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The crystal structure of 3,5-bis(propan-2-yl)-1*H*-pyrazol-4-amine, $C_9H_{17}N_3$

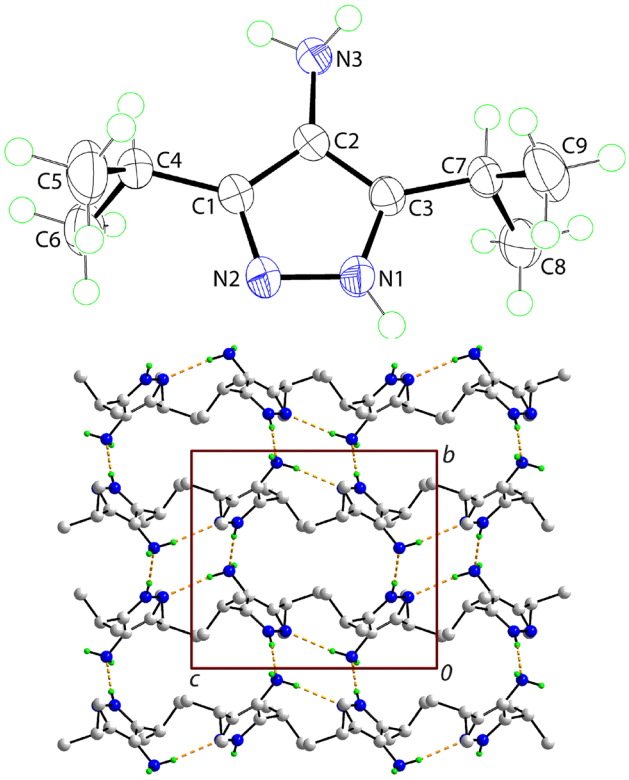

Table 1: Data collection and handling.

Crystal:	Prism, colourless
Size:	0.19 × 0.07 × 0.04 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.07 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB P200, ω-scans
θ_{max}, completeness:	29.8°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15975, 2582, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2127
$N(param)_{refined}$:	122
Programs:	CrysAlis^{PRO} [1], SIR2014 [2], SHELX [3], WinGX and ORTEP [4]

V = 976.75(5) Å^3, Z = 4, $R_{gt}(F)$ = 0.0432, $wR_{ref}(F^2)$ = 0.1223, T = 178(2) K.

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The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Abstract

$C_9H_{17}N_3$, monoclinic, $P2_1/c$ (no. 14), a = 9.5601(3) Å, b = 9.5210(3) Å, c = 10.7651(3) Å, β = 94.564(3)°,

Source of material

To iron powder (0.9995 g, 17.9 mmol) in degassed ethanol (5 mL) was added gradually and drop wise a mixture of 3,5-di-isopropyl-4-nitropyrazole (1.0068 g, 5.10 mmol), prepared as in the literature [5] in degassed ethanol (30 mL) and NH_4Cl (2.7458 g, 51.02 mmol) in degassed distilled water (15 ml). The solution was refluxed at 100 °C for 2 h. After cooling to room temperature, the obtained solution was filtered to remove an unknown black powder. Then, the solution was extracted with diethyl ether (10 mL × 4). The crystallisation was carried out from a mixture of diethylether and n-heptane (1:1 v/v) to yield pale needles with a red-brown tinge (0.4721 g, 2.82 mmol). The colourless crystals for the X-ray study were obtained by slow evaporation of a mixture of dichloromethane and n-heptane (1:1 v/v). Yield: 55%. Anal. Calcd. for $C_9H_{17}N_3$: C, 64.63; H, 10.25; N, 25.12%. Found: C, 64.55; H, 10.26; N, 24.91%. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 2.97 (sep, C(H), 2H, J = 7.0 Hz), 1.29 (d, CH_3, 12H, J = 7.0 Hz). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): δ 21.6 (C(H)), 25.3 (CH_3), 119.9 (pz-4C), 143.7 (pz-3C, pz-5C). **IR** (KBr, cm^{-1}):

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.47275 (10)	0.17033 (10)	0.68661 (9)	0.0249 (2)
H1N	0.5387 (12)	0.1081 (12)	0.6726 (12)	0.030*
N2	0.34837 (10)	0.17139 (10)	0.61700 (9)	0.0273 (2)
N3	0.31020 (9)	0.44672 (10)	0.84709 (8)	0.0222 (2)
H2N	0.3173 (13)	0.4205 (14)	0.9260 (8)	0.027*
H3N	0.2224 (10)	0.4731 (13)	0.8267 (12)	0.027*
C1	0.27106 (11)	0.27139 (12)	0.66664 (10)	0.0238 (2)
C2	0.34845 (11)	0.33464 (10)	0.76847 (9)	0.0198 (2)
C3	0.47736 (11)	0.26740 (11)	0.77825 (9)	0.0212 (2)
C4	0.12207 (11)	0.29831 (14)	0.61499 (11)	0.0301 (3)
H4	0.081467	0.372650	0.667019	0.036*
C5	0.03294 (14)	0.16496 (17)	0.62323 (13)	0.0431 (3)
H5A	0.070151	0.091008	0.571784	0.065*
H5B	−0.064370	0.185392	0.593106	0.065*
H5C	0.036147	0.133383	0.710054	0.065*
C6	0.11468 (14)	0.35035 (14)	0.48039 (12)	0.0366 (3)
H6A	0.170408	0.436328	0.475910	0.055*
H6B	0.016829	0.370069	0.451578	0.055*
H6C	0.152060	0.278028	0.427345	0.055*
C7	0.60226 (11)	0.28694 (12)	0.87017 (10)	0.0257 (2)
H7	0.581459	0.367367	0.925529	0.031*
C8	0.73342 (13)	0.32456 (17)	0.80541 (13)	0.0414 (3)
H8A	0.756801	0.247188	0.750701	0.062*
H8B	0.811805	0.340683	0.868127	0.062*
H8C	0.715946	0.409972	0.755792	0.062*
C9	0.62567 (17)	0.15707 (14)	0.95224 (13)	0.0421 (3)
H9A	0.541606	0.139126	0.996286	0.063*
H9B	0.706024	0.172837	1.012992	0.063*
H9C	0.644398	0.075841	0.900173	0.063*

3374(s) & 3140(vs) ν(N—H); 2965(vs), 2929(s) & 2865(s) ν(C—H); 1599(s) ν(C = N).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.98–1.00 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C). The N-bound H atoms were located from a difference map and refined with N—H = 0.88 ± 0.01 Å and with U_{iso}(H) = 1.2U_{eq}(N). Owing to poor agreement, one reflection affected by the beam-stop, i.e. (1 0 0), was removed from the final cycles of refinement.

Discussion

Pyrazole, a five-membered heterocycle containing two adjacent nitrogen atoms, is one of the more useful motifs found in many small molecules with a wide range of agricultural and pharmaceutical activities [6]. Therefore, the functionalisation of the pyrazole scaffold is an attractive research area with much work accomplished over the last few decades. Moreover, along with metal-organic frameworks [7], covalent organic frameworks (COF's) are now recognised as being of considerable interest [8, 9]. One way of generating covalent bonds in COF's, is to employ Schiff base reactions, that is, a reaction between a primary amine with an aldehyde or a ketone under specific conditions. These a very effective reactions and appropriately substituted pyrazoles functionalised with primary amines can be employed for the construction of COF's [9]. In this context and from a modified literature method [5, 10], it was possible to obtain 3,5-diisopropyl-4-nitropyrazole in ca 75% yield by a nitration reaction with a mixed acid solution of conc. H_2SO_4/conc. HNO_3 (3/1 v/v). The title pyrazole, (I), was then obtained by the reduction of the aforementioned nitro precursor with iron powder/NH_4Cl in ca. 50% yield following a modified synthetic procedure [11].

The molecular structure of (I) is shown in the upper view of the figure (70% displacement ellipsoids). The pyrazole ring is planar with the r.m.s. deviation of the five atoms comprising the ring being only 0.003 Å with the maximum deviations out of the plane being ±0.003 Å for the N1 and N2 atoms, respectively. The observed planarity of the five-membered ring along with the near equivalence of the C1—N2 [1.3421(14) Å] and C3—N1 [1.3499(13) Å] bond lengths, and of the C1—C2 [1.4080(14) Å] and C2—C3 [1.3853(14) Å] bonds, are consistent with substantial delocalisation of π-electron density in the pyrazole ring. The N1—N2 [1.3541(13) Å] bond lengths reflects this observation also. Finally, the exocyclic C2—N3 [1.4276(13) Å] bond is considerably longer than the endocyclic C—N bonds.

There are only three related crystal structures in the literature available for comparison, which reflects the novelty of (I) functionalised with an amine group [10]. The most closely related structure to (I) is in fact the synthetic precursor to (I), which has a nitro group instead of the amine group [5, 10]. Here, the nitro substituent is close to co-planar with the pyrazole ring, forming a dihedral angle of 5.2(5)°. In the t-butyl analogue of the aforementioned [10], the nitro group is twisted out of the plane through the pyrazole ring, forming a dihedral angle of 48.08(11)°. The third structure worthy of mention is the nitroso-substituted analogue of the previous structure where both components of the disordered nitroso group lie approximately in the plane of the ring [12].

A standard analysis of the molecular packing was conducted by employing PLATON [13], which indicated the key role of conventional hydrogen bonding in arranging the molecules into supramolecular layers in the *bc*-plane. A view of the layer is shown in the lower part of

the figure whereby the highly directional pyrazole–N1—H1n···N3(amine) [N1—H1n···N3^{i}: H1n···N3^{i} = 2.131(12) Å, N1···N3^{i} = 3.0149(13) Å with angle at H1n = 174.5(11)° for symmetry operation (i): 1 – *x*, –1/2 + *y*, 3/2 – z] and amine–N3···N2(pyrazole) [N3—H2n···N2^{ii}: H2n···N2^{ii} = 2.233(10) Å, N3···N2^{ii} = 3.1099(13) Å with angle at H2n = 172.5(11)° for (ii): *x*, 1/2 – *y*, 1/2 + *z*] hydrogen bonds connect molecules. The result of these hydrogen bonds is the formation of 10-membered $\{\cdots HN\cdots HNN\}_2$ synthons. There is no apparent role for the amine–H3n atom in directional intermolecular interactions. Indeed, the layers stack along the *a*-axis without directional interactions between them largely owing to the observation that the iso-propyl groups project out of and to either side of the two-dimensional array.

A further analysis of the molecular packing was conducted employing CrystalExplorer [14] following standard methods [15]. The absence of directional interactions between molecules along the a-axis is reflected in the significant contribution to the calculated Hirshfeld surface by H···H contacts which amounts to a rather high 79.9%. The next most significant contribution arise from N···H/H···N contacts [15.3%], in part reflecting the N—H···N hydrogen bonding within the layers, and from C···H/H···C contacts [4.7%].

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