Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

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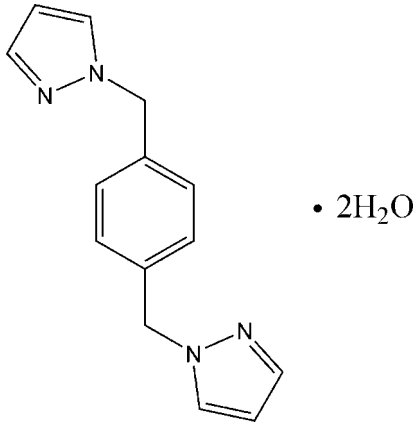
Received 19 February 2009; accepted 2 March 2009

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.048; wR factor = 0.123; data-to-parameter ratio = 18.6.

The asymmetric unit of the title compound, $C_{14}H_{14}N_4{\cdot}2H_2O$ consists of two half-molecules of the main molecule, each situated on an inversion center, and two molecules of water. One-dimensional chains of water molecules are built up by O—H···O hydrogen bonds which are then linked with the main molecule *via* O—H···N hydrogen bonds, forming a two-dimensional supramolecular network in the *ac* plane.

Related literature

For background and the synthesis, see: Chang *et al.* (1993). For similar structures, see: Bourne *et al.* (2006).



Experimental

Crystal data

$C_{14}H_{14}N_4{\cdot}2H_2O$
M_r = 274.32
Monoclinic, $P2_1/c$
a = 4.680 (2) Å
b = 18.640 (8) Å
c = 16.974 (10) Å
β = 91.15 (2)°
V = 1480.6 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 291 K
0.29 × 0.27 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.956, T_{max} = 0.984
14065 measured reflections
3361 independent reflections
1735 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.123
S = 1.00
3361 reflections
181 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H15···N4	0.85	2.08	2.929 (3)	178
O1—H16···O2^{i}	0.85	1.87	2.717 (2)	177
O2—H17···N2^{ii}	0.85	2.08	2.923 (2)	170
O2—H18···O1	0.85	1.89	2.733 (2)	172

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); 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: *SHELXL97*.

The authors acknowledge financial support from the National Natural Science Foundation of China (grant No. 20872030), the Research Foundation of Heilongjiang Provincial Education Department (grant No. 11513073), the Project of the Special Fund of the Science and Technology Innovation People of Harbin (grant No. RC2006QN018001) and Heilongjiang University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2236).

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supplementary materials

Acta Cryst. (2009). E**65**, o690 [**doi:10.1107/S1600536809007521**]

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

A.-E. Shi, Y.-J. Hou, Y.-M. Zhang, G.-F. Hou and J.-S. Gao

Comment

The title compound is not only an excellent flexible ligand, but also a hydrogen bonding acceptor that can be used to construct supramolecular structures (Chang *et al.* (1993). In this paper, we report a two-dimensional supramolecular network similar to that reported earlier (Bourne *et al.* 2006), composed of 1,4-bis((1*H*-pyrazol-1-yl)methyl)benzene and water.

In (I), all bond lengths and angles are normal. The flexible ligand molecules display a '*Z*' shape, with the pyrazole rings on opposite sides of the plane of the phenyl ring (Fig. 1).

In the crystal, one-dimensional water chains are built up by O—H···O hydrogen bonding interactions. The chains are then linked to the ligands (I),*via* O—H···N hydrogen bonds, forming a two-dimensional supramolecular network along the *ac* plane (Fig. 2, Table 1).

Experimental

The title compound was prepared from pyrazole (6.8 g, 100 mmol), Na_2CO_3 (16 g, 100 mmol) and 1,4-bis(bromomethyl)benzene (21.3 g, 50 mmol)in benzene. The solution was refluxed for 3 h. The title compound (4.7 g, 20 mmol) was then dissolved in hot water (30 ml) to give a clear solution and allowed to stand in a desiccator at room temperature for several days after which colorless crystals of (I) were obtained.

Refinement

H atoms bound to C atoms were placed in calculated positions and treated as riding on their parent atoms, with C—H = 0.93 Å (aromatic), C—H = 0.97 Å (methylene), and with U_{iso}(H) = 1.2U_{eq}(C). Water H atoms were initially located in a difference Fourier map, but they were treated as riding on their parent atoms with O—H = 0.85 Å and with with U_{iso}(H) = 1.5U_{eq}(O).

Figures

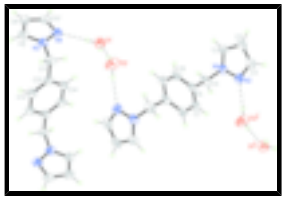

Fig. 1. The molecular structure of (I), showing displacement ellipsoids at the 30% probability level for non-H atoms. Dashed lines indicate the hydrogen-bonding interactions [Symmetry codes; (I) -*x* + 2, -*y* + 1, -*z* + 1]

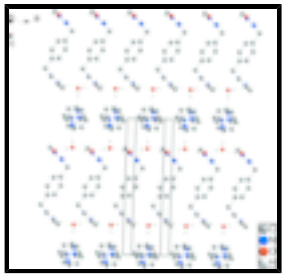

Fig. 2. A partial packing view, showing the two-dimensional network. Dashed lines indicate the hydrogen-bonding interactions. Only H atoms involved in hydrogren bonds are shown.

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

Crystal data

$C_{14}H_{14}N_4 \cdot 2H_2O$	F_{000} = 584
M_r = 274.32	D_x = 1.231 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 8012 reflections
a = 4.680 (2) Å	θ = 6.5–54.9º
b = 18.640 (8) Å	μ = 0.09 mm^{-1}
c = 16.974 (10) Å	T = 291 K
β = 91.15 (2)º	Block, colorless
V = 1480.6 (13) Å^3	0.29 × 0.27 × 0.19 mm
Z = 4	

Data collection

Rigaku R-AXIS RAPID diffractometer	3361 independent reflections
Radiation source: fine-focus sealed tube	1735 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.050
T = 291 K	θ_{max} = 27.5º
ω scan	θ_{min} = 3.3º
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	h = −6→5
T_{min} = 0.956, T_{max} = 0.984	k = −23→24
14065 measured reflections	l = −22→22

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.048	H-atom parameters constrained
$wR(F^2)$ = 0.123	$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max} < 0.001$

3361 reflections	$\Delta\rho_{max} = 0.14$ e Å^{-3}
181 parameters	$\Delta\rho_{min} = -0.13$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8625 (5)	0.35411 (10)	0.69781 (13)	0.0727 (6)
H1	0.7584	0.3209	0.6680	0.087*
C2	1.0682 (5)	0.33893 (11)	0.75233 (13)	0.0784 (6)
H2	1.1345	0.2939	0.7677	0.094*
C3	1.1572 (4)	0.40427 (12)	0.77993 (12)	0.0737 (6)
H3	1.2983	0.4104	0.8187	0.088*
C4	0.6675 (4)	0.46818 (11)	0.63845 (12)	0.0709 (6)
H4	0.6093	0.5124	0.6635	0.085*
H5	0.4963	0.4419	0.6231	0.085*
C5	0.8366 (3)	0.48549 (9)	0.56601 (11)	0.0551 (4)
C6	0.8351 (4)	0.43987 (10)	0.50232 (12)	0.0642 (5)
H6	0.7232	0.3987	0.5034	0.077*
C7	1.0049 (4)	0.54625 (9)	0.56293 (11)	0.0622 (5)
H7	1.0099	0.5779	0.6053	0.075*
C8	0.5827 (4)	0.27680 (10)	−0.07594 (13)	0.0724 (6)
H8	0.6642	0.2909	−0.1230	0.087*
C9	0.3835 (5)	0.22438 (10)	−0.06711 (15)	0.0776 (6)
H9	0.3016	0.1955	−0.1061	0.093*
C10	0.3302 (4)	0.22347 (9)	0.01191 (14)	0.0706 (6)
H10	0.2015	0.1925	0.0354	0.085*
C11	0.8187 (4)	0.36625 (9)	0.01523 (13)	0.0663 (5)
H11	0.9808	0.3674	−0.0195	0.080*
H12	0.8916	0.3612	0.0688	0.080*
C12	0.6550 (3)	0.43624 (8)	0.00771 (11)	0.0527 (4)
C13	0.6725 (4)	0.47764 (9)	−0.05894 (11)	0.0616 (5)
H13	0.7898	0.4630	−0.0995	0.074*
C14	0.4809 (4)	0.45945 (9)	0.06678 (11)	0.0624 (5)
H14	0.4663	0.4324	0.1126	0.075*

N1	0.8358 (3)	0.42535 (8)	0.69450 (8)	0.0559 (4)
N2	1.0191 (3)	0.45779 (8)	0.74505 (9)	0.0660 (4)
N3	0.6401 (3)	0.30445 (7)	−0.00459 (10)	0.0579 (4)
N4	0.4843 (3)	0.27223 (7)	0.05120 (10)	0.0638 (4)
O1	0.4928 (3)	0.31462 (7)	0.21740 (9)	0.0847 (4)
H15	0.4939	0.3031	0.1690	0.127*
H16	0.3374	0.3373	0.2238	0.127*
O2	0.9966 (3)	0.38581 (8)	0.24291 (10)	0.1062 (6)
H17	0.9746	0.4311	0.2421	0.159*
H18	0.8329	0.3663	0.2386	0.159*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0920 (14)	0.0568 (11)	0.0693 (14)	−0.0064 (10)	0.0027 (12)	0.0032 (10)
C2	0.0967 (15)	0.0713 (13)	0.0674 (14)	0.0235 (12)	0.0093 (12)	0.0138 (11)
C3	0.0689 (12)	0.0959 (16)	0.0562 (12)	0.0135 (12)	−0.0021 (10)	0.0092 (11)
C4	0.0529 (10)	0.0895 (13)	0.0704 (14)	0.0117 (9)	0.0054 (10)	0.0187 (11)
C5	0.0413 (9)	0.0633 (10)	0.0605 (12)	0.0094 (8)	−0.0013 (8)	0.0145 (9)
C6	0.0646 (11)	0.0599 (10)	0.0679 (13)	−0.0089 (9)	−0.0060 (10)	0.0122 (10)
C7	0.0708 (11)	0.0571 (10)	0.0587 (12)	0.0052 (9)	−0.0026 (10)	0.0019 (9)
C8	0.0854 (14)	0.0656 (12)	0.0664 (15)	0.0127 (11)	0.0027 (11)	0.0025 (10)
C9	0.0921 (15)	0.0559 (11)	0.0839 (18)	0.0042 (11)	−0.0177 (13)	−0.0075 (11)
C10	0.0695 (12)	0.0487 (10)	0.0935 (18)	−0.0009 (9)	0.0001 (12)	0.0009 (10)
C11	0.0505 (10)	0.0544 (10)	0.0936 (16)	0.0012 (8)	−0.0073 (10)	0.0040 (10)
C12	0.0423 (8)	0.0491 (9)	0.0665 (12)	−0.0049 (7)	−0.0047 (8)	0.0034 (8)
C13	0.0599 (10)	0.0607 (11)	0.0646 (13)	0.0022 (8)	0.0130 (9)	0.0007 (9)
C14	0.0708 (11)	0.0570 (10)	0.0596 (12)	0.0019 (9)	0.0029 (10)	0.0135 (9)
N1	0.0495 (8)	0.0641 (9)	0.0543 (9)	0.0008 (7)	0.0061 (7)	0.0091 (7)
N2	0.0680 (9)	0.0699 (9)	0.0601 (10)	−0.0009 (8)	0.0042 (8)	−0.0023 (8)
N3	0.0561 (8)	0.0491 (7)	0.0682 (11)	0.0080 (7)	−0.0015 (8)	0.0022 (8)
N4	0.0669 (9)	0.0537 (8)	0.0709 (11)	0.0047 (8)	0.0043 (8)	0.0025 (8)
O1	0.0878 (9)	0.0774 (9)	0.0887 (11)	−0.0004 (7)	−0.0012 (8)	0.0027 (8)
O2	0.0867 (10)	0.0885 (10)	0.1433 (16)	0.0021 (8)	0.0031 (10)	−0.0361 (10)

Geometric parameters (Å, °)

C1—N1	1.335 (2)	C9—C10	1.369 (3)
C1—C2	1.352 (3)	C9—H9	0.9300
C1—H1	0.9300	C10—N4	1.331 (2)
C2—C3	1.367 (3)	C10—H10	0.9300
C2—H2	0.9300	C11—N3	1.459 (2)
C3—N2	1.322 (2)	C11—C12	1.517 (2)
C3—H3	0.9300	C11—H11	0.9700
C4—N1	1.460 (2)	C11—H12	0.9700
C4—C5	1.510 (2)	C12—C13	1.373 (2)
C4—H4	0.9700	C12—C14	1.375 (2)
C4—H5	0.9700	C13—C14^{ii}	1.380 (2)

C5—C6	1.375 (3)	C13—H13	0.9300
C5—C7	1.381 (2)	C14—C13^{ii}	1.380 (2)
C6—C7^{i}	1.374 (3)	C14—H14	0.9300
C6—H6	0.9300	N1—N2	1.345 (2)
C7—C6^{i}	1.374 (3)	N3—N4	1.348 (2)
C7—H7	0.9300	O1—H15	0.8500
C8—N3	1.339 (2)	O1—H16	0.8500
C8—C9	1.361 (3)	O2—H17	0.8500
C8—H8	0.9300	O2—H18	0.8500
N1—C1—C2	107.56 (18)	C10—C9—H9	127.6
N1—C1—H1	126.2	N4—C10—C9	112.01 (18)
C2—C1—H1	126.2	N4—C10—H10	124.0
C1—C2—C3	104.84 (18)	C9—C10—H10	124.0
C1—C2—H2	127.6	N3—C11—C12	111.94 (14)
C3—C2—H2	127.6	N3—C11—H11	109.2
N2—C3—C2	112.08 (19)	C12—C11—H11	109.2
N2—C3—H3	124.0	N3—C11—H12	109.2
C2—C3—H3	124.0	C12—C11—H12	109.2
N1—C4—C5	111.25 (14)	H11—C11—H12	107.9
N1—C4—H4	109.4	C13—C12—C14	118.04 (16)
C5—C4—H4	109.4	C13—C12—C11	120.95 (17)
N1—C4—H5	109.4	C14—C12—C11	121.00 (16)
C5—C4—H5	109.4	C12—C13—C14^{ii}	121.16 (16)
H4—C4—H5	108.0	C12—C13—H13	119.4
C6—C5—C7	118.11 (16)	C14^{ii}—C13—H13	119.4
C6—C5—C4	120.89 (17)	C12—C14—C13^{ii}	120.80 (16)
C7—C5—C4	120.97 (18)	C12—C14—H14	119.6
C7^{i}—C6—C5	121.54 (17)	C13^{ii}—C14—H14	119.6
C7^{i}—C6—H6	119.2	C1—N1—N2	111.26 (16)
C5—C6—H6	119.2	C1—N1—C4	128.31 (17)
C6^{i}—C7—C5	120.36 (17)	N2—N1—C4	119.92 (15)
C6^{i}—C7—H7	119.8	C3—N2—N1	104.26 (16)
C5—C7—H7	119.8	C8—N3—N4	111.25 (16)
N3—C8—C9	107.6 (2)	C8—N3—C11	128.06 (17)
N3—C8—H8	126.2	N4—N3—C11	120.37 (16)
C9—C8—H8	126.2	C10—N4—N3	104.34 (16)
C8—C9—C10	104.80 (19)	H15—O1—H16	105.7
C8—C9—H9	127.6	H17—O2—H18	108.3

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H15···N4	0.85	2.08	2.929 (3)	178
O1—H16···O2^{iii}	0.85	1.87	2.717 (2)	177
O2—H17···N2^{i}	0.85	2.08	2.923 (2)	170

O2—H18···O1	0.85	1.89	2.733 (2)	172

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

Fig. 1

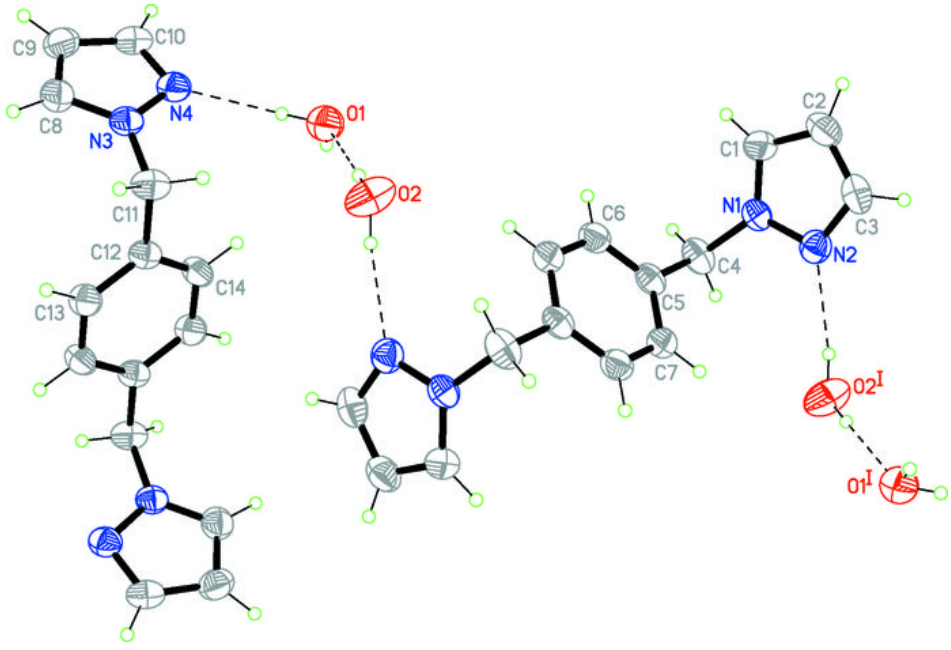

Fig. 2