2,2'-[1,2-Phenylenebis(azanediyl)]di-acetonitrile

Augusto Rivera,[a]* Leonardo Jiménez-Cruz,[a] Mauricio Maldonado,[a] Monika Kučeráková[b] and Michal Dušek[b]

[a]Universidad Nacional de Colombia, Sede Bogotá, Facultad de Ciencias, Departamento de Química, Cra 30 No. 45-03, Bogotá, Código Postal 111321, Colombia, and [b]Institute of Physics ASCR, v.v.i., Na Slovance 2, 182 21 Praha 8, Czech Republic

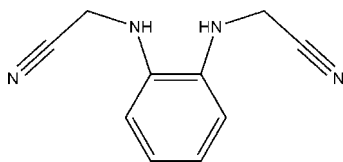Correspondence e-mail: ariverau@unal.edu.co

The title compound, $C_{10}H_{10}N_4$, shows chemical but not crystallographic C_2 symmetry. The two cyanomethyl groups are located in an *anti* position with respect to the aromatic ring. In the crystal, molecules form parallel ladder-like tapes linked through two N—H···N hydrogen bonds. Further weak intramolecular N—H···N hydrogen bonding is responsible for the elongation of one of the $C_{aromatic}$—N bonds.

Related literature

For general background to the title compound, see: Rivera *et al.* (2010). For related structures, see: Rivera *et al.* (2010, 2011); Silversides *et al.* (2006).

Experimental

Crystal data

$C_{10}H_{10}N_4$	$V = 1844.87 (14)$ Å^3
$M_r = 186.2$	$Z = 8$
Orthorhombic, $Pbca$	Cu $K\alpha$ radiation
$a = 7.6404 (3)$ Å	$\mu = 0.69$ mm^{-1}
$b = 15.1703 (7)$ Å	$T = 120$ K
$c = 15.9168 (7)$ Å	$0.17 \times 0.15 \times 0.10$ mm

Data collection

Agilent Xcalibur (Atlas, Gemini ultra) diffractometer	9893 measured reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)	1641 independent reflections
$T_{min} = 0.68$, $T_{max} = 1$	1359 reflections with $I > 3\sigma(I)$
	$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.104$	
$S = 1.55$	
1641 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
133 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N4[i]	0.935 (18)	2.202 (19)	3.0946 (19)	159.2 (16)
N2—H2···N1	0.889 (18)	2.427 (18)	2.7524 (18)	102.0 (13)
N2—H2···N1[ii]	0.889 (18)	2.494 (17)	3.2536 (16)	143.8 (15)

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

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006*.

References

Agilent (2012). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.
Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.
Petříček, V., Dusek, M. & Palatinus, L. (2006). *JANA2006*. Institute of Physics, Praha, Czech Republic.
Rivera, A., Maldonado, M., Casas, J. L., Dušek, M. & Fejfarová, K. (2011). *Acta Cryst.* E**67**, o990.
Rivera, A., Maldonado, M., Ríos-Motta, J., Navarro, M. A. & González-Salas, D. (2010). *Tetrahedron Lett.* **51**, 102–104.
Silversides, J. D., Sparke, A. E. & Archibald, S. J. (2006). *Acta Cryst.* E**62**, o5944–o5946.

supporting information

2,2′-[1,2-Phenylenebis(azanediyl)]diacetonitrile

Augusto Rivera, Leonardo Jiménez-Cruz, Mauricio Maldonado, Monika Kučeráková and Michal Dušek

S1. Comment

The reaction of N^1,N^2-bis((1*H*-benzotriazol-1-yl)methyl)benzene-1,2-diamine with potassium cyanide in DMSO at room temperature gives the title compound in high yield. The two cyanomethyl groups are both *anti* with respect to the planar aromatic ring, no doubt in order to favour intermolecular N—H···N interactions. Intermolecular amine-to-amine and amine-to-cyano hydrogen bonding interactions established "ladder-like" parallel tapes in the crystalline solid (Fig. 2).

  The molecular structure and atom numbering scheme for the title compound are shown in Fig. 1. Its X-ray structure confirms the presence of intramolecular hydrogen bond between the amino groups [N–H, 2.426 (18) Å]. Furthermore the observed C3—N1 bond length [1.4357 (17) Å] is considerably elongated in relation to related structures [1.404 (3) Å] (Rivera *et al.*, 2010), [1.3961 (18) Å] (Silversides *et al.*, 2006) and is longer than the C4—N2 bond [1.4016 (16) Å]. Thus, these results indicate that the intramolecular interaction is responsible for the C3—N1 bond elongation. This is confirmed by the N1—C7 bond length [1.4648 (18) Å] that is longer than N2—C5 bond [1.4457 (19) Å]. Besides, the hybridization of both N1 and N2 atoms are slightly different. In fact, N1 has more sp^2 character [Sα = 347.25°] than N2 [Sα = 330.39°] if compared to sp^3-hybridization [Sα = 328.50°] angle value. Other bond distances and bond angles are in good agreement with the standard values.

S2. Experimental

A mixture of potassium cyanide (0.260 g, 4.00 mmol) and N^1,N^2-bis((1*H*-benzotriazol-1-yl)methyl)benzene-1,2-diamine (0.370 g, 1.00 mmol) was stirred at room temperature in DMSO (5 ml) for 6 h. After quenching by addition of aqueous ammonium chloride a solid formed which was separated and extracted with ethyl acetate.The organic extract was sequentially washed with saturated Na_2CO_3 solution and water, then dried (Na_2SO_4), filtered, and concentrated to give a solid homogeneous by TLC (80% EtOAc/benzene) in 82% yield. Single crystals were obtained by recrystallization from chloroform/methanol by slow evaporation of the solvent at room temperaature, m.p. 399–400 K.

S3. Refinement

All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry, but according to common practice H atoms bonded to C were kept in ideal positions with C–H = 0.96 Å. The coordinates of the amino H atoms were refined. U_{iso}(H) was set to 1.2U_{eq}(C,N). All non-hydrogen atoms were refined using harmonic refinement.
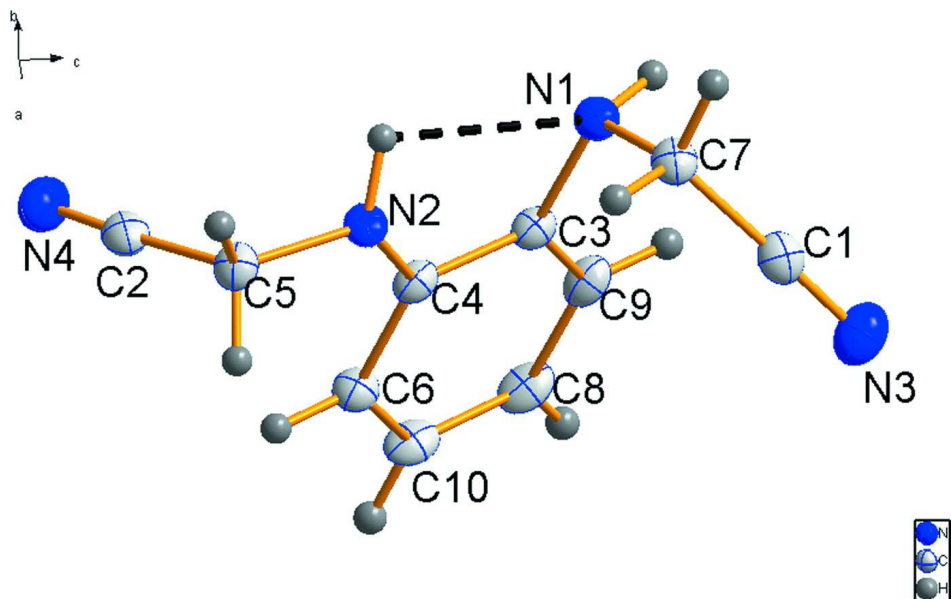
Figure 1

A view of the crystal structure of the tittle compund (**I**) with the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
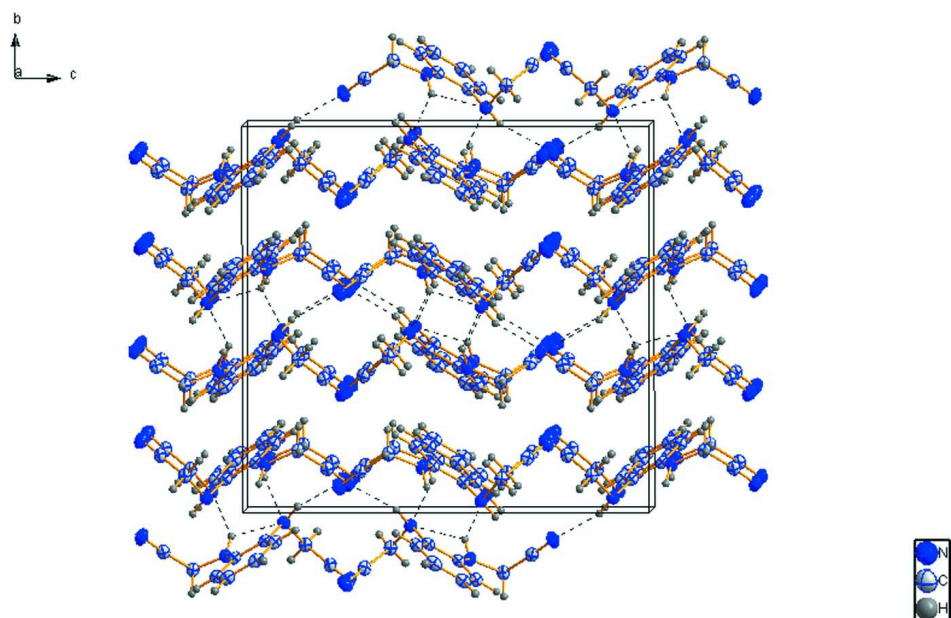
Figure 2

Packing of the molecules of the title compound view along *a* axis. N—H···CN and N—H···N hydrogen bonds are drawn as dashed lines.

2,2′-[1,2-Phenylenebis(azanediyl)]diacetonitrile

Crystal data

$C_{10}H_{10}N_4$	Orthorhombic, *Pbca*
$M_r = 186.2$	Hall symbol: -P 2ac 2ab

$a = 7.6404$ (3) Å
$b = 15.1703$ (7) Å
$c = 15.9168$ (7) Å
$V = 1844.87$ (14) Å^3
$Z = 8$
$F(000) = 784$
$D_x = 1.341$ Mg m^{-3}
Melting point: 399 K

Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å
Cell parameters from 4237 reflections
$\theta = 4.0–67.0°$
$\mu = 0.69$ mm^{-1}
$T = 120$ K
Polygon shape, white
$0.17 \times 0.15 \times 0.10$ mm

Data collection

Agilent Xcalibur (Atlas, Gemini ultra)
    diffractometer
Radiation source: Enhance Ultra (Cu) X-ray
    Source
Mirror monochromator
Detector resolution: 10.3784 pixels mm^{-1}
ω scans
Absorption correction: multi-scan
    (*CrysAlis PRO*; Agilent, 2012)

$T_{min} = 0.68$, $T_{max} = 1$
9893 measured reflections
1641 independent reflections
1359 reflections with $I > 3\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 67.2°$, $\theta_{min} = 5.6°$
$h = -7 \rightarrow 9$
$k = -18 \rightarrow 18$
$l = -18 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.104$
$S = 1.55$
1641 reflections
133 parameters
0 restraints
34 constraints

H atoms treated by a mixture of independent
    and constrained refinement
Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0016I^2)$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Refinement. The refinement was carried out against all reflections. The conventional *R*-factor is always based on *F*. The goodness of fit as well as the weighted *R*-factor are based on *F* and F^2 for refinement carried out on *F* and F^2, respectively. The threshold expression is used only for calculating *R*-factors *etc*. and it is not relevant to the choice of reflections for refinement.

The program used for refinement, Jana2006, uses the weighting scheme based on the experimental expectations, see _refine_ls_weighting_details, that does not force *S* to be one. Therefore the values of *S* are usually larger than the ones from the *SHELX* program.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.67776 (14)	0.46314 (7)	0.09105 (8)	0.0197 (3)
N2	0.59009 (13)	0.37473 (8)	−0.05397 (8)	0.0182 (3)
N3	0.75959 (16)	0.31452 (9)	0.25065 (9)	0.0316 (4)
N4	0.68740 (17)	0.42625 (9)	−0.25896 (9)	0.0314 (4)
C1	0.67383 (17)	0.35295 (9)	0.20428 (10)	0.0228 (4)
C2	0.62292 (17)	0.38628 (9)	−0.20642 (10)	0.0227 (4)
C3	0.81190 (16)	0.41747 (8)	0.04529 (9)	0.0179 (4)
C4	0.76583 (16)	0.37282 (8)	−0.02878 (9)	0.0176 (4)
C5	0.54231 (16)	0.33892 (9)	−0.13496 (9)	0.0200 (4)
C6	0.89448 (16)	0.32671 (9)	−0.07229 (10)	0.0203 (4)
C7	0.57084 (17)	0.40361 (9)	0.14220 (10)	0.0215 (4)

C8	1.11225 (17)	0.37219 (9)	0.02841 (11)	0.0248 (4)
C9	0.98466 (17)	0.41713 (9)	0.07282 (10)	0.0224 (4)
C10	1.06689 (17)	0.32645 (10)	−0.04320 (10)	0.0238 (4)
H1c5	0.417265	0.339719	−0.140823	0.024*
H2c5	0.57431	0.277778	−0.137292	0.024*
H1c6	0.864639	0.294979	−0.122465	0.0244*
H1c7	0.508788	0.363609	0.106188	0.0258*
H2c7	0.481985	0.436862	0.17073	0.0258*
H1c8	1.23154	0.372856	0.047341	0.0298*
H1c9	1.015681	0.44837	0.123117	0.0268*
H1c10	1.154716	0.294105	−0.073369	0.0286*
H1	0.732 (2)	0.5050 (12)	0.1255 (12)	0.0237*
H2	0.536 (2)	0.4245 (12)	−0.0403 (12)	0.0219*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0140 (5)	0.0231 (6)	0.0221 (7)	0.0001 (4)	−0.0013 (5)	−0.0013 (5)
N2	0.0087 (5)	0.0257 (6)	0.0202 (7)	0.0023 (4)	0.0000 (5)	−0.0013 (5)
N3	0.0229 (6)	0.0399 (7)	0.0319 (8)	−0.0047 (6)	−0.0020 (6)	0.0091 (6)
N4	0.0267 (6)	0.0389 (7)	0.0287 (8)	0.0053 (6)	0.0054 (6)	0.0065 (6)
C1	0.0167 (7)	0.0287 (7)	0.0231 (8)	−0.0035 (6)	0.0041 (6)	−0.0004 (6)
C2	0.0154 (6)	0.0286 (7)	0.0241 (9)	0.0052 (6)	−0.0007 (6)	−0.0013 (6)
C3	0.0117 (6)	0.0210 (6)	0.0210 (8)	−0.0002 (5)	0.0014 (5)	0.0041 (5)
C4	0.0101 (6)	0.0217 (6)	0.0211 (8)	−0.0006 (5)	0.0001 (5)	0.0045 (5)
C5	0.0124 (6)	0.0268 (7)	0.0208 (8)	−0.0011 (5)	−0.0006 (6)	0.0008 (5)
C6	0.0131 (6)	0.0249 (7)	0.0229 (8)	0.0011 (5)	0.0019 (6)	0.0012 (6)
C7	0.0137 (6)	0.0285 (7)	0.0223 (8)	0.0013 (5)	0.0007 (6)	−0.0007 (6)
C8	0.0094 (6)	0.0300 (7)	0.0350 (9)	−0.0019 (5)	−0.0030 (6)	0.0081 (6)
C9	0.0153 (6)	0.0262 (7)	0.0256 (9)	−0.0038 (5)	−0.0042 (6)	0.0051 (6)
C10	0.0107 (6)	0.0284 (7)	0.0324 (9)	0.0028 (5)	0.0043 (6)	0.0064 (6)

Geometric parameters (Å, º)

N1—C3	1.4357 (17)	C4—C6	1.3911 (19)
N1—C7	1.4648 (18)	C5—H1c5	0.96
N1—H1	0.935 (18)	C5—H2c5	0.96
N2—C4	1.4016 (16)	C6—C10	1.3963 (18)
N2—C5	1.4457 (19)	C6—H1c6	0.96
N2—H2	0.889 (18)	C7—H1c7	0.96
N3—C1	1.146 (2)	C7—H2c7	0.96
N4—C2	1.144 (2)	C8—C9	1.384 (2)
C1—C7	1.479 (2)	C8—C10	1.379 (2)
C2—C5	1.480 (2)	C8—H1c8	0.96
C3—C4	1.404 (2)	C9—H1c9	0.96
C3—C9	1.3908 (18)	C10—H1c10	0.96
C3—N1—C7	112.49 (10)	H1c5—C5—H2c5	105.18

C3—N1—H1	108.1 (10)	C4—C6—C10	120.20 (14)
C7—N1—H1	109.8 (11)	C4—C6—H1c6	119.9
C4—N2—C5	119.29 (11)	C10—C6—H1c6	119.9
C4—N2—H2	113.2 (11)	N1—C7—C1	113.27 (11)
C5—N2—H2	114.8 (12)	N1—C7—H1c7	109.47
N3—C1—C7	177.27 (15)	N1—C7—H2c7	109.47
N4—C2—C5	176.55 (16)	C1—C7—H1c7	109.47
N1—C3—C4	118.67 (11)	C1—C7—H2c7	109.47
N1—C3—C9	121.29 (13)	H1c7—C7—H2c7	105.38
C4—C3—C9	120.04 (12)	C9—C8—C10	119.55 (13)
N2—C4—C3	118.05 (12)	C9—C8—H1c8	120.22
N2—C4—C6	123.02 (13)	C10—C8—H1c8	120.22
C3—C4—C6	118.90 (12)	C3—C9—C8	120.63 (14)
N2—C5—C2	113.45 (11)	C3—C9—H1c9	119.69
N2—C5—H1c5	109.47	C8—C9—H1c9	119.69
N2—C5—H2c5	109.47	C6—C10—C8	120.65 (13)
C2—C5—H1c5	109.47	C6—C10—H1c10	119.67
C2—C5—H2c5	109.47	C8—C10—H1c10	119.67

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N4[i]	0.935 (18)	2.202 (19)	3.0946 (19)	159.2 (16)
N2—H2···N1	0.889 (18)	2.427 (18)	2.7524 (18)	102.0 (13)
N2—H2···N1[ii]	0.889 (18)	2.494 (17)	3.2536 (16)	143.8 (15)

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