

Structural and DFT Studies on Molecular Structure of Pyridino-1-4- η -cyclohexa-1,3-diene and 2-Methoxycyclohexa-1,3-diene Irontricarbonyl Complexes

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Abstract: We report a molecular simulation of Pyridino-1-4- η -cyclohexa-1,3-diene and 2-methoxycyclohexa-1,3-diene irontricarbonyl complexes. In this work we employed the Density Functional Theory (DFT) in our calculations to predict the dipole moment, spectra, HOMO-LUMO energies, and chemical reactivity parameters including chemical potential, global chemical hardness, electrophilicity index and polarizability revealing that the complexes are highly reactive. The calculated values were compared with the available experimental values for these compounds as a means of validation. A very good agreement has been obtained between B3LYP theoretical results and the experimental results. We also calculated the excitation wavelength with time-dependent density functional theory and observed a mixture of singlet-singlet and singlet to triplet excitation energies.

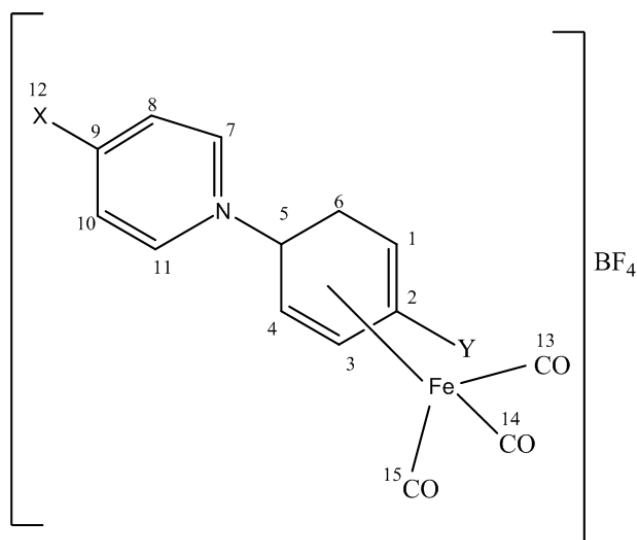
Keywords: Density Functional Theory, HOMO-LUMO Energy Band Gap, ¹H, ¹³C NMR Spectra, Chemical Potential, Electrophilicity

1. Introduction

The synthesis of novel compounds is of prime importance. Qualitative Structure Activity Relationship (QSAR) is an important predictive tool for a preliminary evaluation of the activity of chemical compounds, this can be achieved by using computer-aided models. The Hohenberg and Kohn Sham theorem based Density Functional Theorem (DFT) provide a major boost to the computational chemists in the design and the study of the properties of molecular structures [1-3]. DFT methods are in general capable of generating a variety of isolated molecular properties and the performance of these methods in the description of structures, energetics and molecular properties has received considerable attention in recent times [4-9]. In this paper, we used Quantum chemical calculations based on Density Functional Theory (DFT) for structural and electronic characterization of these organometallic complexes, this is due to the fact that, the

method has been the most accepted framework to develop and generalize a chemical reactivity theory [10-12]. 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 [13-17]. 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 [18-22]. Quantum molecular orbital calculations performed in the framework of DFT approach by using the hybrid B3LYP exchange-functional in combination with the Poples group split valence basis set have been shown to provide excellent compromise between accuracy and computational efficiency

of molecular structures as well as vibrational and NMR spectra of molecules [23-32]. Time-dependent density functional theory (TDDFT) is an important instrument for calculating and elucidating the electronic excited state properties. The theory applies ground state DFT philosophy to time dependent problems by replacing the complicated many-body time-dependent Schrodinger equation by a set of time-dependent single-particle equation whose orbitals yield the same time-dependent density. The commonest time-dependent perturbation is a long wavelength electric field, oscillating with frequency. The field is a weak perturbation of the molecule, and a linear response analysis can be performed, from which the optical absorption spectrum of the molecule due to the electronic excitations can be extracted. The linear response TDDFT predicts the transition frequencies/ excitation energies from electronically ground state to electronic excited states and many other properties [33-37].



X = H, 2-Me, 3-Me, 4-Me and Y = H or OCH₃

Figure 1. Structure of pyridino-1-4-η-cyclohexa-1,3-diene irontricarbonyl.

2. Computational Method

All the calculations were performed using Spartan 10 program package using B3LYP methods which uses the exchange functional proposed by Becke and the correlation functional given by Lee, Yang and Parr [23, 24]. The 6-31 (D) basis set has been used in conjunction with DFT method [25]. This basis set has the advantage of being flexible enough to guarantee reliable theoretical results and being small enough for rapid calculations. It represents an excellent compromise between completeness and economy. The molecular geometry was fully optimized without any constraint with the help of analytical gradient procedure implemented within the program A restricted HF-DFT self-consistent field calculations was carried out using Pulay DIIS and Geometry direct minimization implemented within the program.

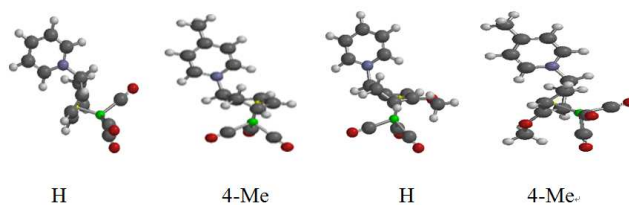


Figure 2. Optimized geometries of pyridino-1-4-η-cyclohexa-1,3-diene irontricarbonyl complexes.

3. Theoretical Background

3.1. Chemical Potential, Hardness and Electronegativity

In the concept framework of DFT, the chemical potential, μ , is a measure of the escaping tendency of an electron from equilibrium as defined by Parr et al [13]. The electronegativity, χ could be written as the partial derivative of the system's energy with respect to the number of electrons, N, at the fixed external potential, $v_{(r)}$:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v_{(r)}} = -\chi \quad (1)$$

Where χ , is the electronegativity.

The global hardness ρ can be seen as the resistance to charge transfer:

$$\rho = \frac{1}{2} \left(\frac{\delta^2 E}{\delta N^2} \right)_{v_{(r)}} \quad (2)$$

According to Mulliken, one has:

$$\mu = \chi = -\frac{1}{2}(I + A) \quad (3)$$

And:

$$\eta = \frac{1}{2}(I - A) \quad (4)$$

Where E and $v_{(r)}$ are electronic energy and external potential of an N-electron system,

Using a finite difference approximation and Koopman's theorem [14-17], the above expressions can be written as:

$$\mu \approx -\frac{1}{2}(I + A) \approx \frac{1}{2}(E_L + E_H) \quad (5)$$

$$\eta \approx \frac{1}{2}(I - A) \approx \frac{1}{2}(E_L - E_H) \quad (6)$$

Parr *et al.*, proposed a new DFT concept called the electrophilicity index, ω , in terms of the above two global activity indices, μ and η , (equation 7).

$$\omega = \frac{\mu^2}{2\eta} = \frac{(I + A)^2}{2(I + A)} = \frac{(E_L + E_H)^2}{2(E_L + E_H)} \quad (7)$$

Where E_H and E_L are the energies of the highest occupied and the lowest unoccupied molecular orbital, I and A, are first ionization potential and electron affinity respectively.

3.2. Electrophilicity Index

This is the relative reactivity of an electrophile. An

electrophile is attracted to electrons that participated in a chemical reaction by accepting electrons to form bond to a nucleophiles [59-61], and because electrophiles accept electrons [62, 63], they are Lewis acids according to the general acid-base theory of Bronsted and Lowry [64,65]. Most electrophiles are positively charged, having an atom which carries a partial positive charge or does not have an octet of electrons. The concept of electrophilicity index was quantitatively introduced by Parr *et al.*, [12], and it is referred to as the stabilization energy when atoms and molecules in their ground states acquire additional electronic charge from the environment.

The electrophilicity index, ω , represents the stabilization energy of the system when it gets saturated by electrons coming from the surrounding: The above formulae are working tools for us to calculate the chemical potential, hardness, and electrophilicity index. 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 yields them in terms of the highest occupied molecular orbital energy, E_H , and the lowest unoccupied molecular orbital energy, E_L .

4. Results and Discussion

4.1. Electronic States

The HOMO and LUMO of these new organometallic

Table 1. Electronic properties of pyridino-1-4- η -cyclohexa-1,3-diene irontricarboxyl complexes.

Y	X	Total energy/a. u	Dipole moment/D	E_{HOMO}/eV	E_{LUMO}/eV	$E_L - E_H = E_g/eV$	Polarizability
H	H	-2084.56	12.21	-9.60	-6.14	3.46	62.12
	2-Me	-2123.90	11.38	-9.56	-5.92	3.64	63.49
	3-Me	-2123.90	11.74	-9.52	-5.96	3.56	63.58
	4-Me	-2123.90	12.03	-9.49	-5.87	3.62	63.57
OCH ₃	H	-2199.09	12.48	-9.33	-6.06	3.27	64.39
	2-Me	-2138.41	11.73	-9.28	-5.83	3.45	65.75
	3-Me	-2138.31	12.11	-9.24	-5.90	3.34	65.85
	4-Me	-2138.41	12.37	-9.23	-5.79	3.44	65.82

4.2. Reactivity Parameters

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 yields 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

compounds are being visualized 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 aqueous state is not taken into consideration.

The HOMO is concentrated on all over the metal and cyclohexa-1,3-diene while the LUMO densities are on methylpyridino moiety, thus giving an insight into the reactivity of these complexes and that the movement of electron is from the metal and the cyclohexa-1,3-diene ring towards the methylpyridine ring. The HOMO and LUMO energies together with calculated energy band gap are collected in shown in Table 1. The orbital energy diagram and the HOMO and LUMO energy diagrams are shown in Figure 3.

Hartree-Fock orbitals. The combination of the two produces conceptual DFT reactivity descriptors that correlate quite well with the reactivity descriptors obtained through Hartree-Fock calculations. The SCF model used in our calculations is a restricted hybrid HF-DFT-SCF calculations using Pulay DIIS + Geometric Direct Minimization. The combination of the two theories produces result which further revalidates Koopman's theorem. The values of electrophilicity index for these complexes revealed that they are capable of reacting with nucleophiles to give new products. The calculated quantities are listed in Table 2.

Table 2. Reactivity parameters pyridino and methylpyridino-1-4- η -cyclohexa-1,3-diene irontricarboxyl complexes.

Substituent Y	X	I/eV	A/eV	μ	η	ω
H	H	9.60	6.14	-7.87	1.73	17.90
	2-Me	9.56	5.92	-7.74	1.82	16.37
	3-Me	9.52	5.96	-7.74	1.78	16.83
	4-Me	9.49	5.87	-7.69	1.81	16.34
OCH ₃	H	9.33	6.06	-7.70	1.64	18.08
	2-Me	9.28	5.83	-7.56	1.73	16.56
	3-Me	9.24	5.90	-7.57	1.67	17.16
	4-Me	9.23	5.79	-7.51	1.72	16.40

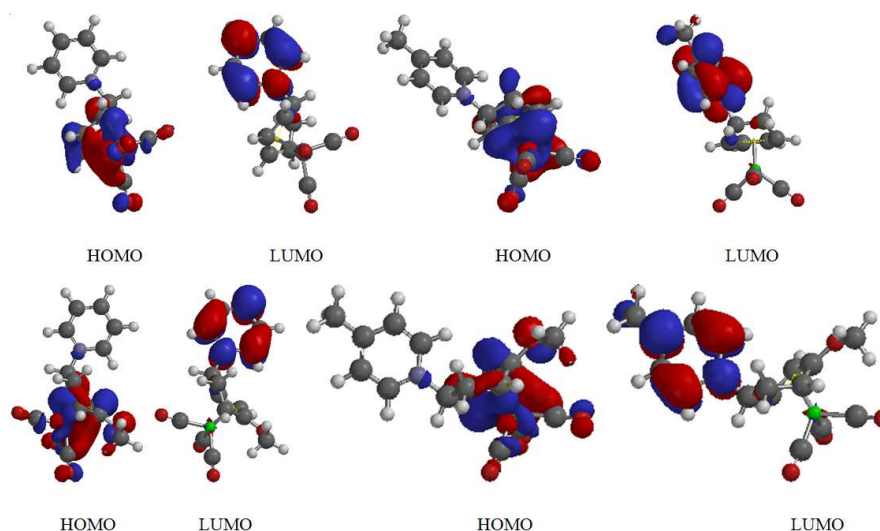


Figure 3. HOMO-LUMO energy diagram of pyridino-1-4- η -cyclohexa-1,3-diene irontricarbonyl complexes.

4.3. NMR Spectra

The ^1H , ^{13}C and ^{15}N NMR spectra of these complexes were analyzed using Spartan 10 programme software. These complexes show well separated overlapping multiplets characteristics of the outer H^1 and H^4 and inner H^2 and H^3 - diene protons. The endo H^6 and exo H^6 protons appeared as shown in the Table 3 and displayed in Figure 4 and figure 5. The H^5 proton adjacent to the N-methylpyridino substituent is shifted downfield. For instance, with the pyridino-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 2.18 – 2.90 ppm. These values are characteristic features of the 1,3-diene derivatives [69-72]. The ^{13}C chemical shifts calculated at the DFT B3LYP levels of theory with 6-31G (D) basis set are presented in Table 3 while the spectra are shown in Figure 4 and Figure 5. The C_1 , C_4 and C_6 atoms appeared at 47.65, 50.83 and 37.23 ppm, while the chemical shifts of C_2 , C_3 and C_5 appeared at 85.91, 80.80 and 79.08 ppm respectively. All

the Aromatic carbons of the pyridine $\text{C}_7 - \text{C}_{11}$ appeared at 120 – 157.20 ppm while Carbonyl carbon due to the presence of oxygen and iron are deshielded and consequently have higher chemical shifts at 208-216 ppm. However, the methylene carbon appeared in the range 19-23 ppm. There are no experimental values for ^{13}C but ^1H NMR values agrees with available experimental values [69-72]. The aromatic carbon to which the methylene carbon is attached is shifted downfield due to the electron releasing ability of the methyl substituent. Its methoxy analogue presents similar results for all the protons but ^{13}C NMR displayed a radical departure due to the influence of the oxygen attached to carbon 2. The C_1 , C_4 and C_6 appeared 139.23, this is attributed to the presence of methoxy group is attached to carbon 2 of the cyclohexa-1,3-diene ring. 47.65, 50.83 and 37.23 while the chemical shifts of C_2 , C_3 , C_4 and C_5 appeared at 63.83, 37.88, 42.64 and 79.04 ppm. The ^1H and ^{13}C NMR spectra data are shown in Table 3 while the spectra are displayed in Figure 4 and Figure 5.

Table 3. NMR Spectra data of pyridino and methylpyridino-1-4- η -2-methoxycyclohexa-1,3-diene irontricarbonyl complexes.

Substituent Y	Proton/Carbon	H	2-Me	3-Me	4-Me
H	H_1	2.71	2.59	2.57	2.68
	H_2	5.80	5.78	5.79	5.76
	H_3	5.57	5.70	5.65	5.55
	H_4	2.35	2.20	2.28	2.32
	H_5	4.80	5.16	4.85	4.70
	H_6^{endo}	2.97	2.70	2.75	2.95
	H_6^{exo}	1.74	1.32	1.51	1.70
	H_7	8.13	-	7.80	7.90
	H_8	7.81	7.62	-	7.51
	H_9	8.39	8.20	8.21	-
	H_{10}	7.93	7.75	7.82	7.63
	H_{11}	8.61	8.68	8.41	8.30
	CH_3	-	2.52-2.90	2.18-2.81	2.58-2.87
	C_1	47.65	45.85	46.22	47.80
C_2	85.91	85.63	85.71	85.55	
C_3	80.80	81.97	81.57	80.73	
C_4	50.83	47.72	48.24	50.48	
C_5	79.08	71.05	78.22	77.30	
C_6	37.23	32.92	36.08	37.07	

Substituent Y	Proton/Carbon	H	2-Me	3-Me	4-Me
OCH ₃	1H	2.84	2.76	2.83	2.81
	2H	-	-	-	-
	3H	5.16	5.34	5.17	5.15
	4H	2.08	1.92	2.05	2.04
	5H	4.56	4.88	4.49	4.47
	6H	2.93	2.73	2.88	2.84
	6'H	1.68	1.33	1.65	1.62
	OCH ₃	3.55-4.10	3.51-4.06	3.54-4.09	3.54-4.08
	8H	8.09	-	7.79	7.86
	9H	7.78	7.58	-	7.48
	10H	8.47	8.16	8.18	-
	11H	7.90	7.73	7.78	7.62
	12H	8.57	8.85	8.33	8.35
	CH ₃	-	2.46-2.84	2.13-2.79	2.57-2.86
	C ₁	139.23	139.51	139.21	139.13
	C ₂	63.87	64.44	64.19	64.06
C ₃	37.88	36.94	38.00	37.82	
C ₄	42.64	39.31	42.48	42.23	
C ₅	79.04	71.33	78.40	77.54	
C ₆	38.59	34.21	38.16	37.98	
C ₇	136.19	148.85	135.79	135.15	
C ₈	122.19	124.43	137.03	122.57	
C ₉	139.35	138.48	140.01	156.80	
C ₁₀	123.03	120.18	122.13	123.64	
C ₁₁	133.99	134.52	131.11	132.59	
OCH ₃	54.08	54.07	53.99	54.00	
C ₁₃	214.46	214.93	214.80	214.52	
C ₁₄	206.90	206.99	207.11	206.99	
C ₁₅	209.60	209.80	209.81	209.81	
C ₁₆	-	20.26	18.91	22.30	

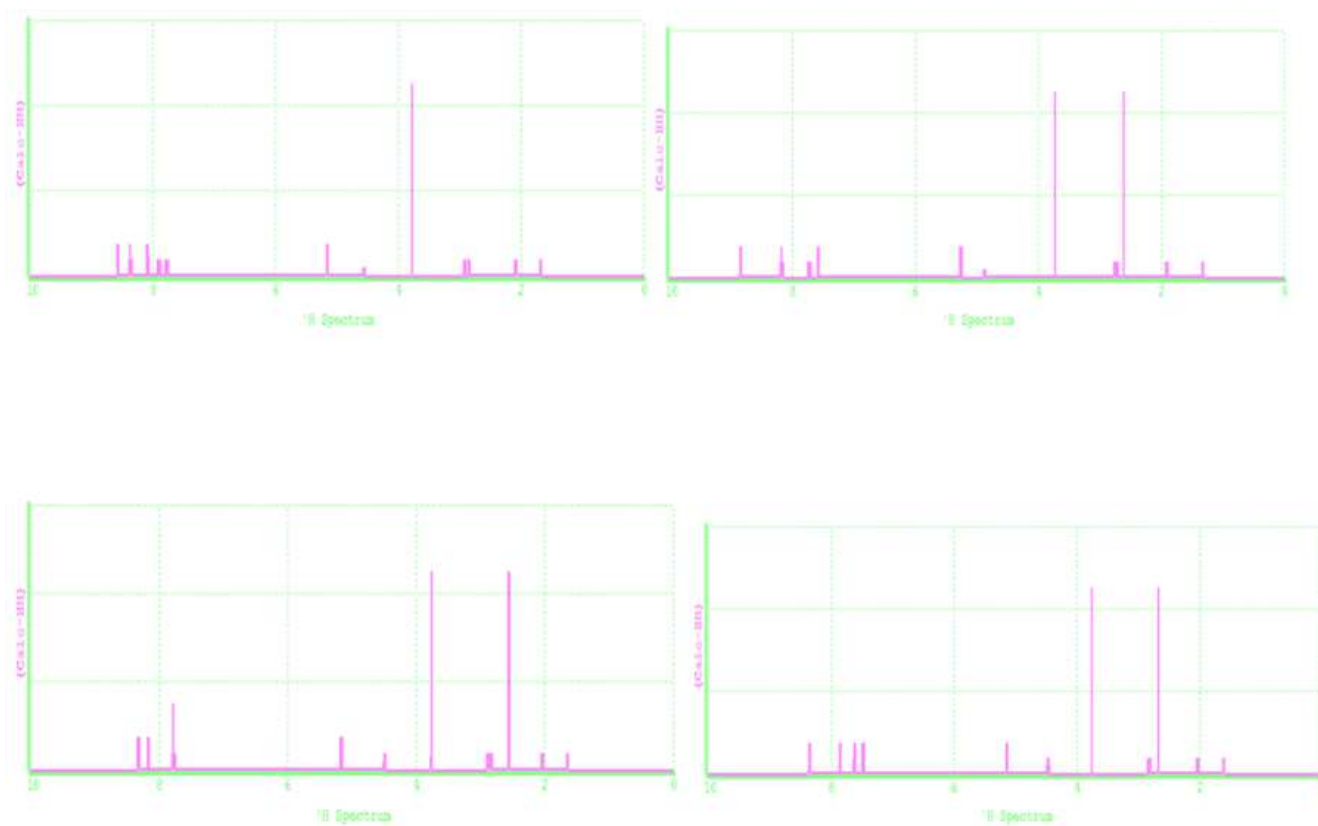


Figure 4. ¹H NMR spectra of pyridino- and methylpyridino-1-4- η -2-methoxycyclohexa-1,3-diene irontricarboxyl complexes.

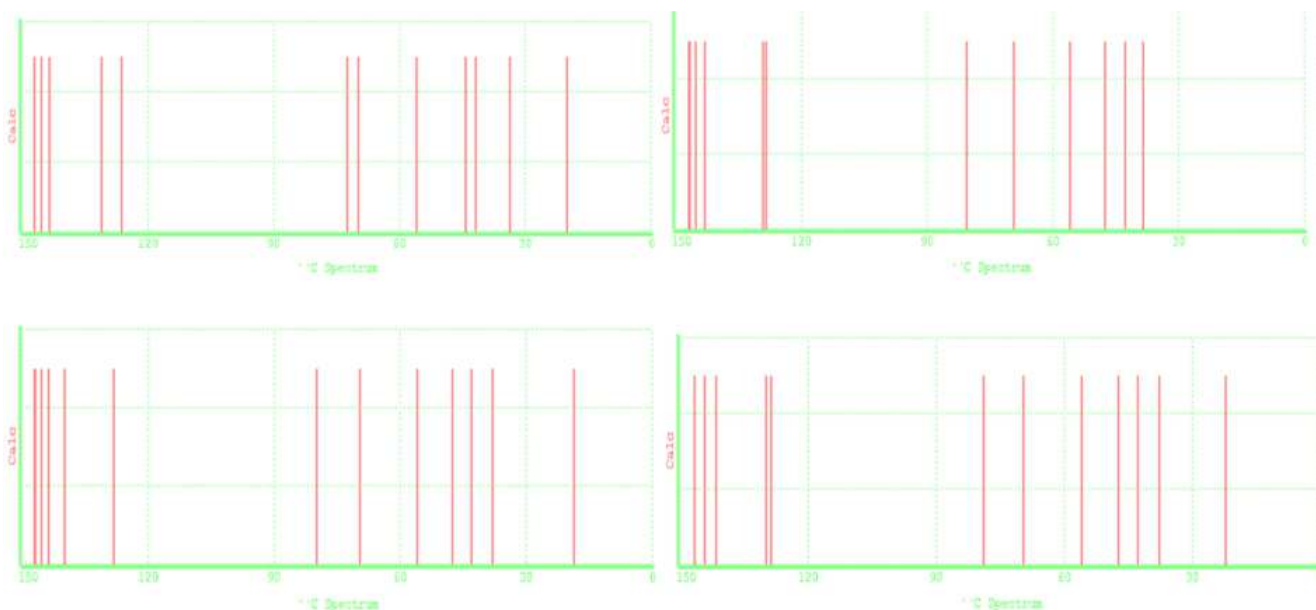


Figure 5. ^{13}C NMR spectra of pyridino- and methylpyridino-1-4- η -cyclohexa-1,3-diene irontricarbonyl complexes.

4.4. Vibrational Analysis

There are 87 and 96 A normal modes of vibration for the pyridino- and the methylpyridino-1-4- η -cyclohexa-1,3-diene irontricarbonyl complexes while its methoxy analogue presents 99 and 108 normal vibrations. We present the calculated vibrational frequencies from gas phase infra-red spectra (Figure 6) 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 complexes shows no large deviation. The complexes have very sharp and strong peak at 2108 - 2165 cm^{-1} corresponding to the stretching vibrations of the $\text{C}\equiv\text{O}$ bond. 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 agree with the experimental values [69-74].



Figure 6. Infra-red spectra of pyridino-1-4- η -cyclohexa-1,3-diene irontricarbonyl.

4.5. Electronic Transitions and UV/Vis Spectra

The Uv-visible absorption spectra of the complexes in the gas phase were calculated using TDDFT, the spectra are shown in Figure 6. There is charge transfer from the irontricarbonyl cyclohexa-1,3-diene ring to the substituted pyridine ring in the excitation process. The absorption bands in the visible region are assigned to the MLCT transitions in which an electron is promoted from molecular orbital belonging to the filled metal shell to the empty π^* orbital of the substituted pyridine. All the organometallics possess

similar spectra features in which the two lower-lying bands that appear in the region 413.94 and 364.44 nm as supported by their oscillator strength 0.0187 are assigned to the $^1\text{MLCT}$ and $^3\text{MLCT}$ transitions. The oscillator strength of these two bands are the same which suggests that the transition from ground state S_0 to $^3\text{MLCT}$ transition is enhanced and become partially allowed due to strong spin-orbit coupling and similar molecular geometry in the excited state singlet and triplet states [75-77].

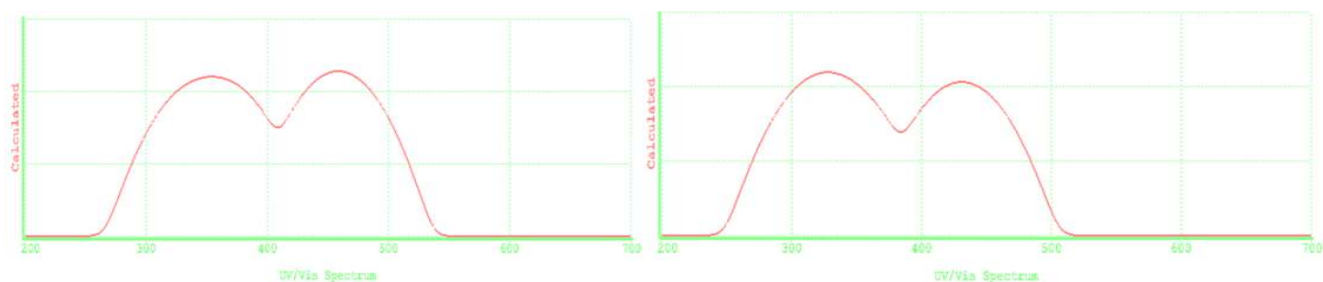


Figure 7. UV-visible spectra of pyridino-1-4- η -cyclohexa-1, 3-diene irontricarboxyl.

5. Conclusion

We have calculated the structure of the novel compound pyridino-1-4- η -cyclohexa-1,3-diene irontricarboxyl using DFT B3LYP with basis set 6-31G(D). Theoretical characterization molecular calculations were carried out on optimized geometries. These calculations include Uv-Visible, Infra-red and NMR. The calculated infra-red and ^1H NMR values agrees with experimental values. We studied the electronic states of these complexes as a function of reactivity parameters. Since the SCF model used in our calculations is a restricted hybrid HF-DFT SCF calculations performed using Pulay DIIS + Geometric Direct Minimization the combination of the two theories produces a result which further validates Koopman's theorem for these complexes. The reactivity indices for these complexes revealed that they are capable of reacting with electron rich compounds to give new products.

The excited state of these complexes is a mixture of singlet and triplet hence the relaxation from the excited state singlet ($S_1 \rightarrow S_0$) gives fluorescence while the relaxation from the excited state triplet to ground state singlet ($T_1 \rightarrow S_0$) results to phosphorescence.

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