



## Structure and stereoisomers of a chelating ligand 3,3'- ([1,1'-biphenyl]-4,4'-diylbis(azanylylidene))bis(indolin-2-one)

### Research article

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#### Abstract

An organic ligand, 3,3'-([1,1'-biphenyl]-4,4'-diylbis(azanylylidene))bis(indolin-2-one), emerged from reaction between benzidine and 1*H*-indole-2,3-dione was structurally analysed. The molecular structure of compounds was confirmed by IR, UV-Vis and NMR spectroscopy. The ratio of geometric isomers in the synthesised product was determined by <sup>1</sup>H-NMR analysis in DMSO-d<sub>6</sub> solution.

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**Keywords:** isatin, benzidine, Schiff base, stereoisomerism, spectroscopy, structural analysis

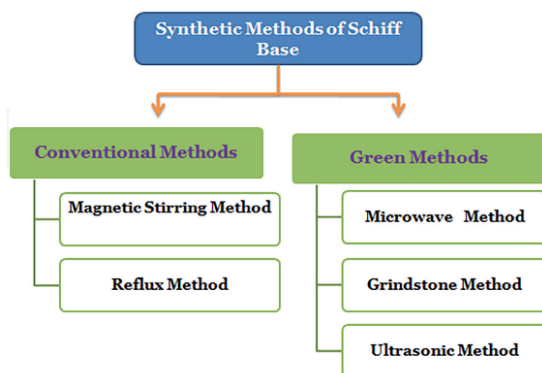
### 1. INTRODUCTION

The imines or Schiff bases was discovered by Italian chemist Hugo Schiff about 161 years ago [1]. They are the most widely used ligands for metallic cations, the discovery being a major step forward for the coordination chemistry [2].

The organic ligand with Schiff base moiety, but especially their complexes with metallic cations, have colossal applications in analytical chemistry [3] and dye technology [4].

Organic ligands with Schiff bases scaffold exhibit biological properties such as antibacterials [5], anti-inflammatories [6], antifungals [7], insecticides [8], anticancer [9], antioxidants and antidiabetes [10], and anti-tuberculosis among many others [11].

The synthesis of imines is carried out from carbonyl compounds and primary amines by both conventional [12] and unconventional routes [13]. The reaction is reversible and generally requires acid or basic catalysts [14]. All methods of synthesis of Schiff bases are summarized in Figure 1.



**Figure 1.** Synthesis of Schiff Base [15].

## 2. MATERIALS AND METHODS

### 2.1. Materials

Reagents, isatin and benzidine are commercial substances from Sigma-Aldrich and were used without further purification.

### 2.2. Apparatus

Ultraviolet-visible spectra were recorded in DMF solution using a Varian Cary spectrometer. The melting temperature of reagents was determined with a Gallenkamp digital melting point

apparatus. The infrared spectra were recorded with the help of an Alpha Bruker Optics spectrometer. <sup>1</sup>H-NMR spectra were acquired on Bruker Avance II spectrometer at 300 MHz in DMSO-d<sub>6</sub>. <sup>13</sup>C-NMR analysis was performed using a Bruker Avance II spectrometer at 75 MHz with DMSO-d<sub>6</sub> as solvent. Chemical shifts  $\delta$  are measured in parts per million (ppm) relative to tetramethylsilane (TMS). The melting point of the product and was done by means of Setsys Evolution, Setaram TG-DTG 92-16 thermobalance under an air flow.

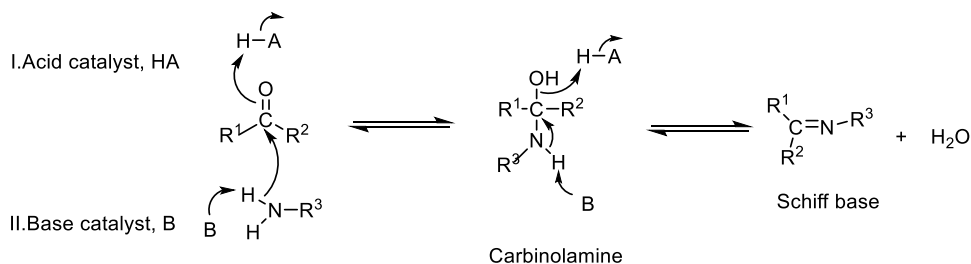
### 2.3. Methods

*Procedure for the conventional synthesis of 3,3'-([1,1'-biphenyl]-4,4'-diylbis(azanylylidene))bis(indolin-2-one) [16]*

4.32 mmol of Benzidine and 2.16 mmol of isatin were dissolved in a 50 mL round bottom flask containing 20 mL of anhydrous methanol. The resulting solution is introduced in a silicone oil bath on a magnetic stirrer hot plate and refluxed for 1.5h. The initial solution has *pH* of 6.5 and dark red color. During the reaction, the solution changes its color to orange. As the reaction product appears, it precipitates at the bottom of the balloon. After cooling to room temperature, the reaction medium is filtered, and the precipitate is washed with its own filtrate, and then washed with hot ethanol. The product is dried in an oven at 110 °C for 4h. Orange crystals of product are obtained. The product is very thermally stable and has a very high melting point 397°C. Yield 90%.

## 3. RESULTS AND DISCUSSION

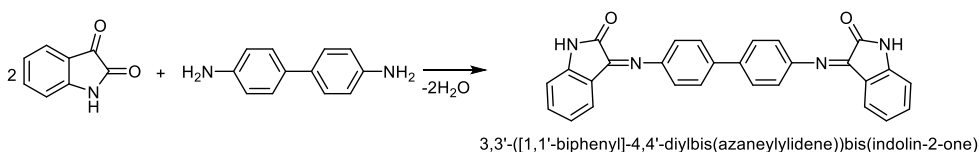
In the Schiff base reaction, the nucleophilic reactant is the primary amine and the electrophilic substrate is the aldehyde or ketone. The reaction is a nucleophilic addition reaction with a carbinolamine as intermediate. The hemiaminal group is dehydrated by either an acid or a base catalyst to the imine group. The reaction mechanism [17, 18] by which the Schiff base is obtained is described in Scheme 1.



**Scheme 1.** Reaction mechanism of Schiff base formation: I-acid-catalyzed pathway, II-base-catalyzed pathway.

To shift the chemical equilibrium towards the reaction product, the water of reaction is sometime removed with a Dean Stark apparatus or using dehydrating agents.

The Schiff base ligand, 3,3'-([1,1'-biphenyl]-4,4'-diylbis(azananylylidene)) bis(indolin-2-one), results from the reaction of isatin with benzidine and has the structure depicted below:

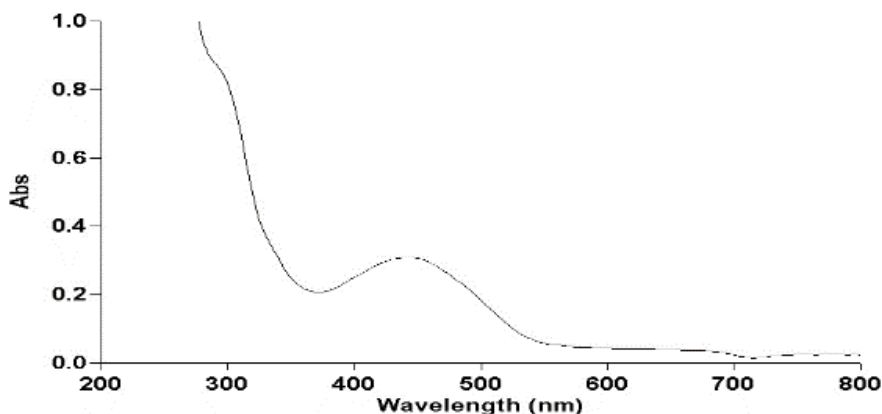


### 3.1. Structural analysis of Schiff base

#### a) UV-visible absorption spectrum

The Schiff base shows an intense absorption band in the visible region of the spectrum (Figure 2, Table 1) at wavelength of 440 nm ( $\epsilon=2446$ ). In the visible spectrum, this wavelength corresponds to blue radiation. So, the compound absorbs intensely in the visible range only one light radiation out of the six, the blue radiation 440 nm. The color of the compound is the color resulting from mixing the other light radiations not absorbed by the substance: violet, green, yellow, orange and red. Among these we distinguished that there are complementary radiations (those that by mixing give white light, improperly also called colorless): violet-yellow (by merging they give colorless) and green-orange (by merging they give colorless). The red radiation remained, therefore the product crystals are orange to red color. The second absorption reveals a very weak band as shoulder

and appear at 694 nm ( $\epsilon=23$ ). A third absorption band exhibits its maximum in ultraviolet region at wavelength of 294 nm ( $\epsilon=6855$ ).



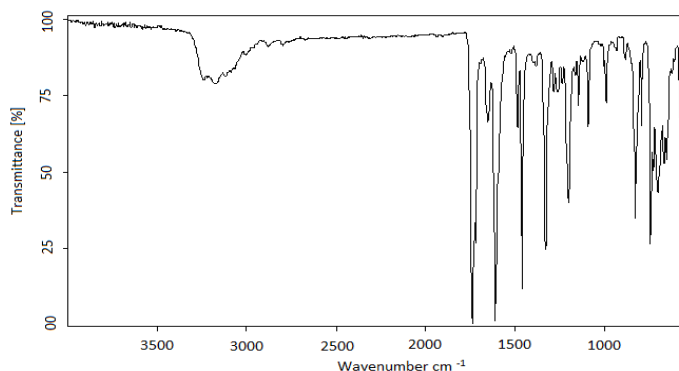
**Figure 2.** UV-VIS spectrum of 3,3'-([1,1'-biphenyl]-4,4'-diylbis(azanylylidene)) bis(indolin-2-one) recorded in DMF  $10^{-4}$  mol/L.

**Table 1.** The electronic absorption bands of 3,3'-([1,1'-biphenyl]-4,4'-diylbis(azanylylidene)) bis(indolin-2-one)

Compound	$\lambda_{\max}$ nm( $\text{cm}^{-1}$ )	Transition	$\epsilon_{\max}$
$\text{C}_{28}\text{H}_{18}\text{N}_4\text{O}_2$	294 (34013)	$\pi \rightarrow \pi^*$	6855
	440 (22727)	$n \rightarrow \pi^*$	2446
	694 (14409)	$\pi \rightarrow \pi^*$	23

#### b) Infrared spectrum

Infrared spectrum of product shows the very intense stretching vibration of imine band ( $\text{C}=\text{N}$ ) at  $1613 \text{ cm}^{-1}$ . The carbonyl group ( $\text{C}=\text{O}$ ) has also a very strong stretching absorption band at frequency of  $1738 \text{ cm}^{-1}$ . The amino group of five-membered 3-imino-1,3-dihydro-2*H*-pyrrol-2-one ring (NH) display symmetric and asymmetric stretching valence vibrations at  $3121 - 3236 \text{ cm}^{-1}$  with medium intensity. At  $1285 \text{ cm}^{-1}$  we observe the  $\nu(\text{C}-\text{N})$  stretching vibration which has a strong absorption of infrared radiation. These bands and the entire IR spectrum (Figure 3) confirm the structure of the imine product.



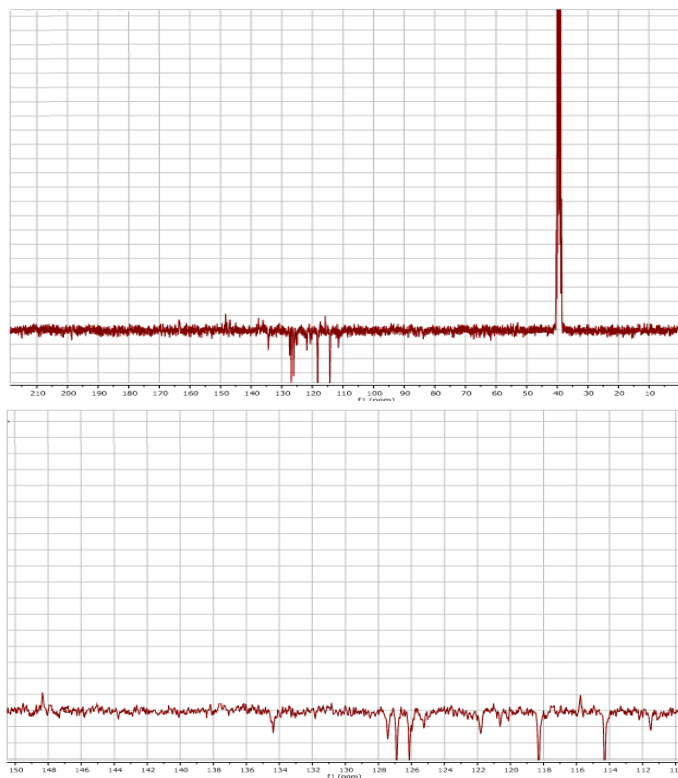
**Figure 3.** IR spectrum of 3'-([1,1'-biphenyl]-4,4'-diylbis(azanylylidene))bis(indolin-2-one).

### c) $^{13}\text{C}$ NMR and $^1\text{H}$ NMR spectra

The synthesized ligand has low solubility in most common organic solvents. However, it dissolves very well in dimethyl sulfoxide and DMSO- $d_6$  solvent was chosen for recording NMR spectra. The recording of  $^{13}\text{C}$  NMR spectrum was done using  $J$ -modulated spin-echo experiment at 75 MHz.

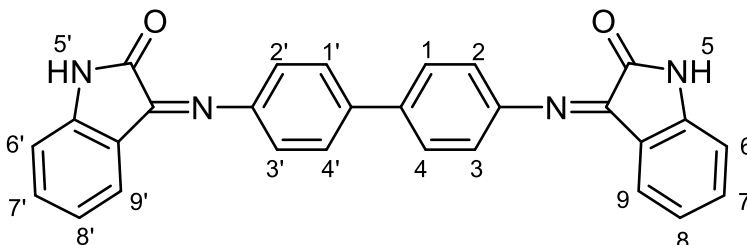
Primary and tertiary carbon atoms display peaks below the baseline, and secondary and quaternary carbon atoms exhibit peaks above the baseline (Figure 4). The values of  $^{13}\text{C}$  chemical shifts ( $\delta$ , ppm) are the following:

Carbon	C <sub>1</sub> ,	C <sub>2</sub> ,C <sub>6</sub>	C <sub>3</sub> ,C <sub>5</sub>	C <sub>4</sub>	C <sub>7</sub>	C <sub>8</sub>
atoms	C <sub>1'</sub>	C <sub>2'</sub> ,C <sub>6'</sub>	C <sub>3'</sub> ,C <sub>5'</sub>	C <sub>4'</sub>	C <sub>7'</sub>	C <sub>8'</sub>
( $\delta$ , ppm)	126.8	121.7	118.3	134.3	148.3	115.7
Carbon	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>
atoms	C <sub>9'</sub>	C <sub>10'</sub>	C <sub>11'</sub>	C <sub>12'</sub>	C <sub>13'</sub>	C <sub>14'</sub>
( $\delta$ , ppm)	127.4	114.2	126.1	120	125.2	111.4



**Figure 4.**  $^{13}\text{C}$  NMR spectrum of 3'-([1,1'-biphenyl]-4,4'-diylbis(azanylylidene)) bis(indolin-2-one). DMSO- $d_6$  peak at 39.5 ppm.

Under similar conditions, the  $^1\text{H}$  NMR spectrum of the compound was recorded at 300 MHz. The protons from residual DMSO present as an impurity in the DMSO- $d_6$  solvent exhibit at 2.55 ppm (quintet) and 3.38 ppm. Also, the protons from the impurities  $\text{H}_2\text{O}$  (singlet) and hemi-deuterated water HOD (triplet 1:1:1) have a prominent absorption in the spectrum at about 3.3 ppm (Figure 5). The proton chemical shifts ( $\delta$ , ppm) and coupling constants ( $J$ , Hz) are as follows:

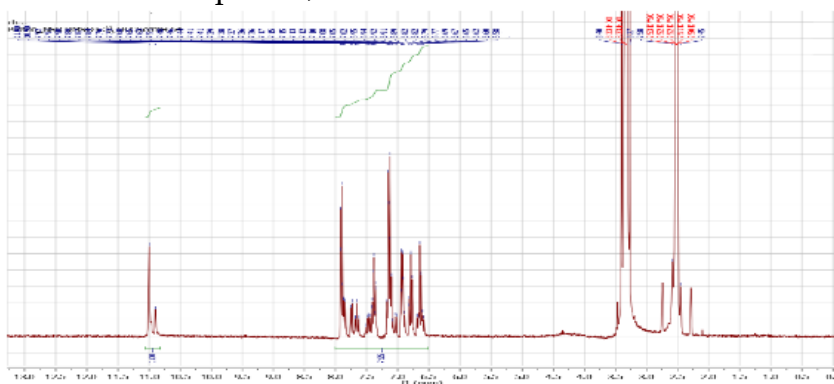


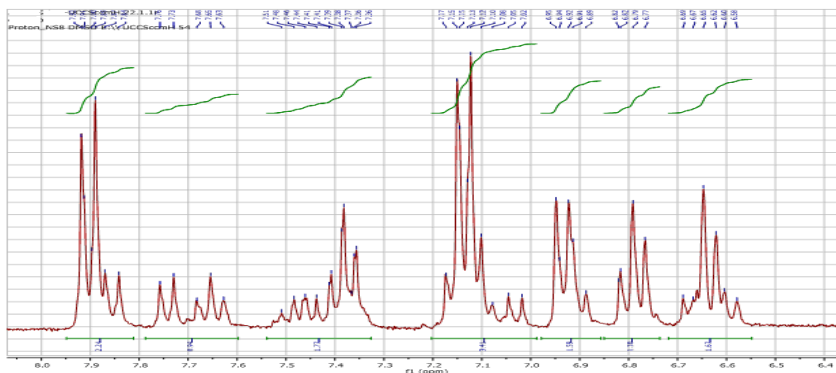
<i>Protons</i>	H1, H1',H4, H4'	H6,H6'	H7,H7'	H8, H8
( $\delta$ , ppm)	6.58-6.82	6.89-6.95	7.01-7.13	7.14-7.20
<i>J</i> (Hz)	9; 6	9; 6; 3	9; 6	9; 6;3
<i>Protons</i>	H9, H9'	H2, H2',H3, H3'	H5, H5'	
( $\delta$ , ppm)	7.36-7.51	7.63-7.92	10.90-11.00	
<i>J</i> (Hz)	6; 3	9; 6		

Integration of the  $^1\text{H}$  NMR signals confirms the number of magnetically equivalent protons that the molecule contains. There are two distinct groups of protons, the aromatic ones on the benzene nucleus and the protons in the isatin moiety. These protons clearly display their distinct absorption peaks in the range  $\delta=6\div 8$  ppm and coupling constant ( $J$ , Hz) can be determined.

The protons on benzidine moiety display at 6.58-6.82 ppm (H1, H1',H4, H4') and 7.63-7.92 ppm (H2, H2',H3, H3'). The protons attached to the benzene ring from isatin moiety exhibit at 6.89-6.95 ppm, 7.01-7.13 ppm, 7.14-7.20 ppm and 7.36-7.51 ppm.

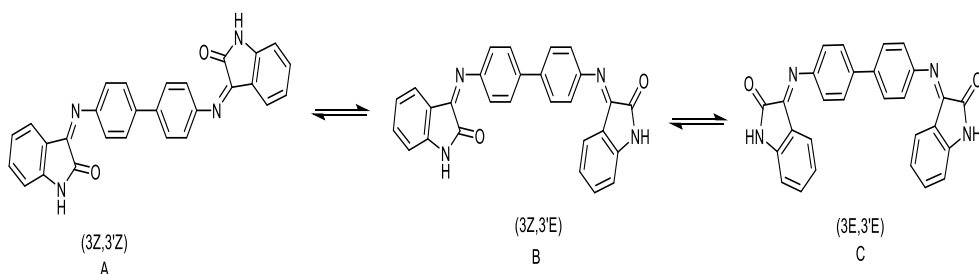
The spin-spin coupling constant ranges from 9 Hz to 3Hz (*ortho* coupling,  $^3J$ ; *meta* coupling,  $^4J$ ; *para* coupling,  $^5J$ ). The presence of the AA'BB' aromatic proton massif in the spectrum is observed. Its analysis can be done manually because the peaks of the massif are well represented [19]. Both  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectra confirm the structure of the compound, too.





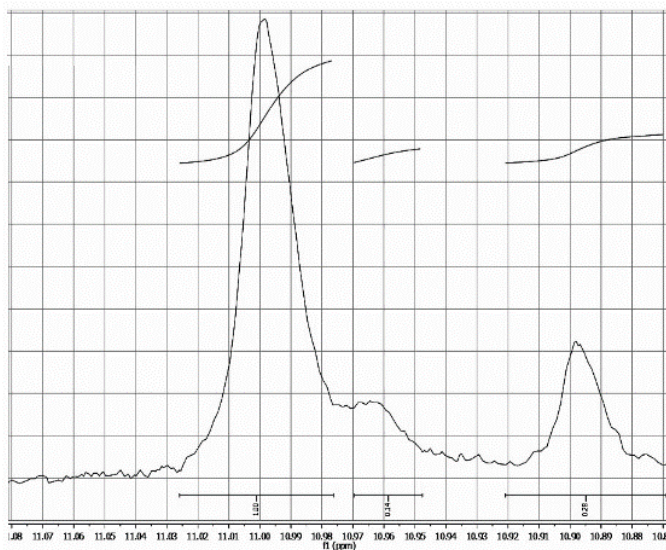
**Figure 5.**  $^1\text{H}$ NMR spectrum of 3'-([1,1'-biphenyl]-4,4'-diylbis(azanylylidene)) bis(indolin-2-one).

The Schiff basis reveals *syn-anti* stereoisomerism (Scheme 2). It can exist in the form of three geometric isomers A (3Z, 3'Z), B(3Z, 3'E'), and C (3E, 3E').



**Scheme 2.** Geometric isomers of 3'-([1,1'-biphenyl]-4,4'-diylbis(azanylylidene)) bis(indolin-2-one).

The concentration of the geometric isomers in  $\text{DMSO-d}_6$  solution at room temperature was determined using the proton absorption signal from the amino group (NH). The presence of three absorption peaks is noted.



**Figure 6.** Signal integrals of amino proton from Schiff base.

The integrals of these peaks have the values:  $I_A=1$ ,  $I_B=0.14$  and  $I_C=0.28$ . Hence, it is easy to obtain [19] the molar proportions of the isomers of the compound: %A=70,4%, %B=9.8%, and %C=19.8%.

The stereoisomer with configuration A (3Z, 3'Z) predominates, and the geometric isomer with configuration C (3E, 3'E) is found in the lowest proportion. Between the two populations of configurational isomers is the geometric isomer B (3Z, 3'E). We expected these variations, since it is observed that configuration A is the least sterically hindered, followed by configuration B and configuration C which is the most congested structure due to the 3-iminoindolin-2-one nucleus.

#### 4. CONCLUSION

A base Schiff, potential ligand in coordination chemistry to form complexes with metal ions, has been synthesized. The structure of the ligand was confirmed by structural analysis. The spectra (IR, UV-vis,  $^1\text{H}$  and  $^{13}\text{C}$  NMR) were explained. The structure of stereoisomers was draw up and their proportion was determined.

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