IJPAC
© Global Research Publications

Vol. 11 • Nos. 1-2 • January-June 2016
pp. 57-62

Natural Bond Orbital, Structural Properties, Density Functional Theory (DFT) Calculations and Charge Distribution for the 2-[(1*h*-pyrrol-2-yl) Methyl]-1*h*-pyrrole Compound

Shahriar Ghamami, Saeedeh Shahbazkhany* and Amir Lashgari

Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran

ABSTRACT: Pyrroles are a significant class of heterocycles due to their uses as bioactive compounds and there have general application in the arena of materials chemistry. In this paper, the optimized geometries and frequencies of the stationary point and the minimum-energy paths of 2-[(1H-Pyrrol-2-yl) meth-yl]-1H-pyrrole are calculated by using the DFT (B3LYP) methods with LANL2DZ basis sets. B3LYP/LANL2DZ calculation results indicated that some selected bond length, bond angles values calculation spectrum for the $C_9H_{10}N_2$ some similarity between calculated and experimental results.

Keywords: DFT, B3LYP/LANL2DZ, Calculation, HOMO, LUMO, Pyrrole Derivatives.

INTRODUCTION

Pyrroles are a significant class of heterocycles due to their uses as bioactive compounds and synthetic intermediates in organic production [1]. Pyrroles have general application in the arena of materials chemistry and as structural elements in molecular recognition trainings [2].

The pyrrole moiety is an amazing compound since its finding this heterocyclic system has been incessantly created in nature at the very heart of many different compounds essential for survival of living organisms. Pyrroles are five membered aromatic structures with the lone pair on nitrogen delocalized over the ring. This gives the ring a total of six π electrons achieving Huckel's rules for aromaticity. As such the pyrrole ring displays reactivity matching to that of an aromatic molecule [3].

The pyrrole comprising heterocyclic derivatives have been described in synthetic and effective biological importance for instance COX-1/COX-2 inhibitors [4-5]. Heterocyclic systems are of common occurrence in nature, mainly in such natural products as nucleic acids, vitamins, proteins and the heme, bile pigments, porphyrins, the pyrrole alkaloids, chlorophyll, antibiotics and polymeric systems [6-9].

Pyrrole derivative are great attention of synthetic significance and extensively used in drug discovery [10] and pharmacological activity such as anti-inflammatory [11], cytotoxicity [12], *and in vitro* cytotoxic activity beside solid tumor models [13-14], treatment of hyperlipidemias [15]. Pyrrole and its derivatives are biochemically important compounds and can be originated as substructures in many natural products [16-17]. Also Electrophilic substitutions of pyrroles, which combine electron-rich π-systems, have been examined intensively [18].

The semiempirical calculations suggest an unlimited deal of understanding of reaction mechanisms, mainly for organic compounds; however, they usually cannot give perfect quantitative answers due to their parametric nature. On the other hand, ab-initio controls are more dependable, but the computational times could be very prohibitive for applications including big molecules. They also suffer from natural errors of small basis sizes and/or prohibition of electron correlation effects [19-20].

We are interested to the biological activities of these title compounds. Thus, for this study, we are achieved computational investigation for pyrrole derivatives. Dipyrromethane (DPM) derivatives have been used as intermediates in key the synthesis of symmetric and

---

* *To whom correspondence be made:*
E-mail: Ikiu2014@gmail.com

nonsymmetrical porphyrins and also used as organometallic ligands.

The crystal structure of the title compound, $C_9H_{10}N_2$, has been reported at 153(K), also all experimental data used in this article take from Acta Cryst [21]. In recent years, computational chemistry is playing an important role in supporting and supplementing the experimental research, and explain the observed results. The present study considers $C_9H_{10}N_2$ whose includes pyrrole. The structure has been confirmed by neutron diffraction studies and is justified by VSEPR theory [22-23].

During this study we report the optimized geometries, assignments and electronic structure calculations for the compound. The main objective of the present study is to assess the performance of the hybrid density functional method B3LYP, with the LANL2DZ basis sets. The comparison between theory and calculation is made. In present work, density functional theory has been used to study the electronic properties of $C_9H_{10}N_2$ to determine HOMO and LUMO of its IR, NMR and RAMAN spectrum [24].

COMPUTATIONAL DETAILS

Theoretical approaches form another different for obtaining evidence on the bonding of such complex structures. Actually, a number of strengths have been made employing semi-empirical quantum mechanical calculations on geometries [25] and small basis ab-initio calculations of pyrroles.

The molecule under study represented in Fig. 1. All the computational studies were carried out using the density functional theory (DFT) methods implemented in the Gaussian 09 [26] suite of programs. The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all stationary points as minima. The molecular properties of the compounds have been computed by DFT using the standard LANL2DZ basis sets. In the DFT calculations the Lee Yang and Parr correlation functional [27] is used together with Becke's three parameters [28] exchange functional B3LYP.

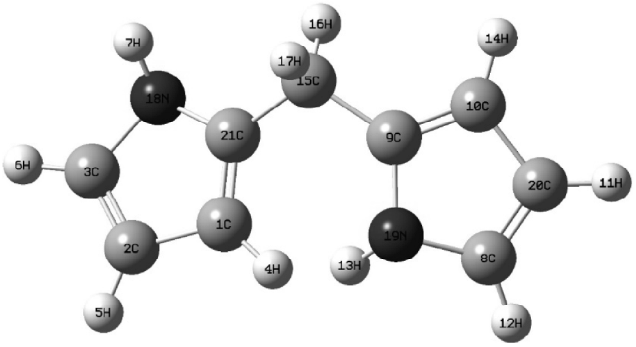


Figure 1: The optimized structure of the $C_9H_{10}N_2$

Harmonic vibrational frequencies (í) in cm^{-1} and infrared intensities (int) in Kilometer per mole of all compounds were used at the same level on the respective fully optimized geometries [29].

RESULTS AND DISCUSSION

Molecular Properties

Theoretical calculation of bond and angle for the compound was determined by optimizing the geometry (Table 1 and Table 2). We could compare the calculation results given in bond lengths and bond angle values with the experimental data (Graph 1 and Graph 2).

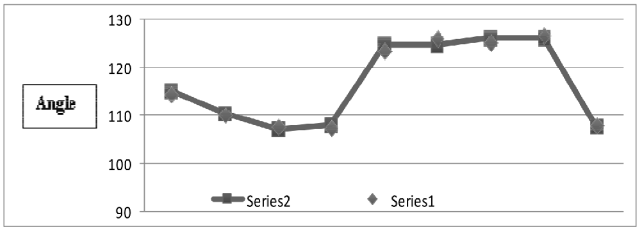
Table 1
Geometrical Parameters Optimized for $C_9H_{10}N_2$ some Selected Bond Lengths

Bond	*Calculated bond lengths (Å)*	*Experimental bond lengths (Å)*
C8-C20	1.392	1.363(3)
C8-N19	1.392	1.369(3)
C9-N19	1.392	1.361(3)
C10-C20	1.438	1.402(3)
C9-C10	1.394	1.370(3)
C9-C15	1.510	1.491(3)
C15-C21	1.513	1.490(3)

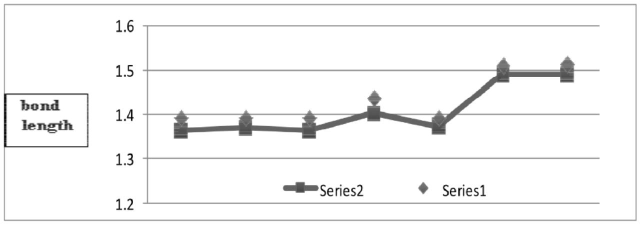
Table 2
Geometrical Parameters Optimized for $C_9H_{10}N_2$ some Selected Angles

Bond	*Calculated angles (°)*	*Experimental angles (°)*
C9-C15-C21	114.4	115.1(2)
C8-N19-C9	110.0	110.5(2)
C2-C1-N5	107.5	107.0(2)
C8-C20-C10	107.3	107.8(2)
C9-N19-H13	123.7	124.8(2)
C8-N19-H13	126.0	124.8(2)
C21-C1-H4	125.2	126.2(2)
C2-C1-H4	126.8	126.2(2)
C21-C1-C2	107.9	107.7(2)

Actually, (Graph 1) shows that calculated angles {series 1} completely accords with experimental angles {series 2} but in (Graph 2) that shows calculated bond lengths (Å) {series 1} had a little difference with experimental bond lengths {series 2}.



Graph 1: Compare calculated angles {series 1} with experimental angles {series 2}.



Graph 2: Compare calculated bond lengths (Å) {series 1} with experimental bond lengths {series2}.

Raman Analysis

The Raman Effect happens when light impinges upon a molecule and interdepends with the electron cloud and the bonds of that molecule. For the extemporary Raman Effect, which is a form of light scattering, a photon motivates the molecule from the ground state to a suitable energy state. When the molecule moderates it emits a photon and it incomes to a different rotational or vibrational state. The difference in energy between the original state and this novel state hints to a shift in the emitted photon's frequency away from the excitation wavelength. The Raman Effect, which is a light scattering phenomenon, should not be muddled with absorption where the molecule is motivated to a discrete energy level.

In this we have carried out computed chemical shift calculations of existing molecule, and the Raman spectrum of *2-[(1H-Pyrrol-2-yl) meth-yl]-1H-pyrrole* ($C_9H_{10}N_2$) are showed in Fig 2.

NMR Analysis

NMR spectroscopy is a suitable technique for identifying and analyzing organic compounds. In this we have carried out computed chemical shift calculations ^{13}C NMR of current molecule. The NMR spectrum of *2-[(1H-Pyrrol-2-yl) meth-yl]-1H-pyrrole* ($C_9H_{10}N_2$) are indicated in Fig 3. Our founding can be interpreted in this way that in ^{13}C NMR spectrum, four carbons that give peak in rang of A {35-55 ppm} are in the strong field,

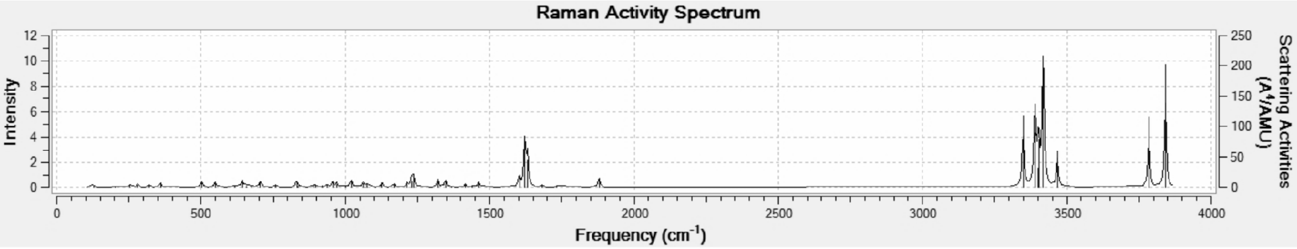


Figure 2: Raman spectra calculated DFT (B3LYP)/LANL2DZ

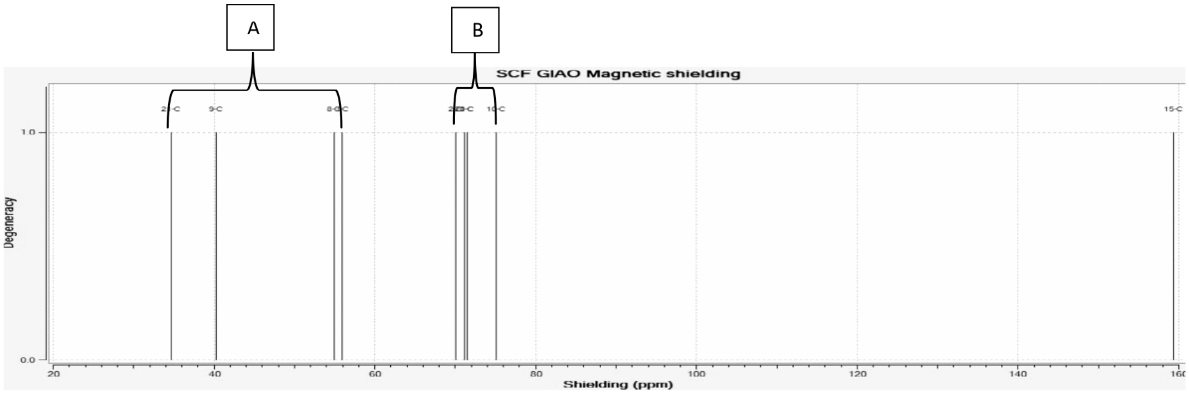


Figure 3: ^{13}C NMR spectra calculated by DFT (B3LYP)/LANL2DZ

because they are connected to the nitrogen atoms and have sp^2 hybrid. Similarly four carbons that give peak in range of B {70-75 ppm} are in the middle field, because they are distance from Nitrogen but have sp^2 hybrid. Whereas sp^2 hybrid give peak in stronger field than sp^3 hybrid, C15 give peak {160 ppm} that existent in weak field, because they are distance from nitrogen atoms and have sp^3 hybrid.

Charge and Electron Density Distribution

The total electron density distribution is a physical property of molecules. The electron density is typically showed as a comparison of the identified electron density with that predictable by spherical models of the atoms and is called deformation electron density. The total electron density was calculated by DFT/ LANL2DZ using ESP type with SCF density matrix and the structure atomic Mulliken charges displayed in Fig 4 that fixed color range from references. Table 3, exhibited that the negative charge of pyrrole ring inclusive the N19 was greater than another ring, and the charge N19 {-0.486} is more than N18 {-0.466}, it show congestion of negative charge was on ring include N19. In the other hand, between all carbons in this compound, the negative charge of C15 {-0.827} and C20 {-0.915} extremely greater than from others, it results that C15 and C20 be able to fulfilment the electrophilic reaction with other compounds. In this condition, hydrogen atoms that connected to these carbons can be separated easier than other. Furthermore, in nucleophilic reactions, the ring include N18 be able to acting and in electrophilic reactions, ring include N19 can be performing.

Table 3
Charge of $C_9H_{10}N_2$

Atom No	*Charge*	*Atom No*	*Charge*
C1	0.033	C10	-0.714
C2	-0.493	C20	-0.915
C3	-0.289	C8	-0.813
C9	0..581	C21	0.930
N18	-0.466	N19	-0.489

Natural Bond Orbitals

Natural bond orbitals (NBOs) are included few-center orbitals that define the Lewis-like molecular bonding pattern of electron pairs in optimally compact form. With a computer program that can calculate NBOs, optimal Lewis constructions be able to found. An optimal Lewis construction can be perfect as that one with the great amount of electronic charge in Lewis orbitals [30]. A little amount of electronic charge in Lewis orbitals demonstrations strong effects of electron delocalization. In resonance structures, major and minor discovery structures may be present.

This analysis is carried out by searching all possible interactions among "filled" (donor) Lewis-type NBOs and "empty" (acceptor) non-Lewis NBOs, and considering their energetic position by 2nd-order perturbation idea. Natural charges have been computed using natural bond orbital (NBO) module instigated in Gaussian 09. Atomic charges and bond orders are imperative factors for our investigation. These quantities are derived from the NBO occupation analysis. The NBO method is wished to Mulliken charges, because the former suggestions and orbital image that is closer to the classical Lewis structure.

The NBO calculated hybridizations are significant parameters for our study. These quantities are derived from the NBO population analysis. The NBO analysis involving hybridizations of selected bonds are calculated at B3LYP methods and LANL2DZ level of theory. Hybridizations for Nitrogen is S^1P^2 but in Fig 5 there are three Hybridizations for Nitrogen that consist of $[S^1 P^{1.77}\_S^1P^{1.88}\_S^1P^{2.44}]$. Average of these three Hybridizations for Nitrogen is $[S^1P^{2.03}]$.

$$(1.77 + 1.88 + 2.44) = 6.09 \rightarrow 6.09/3 = 2.03 \rightarrow S^1P^{2.03}$$

Therefor calculated Hybridizations for Nitrogen is similar to the theory Hybridizations, also the highest percentage of orbital P for Nitrogen is in N-H bond.

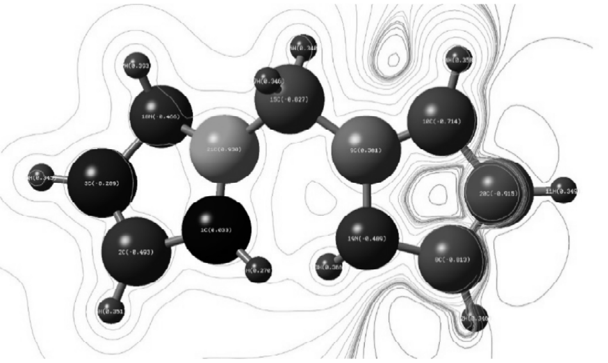


Figure 4: Contour map of electron density and the structure atomic charges with wan der Waals Radii

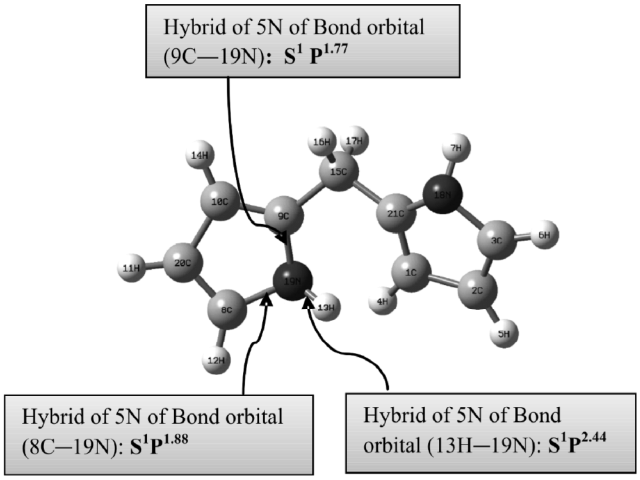

Hybrid of 5N of Bond orbital (9C—19N): $S^1 P^{1.77}$
Hybrid of 5N of Bond orbital (8C—19N): $S^1P^{1.88}$
Hybrid of 5N of Bond orbital (13H—19N): $S^1P^{2.44}$

Figure 5: NBO Hybridizations for N in $C_9H_{10}N_2$.

Frontier Molecular Orbital

Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability. We focus attention on these two orbitals because they are the nearby in energy. These orbitals are closely involved in chemical reactivity, because they are the maximum accessible to electrophiles and nucleophiles, individually. Another key change has to do with the frontier orbitals, the π (HOMO) and π* (LUMO) orbitals [31-32].

Energy difference between HOMO and LUMO orbital is called as energy gap that is a significant factor for structures. The HOMO represents the skill to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron [33]. Highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) and the values are listed are shown in Fig 6. The HOMO–LUMO energies were also calculated at the LANL2DZ, respectively.

IR spectrum

Vibrational spectroscopy is widely used in organic chemistry for the identification of functional groups of organic compounds, the study of molecular conformations, reaction kinetics. IR Spectrum for $C_9H_{10}N_2$ and Vibronic information for the highest pick are Freq: 549.76 Infrared: 269.7305 Raman activity: 6.3824 that showed in Fig 7. Our founding can be interpreted in this way:

According to advanced inorganic chemistry [34], number of vibrational peaks is calculated by following method:

C_1	E
A	1

,

C_1	E
Unshifted atom	21
Contribution pro atom	3
Γtot	63

$$\longrightarrow \quad A = (1\div1)\times\{1\times1\times63\} = 63A$$

$$\Gamma 3_N = 63A$$

Since we do not have x, y, z, R_x, R_y and R_z, thus we do not have translational and rotational contributions, therefore $\Gamma 3_N = \Gamma$ vibrational, it show that this molecule has maximum 63 peaks in IR spectrum.

CONCLUSION

In this research we are interested in studying on $C_9H_{10}N_2$ was chosen to theoretical studies [35]. The optimized geometries and frequencies of the stationary point are calculated by using the DFT (B3LYP) methods with LANL2DZ basis sets. This calculation results indicated that some selected bond length, bond angles values calculation spectrum for the $C_9H_{10}N_2$ some similarity between calculated and experimental results. Calculated angles completely accords with experimental angles, but experimental Bond lengths had a little difference with calculated bond lengths. This results shows that C15 and C20 be able to fulfilment the electrophilic reaction with other compounds. In this condition, hydrogen atoms that connected to these carbons can be separated easier than other. Furthermore, in nucleophilic reactions, the ring include N18 be able to acting and in electrophilic reactions, ring include N19 can be performing. These calculation results indicated that some selected bond length and bond angles values for the $C_9H_{10}N_2$.

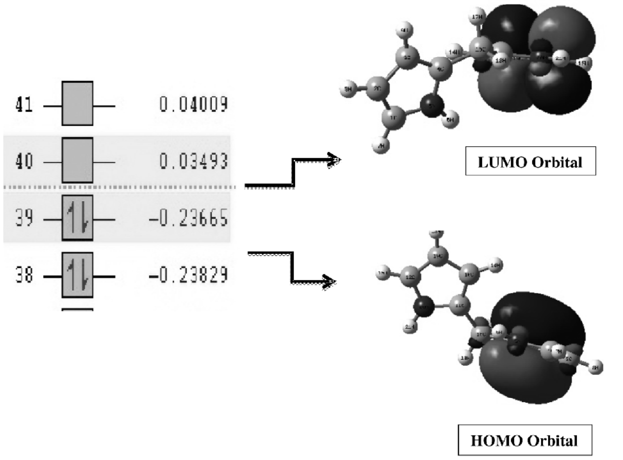


Figure 6: HOMO and LUMO with their energies calculated at DFT (B3LYP)/LANL2DZ

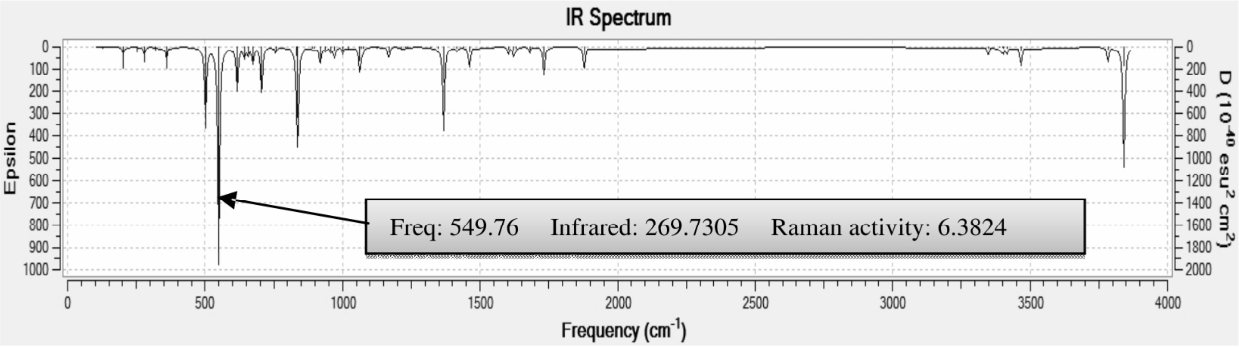


Figure 7: IR spectrum calculated at DFT (B3LYP)/LANL2DZ.

Acknowledgments

We gratefully acknowledge the financial support from the Research Council of Imam Khomeini International University.

References

[1] Jones R A, Pyrroles, Part II, the Synthesis, Reactivity and Physical Properties of substituted Pyrroles, Wiley, New York, **1992.**

[2] Matano Y and Imahori H, Acc. Chem. Res, 42, **2009**, 1193.

[3] Young I S and Kerr M A, Angew. *Chem. Int. Ed,* 42, **2003**, 3023-3026.

[4] Almerico A M, Diana P, Barraja P, Dattolo G, Mingoia F, Loi A G, Scintu F, Milia C, Puddu I and La Colla P, Glycosidopyrroles. Part 1. Acyclic derivatives: 1-(2-hydroxyethoxy)methylpyrroles as potential anti-viral agents, Farmaco, 53(1), **1998**, 33.

[5] Carpio H, Galeazzi E, Greenhouse R, Guzman A, Velarde E and Antonio Y, *Can. J. Chem.* **1982**.

[6] Cartledge J D, Midgley J, Shanson D and Gazzard B G, *J. Antimicrob Chemother*, 40, **1997**, 517.

[7] Jones A, Chemistry of Heterocyclic Compounds, Wiley, New York, **1990**, Vol. 48.

[8] Myers W H, Koontz J I and Harman W D, *J. Am. Chem. Soc*, 114, **1992**, 5684.

[9] Brockmann W T and Tour J M, *J. Am. Chem. Soc,* 117, **1995**, 4437.

[10] Toja E, Depaoli A, Tuan G and Kettenring J, Synthesis. **1987**, 272-274.

[11] Joseph M, Muchowski Stefan H, Unger T, Ackrell J, Cheung P, Gary F and Cook C J, *J. Med. Chem*, 28, **1985**, 1037.

[12] Khanna I K, Weier R M, Yu Y, Collins P W, Miyashiro J M, Koboldt C M, Veenhuizen A W, Currie J L, Seibert K and Isakson P C, *J. Med. Chem*, 40, **1997**, 1619.

13. Burnham B S, Gupton J T, Krumpe K E, Webb T, Shuford J, Bowers B, Warren C, Barnes A E and Hall I H, Arch. Pharm. Pharm. Med. Chem, **1998**, 331-337.

[14] Gupton J T, Burnham B S, Byrd B D, Krumpe K E, Stokes C, Shuford J, Winkle S, Webb T, Warren A E, Barnes C, Henry J and Hall I H, Pharmazie, 54, **1999**, 691.

[15] Justin M H, O'Toole-Colin K, Getzel A, Argenti A and Michael A, Molecules. **2004**, 9, 135.

[16] Higasio Y S and Shoji T, Applied Catalysis, a: General, 221, **2001**, 197-207.

[17] Black D S C, Sci. Synth, 9, **2002**, 441-552.

[18] Katritzky A R and Taylor R, Electrophilic Substitution of Heterocycles, Academic Press, San Diego, **1990**.

[19] Orti E, Sanchez-Marin J and Tomas F, Theor. Chim. Acta, 69, **1986**, 41.

[20] Meyers F, Adant C, Toussaint J M and Bredas J L, Synt. Met, 41, **1991**, 3559.

[21] Chong-Hyeak K, Yea-Sel J, Vincent L, Jonathan L S and Kwang-Jin H, Acta Cryst. **2013**, E69, o1697.

[22] Fleming I, Frontier Orbitals and Organic Chemical Reactions., Wiley, London, **1976**, pp. 125.

[23] Zhang W, Curran D P, Synthetic Application of Fluorous. Tetrahedron, 62, **2006**, 11837-11865.

[24] Smith M C, Ciao Y, Wang H, George S J, Coucouvanis D, Koutmos M, Sturhahn W, Alp E A, Zhao J and Kramer S P, Inorg. Chem, 44, **2005**, 5562-5570.

[25] Tanaka K, Shichiri T, Toriumi M and Yamabe T, Synt. Met, 30, **1989**, 271.

[26] Frisch M J, Trucks G W and Schlegel H B, et al. Gaussian 09 Revision A.02, Gaussian, Inc., PA, Wallingford CT. **2009**.

[27] Lee C, Yang W and Parr R G, Phys. Rev, B 37, **1988**, 785.

[28] Becke A D, Phys. Rev, A 38, **1988**, 3098.

[29] Becke A D, J. Chem. Phys, 98, **1993**, 5648.

[30] Weinhold F and Clark R, Educ. Res. Pract. Eur, 2, **2001**, 91-104.

[31] Jursic B S, Journal of Molecular Structure (Theochem), 497, **2000**, 65-73.

[32] Reshak A H and Sikander A, J. Electrochem. Sci, 8, **2013**, 10396-10423.

[33] Sudha S, Sundaraganesan N, Kurt M, Cinar M and Karabacak M, *Journal of Molecular Structure*, 985, **2011**, 148-156.

[34] Wilkinson G and Cotton F A, Advance inorganic chemistry, Wiley, Canada, 1980.

[35] Simadiras E D, Handy N C and Amos R D, *J. Phys. Chem,* 92, **1988**, 1739.