

Synthesis, Characterization And Computational Studies Of Novel (E)-N-(3,4-Dimethoxybenzylidene)naphthalen-1-amine

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Abstract. Novel (E)-N-(3,4-dimethoxybenzylidene)naphthalen-1-amine (DBNA) ligand has been synthesized by refluxing 1-naphthylamine and 3,4-dimethoxybenzaldehyde in methanolic solution for 5-6 hours. The obtained compound was characterized by UV-Vis, FT-IR and ¹H-NMR. All the spectral data confirmed the structure of the ligand.

1. Introduction

Heterocyclic compounds play important part in organic chemistry because of their specific structure and functions to respond many demands of biochemical systems. Heterocyclic is the majority of pharmaceuticals and biologically active compound[1]. Among heterocyclic compounds, Schiff base ligands derived from aromatic amines and aromatic aldehydes have received significant interest in the development of coordination chemistry[2] and wide range of applications[3]. Schiff base ligands are able to form coordination bond with many different metals and to stabilize them in various oxidation states[4].

Schiff base ligands and their transition metal complexes have been extensively explored as antimicrobial, antifungal, antituberculosis and anticancer agents. Schiff base metal complexes have promising material in clinical, analytical, industrial applications and organic synthesis[5][6]. However, efforts to further studies must be done to improve the functionality of Schiff base derivatives. Therefore, in this paper, we report the synthesis, characterization and computational studies of Schiff base ligand derived from aromatic amine (1-naphthylamine) and aromatic aldehyde (3,4-dimethoxybenzaldehyde).

2. Materials and Method

2.1. Materials

All chemicals used are analytical grade from Merck. 1-naphthylamine, 3,4-dimethoxybenzaldehyde, methanol and acetone.

2.2. Instrumentation

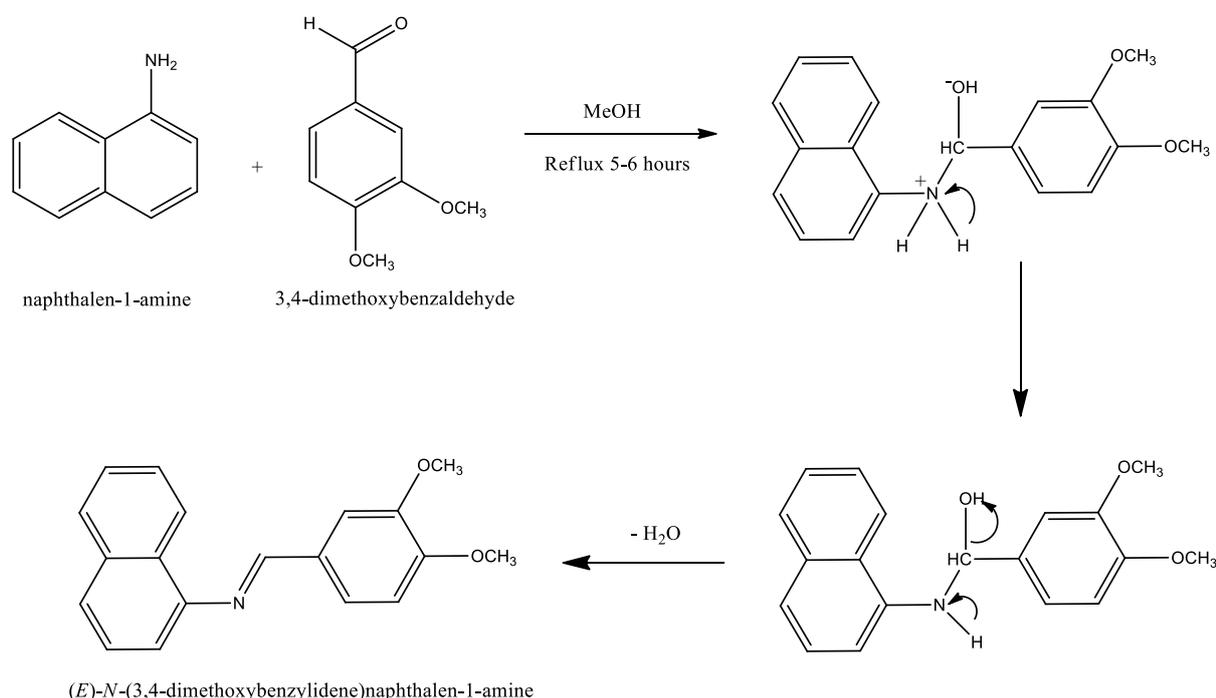
Electronic spectra were investigated by using Agilent spectrophotometer UV-Vis Cary 100. The IR spectra was performed by Fourier Transform Infrared (FTIR) Shimadzu IR prestige-21. ¹H-NMR spectra were recorded using Agilent 500 MHz. Thermal analysis was recorded by TGA and DTA instrument (Exstar SII 7300 series).

2.3 Synthesis of Ligand (E)-N-(3,4-dimethoxybenzylidene)naphthalen-1-amine

Equimolar ratio of 1-naphthylamine (0.859 g, 6 mmol) and 3,4-dimethoxybenzaldehyde (0.997 g, 6 mmol) were dissolved in methanol. The solution was refluxed for 5-6 hours at constant temperature about 60 - 70°C. The reaction progress was monitored by thin layer chromatography. Purification of the obtained compound was done by washing the ligand with methanol. Methanol was added to the resulting compound for recrystallization to yield pure compound.

240, 279 and 317 nm

Brown solid. Yield= 78.5%. m.p=129°C. UV-Vis (200-700 nm); (λ :nm): (240 nm) (279 nm) (317 nm). FT-IR (KBr, cm⁻¹); 3043.67, 3001.24 ($\nu_{\text{CH-Ar}}$) : 2931.80 ($\nu_{\text{C-H}}$) : 2862.36 ($\nu_{\text{O-CH}_3}$) 1627.92 ($\nu_{\text{C=N}}$) : 1577.77, 1510.26 ($\nu_{\text{C=C}}$). ¹H-NMR (CDCl₃), ppm: δ =4.03, 3.97 (O-CH₃), δ =6.95-8.36 (Ar-proton), δ =8.45 (N=CH).



2.4 Computational Method

Computational study towards DBNA has been done using GAMESS[®] software to calculate HOMO and LUMO energy level. In this study, we use Slater Type Orbital Gaussian 3-21, under Density Functional Theory. For the Self-Consistent Field, Restricted Hartree Fock type has been applied with convergence criteria 10⁻⁵.

3. Results and Discussions

UV-Vis Spectral Data

The UV-Vis spectral data of DBNA ligand showed intense peaks at 240, 279 and 317 nm. These intense peaks are assigned to n- π^* transitions for azomethine group (-N=CH-) and π - π^* transitions of conjugated π -bonding systems in ligand (fig.1).

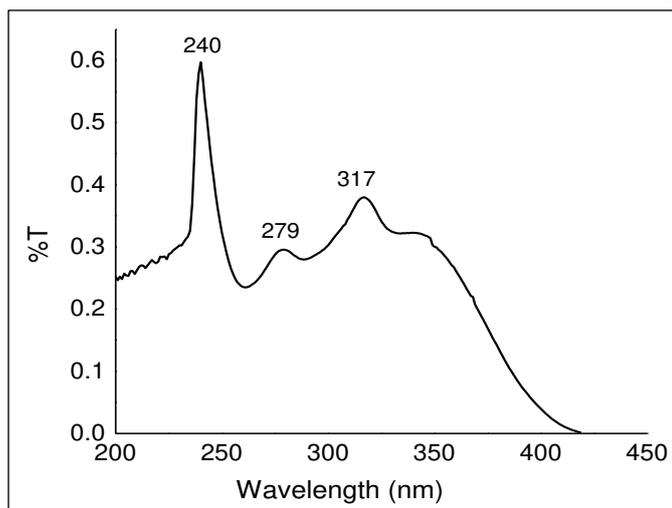


Fig.1 UV-Vis spectrum of DBNA ligand

FTIR Spectral Data

The FTIR spectrum of DBNA (fig. 2) showed stretching band at 1510.26 cm^{-1} and 1577.77 cm^{-1} which were assigned to the absorption of C=C stretching for aromatic ring. The sharp peak at 1627.92 cm^{-1} was observed as C=N stretching frequency in the azomethine group which indicated NH group from naphthylamine moiety was associated with C atom of benzaldehyde gave Schiff base formation. The two methoxy groups (O-CH₃) in the ligand was observed at 2862.36 cm^{-1} . While the aromatic ring moiety were assigned to the absorption band of C-H alkyl stretching at 2931.80 cm^{-1} and C-C aromatic stretching at 3001.24 and 3043.67 cm^{-1} . The pattern of overtone bands in the region $2000\text{--}1850\text{ cm}^{-1}$ indicated of aromatic moiety in the ligand.

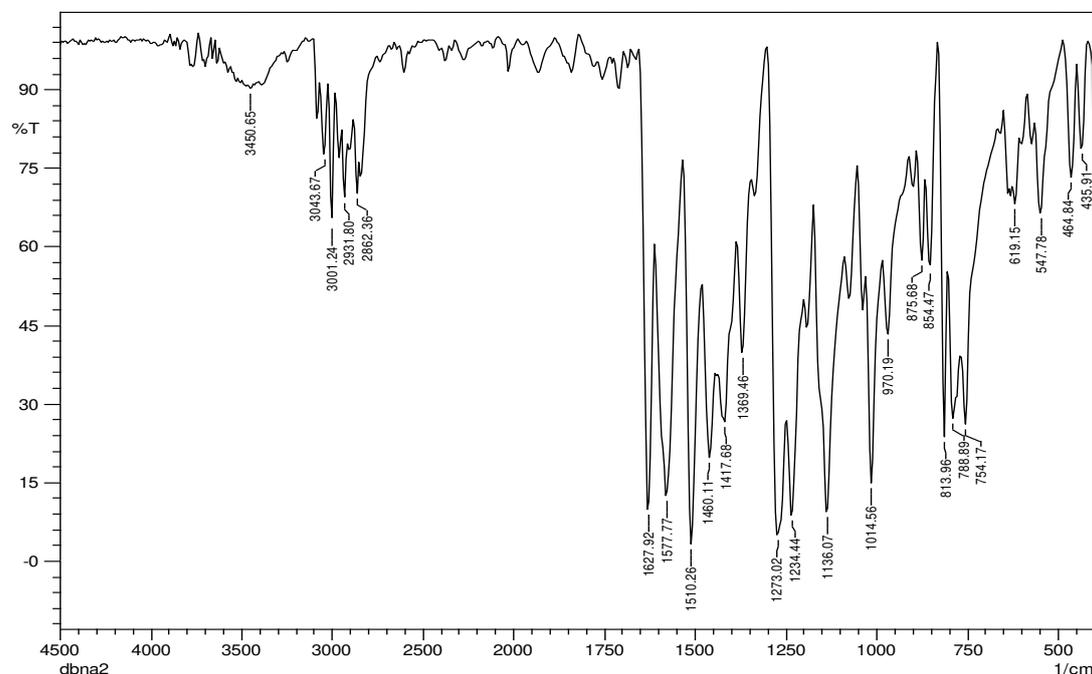


Fig 2. IR spectrum of DBNA ligand

¹H-NMR Spectral Data

The ¹H-NMR spectrum of DBNA was measured in CDCl₃ solvent. The spectrum showed signal at δ 8.45 ppm corresponded to the azomethine proton (N=CH) that bound between naphthalene and benzaldehyde moiety. The two signals at δ =3.97 and 4.03 ppm refer to methoxy groups (O-CH₃) bound

to the benzaldehyde moiety. Other signals in the region $\delta=6.95-8.36$ ppm could be attributed to the protons of aromatic rings of the ligand.

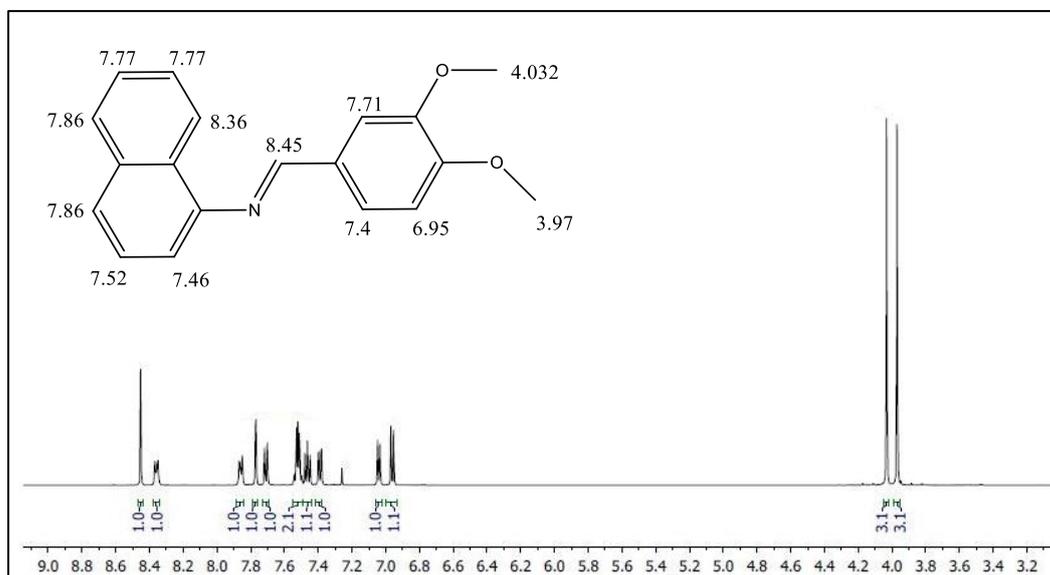


Fig 3. ¹H-NMR Spectrum of DBNA ligand

Computational Studies

HOMO and LUMO energy level of DBNA molecule has been calculated for any needs of complex's synthesis. This calculation will be able to be used in the future to predict properties of the ligand and also depict how the complex can be used in various aspect. The frontier molecular orbital energies (i.e., E_{HOMO} and E_{LUMO}) are significant parameters for the prediction of the reactivity and stability of a chemical compound. The E_{HOMO} is often associated with the electron donating ability (Ionization energy) of a molecule. The E_{LUMO} indicates the ability of the molecule to accept electrons (Electron affinity). By comparing HOMO and LUMO energy level from 2 molecules can indicates the tendency of the molecules to donor or to accept electrons. From the calculation, the HOMO energy level of DBNA molecules as represent in fig.4 is -5.27360808 eV, while the LUMO energy level (fig.5) is 4.43821196 eV.

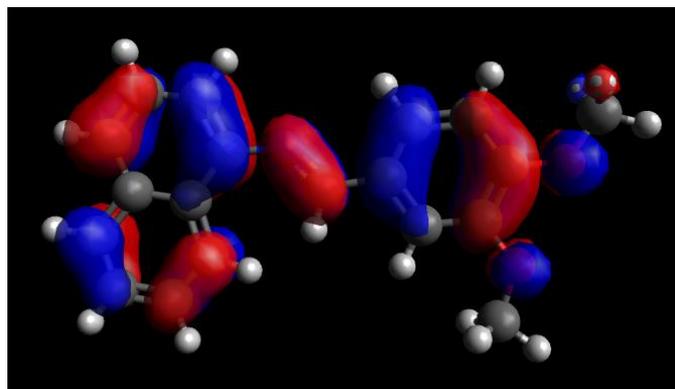


Fig.4 HOMO surface of DBNA

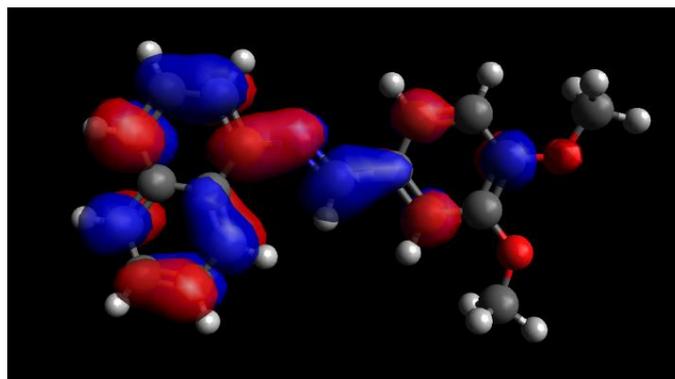


Fig.5 LUMO surface of DBNA

4. Conclusion

Novel (E)-N-(3,4-dimethoxybenzylidene)naphthalen-1-amine have been synthesized and characterized by various spectroanalytical method, they are UV-Vis, FT-IR and $^1\text{H-NMR}$. Spectroanalytical studies revealed the correct structure of the molecule as expected. FT-IR spectral data showed particular bonding which correspond to C=C, C=N, O-CH₃, C-C aromatic and C-H alkyl. $^1\text{H-NMR}$ also depict azomethine proton (N=CH), methoxy group and protons of aromatic ring in the ligand. Computational studied has been done as an initial step to prove the tendency of electron donor-acceptor of the ligand.

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Acknowledgments

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