

2-[(1*H*-Pyrrol-2-yl)methyl]-1*H*-pyrrole

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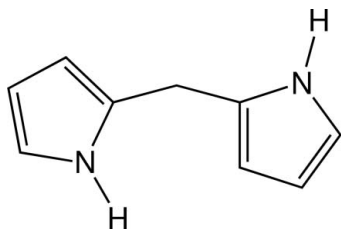
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Key indicators: single-crystal X-ray study; $T = 153$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.057; wR factor = 0.132; data-to-parameter ratio = 17.9.

In the title compound, $\text{C}_9\text{H}_{10}\text{N}_2$, the two pyrrole ring planes are twisted by a dihedral angle of $69.07(16)^\circ$ and the $\text{C}-\text{C}-\text{C}$ methane angle is $115.1(2)^\circ$. In the crystal, molecules are connected into layers in the bc plane by $\text{N}-\text{H}\cdots\pi$ interactions.

Related literature

For synthesis of symmetric and non-symmetric porphyrins, see: Shanmugathasan *et al.* (2000); Bonifazi *et al.* (2005); Fendt *et al.* (2009). For their applications as organometallic ligands, see: Ganesan *et al.* (2001); Gao *et al.* (2004).



Experimental

Crystal data

$\text{C}_9\text{H}_{10}\text{N}_2$
 $M_r = 146.19$
Monoclinic, $P2_1$
 $a = 6.048(3)$ Å
 $b = 7.312(4)$ Å
 $c = 9.024(5)$ Å
 $\beta = 100.78(1)^\circ$

$V = 392.0(4)$ Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 153$ K
 $0.32 \times 0.08 \times 0.06$ mm

Data collection

Rigaku SCX-Mini diffractometer
with Mercury 2 CCD
Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)
 $T_{\min} = 0.976$, $T_{\max} = 0.996$
4179 measured reflections
1786 independent reflections
1374 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.132$
 $S = 1.05$
1786 reflections
100 parameters
61 restraints
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.19$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$Cg1$ and $Cg2$ are the centroids of the $\text{N}1/\text{C}1-\text{C}4$ and $\text{N}2/\text{C}6-\text{C}9$ rings, respectively.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}1-\text{H}1\text{N}\cdots Cg1^i$	0.88	2.53	3.357 (3)	156
$\text{N}2-\text{H}2\text{N}\cdots Cg2^{ii}$	0.88	2.53	3.363 (3)	159

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

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5264).

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supporting information

Acta Cryst. (2013). E69, o1697 [doi:10.1107/S1600536813028365]

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S1. Comment

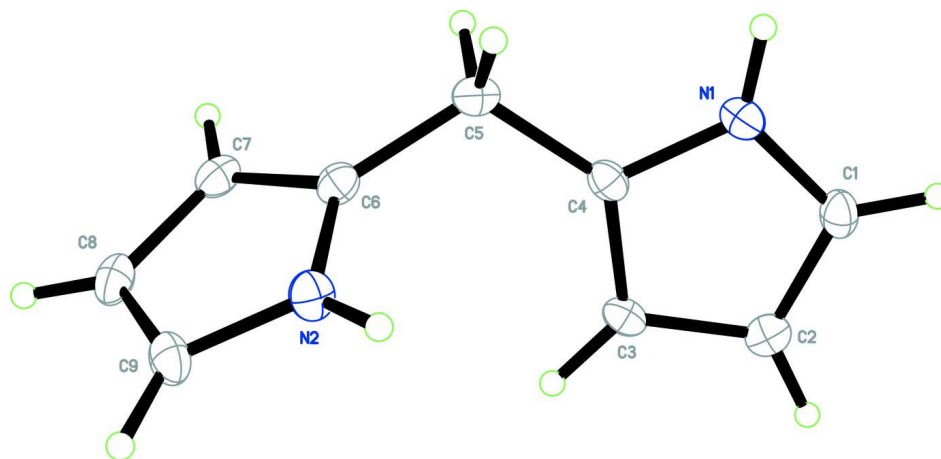
Dipyrromethane (DPM) derivatives have been used as key intermediates in the synthesis of symmetric and non-symmetric porphyrins (Shanmugathan *et al.*, 2000; Bonifazi *et al.*, 2005; Fendt *et al.*, 2009) and also used as organometallic ligands (Ganesan *et al.*, 2001; Gao *et al.*, 2004). DPMs are typically electron rich and prone to oxidation; this is particularly true in the case of unsubstituted DPMs, which benefit from oxygen-free conditions for isolation and long-term storage. Low temperatures are also beneficial. This sensitivity has made it difficult to obtain unsubstituted dipyrromethanes in the form of X-ray diffraction-grade crystals. Here, we report the crystal structure of 2-(1*H*-pyrrol-2-ylmethyl)-1*H*-pyrrole that in crystalline form is stable in air under ambient conditions. The molecular structure of the title compound is shown in Fig. 1. The configuration of two pyrrole ring planes are approximately perpendicular to each other, with the C4—C5—C6 methane angle of 115.1 (2)°.

S2. Experimental

For the synthesis of DPM, the solution of paraformaldehyde (0.9 g, 29.97 mmol) in pyrrole (110 ml, 1.58 mol) with InCl₃ (0.3 g, 1.42 mmol) was stirred for 1 h at 70 °C under nitrogen atmosphere. After addition of NaOH (5 pellets), the reaction solution was stirred for 1 h at room temperature and then concentrated under vacuum (20 mmHg) at 70 °C. To the reaction mixture was poured 1 N NaOH solution (100 ml) and ethyl acetate (100 ml), then the organic layer was dried (Na₂SO₄), and distilled to afford DPM (4.37 g, 50% yield) as a dark brown syrup. The crystals of the title compound suitable for X-ray analysis were collected in the form of long needles from the pyrrole-rich distillate after being stored in a freezer for few days.

S3. Refinement

H atoms were placed in calculated positions using a riding model with N—H = 0.88 Å and C—H = 0.95 and 0.99 Å for pyrrole and methane H, respectively, and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$.

**Figure 1**

The molecular structure of the title compound with 25% probability displacement ellipsoids.

2-[(1*H*-Pyrrol-2-yl)methyl]-1*H*-pyrrole

Crystal data

$C_9H_{10}N_2$

$M_r = 146.19$

Monoclinic, $P2_1$

Hall symbol: $P\ 2yb$

$a = 6.048\ (3)\ \text{\AA}$

$b = 7.312\ (4)\ \text{\AA}$

$c = 9.024\ (5)\ \text{\AA}$

$\beta = 100.78\ (1)^\circ$

$V = 392.0\ (4)\ \text{\AA}^3$

$Z = 2$

$F(000) = 156$

$D_x = 1.238\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71075\ \text{\AA}$

Cell parameters from 4189 reflections

$\theta = 3.0\text{--}27.5^\circ$

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

$T = 153\ \text{K}$

Needle, colourless

$0.32 \times 0.08 \times 0.06\ \text{mm}$

Data collection

Rigaku SCX-Mini with Mercury 2 CCD diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.976$, $T_{\max} = 0.996$

4179 measured reflections

1786 independent reflections

1374 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.063$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -7 \rightarrow 7$

$k = -9 \rightarrow 9$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.132$

$S = 1.05$

1786 reflections

100 parameters

61 restraints

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

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2]$

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

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

$\Delta\rho_{\max} = 0.19\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.23\ \text{e \AA}^{-3}$

Absolute structure: nd

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. The direction of the twofold screw axis could not be reliably determined.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2619 (4)	-0.0035 (4)	0.5615 (3)	0.0353 (6)
H1	0.3300	-0.0409	0.6603	0.042*
C2	0.3488 (4)	0.1182 (4)	0.4732 (3)	0.0331 (6)
H2	0.4887	0.1802	0.4991	0.040*
C3	0.1930 (4)	0.1352 (3)	0.3367 (3)	0.0298 (6)
H3	0.2088	0.2109	0.2538	0.036*
C4	0.0136 (4)	0.0222 (4)	0.3451 (2)	0.0284 (5)
C5	-0.2014 (4)	-0.0146 (4)	0.2387 (2)	0.0348 (6)
H5A	-0.3267	0.0374	0.2818	0.042*
H5B	-0.2242	-0.1486	0.2310	0.042*
C6	-0.2144 (4)	0.0606 (3)	0.0837 (3)	0.0301 (6)
C7	-0.3568 (4)	0.1863 (4)	0.0037 (3)	0.0342 (6)
H7	-0.4721	0.2516	0.0396	0.041*
C8	-0.3029 (4)	0.2019 (4)	-0.1402 (3)	0.0362 (6)
H8	-0.3761	0.2785	-0.2195	0.043*
C9	-0.1268 (4)	0.0876 (4)	-0.1462 (2)	0.0367 (6)
H9	-0.0530	0.0711	-0.2294	0.044*
N1	0.0597 (4)	-0.0620 (3)	0.4825 (2)	0.0344 (6)
H1N	-0.0283	-0.1423	0.5153	0.041*
N2	-0.0764 (3)	0.0011 (3)	-0.0094 (2)	0.0336 (5)
H2N	0.0302	-0.0813	0.0148	0.040*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0380 (14)	0.0427 (15)	0.0244 (12)	0.0079 (13)	0.0037 (11)	-0.0002 (12)
C2	0.0322 (13)	0.0322 (14)	0.0356 (13)	-0.0001 (11)	0.0082 (11)	-0.0078 (11)
C3	0.0366 (13)	0.0265 (13)	0.0292 (12)	-0.0002 (10)	0.0135 (11)	0.0000 (10)
C4	0.0349 (12)	0.0269 (13)	0.0249 (11)	0.0027 (10)	0.0096 (10)	0.0001 (9)
C5	0.0311 (12)	0.0358 (14)	0.0388 (14)	-0.0030 (11)	0.0103 (11)	0.0009 (11)
C6	0.0281 (12)	0.0290 (14)	0.0322 (13)	-0.0035 (10)	0.0030 (10)	-0.0048 (10)
C7	0.0248 (13)	0.0328 (14)	0.0438 (15)	0.0010 (11)	0.0031 (11)	0.0001 (11)
C8	0.0343 (14)	0.0296 (14)	0.0394 (14)	-0.0002 (11)	-0.0070 (12)	0.0034 (11)
C9	0.0459 (14)	0.0375 (16)	0.0248 (13)	-0.0032 (13)	0.0016 (11)	-0.0026 (11)
N1	0.0388 (12)	0.0334 (13)	0.0323 (11)	-0.0030 (10)	0.0100 (10)	0.0038 (9)

N2	0.0371 (11)	0.0287 (11)	0.0345 (11)	0.0064 (10)	0.0058 (9)	0.0006 (9)
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Geometric parameters (Å, °)

C1—C2	1.363 (4)	C5—H5B	0.9900
C1—N1	1.364 (3)	C6—N2	1.361 (3)
C1—H1	0.9500	C6—C7	1.370 (3)
C2—C3	1.410 (3)	C7—C8	1.402 (3)
C2—H2	0.9500	C7—H7	0.9500
C3—C4	1.377 (3)	C8—C9	1.363 (3)
C3—H3	0.9500	C8—H8	0.9500
C4—N1	1.365 (3)	C9—N2	1.369 (3)
C4—C5	1.490 (3)	C9—H9	0.9500
C5—C6	1.491 (3)	N1—H1N	0.8800
C5—H5A	0.9900	N2—H2N	0.8800
C2—C1—N1	107.8 (2)	N2—C6—C7	106.7 (2)
C2—C1—H1	126.1	N2—C6—C5	122.0 (2)
N1—C1—H1	126.1	C7—C6—C5	131.2 (2)
C1—C2—C3	107.5 (2)	C6—C7—C8	108.1 (2)
C1—C2—H2	126.3	C6—C7—H7	125.9
C3—C2—H2	126.3	C8—C7—H7	125.9
C4—C3—C2	107.7 (2)	C9—C8—C7	107.8 (2)
C4—C3—H3	126.2	C9—C8—H8	126.1
C2—C3—H3	126.2	C7—C8—H8	126.1
N1—C4—C3	107.0 (2)	C8—C9—N2	107.0 (2)
N1—C4—C5	120.6 (2)	C8—C9—H9	126.5
C3—C4—C5	132.4 (2)	N2—C9—H9	126.5
C4—C5—C6	115.1 (2)	C1—N1—C4	110.1 (2)
C4—C5—H5A	108.5	C1—N1—H1N	124.9
C6—C5—H5A	108.5	C4—N1—H1N	124.9
C4—C5—H5B	108.5	C6—N2—C9	110.5 (2)
C6—C5—H5B	108.5	C6—N2—H2N	124.8
H5A—C5—H5B	107.5	C9—N2—H2N	124.8
N1—C1—C2—C3	0.5 (3)	C5—C6—C7—C8	-177.2 (2)
C1—C2—C3—C4	-0.1 (3)	C6—C7—C8—C9	-0.7 (3)
C2—C3—C4—N1	-0.4 (3)	C7—C8—C9—N2	1.1 (3)
C2—C3—C4—C5	178.4 (3)	C2—C1—N1—C4	-0.8 (3)
N1—C4—C5—C6	-170.1 (2)	C3—C4—N1—C1	0.7 (3)
C3—C4—C5—C6	11.2 (4)	C5—C4—N1—C1	-178.3 (2)
C4—C5—C6—N2	64.4 (3)	C7—C6—N2—C9	0.6 (3)
C4—C5—C6—C7	-118.6 (3)	C5—C6—N2—C9	178.2 (2)
N2—C6—C7—C8	0.1 (3)	C8—C9—N2—C6	-1.0 (3)

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the N1/C1–C4 and N2/C6–C9 rings, respectively.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1N···Cg1 ⁱ	0.88	2.53	3.357 (3)	156
N2—H2N···Cg2 ⁱⁱ	0.88	2.53	3.363 (3)	159

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