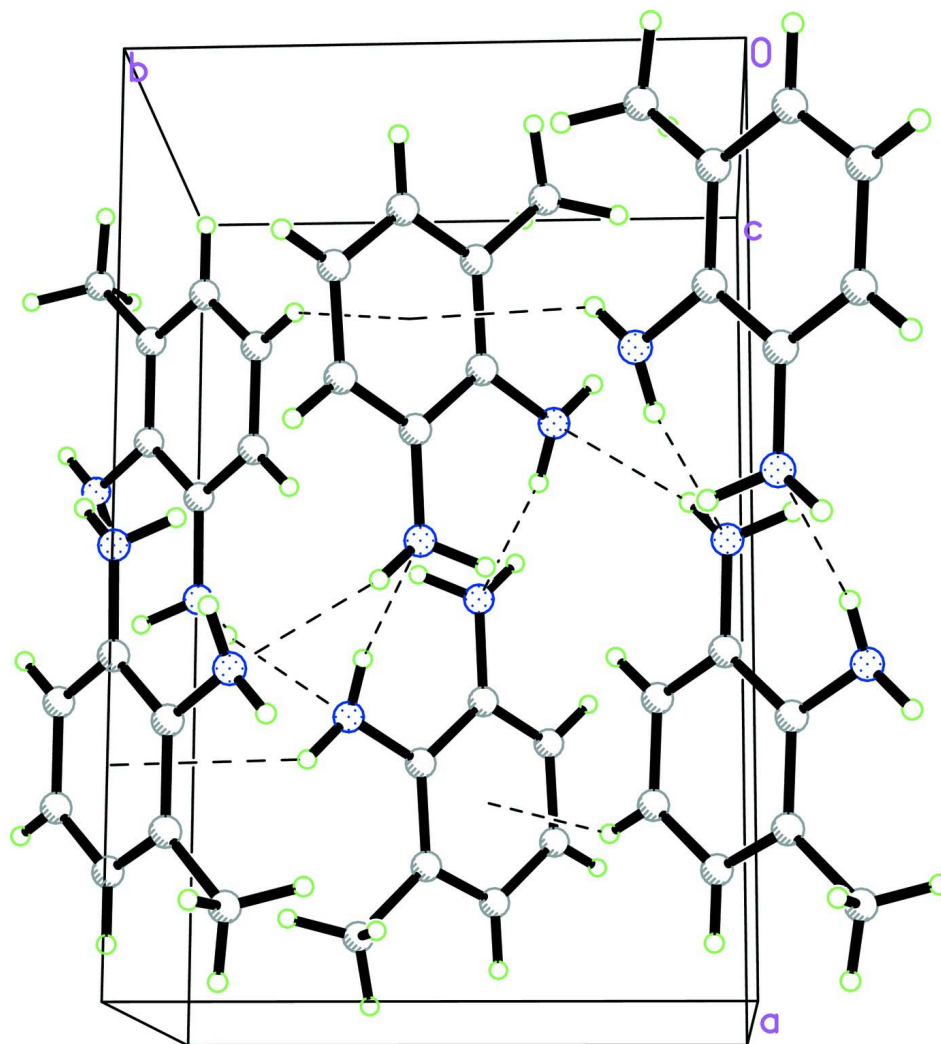


Figure 1

The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

A packing diagram of (I). Hydrogen bonds are shown by dashed lines.

3-Methylbenzene-1,2-diamine

Crystal data

$C_7H_{10}N_2$

$M_r = 122.17$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 11.836\ (2)\ \text{\AA}$

$b = 7.7160\ (15)\ \text{\AA}$

$c = 7.7430\ (15)\ \text{\AA}$

$\beta = 90.72\ (3)^\circ$

$V = 707.1\ (2)\ \text{\AA}^3$

$Z = 4$

$F(000) = 264$

$D_x = 1.148\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 9\text{--}13^\circ$

$\mu = 0.07\ \text{mm}^{-1}$

$T = 291\ \text{K}$

Needle, colourless

$0.3 \times 0.2 \times 0.1\ \text{mm}$

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.979$, $T_{\max} = 0.993$

2693 measured reflections

1300 independent reflections

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

$R_{\text{int}} = 0.060$

$\theta_{\max} = 25.4^\circ$, $\theta_{\min} = 1.7^\circ$

$h = -14 \rightarrow 14$

$k = -9 \rightarrow 9$

$l = 0 \rightarrow 9$

3 standard reflections every 200 reflections

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.124$

$S = 1.00$

1300 reflections

110 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

$w = 1/[\sigma^2(F_o^2) + (0.073P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.13 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.15863 (14)	0.55588 (19)	0.1128 (2)	0.0551 (5)
H1	0.0829	0.5612	0.0799	0.066*
C2	0.23534 (15)	0.6592 (2)	0.0300 (2)	0.0578 (5)
H2	0.2116	0.7340	-0.0573	0.069*
C3	0.34751 (13)	0.65096 (18)	0.07727 (19)	0.0493 (4)
H3	0.3996	0.7206	0.0211	0.059*
C4	0.38402 (12)	0.54018 (16)	0.20768 (17)	0.0408 (4)
C5	0.30472 (12)	0.43631 (17)	0.29360 (17)	0.0399 (4)
C6	0.19124 (12)	0.44367 (18)	0.2446 (2)	0.0478 (4)
C7	0.10562 (18)	0.3339 (3)	0.3346 (3)	0.0760 (6)
N1	0.49730 (11)	0.5349 (2)	0.26271 (18)	0.0508 (4)
N2	0.34528 (14)	0.32174 (18)	0.42184 (19)	0.0525 (4)
H1A	0.5472 (17)	0.596 (3)	0.199 (3)	0.072 (6)*
H1B	0.5231 (14)	0.430 (3)	0.290 (2)	0.066 (6)*
H2A	0.4043 (19)	0.350 (3)	0.478 (3)	0.086 (7)*

H2B	0.2929 (18)	0.257 (2)	0.474 (3)	0.074 (6)*
H7A	0.031 (2)	0.350 (3)	0.279 (3)	0.097 (7)*
H7B	0.127 (2)	0.211 (3)	0.323 (3)	0.111 (8)*
H7C	0.1046 (18)	0.375 (3)	0.458 (3)	0.091 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0485 (9)	0.0534 (9)	0.0630 (10)	0.0031 (7)	-0.0144 (8)	-0.0054 (8)
C2	0.0675 (11)	0.0475 (9)	0.0578 (10)	-0.0018 (8)	-0.0169 (8)	0.0077 (8)
C3	0.0583 (10)	0.0435 (8)	0.0461 (9)	-0.0086 (7)	-0.0023 (7)	0.0014 (7)
C4	0.0458 (8)	0.0359 (7)	0.0408 (8)	-0.0009 (6)	0.0020 (6)	-0.0065 (6)
C5	0.0445 (8)	0.0354 (7)	0.0398 (7)	0.0032 (6)	0.0025 (6)	-0.0045 (6)
C6	0.0424 (8)	0.0444 (8)	0.0566 (9)	-0.0021 (6)	0.0008 (7)	-0.0062 (7)
C7	0.0493 (11)	0.0862 (16)	0.0926 (17)	-0.0115 (10)	0.0066 (11)	0.0150 (13)
N1	0.0437 (8)	0.0531 (9)	0.0558 (8)	-0.0016 (6)	0.0033 (6)	0.0063 (7)
N2	0.0482 (8)	0.0534 (8)	0.0557 (8)	0.0009 (7)	0.0021 (7)	0.0128 (7)

Geometric parameters (Å, °)

C1—C2	1.373 (2)	C5—N2	1.4092 (19)
C1—C6	1.389 (2)	C6—C7	1.499 (2)
C1—H1	0.9300	C7—H7A	0.98 (2)
C2—C3	1.374 (2)	C7—H7B	0.99 (2)
C2—H2	0.9300	C7—H7C	1.01 (2)
C3—C4	1.388 (2)	N1—H1A	0.91 (2)
C3—H3	0.9300	N1—H1B	0.89 (2)
C4—N1	1.4023 (19)	N2—H2A	0.84 (2)
C4—C5	1.408 (2)	N2—H2B	0.90 (2)
C5—C6	1.392 (2)		
C2—C1—C6	121.70 (15)	C1—C6—C5	118.94 (14)
C2—C1—H1	119.2	C1—C6—C7	120.69 (16)
C6—C1—H1	119.2	C5—C6—C7	120.37 (15)
C1—C2—C3	119.44 (15)	C6—C7—H7A	109.4 (13)
C1—C2—H2	120.3	C6—C7—H7B	108.7 (16)
C3—C2—H2	120.3	H7A—C7—H7B	108.3 (19)
C2—C3—C4	120.86 (15)	C6—C7—H7C	106.2 (12)
C2—C3—H3	119.6	H7A—C7—H7C	110.6 (19)
C4—C3—H3	119.6	H7B—C7—H7C	113 (2)
C3—C4—N1	121.78 (14)	C4—N1—H1A	116.5 (12)
C3—C4—C5	119.42 (14)	C4—N1—H1B	115.0 (11)
N1—C4—C5	118.72 (13)	H1A—N1—H1B	112.1 (17)
C6—C5—C4	119.64 (13)	C5—N2—H2A	118.1 (14)
C6—C5—N2	122.45 (14)	C5—N2—H2B	115.9 (12)
C4—C5—N2	117.83 (14)	H2A—N2—H2B	118.8 (19)
C6—C1—C2—C3	0.5 (2)	N1—C4—C5—N2	-5.00 (19)

C1—C2—C3—C4	-0.2 (2)	C2—C1—C6—C5	0.1 (2)
C2—C3—C4—N1	-177.35 (13)	C2—C1—C6—C7	179.18 (17)
C2—C3—C4—C5	-0.6 (2)	C4—C5—C6—C1	-0.9 (2)
C3—C4—C5—C6	1.19 (19)	N2—C5—C6—C1	-177.77 (13)
N1—C4—C5—C6	178.00 (12)	C4—C5—C6—C7	179.99 (16)
C3—C4—C5—N2	178.19 (12)	N2—C5—C6—C7	3.1 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 is the centroid of C1–C6 ring.

<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>
N1—H1 <i>A</i> \cdots N2 ⁱ	0.91 (2)	2.36 (2)	3.237 (2)	163.5 (16)
N2—H2 <i>A</i> \cdots N1 ⁱⁱ	0.84 (2)	2.48 (2)	3.248 (2)	152.2 (19)
C2—H2 \cdots Cg1 ⁱⁱⁱ	0.93	2.85	3.6713 (18)	148
N2—H2 <i>B</i> \cdots Cg1 ^{iv}	0.90 (2)	2.776 (18)	3.5192 (17)	141.2 (16)

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