Geometric and Electronic Investigations of 2,7-bis((3-(pyridin-2-yl)-1H-pyrazol-1-yl) methyl) naphthalene Using Computational Chemistry

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Abstract

Understanding geometric and electronic characterizations of organic molecules that working as flexible ligands; may helpful to predict their chemical behavior either in solution or solid state when reacted with metal ions. We have investigated bis-(3-(pyridin-2-yl)-1H-pyrazol-1-yl)) ligands using computational chemistry. Disubstitutions in position 2,7-naphthyl based ligand; as linker between bis(3-(pyridin-2-yl)-1H-pyrazol-1-yl)) units is our molecule of investigation. HyperChem (V.8) software, semi-empirical, AM1 were used as methods of calculations. Some thermo-physical properties have been calculated such as total energy, dipole moment, binding energy and heat of formation. The calculated total energy was recorded at-118141.72 kcal/mol. The molecule is slightly polar as the dipole moment observed at 0.895D. The energy gap (E_{gap}) between HOMO and LUMO; as one of the most important parameter for molecular stability recorded at 8.29 eV. Moreover, ionization potential (I), electronic affinity (A), global hardness (\(\eta\)), electronegativity (\(\chi\)), electronic chemical potential (\(\mu\)), electrophilicity (\(\omega\)) and chemical softness (S) were calculated. As HOMO and LUMO energy is responsible for molecular reactivity. So, the calculated parameters of molecule may helpful to understanding its chemical behavior. Geometrically, comparison between the single X-ray crystallography and calculated data such as; bond angles and bond lengths were done. The calculated data approximately agreed with the single X-ray crystallography reported data[1].

Keywords
Flexible ligands, 3-(2-pyridyl)pyrazole, coordination chemistry, computational chemistry, HyperChem, Semi-empirical.
النصف تجريبية والدائمة أي ام 3 هي التي استخدمت لأجراء كل الحسابات. بعض الدوال الثيرمو-فيزيائية و غيرها تم حسابها وهي تشتمل الطاقة الكلية وخاصة عزم ثنائي القطب وطاقة الترابط وطاقة التشکل. الطاقة الكلية للمركب تم تشخيصها وهي حققت القيمة السالبة 118141.722 كيلوكلوريو لكل مول. الجزيئة تتعلق السلوك القطبي وذلك من خلال القيمة المتحصل عليها نظريا لدالة عزم ثنائي القطب. الطاقة الفاصلة ما بين مداراً التي تشغل الإلكترونات والمدار المناظر لها والتي لا تحتوي الكترونات تعتبر مؤشرة ذهبية في تقدير استقراره المركبات. فهذه الدالة أعطت القيمة 8.29 الكترون فولت. كذلك بعض الدوال الأخرى تم حسابها مثل طاقة التأين والكهرمغناطيسية وغيرها. كما يمكننا التنبؤ ثانيا على أن قيمة الطاقة التي تفصل المدار الذي تشغل الكترونات الأخرى التي لا تتشكل الطاقة الصلبة عبر مداراً يحتوي الإلكترونات. وللمركبات لذا يمكننا القول أن كل الدوال التي حسبت يمكن أن تكون مؤثرة في تشخيص السلوكي الكيميائي لمركبات الدراسة عند تفاعله مع أيونات المعادن. كما أن الدراسة شملت المقارنة ما بين القيم العملية من التركيب البلوري المذكور لمركبات الدراسة والحوسبة التي تم اجراها لمركبات باستخدام نفس الدوال ووجد ان القيم متفاوتة جداً.
Introduction

Synthesis strategy of 3-(2-pyridyl)pyrazole introduced hybridized molecule with characterization useful to use as ligands in coordination chemistry[2]. In fact, the N-heterocyclic compound working widely as ligands in coordination chemistry[3]. Although, the 3-(2-pyridyl)pyrazole classified as bidentate ligand; connection of Bis-(3-(2-pyridyl)pyrazole) with different linkers such as Naphthyl[4,5] Anthracyl[5], Benzyl[6], and others[7] produced a new systems of tetradentate ligands (figure 1).

Figure 1. Selected examples of Homo/Hetero spacers based on Bis-(3-(2-pyridyl)pyrazole)[8].

Moreover, alkyl spacer reported with bis-(3-(2-pyridyl)pyrazole) units (Figure 2 and 3). Reaction the ligands (see figure 1) with M(II) ions produced unpredictable products[7].

Figure 2. Selected example of Alky spacer based on Bis-(3-(2-pyridyl)pyrazole)[7].
Surprisingly, the Bis-(3-(2-pyridyl)pyrazole) ligands react with octahedral metal ions using stoichiometric ratio M:L; 1:1.5. [9] The formed coordination compounds arranged from $M_2L_3$, $M_4L_6$, $M_6L_9$, $M_8L_{12}$ and others see figure 4.[8] Actually, the tetradeutate ligands used all of their donor atoms to achieve the maximum site occupancy (MSO) principle. Apparently, the self-assembly of metal with Bis-(3-(2-pyridyl)pyrazole) ligands (figure 4) formed unpredictable complexes in different geometry.[8] As the degree of similarity between molecules depend on the most important factor which is electron density.[10] However, the HOMO and LUMO gave indications about the reactivity region of chemical molecules.[11]

Presently, we have been struggling to study the electronic structure of this class of ligand. Additionally, understanding the electronic structure of molecules using some of
computational parameters may provide useful information to predict the geometry of formed molecules. HyperChem release 8.0, semi-empirical, AM1 and geometry optimization have been used to calculate all of parameters. [12]

Calculations method and software
All of the calculations were carried out using HyperChem software V.8. HyperChem TM 8.0 Molecular Modeling program with root mean square (RMS) gradient 0.1 kcal/Åmol using Polak Ribiere algorithm. The calculation methods were Semi-empirical, geometry optimization and AM1 methods. [13] All the investigations were using Personal desktop ((acer)) with Windows XP, a 2.93 GHz Intel (R) core (TM) 2 Duo CPU, and 4.00 GB of RAM.

Results and Discussion
Ligand structure
The chemical structure of the ligand can be seen in figure 5. 3-D view of molecule displayed in figure 6. The crystal structure with atomic numbering of the ligand presented in figure 7. [1] The π-conjugated system linker between two units of bis-(pyrazolyl-pyridine) separated by CH₂ group to increase the arms flexibility. The stability of some cages reported due to the π-π-stacking between the π-conjugated linker. Different isomers of naphthyl spacer have been formed supramolecular coordination cages. [9]

![Figure 5. Structure of 2,7-bis((3-(pyridin-2-yl)-1H-pyrazol-1-yl)methyl)naphthalene ligand.[1]](image)

![Figure 6. 3D view of title compound](image)
The computational analyses were performed to get the molecular geometry of compound and energy minimization studies using HyperChem V.8 software.[13] The expected geometries of the studied ligand were fully optimized geometrically in order to investigate the minimum energy without any symmetry constraints. Table 1 shows the computational results of molecule; the ligand has total energy \(-118141.722\) Kcal/mol, binding energy \(-6341.810\) Kcal/mol, heat formation \(267.353\). It seems that the molecule slightly polar (calc. Dipole moment \(0.895\) Debyes) and may saturation in polar solvents.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Total Energy</th>
<th>Binding energy</th>
<th>Heat of formation</th>
<th>Dipole moment</th>
</tr>
</thead>
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<tr>
<td>L(^{27})NaphPy</td>
<td>(-118141.722)</td>
<td>(-6341.810)</td>
<td>(267.353)</td>
<td>(0.895)</td>
</tr>
</tbody>
</table>

*Total energy (kcal/mol), binding energy (kcal/mol), heat of formation (kcal/mol) and dipole moment (Debyes)

Figure 8 shows Highest Occupied Molecular Orbital (HOMO); Lowest Unoccupied Molecular Orbital (LUMO); Energy gap (HOMO-LUMO) and HOMO/LUMO plot of the ligand. The HOMO/LUMO orbitals give information such as: (i) electronic transtion; (ii) indicate the electrophilic and nucleophilic attraction area in molecule and (iii) most important parameters for chemical reactivity.[11] The energy of HOMO orbital recorded at \(-8.92\) eV; the next higher energy level which is unoccupied because no more electrons are available (LUMO) presented at \(-0.63\) eV. The energy gap (HOMO-LUMO) as very important for indication of molecular stability and electrical transport properties recorded at \(8.29\) eV. Notably, the LUMO orbitla centered at the naphthyl system; whereas the HOMO centered at...
the N-Heterocyclic where the lone pairs presented; which are the most expected chelating centers as seen in figure 6.

![Diagram of HOMO and LUMO molecular orbitals]

**Figure 6. The HOMO/LUMO level, energy gap, plot of HOMO and LUMO molecular orbitals.**

The concepts of electronegativity and hardness could explain important aspects of chemical reactions and could be related to different physico-chemical properties. As well as; main global parameters descriptor for molecular reactivity.[10] The electronic parameters such as the ionization potential ($I$) directly related to HOMO-orbital and recorded at 8.923 eV. The LUMO-orbital directly related to electronic affinity ($A$); its observed at 0.634 eV., global hardness ($\eta$), electronegativity ($\chi$), electronic chemical potential ($\mu$), electrophilicity ($\omega$) and chemical softness ($S$) presented in table 2.

**Table 2. Calculated Electronic properties of ligands: $E_{\text{HOMO}}$(eV), $E_{\text{LUMO}}$(eV), $\text{Egap}$(eV), $I$(eV), $A$(eV), $\eta$(eV), $\mu$(eV), $\chi$(eV) and $\omega$(eV).**

<table>
<thead>
<tr>
<th>Property</th>
<th>$E_{\text{HOMO}}$</th>
<th>$E_{\text{LUMO}}$</th>
<th>$\text{Egap}$</th>
<th>$I$</th>
<th>$A$</th>
<th>$\eta$</th>
<th>$\mu$</th>
<th>$\chi$</th>
<th>$\omega$</th>
<th>$S$</th>
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<tbody>
<tr>
<td>L$_2$NaphPy</td>
<td>-8.923</td>
<td>-0.634</td>
<td>8.288</td>
<td>8.923</td>
<td>0.634</td>
<td>8.605</td>
<td>4.778</td>
<td>9.240</td>
<td>1.326</td>
<td>0.116</td>
</tr>
</tbody>
</table>

**Conclusion**

In conclusion: Geometrically; the data of single crystal agreed with that calculated. Electronic structure calculation provide useful estimates of energetic properties of chemical compound. The calculated electronic-density distribution of the highest occupied molecular (HOMO) orbital of ligand is located over the 3-(2-
pyridyl) pyrazole arms. The lowest unoccupied molecular (LUMO) orbital level of title molecule is distributed over the naphthalene ring. Moreover, we conclude that the molecules slightly polar and stabilized in polar solvents.
References


