

N-Benzyl-3-nitroaniline

Vladimir Stilinović^{a*} and Tomislav Portada^b^aLaboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102 A, HR-10000 Zagreb, Croatia, and^bDepartment of Organic Chemistry and Biochemistry, Ruder Bošković Institute, PO Box 180, HR-10002 Zagreb, Croatia

Correspondence e-mail: vstilinovic@chem.pmf.hr

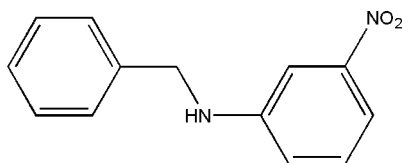
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.034; wR factor = 0.081; data-to-parameter ratio = 8.1.

The molecule of the title compound, $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$, has a bent conformation with a torsion angle about the central C–N bond of $72.55(19)^\circ$. In the crystal, the molecules are connected *via* classical N–H \cdots O and non-classical C–H \cdots O hydrogen bonds into chains along $[10\bar{1}]$. The dihedral angle between the ring planes is $86.0(6)^\circ$.

Related literature

For the synthesis of the title compound, see: Magyarfalvi (2008). For related structures, see: Betz *et al.* (2011); Iwasaki *et al.* (1988).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$ $M_r = 228.25$ Monoclinic, $P2_1$ $a = 5.3359(2)$ Å $b = 19.2285(6)$ Å $c = 5.6017(2)$ Å $\beta = 97.334(3)^\circ$ $V = 570.04(3)$ Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 0.09$ mm⁻¹ $T = 295$ K $0.41 \times 0.29 \times 0.23$ mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer

7072 measured reflections

1280 independent reflections

1093 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.017$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.081$ $S = 1.01$

1280 reflections

158 parameters

3 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.14$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}^{\text{i}}$	0.84 (2)	2.44 (2)	3.263 (2)	166 (2)
$\text{C6}-\text{H6}\cdots\text{O2}^{\text{i}}$	0.93	2.45	3.364 (2)	169
$\text{C13}-\text{H13}\cdots\text{O1}^{\text{ii}}$	0.93	2.67	3.293 (2)	125
$\text{C7}-\text{H7A}\cdots\text{O1}^{\text{iii}}$	0.97	2.61	3.318 (2)	130

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program used to solve structure: *SHELXS97* (Sheldrick, 2008); program used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997), *POV-RAY* (Cason *et al.*, 2002) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PLATON* (Spek, 2009) and *PARST* (Nardelli, 1995).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2302).

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supplementary materials

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N-Benzyl-3-nitroaniline

V. Stilinovic and T. Portada

Comment

The synthesis of the title compound was a part of Preparatory problems for the 40th International Chemistry Olympiad (Magyarfalvi, 2008). It was prepared and crystalized as a part of the laboratory work with high-school students.

The *N*-methyl-3-nitroaniline system is almost perfectly planar (the mean plane of the the phenyl ring is at an angle of 1.5 (2)° with the mean plane of the angle nitro group, and 1.4 (2)° with the mean plane of the central C1—N1—C7. The phenyl substituent is at an angle of 86.0 (2)° to the rest of the molecule. The C1—N1—C7—C8 torsion angle is 72.55 (19)°. This conforamtion is similar to thet reported by Betz *et al.* (2011) for the unsubstituted *N*-benzylaniline.

The molecules are connected into chains along the [1 0 $\bar{1}$] direction by N1—H1 \cdots O1ⁱ classical hydrogen bonds of (N1 \cdots O1ⁱ = 3.263 (2)Å), which are further fortified by non-classical one C6—H6 \cdots O2ⁱ with contact C6 \cdots O2ⁱⁱ of 3.364 (2)Å. Interestingly, in a similar compound, *N*-benzyl-4-nitroaniline (Iwasaki *et al.*, 1988), the N—H \cdots O bonding is entirely absent, which demonstrates the effect of changing the position of the nitro group on tha supramolecular aggregation.

The chains are further interconnected *via* long non-classical C—H \cdots O (C13—H13 \cdots O1ⁱⁱ of 3.293 (2)Å and C7—H7A \cdots O1ⁱⁱⁱ of 3.318 (1)Å) contacts into layers perpendicular to the *b* axis.

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

Experimental

The title compound was prepared using a slightly modified procedure (Magyarfalvi, 2008) and isolated in a form of yellow crystalline powder. A sample of approximately 100 mg of the compound was dissolved in approximately 10 ml of hot ethanol. The solution was left to cool to room temperature, filtered, and the filtrate was left to crystallize by slow evaporation. The single crystalls suitable for X-ray study were obtained after aproximatelly 4 days.

Refinement

The amine hydrogen atom was locates from the electron fiffERENCE map and isotropical refined. All H atoms bonded to carbon atoms were placed geometrically and included in the riding-model approximation with C—H distances of 0.93Å for aryl and 0.97Å for CH₂. In the refinement these H atoms were included with $U_{iso} = 1.2U_{eq}(C)$.

Since there are no heavy atoms in the structure, the Friedel pairs (1186) were merged for the final refinement.

Figures

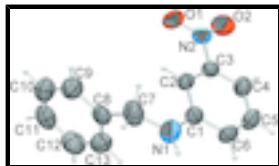


Fig. 1. The molecular structure of title compound with the atom labeling scheme. Displacement ellipsoids are shown at 30% probability level. Hydrogen atoms are shown as a spheres of arbitrary radius.

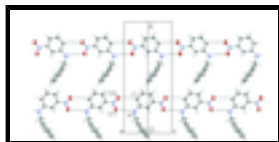


Fig. 2. Chains in the structure of the title compound viewed along the $[1\ 0\ \bar{1}]$ direction. Hydrogen bonds are indicated by dashed lines.

N-benzyl-3-nitroaniline

Crystal data

$C_{13}H_{12}N_2O_2$	$Z = 2$
$M_r = 228.25$	$F(000) = 240$
Monoclinic, $P2_1$	$D_x = 1.33\text{ Mg m}^{-3}$
Hall symbol: $P\ 2y_b$	Mo $K\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$
$a = 5.3359\ (2)\text{ \AA}$	$\theta = 4.6\text{--}54.0^\circ$
$b = 19.2285\ (6)\text{ \AA}$	$\mu = 0.09\text{ mm}^{-1}$
$c = 5.6017\ (2)\text{ \AA}$	$T = 295\text{ K}$
$\beta = 97.334\ (3)^\circ$	Plate, yellow
$V = 570.04\ (3)\text{ \AA}^3$	$0.41 \times 0.29 \times 0.23\text{ mm}$

Data collection

Oxford Diffraction Xcalibur CCD diffractometer	1093 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube graphite	$R_{\text{int}} = 0.017$
φ and ω scans	$\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 3.8^\circ$
7072 measured reflections	$h = -6 \rightarrow 6$
1280 independent reflections	$k = -24 \rightarrow 24$
	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.034$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.081$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2]$
	where $P = (F_o^2 + 2F_c^2)/3$

1280 reflections	$(\Delta/\sigma)_{\max} = 0.003$
158 parameters	$\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$
3 restraints	$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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	$U_{\text{iso}}^*/U_{\text{eq}}$
H1	0.844 (5)	0.2074 (13)	0.076 (5)	0.063 (6)*
C3	0.2527 (3)	0.28407 (9)	0.4595 (3)	0.0412 (4)
C2	0.4146 (3)	0.23191 (9)	0.4090 (3)	0.0423 (4)
H2	0.4181	0.1896	0.4896	0.051*
C1	0.5737 (3)	0.24414 (9)	0.2335 (3)	0.0454 (4)
N2	0.0876 (3)	0.27154 (8)	0.6441 (3)	0.0489 (4)
C6	0.5584 (3)	0.30889 (10)	0.1187 (4)	0.0516 (4)
H6	0.6626	0.318	0.0013	0.062*
C4	0.2364 (4)	0.34794 (9)	0.3472 (4)	0.0528 (5)
H4	0.1244	0.382	0.3858	0.063*
N1	0.7446 (4)	0.19560 (9)	0.1759 (4)	0.0663 (5)
O2	-0.0522 (3)	0.31801 (9)	0.6928 (3)	0.0763 (5)
O1	0.0942 (3)	0.21462 (8)	0.7433 (3)	0.0645 (4)
C5	0.3954 (4)	0.35886 (10)	0.1740 (4)	0.0579 (5)
H5	0.3905	0.4013	0.0939	0.069*
C8	0.5655 (3)	0.07735 (9)	0.2164 (3)	0.0496 (4)
C7	0.7768 (4)	0.12849 (11)	0.2881 (5)	0.0616 (5)
H7A	0.7937	0.1347	0.4612	0.074*
H7B	0.9335	0.1085	0.2492	0.074*
C11	0.1852 (4)	-0.01992 (12)	0.0930 (5)	0.0705 (6)
H11	0.0576	-0.0523	0.0518	0.085*
C13	0.4114 (4)	0.08153 (12)	-0.0021 (3)	0.0666 (6)
H13	0.4348	0.1172	-0.1093	0.08*
C10	0.3354 (5)	-0.02457 (12)	0.3060 (5)	0.0739 (6)
H10	0.3118	-0.0606	0.4115	0.089*
C9	0.5222 (4)	0.02354 (12)	0.3673 (4)	0.0651 (5)
H9	0.6224	0.0197	0.5152	0.078*
C12	0.2233 (5)	0.03297 (16)	-0.0607 (4)	0.0764 (6)
H12	0.1207	0.0363	-0.2075	0.092*

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Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C3	0.0386 (7)	0.0460 (9)	0.0405 (8)	-0.0039 (7)	0.0116 (6)	-0.0028 (6)
C2	0.0431 (8)	0.0405 (8)	0.0456 (9)	-0.0033 (7)	0.0142 (7)	0.0021 (7)
C1	0.0417 (8)	0.0458 (9)	0.0515 (10)	-0.0066 (7)	0.0164 (7)	-0.0044 (7)
N2	0.0472 (8)	0.0573 (9)	0.0444 (8)	-0.0030 (7)	0.0150 (6)	-0.0023 (7)
C6	0.0508 (10)	0.0569 (10)	0.0510 (10)	-0.0126 (9)	0.0211 (8)	0.0032 (8)
C4	0.0524 (10)	0.0441 (10)	0.0643 (12)	0.0042 (8)	0.0163 (9)	0.0017 (8)
N1	0.0602 (10)	0.0540 (10)	0.0943 (13)	0.0002 (8)	0.0470 (10)	-0.0012 (9)
O2	0.0773 (10)	0.0795 (11)	0.0811 (11)	0.0173 (9)	0.0447 (9)	-0.0031 (8)
O1	0.0718 (9)	0.0671 (9)	0.0601 (8)	-0.0025 (7)	0.0301 (7)	0.0108 (7)
C5	0.0603 (11)	0.0484 (11)	0.0671 (12)	-0.0028 (9)	0.0164 (10)	0.0147 (8)
C8	0.0481 (9)	0.0457 (10)	0.0577 (10)	0.0089 (8)	0.0171 (8)	-0.0069 (7)
C7	0.0468 (10)	0.0517 (10)	0.0892 (16)	0.0051 (8)	0.0201 (10)	-0.0067 (10)
C11	0.0620 (12)	0.0589 (12)	0.0913 (17)	-0.0032 (10)	0.0128 (12)	-0.0219 (9)
C13	0.0778 (14)	0.0645 (12)	0.0581 (13)	0.0059 (11)	0.0112 (11)	0.0051 (9)
C10	0.0851 (16)	0.0572 (12)	0.0803 (16)	-0.0117 (12)	0.0134 (13)	0.0030 (11)
C9	0.0722 (12)	0.0600 (12)	0.0617 (12)	-0.0029 (11)	0.0030 (10)	0.0041 (10)
C12	0.0778 (14)	0.0816 (14)	0.0653 (13)	0.0054 (13)	-0.0079 (11)	-0.0111 (10)

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

C3—C2	1.376 (2)	C5—H5	0.93
C3—C4	1.378 (2)	C8—C9	1.374 (3)
C3—N2	1.461 (2)	C8—C13	1.3868 (17)
C2—C1	1.398 (2)	C8—C7	1.511 (3)
C2—H2	0.93	C7—H7A	0.97
C1—N1	1.372 (2)	C7—H7B	0.97
C1—C6	1.399 (3)	C11—C10	1.353 (4)
N2—O2	1.217 (2)	C11—C12	1.364 (4)
N2—O1	1.226 (2)	C11—H11	0.93
C6—C5	1.358 (3)	C13—C12	1.379 (4)
C6—H6	0.93	C13—H13	0.93
C4—C5	1.384 (3)	C10—C9	1.371 (3)
C4—H4	0.93	C10—H10	0.93
N1—C7	1.436 (3)	C9—H9	0.93
N1—H1	0.85 (3)	C12—H12	0.93
C2—C3—C4	124.08 (15)	C9—C8—C13	117.32 (18)
C2—C3—N2	118.44 (14)	C9—C8—C7	120.31 (17)
C4—C3—N2	117.48 (15)	C13—C8—C7	122.36 (19)
C3—C2—C1	118.37 (15)	N1—C7—C8	115.13 (19)
C3—C2—H2	120.8	N1—C7—H7A	108.5
C1—C2—H2	120.8	C8—C7—H7A	108.5
N1—C1—C2	122.14 (17)	N1—C7—H7B	108.5
N1—C1—C6	119.94 (16)	C8—C7—H7B	108.5
C2—C1—C6	117.90 (16)	H7A—C7—H7B	107.5

O2—N2—O1	122.47 (15)	C10—C11—C12	119.1 (2)
O2—N2—C3	118.66 (16)	C10—C11—H11	120.4
O1—N2—C3	118.87 (14)	C12—C11—H11	120.4
C5—C6—C1	121.74 (16)	C12—C13—C8	120.2 (2)
C5—C6—H6	119.1	C12—C13—H13	119.9
C1—C6—H6	119.1	C8—C13—H13	119.9
C3—C4—C5	116.54 (16)	C11—C10—C9	120.4 (2)
C3—C4—H4	121.7	C11—C10—H10	119.8
C5—C4—H4	121.7	C9—C10—H10	119.8
C1—N1—C7	123.70 (18)	C10—C9—C8	121.9 (2)
C1—N1—H1	117.6 (17)	C10—C9—H9	119.1
C7—N1—H1	118.6 (17)	C8—C9—H9	119.1
C6—C5—C4	121.36 (17)	C11—C12—C13	121.1 (2)
C6—C5—H5	119.3	C11—C12—H12	119.4
C4—C5—H5	119.3	C13—C12—H12	119.4

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

<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 \cdots O1 ⁱ	0.84 (2)	2.44 (2)	3.263 (2)	166 (2)
C6—H6 \cdots O2 ⁱ	0.93	2.45	3.364 (2)	169
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Fig. 1

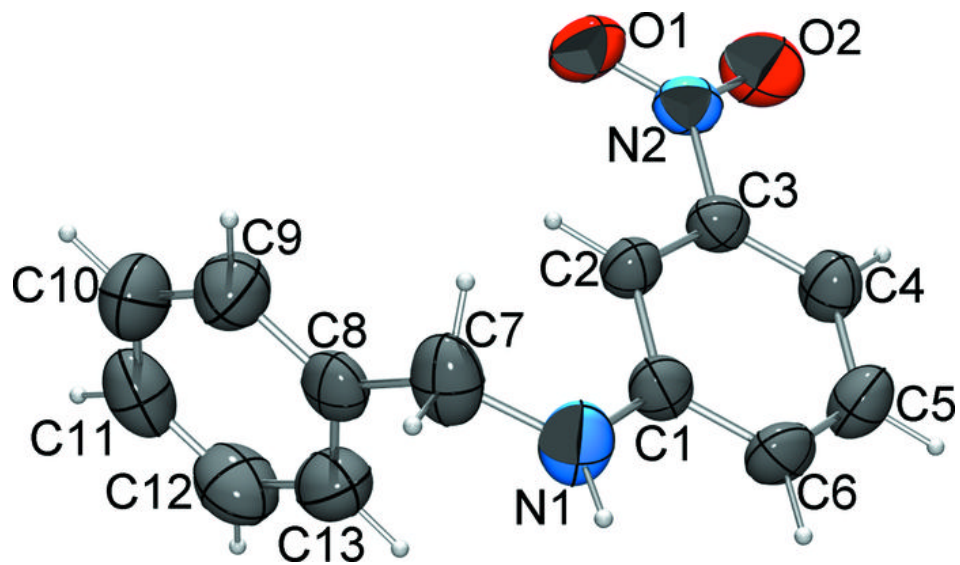


Fig. 2

