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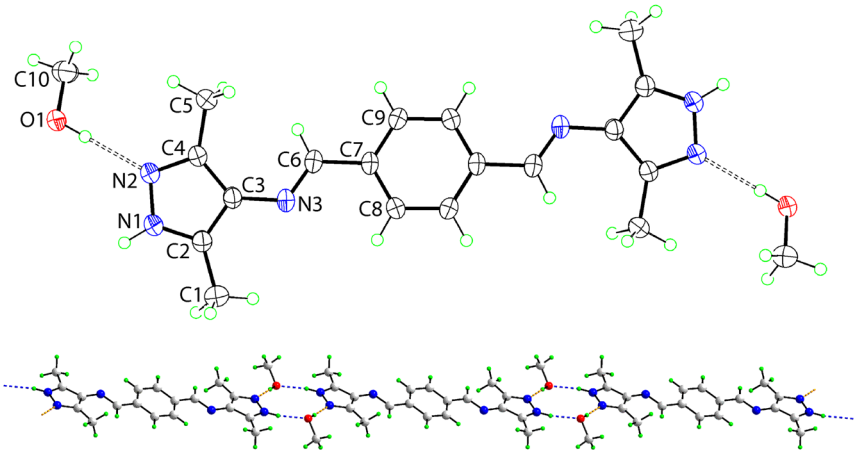
Crystal structure of [*N*(*E*),*N*′(*E*)]-*N*,*N*′-(1,4-phenylenedimethylidyne)bis-3,5-dimethyl-1*H*-pyrazol-4-amine di-methanol solvate, $C_{18}H_{20}N_6{\cdot}2(CH_3OH)$



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Abstract

$C_{18}H_{20}N_6{\cdot}2(CH_3OH)$, triclinic, $P\bar{1}$ (no. 2), a = 5.0063(2) Å, b = 8.5627(5) Å, c = 12.8216(6) Å, α = 77.898(4)°, β = 89.301(4)°, γ = 76.601(4)°, V = 522.40(5) Å^3, Z = 1, $R_{gt}(F)$ = 0.0577, w$R_{ref}(F^2)$ = 0.1642, 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:	Colourless prism
Size:	0.17 × 0.07 × 0.04 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.08 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB P200, ω
θ_{max}, completeness:	29.7°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8294, 2669, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2051
$N(param)_{refined}$:	136
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-dimethyl-1-pyrazole (0.053 g, 0.48 mmol) with terephthaladehyde (0.033 g, 0.25 mmol) in anhydrous methanol (15 mL) over molecular sieves 3 Å (0.5 g) was conducted at room temperature overnight. The solution was filtered to remove the molecular sieves after which the solvent was removed in vacuo. Yellow crystals of (I), were obtained by slow evaporation of the residue from its anhydrous methanol solution held at room temperature (0.040 g, 0.13 mmol, 54 % yield).

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
N1	0.3758 (3)	−0.27589 (16)	0.82786 (10)	0.0350 (3)
H1N	0.329 (4)	−0.3717 (15)	0.8503 (15)	0.042*
N2	0.5405 (3)	−0.23138 (16)	0.89468 (10)	0.0346 (3)
N3	0.3982 (3)	0.10752 (16)	0.66471 (10)	0.0337 (3)
C1	0.1236 (4)	−0.1783 (2)	0.65202 (14)	0.0442 (4)
H1A	0.151246	−0.105427	0.584907	0.066*
H1B	−0.068617	−0.148170	0.671361	0.066*
H1C	0.168654	−0.292264	0.643182	0.066*
C2	0.3058 (3)	−0.16136 (18)	0.73820 (12)	0.0317 (3)
C3	0.4296 (3)	−0.03423 (18)	0.74546 (12)	0.0298 (3)
C4	0.5752 (3)	−0.08483 (18)	0.84572 (12)	0.0303 (3)
C5	0.7477 (4)	−0.0015 (2)	0.89961 (13)	0.0377 (4)
H5A	0.648999	0.112537	0.896667	0.057*
H5B	0.921213	−0.003127	0.863169	0.057*
H5C	0.785841	−0.059339	0.974294	0.057*
C6	0.5444 (4)	0.2089 (2)	0.66352 (13)	0.0425 (4)
H6	0.678715	0.188058	0.719540	0.051*
C7	0.5171 (3)	0.35839 (19)	0.57931 (12)	0.0342 (4)
C8	0.3373 (5)	0.3925 (2)	0.49430 (15)	0.0551 (6)
H8	0.224744	0.319108	0.488502	0.066*
C9	0.6821 (5)	0.4661 (3)	0.58376 (17)	0.0684 (7)
H9	0.811728	0.442470	0.641721	0.082*
O1	0.7078 (3)	−0.41208 (15)	1.09962 (10)	0.0446 (3)
H1O	0.663 (5)	−0.360 (3)	1.0361 (10)	0.067*
C10	0.9649 (4)	−0.3865 (2)	1.12671 (17)	0.0519 (5)
H10A	1.072846	−0.372152	1.062606	0.078*
H10B	1.063959	−0.481744	1.179626	0.078*
H10C	0.936004	−0.287816	1.156669	0.078*

Anal. Calcd. for $C_{18}H_{20}N_6{\cdot}0.5(CH_3OH)$: C 66.05, H 6.59, N 24.98 %. Found: C 66.27, H 6.35, N 25.24 %. **^{1}H NMR** (CD_3OD, 500 MHz): δ 2.39 (s, 12H, CH_3), 3.34 (s, CH_3OD), 7.98 (s, 4H, (C_6H_4)), 8.64 (s, 2H, CH=N); N–H not observed. **IR** (KBr, cm^{-1}): 3231 s ν(N–H), 1609 w ν(C=N), 1583 w, 1146 m, 1098 s. **Solution UV–vis** (CH_3OH, λ_{max}, nm) (ε, M^{-1} cm^{-1}): 230 (8820), 297 (6530), 366 (15,340). **Solid-state UV–vis** (nujol, λ_{max}, nm): 242, 304, 379.

2 Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding with U_{iso}(H) = 1.2–1.5 U_{eq}(C). The O- and N-bound H atoms were located from a difference Fourier map and refined with O–H = 0.84 Å and N–H = 0.88 Å, and with U_{iso}(H) = 1.5 U_{eq}(O) and 1.2 U_{eq}(N).

3 Comment

Covalent organic frameworks (COFs) are a new class of materials obtained from reactions between appropriate organic precursors to yield strong covalent bonds to afford stable and porous crystalline materials [5]. COF linkages normaly rely on controlled B–O, C–N, C=N, C=C and B=N bond formation [6]. A convenient synthetic protocol for C=N bond formation arises from the reaction of an aliphatic or aromatic amine with a carbonyl compound via nucleophilic addition, to form a hemiaminal, followed by dehydration to generate an imine; this is well-known as Schiff base synthesis [7]. Recently [8], the structure of a potential precursor molecule for COFs was obtained through Schiff base synthesis via the reaction of 4-amino-3,5-diisopropyl-1-pyrazole, L^1HpzNH_2 [9], with terephthalaldehyde (benzene-1,4-dicarboxaldehyde). Herein, in continuation of these studies, the title compound (I, systematic name: (*NE*)-*N*-({4-[*N*-(3,5-dimethyl-1H-pyrazol-4-yl)carboximidoyl]phenyl}methylidene)-3,5-dimethyl-1H-pyrazol-4-amine was obtained by the reaction of a less hindered methyl substituted 4-amino-3,5-dimethyl-1-pyrazole (L^0HpzNH_2) with terephthalaldehyde in anhydrous methanol solution. This amino pyrazole was obtained by the direct nitration of acetylacetone with sodium nitrite ($NaNO_2$) which was reported previously [10].

In the IR spectrum, (I) displays a new, characteristic absorption band at 3231 cm^{-1}, assigned to ν(N–H) stretching, in contrast to a no longer present sharp band at 3345 cm^{-1} observed in the spectrum of L^0HpzNH_2, which is assigned to ν(N–H_2) stretching. In the UV–vis spectrum of (I), new absorption bands at 230, 297 and 366 nm are observed which is clearly different from the UV spectrum of L^0HpzNH_2, which shows a single absorption at 237 nm. The band positions for (I) were almost the same as those observed for the L^1HpzNH_2 derivative [8]. A similar pattern of absorptions were also observed in the solid-state UV–vis spectrum, indicating the solid-state structure is retained in both phases. The expected signals in the ^{1}H NMR were observed. The molecular structure of (I) was established by X-ray crystallography on a freshly recrystallised sample and shown to be a di-methanol solvate, i.e. (I)·2MeOH.

The molecular structures of the three-molecule aggregate in (I)·2MeOH is shown in the upper view of the figure (50 % displacement ellipsoids, the dashed lines indicate O–H···N hydrogen bonds and unlabelled atoms are related by the symmetry operation 1 – *x*, 1 – *y*, 1 – *z*). The crystallographic asymmetric-unit of (I) comprises half a (1,4-phenylenedimethylidyne)bis-3,5-dimethyl-1H-pyrazol-

4-amine molecule, being disposed about a centre of inversion, and a solvent methanol molecule. The pyrazolyl ring is strictly planar with the pattern of bond lengths within the ring being suggestive of considerable delocalisation of π-electron density. Thus, the nominal double-bonds, i.e. C4–N2 [1.3291(19) Å] and C2–C3 [1.391(2) Å], are longer than the expected bond lengths while each of the N1–N2 [1.3636(18) Å], C2–N1 [1.3357(19) Å] and C3–C4 [1.419(2) Å] bond lengths are shorter than expected for single bonds. The imine–C6=N3 bond length is 1.256(2) Å, and the C3–N3 link between these residues is 1.3994(18) Å.

The planarity in the phenyl ring extends to the terminal substituents as evidenced in the C3–N3–C6–C7 torsion angle of 179.61(15)° but a twist occurs about the C3–N3 bond with the C4–C3–N3–C6 torsion angle being 12.2(3)°; the dihedral angle between the five- and six-membered rings is 9.87(6)°. Thus, globally, the molecule is twisted.

Related structures in the literature include the precursor molecule, i.e. 3,5-dimethyl-4-aminopyrazole, which exhibits similar delocalisation of π-electron density in the pyrazolyl ring [10]. An accompanying publication describes the structure of the non-solvated di-isopropyl derivative, which also exhibits an analogous electronic structure in the five-membered ring and which forms a dihedral angle of 29.76(7)° with the central six-membered ring [8]; this molecule is located about an inversion centre.

In the crystal of (I), the methanol–O–H atom forms a hydrogen bond with the pyrazolyl–N2 atom of the ring [O1–H1o···N2: H1o···N2 = 1.940(15) Å, O1···N2 = 2.7838(18) Å with angle at H1o = 176(2)°], as indicated in the upper view of the figure. A reciprocating pyrazolyl–N–H···O(methanol) hydrogen bond [N1–H1n···O1^{i}: H1n···O1^{i} = 1.881(15) Å, N1···O1^{i} = 2.7651(19) Å with angle at H1n = 170.7(18)° for symmetry operation (i) $1-x, -1-y, 2-z$] is formed which results in the formation of a centrosymmetric, 10-membered $\{\cdots HO\cdots HNN\}_2$ synthon. As illustrated in the lower view of the figure, a linear chain, along [0 2 –1], incorporates these hydrogen bonds. The other directional interaction operating in the crystal is of the type methyl–C–H···π [C5–H5b···Cg(N1,N2,C1–C3)^{ii}: H5b···Cg(N1,N2,C1–C3)^{ii} = 2.80 Å, C5···Cg(N1,N2,C1–C3)^{ii} = 3.698(2) Å with angle at H5b = 153° for (ii) $1+x, y, z$]. The C–H···π interactions link the chains into a two-dimensional array parallel to (0 1 2). The layers stack along the b-axis and are off-set with respect to each other. The ···ABA··· stacking patterns allows for the construction of rectangular channels in which reside the methanol molecules.

To gain further information on the molecular packing, the Hirshfeld surfaces and the full and delineated two-dimensional fingerprint plots were calculated with Crystal Explorer 21 [11] in accord with literature protocols [12]. These calculations show that H···H contacts contribute 56.7 % to the calculated surface, consistent with the stacking of layers observed in the crystal. The remaining significant surface contacts also involve hydrogen, i.e. C···H/H···C [21.2 %], N···H/H···N [12.5 %] and O···H/H···O [9.3 %]. The only contribution to the surface contacts not involving hydrogen are O···C/C···O contacts at a mere 0.2 %.

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