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3-(1*H*-Pyrrol-2-yl)-1*H*-pyrazole forms an unusual hydrogen-bonded two-dimensional (3,4)-connected net

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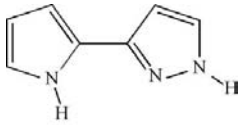
The title compound, $C_7H_7N_3$, is the first crystallographically characterized 1*H*-pyrrolyl-1*H*-pyrazole derivative and contains two unique molecules in its asymmetric unit ($Z' = 2$). These molecules associate into centrosymmetric tetramers through N—H···N hydrogen bonding, including a cyclic dimerization of one of the two unique pyrazole rings. These tetramers are linked further by two weaker N—H···π contacts to give a novel two-dimensional (3,4)-connected net with a $(3^2.8)_2(3.8^2)_2$ topology.

Comment

The 1*H*-pyrazole ring is an attractive synthon in inorganic supramolecular chemistry, since it possesses a metal-binding Lewis basic N-donor, and a Lewis acidic pyrrolic N—H group, in adjacent sites. A pyrazole ring can therefore bind a metal cation and anion simultaneously, and several 1*H*-pyrazole complexes have proved to be useful hosts for inorganic anions (Pérez & Riera, 2008). As part of our own investigations of the supramolecular chemistry of N—H pyrazole derivatives (Renard *et al.*, 2002, 2006; Liu *et al.*, 2004; Pask *et al.*, 2006; Jones *et al.*, 2006), we have achieved the first synthesis of the title compound, (I). Given the well known ability of pyrrole



(I)

derivatives to act as anion hosts in their own right (Sessler, Camiolo & Gale, 2003), the combination of pyrrole and pyrazole groups in (I) makes it a potentially useful reagent for supramolecular chemistry. The Cambridge Structural Database (CSD, Version of July 2009; Allen, 2002) contains no other 1*H*-pyrrolyl-1*H*-pyrazole derivatives, although protonated and *N*-methylated derivatives of 3,5-bis(pyrrol-2-yl)pyrazole have been crystallographically characterized (Maeda *et al.*, 2007).

The asymmetric unit of (I) contains two unique molecules, labelled *A* and *B* (Fig. 1). The molecules adopt essentially the same conformation, with the 3-substituted tautomer at the pyrazole ring and *syn*-pyrrole and pyrazole groups that are almost coplanar. The dihedral angle between the least-squares planes of the two heterocyclic rings is 4.57 (11)° for molecule *A* and 10.15 (7)° for molecule *B*. Molecules *A* and *B* associate through the N6*B*—H6*B*···N2*A* hydrogen bond between the pyrrole group of molecule *A* and the pyrazole ring of molecule *B* (Fig. 1). Molecule *B* then forms a hydrogen-bonded dimer with its symmetry equivalent related by the inversion centre at $(0, 0, \frac{1}{2})$, their pyrazole rings forming a cyclic dimer through the N1*B*—H1*B*···N2*B*^{iii} interaction [symmetry code: (iii) $-x, -y, 1 - z$] and its symmetry equivalent (Fig. 1). This cyclic dimer motif is common in crystalline pyrazoles substituted at the C3 and/or C5 positions (Claramunt *et al.*, 2006). It is noteworthy that (I) does not adopt the alternative supramolecular dimer motif that is often exhibited by crystalline (1*H*-pyrrol-2-yl)-aldimines (Fig. 2; see *e.g.* Franceschi *et al.*, 2001; Sessler,

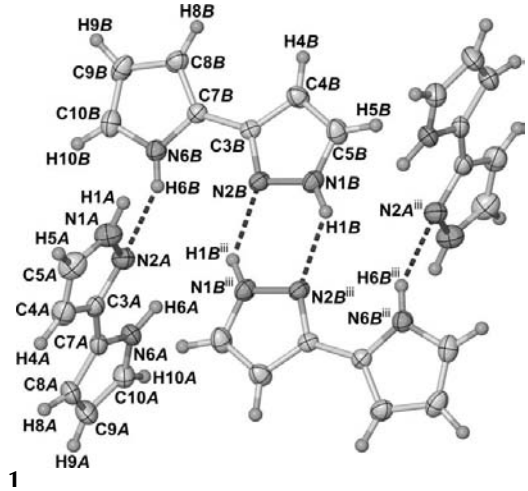


Figure 1
A view of the centrosymmetric hydrogen-bonded tetramer in the crystal structure of (I), showing the atom-numbering scheme employed. The additional intermolecular N—H···π interactions linking these tetramers into a two-dimensional network are not shown. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (iii) $-x, -y, 1 - z$.]

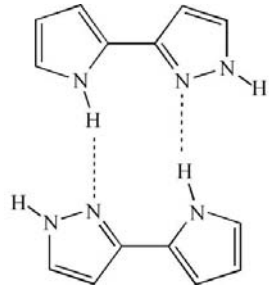


Figure 2
Alternative dimer structure which could have been adopted by (I), based on the cyclic dimer motif exhibited by (1*H*-pyrrol-2-yl)aldimines (Munro *et al.*, 2006).

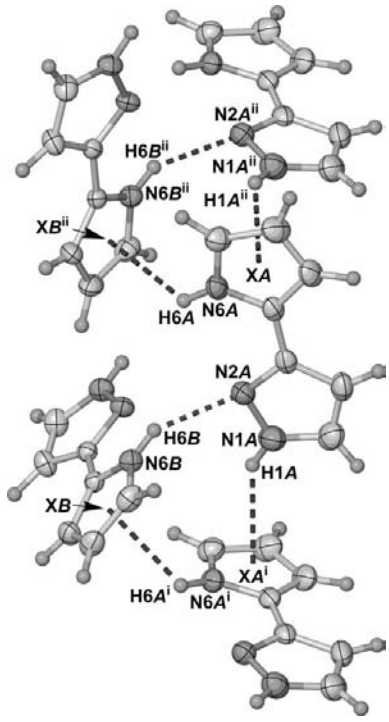


Figure 3
View of the intermolecular environment about molecule *A*, showing the N—H···N and N—H···π interactions. See Fig. 1 for the full atom-numbering scheme. [Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.]

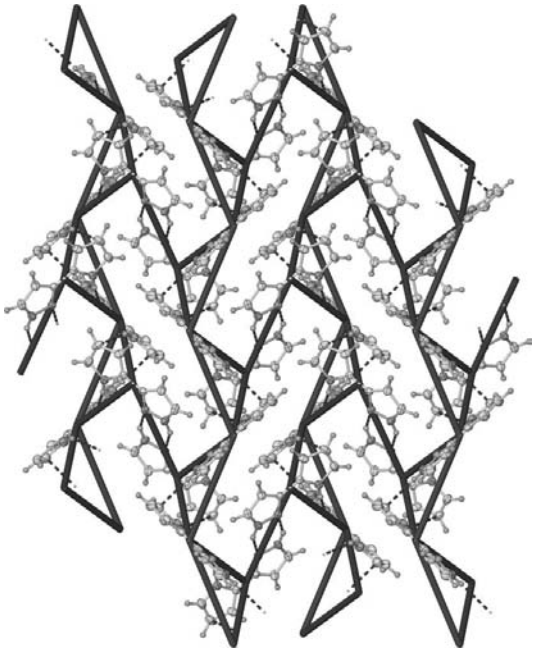


Figure 4
The topology of the $(3.8^2)_2(3^2.8^2)_2$ net formed by the intermolecular N—H···N and N—H···π hydrogen bonds in (I). The view is parallel to the $(10\bar{1})$ plane, with the *b* axis horizontal. The intermolecular links are between the centroids of each molecule.

Berthon-Gelloz *et al.*, 2003; Matsui *et al.*, 2004; Munro *et al.*, 2006; Carabineiro *et al.*, 2007; Wang *et al.*, 2007).

The two N—H groups in molecule *A* form intermolecular N—H···π contacts to the two unique pyrrole rings; these are N1*A*—H1*A*···*XA*^{i} and N6*A*—H6*A*···*XB*^{ii} [symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$], where *XA* and *XB* are the centroids of the pyrrole rings of molecules *A* and *B*, respectively (Fig. 3 and Table 1). The H···π distances (2.55 and 2.68 Å, respectively) are longer than the N—H···N hydrogen bonds in the structure, but still 0.2–0.4 Å shorter than the sum of the van der Waals radii of an aromatic group and an H atom (Pauling, 1960). In total, molecule *A* forms N—H···N or N—H···π contacts to four other adjacent molecules, while molecule *B* is connected to three neighbours. These interactions combine to give a puckered two-dimensional (3,4)-connected network running parallel to the crystallographic $(10\bar{1})$ plane. The topology of the network is $(3.8^2)_2(3^2.8^2)_2$ in the short Schläfli notation (Fig. 4). While several different two-dimensional (3,4)-connected nets have been reported before, to our knowledge, this example is new. The most common topology of this type in molecular crystals is $(4.6^2)(4^2.6^2.8^2)$, which has been observed on at least five previous occasions (Zhong *et al.*, 2001; Zheng *et al.*, 2004; Xu *et al.*, 2006; Xue *et al.*, 2008; Li *et al.*, 2008). Other known (3,4)-connected two-dimensional networks in metal–organic stuctures include $(3.8^2)(4^2.8^2)$ (Zhong *et al.*, 2008), $(4^2.6)(4^2.6^4)$ (Qi *et al.*, 2008) and the V_2O_5 net $(4^2.6)(4^2.6^3.8)$ (Li *et al.*, 2009).

Experimental

Compound (I) was prepared following the procedure of Lin & Lang (1977). A solution of 2-acetylpyrrole (20 g, 0.18 mol) in dimethylformamide dimethyl acetal (100 g, 0.84 mol) was refluxed under N_2 for 48 h. Evaporation of the solvent gave a dark-brown solid residue that was purified by dissolution in CH_2Cl_2 and filtration through a silica plug. Pure 3-dimethylamino-1-(1*H*-pyrrol-2-yl)prop-2-en-1-one was obtained from the resultant solution as a yellow solid by addition of ethyl acetate. A solution of this intermediate (12 g, 0.073 mol) and hydrazine monohydrate (25 g, 0.50 mol) in methanol (200 ml) was refluxed for 6 h. The reaction was quenched with water and the solution extracted with CH_2Cl_2 (3 × 100 ml). Evaporation of the extracts to dryness yielded an orange oil which slowly solidified upon storage at 253 K. Two further recrystallizations from CH_2Cl_2–hexanes (3:1 *v*/*v*) afforded analytically pure yellow crystals of (I) (yield 5.5 g, 57%), one of which was used for analysis. Analysis found: C 62.9, H 5.3, N 31.5%; calculated for $C_7H_7N_3$: C 63.1, H 5.3, N 31.6%. ^{1}H NMR [$(CD_3)_2SO$, 298 K]: δ 6.09 (*d*, *J* = 2.6 Hz, 1H), 6.41 (*s*, 1H), 6.47 (*d*, *J* = 2.0 Hz, 1H), 6.79 (*d*, *J* = 1.3 Hz, 1H), 7.62 (*s*, 1H), 11.14 (*br s*, 1H), 12.72 (*br s*, 1H); EI MS *m*/*z*: 133.0 ([*M*]$^+$), 104.0 ([*M*—N_2]$^+$).

Crystal data

$C_7H_7N_3$
M_r = 133.16
Monoclinic, $P2_1/n$
a = 10.442 (2) Å
b = 13.004 (2) Å
c = 10.8849 (19) Å
β = 111.119 (9)°
V = 1378.7 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 150 K
0.18 × 0.15 × 0.09 mm

Data collection

Bruker X8 APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.795, T_{max} = 0.925
17932 measured reflections
3601 independent reflections
2789 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

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

XA and *XB* are the centroids of the pyrazole rings of molecules *A* and *B*, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*A*···*XA*^{i}	0.90 (2)	2.55 (2)	3.31	143
N6*A*—H6*A*···*XB*^{ii}	0.911 (16)	2.68	3.32	127
N1*B*—H1*B*···N2*B*^{iii}	0.892 (15)	2.193 (15)	2.9512 (15)	142.5 (13)
N6*B*—H6*B*···N2*A*	0.880 (16)	2.204 (16)	2.9952 (16)	149.3 (13)

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	237 parameters
$wR(F^2) = 0.111$	All H-atom parameters refined
$S = 1.02$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
3601 reflections	$\Delta\rho_{min} = -0.18$ e Å^{-3}

The pyrrole and pyrazole rings in molecules *A* and *B* were distinguished by the isotropic displacement parameters of atoms N1 and C10, by the absence of an H atom on atom N2 in the Fourier map, and by the short hydrogen bonds accepted by both pyrazole N2 atoms. All H atoms were located in a difference Fourier map and allowed to refine freely. The refined C—H distances are in the range 0.952 (17)–1.001 (15) Å and the N—H distances are in the range 0.880 (16)–0.911 (16) Å.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: local program.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3214). Services for accessing these data are described at the back of the journal.

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