

## THEORETICAL CHARACTERIZATION OF A IMIDAZOPHENANTHROLINE DERIVED LIGAND BY THE DENSITY FUNCTIONAL METHOD

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### Abstract

The biological and physiological activities of heterocyclic ligands are important research fields. As those ligands are components of many natural substances, their synthesis lead to the new products. The prior theoretical examination of ligands, to be synthesized, is necessary due to the fact that determining the proper experimental conditions and taking precautions against the possible experimental errors are necessary processes. Moreover, the theoretical calculations can model instable molecules and their trans-states, giving opportunity to simulate molecules and reaction mechanisms which cannot be observed experimentally. A new ligand with N and O donor atoms, namely (E)-N-(4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenyl)-1-(furan-2-yl)methanimine, was simulated using density functional theory. The base set was B3LYP/6-311G ++ (2d, p) in Gaussian G09w packet program. After the geometry of ligand was minimized, the NMR spectrum and FT-IR spectrum of the chemical were also calculated on the found structure. The bond lengths, bond angles, dihedral angles of the ligand together with the molecular electrostatic potential map, the Mulliken atomic charges, the dipole moments, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies were determined. The ligand can be supposed to make coordination bonds with two metal ions, and therefore became a good candidate of metal ion carrier, or catcher.

**Keywords:** Imidazophenanthroline, Furan, DFT/B3LYP.

### INTRODUCTION

Heterocyclic molecules as ligands are important in their usage against bacteria biological functions [1,2]. These molecules act as ligands because of having various donor atoms such as O, N, and S. They can form complexes with many transition metals [3,4]. In particular, imidazophenanthroline derivatives play a key role in the application of a wide variety of multifunctional compounds.

Imidazophenanthroline analogues and their metal complexes have been found to be ideal DNA probes due to their diverse DNA binding modes, effective DNA photocleavage effects, and distinct photophysical and electrochemical properties [5,6]

In general, the theoretical modeling of such molecules or ligands before the

synthesis is useful for shaping the relevant reaction mechanisms. Even if the molecule is unstable, it can theoretically be shaped. When the template method is used without the formation of the molecule, they can act as ligands in the composition of the targeted complexes. In this case, it is theoretically possible to shape the molecule and examine it as if it were synthesized. On the other hand, the experimental determination of the geometric structure of a molecule or the positions of its atoms relative to each other can only be determined by the X-ray diffraction method, which requires crystal formation. Considering that a chemical cannot always be obtained in crystalline form, it is clear that theoretical description of the molecule would be beneficial. Because it is possible to verify the molecule by

comparing the calculated NMR, FT-IR and UV spectra of the theoretically obtained molecule with the corresponding experimental spectra [7,8,9].

Gaussian computations are used to conduct research in established or emerging areas of interest in chemistry. It is useful for studying molecules and describing potential reactions, including compounds that are impossible or very difficult to study experimentally. The ligand with N and O donors under study can be named (E)-N-(4-(1H-imidazo[4,5-f] [1,10] phenanthroline-2-yl) phenyl)-1-(furan-2-yl) methanimine. Its geometrical structure has been theoretically elucidated and its optical, geometric and chemical properties have been calculated.

## FINDINGS

### Molecular Geometry

The minimized structure of the ligand having minimized energy as -1272.931927 au in the gas phase is shown in Figure 1. The dipole moment is 6.654402 Debye, and symmetry group of the molecule is found to be C1.

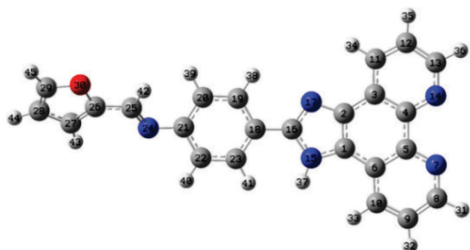


Fig. 1 The suitable structure of the ligand with the lowest theoretically calculated energy.

The bond lengths between the atoms of the ligand are shown in Table 1 while the important bond and dihedral angles are shown in Table 2.

Table 1. Interatomic bond lengths of the ligand

Selected Bond Lengths (Å)	Selected Bond Lengths (Å)
1.36 (C28-C29)	1.38 (C16-N15)
1.35 (C29-O30)	1.00 (N15-H37)
1.07 (C29-H45)	1.38 (N15-C1)
1.37 (O30-C26)	1.32 (C16-N17)
1.44 (C25-C26)	1.39 (C1-C2)
1.09 (C25-H42)	1.43 (C2-C2)
1.28 (C25-N24)	1.42 (C3-C4)
1.40 (N24-C21)	1.35 (C4-N14)
1.40 (C21-C22)	1.32 (N14-C13)
1.46 (C18-C16)	1.08 (C13-H36)

Table 2. Bond and dihedral angles between atoms of the ligand

Selected Bond Angles (°)	Selected Dihedral Angles (°)
116.2 (O30-C26-C25)	-179.9 (H45-C29-O30-C26)
109.5 (O30-C26-C27)	0.024 (C29-O30-C26-C27)
125.3 (C26-C27-H43)	178.1 (O30-C26-C25-N24)
115.2 (C26-C25-H42)	-0.870 (O30-C26-C25-H42)
121.9 (C26-C25-N24)	176.8 (C26-C25-N24-C21)
120.3 (C25-N24-C21)	-36.204 (C25-N24-C21-C20)
117.8 (N24-C21-C22)	146.5 (C25-N24-C21-C22)
118.5 (C21-C22-H40)	179.9 (N24-C21-C22-C23)
119.3 (C19-C18-C16)	-1.464 (C21-C22-C23-C18)
123.7 (C18-C16-N15)	-2.789 (C23-C18-C16-N15)
126.0 (C16-N15-H37)	-179.8 (C18-C16-N15-C1)
107.4 (C16-N15-C1)	179.9 (C16-N15-C1-C6)
104.9 (N15-C1-C2)	-0.015 (N15-C1-C6-C10)
120.7 (C1-C2-C3)	-179.9 (N15-C1-C6-C3)
123.2 (C2-C3-C11)	0.050 (C1-C6-C10-H33)

The C25-N24 imine bond length in the ligand is 1.28 Å which is compatible with the calculated imine bond length value of 1.276 Å N,N'-(ethane-1,2-diylbis (4,1-phenylene)) bis (1-(thiophen-2-yl) metanimine) molecule[13]. The 1.36 Å double-bond carbon-carbon length (C28-C29) and 1.44 Å single-bond length (C26-C25) in the quintuple ring correspond to the lengths of 1.375 Å and 1.416 Å, respectively, in the last referred molecule. Dihedral angles disrupt the planarity of the ligand's tail.

### Molecular Orbital Analyzes and Electronic Properties

Leading molecular orbital energies, abbreviated as HOMO and LUMO, play a major role in determining the electronic and optical properties of a molecule. The energy difference between HOMO-LUMO levels is shown in Figure 2 along with the molecular orbital distributions. The less the energy difference between these two molecular orbitals, the molecule becomes more polarized. A large energy difference indicates that the molecule's ability to react is low.

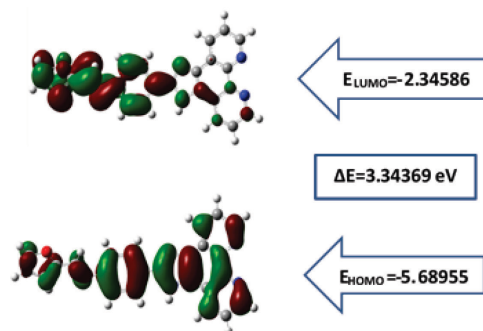


Fig. 2. HOMO and LUMO three-dimensional representations and energy values

While the HOMO energy, which represents the ability of the molecule to donate electrons, is -5.68955 eV, and the LUMO energy, which represents the ability to withdraw electrons, is -2.34586 eV, according to these data, the energy gap is 3.34369 eV. The small energy gap makes the formation of the molecule easier [14].

In relation to HOMO and LUMO energies, the electronic properties of the molecule are listed in Table 3 by obtaining the ionization potential IP, electron affinity EA, electronegativity of the ligand  $\chi$ , chemical potential  $\mu$ , chemical hardness  $\eta$ , chemical softness  $\sigma$  and electrophilicity index  $\omega$  [15,16].

**Table 3.** Electronic structure parameters of the ligand and their values

Parameter	Value
IP (eV)	5.68955
EA (eV)	2.34586
$\Delta E$	3.34369
$\chi$ (eV)	4.01770
$\mu$ (eV)	-4.01770
$\eta$ (eV)	1.67184
$\sigma$ (eV <sup>-1</sup> )	0.59814
$\omega$	4.82974

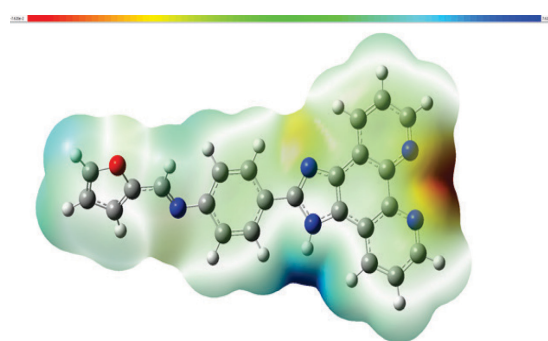
IP: - $E_{\text{HOMO}}$ , EA: - $E_{\text{LUMO}}$ ,  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ,  
 $\chi = (\text{IP} + \text{EA})/2$ ,  $\mu = -\chi$ ,  $\eta = (\text{IP} - \text{EA})/2$ ,  $\sigma = 1/\eta$ ,  $\omega = \mu^2/2\eta$

### Molecular Electrostatic Potential Surface

When the results given in Table 3 were compared with the results obtained for the 1, 3, 5-triphenylbenzene molecule in crystal form in a previous study, it was seen that although the two are very different molecules, their electronic properties are numerically very close to each other [16]. However, the value of  $\omega = 4.82974$  eV, which indicates biological activity, is greater than that of 1, 3, 5-triphenylbenzene, whose electrophilic index is  $\omega = 2.931$  eV. The same applies to the chemical softness parameter  $\sigma$ , which is a measure of chemical reactivity.

Molecular electrostatic potential map (MEP) shown in Figure 3 is used to determine the positive and negative regions of the ligand. The red regions on the map indicate partial negative charge, and blue regions indicate partial positive charge.

Regions containing fewer electrons are shown in yellow, while neutral regions are shown in green.

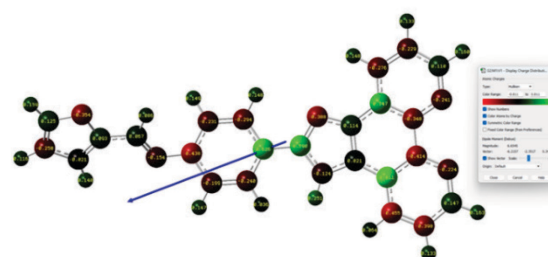


**Fig.3.** Molecular electrostatic potential map of the ligand.

In the MEP map of the ligand shown above, the color codes of the electronic potential surfaces vary between  $-7.620 \text{ e}^{-2}$  (red) and  $7.620 \text{ e}^{-2}$  (blue). Accordingly, the geometric location and energy of bonding in interactions with metals are determined by the red regions.

### Mulliken Atomic Charge Distribution

The electron distribution in a molecule is also determined by the Mulliken atomic charge distribution. The Mulliken distribution of the examined molecule is shown in Figure 4. In color codes, the red color indicates the largest negative charge of -0.811, while the green color codes for a positive charge of +0.811. In the structure, carbon atoms bonded with nitrogens are seen as the most negative centers.



**Fig. 4.** Mulliken atomic charges of the ligand

### Theoretical NMR Chemical Shift Values

The GIAO method was used to obtain theoretical  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR chemical shifts are shown in Table 4 and Table 5, respectively.

**Table 4.** <sup>1</sup>H-NMR chemical shift values (TMS δ/ppm).

δ/ppm	Atom	δ/ppm	Atom
9.9	H37	7.9	H35
9.6	H36	7.9	H45
9.6	H31	7.9	H32
9.5	H34	7.8	H40
9.3	H38	7.8	H43
8.8	H42	7.6	H39
8.5	H33	6.9	H44
8.0	H41		

**Table 5.** <sup>13</sup>C-NMR chemical shift values (TMS δ/ppm).

δ/ppm	Atom	δ/ppm	Atom
162.5	C26	132.5	C18
159.6	C21	130.8	C22
153.4	C16	129.5	C1
153.0	C13	129.1	C3
152.6	C5	128.7	C10
152.2	C8	126.0	C23
152.1	C4	125.8	C12
151.6	C25	124.6	C9
150.5	C29	122.0	C6
144.5	C2	120.8	C20
133.8	C19	117.0	C28
133.5	C11	116.6	C27

For the ligand, the chemical shift value of the proton of HCN was calculated as 8.8 ppm, and the imidazole proton was calculated as 9.9 ppm. The chemical shift value for the CH carbon was found to be 151.6 ppm, and the chemical shift values of the carbons in the ring were found to be between 116.6-162.5 ppm. When compared with the literature, the chemical shift values appear to be compatible [13, 17].

### Theoretical Vibration Frequencies

The calculated vibration frequencies and their assigned modes are presented in Table 6. As it is well known, there might be small deviations between the vibration frequencies calculated in quantum chemical methods such as the DFT level and the experimental vibration frequencies. These deviations are due to non-harmonic and band aliasing effects in experimental measurements [18]. The deviations are minimized by multiplying the theoretically calculated frequencies by 0.9613, which is the scale factor suitable for the 6-311G++ (2d, p) basis set.

**Table 6.** Selected FT-IR vibration frequencies and modes.

Mod	k (cm <sup>-1</sup> )	Atoms
v NH	3532	v N15-H37
v CH	3155	v C29-H45, v C28-H44, v C27-H43
v CH	3083	v C19-H38, v C20-H39
v CH	3061	v C11-H34, v C12-H35, v C13-H36
v CH	3041	v C18-H33, v C9-H32, v C8-H31
v CH	2922	v C25-H42
v CN	1609	v C25-N24
v CC	1506	v C16-C18
v CN	1470	v C4-N14, v C5-N7
δ HCC	1470	δ H36-C13-C12, δ H31-C8-C9
δ HCN	1470	δ H31-C8-N7, δ H36-C13-N14
δ HCC	994	δ H44-C28-C27, δ H43-C27-C28
δ COC	994	δ C26-O30-C29
δ CCC	989	δ C19-C18-C23, δ C20-C21-C22
γ NCCC	823	γ N7-C5-C6-C18, γ N14-C4-C3-C2
γ CNCC	718	γ C13-N14-C4-C3
γ CCNC	718	γ C12-C13-N14-C4, γ C9-C8-N7-C5
γ CCCC	522	γ C21-C22-C23-C18, γ C21-C20-C19-C18

v: stretching, δ: in-plane bending, γ: out-of-plane bending

According to the FT-IR spectrum, all v CH stretching peaks are between 3155-2922 cm<sup>-1</sup>, v NH stretching peak is at 3532 cm<sup>-1</sup>, v C=N stretching peak is at 1609 cm<sup>-1</sup>, v C-C stretching peak is at 1506 cm<sup>-1</sup>, and v C-N stretching peak was calculated at 1470 cm<sup>-1</sup>. Vibrations due to in-plane bending and out-of-plane bending were found in the range of 1547-400 cm<sup>-1</sup>. When compared to the literature, the vibration values appear to be compatible [13,17].

### CONCLUSION

By minimizing the energy of the (E)-N-(4-(1H-imidazo [4,5-f] [1,10] phenanthroline-2-yl) phenyl)-1-(furan-2-yl) methanimine in the gas phase, the geometric parameters such as interatomic bond lengths, bond angles and dihedral angles were calculated. The NMR and FT-IR spectra were also calculated using the minimized geometry and results compatible with the concerning data in

literature. Using HOMO-LUMO energies, the electronegativity, chemical potential, chemical softness, chemical hardness and electrophilicity index of the ligand were calculated. It was determined from the MEP map that the regions where the nitrogen of the ligand are located will exhibit nucleophilic behavior. The information obtained here about the ligand will make it easier to synthesize it.

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