

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

1,4-Bis[(1*H*-pyrazol-1-yl)methyl]benzene

 Gui-Ying Dong,^{a*} Tong-Fei Liu,^a Cui-Huan Jiao,^a
 Xiao-Chen Deng^b and Xiao-Ge Shi^b
^aCollege of Chemical Engineering, Hebei United University, Tangshan 063009, People's Republic of China, and ^bQian'an College, Hebei United University, Tangshan 063009, People's Republic of China

Correspondence e-mail: tsdgying@126.com

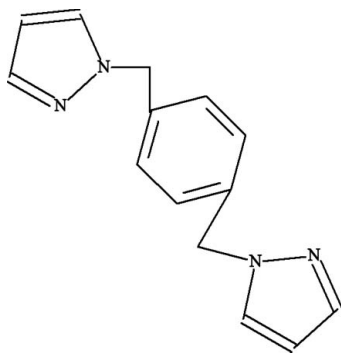
Received 6 June 2011; accepted 10 June 2011

 Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.033; wR factor = 0.064; data-to-parameter ratio = 13.4.

In the title compound, $\text{C}_{14}\text{H}_{14}\text{N}_4$, the center of the phenylene group is a crystallographic center of inversion. The compound is composed of three aromatic rings displaying a *Z*-like conformation. The dihedral angle between the pyrazole rings and the central phenyl ring is 83.84 (9)°.

Related literature

For background and coordination compounds with related ligands, see: Chang *et al.* (1993); Hou *et al.* (2010); Liu *et al.* (2011). For the crystal structure of the title compound with two solvent water molecules, see: Shi *et al.* (2009).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{14}\text{N}_4$	$V = 626.01$ (17) Å ³
$M_r = 238.29$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.6088$ (8) Å	$\mu = 0.08$ mm ⁻¹
$b = 6.8183$ (10) Å	$T = 295$ K
$c = 16.526$ (3) Å	$0.20 \times 0.20 \times 0.19$ mm
$\beta = 97.900$ (15)°	

Data collection

Bruker SMART CCD area-detector diffractometer	2464 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1109 independent reflections
$T_{\min} = 0.956$, $T_{\max} = 0.996$	580 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	1 restraint
$wR(F^2) = 0.064$	H-atom parameters constrained
$S = 0.80$	$\Delta\rho_{\text{max}} = 0.10$ e Å ⁻³
1109 reflections	$\Delta\rho_{\text{min}} = -0.11$ e Å ⁻³
83 parameters	

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors thank Hebei United University for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2296).

References

- Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chang, W.-K., Sheu, S.-C., Lee, G.-H., Wang, Y., Ho, T.-I. & Lin, Y.-C. (1993). *J. Chem. Soc. Dalton Trans.* pp. 687–694.
- Hou, G. F., Bi, L. H., Li, B. & Wu, L. X. (2010). *Inorg. Chem.* **49**, 6474–6483.
- Liu, T. F., Zhang, M. X., Zhang, W. G. & Cui, G. H. (2011). *Chin. J. Struct. Chem.* **30**, 508–513.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shi, A.-E., Hou, Y.-J., Zhang, Y.-M., Hou, G.-F. & Gao, J.-S. (2009). *Acta Cryst.* **E65**, o690.

supporting information

Acta Cryst. (2011). E67, o1685 [doi:10.1107/S1600536811022537]

1,4-Bis[(1*H*-pyrazol-1-yl)methyl]benzene

Gui-Ying Dong, Tong-Fei Liu, Cui-Huan Jiao, Xiao-Chen Deng and Xiao-Ge Shi

S1. Comment

Over the past few years, efforts have been focused on the investigation of coordination polymers with flexible ligands. Flexible ligands with two or more pyrazolyl moieties such as 1,4-bis[(1*H*-pyrazol-1-yl)-methyl]-benzene find numerous applications in constructing metal–organic coordination polymers (Chang *et al.* 1993; Hou *et al.* 2010; Liu *et al.* 2011). The crystal structure of the title compound including two water molecules of hydration has previously been described (Shi *et al.* 2009). We report here the crystal structure of the title compound without any solvent molecules in the crystal lattice.

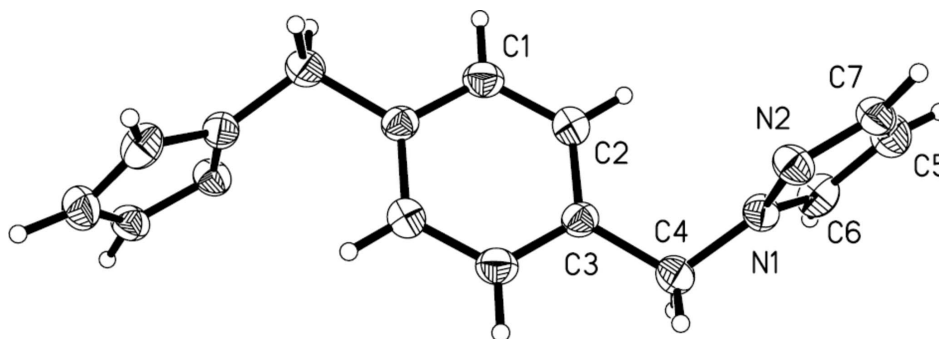
In (I), the center of the phenylene group is an inversion centre, so that the asymmetric unit consists of one-half of the title compound (Fig. 1). 1,4-Bis[(1*H*-pyrazol-1-yl)-methyl]-benzene is composed of three aromatic rings, displaying a Z shape, with the pyrazole rings on opposite sides of the plane of the phenyl ring. The whole molecule is nonplanar, the dihedral angle of the pyrazoles with respect to the central phenyl group are 83.84 (9)°. The average bond distances and angles for the pyrazole ring are in agreement with those of previously reported related pyrazole complexes and the hydrated title compound (Liu *et al.* 2011; Shi *et al.* 2009). In contrast to the structure of the same compound with additional water molecules of hydration (Shi *et al.* 2009), the dihedral angles of the pyrazole units with respect to the central phenyl group are 76.9 (1)° and 74.5 (1)°, respectively. The hydrated compound further forms a two-dimensional supramolecular network by the hydrogen bond interactions including the water molecules.

S2. Experimental

(I) was obtained as an unexpected product in an attempt to construct a supramolecular Zn complex under hydrothermal conditions. A mixture of Zn(NO₃)₂·6H₂O (166 mg, 1 mmol), phthalic acid (150 mg, 1 mmol), NaOH (80 mg, 2 mmol) and 1,4-Bis[(1*H*-pyrazol-1-yl)-methyl]-benzene (238 mg, 1 mmol) in H₂O (12 ml) was placed in a Teflon-lined stainless vessel and heated to 453 K for 72 h. Then, the reaction system was cooled to room temperature during 24 h to give rise to colourless crystals, which were collected and washed with water. Yield 0.024 g (10% of used (I)). Analysis calculated for C₁₄H₁₄N₄ (238.29): C 70.57, H 5.92, N 23.51%; found: C 70.38, H 5.78, N 23.38%.

S3. Refinement

H atoms were placed in calculated positions, with C—H = 0.93 Å or C—H = 0.97 Å and refined with a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Restraints (DELU) were applied to the U_{ij} parameters of atoms C3 and C4.

**Figure 1**

The molecular structure of (I), showing displacement ellipsoids at the 30% probability level for non-hydrogen atoms.

1,4-Bis[(1*H*-pyrazol-1-yl)methyl]benzene

Crystal data

$C_{14}H_{14}N_4$

$M_r = 238.29$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 5.6088\ (8)\ \text{\AA}$

$b = 6.8183\ (10)\ \text{\AA}$

$c = 16.526\ (3)\ \text{\AA}$

$\beta = 97.900\ (15)^\circ$

$V = 626.01\ (17)\ \text{\AA}^3$

$Z = 2$

$F(000) = 252$

$D_x = 1.264\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1865 reflections

$\theta = 5.3\text{--}24.1^\circ$

$\mu = 0.08\ \text{mm}^{-1}$

$T = 295\ \text{K}$

Block, colourless

$0.20 \times 0.20 \times 0.19\ \text{mm}$

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.956$, $T_{\max} = 0.996$

2464 measured reflections

1109 independent reflections

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

$R_{\text{int}} = 0.033$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -6 \rightarrow 6$

$k = -6 \rightarrow 8$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.064$

$S = 0.80$

1109 reflections

83 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

$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2]$

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

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

$\Delta\rho_{\max} = 0.10\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.11\ \text{e \AA}^{-3}$

Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.043 (3)

Special details

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
N2	0.3304 (2)	0.6599 (2)	0.19489 (8)	0.0484 (4)
N1	0.1491 (2)	0.76019 (19)	0.15110 (8)	0.0450 (4)
C2	0.3728 (3)	0.8298 (3)	0.00568 (11)	0.0536 (5)
H2B	0.2880	0.7135	0.0088	0.064*
C7	0.2330 (3)	0.4880 (3)	0.20879 (10)	0.0502 (5)
H7A	0.3157	0.3862	0.2378	0.060*
C1	0.5185 (3)	0.8528 (2)	-0.05491 (11)	0.0525 (5)
H1A	0.5294	0.7517	-0.0920	0.063*
C3	0.3522 (3)	0.9770 (3)	0.06120 (10)	0.0436 (4)
C6	-0.0531 (3)	0.6553 (3)	0.13893 (11)	0.0555 (5)
H6A	-0.1998	0.6959	0.1108	0.067*
C4	0.1899 (3)	0.9606 (2)	0.12664 (11)	0.0562 (5)
H4A	0.2606	1.0340	0.1742	0.067*
H4B	0.0360	1.0203	0.1068	0.067*
C5	-0.0058 (3)	0.4783 (3)	0.17507 (12)	0.0588 (5)
H5A	-0.1111	0.3735	0.1767	0.071*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0428 (8)	0.0432 (10)	0.0573 (10)	0.0048 (8)	0.0001 (7)	0.0053 (8)
N1	0.0420 (8)	0.0448 (9)	0.0484 (9)	0.0056 (8)	0.0074 (7)	0.0057 (8)
C2	0.0598 (11)	0.0468 (12)	0.0558 (12)	-0.0024 (9)	0.0134 (10)	0.0014 (11)
C7	0.0593 (13)	0.0408 (12)	0.0504 (12)	0.0055 (10)	0.0072 (10)	0.0036 (10)
C1	0.0626 (11)	0.0460 (12)	0.0490 (12)	0.0036 (10)	0.0076 (10)	-0.0051 (10)
C3	0.0454 (10)	0.0443 (11)	0.0413 (11)	0.0087 (9)	0.0067 (8)	0.0027 (10)
C6	0.0352 (10)	0.0744 (15)	0.0559 (12)	0.0007 (11)	0.0025 (8)	-0.0021 (12)
C4	0.0635 (11)	0.0458 (12)	0.0614 (13)	0.0138 (9)	0.0165 (10)	0.0119 (10)
C5	0.0551 (13)	0.0566 (14)	0.0653 (13)	-0.0144 (10)	0.0100 (11)	-0.0042 (12)

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

N2—C7	1.3264 (19)	C1—C3 ⁱ	1.380 (2)
N2—N1	1.3504 (16)	C1—H1A	0.9300
N1—C6	1.3324 (18)	C3—C1 ⁱ	1.380 (2)
N1—C4	1.4518 (19)	C3—C4	1.511 (2)

C2—C3	1.375 (2)	C6—C5	1.356 (2)
C2—C1	1.386 (2)	C6—H6A	0.9300
C2—H2B	0.9300	C4—H4A	0.9700
C7—C5	1.380 (2)	C4—H4B	0.9700
C7—H7A	0.9300	C5—H5A	0.9300
C7—N2—N1	104.04 (12)	C2—C3—C4	122.52 (16)
N2—N1—C6	111.81 (13)	C1 ⁱ —C3—C4	119.39 (16)
N2—N1—C4	119.33 (14)	N1—C6—C5	107.47 (15)
C6—N1—C4	128.81 (16)	N1—C6—H6A	126.3
C3—C2—C1	120.76 (16)	C5—C6—H6A	126.3
C3—C2—H2B	119.6	N1—C4—C3	113.74 (14)
C1—C2—H2B	119.6	N1—C4—H4A	108.8
N2—C7—C5	111.86 (16)	C3—C4—H4A	108.8
N2—C7—H7A	124.1	N1—C4—H4B	108.8
C5—C7—H7A	124.1	C3—C4—H4B	108.8
C3 ⁱ —C1—C2	121.18 (16)	H4A—C4—H4B	107.7
C3 ⁱ —C1—H1A	119.4	C6—C5—C7	104.82 (16)
C2—C1—H1A	119.4	C6—C5—H5A	127.6
C2—C3—C1 ⁱ	118.07 (15)	C7—C5—H5A	127.6

Symmetry code: (i) $-x+1, -y+2, -z$.