



organic compounds

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3,4-Diaminobenzonitrile

David K. Geiger* and Dylan E. Parsons

Department of Chemistry, State University of New York-College at Geneseo, 1
College Circle, Geneseo, NY 14454, USACorrespondence e-mail: geiger@geneseo.edu

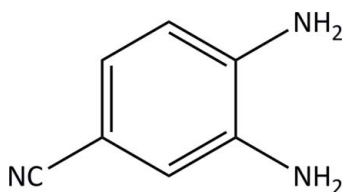
Received 18 February 2013; accepted 22 February 2013

Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å;
R factor = 0.052; wR factor = 0.128; data-to-parameter ratio = 11.1.

The non-H atoms in the structure of the title molecule, $\text{C}_7\text{H}_7\text{N}_3$, are almost coplanar (r.m.s. deviation = 0.018 Å). The two amine groups each donate two and accept one weak $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds. $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonding between the amine and nitrile groups results in chains parallel to [101] in the crystal structure. The chains are cross-linked by $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds between amine groups, giving rise to an infinite three-dimensional network.

Related literature

For the crystal structures of related compounds, see: Czapik & Gdaniec (2010); Stålhandske (1981).



Experimental

Crystal data

 $\text{C}_7\text{H}_7\text{N}_3$
 $M_r = 133.16$
Monoclinic, $P2_1/c$
 $a = 8.858$ (3) Å
 $b = 10.536$ (4) Å
 $c = 8.160$ (3) Å
 $\beta = 116.213$ (12)° $V = 683.2$ (4) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 200$ K
 $0.50 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART X2S CCD
diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2010)
 $T_{\min} = 0.85$, $T_{\max} = 0.99$ 2149 measured reflections
1188 independent reflections
662 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.128$
 $S = 0.96$
1188 reflections
107 parametersH atoms treated by a mixture of
independent and constrained
refinement
 $\Delta\rho_{\max} = 0.18$ e Å⁻³
 $\Delta\rho_{\min} = -0.19$ e Å⁻³**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{N2}^{\text{i}}$	0.89 (3)	2.37 (3)	3.251 (4)	168 (3)
$\text{N1}-\text{H1B}\cdots\text{N3}^{\text{ii}}$	0.91 (3)	2.31 (3)	3.147 (4)	154 (3)
$\text{N2}-\text{H2A}\cdots\text{N1}^{\text{iii}}$	0.90 (3)	2.36 (3)	3.246 (4)	173 (2)
$\text{N2}-\text{H2B}\cdots\text{N3}^{\text{ii}}$	0.93 (3)	2.42 (3)	3.303 (4)	159 (3)

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

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XSELL* (Bruker, 2010) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

This work was supported by a Congressionally directed grant from the US Department of Education (grant No. P116Z100020) for the X-ray diffractometer

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QK2053).

References

- Bruker (2010). *APEX2*, *SAINT*, *SADABS* and *XSELL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Czapik, A. & Gdaniec, M. (2010). *Acta Cryst.* **C66**, o198–o201.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Stålhandske, C. (1981). *Cryst. Struct. Commun.* **10**, 1081–1086.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2013). E69, o452 [doi:10.1107/S1600536813005151]

3,4-Diaminobenzonitrile

David K. Geiger and Dylan E. Parsons

S1. Comment

Single crystals of the title compound were obtained during its purification by recrystallization for use in the synthesis of an organometallic complex. Figure 1 shows a view of the title molecule with the atom numbering scheme. The non-hydrogen atoms are planar with a r. m. s. deviation of 0.018 Å. The maximum deviation is for C1, which is 0.034 (2) Å out of the plane. The benzene ring is planar with a maximum deviation of 0.008 (2) Å for C4. The amine nitrogens are decidedly pyramidal with H-N-H angles of 113 (3)° and 112 (2)° for N1 and N2, respectively. N1 and N2 are 0.056 (4) and 0.073 (4) Å, respectively, below the benzene plane. All four of the hydrogen atoms of the amine groups are on the opposite side of the benzene plane from the amine nitrogen atoms. The nitrile group carbon and nitrogen atoms are 0.046 (4) and 0.086 (5) Å, respectively, out of the benzene plane and are on the opposite side as the amine nitrogens. The nitrile is linear (C4-C7-N = 179.2 (3)°).

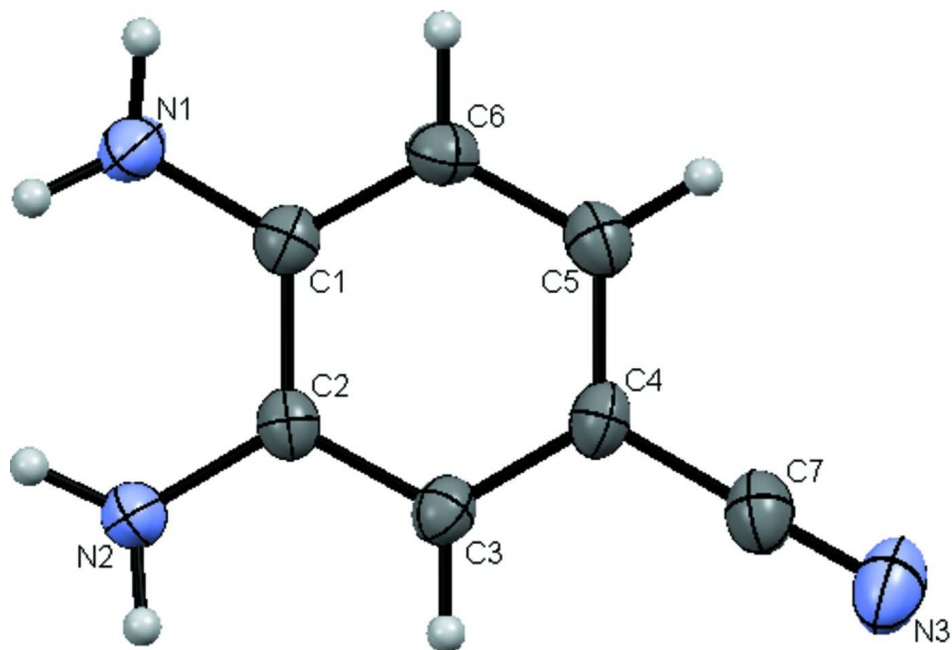
There are two known crystalline forms of 1,2-diaminobenzene (Stålhandske, 1981; Czapik & Gdaniec, 2010). In both forms, one of the N-H bonds of each amine group is coplanar with the benzene ring and an intramolecular N-H...N interaction is exhibited. Intermolecular hydrogen bonding results in layers that are joined by additional hydrogen-bonding interactions. The two forms are isostructural in two dimensions, but differ in the stacking of the layers (Czapik & Gdaniec, 2010). Figure 2 shows the hydrogen-bonding network exhibited by the title compound. In contrast to 1,2-diaminobenzene, no intramolecular hydrogen-bonding is observed. Parallel chains of molecules with an interplanar spacing of 3.32 Å are formed by hydrogen-bonds involving one hydrogen atom from each of the amines and the nitrile group on adjacent molecules. The chains run parallel to [101] and are crosslinked by hydrogen bonds between amine groups.

S2. Experimental

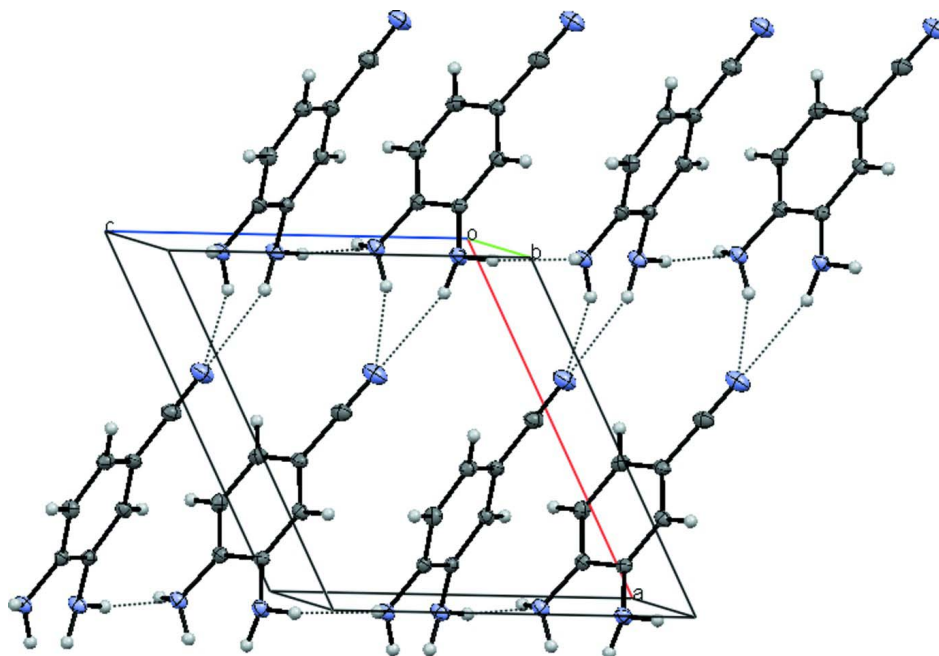
The compound was obtained commercially (Sigma-Aldrich). Single crystals were grown by slow evaporation of an ethanolic solution.

S3. Refinement

The H atoms bonded to carbon were refined using a riding model with C—H = 0.95 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$. The coordinates and isotropic thermal parameters of the amine H atoms were refined freely.

**Figure 1**

Perspective view of the title molecule. Displacement ellipsoids of the nonhydrogen atoms are drawn at the 50% probability level.

**Figure 2**

A view of the unit cell showing the chains parallel to $[101]$ resulting from H-bonding between amine and nitrile groups and the cross-linking H-bonds between amine groups. Displacement ellipsoids of the nonhydrogen atoms are drawn at the 25% probability level.

3,4-Diaminobenzonitrile

*Crystal data*C₇H₇N₃ $M_r = 133.16$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 8.858 (3) \text{ \AA}$ $b = 10.536 (4) \text{ \AA}$ $c = 8.160 (3) \text{ \AA}$ $\beta = 116.213 (12)^\circ$ $V = 683.2 (4) \text{ \AA}^3$ $Z = 4$ $F(000) = 280$ $D_x = 1.294 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 516 reflections

 $\theta = 2.6\text{--}21.2^\circ$ $\mu = 0.08 \text{ mm}^{-1}$ $T = 200 \text{ K}$

Prism, colourless

 $0.50 \times 0.20 \times 0.10 \text{ mm}$ *Data collection*

Bruker SMART X2S CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.33 pixels mm^{-1} ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2010)

 $T_{\min} = 0.85$, $T_{\max} = 0.99$

2149 measured reflections

1188 independent reflections

662 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.039$ $\theta_{\max} = 25.2^\circ$, $\theta_{\min} = 3.2^\circ$ $h = -10 \rightarrow 10$ $k = -12 \rightarrow 11$ $l = -5 \rightarrow 9$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.052$ $wR(F^2) = 0.128$ $S = 0.96$

1188 reflections

107 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

 $w = 1/[\sigma^2(F_o^2) + (0.0526P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.18 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.19 \text{ e \AA}^{-3}$ *Special details*

Experimental. 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 $F^2 > 2\sigma(F^2)$ 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.

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	1.0289 (3)	0.4587 (3)	0.7729 (3)	0.0317 (7)
H1A	1.025 (3)	0.538 (3)	0.809 (4)	0.053 (10)*
H1B	1.135 (4)	0.433 (3)	0.798 (4)	0.063 (11)*
N3	0.3764 (3)	0.3161 (2)	−0.0415 (3)	0.0495 (8)
N2	1.0370 (3)	0.2330 (2)	0.5881 (3)	0.0327 (7)
H2A	1.044 (3)	0.180 (3)	0.507 (4)	0.035 (8)*
H2B	1.142 (4)	0.264 (3)	0.670 (4)	0.068 (11)*
C1	0.8972 (3)	0.4302 (2)	0.6030 (3)	0.0259 (7)
C2	0.9008 (3)	0.3168 (2)	0.5098 (3)	0.0253 (7)
C3	0.7650 (3)	0.2879 (2)	0.3464 (3)	0.0276 (7)
H3	0.7664	0.2122	0.2838	0.033*
C4	0.6251 (3)	0.3686 (3)	0.2712 (3)	0.0298 (7)
C7	0.4877 (3)	0.3387 (3)	0.0985 (4)	0.0366 (8)
C5	0.6212 (3)	0.4783 (3)	0.3641 (3)	0.0323 (8)
H5	0.5262	0.5329	0.3150	0.039*
C6	0.7562 (3)	0.5071 (3)	0.5275 (3)	0.0305 (7)
H6	0.7525	0.5820	0.5905	0.037*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0325 (16)	0.0300 (17)	0.0274 (13)	−0.0019 (12)	0.0086 (13)	−0.0039 (12)
N3	0.0410 (15)	0.0481 (18)	0.0418 (15)	−0.0042 (13)	0.0022 (14)	0.0047 (13)
N2	0.0311 (14)	0.0309 (15)	0.0300 (13)	0.0049 (12)	0.0080 (12)	−0.0032 (12)
C1	0.0271 (15)	0.0256 (16)	0.0251 (14)	−0.0025 (12)	0.0115 (13)	0.0030 (12)
C2	0.0233 (14)	0.0259 (16)	0.0268 (14)	−0.0006 (12)	0.0111 (13)	0.0047 (13)
C3	0.0278 (14)	0.0264 (17)	0.0258 (14)	−0.0028 (12)	0.0092 (13)	0.0008 (12)
C4	0.0237 (14)	0.0338 (18)	0.0277 (15)	−0.0037 (13)	0.0074 (13)	0.0011 (13)
C7	0.0305 (16)	0.036 (2)	0.0387 (17)	0.0015 (13)	0.0108 (16)	0.0062 (14)
C5	0.0272 (15)	0.0324 (19)	0.0366 (16)	0.0020 (13)	0.0134 (14)	0.0036 (13)
C6	0.0345 (16)	0.0252 (16)	0.0327 (16)	0.0016 (13)	0.0156 (14)	−0.0015 (12)

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

N1—C1	1.395 (3)	C2—C3	1.379 (3)
N1—H1A	0.89 (3)	C3—C4	1.401 (3)
N1—H1B	0.91 (3)	C3—H3	0.9500
N3—C7	1.157 (3)	C4—C5	1.392 (4)
N2—C2	1.401 (3)	C4—C7	1.432 (3)
N2—H2A	0.90 (3)	C5—C6	1.375 (3)
N2—H2B	0.93 (3)	C5—H5	0.9500
C1—C6	1.384 (3)	C6—H6	0.9500
C1—C2	1.424 (3)		
C1—N1—H1A	113.1 (17)	C2—C3—H3	119.5

C1—N1—H1B	119 (2)	C4—C3—H3	119.5
H1A—N1—H1B	113 (3)	C5—C4—C3	119.7 (2)
C2—N2—H2A	112.9 (16)	C5—C4—C7	120.2 (2)
C2—N2—H2B	119 (2)	C3—C4—C7	120.0 (2)
H2A—N2—H2B	112 (2)	N3—C7—C4	179.2 (3)
C6—C1—N1	120.7 (3)	C6—C5—C4	119.4 (2)
C6—C1—C2	118.8 (2)	C6—C5—H5	120.3
N1—C1—C2	120.4 (2)	C4—C5—H5	120.3
C3—C2—N2	120.6 (2)	C5—C6—C1	122.0 (3)
C3—C2—C1	119.1 (2)	C5—C6—H6	119.0
N2—C2—C1	120.2 (2)	C1—C6—H6	119.0
C2—C3—C4	121.0 (2)		

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1A...N2 ⁱ	0.89 (3)	2.37 (3)	3.251 (4)	168 (3)
N1—H1B...N3 ⁱⁱ	0.91 (3)	2.31 (3)	3.147 (4)	154 (3)
N2—H2A...N1 ⁱⁱⁱ	0.90 (3)	2.36 (3)	3.246 (4)	173 (2)
N2—H2B...N3 ⁱⁱ	0.93 (3)	2.42 (3)	3.303 (4)	159 (3)

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