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COPPER(II) IONS MEDIATED CRYSTAL FORMATION OF 3-(3-HYDROXY PHENYL)-1-PHENYL-1H-PYRAZOLE-4-CARBALDEHYDE

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ABSTRACT. Schiff base obtained from 3-hydroxyacetophenone and phenylhydrazine was subjected to Vilsmeier-Haack reaction to obtain 3-(3-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (**2**). Successful formation of crystals of **2** was achieved using copper ions (Cu^{2+}) as template. Present paper reports study of spectroscopic characterization and single-crystal X-ray study of **2**. Hydrogen bonding network between **2** and water molecules enable the formation of 2D layer along *ab*-plane supported also by $\pi \cdots \pi$ stacking interactions of parallel molecules in head-to-head fashion.

KEY WORDS: Cu^{2+} assisted crystal growth, Pyrazole-4-carbaldehyde, X-ray crystal study, Hydrogen bonding study

INTRODUCTION

Vilsmeier-Haack reaction allows the formylation of electron-rich arenes. Classical Vilsmeier-Haack reaction [1-3] involves electrophilic substitution of a suitable carbon nucleophile with a chloromethyleneiminium salt. Hydrolysis of iminium salt affords aldehyde derivative and this transformation ($\text{Ar-H} \rightarrow \text{Ar-CHO}$) is the most widely studied outcome of this protocol. This reaction has a broad application as iminium salt can be converted to compounds with various functional groups based on the reagent used in later step. For example, the intermediate iminium salt can be converted to nitrile derivative (Ar-CN) by treatment with hydroxylamine [4].

It is also one of the well-established reactions for the synthesis of pyrazole-4-carbaldehyde compounds where hydrolysis of iminium salt gives the final product. Pyrazole is also an important scaffold in many natural products. Pyrazole containing compounds are usually associated with activities such as antifungal [5], anti-inflammatory [6], insecticidal [7] and antiviral [8] properties. Substituted pyrazoles showed selective anti-proliferative actions on many human cancer cells and hold promise as inhibitors of cellular proliferation [9-13]. Anti-cancer activity of Schiff bases of pyrazole-4-carbaldehyde derivatives are also reported [14].

EXPERIMENTAL

Material and method

All the starting materials and solvents were purchased from commercial sources and were used without further purification. Microwave oven of Samsung, 800W output with digital timer and clock was used for synthesis. Melting points were determined in open capillaries using Electro thermal melting point apparatus and are uncorrected. Progress of reactions was monitored by TLC. Infrared (IR) spectra ($4000\text{--}600\text{ cm}^{-1}$) of the samples were recorded using a Perkin-Elmer Spectrum 100, equipped with a Specac Golden Gate Diamond ATR as a solid sample support. ^1H NMR spectra were recorded with a Bruker Avance III 500 NMR spectrometer with TMS as

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internal reference. MS spectra were recorded with an Agilent 6624 Accurate Mass TOF LC/MS instrument (ESI ionization). Elemental (C, H, N) analyses were obtained using Perkin–Elmer 2400 Series II CHNS/O Elemental Analyzer.

Synthesis of 1-phenyl-3-hydroxy-1H-pyrazole-4-carbaldehyde (2)

Compound was synthesized as reported in literature [15]. A mixture of 3-hydroxyacetophenone (1.36 g, 10.0 mmol), phenylhydrazine (1.08 g, 10.0 mmol), 1 drop of conc. HCl was prepared in a 100 mL conical flask. Ethanol (5 mL) was added as microwave active energy dissipater solvent and the reaction mixture was subjected to microwave irradiation of 20 s at 450 W. The microwave irradiation was carried out in batches of 5 s each for a period of 2 min. The resultant dry solid **1** was dissolved in excess of DMF in an ice bath followed by addition of POCl₃ (15 mmol, 2.30 g) with continuous stirring at cold conditions maintaining temperature at about 8 to 10 °C. The reaction mixture was allowed to attain room temperature and heated at about 80 °C for 1 h in a 150 mL beaker. The reaction mixture, upon hydrolysis by distilled water, gave off white colored solid. The solid obtained was washed with water to remove excess of HCl, filtered and dried. It was recrystallized with ethanol to obtain pure compound **2** as sticky mass. Yield 72% (1.90 g). Melting point 90-91 °C. MS (ESI+) *m/z*: 265.0976 (MH⁺), HRMS: calcd for C₁₆H₁₃N₂O₂: 265.0972, found: 265.0976. ¹H NMR (500 MHz, CDCl₃, ppm): 6.90 (s, 1H, Ar-H), 7.43 (t, 1H, Ar-H, J = 7.42), 7.99 (d, 2H, Ar-H, J = 7.74), 7.29–7.36 overlap (t, 1H, and d, 2H, Ar-H, J = 7.65 and 7.68, respectively), 7.58 (t, 2H, Ar-H, J = 7.57), 9.29 (s, 1H, pyrazolic CH), 9.65 (s, 1H, NH), 9.98 (s, 1H, CHO). IR (ν_{max}/cm⁻¹): 3129 (Ar-OH stretch), 3049 (Ar-CH stretch), 2887 (C-H aldehyde stretch), 1661 (C=O), 1597 (C=N stretch), 1508 (C–N stretch), 1215 (N–N stretch).

Crystal growth of 2

Compound **2** was obtained as sticky mass even after repeated attempts for crystal growth in ethanol or chloroform. **2** is insoluble in aqueous ethanol. However, it is soluble when 10 mL of 0.1 M solution of copper sulfate was added to 30 mL solution of **2** in 70% ethanol. This solution was heated for 5 to 10 min to obtain a clear solution. It was allowed to cool to room temperature and filtered. The filtrate was kept overnight in dark chamber without disturbance to obtain fine crystals of **2**.

IR spectra of the compound shows stretching band at 3129 cm⁻¹ for the phenolic –OH group. Stretching band for C–H proton of aldehyde group is observed at 2887 cm⁻¹ and the carbonyl stretching frequency for aldehyde group is observed at 1661 cm⁻¹. The C=N, C–N and N–N stretching frequencies for the bonds in pyrazole ring are observed at 1597 cm⁻¹, 1508 cm⁻¹ and 1215 cm⁻¹, respectively.

¹H NMR spectra of the compound recorded at 500 MHz in CDCl₃ showed singlet at δ 6.90 for one proton of C–H of aromatic ring adjacent to phenolic –OH. Peaks from the range of δ 7.29–7.36 are an overlap of one triplet of proton and a doublet for two protons of the aryl C–H protons from phenolic ring. Two aromatic protons from the other phenyl ring shows doublet in the range of δ 7.98. The peak at δ 7.58 can be attributed to two aromatic protons of the phenyl ring. The proton at the *para* position of the phenyl ring is observed at δ 7.43. A singlet is observed at δ 9.29 for pyrazolic CH, singlet at δ 9.65 is observed for NH of the pyrazole ring and the singlet for one proton of aldehyde group is observed at δ 9.98.

X-ray crystallographic study

Single-crystal X-ray diffraction data were collected on an Agilent Technologies SuperNova Dual diffractometer with an Atlas detector using monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. The data were processed using CrysAlis Pro [16]. Structure was solved

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by direct methods using SHELXT2014 [17] and refined on F^2 using full-matrix least-squares procedures using SHELXL2017 [18] integrated in Olex2 [19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were readily located in a difference Fourier maps and were subsequently treated as riding atoms in geometrically idealized positions, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Hydrogen atoms in water molecule and hydroxy group have been located by difference Fourier maps and refined restraining the bond lengths and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. CCDC 1899454 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. Crystallographic data are listed in Table 1.

Table 1. Crystallographic data for **2**.

Compound code	2
CCDC number	1899454
Molecular formula	C ₁₆ H ₁₄ N ₂ O ₃
Molecular weight	282.29
Crystal system	Monoclinic
Space group	<i>I</i> 2/ <i>a</i>
<i>a</i> (Å)	22.1406(14)
<i>b</i> (Å)	3.8803(3)
<i>c</i> (Å)	31.682(2)
α (°)	90
β (°)	90.191(7)
γ (°)	90
<i>V</i> (Å ³)	2721.8(3)
<i>Z</i>	8
D_{calc} (g cm ⁻³)	1.378
μ (mm ⁻¹)	0.097
<i>F</i> (000)	1184
Reflections collected	11094
Independent reflections	3096
R_{int}	0.0551
Parameters	199
R_1, wR_2 [$I > 2\sigma(I)$] ^a	0.0529, 0.1141
R_1, wR_2 (all data) ^a	0.0994, 0.1383
GOF ^b	1.014
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ (e Å ⁻³)	0.244, -0.223

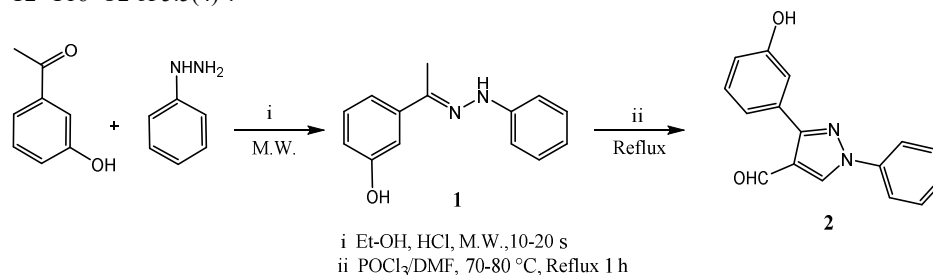
^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. ^b $S = \{ \sum [(F_o^2 - F_c^2)^2] / (n/p) \}^{1/2}$ where *n* is the number of reflections and *p* is the total number of parameters refined.

RESULTS AND DISCUSSION

Titled compound **2** was obtained in two-step procedure (Scheme 1). From the starting material 3-hydroxyacetophenone and phenylhydrazine a Schiff base formed under microwave conditions and further transformed *via* Vilsmeier-Haack reaction using POCl₃ to obtain 3-(3-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**2**). Compound **2** was obtained as sticky mass even after repeated recrystallizations. Attempts to obtain crystals of **2** suitable for XRD analysis by employing evaporation method at room temperature using common organic solvents like methanol, ethanol and chloroform or various combinations of solvents were not successful. However, successful formation of crystals of **2** was achieved by metal assisted method using copper sulfate as template. Usually such reactions lead to formation of a coordination complex of ML₂ type if ligand geometry is favorable for formation of five or six membered ring. In this

case, there is no formation of coordination complex like ML_2 type. Instead, the metal ion (Cu^{2+}) only helps in formation of hydrated crystal of the compound (**2**).

In the crystal structure all the bond lengths are within normal ranges [20] (Figure 1). In the compound the pyrazole ring N1/N2/C1–C3 is essentially planar with the maximum deviation from planarity of 0.002(2) Å for atom C3. The phenyl ring C4–C9 slightly deviates from the plane of the pyrazole ring with dihedral angle between rings of 14.34(11)°. On the other hand, the dihedral angle between pyrazole and phenolic ring C10–C15 is much larger being 41.63(11)°. Formyl group is almost in plane with the pyrazole ring with the dihedral angle C3–C2–C16–O2 of 5.5(4)°.



Scheme 1. Synthesis of 1-phenyl-3-hydroxy-1*H*-pyrazole-4-carbaldehyde.

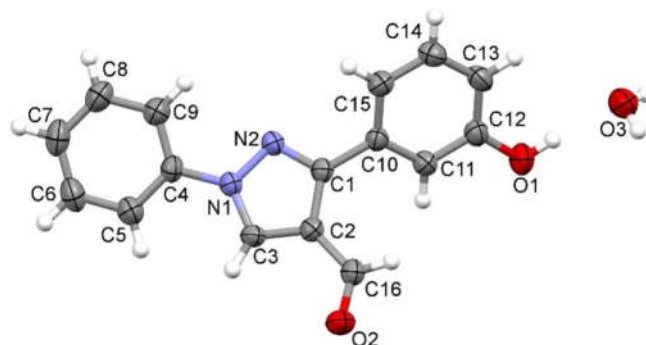
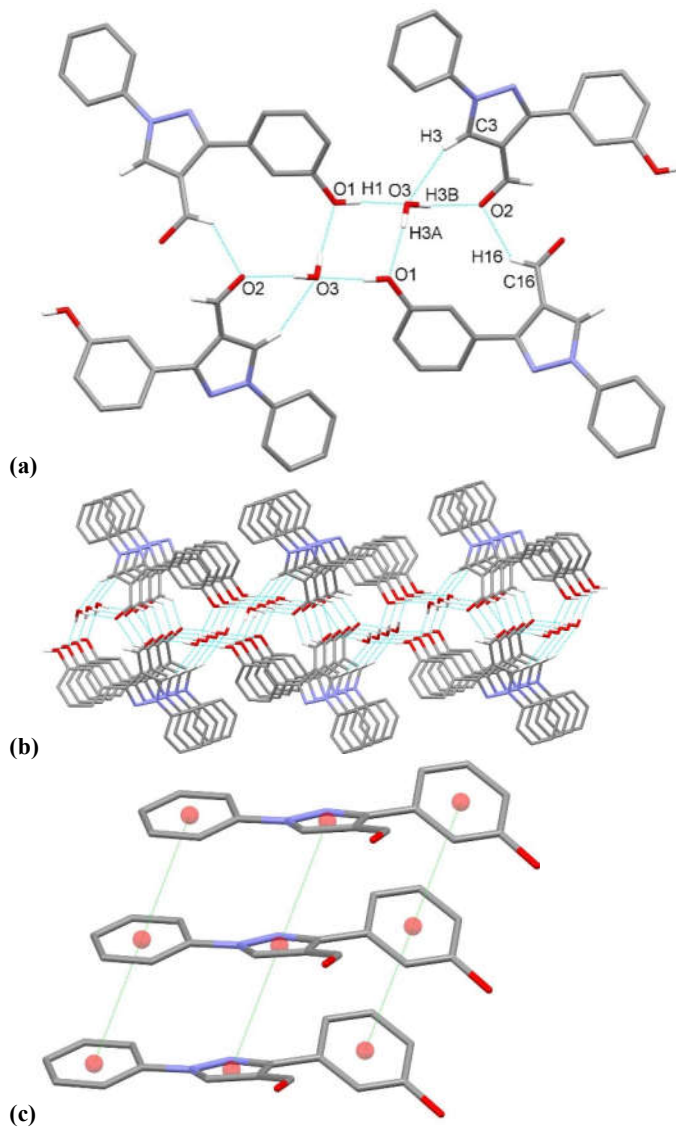


Figure 1. Molecular structures and atom numbering scheme for **2**. Probability ellipsoids are drawn at the 50% level.

Crystal structures of phenyl derivatives of pyrazole-4-carbaldehyde with several different substituents on phenyl ring, like 2-hydroxy, 4-bromo, 4-chloro, 4-methoxy, 4-methyl and 3,4-dimethoxy have been reported [14, 21-30]. However, the presence of hydroxy group enables the formation of different hydrogen bonded networks compared to the other reported derivatives. This is also the case when compared with 2-hydroxy substituent, since intramolecular hydrogen bond between 2-hydroxy and the pyrazole N atom is observed [21, 23, 24].

Hydrogen bonding $O1-H1 \cdots O3$ between hydroxy group of **2** as a hydrogen bond donor and the water molecule as hydrogen bond acceptor and a $O3-H3A \cdots O1$ between the water molecule as hydrogen bond donor and hydroxy group of **2** as a hydrogen bond acceptor enables the formation of a $R_4^4(8)$ graph set motif [31] connecting two **2** molecules and two water molecules (Table 2). Furthermore, water molecule forms as a hydrogen bond donor $O3-H3B \cdots O2$ interaction with the adjacent **2** molecule forming $R_2^2(7)$ graph set motif in cooperation with $C3-H3 \cdots O3$ interaction. $R_3^3(12)$ graph set motif is also present due to the $C16-H16 \cdots O2$ hydrogen

bonding between formyl groups of two adjacent **2** molecules and the hydrogen bonds formed by water molecule as hydrogen bond donor (Figure 2, Table 2). These hydrogen bonding enable the formation of layer along *ab*-plane supported also by $\pi\cdots\pi$ stacking interactions of parallel molecules in head-to-head fashion with centroid-to-centroid distance of 3.880(2) Å and ring slippages of 1.627 Å between pyrazole rings, 1.645 Å between phenyl rings, and 1.694 Å between phenolic rings (Figure 2).



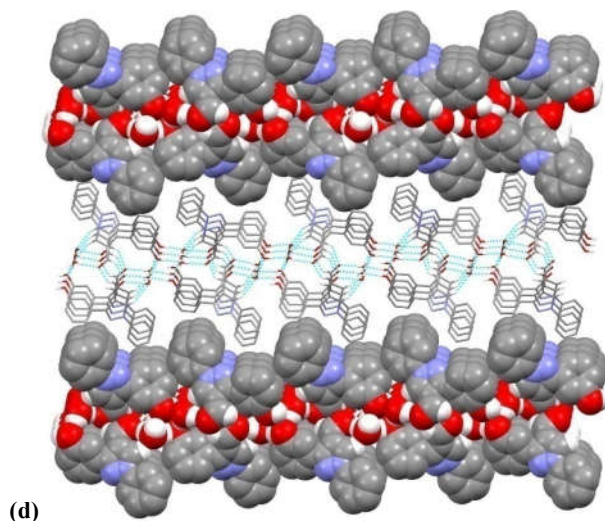


Figure 2. (a) Hydrogen bonding in **2** (blue dashed lines). Hydrogen atoms not involved in the motif shown have been omitted for clarity. (b) Hydrogen-bonded layer along *ab*-plane. (c) $\pi \cdots \pi$ stacking interactions along *b*-axis. Hydrogen atoms and water molecules have been omitted for clarity. (d) Packing of layers.

Table 2. Hydrogen bond geometry of **2**.

D–H \cdots A	D–H (Å)	H \cdots A (Å)	D \cdots A (Å)	D–H \cdots A (°)	Symmetry code
O1–H1 \cdots O3	0.853(17)	1.877(18)	2.726(2)	173(3)	x, y, z
O3–H3A \cdots O1	0.869(18)	2.015(19)	2.875(3)	169(3)	$1/2 - x, -1/2 - y, 1/2 - z$
O3–H3B \cdots O2	0.880(18)	2.011(19)	2.880(2)	169(3)	$1/2 + x, -y, z$
C3–H3 \cdots O3	0.93	2.36	3.211(3)	152.4	$-1/2 + x, -y, z$
C16–H16 \cdots O2	0.93	2.55	3.287(3)	136.7	$1 - x, -1/2 + y, 1/2 - z$

CONCLUSION

The formation of Schiff base from 3-hydroxyacetophenone and phenyl hydrazine and further transformation by Vilsmeier-Haack reaction gave 3-(3-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbaldehyde (**2**). Successful formation of crystals of **2** was achieved by metal assisted method using copper sulphate as template. In the crystal structure hydrogen bonding network between **2** and water molecules enable the formation of 2D layer along *ab*-plane supported also by $\pi \cdots \pi$ stacking interactions of parallel molecules in head-to-head fashion.

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