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# 3-Nitrobenzaldehyde

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**Keywords:** crystal structure; $\pi$–$\pi$ stacking interactions; nitrobenzaldehyde.

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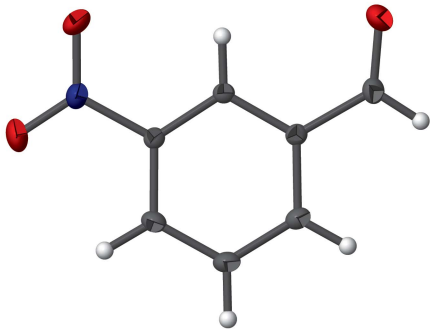
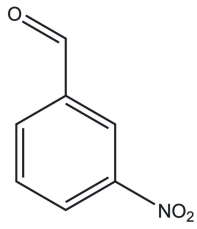
**Structural data**: full structural data are available from iucrdata.iucr.org

Polymorph I of the title compound, $C_7H_5NO_3$, is approximately planar: the dihedral angle between the benzene ring and the nitro group is 10.41 (4)° and the aldehyde O atom deviates from the ring plane by 0.165 (1) Å. In the crystal, aromatic $\pi$–$\pi$ stacking interactions are observed [centroid–centroid separation = 3.7363 (5) Å].

**3D view**



**Chemical scheme**




## Structure description

The existence of two polymorphic forms of the title compound, $C_7H_5NO_3$, has been known for almost eighty years (Lindpaintner, 1939); however, to date no crystal structure of the title compound has been reported. Here, we present the crystal structure of the stable polymorph (polymorph I). For the crystal structure of the closely related compound 2-nitrobenzaldehyde, see Coppens & Schmidt (1964) and Coppens (1964) and for the crystal structure of 4-nitrobenzalhyde, see Jackisch *et al.* (1989) and King & Bryant (1996).

The molecular structure of the title compound is shown in Fig. 1. The dihedral angle between the benzene ring and the nitro group is 10.41 (4)° and the aldehyde O atom deviates from the ring plane by 0.165 (1) Å. In the crystal, aromatic $\pi$–$\pi$ stacking interactions are observed [centroid–centroid separation = 3.7363 (5) Å].

The melting point of the stable polymorph is 327 K, while the melting point of polymorph II is 322 K, as determined using the onset temperature of differential scanning calorimetry.

## Synthesis and crystallization

A 100 mg mL$^{-1}$ solution of 3-nitrobenzaldehyde (Merck, no indication of purity given) in acetone was filtered to obtain a clear yellow solution. Slow evaporation of a 1:1 mixture

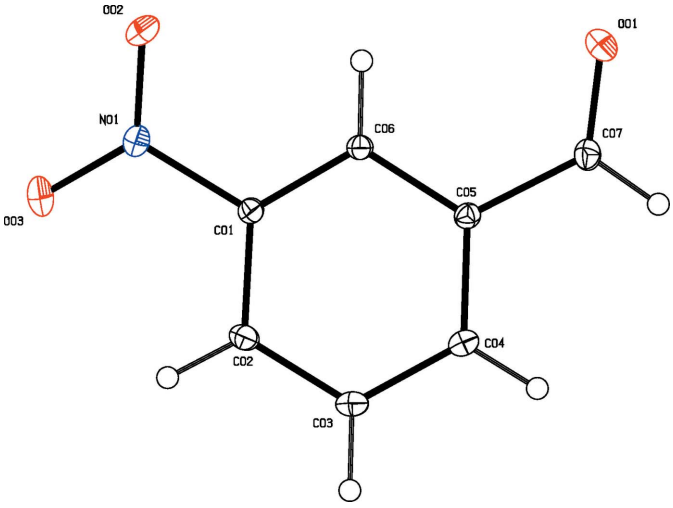



**Figure 1**
The molecular structure of the title compound, showing displacement ellipsoids drawn at the 30% probability level.

of this solution and heptane resulted in large colourless needle-shaped crystals of the title compound after two days.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

**Table 1**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_7H_5NO_3$ |
| $M_r$ | 151.12 |
| Crystal system, space group | Monoclinic, $P2_1$ |
| Temperature (K) | 150 |
| $a$, $b$, $c$ (Å) | 3.7363 (2), 7.0071 (3), 12.5877 (6) |
| $\beta$ (°) | 94.8144 (16) |
| $V$ (Å$^3$) | 328.39 (3) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.12 |
| Crystal size (mm) | 0.48 × 0.17 × 0.09 |
| | |
| Data collection | |
| Diffractometer | Bruker D8 Quest *APEX3* |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2011) |
| $T_{min}$, $T_{max}$ | 0.713, 0.748 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 18662, 4005, 3735 |
| $R_{int}$ | 0.021 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.909 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.030, 0.089, 1.05 |
| No. of reflections | 4005 |
| No. of parameters | 100 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.38, −0.21 |
| Absolute structure | Flack $x$ determined using 1595 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013). |
| Absolute structure parameter | −0.02 (13) |

Computer programs: *APEX3* (Bruker, 2012), *PEAKREF* (Schreurs, 2013), *SAINT* (Bruker, 2012), *SHELXT2014/4* (Sheldrick, 2015*a*), *SHELXL2016/6* (Sheldrick, 2015*b*), *PLATON* (Spek, 2009) and *ShelXLe* (Hübschle *et al.*, 2011).

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# full crystallographic data

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## 3-Nitrobenzaldehyde

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### 3-Nitrobenzaldehyde

*Crystal data*

$C_7H_5NO_3$
$M_r$ = 151.12
Monoclinic, $P2_1$
$a$ = 3.7363 (2) Å
$b$ = 7.0071 (3) Å
$c$ = 12.5877 (6) Å
$\beta$ = 94.8144 (16)°
$V$ = 328.39 (3) Å$^3$
$Z$ = 2
$F(000)$ = 156
$D_x$ = 1.528 Mg m$^{-3}$
Melting point: 327 K
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 9919 reflections
$\theta$ = 2.9–40.3°
$\mu$ = 0.12 mm$^{-1}$
$T$ = 150 K
Needle, colourless
0.48 × 0.17 × 0.09 mm

*Data collection*

Bruker D8 Quest APEX3 diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 10.4 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2011)
$T_{min}$ = 0.713, $T_{max}$ = 0.748
18662 measured reflections
4005 independent reflections
3735 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.021
$\theta_{max}$ = 40.3°, $\theta_{min}$ = 3.3°
$h$ = −6→6
$k$ = −12→12
$l$ = −22→22

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.089
$S$ = 1.05
4005 reflections
100 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2 + 0.0066P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$
Absolute structure: Flack $x$ determined using 1595 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013).
Absolute structure parameter: −0.02 (13)

*Special details*

**Experimental**. Polymorph I

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O01 | 0.3805 (2) | 0.36964 (11) | 0.47803 (5) | 0.02774 (14) |
| O02 | 0.5659 (2) | 0.81726 (10) | 0.79109 (6) | 0.02858 (15) |
| O03 | 0.3141 (2) | 0.75360 (14) | 0.93565 (6) | 0.03273 (17) |
| N01 | 0.39008 (18) | 0.71338 (9) | 0.84537 (5) | 0.01838 (11) |
| C01 | 0.26607 (18) | 0.52935 (9) | 0.79964 (5) | 0.01429 (10) |
| C02 | 0.1223 (2) | 0.39635 (11) | 0.86644 (6) | 0.01736 (12) |
| H02 | 0.101303 | 0.424953 | 0.939430 | 0.021* |
| C03 | 0.0102 (2) | 0.22081 (11) | 0.82413 (6) | 0.01891 (13) |
| H03 | −0.087439 | 0.127606 | 0.868273 | 0.023* |
| C04 | 0.0419 (2) | 0.18223 (10) | 0.71667 (6) | 0.01706 (12) |
| H04 | −0.036577 | 0.062838 | 0.687503 | 0.020* |
| C05 | 0.18828 (17) | 0.31822 (9) | 0.65163 (5) | 0.01416 (10) |
| C06 | 0.30344 (19) | 0.49536 (10) | 0.69286 (5) | 0.01405 (10) |
| H06 | 0.403384 | 0.588642 | 0.649244 | 0.017* |
| C07 | 0.2287 (2) | 0.26924 (11) | 0.53892 (6) | 0.01863 (12) |
| H07 | 0.129789 | 0.151915 | 0.512489 | 0.022* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O01 | 0.0390 (3) | 0.0266 (3) | 0.0188 (2) | −0.0037 (3) | 0.0094 (2) | −0.0013 (2) |
| O02 | 0.0373 (3) | 0.0184 (2) | 0.0311 (3) | −0.0106 (3) | 0.0088 (3) | −0.0032 (2) |
| O03 | 0.0461 (4) | 0.0320 (3) | 0.0209 (3) | −0.0065 (3) | 0.0074 (3) | −0.0112 (3) |
| N01 | 0.0201 (3) | 0.0162 (2) | 0.0187 (2) | −0.00059 (19) | 0.00057 (19) | −0.00306 (18) |
| C01 | 0.0145 (2) | 0.0137 (2) | 0.0148 (2) | −0.00082 (17) | 0.00209 (18) | −0.00065 (17) |
| C02 | 0.0185 (3) | 0.0190 (3) | 0.0148 (2) | −0.0012 (2) | 0.0030 (2) | 0.00250 (19) |
| C03 | 0.0203 (3) | 0.0171 (3) | 0.0196 (3) | −0.0025 (2) | 0.0034 (2) | 0.0042 (2) |
| C04 | 0.0173 (3) | 0.0139 (2) | 0.0200 (3) | −0.00153 (19) | 0.0015 (2) | 0.0017 (2) |
| C05 | 0.0143 (2) | 0.0129 (2) | 0.0153 (2) | 0.00052 (19) | 0.00169 (18) | 0.00008 (19) |
| C06 | 0.0148 (2) | 0.0132 (2) | 0.0145 (2) | −0.00045 (17) | 0.00272 (17) | 0.00045 (17) |
| C07 | 0.0216 (3) | 0.0172 (2) | 0.0174 (3) | 0.0010 (2) | 0.0028 (2) | −0.0031 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O01—C07 | 1.2152 (10) | C03—C04 | 1.3941 (10) |
| O02—N01 | 1.2262 (9) | C03—H03 | 0.9500 |
| O03—N01 | 1.2271 (9) | C04—C05 | 1.3974 (9) |
| N01—C01 | 1.4711 (9) | C04—H04 | 0.9500 |

| | | | |
|---|---|---|---|
| C01—C06 | 1.3836 (9) | C05—C06 | 1.3992 (10) |
| C01—C02 | 1.3928 (9) | C05—C07 | 1.4797 (9) |
| C02—C03 | 1.3909 (11) | C06—H06 | 0.9500 |
| C02—H02 | 0.9500 | C07—H07 | 0.9500 |
| | | | |
| O03—N01—O02 | 123.79 (8) | C03—C04—C05 | 120.36 (6) |
| O03—N01—C01 | 118.29 (7) | C03—C04—H04 | 119.8 |
| O02—N01—C01 | 117.92 (6) | C05—C04—H04 | 119.8 |
| C06—C01—C02 | 123.15 (6) | C04—C05—C06 | 120.73 (6) |
| C06—C01—N01 | 118.48 (6) | C04—C05—C07 | 118.69 (6) |
| C02—C01—N01 | 118.36 (6) | C06—C05—C07 | 120.56 (6) |
| C03—C02—C01 | 118.65 (6) | C01—C06—C05 | 117.39 (6) |
| C03—C02—H02 | 120.7 | C01—C06—H06 | 121.3 |
| C01—C02—H02 | 120.7 | C05—C06—H06 | 121.3 |
| C02—C03—C04 | 119.72 (6) | O01—C07—C05 | 124.13 (7) |
| C02—C03—H03 | 120.1 | O01—C07—H07 | 117.9 |
| C04—C03—H03 | 120.1 | C05—C07—H07 | 117.9 |
| | | | |
| O03—N01—C01—C06 | 170.48 (8) | C03—C04—C05—C06 | −0.38 (10) |
| O02—N01—C01—C06 | −10.01 (10) | C03—C04—C05—C07 | 177.92 (7) |
| O03—N01—C01—C02 | −10.63 (11) | C02—C01—C06—C05 | 0.25 (10) |
| O02—N01—C01—C02 | 168.88 (7) | N01—C01—C06—C05 | 179.09 (6) |
| C06—C01—C02—C03 | −0.08 (11) | C04—C05—C06—C01 | −0.02 (9) |
| N01—C01—C02—C03 | −178.92 (7) | C07—C05—C06—C01 | −178.30 (6) |
| C01—C02—C03—C04 | −0.34 (11) | C04—C05—C07—O01 | −173.33 (8) |
| C02—C03—C04—C05 | 0.56 (11) | C06—C05—C07—O01 | 4.98 (12) |