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Crystal Structure and Characterization of Novel Schiff Base: (Z)-4-(((2-hydroxy phenyl)amino)(phenyl)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one

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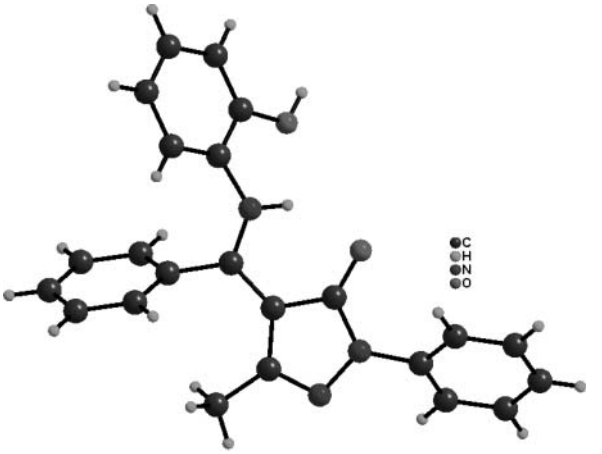
GRAPHICAL ABSTRACT



The crystal structure of the amine tautomer of the new Schiff base derived from 5-methyl-2-phenyl-4-benzoyl pyrazolin-3-one with 2-amino phenol was obtained using single crystal X-ray diffraction (XRD). Weak interactions including intermolecular forces, metal–ion coordination, electrostatic forces, van der Waals interactions, and donor–acceptor interactions are responsible for the organized entities of higher complexity.

A novel Schiff base crystal: (Z)-4-(((2-hydroxy phenyl)amino)(phenyl)methylene)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one was synthesized and grown from alcoholic

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solution. Single crystal X-ray diffraction (XRD) shows that the compound crystallizes in the triclinic crystal system with space group p-1 with a = 7.1822(3) Å, b = 11.0015(4)Å, c = 13.6353(5) Å; α = 111.715(10)°, β = 92.255 (2)°, γ = 106.002 (2)°, and Z = 2. FTIR, UV/Vis, H^1 NMR, and CHN have been employed to characterize the crystal. Thermal stability and the weak interactions among the neutral entities have also been investigated.

Keywords Pyrazole derivatives; Schiff base; tautomer; thermo gram; weak interactions; X-ray structure

1. Introduction

In 1864, the German chemist Hugo Schiff developed a new class of organic compounds [1]. This group of compounds, imines, is often referred to as Schiff bases in his honor. The preparation of these compounds is simple. They are prepared by condensing a carbonyl compound with an amine, generally refluxing in alcohol. Schiff bases are often used as ligands in inorganic chemistry. Pyrazole derivatives are used as starting materials for the synthesis of biologically active compounds [2] and for the construction of condensed heterocyclic systems [3,4]. Moreover, particular interest exists due to the ability of these compounds to exhibit several tautomeric forms, such as CH, OH, and NH [5–8]. These Schiff base ligands have been studied extensively due to their ease of synthesis and their ability to be readily varied both sterically and electronically.

The chemistry of Schiff bases is very diverse. The ligands can coordinate anywhere from a monodentate [9] to a nanodentate [10] fashion to a metal ion. Schiff bases and their metal complexes have been studied for use as antibacterial agents [11–13], antifungal agents [14,15], antitumor drugs [16–18], catalysts [19–21], and in coordination chemistry [22–25].

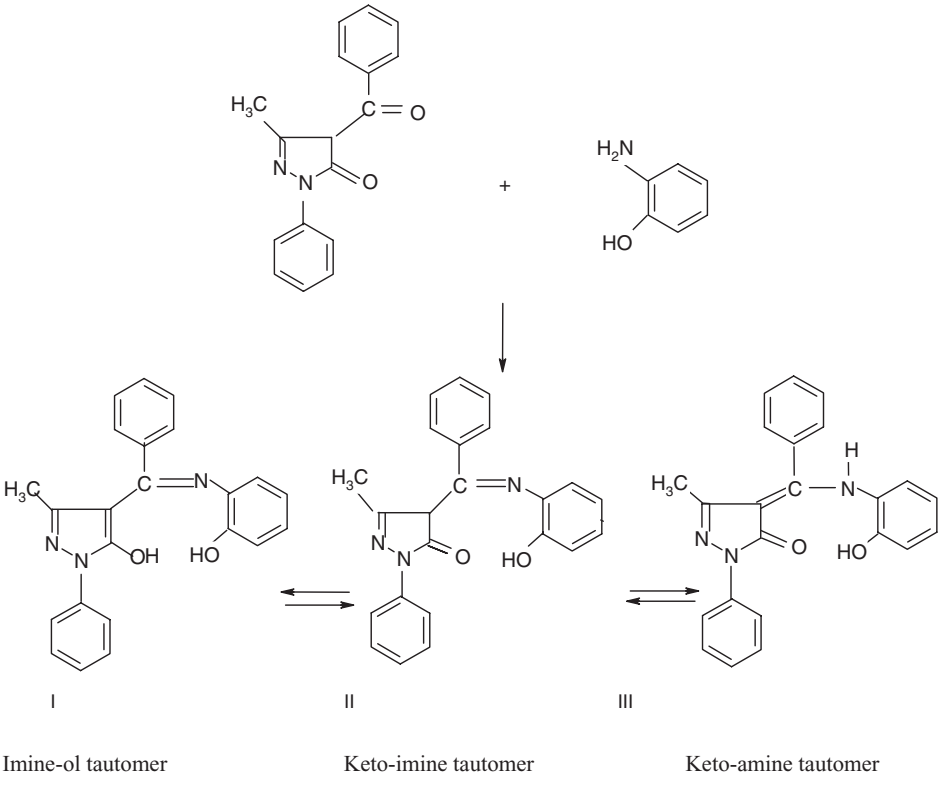
Recently, some Schiff bases from 3-methyl-1-(4′-methylphenyl)-2-pyrazoline-5-one and aromatic amines were prepared, and their molecular structures were determined. These ligands can exist in three tautomeric forms: keto-imine, imine-ol, and keto-amine, although the keto-amine form is predominant in the solid state [26].

Although, the binding ability of Schiff bases to metal has been extensively studied, their interactions with each other have not been studied as much. In Schiff base compounds, the imine nitrogen acts as inter- or intramolecular hydrogen-bond acceptor. The hydrogen-bond interactions are important because of their applications in the pharmaceutical industry. The type and strength of the interactions between the molecules in the formulations can affect the uptake of medication in the body. Moreover, the weak interactions that are bearing on the organized entities of higher complexity, result from the association of two or more chemical species held together by intermolecular forces, metal–ion coordination, electrostatic forces, van der Waals interactions, and donor–acceptor interactions to be focused.

As a part of our ongoing studies into the structure and utility of pyrazole Schiff base ligands, we report the synthesis, spectral properties, crystal structure, tautomerism, and the weak interactions of the Schiff base prepared from the condensation of 5-methyl-2-phenyl-4-benzoyl pyrazolin-3-one with 2-amino phenol.

2. Experimental

All chemicals were purchased from commercial sources and used as received. The infrared (IR) spectrum was recorded on a PerkinElmer spectrophotometer of RXI model



Scheme 1. Synthetic pathway and possible tautomeric forms of the Schiff base.

(PerkinElmer, Waltham, MA). The UV/Visible (UV/Vis) spectrum was recorded in dichloromethane solution on a Systronics 2202 double beam spectrophotometer (Systronics, Gujarat, India). The elemental analyses were obtained from SAIF (Cochin, India). The ^{1}H NMR spectrum was carried out at Sri Ramachandra University (Chennai, India) using tetramethyl silane (TMS) as an internal standard. The thermo gravimetric-differential thermal analysis (TG-DTA) analyses were collected from Central Electrochemical Research Institute (Karaikudi, India). The X-ray diffraction (XRD) analysis was carried out at the Indian Institute of Technology (Chennai, India).

2.1 Synthesis of Schiff Base

A mixture of 5-methyl-2-phenyl-4-benzoyl pyrazolin-3-one (5 mmol, 1.845 g) and 2-amino phenol (5 mmol, 0.545 g) were taken in a round-bottomed flask with 40 mL of ethanol, and refluxed under water bath for about 3 h. The resulting mixture is tested for the completion of reaction by thin layer chromatography and allowed to stand overnight. The colorless crystals formed are separated and dried. Scheme 1 shows the synthesis of the Schiff base and its various possible forms of tautomerism.

2.2 X-ray Crystallography

Crystal data collection parameters are given in Table 1. Data were collected on SADABS (Bruker, 1999). Data collection and cell refinement were performed using APEX2/SAINT

Table 1. Crystal data and structure refinement of the new Schiff base

CCDC entry no.	835665
Empirical formula	$C_{23}\ H_{19}\ N_3\ O_2$
Formula weight	369.41
Color and habit	Colorless, cubical
Crystal size (mm)	$0.30 \times 0.25 \times 0.20$
Temperature (K)	293 (2)
Space group	p-1
a (Å)	7.1822 (3)
b (Å)	11.0015 (4)
c (Å)	13.6352 (5)
α (°)	111.7150 (10)
β (°)	92.255 (2)
γ (°)	106.002 (2)
Volume (Å^3)	950.02 (6)
Z	2
D_{calc} (Mg m^{-3})	1.291
Absorption coeff. (mm^{-1})	0.084
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9833 and 0.9752
F (000)	388
R indices [$I > 2\sigma(I)$]	$R1 = 0.0391$, w$R2 = 0.1054$
R indices (all data)	$R1 = 0.0440$, w$R2 = 0.1102$
Largest peak/hole (e Å^{-3})	0.193 and 0.201

(Bruker, 2004, Madison, WI). The structure was solved by direct methods using SIR929 [27]. The refinements were completed using the program SHELXL-97 [28].

3 Results and Discussion

The compound was stable at room temperature and possessed good keeping qualities. It was nonhygroscopic solid, insoluble in n-hexane, petroleum ether, and toluene, and soluble in chloroform, dichloromethane, and ethyl acetate. Analytical data of the compound are in good agreement with its formulation, and its respective data are shown in Table 2.

3.1 IR and UV/Vis Spectroscopy

The resulting compound has a strong absorption at 3650 cm^{-1} in the IR, confirming the presence of N−H bond in the Schiff base. The IR absorptions at 1745 cm^{-1} and 1135 cm^{-1},

Table 2. Analytical data of the Schiff base

		Analytical data % (found/calcd.)		
Compound	Yield %	C	H	N
$C_{23}\ H_{19}\ N_3\ O_2$	76	74.41 (74.38)	4.96 (4.97)	11.25 (11.23)

clearly indicating the presence of C=O, C−O, respectively. The absorption at 3203 cm^{-1} is due to the presence of –OH group. The UV/Vis spectra of the Schiff base in dichloromethane have the transitions in the range 299–430 nm, which were assigned to the ligand centered transitions.

3.2 ^{1}H NMR Spectroscopy

The tautomerism of this compound in solution and solid state has been the subject of studies. From the ^{1}H NMR spectra, it was inferred that the resulted Schiff base exist as a mixture of tautomers (II) and (III) (Scheme 1) in $CDCl_3$ solution. The phenolic proton leads to a singlet of integration intensity equivalent to one hydrogen at 12.8 ppm. This leads to the conclusion that there is no existence of imine-ol tautomer in $CDCl_3$. The aromatic protons give multiplet around 6.3–8 ppm. The singlet at 1.3 ppm indicates the presence of methyl protons. The two singlets at 0.8 ppm and 3.5 ppm are assigned to N−H proton of keto-amine tautomer and C−H proton of the keto-imine tautomer, respectively. Moreover, the equal intensities of these two tautomers conclude that they are present in equal ratio in $CDCl_3$ solution.

3.3 Thermo Gravimetric Analysis

The thermal behavior of Schiff base has been studied as TG-DTA. Figure 1 represents the thermal properties of Schiff base crystal carried out by TG-DTA. The thermo gram indicates

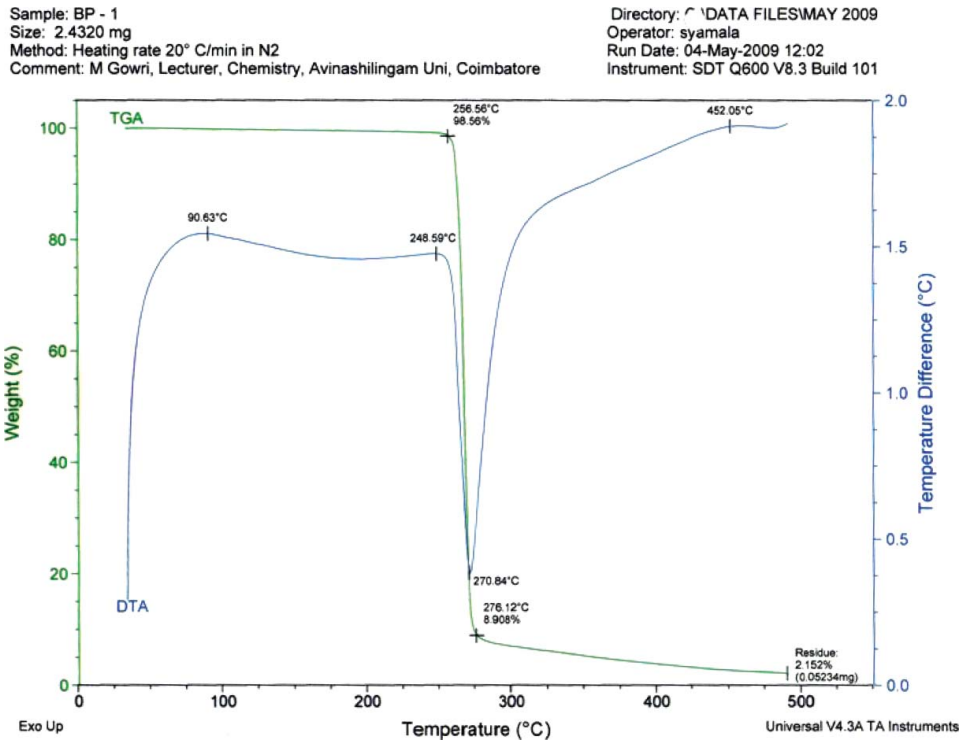


Figure 1. TG-DTA of the newly synthesized Schiff base.

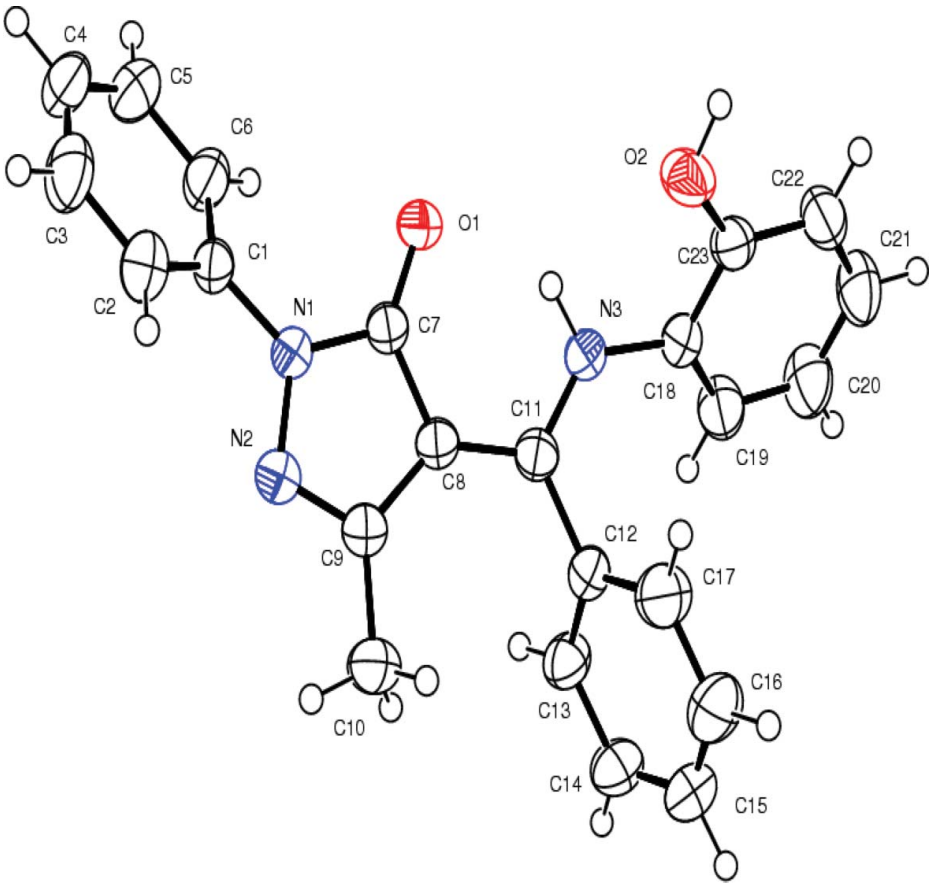


Figure 2. ORTEP diagram of the new compound showing atom numbering scheme.

that the compound is stable up to 256.5°C, and above this temperature, steady and gradual weight loss is noticed. About 90% of weight loss was noticed in between the temperature range 256°C and 276°C. Beyond the temperature 276°C, there is slow decomposition of the compound up to 485°C leaving 2.15% as residue.

Table 3. Summary of selected bond lengths (Å) of the new Schiff base

Bond	Length
C1−N1	1.4144
O1−C7	1.2550
N3−H	0.90
O2−C23	1.3521
C11−N3	1.3243
C11−C12	1.4810
N 1−N 2	1.3942
C8−C11	1.3978

Table 4. Summary of selected bond angles (°) of the new Schiff base

Bond	Angle
C11—N3—C18	130.32
N3—C11—C12	118.86
N1—C7—C8	104.96
C7—N1—N2	112.29
N2—C9—C10	118.59
C9—C10—H10	109.50
C8—C9—C10	129.86

Table 5. Intramolecular hydrogen-bond geometry (Å, °) in the Schiff base

D—H···A	D—H	H···A	D···A	D—H···A
O2—H 2···O1	0.90 (2)	1.82 (2)	2.6824 (14)	159.4 (19)

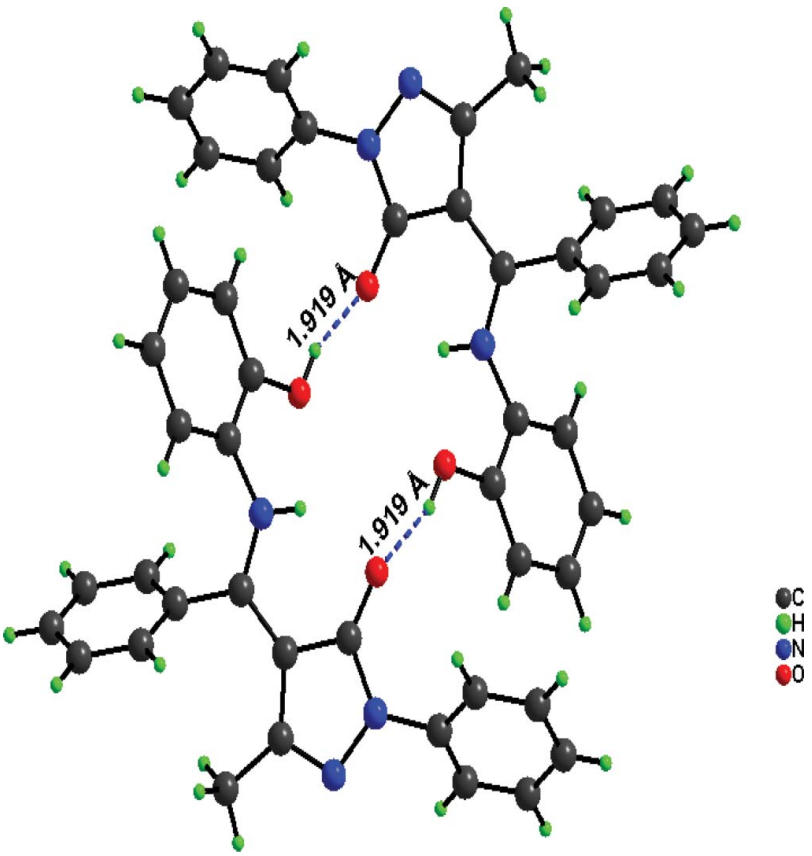


Figure 3. O—H···O interactions in between the molecules with its bond length.

3.4 X-ray Diffraction Studies

The molecular structure of the compound was determined using single crystal XRD analysis. The Schiff base belongs to the triclinic crystal system with space group p-1 with two molecules in the unit cell (half of the molecule in the asymmetric unit). The lattice parameters obtained are: $a = 7.1822(3)$ Å, $b = 11.0015(4)$ Å, $c = 13.6353(5)$ Å, $\alpha = 111.715(10)^\circ$, $\beta = 92.255(2)^\circ$, $\gamma = 106.002(2)^\circ$, and volume = 950.02 (6) A^3. The crystal structure of the compound with atom numbering scheme is shown in Fig. 2. The selected bond lengths and bond angles are given in Tables 3 and 4. The diffraction data reveal that the nitrogen atom from 2-aminophenol exist as N−H group, the bond between the C8 and C11 carbon atoms is double bond, and it further concludes that the resulting Schiff base

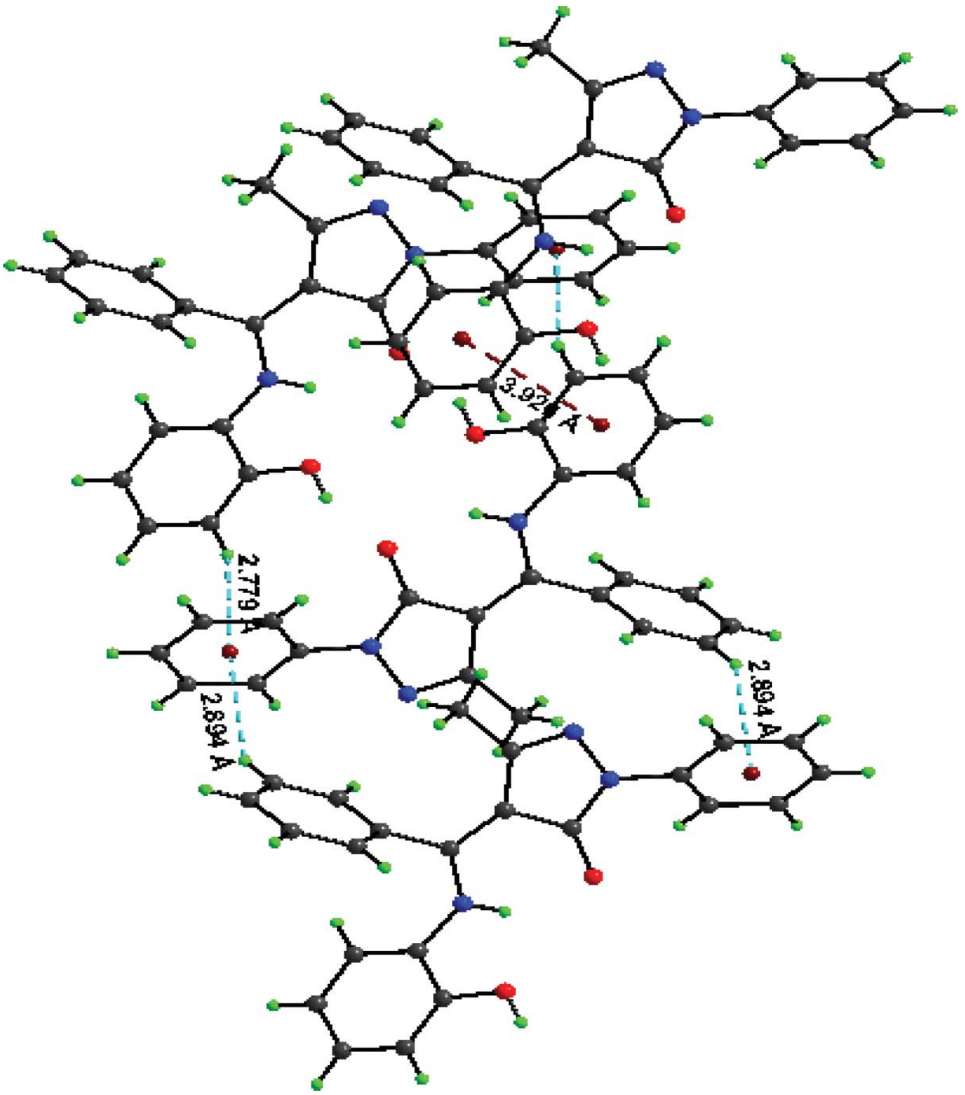


Figure 4. C−H$\cdots\pi$ and $\pi\cdots\pi$ interactions in between the molecules with their bond lengths.

Table 6. Summary of bond distance of various types of weak interactions of the Schiff base

Weak interactions	Bond distance (Å)
C–H···O intramolecular	2.621 (10), 2.646 (11)
C–H···O intermolecular	2.743 (17), 2.758 (10)
O–H···O intermolecular	1.919 (6)
$\pi\cdots\pi$	3.926 (7)
C–H···π	2.779 (7), 2.894 (4)
N–H···O intramolecular	2.404 (8)

is present as keto-amine tautomeric form rather than the keto-imine in the solid state. The crystallographic data have been deposited in the Cambridge structure database (CCDC – 835665).

3.4 Weak Interaction Studies

With the help of XRD analysis, the possible weak interactions of the resulting Schiff base were also studied. The molecular structure is primarily stabilized by a strong intramolecular O2–H2···O1 hydrogen bond [O2–H2 = 0.90(2) Å, H2···O1 = 1.182(2) Å,

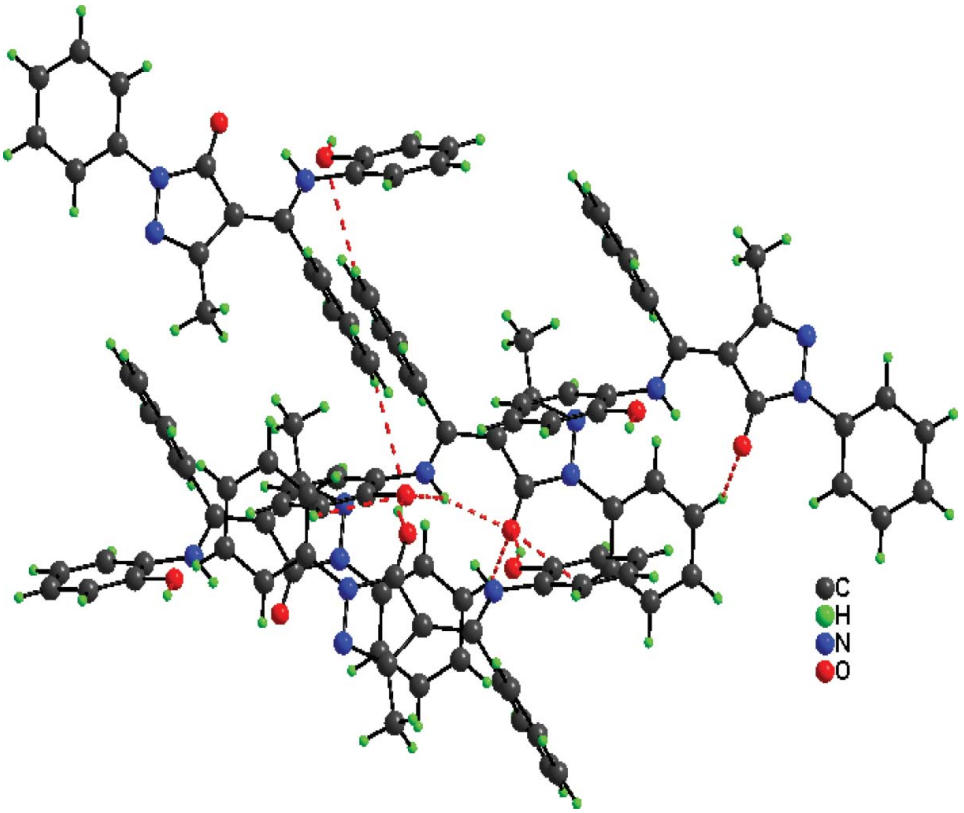


Figure 5. C–H···O interactions in between the molecules.

O2···O1 = 2.6824(14) Å, and the angle O2–H2···O1 = 159.4(19)°] leading to the formation of a pseudo nine-membered hydrogen-bonded pattern, thus locking the molecular conformation and eliminating conformational flexibility. Table 5 shows the intramolecular hydrogen-bond geometry in the Schiff base. Further, the crystal structure is stabilized by intermolecular interactions into a three-dimensional framework structure by the combination of O—H···O, C—H···π, π···π, and C—H···O interactions. Figures 3–5 represent O—H···O, C—H···π, π···π, and C—H···O interactions, respectively. Table 6 shows the summary of bond distances of various types of weak interactions of the Schiff base. The supramolecular aggregation in this structure is thus limited to the O—H···O, C—H···π, π···π, and C—H···O interactions, giving overall stability to the structure. Weak interactions between the neutral molecules provide a platform for discussing the field of weak interactions and to uncover new research directions.

4. Conclusion

The ^{1}H NMR spectra reveal that this compound exists as mixture of keto-amine and keto-imine tautomer in equal ratio in $CDCl_3$ solution. The crystal structure of the Schiff base was determined using single crystal XRD analysis. The high-resolution XRD measurements substantiate the good quality of the crystal. The XRD data confirm the presence of keto-amine tautomer of Schiff base in the solid state among the three possible tautomers. The thermal behavior of crystals was studied using TG-DTA. The weak interaction studies show the presence of supramolecular network among the neutral entities.

Supplementary Material

CCDC – 835665 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or emailing data_request@ccdc.cam.ac.uk. or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK.

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