

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

Adel M. Najar & Mona H. Ali Bnhmad & Yasamin G. Botaima & Marow S. Nawajee &

Marow H. Saleh

Department of Chemistry, Benghazi University, Elmarj, Libya



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

### 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 -118141.722 kcal/mol. The molecule is slightly polar as the dipole moment observed at 0.895D. The energy gap ( $E_{\text{gap}}$ ) 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.

### الملخص :

فهم خصائص التركيب الهندسي و الإلكتروني للمركبات العضوية التي تعمل كعضائد مرنة يمكن أن تؤدي إلى فهم السلوك الكيميائي الذي تسلكه في المحلول وكذلك في الحالة الصلبة وخصوصا عند تفاعلها مع ايونات المعادن. هنا شخصنا مركب الدراسة الذي يعمل كعضيده باستخدام الكيمياء الحاسوبية. التعويض الثنائي في الموقع رقم 2 والموقع رقم 7 في جزيئة النفتالين والتي تعمل كرابط بين مجموعتي بيريديل بيرازول في جزئي الدراسة. البرنامج هاير كيم الاصدار الثامن والطريقة

## العدد التاسع والأربعون / أكتوبر / 2020

النصف تجريبية والداله اي ام 3 هي التي استخدمت لأجراء كل الحسابات. بعض الدوال الثيرمو-فيزيائية و غيرها تم حسابها وهي تشمل الطاقة الكلية وخاصة عزم ثنائي القطب وطاقة الترابط وطاقة التشكيل. الطاقة الكلية للمركب تم تشخيصها وهي حققت القيمة السالبة 118141.722 كيلوكالوري لكل مول . الجزئية تسلك السلوك القطبي وذلك من خلال القيمة المتحصل عليها نظريا لدالة عزم ثنائي القطب. الطاقة الفاصلة ما بين مدارات التي تشغل الإلكترونات والمدارات المناظرة لها والتي لا تحتوي الكترونات تعتبر مؤشرة ذو اهمية في تقييم استقراره المركبات فهذه الدالة اعطت القيمة 8.29 الكترون فوالت. كذلك بعض الدوال الأخرى تم حسابها مثل طاقة التأين و الكهروسالبية وغيرها. كما يمكننا التنويه ثانيا على أن قيمة الطاقة التي تفصل المدات التي تشغل الكترونات والأخرى التي لا تشغلها تعتبر مؤشر كبير للنشاط الكيميائي للمركب لذا يمكننا القول ان كل الدوال التي حسبت يمكن ان تساعدنا في تشخيص السلوك الكيميائي لمركب الدراسة عند تفاعله مع ايونات المعادن. كما أن الدراسة شملت المقارنة ما بين قيم العملية من التركيب البلوري المنتظم لمركب الدراسة والحسابات التي تم اجرائها للمركب باستخدام نفس الدوال ووجد ان القيم متقاربة 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).

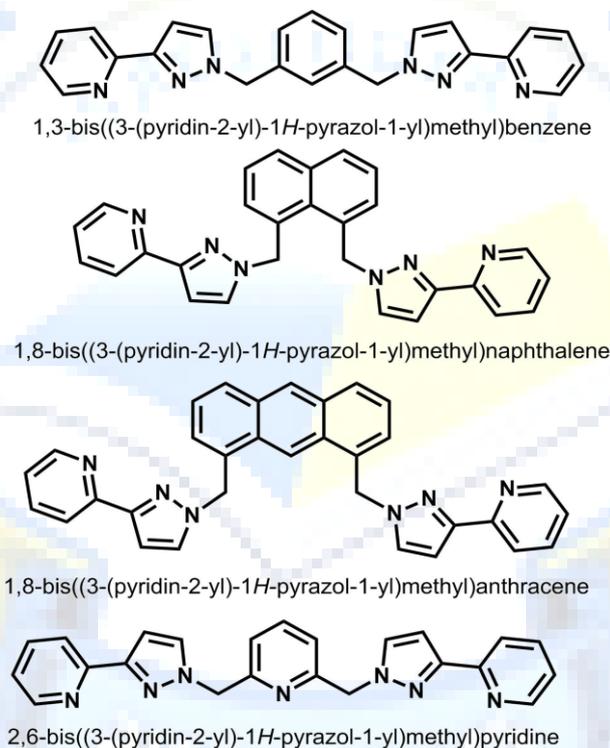


Figure 1. Selected examples of Homo/Hetero spacers based on Bis-(3-(2-pyridyl)pyrazole)[8].

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].

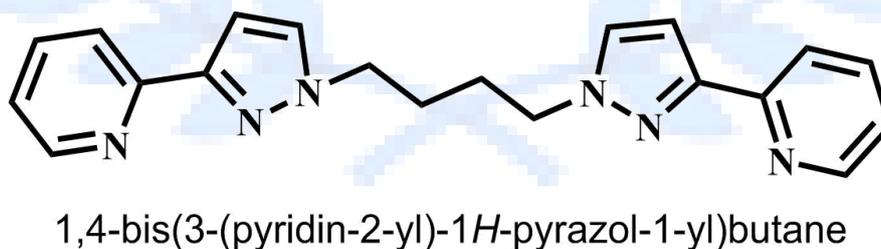


Figure 2. Selected example of Alky spacer based on Bis-(3-(2-pyridyl)pyrazole)[7].

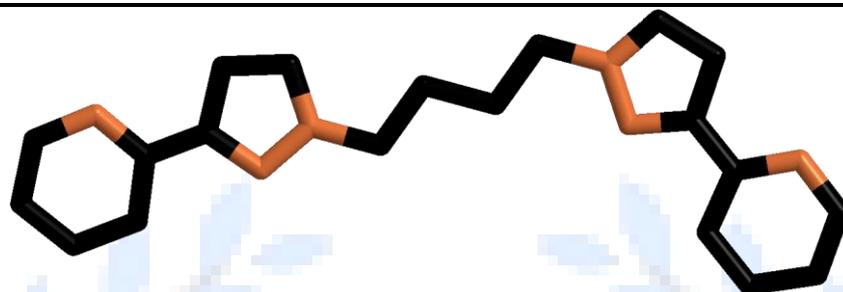


Figure 3. 3D view of Alky spacer based on Bis-(3-(2-pyridyl)pyrazole).[7]

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 tetradentate 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]

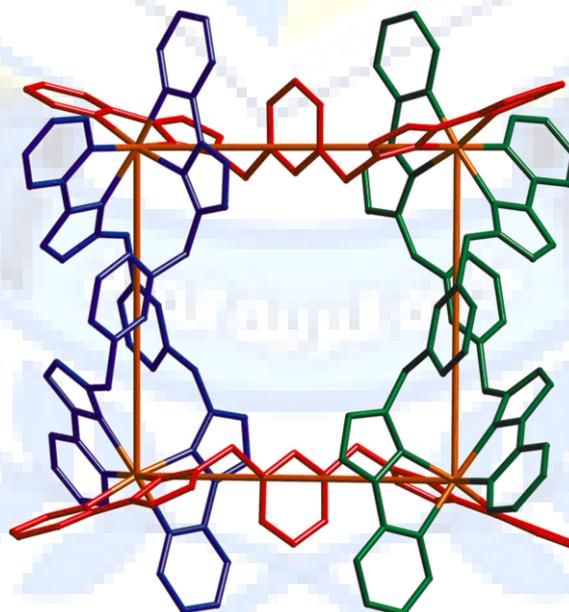


Figure 4. Crystal structure of Selected example  $M_4L_6$ ;  $[Ni_4(L^{26Py})_6](BF_4)_8$ . [6]

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  $\pi$ -conjugated system linker between two units of bis-(pyrazolyl-pyridine) separated by CH<sub>2</sub> group to increase the arms flexibility. The stability of some cages reported due to the  $\pi$ - $\pi$ -stacking between the  $\pi$ -conjugated linker. Different isomers of naphthyl spacer have been formed supramolecular coordination cages.[9]

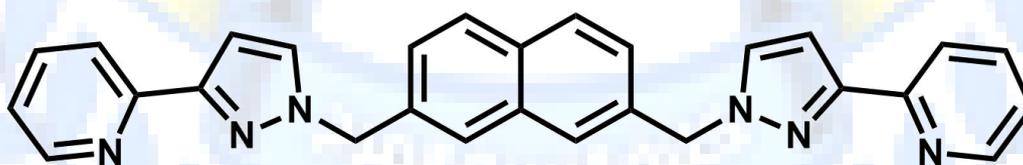


Figure 5. Structure of 2,7-bis((3-(pyridin-2-yl)-1H-pyrazol-1-yl)methyl)naphthalene ligand.[1]

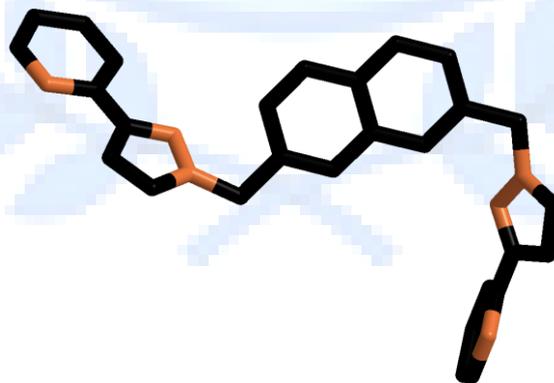


Figure 6. 3D view of title compound

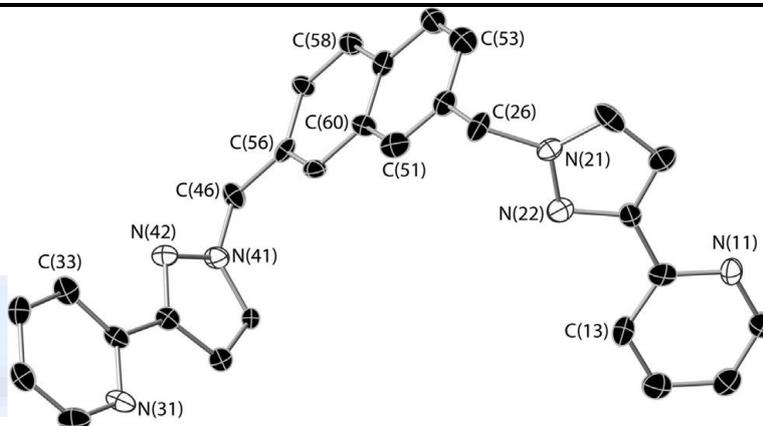


Figure 7. Crystal Structure of  $L^{27NaphPy}$ . [1]

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 (calcu. Dipole moment 0.89595 Debye) and may be stabilized in polar solvents.

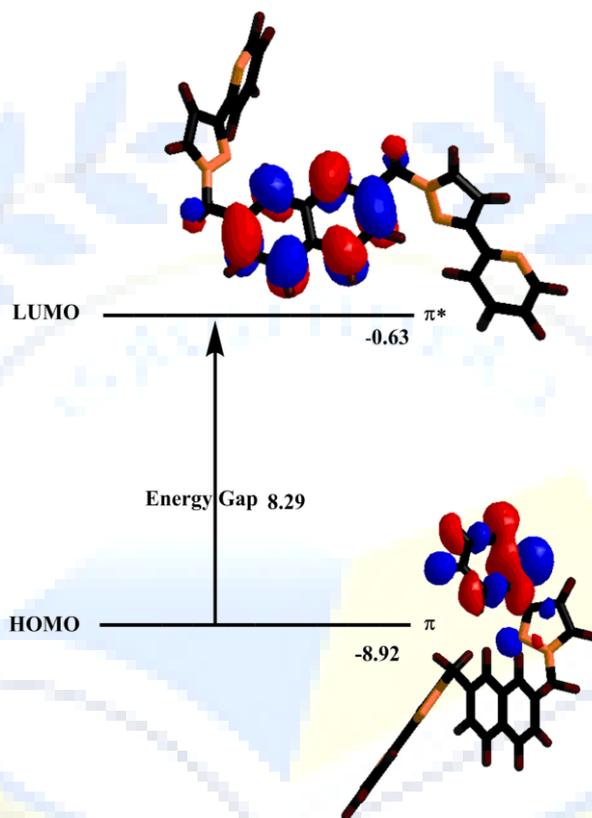
Table 1. Calculated thermo-physical properties

Molecules	Total Energy	Binding energy	Heat of formation	Dipole moment
$L^{27NaphPy}$	-118141.722	-6341.810	267.353	0.895

\*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 transition; (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 orbital 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.



**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:  $E_{HOMO}$ (eV),  $E_{LUMO}$ (eV),  $E_{gap}$ (eV),  $I$ (eV),  $A$ (eV),  $\eta$ (eV),  $\mu$ (eV),  $\chi$ (eV) and  $\omega$ (eV).**

Property	$E_{HOMO}$	$E_{LUMO}$	$E_{gap}$	$I$	$A$	$\eta$	$\mu$	$\chi$	$\omega$	$S$
$L^{27NaphPy}$	-8.923	-0.634	8.288	8.923	0.634	8.605	4.778	9.240	1.326	0.116

## 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-

العدد التاسع والأربعون / أكتوبر / 2020

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

- [1] Z. N. Zubaidi, A. J. Metherell, E. Baggaley, and M. D. Ward, "Ir ( III ) and Ir ( III ) / Re ( I ) complexes of a new bis ( pyrazolyl-pyridine ) bridging ligand containing a naphthalene-2 , 7-diyl spacer : Structural and photophysical properties," *Polyhedron*, vol. 133, pp. 68–74, 2017.
- [2] S. Trofimenko, "Geminal Poly(1-pyrazolyl)alkanes and Their Coordination Chemistry," *J. Am. Chem. Soc.*, 1970.
- [3] M. D. Ward, J. A. McCleverty, and J. C. Jeffery, "Coordination and supramolecular chemistry of multinucleating ligands containing two or more," vol. 222, pp. 251–272, 2001.
- [4] S. P. Argent *et al.*, "Coordination chemistry of tetradentate N-donor ligands containing two pyrazolyl-pyridine units separated by a 1,8-naphthyl spacer: Dodecanuclear and tetranuclear coordination cages and cyclic helicates," *Inorg. Chem.*, 2006.
- [5] I. S. Tidmarsh *et al.*, "Octanuclear cubic coordination cages," *J. Am. Chem. Soc.*, 2008.
- [6] A. M. Najar, I. S. Tidmarsh, H. Adams, and M. D. Ward, "," *Inorg. Chem.*, vol. 48, no. 24, 2009.
- [7] K. L. V. Mann, J. C. Jeffery, J. A. McCleverty, and M. D. Ward, "Synthesis and coordination chemistry of the tetradentate chelating ligand 1,3-bis[3-(2-pyridyl)pyrazol-1-yl]propane: Crystal structures of complexes with FeII, CuII, ZnII, AgI and PbII," *J. Chem. Soc. - Dalt. Trans.*, 1998.
- [8] A. N. Gusev, V. F. Shulgin, and M. A. Kiskin, "Self-Assembly of Polynuclear Complexes Based on Spacer- Armed Pyridylazoles," *J. Struct. Chem.*, vol. 60, no. 3, pp. 335–355, 2019.
- [9] A. M. Najar, I. S. Tidmarsh, and M. D. Ward, "," no. Scheme 1, pp. 3642–3650, 2010.
- [10] J. P. T. Bultinck, Patrick, Winter, Hans DeWi If ried Langenaeker, Ed., *Computational Medical Chemistry for Drug discovery*. NEW YORK: Taylor & Francis Group LLC, 2004.
- [11] M. J. Islam, A. Zannat, A. Kumer, N. Sarker, and S. Paul, "The prediction and theoretical study for chemical reactivity, thermophysical and biological activity of morpholinium nitrate and nitrite ionic liquid crystals: A DFT study," *Adv. J. Chem. A*,

vol. 2, no. 4, pp. 316–326, 2019.

- [12] W. F. Coleman and C. R. Arumainayagam, “HyperChem 5 (by Hypercube, Inc.),” *J. Chem. Educ.*, 1998.
- [13] H. oem Software, “No Title HyperChem Professional 8.0, (Molecular modeling system) Hypercube.” 2010.

