

Synthesis and Fluorescence Spectrum of N, N' Bis (2-Hydroxy Benzylidene) Benzidine with Different Solvents and Different PH

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Abstract: In this study, a fluorescent compound; N, N'-Bis (2-Hydroxy Benzylidene) Benzidine, ($C_{26}H_{20}N_2O_2$) prepared and calculated by FT-IR, 1H NMR, UV-Vis and fluorescence procedures. The 1H NMR field examined in Chloroform-d solvent. The Fourier Transform-Infrared FT-IR in hard case detected in the area 4000-600 cm^{-1} . The absorption spectrum of the Bis (2-Hydroxy Benzylidene) Benzidine resolved in tetrahydrofuran registered on the range 250-800nm. The fluorescence spectrum show in the region 520-700nm in different pH at room temperature. Photoluminescent properties of the title compound examined in tetrahydrofuran, Chloroform, acetone, and Toluene. The intensity and Stoke's move of N, N' Bis (2-Hydroxy Benzylidene) Benzidine in THF solvent found greater than other solvents. The structural value, fundamental vibration modes, Proton Nuclear magnetic resonance isotropic chemical changes, and absorption spectrum of the N, N'-Bis (2-Hydroxy Benzylidene) Benzidine computed by density functional theory (DFT) using B3LYP/6-311G (d, p) basis set.

Keywords: Fluorescence, N, N' Bis (2-Hydroxy Benzylidene) Benzidine, Solvent Effect, PH Effect, Density Functional Theory (DFT)

1. Introduction

The Fluorescent compounds now overwhelm the line of molecular sensors for chemical studies and biologically on account of them to offer priority to high discovery sensitivity, low noise, and large active domains [1, 2]. These characteristics will be especially apparent in the change of modern optical analytical tools high thoroughness. Fluorescent compounds offering high absorptivity and fluorescence quantum produce, which participate in the cause that they are the greatest significant clan of luminescent analyses [3]. The evolution of luminescence probes and sensors is the topic of dense research both in organic and health science [4]. Fluorescent compounds which syntheses from molecules are strong apparatus to imagine the organic procedure in active cells and creatures. Since detection of aromatic fluorescent composites in the end nineteenth century, endeavours have

prepared to "see" the conduct of exact biomolecules in active systems using dye as database. Also, many fluorescent sensors or organic sensors, which acquainted as molecules that offer an alteration in fluorescence ownerships in the presence of their essential molecule studied and applied to biological studying. Presently, a change of sensors is a ready that metallic ions, enzyme liveliness, pH, and sensor molecules [5]. Fluorescence is a strong implement for examining the construction and dynamics of substance or active systems at a molecular field. Solid surfaces, Polymers, proteins, liquid of surfactants, organic membranes, nuclei acids and organism cells are famous samples of systems in which assessment of the factors like polarity, instruction, liquids, electrical potential and molecular mobility is conceivable by incomes fluorescent molecules taking the role of sensors [6, 7, 8]. The many applications of fluorescence compounds confirm the requirement for an account of the fluorescence

characteristics of this molecule in a liquid solution. Specially, a characterization of the effects of solvent, pH, concentration, irradiation, and excitation wavelength possibly increases the sensitivity and usage of enzyme and other determinations as well as clarify other observations of living and chemical advantage [9]. In this study, the synthesis new fluorescent Schiff base compound by reaction to benzidine and 2-Hydroxy benzylidene. The compound named N, N' bis (2-hydroxy benzylidene) benzidine synthesized by standard processes and described by the elemental analysis and determination of the melting point (figure 1).

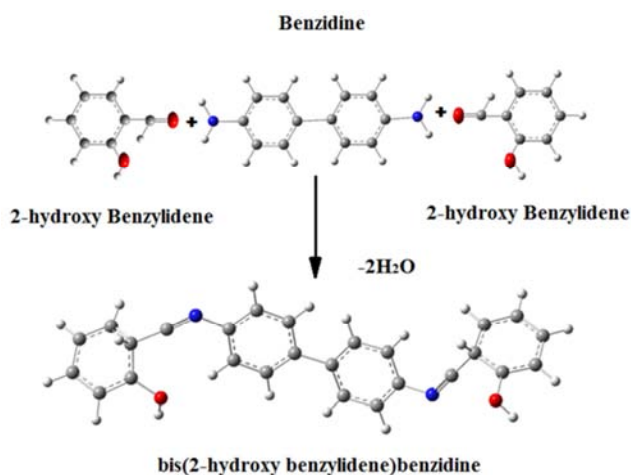


Figure 1. Synthesis of N, N' bis (2-hydroxy benzylidene) benzidine.

2. Materials and Methods

All Chemical Materials utilized for the preparing of Bis (2-hydroxy benzylidene) Benzidine with a stated purity of 99%. Benzidine from fluka chemicals. (2-hydroxy benzylidene) from the Sigma Chemical Company. (USA), the solvents such as benzene, tetrahydrofuran, Ethanol, Chloroform, Toluene and Aceton were of high purity also utilized without additional purification.

Synthesis of Bis (2-hydroxy benzylidene) Benzidine

The Schiff base synthesized from the mixing (two moles) 2-hydroxy benzylidene, with benzidine (one mole) in 25ml benzene and (3-4) droplets of glacial acetic acid. This blend refluxed on aqueous baths for more ten hours. A result masses discrete out on cooling, filtered off.

Yield: 75%. Colour: Yellow. Melting Point: 210-212°C. Molecular formula $C_{26}H_{20}N_2O_2$. FT-IR (KBr, ν , cm^{-1}): 1616 ($C=N$), 1568 ($C=C$), 3554 (OH), 3057 (C-H). UV-Vis (THF): λ_{max} / nm (log ϵ) 400. 1H NMR (300 MHz, Chloroform- d_6 , δ , ppm): 7.2, 7.34-7.76 and 8.68 ppm are the proton signals due to the solvent, protons of aromatic and azomethine ($-CH=N-$) proton one-to-one, the proton signal of phenolic ($-OH$) proton disappear

3. Experimental Parts

The Experimental characterizations of the compound

considered by FT-IR, 1H NMR, absorbance spectrum and fluorescence spectrum techniques. Under is an explanation of these techniques.

3.1. FT-IR Spectrum

Fourier transform-infrared spectra (FT-IR) calculations were used the KBr technique utilizing a Shimadzu corporation 8400S FTIR spectrometer. The FT-IR spectrum calculated in the region of $4000-400\text{ cm}^{-1}$.

3.2. UV-Vis Spectrum

All absorbance spectrum of the Bis (2-hydroxy benzylidene) Benzidine studied in the range 200–800 NM is utilizing a Perkin Elmer Lambda 35 UV-Vis spectrometer.

3.3. 1H NMR Spectrum

1H Proton magnetic resonance spectrum studied (299K) on AV300 MHz spectrometer. The composite resolved in Chloroform- d solvent. Chemical shifts studied in ppm proportional to tetramethylsilane (TMS) for 1H NMR. 1H Proton magnetic resonance spectrum gained at 300 MHz of the base frequency.

3.4. Fluorescence Spectrum

A Shimadzu RF-5301PC spectrofluorophotometer utilized in fluorescence computations. The spectrum of the title compound gained in THF solvent, the concentration was 2×10^{-5} M.

3.5. Computational Systems

The structural geometry, with no similarity constrains, studied by Gaussian 09 package utilized density functional theory (DFT) computing with a cross functional B3LYP (Becke's three parameter reciprocity functionality integrated with the LYP incline modified association useful) at the foundation set 6-311G (d,p) by the Berny way [13] to study all constant points as a minimum. The computed vibrational frequencies determined that the structure was steady (no fantasy frequency). The TD-DFT way has commonly found a powerful and accurate way of characterizing low-lying excited cases of combined molecules and useful to dissolve many of chemical and physical issues. Based on the studied geometry and by utilizing time-dependent density functional model (TD-DFT) ways in a vacuum, the allowable excitation and oscillator powers of the electronic absorption spectrum prognosticated. Lastly, the Nuclear Magnetic Resonance (NMR) chemical shift performed utilizing Gauge Independent Atomic Orbital (GIAO) way [14, 15].

4. Results and Discussion

4.1. Vibrational Frequencies

The theoretical FT-IR at DFT/B3LYP level of 6-311G (d,p) basis set of the title compound is given in Figure (2). furthermore, the FT-IR spectrum of the Benzidine and Bis

(2-hydroxy benzylidene) benzidine are given in Figures (3), (4). The vibrational frequencies of the fundamental types of Bis (2-hydroxy benzylidene) benzidine spotted nearby the theoretical IR frequencies, the IR computations of the title

compound are shown in table (1). The omission unharmonicity in a actual system, the vibrational frequency theory for Bis (2-hydroxy benzylidene) benzidine with B3LYP/6-311G (d, p) are little larger than the studied values.

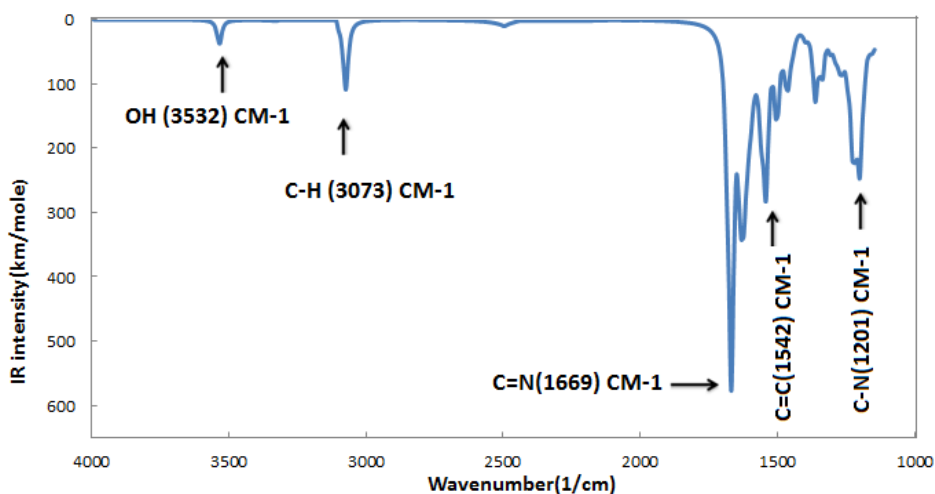


Figure 2. Theoretical FT-IR spectrum of bis (2-hydroxy benzylidene) benzidine.

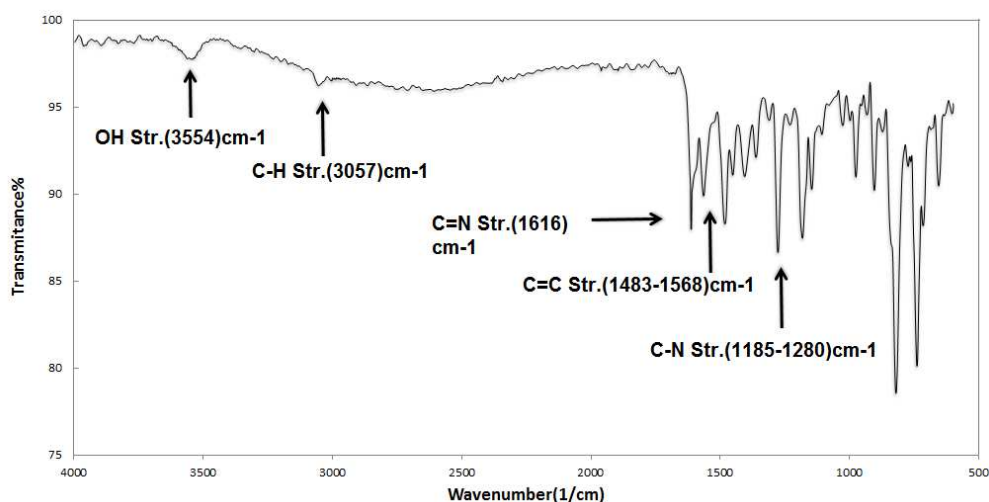


Figure 3. Experimental FT-IR spectrum of bis (2-hydroxy benzylidene) benzidine.

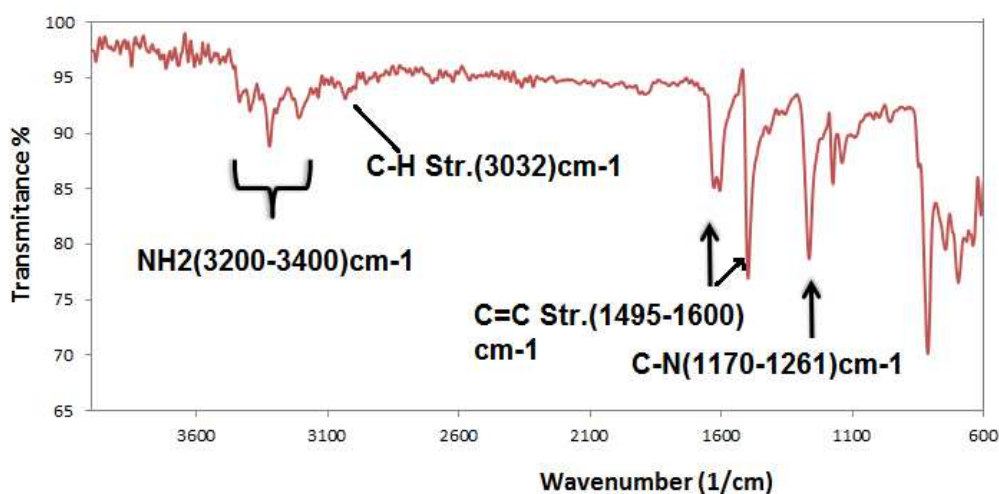


Figure 4. FT-IR spectrum of benzidine.

Table 1. Theoretical and Experimental FT-IR spectroscopy for bis (2-hydroxy benzyldene) benzidine.

compound	(OH)	(C=N)	(C-N)	(C-H)	(C=C)	(NH ₂)
Benzidine	-	-	1170-1261	3032	1495-1600	3200-3400
Experimental bis (2-hydroxy benzyldene) benzidine	3554	1616	1185-1280	3057	1483-1568	-
Theoretical bis (2-hydroxy benzyldene) benzidine	3532	1669	1200	3073	1542	-

4.1.1. C-H Vibrations

The aromatic compound displays the vibration modes of C-H in the domain 3000-3100 cm^{-1} [16]. The band of C-H extending vibrations of the bis (2-hydroxy benzyldene) benzidine was 3057 cm^{-1} . DFT calculations predict refer to modes 3073 cm^{-1} for B3LYP/6-311G (d, p) levels of the model. The computations presented that the theoretical and experimental data closely coincide and these projects are in decent nearby with literature values [17].

4.1.2. C-C Vibrations

In Benzene rings the C=C stretching modes are appearing in the spectral domain 1650-1400 cm^{-1} [18]. In the title compound, the stretching vibrations of C=C found at 1483-1568 cm^{-1} . These calculations agree with theoretical way and in addition to nearby with the literature values [17].

4.1.3. C=N Vibrations

The new peak appears at 1616 cm^{-1} after the condensation reaction indicating amine (CH=N) bond. -NH₂ peaks of benzidine vanish in the FT-IR spectrum of Bis (2-hydroxy benzyldene) benzidine. This result agrees with the studied vibrations 1669 cm^{-1} obtained from DFT for B3LYP/6-311G (d, p). The consequences presented that the theoretical results closely accord with experimental and as well as with the literature data [19].

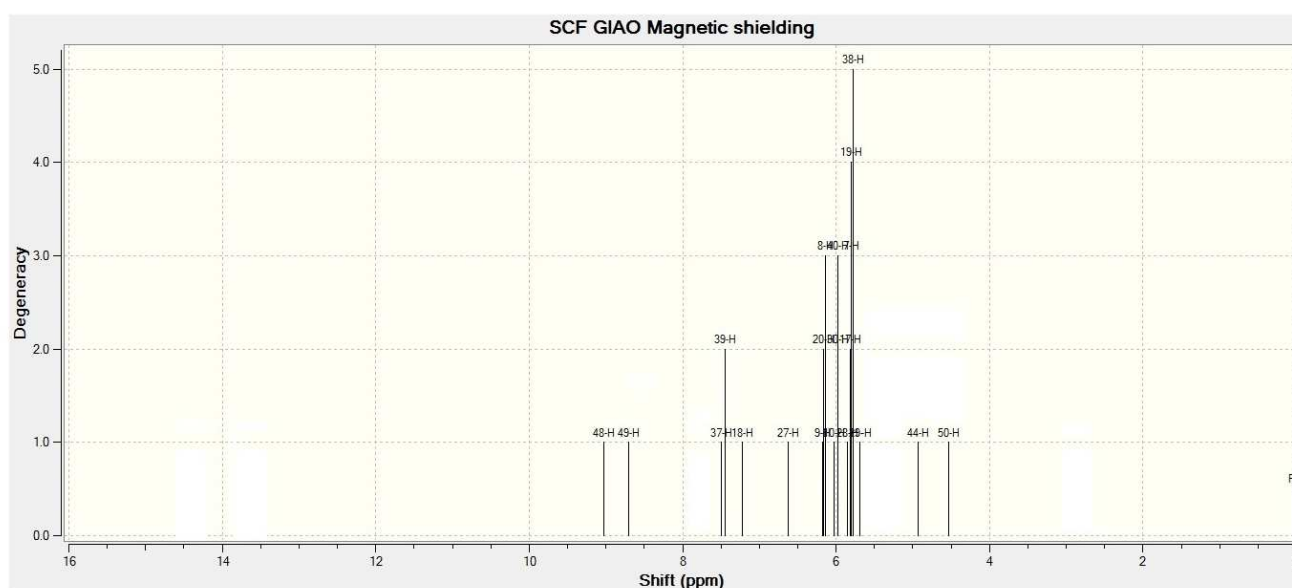
4.1.4. OH Group

The OH group of alcohols and phenols presents a powerful

stretch in the area between 3200 and 3650 cm^{-1} [17]. In states where hydrogen bonding is present (as it would be in neat fluids, unless it was banned by steric hindrance) this absorption is fairly wide and typically between 3200 and 3600 cm^{-1} [17, 19]. The IR spectrum of Bis (2-hydroxy benzyldene) benzidine at 3554 cm^{-1} with strong and medium assigned of the title compound. These results are a good agreement with B3LYP/6-311G (d, p) way and in addition to the literature data [17,19].

4.2. NMR Spectrum for the N, N Bis (2-Hydroxy Benzyldene) Benzidine

Experimental ¹H-NMR spectrum of Bis (2-hydroxy benzyldene) benzidine is given in Figure (6). The molecular geometry of Schiff bases established in this spectrum. NMR spectral data abridged as follows: ¹H NMR/CDCL₃/δ ppm: The proton signals of solvent at 7.24ppm., 7.34-7.76 ppm is due to the protons of aromatic and azomethine (-CH=N-) proton at 8.68ppm, the proton of phenolic (-OH) is disappear because a protic deuterated solvent is used (e.g., D₂O or CD₃OD), then the OH proton will exchange with the deuterium and the peaks will shrink or disappear entirely, since D (2H) does not show up in the 1H NMR spectrum. The theoretical spectrum, which studied with GIAO way using DFT/B3LYP/6-311G (d, p) way agrees with Experimental ¹H-NMR spectrum, using Gaussian 09 package to perform The NMR spectra calculations, as shown figure (5).

**Figure 5.** Theoretical¹H NMR of Bis (2-hydroxy benzyldene) benzidine compound.

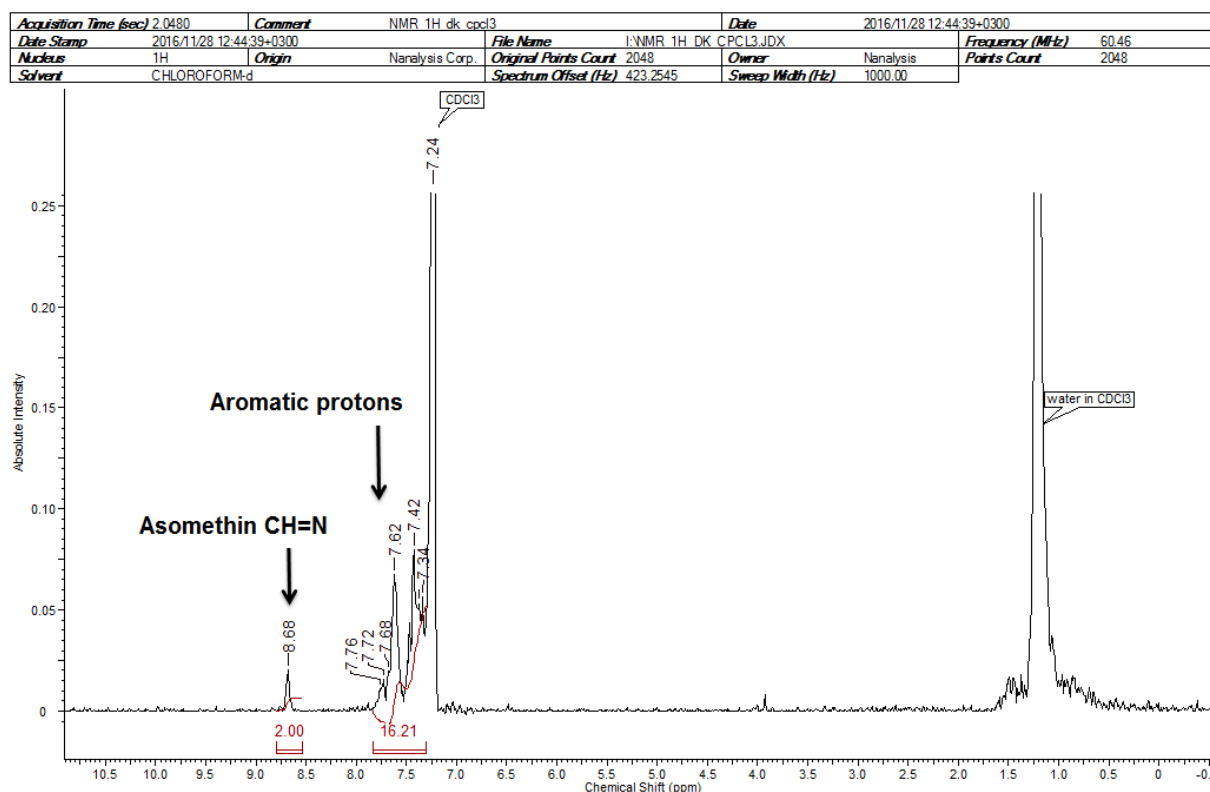


Figure 6. Experimental ^1H NMR of Bis (2-hydroxy benzylidene) benzidine in CDCl_3 solvent.

4.3. UV/Vis Spectrum

Quantum calculations were approved to the electronic properties of N, N' Bis (2-hydroxy benzylidene) benzidine. The TD-DFT/B3LYP way utilizing 6-311G (d, p) basis sets utilized to define the excited states for examining the UV-Vis absorption spectrum of the title compound. The experimental and theoretical absorption spectrum of the title compound

can be seen in Figures (7), (8). From the figures, UV-Vis spectrum of the title compound displays one peak at 380 nm. From TD-DFT (C-PCM) /B3LYP method, the theoretical absorption bands expected at 400 nm at 6-311G (d, p) basis set and in addition to can show the data are the closest with compared to the experimental data.

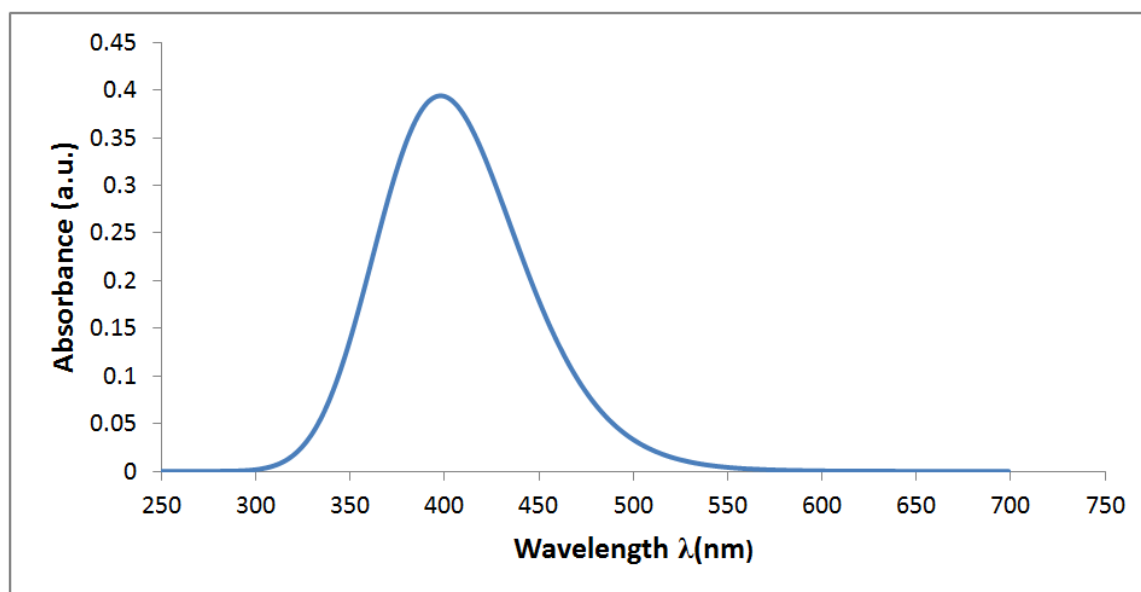


Figure 7. Theoretical electronic spectrum for Bis (2-hydroxy benzylidene) benzidine

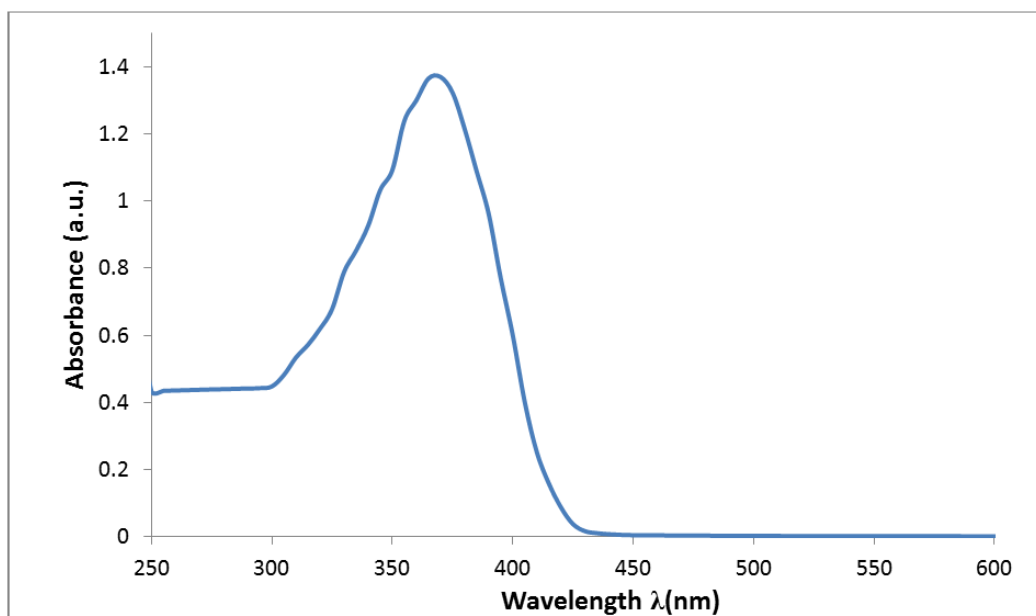


Figure 8. Experimental electronic spectrum for Bis (2-hydroxy benzylidene) benzidine.

4.4. Fluorescence Characteristics

The fluorescence spectrum of Bis (2-hydroxy benzylidene) benzidine in tetrahydrofuran solvent at the concentration of 2×10^{-5} M at pH (6) and room temperature shown in Figure (9). From this figure displays a production peak at 553 nm and excited at 400 nm. The fluorescence amount was a good, this is because of prepared aromatic compound usually

contain of interconnected aromatic circle structure of 2-hydroxy benzylidene attached to the central structure, conjoining numerous ring structures increase the concentration of states and lets for a lower band gap substantial, letting electronic HOMO/LUMO excitation at lesser energies [20].

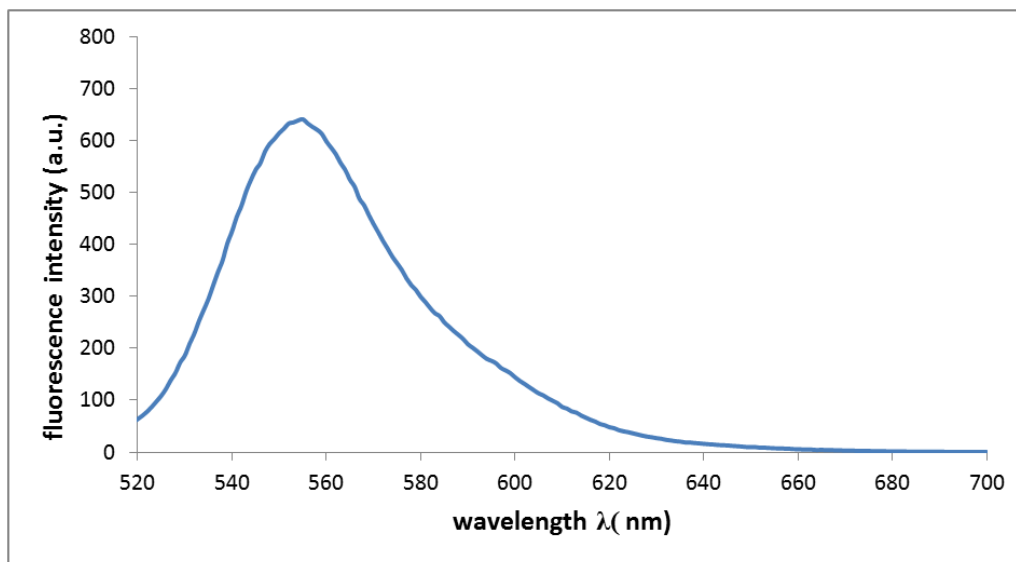


Figure 9. Fluorescence emission Spectrum of Bis (2-hydroxy benzylidene) benzidine.

4.4.1. Effect of pH on Fluorescence Spectrum

The intensity of Aggregation Induced Enhanced Emission (AIEE) of the System influence really by the PH of the medium [17]. The effect of acidic on the spectrum of N, N' Bis (2-hydroxy benzylidene) benzidine was examined by NaOH and HCl in aqueous can be seen in Figures (10, 11). Bis (2-hydroxy benzylidene) benzidine can exist in the next forms of different pH: (i) pH (5 to 7) High form (ii) pH (8 to

10) Low form and (iii) at pH (2 to 5) middle forms. The fluorescence intensity upsurges with increasing of pH (2 to 5). The intensity constant up to pH (5-7). The acidic domain was suitable for the stability of the compound name. Finally, it decreases up to pH=10. The finest value for the fluorescence amount of PH (6), this mean that quantum yield was very good at this point.

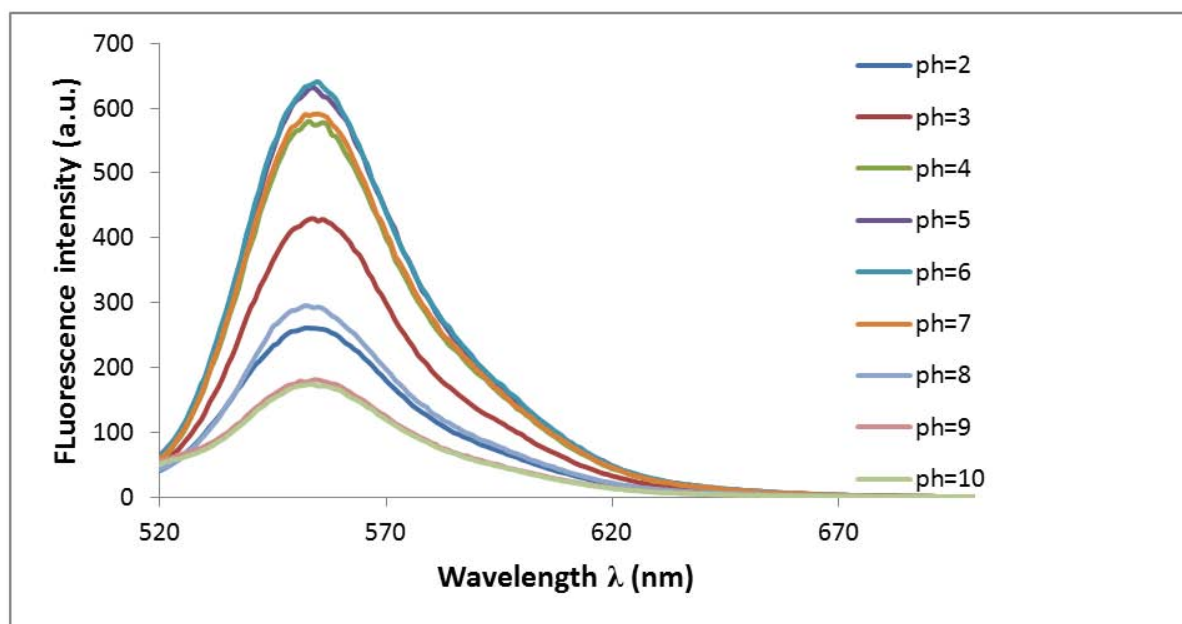


Figure 10. Effect of pH of fluorescence intensity of Bis (2-hydroxy benzylidene) benzidine.

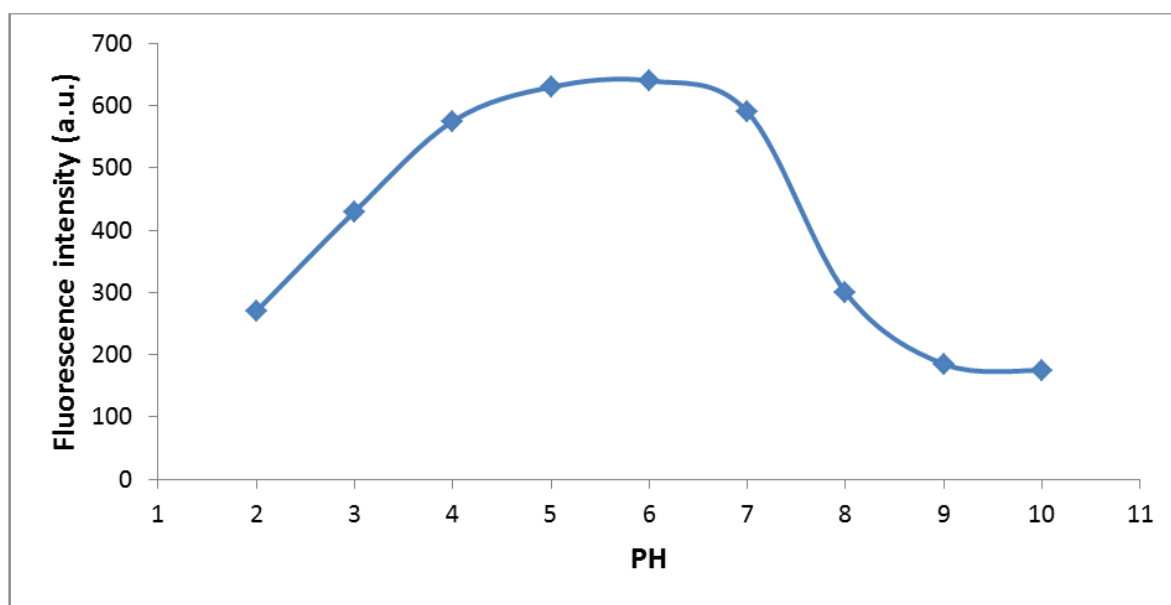


Figure 11. Effect of pH of fluorescence intensity of bis (2-hydroxy benzylidene) benzidine.

4.4.2. Effect of Solvent on Fluorescence Spectral Properties

In Table (2) determined the best emission and excitation wavelengths of N, N' Bis (2-hydroxy benzylidene) benzidinein with different solvents. According to the results, Bis (2-hydroxy benzylidene) benzidinein has the maximum emission in THF solvent. The Stoke's shift ($\Delta\lambda_{ST}$) in all using solvents was studied as in the literature [21] and can be seen in Table (1). The higher Stoke's shift provisions very little background signals and allows the usage of the cmpound in the construction of a fluorescence sensors. Bis (2-hydroxy benzylidene) benzidinein in THF solution had higher Stoke's shift with the value of 128 nm, in comparison with the other solvents as seen in Table (2). This indicates that the usage of

Bis (2-hydroxy benzylidene) benzidinein as fluorophore is useful in THF solution. The emission spectra of Bis (2-hydroxy benzylidene) benzidine in different solvents shown in Figure (12).

Table 2. Fluorescence spectra related data of Bis (2-hydroxy benzylidene) benzidinein.

Solvent	$\lambda_{max} (Ex)$	$\lambda_{max} (Em)$	I (Em)	$\Delta\lambda_{ST}$
THF	400	553	640	153
CDCL ₃	428	532	575	104
Toluene	429	534	610	105
Acetone	427	529	270	102

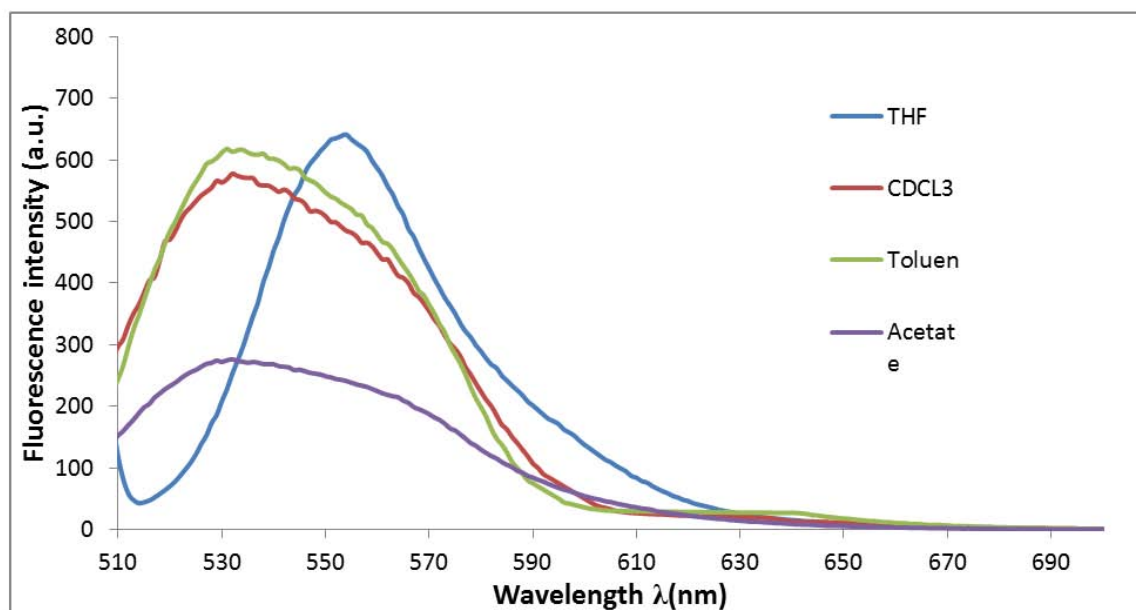


Figure 12. Emission spectra of Bis (2-hydroxy benzylidene) benzidine in different solvents.

5. Conclusion

The new N, N' Bis (2-Hydroxy Benzylidene) Benzidine was synthesized. Uses the fluorescence spectrum, FT-IR, absorbance spectrum, and NMR techniques to study Characterizations of the title compound. Theoretical results of FT-IR, UV-vis, and NMR uses a DFT/B3LYP way with 6-311G (d, p) basis set. The fluorescence intensity of the title compound in different solvents was defining. Stoke's shift values in the different solvents presented that THF was the finest solvent. It was strong the effect of pH on the Fluorescence intensity, the finest value for Fluorescence intensity of pH (5 to 7). This result of the PH value will increase quantum efficiency. Fluorescence intensities of N, N' Bis (2-Hydroxy Benzylidene) Benzidine in several solvents were studied. Stoke's shift values in the several solvents showed that THF was the finest solvent to use N, N' Bis (2-Hydroxy Benzylidene) Benzidine as fluorescent probes.

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