

Original article

Synthesis, Characterization and PXRD Crystal Structure of Benzidinedioxime

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Abstract

Recently Schiff bases compounds were played an importance role in the preparation of novelty complex compounds, and they are used in many fields such as industrial technology, pharmaceutical, biochemistry, and physiology. The benzidinedioxime Schiff base N-((2E,3E)-3-[(4'-((Z)-[(3E)-3-(hydroxyimino)butan-2-ylidene]amino)[1,1'-biphenyl]-4yl)imino]butan-2-ylidene) hydroxylamine is synthesized by the condensation reaction of benzidine with diacetylmonoxime in the (1:2) mole ratios respectively. The chemical structure, electronic properties, and crystal structure of benzidinedioxime were investigated using different techniques including elemental analysis, powder X-ray diffraction (PXRD), FTIR, UV-Visible and NMR spectroscopy. The FT-IR, NMR, and elemental analysis confirmed that two moles of diacetylmonoxime and one mole of benzidine reacted to formation of the Schiff base. The UV-Vis spectrum revealed smooth and strong peaks due to electronic vibration and rotation transitions indicating $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, and $\pi \rightarrow \pi^*$ electronic transitions. Benzidinedioxime has a triclinic space group with P1(1) point groups. The NMR analyses showed two peaks at different chemical shifts for both the biphenyl and dimethyl groups in different environments.

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Introduction

Schiff bases have played an important role in the development of coordination chemistry (Arun, 2011). Schiff base metal

complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas (Arun, 2011). A Schiff base is a nitrogen analogy of an aldehyde or ketone in which the C=O group is replaced by C=N-R, where R may be an

alkyl or an aryl group. It is usually formed by the condensation of an aldehyde or ketone with a primary amine (Carey, 2000, Vogel and Houk, 2019). Schiff bases that contain aryl substituents are substantially more stable and more readily synthesized, while those that contain alkyl substituents are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and are readily polymerizable (Cimerman et al., 2000), while those of aromatic aldehydes having effective conjugation are more stable (Perry et al., 1986, Kabak et al., 1999). Schiff bases are used in different fields such as industrial technology (plastic industries, liquid-crystal technology), pharmaceutical (dye and mechanistic investigations of the drugs) (Abuamer et al., 2014), biochemistry and physiology (antimalarial, antibacterial, antifungal, and antiviral) (Akila et al., 2017, da Silva et al., 2011). Schiff bases are among the best ligands used in the synthesis of coordination compounds. They, generally, lead to the formation of stable complexes with most of the transition metals (Asadi et al., 2011, Chamayou et al., 2011, Monfared et al., 2011). A large number of benzidine Schiff base ligands were synthesized by the reaction of one or both amino groups in benzidine with carbonyl compounds. Benzidine played an important role in the synthesis of Schiff base complexes that are widely used in biological fields and biological modelling applications (Akila et al., 2017, Kabak et al., 1999, Akhter et al., 2017, More et al., 2019). N, N'-bis(salicylaldehyde)benzidine, (C₂₆H₂₀N₂O₂) is synthesised from the condensation of benzidine and salicylaldehyde in 1:2 mole ratio (Saleh and Kafi, 2016). Other benzidine Schiff bases have been synthesized from the reaction of (ethoxymethylene)pentane-2,4-dione and 3,3'-diaminobenzidine in the presence of calculated amounts of KOH as a catalyst (Alsalihi, 2019), and by the reaction of glyoxal/diacetyl and 2-aminophenol with benzidine in 1:2:2 mol ratio respectively (Akila et al., 2017).

2. Materials and methods

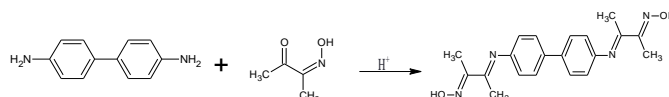
2.1. Materials

Benzidine (99%, Riedel-de-Haen AG, Germany), diacetylmonoxime (99%, (Trust Chemical Laboratories, India), ethanol (99.9%, (Duksan, Germany), diethyl ether (97.5%, (Alpha Chemika, India, dimethyl sulphoxide (99.9, Alpha Chemika, India), glacial acetic acid (85%, Alpha Chemika, India) were used as received.

2.2 Methods

2.2.1. Preparation of benzidinedioxime Schiff base

To benzidine (2.00 g, 10 mmol) dissolved in 50 mL of absolute hot ethanol was added to (2.22 g, 20 mmol) 2, 3 butanedionemonoxime dissolved in 20 mL of absolute ethanol. A few drops of glacial acetic acid were added to the mixture. The mixture was refluxed with stirring for 8 h. The solution was left to cool at room temperature. The precipitate that formed was filtered and washed with cold ethanol and ether. The isolated precipitate was recrystallized using an ethanol/ether mixture in a 1:1 volume ratio.



2.2.2. Characterization of benzidinedioxime Schiff base using FT-IR

A small amount of the benzidinedioxime Schiff base was mixed thoroughly with potassium bromide and compressed into a thin transparent pellet using a hydraulic presser. The FT-IR spectra of the samples were obtained using a SHIMADZU IR-spectrometer in the wavenumber range of 4000 to 400 cm⁻¹.

2.2.3. Nuclear magnetic resonance measurement (NMR)

The NMR spectrum was obtained from a benzidine dioxime solution in DMSO D₆ (0.05 mM) using Bruker DPX 250 and 300 MHz spectrometers. Standard pulse sequences were used for the ¹³C, ¹H one-bond, and long-range HMBC spectra.

2.2.4. Elemental analysis measurement

The elemental analysis of benzidinedioxime was determined using Flash EA 1112 CHN Analyzer.

2.2.5. Electronic properties

The electronic spectra of the compounds were obtained using a Shimadzu 160 UV-Visible spectrophotometer over the range (200–1000 nm) using a quartz cell of 1.0 cm length with a concentration of 1.43 mmol L⁻¹ of samples in dimethyl sulphoxide at 25°C.

2.2.6. Powder X-ray diffraction (PXRD)

The crystalline phases and unit cell parameters of the powders were determined by XRD, using a Shimadzu 7000 X-ray diffractometer. At room temperature, data were collected for a 2θ range of 20–80° at a step size of 0.02° and a 5 second count time.

3. Results and discussion

3.1. Fourier transform-infrared (FT-IR) analyses of ligand

FT-IR spectroscopy measurements were performed to examine the functional groups present in the ligand in the range of 4000 cm^{-1} to 400 cm^{-1} .

The FT-IR spectrum of the ligand is shown in Table 3.1. This spectrum confirms the proposed structure. After the condensation reaction, a new peak appeared at 1616 cm^{-1} indicating the formation of an imine $\text{CH}=\text{N}$ bond. This wave number is in agreement with literature data (Saleh and Kafi, 2016).

Table 3.1: characteristic infrared absorption frequencies of benzidinedioxime

Wave number (cm^{-1})	Functional groups
3365, 3296	O-H stretching vibrations of the oxime group
2775	stretching vibrations of saturated C–H
1617	C=N stretching vibrations of imine
1463	C-H bending vibration
1488, 1362, 1258	C=C stretching vibrations of the aromatic ring
970	C-N stretching vibration

3.2. ^1H -NMR and ^{13}C -NMR of ligand

Figure 3.1: shows the ^1H -NMR spectrum of (3Z, 2'E, 3'Z)-N2, N2'-biylbis (N3-hydroxybutane-2,3-diimine). The peaks at 2 ppm in the H-NMR spectrum correspond to the doublet methyl groups $-\text{CH}_3$ at the same environment (Gwaram et al., 2012, Akitt and Mann, 2017, Jacobsen, 2007). The protons of the carbon next to the oxime linkages, $\text{CH}_3\text{-C}=\text{N-OH}$ resonated at 2.5 ppm. The aromatic protons of the biphenyl ring appeared as a quartet to signal around 6.52 – 6.8 ppm and 7.14 – 7.63 ppm in different environments (Gwaram et al., 2012, Akitt and Mann, 2017,

Jacobsen, 2007). The protons attached to oxime appeared to signal at 11.82 ppm. In the ^{13}C -NMR Figure 3:2, the imine groups $-\text{N}=\text{C}-\text{C}$ adjacent to the aromatic ring appeared at 167.56 ppm, whereas, $-\text{N}=\text{C}-\text{C}$ of the oxime group can be seen at 150.4 ppm. The carbon-carbon double bonds $-\text{C}=\text{C}-$ of the phenyl ring are observed at 122.8 – 148.07 ppm. In addition, the peaks at 9.1 and 15.8 ppm correspond to the $-\text{CH}_3$ groups in different environments (Akitt and Mann, 2017, Jacobsen, 2007).

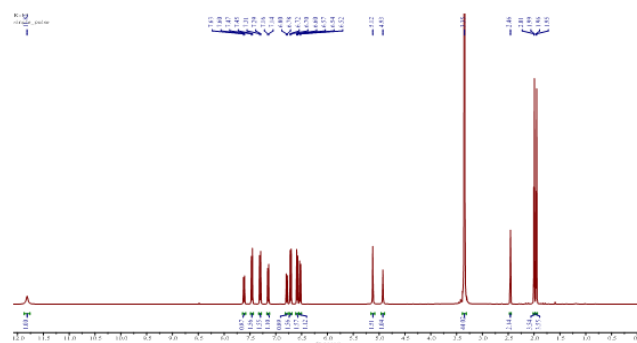


Figure 3.1: ^1H -NMR spectrum of benzidinedioxime

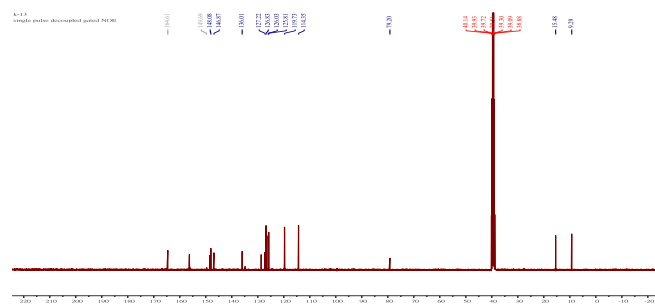


Figure 3.2: ^{13}C -NMR spectrum of benzidinedioxime

3.3. Elemental composition

The composition of the coordinative compounds was determined by the C, H, N, and metal contents. Analytical results indicated a good purity of the compound. The proposed formula and elemental analysis data of the complexes were produced as shown in Table 3.2.

Table 3.2: Calculation and theoretical percentage of C, H, and N in benzidinedioxime

$\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_2$	Calculation percentage %	Theoretical percentage %

C	H	N	C	H	N
71.77	6.43	15.14	68.5	6.29	16.00

3.4. Electronic properties

The ligand was scanned in 200-1000 nm. The spectrum is shown where many noise peaks due to electronic, vibration, and rotation transition are seemed. The spectrum has appeared strong peak at 225 nm that indicated to $n \rightarrow \pi^*$ transition of saturated compound CH_3 containing atoms with unpaired electrons (non-bonding electrons) Figure 3.3 (Sharma, 2013). Peaks resulting from $n \rightarrow \pi^*$ transition are shifted to a shorter wavelength with increasing solvent polarity (Sharma, 2013).

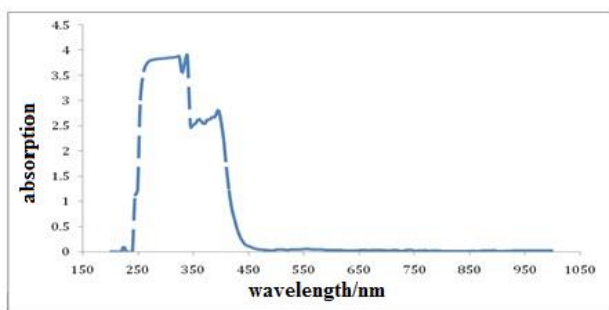


Figure 3.3: Electronic properties of benzidinedioxime

Figure 3.3: displays electronic transitions at around 300-350 nm that indicate high electronic transitions in the UV region. The spectrum shows a sharp peak at around 300-350 nm indicated to $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ (Kudrat-E-Zahan and Haque, 2019, Sharma, 2013, Pavia et al., 2013), the sharp absorption in 400 nm due to $\pi \rightarrow \pi^*$ electronic transition of conjugated unsaturated compound Figure 3.4 (Pavia et al., 2013). It is important to mention electronic properties were reported by other researchers as a main constituent of the benzidine ligand.

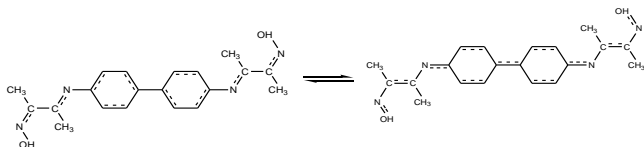


Figure 3.4: Conjugation of benzidinedioxime

3.5. Powder X-ray diffraction

The crystal structure of benzidinedioxime was determined by powder-crystal X-ray diffraction. The diffraction pattern for every phase is as unique as a fingerprint. The peaks pattern of benzidinedioxime in Figure 3.5 has reported it is a single structure and almost all of the crystals were grown in the same phase.

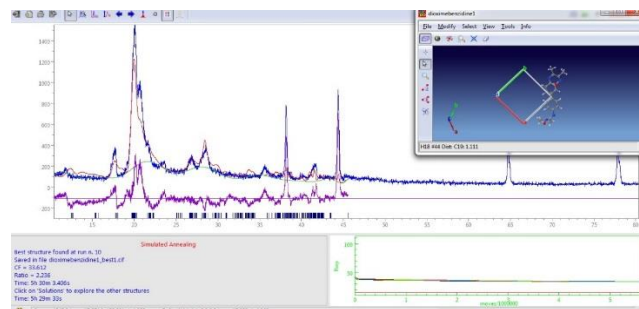


Figure 3.5 Analysis of the PXRD spectrum of benzidinedioxime using the EXPO software program

Figure 3.5 illustrates the analysis of the PXRD spectrum of benzidinedioxime using the EXPO software program. The blue line is the absorbed pattern, the red line is the calculated pattern, the green line is the calculated background and is inscribed at the base of the observed pattern. The violet pattern at the bottom is the difference between observed and calculated values. A minor reference peak is not observed in the data then that is a good match. A minor reference peak could be lost in the background noise so it may be acceptable if they are not observed.

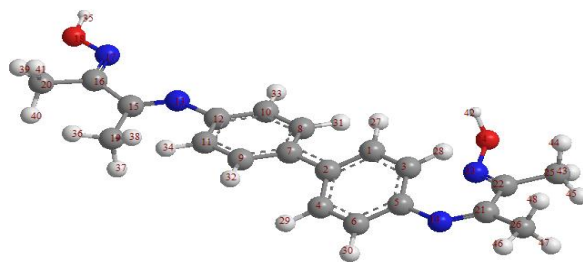


Figure 3.6: PXRD Crystal structure of benzidine dioxime was solved by using EXPO 2014 software.

The crystal structure was solved by using the direct method within EXPO 2014 software and is found to be having the molecular formula $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_2$, molecular weight 350. The crystal system has a triclinic space group P1 (1) with $a = 9.96474 \text{ \AA}$, $b = 9.84346 \text{ \AA}$, $c = 992847 \text{ \AA}$, and $\alpha = 98.853^\circ$, $\beta = 91.032^\circ$.

α , $\gamma = 88.809$ A°. The crystal structure of benzidinedioxime has no plane of symmetry. One of the phenyl rings is perpendicular to the other phenyl ring and the two diacetylmonoxime substituents are not in the same plane as well. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analyses in Figure 3.6 confirmed this result. They have shown only two peaks in different chemical shifts for the biphenyl and dimethyl groups in different environments.

Conclusion

The newly synthesized Schiff base $\text{N,N}'$ -([1,1-biphenyl]-4,4-diylbis-[azanylylidene butane-3,2 diylidenedihydroxylamine]) was synthesized and characterized by FTIR, UV-visible, NMR spectroscopy, elemental analysis, and powder X-ray diffraction. All analyses confirmed that the reaction of benzidine with diacetylmonoxime in the molar ratio 1:2. ^1H - ^{13}C -NMR spectroscopy and powder X-ray diffraction analyses have shown the absence of the plane symmetry.

Conflicts of interest

The authors whose names are listed immediately above certify that they have did not receive support from any organization for the submitted work. No funding was received to assist with the preparation of this manuscript. No funding was received for conducting this study. No funds, grants, or other support were received.

Data Availability:

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

Software:

PXRD data were analyzed by EXPO software EXPO2014 installation <http://www.ba.ic.cnr.it/softwareic/expo/expo2014-installation/>

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