Density Functional Theory and Reactivity Parameters of Dimethylpyridino-1-4-η-Cyclohexa-1,3-diene iron tricarbonyl Complexes

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Abstract

We present the density-functional theoretical results of structural, electronics, and Characterization of simulated dimethylpyridino-1-4-η-cyclohexa-1,3-diene iron tricarbonyl complexes using infra-red, Uv-visible and NMR spectroscopy. The chemical concepts treated include frontier orbitals (HOMO/LUMO), chemical potential, global chemical hardness as well as electrophilicity index.

Keywords: Electrophilicity index, Chemical hardness, vibrational analysis, ionization energy, electron affinity

Introduction

Conceptual density functional theory (DFT) has been widely used to predict the properties and reactivities of various molecular systems.[1-2] It has proved to be successful as a simple working tool in elucidating chemical reactivity as well as site selectivity. The chemical concepts, reactivity indices such as frontier orbitals (HOMO-LUMO), electronegativity/chemical potential, global chemical hardness and electrophilicity e.t.c. have attracted considerable attention in recent times. Theoretical investigations into the physical and chemical properties of complexes are also important in order to study the relationship between structures, properties and performance and to assist in the development and synthesis of new derivatives with improved properties.[3-8] The quantitative structural activity relationship (QSAR) is a mathematical representation of activity in terms of structural descriptors of series of homologue molecules. The main aim of QSAR is to look for new molecules with required properties using chemical intuition and experience transformed into mathematically quantified and computerized form. Once a correlation is established, the structure of any number of compounds with desired properties can be predicted. Thus the quantum mechanical methodology saves resources. Semi empirical studies on the geometry, thermodynamics, electronic and vibrational states of dimethylpyridino-1-4-η-cyclohexa-1,3-diene iron tricarbonyl complexes have been reported[9]. In this paper, we used Quantum chemical calculations based on Density Functional Theory (DFT) for structural and electronic characterization of these novel organometallic complexes. The DFT has been the most accepted framework to develop and generalize a chemical reactivity theory.[10-13] The calculated properties for the stable structures include dipole moment, spectra (vibration and NMR), the HOMO-LUMO energy band gaps, vertical ionization energies and electron affinities. All the calculations were made using the DFT hybrid functional B3LYP with the basis set 6-31G(D). A suitable description of DFT with B3LYP and basis set 6-31G(D) is available in any computational chemistry text book.[14-18] Generally, the DFT results can be credited with a higher confidence in the quantitative respects due to their treatment of correlation effects, while the regular DFT functional face intrinsic problems in the long range.[19-23] Quantum molecular orbital calculations performed in the framework of DFT approach by using the hybrid B3LYP exchange-functional[24-25] in combination with the Poples group split valence basis set,[26] have been shown to provide excellent compromise between accuracy and computational efficiency of molecular structures as well as vibrational and NMR spectra of molecules.[27-34] All the calculations were performed using Spartan 08V111.[35]

Theoretical Background:

Chemical hardness, chemical potential, electronegativity and electrophilicity index are a number of reactivity parameters that have been defined based on density functional theory.[11-13] The stability of molecules is related to hardness.[12]. Pauling[4] introduced the concept of electronegativity as the power of an atom in a molecule to attract electron to it. Chemical potential, (μ), global chemical hardness (η), electronegativity (χ) are defined as follows:

$$\mu = \left(\frac{\delta E}{\delta N}\right)_{v(r)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. (1)$$

$$\eta = \frac{1}{2}\left(\frac{\delta^2 E}{\delta N^2}\right)_{v(r)} = \frac{1}{2}\left(\frac{\delta \mu}{\delta N}\right)_{v(r)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2)$$

$$\chi = -\mu = -\left(\frac{\delta E}{\delta N}\right)_{v(r)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. (3)$$

Where E and v(r) are the electronic energy and the external potential of an N- electron system.

Using Koopman's theorem for closed-shell molecules, μ, η, χ can be defined as follows:

$$\mu \approx \frac{1}{2}(I + A) \approx \frac{1}{2}(E_H + E_L) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$\eta \approx \frac{1}{2}(I - A) \approx \frac{1}{2}(E_L - E_H) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$\chi = \frac{1}{2}(I + A) = \frac{1}{2}(E_H - E_L) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

I = -E_{HOMO} and A= E_{LUMO}, where I and A are ionization and electron affinity of the molecules. Electron affinity refers to the capacity of the molecules to accept one electron from donor while the ionization potential refers to the ability of the molecules to lose electrons.

Electrophilicity Index:

According to Parr et al[12], It is a measure of energy lowering due to the maximal electron flow between donor and acceptor. It is defined quantitatively as in equation 7.

$$\omega = \frac{\mu^2}{2\eta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where two molecules react, the one that will act as nucleophile/electrophile depends on which has a higher/lower electrophilicity index. The new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge, ΔN, from the environment. The electrophilicity index is a descriptor of reactivity that allows a quantitative classification of the global electrophilicity nature of a molecule within a relative scale. The usefulness of this new reactivity parameter has been demonstrated in understanding the reaction between –diene and dienophile.
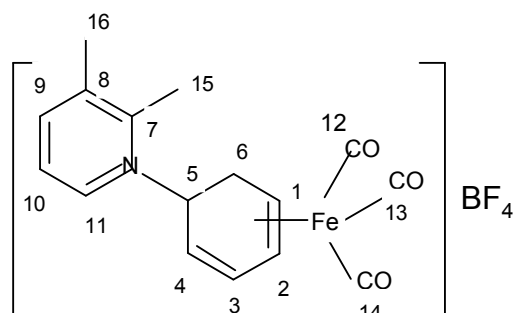

Figure 1: Structure of dimethylpyridino-1-4-η-cyclohexa-1,3-diene iron tricarbonyl complexes.

Computational details.

The hybrid density form used here is Becke's three-parameter hybrid exchange functional[24] with the Lee, Yang, and Parr's correlation functional[25-26] (B3LYP). All the calculations in this work have adopted the 6-31G(D) basis set. Based on the C1 symmetry, the pyridine ring has been exohedrally methylated by replacing two Hydrogen atoms with methyl groups and calculations were made at the B3LYP/ 6-31G(D) level of theory. Some properties have been investigated for the stable structures and these include dipole moment, polarizability, Infra-red and NMR spectra, HOMO and LUMO energies, vertical ionization energies and electron affinities. All the calculations were performed using Spartan '08 programmed package. Figures 1 and 2 represent the structure and optimized structures of the novel organometallic complexes respectively.
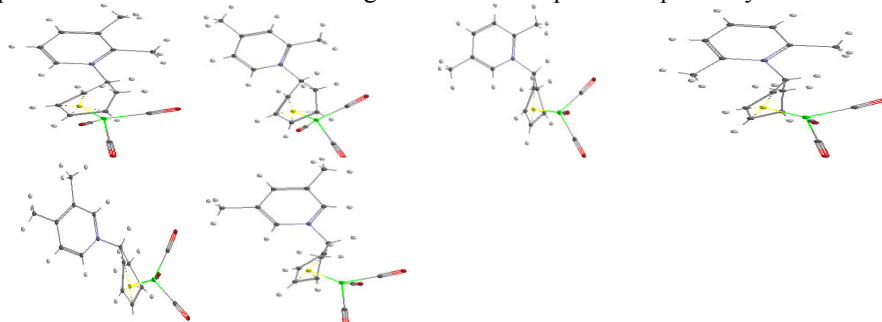

Figure 2: Optimized geometry of X,X-dimethylpyridino-1-4-η-cyclohex-1,3-diene iron tricarbonyl complexes.

Results and discussion:

NMR Spectra: The ^1H, ^{13}C and ^{15}N NMR spectra of these complexes were analyzed using Spartan '08 programme software. These complexes show well separated overlapping multiplets characteristics of the outer H^1 and H^4 and inner H^3-diene protons. The endo H^6 and exo H^6 all appeared as shown in Table 1 and displayed

in Figure 3. The H^5 proton adjacent to the N-methylpyridino substituent is shifted downfield. For instance, with the 2,3-dimethylpyridino-1-4-η-cyclohexa-1,3-diene complex, the Aromatic protons of the pyridine group appear as triplets and doublets while the methylene protons appeared as singlet between 2.35-2.81ppm. These values are characteristic features of the 1,3-diene derivatives[36-39]. The ^{13}C chemical shifts calculated at the DFT B3LYP levels of theory with 6-31G(D) basis set are presented in Table 2 while the spectra are shown in Figure 4. The C_1, C_4 and C_6 atoms appeared 45.97. 48.22 and 36.25ppm respectively while the chemical shifts of C_2, C_3 and C_5 atoms appeared respectively at 85.62, 81.84 and 71.08ppm. All the Aromatic carbons of the pyridine $C_7 - C_{11}$ appeared between 120 and 157.20ppm while the carbonyl carbon due to the presence of oxygen and iron is deshielded and therefore has a higher chemical shifts at 208-216ppm. However, the methylene carbon appeared in the range 19-23ppm. The aromatic carbon to which the methylene carbon is attached is shifted downfield due to the electron releasing ability of the methyl substituent.

Table 1: ^1H N.M.R. Chemical shifts in ppm of X,X-dimethylpyridino-1-4-η-cyclohex-1,3-diene iron tricarbonyl complexes.

Proton	2,3-diMe	2,4-diMe	2,5-diMe	2,6-diMe	3,4-diMe	3,5-diMe
H_1	2.59	2.57	2.61	2.76	2.53	2.62
H_2	5.77	5.75	5.77	5.62	5.77	5.78
H_3	5.68	5.68	5.63	5.66	5.64	5.56
H_4	2.18	2.17	2.22	2.07	2.23	2.29
H_5	5.16	5.07	5.08	5.40	4.83	4.69
$H_{6\ endo}$	2.70	2.68	2.71	2.49	2.68	2.82
H_6 exo	1.33	1.28	1.43	1.71	1.45	1.62
H_7	8.04	7.32	7.49	7.46	7.66	7.61
H_8	7.60	7.48	8.00	8.00	7.58	8.00
H_9	8.54	8.46	8.29	7.43	8.27	8.07
H_{10}	2.75	2.35	2.53	2.59	2.49	2.74
H_{11}	2.24	2.80	2.50	2.65	2.50	2.71
H_{12}	2.61	2.70	2.79	2.98	2.24	2.10
H_{13}	2.40	2.48	2.74	2.65	2.58	2.75
H_{14}	2.65	2.45	2.77	3.17	2.57	2.79
H_{15}	2.61	2.81	2.17	2.49	2.48	2.19

Table 2: ^{13}C N.M.R. Chemical shifts in ppm of X, X-dimethylpyridino-1-4-η-cyclohex-1,3-diene iron tricarbonyl complexes.

| Carbon	2,3-diMe	2,4-diMe	2,5-diMe	2,6-diMe	3,4-diMe	3,5-diMe
C1	45.97	46.20	46.44	46.74	46.02	47.00
C2	85.62	85.56	85.04	85.04	85.62	85.65
C3	81.84	81.84	82.01	81.92	81.70	81.17
C4	48.22	47.53	49.50	47.46	47.61	50.11
C5	71.08	69.57	69.88	69.75	76.49	77.84
C6	32.65	32.99	34.09	27.36	35.46	36.45
C7	148.21	147.51	145.78	151.02	134.72	133.39
C8	136.33	125.27	123.90	123.29	135.78	136.01
C9	140.00	155.58	139.56	137.53	155.89	141.09
C10	119.29	120.89	134.71	124.80	123.48	136.66
C11	131.59	132.49	133.81	151.18	129.59	130.42
C12	215.32	215.38	215.38	215.95	215.26	214.87
C13	208.70	208.72	208.79	208.77	208.88	208.67
C14	208.65	208.67	208.55	209.16	208.66	208.59
C15	16.25	20.07	19.87	22.71	18.41	18.68
C16	21.35	22.04	18.82	25.37	21.41	19.07
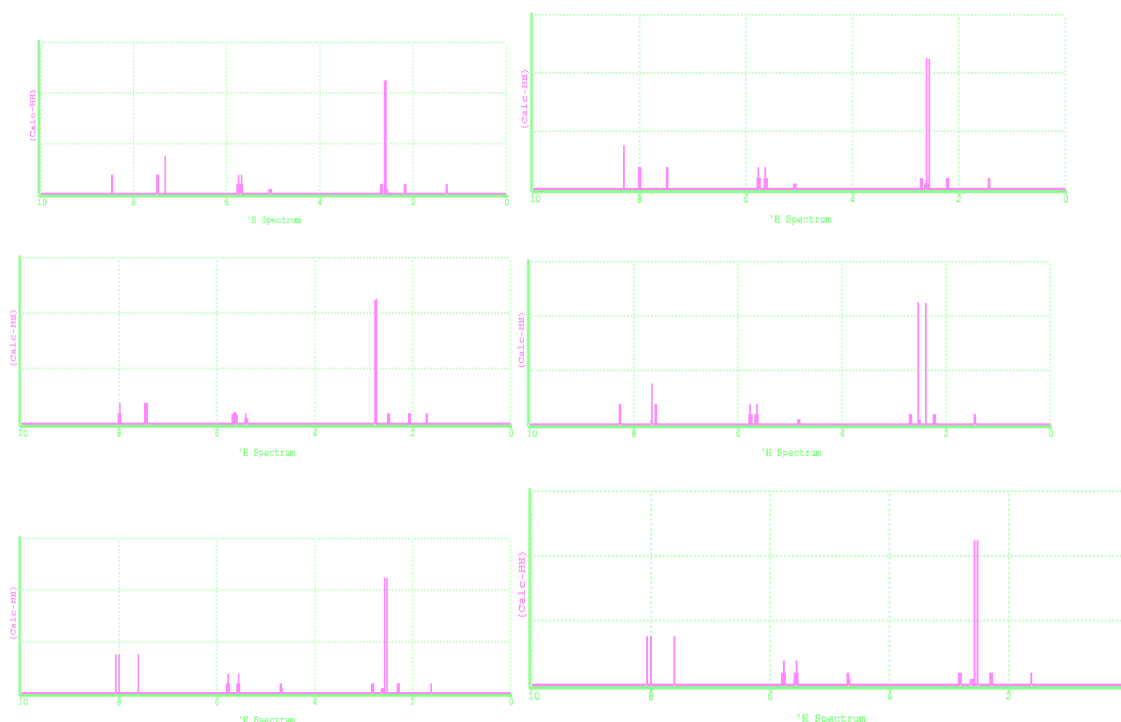
Figure 3: ^{1}Hn.m.r spectra of X,X-dimethylpyridino-1-4-η-cyclohex-1,3-diene iron tricarbonyl complexes
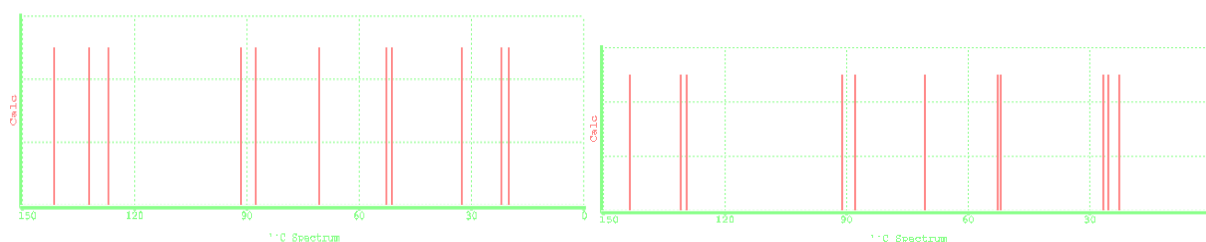

Figure 4: ^{13}C n.m.r. spectra of X,X-dimethylpyridino-1-4-η-cyclohex-1,3-diene iron tricarbonyl complexes.

Vibrational analysis: There is no obvious deviation in optimized geometries for these dimethylpyridino-1-4-η-cyclohexa-1,3-diene iron tricarbonyl complexes. We present the calculated vibrational frequencies from gas phase infra-red spectra of the complexes without any scale factor. The absence of any imaginary frequency indicates that all the optimized structures correspond to the minimum point on the intramolecular potential energy surface. Analysis of the calculated vibrational frequencies of the six complexes shows no large deviation. We observed that the complexes have very sharp peak between $2103cm^{-1}$ - $2170cm^{-1}$corresponding to the stretching vibration of the C≡O bond[36-39]. It is clearly seen that these groups have corresponding IR signatures which are expected to provide useful information for further studies. Our theoretical   vibrational frequencies may form the basis of reference for further theoretical studies.
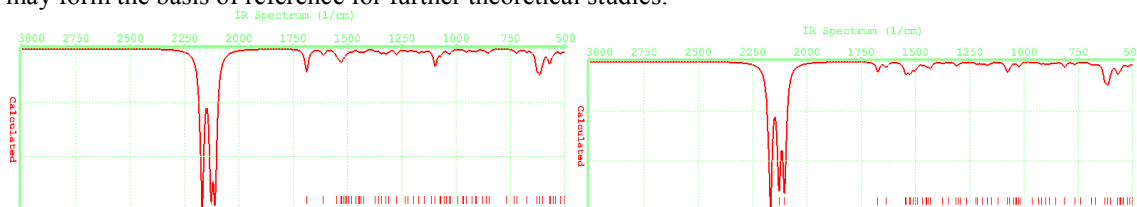

Figure 5: Infra-red spectra of X,X-dimethylpyridino-1-4-η-cyclohex-1,3-diene iron tricarbonyl complexes.

 Uv-visible: The ultra-violet spectrum of these novel species were calculated with DFT. The results in Table 3 show the first five electronic transition states in nanometer (nm), the oscillation strengths(f) that can give an idea of intensity of the transition, and orbital assignments, indicating the percentage of any H-n → L+n transition taking place in the ultraviolet region, close to but out of the visible region. The calculated uv absorption band is between 305nm-308nm while the 3,4 dimethyl and 3,5-dimethyl groups exhibit the peak 325nm (3.152) and 404.27nm (0.021).

Table 3: Uv visible spectrometric studies of new dimethylpyridino-1-4--η-cyclohexa-1,3-diene iron tricarbonyl complexes.

| Substituent	Wavelength λ / nm	Intensity
2,3-(Me)$_2$	308	0.021
	313	0.005
	319	0.005
	321	0.001
	325	3.000
	386	0.010
2,4-(Me)$_2$	308	0.028
	311	0.004
	316	0.002
	319	0.002
	325	0.0003
	382	0.009
2,5-(Me)$_2$	308	0.019
	314	0.003
	322	0.009
	327	0.005
	329	0.0002
	398	0.013
	305	0.025
	312	0.001
	327	0.007
	329	0.0009
	322	0.015
	396	0.022
2,6-(Me)$_2$		
3,4-(Me)$_2$	309	0.025
	314	0.005
	320	0.008
	323	0.0003
	326	3.154
	391	0.011
3,5-(Me)$_2$	309	0.025
	312	0.001
	327	0.007
	329	0.0009
	332	0.015
	396	0.022
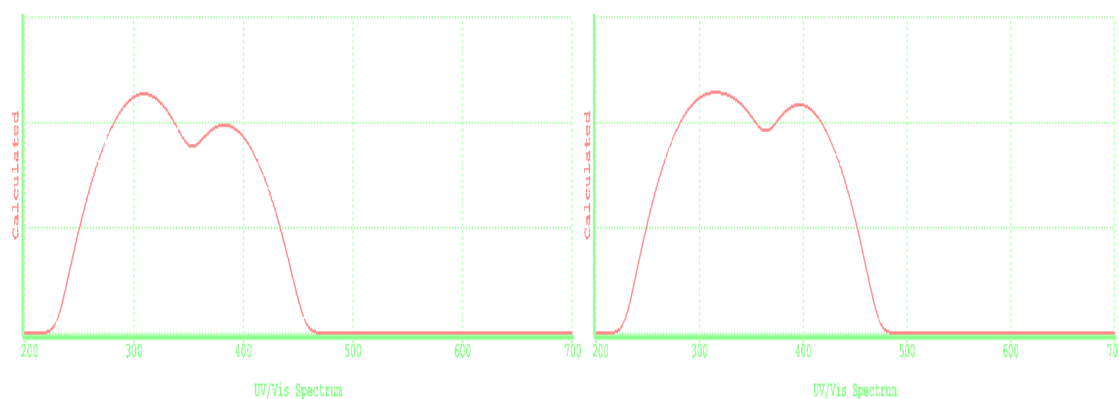
Figure 6: Uv-visible spectra of X,X-dimethylpyridino-1-4-η-cyclohex-1,3-diene iron tricarbonyl complexes.
Polarizability: This is the ability of these molecules to acquire a dipole moment, p, in an electric field, E. The appearance of p is due to the displacement of electric charges in atomic systems under the influence of E and the

moment, p, disappears when no electric field is present. The concept of polarizability is generally not applied to particles having permanent dipole moment such as polar molecules.

$p = \propto E$ Where α is a quantitative measure of polarizability and is sometimes called molecular polarizability for some molecules. The value of α may depend on the direction of E: this is known as anisotropic polarizability. It is calculated as the average of the polarizability tensor, α, which is $\propto = \frac{1}{3}(\propto_{xx} + \propto_{yy} + \propto_{zz})$.

Dipole moment: The molecular dipole moment is the simplest experimental measure of the distribution of charge in a molecule. The accuracy of the overall distribution of electrons in a molecule is difficult to quantify since it involves all the multipoles. The result for the dipole moment and polarizability of these molecules may provide an insight into their solubility and chemical reactivities as well as their potential application in the synthesis of new organometallic derivatives.

Electronic States: It is expedient to visualize the HOMO and LUMO of these new organometallic compounds because the relative ordering of occupied and virtual orbital provide a reasonable qualitative indication of both ground and excited state properties. The HOMO of these complexes possess a π-bonding character within the subunit and π-antibonding character excited state properties between the consecutive subunits. On the other hand, the LUMO possesses a π-antibonding character within the subunit and a π-bonding character between the subunits. In practice, the HOMO and LUMO energies are obtained from an empirical formula based on the onset of oxidation-reduction of peaks measured by cyclic voltametry. Theoretically the HOMO and LUMO energies are calculated using DFT B3LYP (6-31G(D)). These calculations however, do not have solid-state packing effect and aqeous state is not taken into consideration. The HOMO and LUMO densities are all over the cyclohexa-1,3-diene and dimethylpyridino moiety respectively, thus giving an insight into the reactivity of the complexes. The HOMO and LUMO energies together with calculated energy band gap are shown in Table 4. The orbital energy diagram and the HOMO and LUMO energy diagrams are displayed in Figures 7 and 8 respectively.

Table 4: Total energy, Dipole moment, Polarizability and Energy band gaps for X, X-dimethylpyridino-1-4-η-cyclohex-1,3-diene iron tricarbonyl complexes.

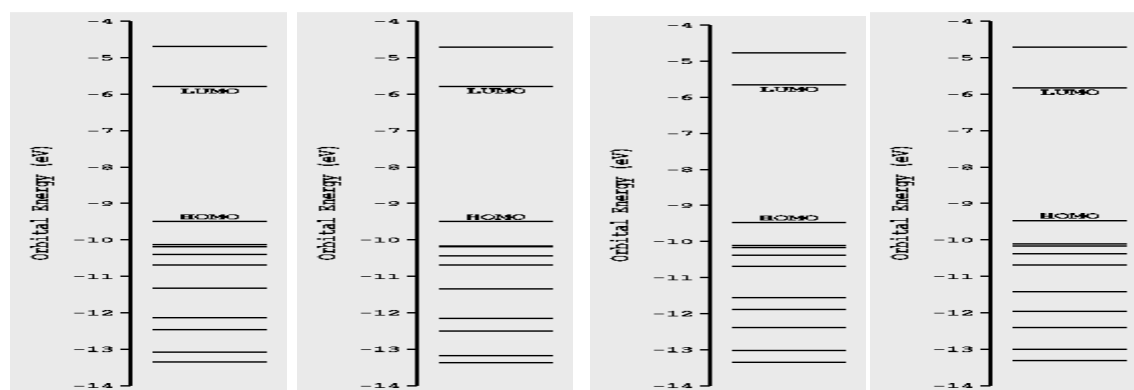| X,X-diMethyl	Total Energy/ a.u	Dipole moment/D	EHOMO/ eV	ELUMO/ eV	Energy band gap/eV	Polarizability
2,3-Me	-2163.21	10.83	-9.51	-5.72	3.89	64.89
2,4-Me	-2163.20	11.21	-9.47	-5.65	3.82	64.93
2,5-Me	-2163.21	10.96	-9.49	-5.79	3.70	64.96
2,6-Me	-2163.20	10.61	-9.50	-5.78	3.72	64.83
3,4-Me	-2163.21	11.54	-9.44	-5.69	3.75	64.99
3,5-Me	2163.21	11.26	-9.64	5.82	3.82	65.04

Figure 7: Orbital energies of X,X-dimethylpyridino-1-4-η-cyclohex-1,3-diene iron tricarbonyl complexes.
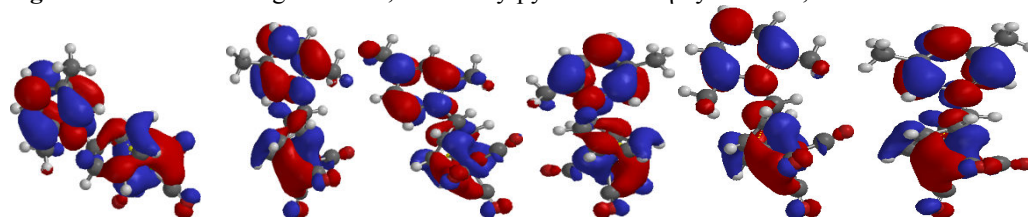

Figure 8: HOMO-LUMO Energy diagram of X,X-dimethylpyridino-1-4-η-cyclohex-1,3-diene iron tricarbonyl complexes.

Reactivity parameters: All the calculated reactivity parameters are based on the values of the chemical

potential, μ, and the global chemical hardness, η. They were calculated using finite difference and the frozen orbital approximations, which yield them in terms of the highest occupied molecular orbital energy E_H, and the lowest unoccupied molecular orbital energy E_L. The validity of the Koopman's theorem within the DFT approximation is still controversial. However, it has been shown that the Kohn Sham orbitals may differ in shape and energy from the Hartree-Fock orbitals and the combination of the two produces conceptual DFT reactivity descriptors that correlate quite well with the reactivity descriptors obtained from the combination of these two theories i.e Hartree-Fock and Density Functional theory. Thus, it is expedient to calculate the electronegativity, global hardness and global electrophilicity index for these complexes using both approximations in order to verify the quality of the procedures. Since the SCF model used in our calculations is a restricted hybrid HF-DFT self consistent field (SCF), calculations performed using Pulay DIIS + Geometric Direct Minimization. The combination of the two theories is expected to produce a result that validates Koopman's theorem, however we employed both DFT B3LYP with basis set 6-31G(D) and Hartree-Fock with basis set 6-31G(D) and observed that the DFT procedure underestimated the LUMO energy in comparison to Hartree-Fock procedure. The calculated HOMO and LUMO energies for density functional theory DFT, B3LYP with basis set 6-31G(D) are -9.50eV and -5.78eV with a band gap of 3.72eV compared with the calculated energies of HOMO and LUMO values of -10.42eV and -1.27eV and band gap energy of 9.15eV obtained for Hartree-Fock with basis set 6-31G(D). The results for the vertical ionization energies and electron affinities of these complexes obtained through energy difference between the ionized and neutral state, calculated from the optimized geometry of the molecule are listed and collected in Table 5. The values of the electronegativity, global hardness and global electrophilicity were calculated using I and A, and are also collected and listed in Table 5.

Table 5: Reactivity global indexes of the structure of new dimethylpyridino-1-4--η-cyclohexa-1,3-diene iron tricarbonyl complexes.

X,X-diMethyl	I/eV	A/eV	μ/Ev	χ/eV	η/eV	ω/eV
2,3-Me	9.51	5.72	-7.62	7.62	1.95	14.89
2,4- Me	9.47	5.65	-7.56	7.56	1.91	14.96
2,5- Me	9.49	5.79	-7.64	7.64	1.85	15.80
2,6- Me	9.50	5.78	-7.64	7.64	1.86	15.69
3,4- Me	9.44	5.69	-7.57	7.57	1.88	15.28
3,5- Me	9.64	5.82	-7.73	7.73	1.91	15.64

Conclusion

We have determined the structure of the novel compound, dimethylpyridino-1-4-η-cyclohexa-1,3-diene iron tricarbonyl complexes using DFT B3LYP with basis set 6-31G(D) and compared the calculated energies values with Hartree-Fock with basis set 6-31(D) using Koopman's theorem. Quantum molecular orbital calculations carried out on optimized geometries; include Uv-Visible, Infra-red and NMR. Since the SCF model used in our calculations is a restricted hybrid HF-DFT SCF, calculations were performed using Pulay DIIS + Geometric Direct Minimization. The combination of the two theories produces a result for these complexes. The shape of the frontier orbitals of these complexes were displayed as well as some electronic parameters such as the total energy, the dipole moment and the polarizability while the reactivity parameters such as the chemical potential, electronegativity and electrophilicity index were calculated. Results suggest that under suitable conditions, these complexes will react with suitable nucleophiles to give new products.

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