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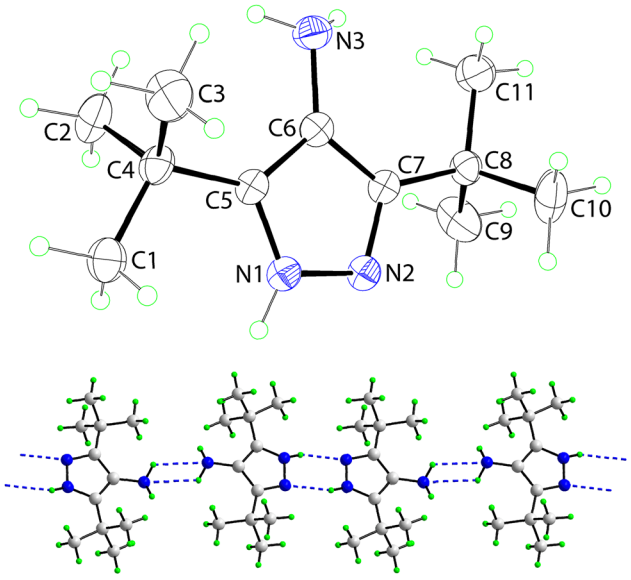
Crystal structure of 3,5-bis(*t*-butyl)-1*H*-pyrazol-4-amine, $C_{11}H_{21}N_3$



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Abstract

$C_{11}H_{21}N_3$, monoclinic, $P2_1/c$ (no. 14), a = 11.2439(9) Å, b = 9.7110(6) Å, c = 11.9008(9) Å, β = 112.832(9)°, V = 1197.63(17) Å^3, Z = 4, $R_{gt}(F)$ = 0.0775, w$R_{ref}(F^2)$ = 0.2318, T = 178 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.39 × 0.24 × 0.17 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	0.07 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB P200, ω scan
θ_{max}, completeness:	27.5°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8,825, 2,739, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1971
$N(param)_{refined}$:	158
Programs:	CrysAlis^{PRO},[1] Il Milone[2], SHELX[3], WinGx[4]

1 Source of material

The synthesis of (I) was accomplished in a three-step process. **LHpzH**, 3,5-bis(*t*-butyl)-1*H*-pyrazole, was obtained by a modified literature method,[5] by the reaction of 2,2,6,6-tetramethyl-3,5-heptanedione (10.0 g, 54.3 mmol) with hydrazine monohydrate (8.8 mL, 181 mmol, 3.3 equiv.) in ethanol (35 mL) at 373 K for 8 h. After the reaction, the solution was dried under vacuum. Crystallization was carried out at 273 K from dichloromethane solution to yield colourless crystals (8.71 g, 48.3 mmol, 89 % yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.30 (s, 18H, C(CH_3)$_3$), 5.90 (s, 1H, pz-4*H*), amine-NH not observed. IR (KBr, cm^{-1}): 3234 s ν(N–H), 2966 s ν(C–H), 2904 s ν(C–H), 2866 s ν(C–H), 1570 s ν(C=N). **LNO$_2$pzH**, 3,5-bis(*t*-butyl)-1*H*-pyrazol-4-nitro, was obtained by a modified literature method.[6] The nitration reaction of LHpzH (5.00 g, 27.7 mmol) was achieved using a mixture of concentrated nitric acid (8 mL) and concentrated sulfuric acid (18 mL). After heating at 373 K for 3 h, the cooled reaction mixture was neutralised with sodium hydroxide solution. After the filtration of the precipitated yellow-white powder, the obtained powder was carefully washed with distilled water. Crystallization from dichloromethane solution at 273 K yielded pale-yellow crystals (4.38 g 19.4 mmol, 70 % yield). Anal. calcd. for $C_{11}H_{19}N_3O_2$: C 58.64, H 8.50, N 18.65 %. Found: C 58.43, H 8.68, N 18.70 %. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.40 (s, 18H, C(CH_3)$_3$), NH not observed. IR (KBr, cm^{-1}): 3288 s ν(N–H), 2965 s ν(C–H), 2932 s ν(C–H), 2872 s ν(C–H), 1561 s ν(C=N). **LNH$_2$pzH** 3,5-bis(*t*-butyl)-1*H*-pyrazol-4-amine (I), was obtained by a hydrogenation reaction with palladium on carbon (10 %) catalyst under H_2 (1 atm). After drying, LNO_2pzH (1.00 g, 4.44 mmol) and Pd/C catalyst (1.0 g) were

suspended in methanol (30 mL), and the atmosphere was changed from Ar to H_2. The reaction was performed for 45 h at room temperature. The obtained reaction mixture was filtered through Celite to remove undissolved solids. The filtrate was crystallized at 243 K to yield a colourless powder (0.54 g, 2.76 mmol, 62 % yield). Crystals suitable for single crystal analysis were obtained from its methanol solution held at 243 K. Anal. calcd. for $C_{11}H_{21}N_3{\cdot}1/3(H_2O)$ (bulk material): C 65.63, H 10.85, N 20.87 %. Found: C 65.86, H 10.84, N 20.64 %. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 1.30 (s, 18H, C(CH_3)$_3$), NH not observed. **IR** (KBr, cm^{-1}): 3424 s ν(NH_2), 3284 s ν(N–H), 2962 s ν(C–H), 2930 s ν(C–H), 2867 s ν(C–H), 1577 s ν(C=N).

2 Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.98 Å) and refined as riding with U_{iso} (H) = 1.5U_{eq} (C). The coordinates of the N-bound H atom were refined freely and with U_{iso} (H) = 1.2U_{eq} (N). Near the conclusion of the refinement, three residual electron density peaks, in positions rotated by approximately 60° to the C8-*t*-butyl group were evident. These were refined isotropically. The second orientation of the C8-*t*-butyl group converged with a site occupancy = 0.151(6). Owing to poor agreement, one reflection, i.e. (–1 3 3), was omitted from the final cycles of refinement.

3 Discussion

The functionalisation of pyrazole, an important five-membered heterocycle containing two adjacent nitrogen atoms, is an attractive research area with much work accomplished over the last few decades. Recent work has focussed upon incorporating an amino group as a functional substituent in the ring. Thus, the structure of 3,5-bis(propan-2-yl)-1*H*-pyrazol-4-amine (II) (denoted as L1NH_2pzH)[7] and its cobalt dichlorido complex [$CoCl_2$(L1NH_2pzH)$_2$][8] were reported recently. Herein, the synthesis and structure of the title pyrazole, 3,5-bis(*t*-butyl)-1*H*-pyrazol-4-amine, LNH_2pzH, (I), with more bulky *tert*-butyl substituents in the 3- and 5-positions of the pyrazolyl ring, are described.

After the nitration reaction of LHpzH with a mixture of concentrated nitric acid and concentrated sulfuric acid, the known compound LNO_2pzH was obtained in 70 % yield.[6] The hydrogenation reaction of LNO_2pzH with palladium on carbon (10 %) catalyst under an H_2 (1 atm) atmosphere yielded a colourless powder of LNH_2pzH in 62 % yield. The related compound (II) was also obtained from L1NO_2pzH by the hydrogenation reaction with palladium on carbon (10 %) catalyst in 76 % yield and also through reduction of L1NO_2pzH by iron powder/NH_4Cl.[7]

The IR spectrum of (I) features a characteristic absorption band at 3424 cm^{-1}, assigned to amine–NH_2 stretching and a strong absorption band at 3284 cm^{-1} is assigned to pyrazolyl-N-H stretching. The expected signal in the ^{1}H NMR spectrum of (I) was 1.37 ppm (methyl-H), which was shifted compared to those of the precursors, LNO_2pzH, at 1.40 ppm, and LHpzH, at 1.30 ppm. The solid-state structure determination of (I) was achieved through X-ray crystallography.

The molecular structure of (I) is illustrated in the upper view of the figure (35 % displacement ellipsoids; the disorder component of the C8-*t*-butyl group is omitted for clarity). The molecule comprises a planar pyrazolyl ring with the maximum deviation from the least-squares plane being 0.005(2) Å for the N2 atom; the amine-N3 atom lies 0.030(3) Å out of the plane. An amine group is bound at the ring-C6 position and the *t*-butyl groups are connected at the C5 and C7 positions. The confirmation of protonation at the pyrazolyl-N1 atom is manifested by the significantly wider angle at the N1 atom compared with the N2 atom, i.e. C5–N1–N2 = 111.28(19)° cf. C7–N2–N1 = 106.98(18)°. Significant delocalisation of π-electron density over the five-membered ring is indicated by the experimental equivalence of the N1–C5 and N2–C7 [1.336(3) and 1.339(3) Å] and of the C5–C6 and C6–C7 [1.394(3) and 1.400(3) Å] bond lengths. The same conclusions are made for the methyl[9] and *i*-propyl[7] analogues. The N1–N2 and C6–N3 bond lengths in (I) are 1.353(3) and 1.419(3) Å, respectively.

In the molecular packing, supramolecular chains aligned along [1 0 1] feature N–H···N hydrogen-bonding interactions, see the lower view of the figure. Thus, a pair pyrazolyl-N–H···N(pyrazolyl) hydrogen bonds [N1–H1···N2^i: H1···N2^i = 2.10(2) Å, N1–N2^i = 2.902(3) Å with angle at H1n = 152.5(18)° for symmetry operation i: 1-x, 2-y, -z] assemble over a centre of inversion to form a six-membered {···HNN}$_2$ synthon. Similarly, a pair amine-N–H···N(amine) hydrogen bonds [N3–H2···N3^{ii}: H2…N3^{ii} = 2.53(3) Å, N3···N3^{ii} = 3.051(3) Å with angle at H2n = 119(2)° for ii: 2-x, 2-y, 1-z] assemble over a centre of inversion to form a four-membered {···HN}$_2$ synthon. The linear chains are connected into a three-dimensional architecture by methyl-C–H···π(pyrazolyl) interactions [C1–H1···Cg(N1,N2,C5–C7)^{iii}: H1···Cg(N1,N2,C5–C7)^{iii} = 2.59 Å; C···Cg(N1,N2,C5–C7)^{iii} = 3.545(3) Å with angle at H1a = 166° for iii: 1-x, –1/2+y, 1/2-z] which occur about a 2_1 screw axis aligned along the b-axis. There is no apparent role in the molecular packing for the amine-H3n atom.

The molecular packing pattern in (I) contrasts those observed in the crystals of the methyl[9] and i-propyl[7]

derivatives. In the former, a three-dimensional architecture features N–H···N hydrogen bonds operating in three-dimensions as each donor/acceptor site participates in at least one N–H···N hydrogen bond.[9] In the crystal of the *i*-propyl derivative, supramolecular layers feature N–H···N hydrogen bonds but one of the amine-H atoms does not participate in a directional intermolecular contact,[7] as in the crystal of (I).

Finally, an analysis of the nature of and relative contributions to the calculated Hirshfeld surfaces and two-dimensional fingerprint plots in the crystals of (I) and the *i*-propyl and methyl derivatives was undertaken employing CrystalExplorer[10] and standard procedures.[11] For the methyl species, calculations were performed on each of the disorder (60° degree rotation for one of the methyl groups) and the reported percentages are average values. For the *t*-butyl derivatives, only the major component of the disordered *t*-butyl group was considered. In each crystal there are only three types of surface contacts evident, namely H···H, N···H/H···N and C···H/H···C contacts. These were found to systematically follow trends in accord with the number of hydrogen atoms in the molecule. Thus, H···H contacts increased in the order of the methyl to *i*-propyl to *t*-butyl derivatives, viz. 61.5, 79.9 and 83.9 %, respectively. Consequently, the percentage contributions from the N···H/H···N (25.5, 15.3 and 12.2 %, respectively) and C···H/H···C (13.0, 4.7 and 3.9 %, respectively) diminished passing from the methyl to *i*-propyl to *t*-butyl.

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