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4-(Pyrrol-1-yl)-1,2,4-triazole

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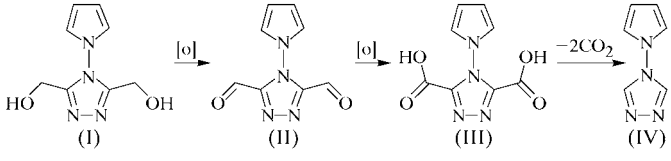
The asymmetric unit of the title compound, $C_6H_6N_4$, comprises one and a half molecules with a C_2 axis through the second molecule. Each molecule consists of two planar five-membered rings connected by a triazole–pyrrole N—N bond with the triazole ring close to being at right angles to the pyrrole ring. The molecules are linked by C—H···N hydrogen bonds and weaker offset face-to-face π–π interactions.

Comment

1,2,4-Triazole derivatives are a class of organic heterocyclic molecules which are of interest for two main reasons. Firstly, they often show biological, such as antifungal, activity (Sweetman & Martindale, 2005); secondly, their iron(II) complexes often exhibit spin crossover behaviour (Klingele, Moubaraki, Cashion, Murray & Brooker, 2005; Haasnoot, 2000; Kahn, 1999). Our interest lies in the latter area, and we have been actively developing synthetic routes to carefully designed triazole ligands (Beckmann *et al.*, 2003; Depree *et al.*, 2003; Klingele & Brooker, 2004; Klingele, Moubaraki, Murray & Brooker, 2005; Brandt *et al.*, 2007) for the purpose of accessing novel spin crossover materials (Klingele, Moubaraki, Cashion, Murray & Brooker, 2005). As part of this study, we decided to attempt to oxidize the dialcohol (I) (see scheme) that we had prepared earlier (Klingele, Moubaraki, Murray & Brooker, 2005) to the dialdehyde (II) using manganese dioxide. As the dialcohol is not very soluble, the reaction was carried out in refluxing 1,4-dioxane rather than at room temperature. Instead of the dialdehyde (II), compound (IV) as presented here was obtained in high yield.



Compound (IV) has been deliberately prepared previously as part of a study of heterocyclic cations and anions (Katritzky & Suwinski, 1974), as a precursor for the preparation of *N*-cyanamidoimines (Olofson & Pepe, 1979) and for comparison with other heterocyclic compounds (De Mendoza *et al.*, 1980). In these deliberate preparations it was made by the simple reaction of 4-amino-1,2,4-triazole with 2,5-diethoxytetrahydrofuran in acetic acid. Our accidental synthesis of (IV) from (I) is presumed to have occurred (see scheme) *via* a combination of over-oxidation, 'beyond' (II) to the dicarboxylic acid (III), followed by double decarboxylation, leaving 3,5-unsubstituted (IV). The decarboxylation of acid-substituted triazole rings was first reported in 1907 (Curtius *et al.*, 1907) and a mechanism proposed later (Dyson & Hammick, 1937). The only other structurally characterized (uncoordinated) compound featuring a triazole–pyrrole N—N connection between a 1,2,4-triazole and a pyrrole ring is 3,5-di-2-pyridyl-N^4-(pyrrol-1-yl)triazole (Mandal *et al.*, 1993; Klingele *et al.*, 2006).

The asymmetric unit comprises one and a half molecules, as a C_2 axis runs through the second molecule (Figs. 1 and 2, and Table 1). Each molecule consists of two planar five-membered rings, *viz.* one triazole ring and one pyrrole ring, connected by an N—N bond. In both cases, the triazole ring is almost at right angles to the pyrrole ring [the interplanar angles are 82.43 (8) and 74.41 (7)°]. The formulation of (IV) is therefore confirmed to be as shown in the scheme. Within experimental error, the bond lengths and angles in the two independent molecules are identical (Table 1). Likewise, the intra-ring torsion angles of the pairs of analogous rings are identical, although the inter-ring torsion angles differ (Table 1).

The bond lengths and angles in the triazole rings (Table 1) are within 0.012 Å of those seen in 4,4′-bitriazole (Domiano, 1977). The bond lengths in the pyrrole rings (Table 1) are within 0.007 Å of those seen in 1*H*-pyrrole (Allen *et al.*, 1987). The triazole–pyrrole N—N bond lengths (Table 1) are intermediate between those expected for an N—N single bond (1.425 Å) and an N—N double bond (1.240 Å) (Allen *et al.*, 1987), indicating that some delocalization is occurring. The N—N inter-ring bond length observed in (IV) is identical to that in 4,4′-bitriazole (1.380 Å; Domiano, 1977).

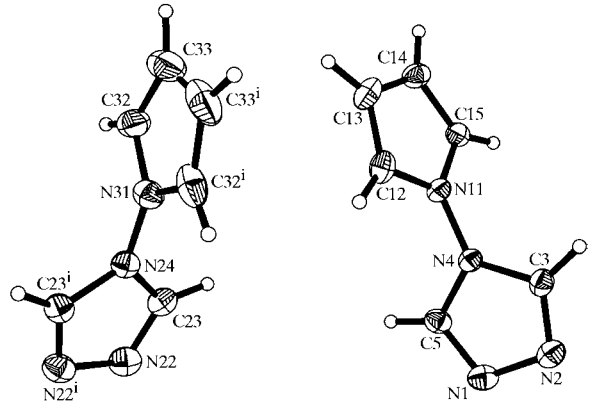


Figure 1
The molecular structure and atom-numbering scheme for the two molecules of (IV), with displacement ellipsoids drawn at the 50% probability level and H atoms shown as spheres of arbitrary radii. [Symmetry code: (i) $-x, y, -z+\frac{3}{2}$.]

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Weak offset face-to-face π–π interactions (Hunter & Sanders, 1990; Janiak, 2000) with a centroid–centroid distance of 3.507 (2) Å and an angle of 20.2 (1)° between the mean planes, are present between each of the N22/C23/N24/C23^{i}/N22^{i} triazole rings [symmetry code: (i) $-x, y, -z+\frac{3}{2}$], leading to stacking of these triazole rings along the *c* axis, as shown in Fig. 2. The other triazole ring and the pyrrole rings are not involved in such π–π interactions.

There are three significant C—H···N interactions (Steiner, 1998; Desiraju & Steiner, 1999), all of which are intermolecular (Table 2 and Fig. 2). One of these provides further connections between the adjacent symmetry-generated offset π–π stacked (along the *c* axis) N22-triazole rings. The remaining two C—H···N interactions link the other independent set of molecules, those containing N1, to their symmetry-related sets of neighbouring N1 molecules, generating ribbons along the *b* axis. The N22-triazole rings lie between the ribbons of N1-triazole rings.

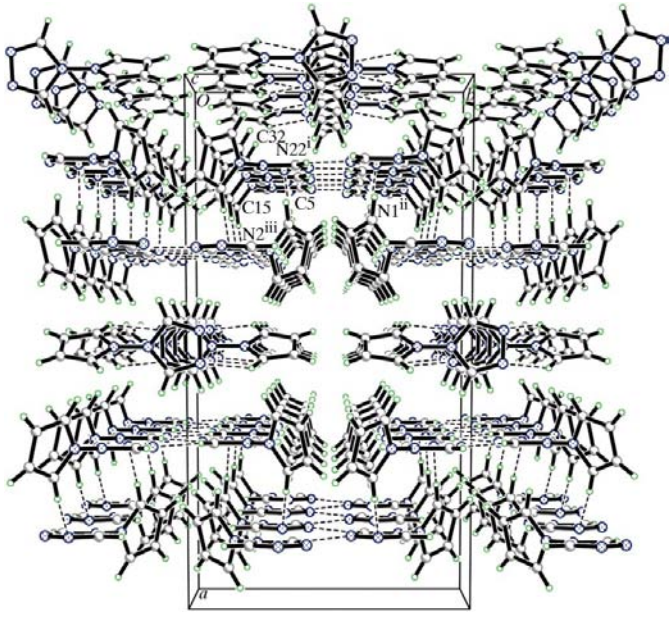

Figure 2
The crystal packing of (IV), viewed down the *c* axis. The intermolecular C—H···N interactions are shown (dashed lines). The stacks of offset face-to-face N22/C23/C24/C23^{i}/N22^{i} triazole rings, weakly π–π stacked along the *c* axis, can be clearly seen as these triazole rings are almost perpendicular to the *c* axis. See Tables 1 and 2 for symmetry codes.

Experimental

To a partially dissolved mixture of 3,5-bis(hydroxymethyl)-4-(pyrrol-1-yl)-1,2,4-triazole (2.00 g, 10.3 mmol) in dry 1,4-dioxane (1200 ml, freshly distilled from sodium metal) was added manganese dioxide (10.80 g, from Aldrich). The resulting brown suspension was refluxed for 4 h and then filtered through a pad of Celite on a glass sinter. The filtrate was collected and evaporated to dryness *in vacuo*, yielding 1.40 g (7.35 mmol, 71%) of an off-white crystalline solid. Single crystals were grown by slow evaporation of an acetone solution of the solid (m.p. 408 K). For other details, see supplementary data.

Crystal data

$C_6H_6N_4$
M_r = 134.15
Monoclinic, $C2/c$
a = 22.9326 (11) Å
b = 12.1235 (6) Å
c = 7.0111 (3) Å
β = 96.707 (2)°
V = 1935.91 (16) Å^3
Z = 12
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 93 (2) K
0.5 × 0.3 × 0.1 mm

Data collection

Bruker Kappa-APEXII area-detector diffractometer
Absorption correction: multi-scan (*SCALE*; Bruker, 2004)
T_{min} = 0.834, T_{max} = 1.000
20165 measured reflections
1997 independent reflections
1834 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.089
S = 1.10
1997 reflections
173 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.4056 (15)	N22—N22^{i}	1.408 (2)
N4—N11	1.3802 (13)	N24—N31	1.375 (2)
C3—N4—N11—C15	75.14 (16)	C23—N24—N31—C32	82.73 (9)
C5—N4—N11—C12	74.08 (16)		

Symmetry code: (i) $-x, y, -z+\frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···N1^{ii}	0.942 (16)	2.353 (16)	3.2479 (16)	158.6 (12)
C15—H15···N2^{iii}	0.955 (15)	2.521 (15)	3.4261 (16)	158.3 (11)
C32—H32···N22^{ii}	0.926 (18)	2.528 (18)	3.325 (2)	144.3 (14)

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

The coordinates and U_{iso}(H) values for the H atoms were freely refined [C—H = 0.923 (16)–0.978 (15) Å].

Data collection: *SMART* (Bruker, 2004); cell refinement: *SMART* and *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2004); software used to prepare material for publication: *enCIFer* (Version 1.2; Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3049). Services for accessing these data are described at the back of the journal.

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