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2-Chloro-5-nitroaniline

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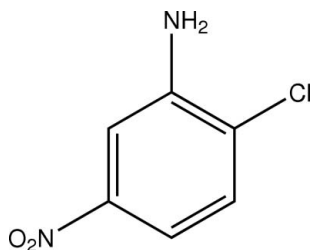
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.023; wR factor = 0.061; data-to-parameter ratio = 11.8.

The molecule of the title compound, $\text{C}_6\text{H}_5\text{ClN}_2\text{O}_2$, is close to being planar (rms deviation = 0.032 Å for all non-H atoms), with a maximum deviation of -0.107 (3) Å for an O atom. In the crystal structure, intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ interactions link the molecules into a three-dimensional network.

Related literature

For applications of substituted nitrobenzene and aniline derivatives, see: Heinisch *et al.* (1997); Wang *et al.* (2000); Yosuke *et al.* (2003); Zou *et al.* (1997). For a related structure, see: Zhang *et al.* (2004). For bond-length data, see: Allen *et al.* (1987). For synthesis, see: Suwanprasop *et al.* (2003).



Experimental

Crystal data

 $\text{C}_6\text{H}_5\text{ClN}_2\text{O}_2$ $M_r = 172.57$

Monoclinic, $P2_1/n$
 $a = 13.6233$ (10) Å
 $b = 3.7445$ (3) Å
 $c = 13.6420$ (9) Å
 $\beta = 91.768$ (5)°
 $V = 695.58$ (9) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.49$ mm⁻¹
 $T = 173$ K
 $0.35 \times 0.34 \times 0.29$ mm

Data collection

Stoe IPDSII two-circle diffractometer
 Absorption correction: multi-scan (MULABS; Blessing, 1995)
 $T_{\min} = 0.847$, $T_{\max} = 0.871$

5108 measured reflections
 1300 independent reflections
 1266 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.061$
 $S = 1.06$
 1300 reflections
 110 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.20$ e Å⁻³
 $\Delta\rho_{\min} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|----------|-------------|-------------|---------------|
| $\text{N2}-\text{H2A}\cdots\text{O1}^i$ | 0.85 (2) | 2.33 (2) | 3.1521 (18) | 163.2 (19) |
| $\text{N2}-\text{H2B}\cdots\text{N2}^{ii}$ | 0.88 (3) | 2.44 (2) | 3.1452 (19) | 137.4 (18) |

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

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-RED* (Stoe & Cie, 2001); data reduction: *X-RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2694).

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supplementary materials

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2-Chloro-5-nitroaniline

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Comment

Substituted nitrobenzene and aniline derivatives are valuable as intermediates towards a variety of dye and pigments, heterocycles, pesticides, rubber chemicals and agricultural products, and are useful as textile printing agents, nickel stripping agents and polymerization catalysts. Thus, then title compound is an important intermediate or starting point in the syntheses of alkyl derivatives of 2-aminobenzenethiols substituted by chloro and nitro groups (Wang *et al.*, 2000), donor-bridge-acceptor' triad compounds containing the aromatic sulfur bridges (Yosuke *et al.*, 2003), pyridazinobenzodiazepin-5-ones as non-nucleoside HIV Reverse Transcriptase Inhibitors (Heinisch *et al.*, 1997) and 2-chloro-5,6-dihalo-*D*-ribofuranosylbenzimidazoles as potential agents for human cytomegalovirus infections (Zou *et al.*, 1997). We report herein the crystal structure of the title compound, as a key starting point towards many heterocycles.

In the molecule of the title compound (Fig 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges, and may be compared with the corresponding values in *N*-tert-butyl-4-chloro-5-methyl-2-nitroaniline (Zhang *et al.*, 2004). Ring A (C1–C6) is, of course, planar. Atoms Cl1, O1, O2, N1 and N2 are 0.019 (3), 0.104 (3), -0.107 (3), 0.003 (3) and -0.066 (3) Å away from the ring plane, respectively. So, the molecule is nearly planar.

In the crystal structure, intermolecular N—H···O and N—H···N hydrogen bonds (Table 1) link the molecules into a network, in which they may be effective in the stabilization of the structure.

Experimental

The title compound was prepared by nitration and selective reduction of 4-nitroaniline according to the literature method (Suwanprasop *et al.*, 2003). Recrystallization from methanol afforded the title compound. Anal. calcd. for C₆H₅ClN₂O₂: C, 41.76; H, 2.92; N, 16.23%; found: C, 41.71; H, 2.97; N, 16.16%

Refinement

H atoms (for NH₂) were located in a difference synthesis and refined isotropically. The remaining H atoms were positioned geometrically, with C—H = 0.95 Å for aromatic H and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

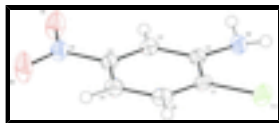


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

2-Chloro-5-nitroaniline

Crystal data

$C_6H_5ClN_2O_2$

$M_r = 172.57$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 13.6233$ (10) Å

$b = 3.7445$ (3) Å

$c = 13.6420$ (9) Å

$\beta = 91.768$ (5)°

$V = 695.58$ (9) Å³

$Z = 4$

$F_{000} = 352$

$D_x = 1.648$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 7189 reflections

$\theta = 3.4$ – 25.9 °

$\mu = 0.49$ mm⁻¹

$T = 173$ K

Block, orange

$0.35 \times 0.34 \times 0.29$ mm

Data collection

Stoe IPDSII two-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173$ K

ω scans

Absorption correction: multi-scan (MULABS; Blessing, 1995)

$T_{\min} = 0.847$, $T_{\max} = 0.871$

5108 measured reflections

1300 independent reflections

1266 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\text{max}} = 25.5$ °

$\theta_{\text{min}} = 3.4$ °

$h = -16$ → 14

$k = -4$ → 4

$l = -16$ → 16

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.061$

$S = 1.06$

1300 reflections

110 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.0466P]$

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

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

$\Delta\rho_{\text{max}} = 0.20$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Extinction correction: SHELXL97 (Sheldrick, 2008),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.034 (4)

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 | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|--------------|----------------------------------|
| C11 | 0.91913 (3) | 0.59906 (8) | 0.62642 (3) | 0.02963 (14) |
| O1 | 0.50548 (9) | 0.8247 (4) | 0.37207 (9) | 0.0385 (3) |
| O2 | 0.60383 (10) | 1.0787 (4) | 0.27322 (9) | 0.0475 (4) |
| N1 | 0.58750 (10) | 0.9201 (3) | 0.34951 (9) | 0.0258 (3) |
| N2 | 0.70761 (10) | 0.4832 (4) | 0.66629 (9) | 0.0255 (3) |
| H2B | 0.7582 (18) | 0.367 (5) | 0.6920 (18) | 0.043 (6)* |
| H2A | 0.6514 (17) | 0.384 (4) | 0.6685 (15) | 0.029 (5)* |
| C1 | 0.82203 (10) | 0.6968 (3) | 0.54548 (10) | 0.0215 (3) |
| C2 | 0.72634 (11) | 0.6173 (3) | 0.57428 (10) | 0.0203 (3) |
| C3 | 0.64960 (10) | 0.6935 (3) | 0.50720 (10) | 0.0206 (3) |
| H3 | 0.5836 | 0.6427 | 0.5230 | 0.025* |
| C4 | 0.67060 (10) | 0.8434 (3) | 0.41772 (10) | 0.0206 (3) |
| C5 | 0.76477 (11) | 0.9244 (3) | 0.38893 (11) | 0.0231 (3) |
| H5 | 0.7764 | 1.0285 | 0.3269 | 0.028* |
| C6 | 0.84118 (11) | 0.8461 (4) | 0.45509 (11) | 0.0248 (3) |
| H6 | 0.9070 | 0.8952 | 0.4383 | 0.030* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|--------------|------------|--------------|---------------|---------------|
| C11 | 0.0223 (2) | 0.03330 (19) | 0.0329 (2) | 0.00210 (13) | -0.00586 (12) | -0.00076 (14) |
| O1 | 0.0221 (6) | 0.0617 (7) | 0.0315 (6) | -0.0054 (5) | -0.0011 (4) | 0.0122 (5) |
| O2 | 0.0374 (7) | 0.0750 (10) | 0.0298 (6) | -0.0099 (6) | -0.0040 (5) | 0.0271 (6) |
| N1 | 0.0252 (7) | 0.0302 (6) | 0.0218 (6) | -0.0012 (5) | 0.0000 (5) | 0.0029 (5) |
| N2 | 0.0266 (7) | 0.0291 (6) | 0.0206 (6) | -0.0039 (6) | -0.0011 (5) | 0.0041 (5) |
| C1 | 0.0215 (7) | 0.0184 (5) | 0.0245 (7) | 0.0006 (5) | -0.0014 (5) | -0.0047 (5) |
| C2 | 0.0246 (7) | 0.0181 (6) | 0.0182 (7) | -0.0004 (5) | 0.0014 (5) | -0.0026 (4) |
| C3 | 0.0204 (6) | 0.0216 (6) | 0.0201 (6) | -0.0019 (5) | 0.0034 (5) | -0.0021 (5) |
| C4 | 0.0222 (7) | 0.0196 (6) | 0.0198 (6) | 0.0001 (5) | 0.0006 (5) | -0.0015 (5) |
| C5 | 0.0257 (7) | 0.0235 (6) | 0.0203 (7) | -0.0021 (5) | 0.0060 (6) | -0.0007 (5) |
| C6 | 0.0199 (7) | 0.0247 (6) | 0.0301 (7) | -0.0009 (5) | 0.0054 (5) | -0.0027 (5) |

supplementary materials

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------------|--------------|--------------|--------------|
| N1—O1 | 1.2216 (19) | C2—C3 | 1.397 (2) |
| N1—O2 | 1.2245 (18) | C3—C4 | 1.382 (2) |
| N2—H2B | 0.88 (3) | C3—H3 | 0.9500 |
| N2—H2A | 0.85 (2) | C4—C5 | 1.387 (2) |
| C1—C6 | 1.386 (2) | C4—N1 | 1.4713 (18) |
| C1—C2 | 1.405 (2) | C5—C6 | 1.388 (2) |
| C1—C11 | 1.7357 (14) | C5—H5 | 0.9500 |
| C2—N2 | 1.3830 (18) | C6—H6 | 0.9500 |
| O1—N1—O2 | 123.19 (14) | C4—C3—C2 | 119.37 (12) |
| O1—N1—C4 | 118.40 (12) | C4—C3—H3 | 120.3 |
| O2—N1—C4 | 118.41 (13) | C2—C3—H3 | 120.3 |
| C2—N2—H2B | 112.2 (15) | C3—C4—C5 | 123.90 (13) |
| C2—N2—H2A | 112.4 (14) | C3—C4—N1 | 117.51 (12) |
| H2B—N2—H2A | 117.7 (18) | C5—C4—N1 | 118.59 (13) |
| C6—C1—C2 | 122.42 (13) | C4—C5—C6 | 116.84 (13) |
| C6—C1—C11 | 119.36 (11) | C4—C5—H5 | 121.6 |
| C2—C1—C11 | 118.22 (11) | C6—C5—H5 | 121.6 |
| N2—C2—C3 | 120.88 (13) | C1—C6—C5 | 120.38 (13) |
| N2—C2—C1 | 121.98 (13) | C1—C6—H6 | 119.8 |
| C3—C2—C1 | 117.09 (13) | C5—C6—H6 | 119.8 |
| C6—C1—C2—N2 | -177.05 (13) | N1—C4—C5—C6 | -179.64 (12) |
| C11—C1—C2—N2 | 3.57 (17) | C2—C1—C6—C5 | 0.2 (2) |
| C6—C1—C2—C3 | 0.33 (19) | C11—C1—C6—C5 | 179.57 (10) |
| C11—C1—C2—C3 | -179.04 (9) | C4—C5—C6—C1 | -0.5 (2) |
| N2—C2—C3—C4 | 176.87 (12) | C3—C4—N1—O1 | -5.21 (19) |
| C1—C2—C3—C4 | -0.55 (19) | C5—C4—N1—O1 | 174.73 (13) |
| C2—C3—C4—C5 | 0.2 (2) | C3—C4—N1—O2 | 174.29 (13) |
| C2—C3—C4—N1 | -179.82 (12) | C5—C4—N1—O2 | -5.8 (2) |
| C3—C4—C5—C6 | 0.3 (2) | | |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|----------|-------------|-------------|---------------|
| N2—H2A \cdots O1 ⁱ | 0.85 (2) | 2.33 (2) | 3.1521 (18) | 163.2 (19) |
| N2—H2B \cdots N2 ⁱⁱ | 0.88 (3) | 2.44 (2) | 3.1452 (19) | 137.4 (18) |

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

Fig. 1

