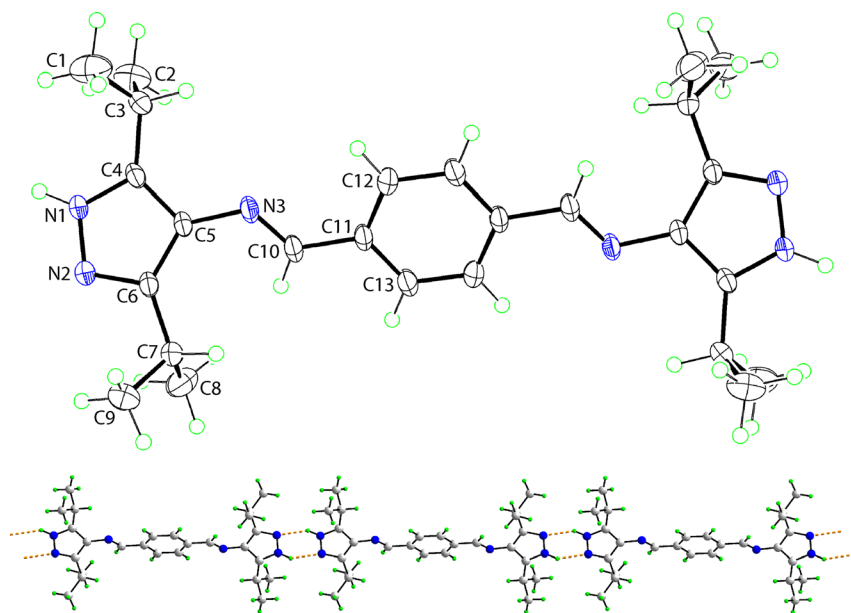


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Crystal structure of $[N(E),N'(E)]$ - N,N' -(1,4-phenylenedimethyldiyn)bis-3,5-bis(propan-2-yl)-1*H*-pyrazol-4-amine, $C_{26}H_{36}N_6$



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Abstract

$C_{26}H_{36}N_6$, triclinic, $P\bar{1}$ (no. 2), $a = 5.7137(2)$ Å, $b = 10.4374(3)$ Å, $c = 11.1141(3)$ Å, $\alpha = 104.980(3)^\circ$, $\beta = 94.279(3)^\circ$, $\gamma = 93.876(3)^\circ$, $V = 635.89(3)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0503$, $wR_{ref}(F^2) = 0.1220$, $T = 178$ K.

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The molecular 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.

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	$0.07 \times 0.06 \times 0.01$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.07 mm^{-1}
Diffractionmeter, scan mode:	Rigaku XtaLAB P200, ω
θ_{max} , completeness:	29.5° , >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	21,711, 3240, 0.053
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2113
$N(\text{param})_{\text{refined}}$:	152
Programs:	CrysAlis ^{PRO} [1], IL MILIONE [2], SHELX [3], WinGX/ORTEP [4]

1 Source of material

Under an argon atmosphere, the reaction of 4-amino-3,5-diisopropyl-1-pyrazole (0.1004 g, 0.600 mmol) with terephthalaldehyde (0.0439 g, 0.327 mmol) in anhydrous methanol (10 mL) was conducted at room temperature for four days. The solvent was then removed in vacuo. Yellow crystals of (I), were obtained by the slow evaporation at room temperature from an anhydrous methanol and n-heptane solution (4:1 v/v) of (I). Yield: 0.0454 g, 0.105 mmol,

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
N1	0.1000 (2)	0.12351 (11)	0.46106 (11)	0.0293 (3)
H1N	0.133 (3)	0.1034 (15)	0.5329 (10)	0.035 [*]
N2	−0.0513 (2)	0.03672 (11)	0.37231 (11)	0.0292 (3)
N3	0.0993 (2)	0.30851 (11)	0.23643 (10)	0.0260 (3)
C1	0.5676 (3)	0.28535 (19)	0.54768 (19)	0.0532 (5)
H1A	0.527942	0.225032	0.599105	0.080 [*]
H1B	0.678888	0.359121	0.596878	0.080 [*]
H1C	0.639602	0.236620	0.474085	0.080 [*]
C2	0.2369 (3)	0.42227 (16)	0.61729 (16)	0.0453 (4)
H2A	0.098711	0.460681	0.588170	0.068 [*]
H2B	0.352990	0.494022	0.665484	0.068 [*]
H2C	0.188932	0.365351	0.670439	0.068 [*]
C3	0.3449 (3)	0.34005 (14)	0.50578 (14)	0.0303 (4)
H3	0.391519	0.400907	0.453679	0.036 [*]
C4	0.1730 (2)	0.23160 (13)	0.42531 (13)	0.0243 (3)
C5	0.0581 (2)	0.21652 (13)	0.30708 (12)	0.0232 (3)
C6	−0.0787 (2)	0.09167 (13)	0.27724 (12)	0.0237 (3)
C7	−0.2304 (3)	0.01690 (13)	0.16101 (13)	0.0279 (3)
H7	−0.185876	0.054919	0.091160	0.033 [*]
C8	−0.4896 (3)	0.03591 (18)	0.17697 (15)	0.0435 (4)
H8A	−0.536192	0.002564	0.247220	0.065 [*]
H8B	−0.585968	−0.013431	0.100224	0.065 [*]
H8C	−0.513273	0.130798	0.193737	0.065 [*]
C9	−0.1904 (3)	−0.13078 (15)	0.12481 (16)	0.0457 (4)
H9A	−0.021933	−0.140534	0.118713	0.069 [*]
H9B	−0.278414	−0.174477	0.043833	0.069 [*]
H9C	−0.244996	−0.172129	0.188661	0.069 [*]
C10	−0.0620 (3)	0.32335 (13)	0.15701 (13)	0.0263 (3)
H10	−0.210474	0.273495	0.148718	0.032 [*]
C11	−0.0273 (2)	0.41457 (13)	0.07777 (12)	0.0247 (3)
C12	0.1824 (3)	0.49322 (14)	0.08688 (14)	0.0307 (3)
H12	0.308503	0.489268	0.146214	0.037 [*]
C13	−0.2088 (3)	0.42275 (14)	−0.01003 (14)	0.0312 (3)
H13	−0.353387	0.369568	−0.017252	0.037 [*]

35 % yield. The yield was improved (up to 61 %) by dehydration with molecular sieves 3 Å in methanol/n-heptane solution. **Anal. Calcd.** for C₂₆H₃₆N₆: C 72.19, H 8.39, N 19.42 %. **Found:** C 71.91, H 8.56, N 19.30 %. **¹H NMR** (CDCl₃, 500 MHz): δ 1.35 (d, 24H, 7 Hz, CH(CH₃)₂), 3.23 (sept, 4H, 7 Hz, CH(CH₃)₂), 7.93 (s, 4H, (C₆H₄)), 8.48 (s, 2H, CH=N); NH not obs. **¹³C{¹H} NMR** (CD₃OD, 125 MHz): δ 22.8 (CH(CH₃)₂), 26.3 (CH(CH₃)₂), 27.9 (CH(CH₃)₂), 128.6 (4C-pyz), 129.7 (2,3,4,5C-benzene), 140.7 (1,6C-benzene), 152.4 (3,5C-pyz), 159.6 (CH=N). **IR** (KBr, cm^{−1}): 3207 s ν(N–H), 3118 s, 3050 s, 2962 s ν(C–H), 2926 s ν(C–H), 2869 s ν(C–H), 1609 m ν(C=N), 1488 s, 1012 s. **Far-IR** (CsI, cm^{−1}): 633 s, 539 s, 243 m. **Raman** (neat solid, cm^{−1}): 1599 s, 1559 s, 1224 m, 1161 m. **Solution UV–vis** (CH₃OH, λ_{max}, nm) (ε, M^{−1} cm^{−1}): 231 (18,450), 291 (16,820), 370 (23,190). **Solid UV–vis**

(Nujol, λ_{max}, nm): 236, 305, 394. **Diffuse Reflectance** (solid, nm): 238, 300, 396.

2 Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C). The N-bound H atom was located in a difference Fourier map and refined with N–H = 0.88 Å and with *U*_{iso}(H) = 1.2*U*_{eq}(N). Owing to poor agreement, three reflections, i.e. (0 1 0), (0 0 1) and (0 −1 1), were omitted from the final cycles of refinement.

3 Comment

Recently, the crystal structure of amine group-introduced pyrazole, i.e. 4-amino-3,5-diisopropyl-1-pyrazole (L¹HpzNH₂) was described [5]. The compound was obtained by the reduction 4-nitro-3,5-diisopropyl-1-pyrazole with iron powder [5]. The synthetic method and structure of this molecule can be compared to the analogous molecule with methyl groups replacing the isopropyl substituents, i.e. 4-amino-3,5-methyl-1-pyrazole [6]. Originally, 4-amino-3,5-methyl-1-pyrazole was obtained by the direct nitration of acetylacetone with sodium nitrite (NaNO₂). This amino group can readily react with aldehydes to generate covalent organic frameworks [7–9]. Thus, L¹HpzNH₂ can react readily with terephthalaldehyde (benzene-1,4-dicarboxaldehyde) to yield the title compound I; systematic name: (NE)–N-[(4-{N-[3,5-bis(propan-2-yl)-1H-pyrazol-4-yl]carboximidoyl}phenyl)-methylidene]-3,5-bis(propan-2-yl)-1H-pyrazol-4-amine.

New characteristic absorption bands were observed in the IR spectrum of (I). Thus, the sharp N–H₂ stretching band in the spectrum of the L¹HpzNH₂ precursor at 3374 cm^{−1} disappeared and the band at 3211 cm^{−1} was shifted to 3207 cm^{−1} in the spectrum of (I). The C=N stretching bands of L¹HpzNH₂ at 1599 cm^{−1} was clearly separated into two bands at 1609 and 1575 cm^{−1}, and the C=O band at 1693 cm^{−1}, due to terephthalaldehyde, disappeared. In addition, new absorption bands at 231 nm (ε, 18,450 M^{−1} cm^{−1}), 291 nm (ε, 16,820 M^{−1} cm^{−1}) and 370 (ε, 23,190 M^{−1} cm^{−1}) in the UV–vis spectrum of (I), which were clearly different from the spectrum of L¹HpzNH₂, i.e. an absorption appeared at 238 nm (ε, 4130 M^{−1} cm^{−1}). The new bands in the spectrum of (I) were also observed in both the solid-state UV–vis and diffuse reflectance spectra, indicating the solid-state structure is retained in solution. The ¹H and ¹³C{¹H} NMR

exhibited the anticipated signals and in the case of 1H NMR, integration; no resonances were observed for imine N–H.

The molecular structure of (I) was established by X-ray crystallography and is represented in the upper image of the figure (50 % displacement ellipsoids). The molecule is disposed about a centre of inversion and unlabelled atoms are related by the symmetry operation (i): $-x, 1 - y, -z$. As anticipated, the 1H-pyrazole ring is strictly planar (r.m.s. = 0.010 Å) with the maximum deviation of 0.009(1) Å noted for the C4 atom. Within the ring, the formal C6=N2 [1.3307(17) Å] and C4=C5 [1.3903(19) Å] double bonds are longer than their standard values, and at the same time the formal N1–N2 [1.3585(16) Å], C4–N1 [1.3406(17) Å] and C5–C6 [1.4210(18) Å] single bonds are shorter than their standard values. These results confirm the extensive delocalisation of π -electron density over the five-membered ring. The imine C10=N3 bond length is 1.2736(17) Å, and the C5–N3 link between these residues is 1.4074(16) Å. The overall molecule of (I) is non-planar, there being a twist about the C5–N3 bond [the C4–C5–N3–C10 torsion angle = $-152.37(14)^\circ$] as seen in the dihedral angle of $29.76(7)^\circ$ between the five- and six-membered rings. With respect to the pyrazole-bound isopropyl groups, the methine–H atoms are orientated to be directed towards the centre of the molecule.

There are no structural precedents in the literature for molecules related to (I) where a pyrazole ring is directly connected to an imine functionality. However, in an accompanying publication [10], this connectively is described in the di-methanol solvate of the all-methyl analogue of (I). The pyrazole exhibits the same attributes/electronic structure as described for (I). There are examples of molecules whereby the pyrazole ring is connected to a nitrogen atom as in (I) but that nitrogen atom is connected to two carbon atoms, for example when the nitrogen atoms are incorporated at opposite ends of a naphthalene diimide molecule [11]. In the context of the motivation of the synthesis of (I) and related derivatives, it should be mentioned that coordination polymers are formed [12] by molecules of the aforementioned type in their neutral form [11].

Employing PLATON [13], an analysis of the molecular packing suggests the presence of both N–H $\cdots$ N and C–H $\cdots$ π directional interactions between molecules. Thus, pyrazole–N–H $\cdots$ N(pyrazole) hydrogen bonds [N1–H1n $\cdots$ N2ⁱⁱ: H1n $\cdots$ N2ⁱⁱ = 2.060(15) Å, N1 $\cdots$ N2ⁱⁱ = 2.8141(17) Å with angle at H1n = $142.2(14)^\circ$ for (ii): $-x, -y, 1 - z$] link molecules into supramolecular chains. The chain, illustrated in the lower view of the figure (the N–H $\cdots$ N hydrogen bonds are shown as orange dashed lines), is orientated along [0 1 $\bar{1}$] and features centrosymmetric, six-membered $\{\cdots HNN\}_2$ synthons. The chains are connected laterally by methyl–C–H $\cdots$ π (pyrazole) [C1–H1c $\cdots$ Cg(pyrazole)ⁱⁱⁱ: H1c $\cdots$ Cg(pyrazole)ⁱⁱⁱ = 2.78 Å with

angle at H1c = 149° for (iii) $1 + x, y, z$] resulting in supramolecular layers parallel to (0 1 1). Layers stack in an off-set fashion so the alkyl residues occupy regions defined by the phenyl rings of adjacent layers, but without directional interactions between them.

The above geometric analysis of the molecular packing was complemented by the calculation of the Hirshfeld surfaces and of the full and delineated two-dimensional fingerprint plots, using CRYSTAL EXPLORER 21 [14] and literature protocols [15]. All surface contacts in the crystal of (I) involve H, with the majority being of the type H $\cdots$ H, i.e. 69.7 %. The remaining contacts comprise C $\cdots$ H/H $\cdots$ C [16.7 %] and N $\cdots$ H/H $\cdots$ N [13.6 %] contacts.

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