

## 3-Nitrobenzonitrile

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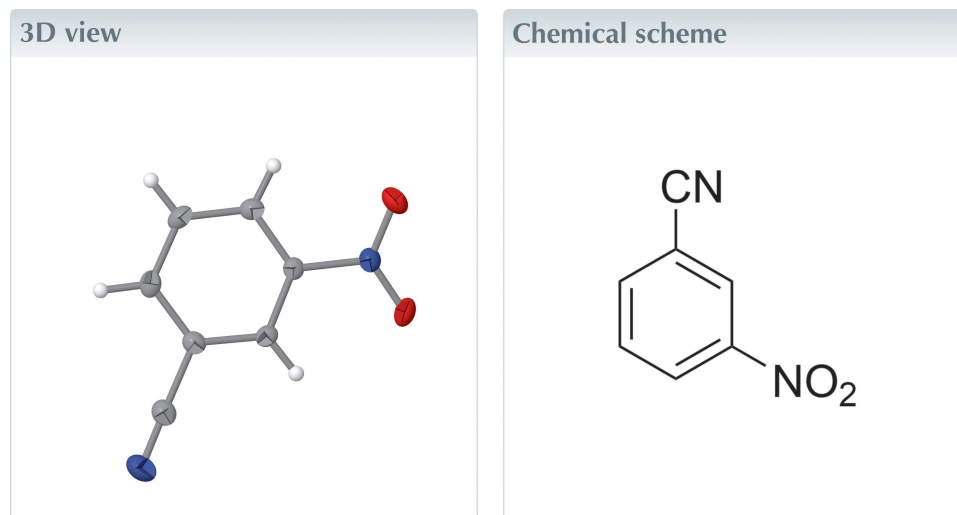
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**Keywords:** nitro; nitrile; benzonitrile; crystal structure.**CCDC reference:** 2295676**Structural data:** full structural data are available from iucrdata.iucr.org

The crystal structure of 3-nitrobenzonitrile,  $C_7H_4N_2O_2$ , was elucidated by low-temperature single-crystal X-ray diffraction. The compound crystallizes in the Sohncke space group  $P2_1$  and features two molecules in the unit cell. Aromatic  $\pi$ - $\pi$  stacking leads to stacks of molecules in the [100] direction. The absolute structure was established from anomalous dispersion.



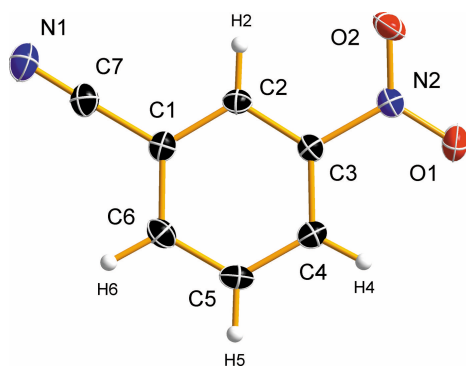
### Structure description

3-Nitrobenzonitrile crystallizes in the monoclinic Sohncke space group  $P2_1$  with one molecule in the asymmetric unit (Fig. 1). The nitro group is not coplanar with the benzene ring, but slightly tilted. The corresponding angle between the benzene ring and  $NO_2$  plane normals is  $11.22(6)^\circ$  with atom O1 located  $0.163(3)$  Å below and atom O2  $0.253(3)$  Å above the plane of the benzene ring.

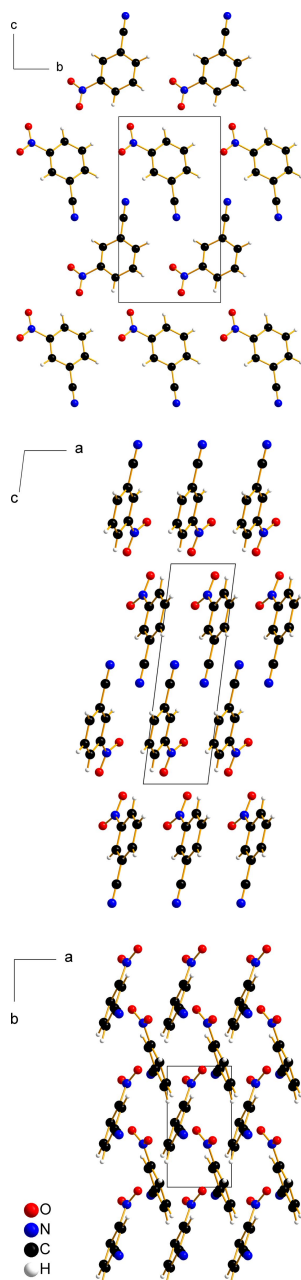
This tilt of the  $NO_2$  group is presumably the result of the crystal packing, which locks the orientation of the  $NO_2$  group. The corresponding non-coplanar orientation of the  $NO_2$  group induces the asymmetry of the molecule and, in turn, the chirality of the crystal. In solution, where the barriers for the rotation of the nitro group are usually low, for instance,  $19 \text{ kJ mol}^{-1}$  in nitrobenzene determined by gas-phase electron diffraction (Borisenko & Hargittai, 1996), the rotation is not hindered, and the molecule can readily adopt different conformations.

The C–C and C–H bonds of the benzene ring span the ranges  $1.3851(19)$ – $1.397(2)$  Å and  $0.91(3)$ – $0.96(2)$  Å, respectively. The substituents are bonded to the benzene ring by a C–N bond of  $1.4697(19)$  Å in the case of the nitro group and a C–C bond of  $1.447(2)$  Å in the case of the nitrile group. The observed N–O distances of the nitro group are essentially equal [ $1.2258(17)$  and  $1.2262(18)$  Å]. The length of the C $\equiv$ N triple bond in the nitrile group is  $1.141(2)$  Å. In the crystal (Fig. 2), the molecules are  $\pi$ -stacked along the shortest crystallographic axis,  $a$ , with an interplanar distance of  $3.3700(9)$  Å.

Of the three positional isomers of nitrobenzonitrile, only the crystal structure of 4-nitrobenzonitrile has been previously reported (Cambridge Structural Database



**Figure 1**  
The molecular structure of the title compound showing 50% displacement ellipsoids. Hydrogen atoms are depicted as spheres of arbitrary radius.



**Figure 2**  
Packing diagrams and the unit cell of the title compound viewed along [100] (top), [010] (middle) and [001] (bottom).

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	148.12
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	3.73339 (4), 6.97307 (5), 12.87327 (9)
$\beta$ (°)	97.1579 (8)
<i>V</i> (Å <sup>3</sup> )	332.52 (1)
<i>Z</i>	2
Radiation type	Cu <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.95
Crystal size (mm)	0.28 × 0.06 × 0.04
Data collection	
Diffractometer	XtaLAB Synergy-S, Dualflex, Eiger2 R CdTe 1M
Absorption correction	Gaussian ( <i>CrysAlis PRO</i> ; Rigaku OD, 2023)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.565, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	10190, 1360, 1353
<i>R<sub>int</sub></i>	0.025
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.629
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.024, 0.069, 1.09
No. of reflections	1360
No. of parameters	116
No. of restraints	1
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.17, -0.17
Absolute structure	Flack <i>x</i> determined using 611 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.02 (5)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *OLEX2.solve* (Dolomanov *et al.*, 2009), *SHELXL2019/3* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

refcode PNBZNT; Higashi & Osaki, 1977). It also crystallizes in the Sohncke space group *P*2<sub>1</sub> and the tilt angle of the nitro group out of the benzene ring plane (10.3°) is similar to the angle reported herein for the *meta* isomer [11.22 (6)°].

### Synthesis and crystallization

The title compound was obtained by decomposition of the corresponding diazonium salt in ethanol. The diazonium salt was synthesized by the previously published procedure (Mihelač *et al.*, 2021). *p*-Toluenesulfonic acid monohydrate (570.7 mg; 3 mmol) was dissolved in 15 mL of ethyl acetate and 2-amino-5-nitrobenzonitrile (489.3 mg; 3 mmol) was added to the solution. The dropwise addition of *tert*-butyl nitrite (1068  $\mu$ L, 9 mmol) resulted in the formation of a yellow solution, which was stirred for 5 minutes at room temperature. The yellow precipitate of 2-cyano-4-nitrobenzenediazonium tosylate was obtained by filtration and washed thoroughly with ethyl acetate. This solid was then dissolved in 10 mL of EtOH and stirred for 3 days at room temperature. 3-Nitrobenzonitrile was isolated by filtration as an off-white solid. Single crystals were grown from a concentrated ethanol solution at -20 °C. A crystal suitable for single-crystal X-ray

diffraction analysis was selected under a polarizing microscope and mounted on a MiTeGen Dual Thickness MicroLoop LD using Baysilone-Paste (Bayer-Silicone, mittelviskos).

### Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 1. The positions of the hydrogen atoms were freely refined, including their isotropic displacement parameter  $U$  (Cooper *et al.*, 2010). The absolute structure was established based on the anomalous dispersion effects [Flack  $x = 0.02$  (5); Hooft  $y = 0.05$  (3); Parsons *et al.* (2013); Hooft *et al.* (2008)].

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## full crystallographic data

*IUCrData* (2023). **8**, x230814 [<https://doi.org/10.1107/S2414314623008143>]

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*Crystal data*

$C_7H_4N_2O_2$

$M_r = 148.12$

Monoclinic,  $P2_1$

$a = 3.73339$  (4) Å

$b = 6.97307$  (5) Å

$c = 12.87327$  (9) Å

$\beta = 97.1579$  (8)°

$V = 332.52$  (1) Å<sup>3</sup>

$Z = 2$

$F(000) = 152$

$D_x = 1.479$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å

Cell parameters from 9014 reflections

$\theta = 3.5\text{--}75.7^\circ$

$\mu = 0.95$  mm<sup>-1</sup>

$T = 100$  K

Needle, colourless

0.28 × 0.06 × 0.04 mm

*Data collection*

XtaLAB Synergy-S, Dualflex, Eiger2 R CdTe

1M

diffractometer

Radiation source: micro-focus sealed X-ray

tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

Detector resolution: 13.3333 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: gaussian

(CrysAlisPro; Rigaku OD, 2023)

$T_{\min} = 0.565$ ,  $T_{\max} = 1.000$

10190 measured reflections

1360 independent reflections

1353 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 75.9^\circ$ ,  $\theta_{\min} = 3.5^\circ$

$h = -4 \rightarrow 4$

$k = -8 \rightarrow 8$

$l = -16 \rightarrow 16$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.069$

$S = 1.09$

1360 reflections

116 parameters

1 restraint

Primary atom site location: iterative

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.0377P]$

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

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

$\Delta\rho_{\max} = 0.17$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.17$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using

611 quotients  $[(I^-)-(I)]/[(I^+)+(I)]$  (Parsons *et al.*, 2013)

Absolute structure parameter: 0.02 (5)

*Special details*

**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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.2952 (4)	0.11413 (19)	0.94632 (9)	0.0316 (3)
O2	0.5449 (3)	0.03136 (17)	0.81028 (9)	0.0294 (3)
N1	0.2525 (4)	0.5665 (2)	0.45848 (11)	0.0323 (4)
N2	0.3724 (3)	0.14375 (19)	0.85792 (10)	0.0199 (3)
C1	0.1823 (4)	0.5195 (2)	0.65436 (11)	0.0192 (3)
C2	0.2895 (4)	0.3452 (2)	0.70086 (12)	0.0179 (3)
C3	0.2551 (4)	0.3250 (2)	0.80620 (11)	0.0171 (3)
C4	0.1192 (4)	0.4678 (2)	0.86529 (12)	0.0195 (3)
C5	0.0164 (4)	0.6403 (2)	0.81697 (12)	0.0215 (3)
C6	0.0461 (4)	0.6674 (2)	0.71128 (13)	0.0218 (3)
C7	0.2185 (4)	0.5471 (3)	0.54475 (12)	0.0236 (3)
H2	0.387 (6)	0.249 (4)	0.6661 (17)	0.031 (6)*
H4	0.108 (5)	0.445 (3)	0.9361 (16)	0.018 (5)*
H6	-0.009 (5)	0.790 (4)	0.6782 (15)	0.024 (5)*
H5	-0.071 (6)	0.738 (4)	0.8528 (17)	0.028 (5)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0389 (7)	0.0334 (7)	0.0230 (5)	0.0024 (5)	0.0053 (5)	0.0092 (5)
O2	0.0321 (6)	0.0201 (6)	0.0368 (6)	0.0076 (5)	0.0073 (5)	0.0018 (5)
N1	0.0338 (8)	0.0387 (9)	0.0252 (6)	-0.0019 (6)	0.0064 (6)	0.0066 (6)
N2	0.0181 (6)	0.0192 (6)	0.0220 (6)	-0.0006 (5)	0.0014 (4)	0.0019 (5)
C1	0.0167 (6)	0.0217 (8)	0.0192 (6)	-0.0029 (5)	0.0016 (5)	0.0008 (6)
C2	0.0151 (7)	0.0184 (7)	0.0206 (6)	-0.0003 (5)	0.0034 (5)	-0.0018 (6)
C3	0.0148 (6)	0.0165 (7)	0.0199 (6)	-0.0017 (5)	0.0018 (5)	0.0006 (5)
C4	0.0165 (7)	0.0231 (7)	0.0190 (7)	-0.0010 (6)	0.0021 (5)	-0.0023 (6)
C5	0.0183 (7)	0.0202 (7)	0.0258 (7)	0.0016 (6)	0.0020 (5)	-0.0070 (6)
C6	0.0181 (7)	0.0190 (8)	0.0275 (7)	0.0005 (6)	-0.0004 (5)	0.0013 (6)
C7	0.0214 (7)	0.0246 (7)	0.0247 (7)	-0.0022 (6)	0.0027 (6)	0.0029 (6)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—N2	1.2258 (17)	C2—H2	0.91 (3)
O2—N2	1.2262 (18)	C3—C4	1.387 (2)
N1—C7	1.141 (2)	C4—C5	1.386 (2)
N2—C3	1.4697 (19)	C4—H4	0.93 (2)
C1—C2	1.392 (2)	C5—C6	1.392 (2)
C1—C6	1.397 (2)	C5—H5	0.91 (2)
C1—C7	1.447 (2)	C6—H6	0.96 (2)
C2—C3	1.3851 (19)		
O1—N2—O2	123.75 (13)	C4—C3—N2	118.53 (12)
O1—N2—C3	118.31 (12)	C3—C4—H4	118.7 (12)
O2—N2—C3	117.93 (12)	C5—C4—C3	118.46 (13)

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C2—C1—C6	121.55 (14)	C5—C4—H4	122.8 (12)
C2—C1—C7	118.61 (14)	C4—C5—C6	120.34 (14)
C6—C1—C7	119.84 (14)	C4—C5—H5	121.5 (14)
C1—C2—H2	123.1 (14)	C6—C5—H5	118.1 (14)
C3—C2—C1	116.93 (13)	C1—C6—H6	119.6 (12)
C3—C2—H2	119.9 (14)	C5—C6—C1	119.42 (14)
C2—C3—N2	118.16 (12)	C5—C6—H6	120.9 (12)
C2—C3—C4	123.30 (13)	N1—C7—C1	178.69 (17)
O1—N2—C3—C2	-169.59 (13)	C2—C1—C6—C5	0.0 (2)
O1—N2—C3—C4	11.0 (2)	C2—C3—C4—C5	-0.8 (2)
O2—N2—C3—C2	11.01 (19)	C3—C4—C5—C6	0.7 (2)
O2—N2—C3—C4	-168.36 (13)	C4—C5—C6—C1	-0.3 (2)
N2—C3—C4—C5	178.55 (12)	C6—C1—C2—C3	0.0 (2)
C1—C2—C3—N2	-178.92 (13)	C7—C1—C2—C3	179.18 (13)
C1—C2—C3—C4	0.4 (2)	C7—C1—C6—C5	-179.21 (13)

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