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# Semi-empirical (PM3) studies of new pyridino-1-4-η-2-methoxycyclohexa-1,3-diene iron tricarbonyl complexes

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## ABSTRACT

Theoretical studies on the geometries, electronic states, thermodynamic parameters and vibrational frequencies of new pyridino-1,4-η-2-methoxycyclohexa-1,3-diene complexes were carried out. The theoretical ground state geometries electronic structure, thermodynamic properties and vibrational frequencies were obtaianed using PM3 method. The geometries,electronic states, thermodynamic properties and vibrational frequencies are discussed. The results show that all the complexes studied are thermodnamically stable.          © 2011 Trade Science Inc. - INDIA

## INTRODUCTION

The kinetics and synthetic studies of additon of pyridines to 1,5-η-2-methoxycyclohexadienyl iron tricarbonyl cation have been reported[1-4]. in the Literature. Semi-empirical PM3 have been known to produce good and suitable calculations for Inorganic transition metal complexes and organometallic compounds[5]. Theoretical chemistry of organometallic compounds is fast undergoing rapid progress of recent due to the fact that many novel compounds are being dis-

covered and many inaccessible organic compounds of medicinal interest are being synthesized through organometallic synthetic route[6-8]. Various theoretical studies have been carried out on a number of organometallic compounds involving the first row transition metals.[5] Computational chemistry have succeeded in calculating the properties of compounds within limit of accuracy of the experimental values. Theoretical studies in chemistry are now in advanced state with the structures,properties of compounds being routinely calculated[9,10]. However, little is known in Organometallic
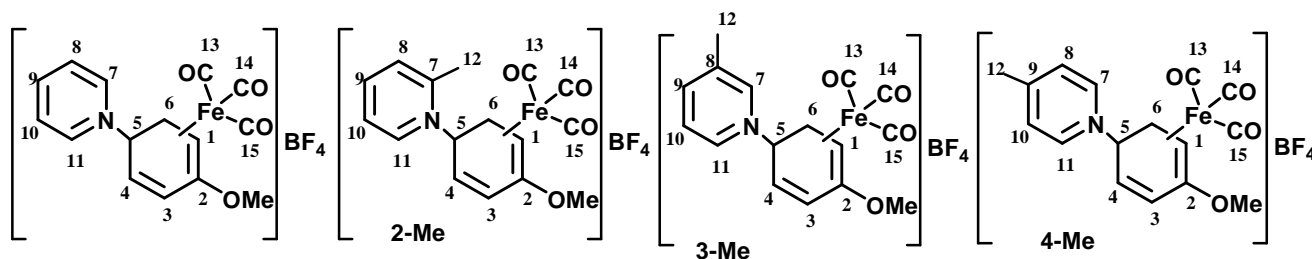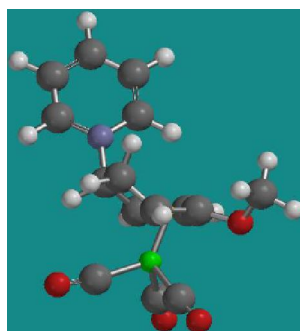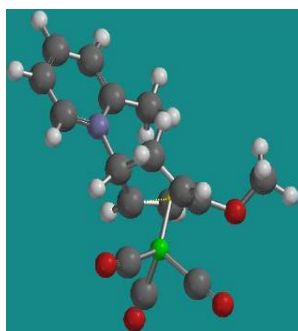


**Figure 1 : Structure of the new pyridino derivatives of 1,4-η-2-methoxycyclohexa- 1,3-diene iron tricarbonyl complexes**

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**Pyridino-1-4- η-2-methoxy-cyclohexa-1,3-diene irontri-carbonyl complex**

**2-methylpyridino-1-4- η- 2-methoxycyclohexa-1,3-diene irontricarbonyl complex**

**3-methylpyridino-1-4- η- 2-methoxycyclohexa-1,3-diene irontricarbonyl complex**

**4-methylpyridino-1-4- η-2-methoxycyclohexa-1, 3-diene irontricarbonyl complex**

**Figure 2 : Optimized structures of. the new pyridino derivatives of 1,4-η-2-methoxycyclohexa-1,3-diene iron tricarbonyl complexes. (the $BF_4$ ion is excluded for clarity)**



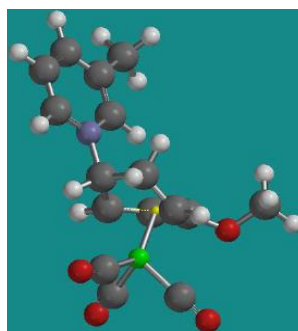**Pyridino-1-4-η-2-methoxy-cyclohexa-1, 3-diene irontri-carbonyl complex**

**2-methylpyridino-1-4-η-2-methoxycyclohexa-1,3-diene irontricarbonyl complex**

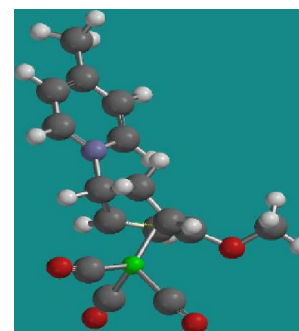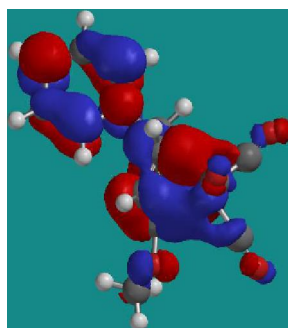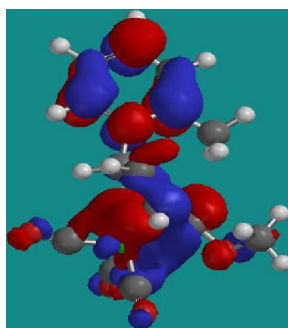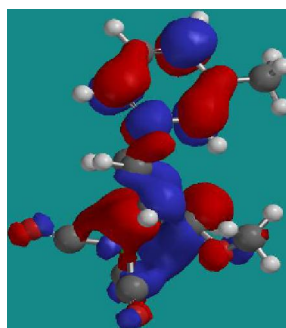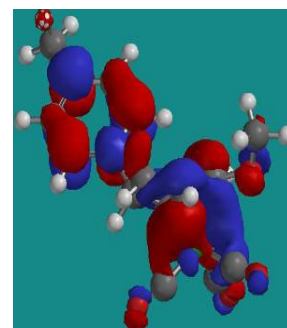**3-methylpyridino-1-4-η-2-methoxycyclohexa-1,3-diene irontricarbonyl complex**

**4-methylpyridino-1-4-η-2-methoxycyclohexa-1,3-diene irontricarbonyl complex**

**Figure 3 : HOMO-LUMO Energy diagram of optimized geometries of. the new pyridino derivatives of 1,4-η-2-methoxycyclohexa-1,3-diene iron tricarbonyl complexes**

systems.

In this paper, the geometries, electronic structure, dipole moment, thermodynamic parameters and vibrational frequencies are reported for a number of pyridino derivatives of 1,4-η-2-methoxycyclohexa-1,3-diene iron tricarbonyl complexes. The structures of the complexes are shown in figure 1.

## COMPUTATIONAL METHODOLOGY

All the pyridino-1,4-η-2-methoxycyclohexa-1,3-diene iron tricarbonyl complexes, (Figure 1), were modeled. Initial geometries were fully optimized using Semi-empirical method at PM3 level. The calculations were carried out to evaluate the geometries, electonic structure, dipole moment, thermodynamic parameters and vibrational frequencies using Spartan '06111exe running on intel processor 1.60GHz computer. The

optimized geometries of the new pyridino derivatives of 1,4-η-2-methoxycyclohexa-1,3-diene irontricarbonyl complexes are shown in figure 2.

## RESULTS AND DISCUSSION

**Geometric parameters**

For all organometallics, the geometrical parameters were obtained after total optimization of the equilibrum geometries by Semi-empirical PM3. In order to investigate the effect of the substituent on the pyridine ring, the geometries were compared with the parent pyridino-1,4-η-cyclohexa-1,3-dieneirontricarbonyl complex. For unsubstituted pyridino-1,4-η-cyclohexa-1,3-diene complex at PM3 level, calculations predict the bond lenght, bond angles and dihedral angles with remarkable changes.The effect of the methyl group grafted on the position 2,3 and 4 of the pyridine ring was clearly ob-
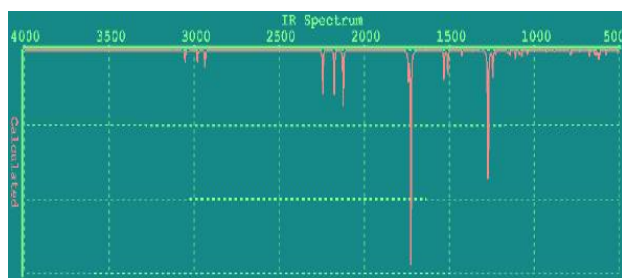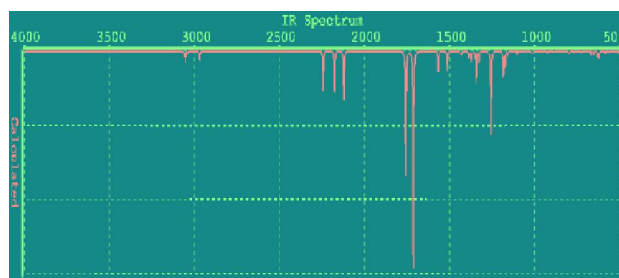
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**Pyridino-1-4-η-2-methoxycyclohexa-1,3-diene irontricarbo- nyl complex**



**2-methylpyridino-1-4-η-2-methoxycyclohexa-1,3-diene iron-tricarbonyl complex**
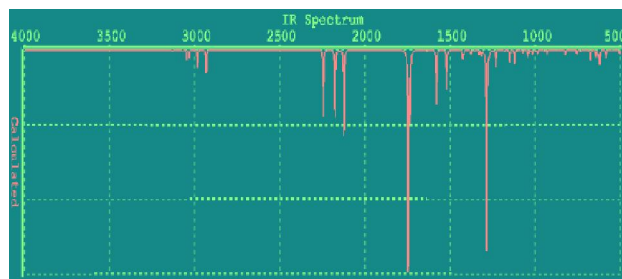


**3-methylpyridino-1-4-η-2-methoxycyclohexa-1,3-diene irontricarbonyl complex**



**4-methylpyridino-1-4-η-2-methoxycyclohexa-1,3-diene irontricarbonyl**

**Figure 4 : Infra-red spectra data showing virational frequencies and intensities for the new pyridino derivatives of 1,4-η-2-methoxycyclohexa-1,3-diene iron tricarbonyl complexes**
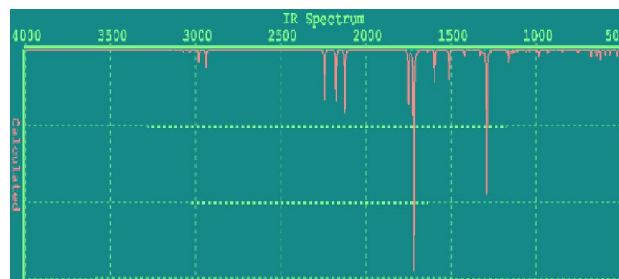
served with the increase in bond length adjacent to the methyl group resulting from the strong electron-donating effect of the substituent.

The ground state geometrical parameters were compaired with those of the unsubstituted 1,4-η -cyclohexa-1,3-diene irontricarbonyl complex.The replacement of hydrogen with the methoxy group resulted in the increase in bond length within the cyclohexa-1,3-diene ring. For instance, the bond length of $C_2$-$C_3$ generally increased when compared to the unsubstituted diene derivatives. For each compound, there were remarkables changes in bond length with the bond distances of C- H occuring within the range of 1.088A°-1.126A°. While the C-C and C = C bonds are within the range of 1.373A°-1.545A° and 1.373A°-1.488A° respectively. The metal- carbon bond distances range from 1.736A° to 1.806A°, while the metal-ligand bond appear to be unchanged at 1.663A°. However, the bond angles and dihedral angles exhibit changes which depend on the position of the methyl. (TABLE 1).

**Electronic properties**

To be able to explain the electronic properties of these novel compounds, it is expedient to visualize the HOMO and the LUMO for these new organometallic compounds because the relative ordering of occupied and virtual orbitals provide a reasonable qualitative indication of both ground and excited state properties. The HOMO of these complexes possesses a π-bonding character within subunit and π -antibonding character exited 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 were obtained from 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 Semi-empirical PM3.These calculations however, do not have solid-state packing effect and aqeuous state is not taken into consideration.Even if these energy levels are not accurate, it is still possible to use them to obtain information by comparing them with other compounds. TABLE 2, lists the theoretical electronic parameters for these new organometallics. The calculated electronic properties (energy band gap LUMO-HOMO) of the X-substituted pyridino-1,4-η-2-methoxycyclohexa-1,3-dieneirontricarbonyl complexes are 7.21eV,7.20eV, 7.18eV and 7.24eV respec-

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**TABLE 1 : Geometrical parameters of 1-4-η-2-methoxy-cyclohexa-1,3-diene iron tricarbonyl complexes showing selected bond length, bond angles and dihedral angles**

| Bond length/A° | H | 2-Me | 3-Me | 4-Me |
|---|---|---|---|---|
| $C_1$-$C_2$ | 1.417 | 1.417 | 1.417 | 1.417 |
| $C_2$-$C_3$ | 1.486 | 1.487 | 1.486 | 1.486 |
| $C_3$-$C_4$ | 1.488 | 1.487 | 1.488 | 1.488 |
| $C_4$-$C_5$ | 1.545 | 1.535 | 1.545 | 1.545 |
| $C_5$-$C_6$ | 1.489 | 1.490 | 1.489 | 1.489 |
| $C_6$-$C_1$ | 1.491 | 1.492 | 1.491 | 1.491 |
| $C_2$-$O_1$ | 1.375 | 1.376 | 1.375 | 1.375 |
| $O_1$-$C_{12}$ | 1.414 | 1.414 | 1.414 | 1.414 |
| $C_5$-N | 1.529 | 1.535 | 1.528 | 1.528 |
| $C_7$-N | 1.371 | 1.382 | 1.370 | 1.373 |
| $C_{11}$-N | 1.374 | 1.383 | 1.372 | 1.375 |
| $C_7$-$C_8$ | 1.393 | 1.406 | 1.398 | 1.373 |
| $C_8$-$C_9$ | 1.393 | 1.386 | 1.400 | 1.400 |
| $C_9$-$C_{10}$ | 1.395 | 1.396 | 1.392 | 1.402 |
| $C_{10}$-$C_{11}$ | 1.391 | 1.385 | 1.393 | 1.388 |
| Fe-Lig | 1.662 | 1.663 | 1.662 | 1.662 |
| Fe-$C_{13}$ | 1.737 | 1.796 | 1.796 | 1.796 |
| Fe-$C_{14}$ | 1.804 | 1.804 | 1.736 | 1.736 |
| Fe-$C_{15}$ | 1.797 | 1.796 | 1.806 | 1.806 |
| $C_{13}$-$O_2$ | 1.157 | 1.157 | 1.157 | 1.147 |
| $C_{14}$-$O_3$ | 1.145 | 1.147 | 1.147 | 1.147 |
| $C_{15}$-$O_4$ | 1.147 | 1.145 | 1.145 | 1.145 |
| **Bond angles in degrees** | | | | |
| Angles/° | H | 2-Me | 3-Me | 4-Me |
| $C_{13}$-Fe-$C_{14}$ | 94.63 | 96.52 | 96.63 | 96.63 |
| $C_{14}$-Fe-$C_{15}$ | 92.49 | 96.04 | 94.62 | 94.67 |
| $C_{13}$-Fe-$C_{15}$ | 96.63 | 96.52 | 92.55 | 92.53 |
| Lig-Fe-$C_{15}$ | 118.38 | 118.34 | 118.59 | 118.59 |
| $C_2$-$O_1$-$C_{12}$ | 114.96 | 114.67 | 114.94 | 115.00 |
| Fe-lig-$C_2$ | 103.69 | 103.30 | 103.65 | 103.66 |
| Fe-lig-$C_1$ | 80.55 | 80.63 | 80.56 | 80.56 |
| Fe-$C_{15}$-$O_4$ | 174.77 | 177.13 | 177.18 | 177.14 |
| $C_5$-N-$C_7$ | 120.12 | 124.74 | 119.91 | 120.09 |
| $C_5$-N-$C_{11}$ | 119.84 | 116.14 | 119.85 | 120.01 |
| **(c) Dihedral angles in degrees** | | | | |
| Angles/° | H | 2-Me | 3-Me | 4-Me |
| $C_{15}$-Fe-lig-$C_3$ | 101.09 | 101.11 | 101.67 | 101.69 |
| $C_{12}$-$O_1$-$C_2$-$C_1$ | -67.14 | -68.39 | -67.45 | -66.83 |
| $C_4$-$C_5$-N-$C_7$ | -41.78 | -51.62 | -43.51 | -43.70 |
| $C_{10}$-$C_{11}$-N-$C_5$ | 179.61 | 179.47 | 179.69 | 179.70 |
| $C_{11}$-N-$C_7$-$C_8$ | -0.32 | -1.13 | -0.26 | -0.28 |
| $C_2$-$C_3$-lig-Fe | -104.85 | -104.44 | -104.81 | -104.83 |

**TABLE 2 : Values of dipole moment, HOMO-LUMO energies, Eg calculated for all the complexes**

| X-pyridino-- | Dipole moment/debye | HOMO energy /eV | LUMO energy /eV | Band gap/ eV |
|---|---|---|---|---|
| H | 6.69 | -5.08 | -12.29 | 7.21 |
| 2-Me | 6.62 | -5.00 | -12.30 | 7.20 |
| 3-Me | 5.58 | -4.97 | -12.25 | 7.18 |
| 4-Me | 5.24 | -4.99 | -12.23 | 7.24 |

**TABLE 3 : Thermodynamic parameters for the pyridino complexes at 298.15K**

| X-pyridino | Heat of formation $\Delta H_f$ kJmol$^{-1}$ | Free Energy $\Delta G$/ kJmol$^{-1}$ | Entropy $\Delta S$ /Jmol$^{-1}$K$^{-1}$ | Enthalpy/ $\Delta H$ kJmol$^{-1}$ |
|---|---|---|---|---|
| H | -976.54 | -420.10 | 616.03 | -237.33 |
| 2-Me | -1001.90 | -371.57 | 630.71 | -183.52 |
| 3-Me | -1021.94 | -398.59 | 649.75 | -204.87 |
| 4-Me | -1024.46 | -401.13 | 649.26 | -207.56 |

tively for X = H, 2-Me, 3-Me and 4-Me. There is no significant change in the opto-electronic properties of these complexes. The LUMO-HOMO diagram are presented in figure 3.

### Thermodynamic parameters and stabilities

The formation of these complexes are spontaneous. Thermodynamic stabilities are expected when $\Delta H$ and $\Delta G$ are negative. The more negative these values are and the more positive $\Delta S$, the more stable would be the pyridino complexes. A closer look at TABLE 3 confirms that the formation of 4-methylpyridino-1,4-η-2-methoxycyclohexa-1,3-dieneirontricarbonyl complex is more rapid than that of 2-methylpyridino and 3-methylpyridino organometallic complexes, hence the order of stability is H > 4-Me > 3-Me > 2-Me. All the calculated free energy values are negative and the calculated enthalpies are negative while all entropies are positive thus confirming that the formation of these complexes is spontaneous. There are no experimental or theoretical data for comparison. However, the present calculations reveal that all the complexes are thermodynamically stable as shown in TABLE 3.

### Vibrational frequencies

The calculated vibrational frequencies of the complexes are shown in figure 4. According to group representation theory in Chemistry, we can deduce that there are 99 and 108 vibrational modes for the pyridino- and methylpyridino-derivatives. Among these normal modes,

**TABLE 4 : Vibrational frequencies and intensities of new pyridino-1,4-η-2-methoxy cyclohexa-1,3-diene irontricarbonyl complexes**

| X-pyridino/assigned peaks | Bond | Frequency/ cm$^{-1}$ | Intensity |
|---|---|---|---|
| H | N-C$_7$ | 1272 | 3723 |
| | N=C$_{11}$ | 1727 | 6384 |
| | | 2123 | 1630 |
| | C≡O | 2176 | 1301 |
| | | 2244 | 1261 |
| 2-Me | N-C$_7$ | 1270 | 2595 |
| | N=C$_{11}$ | 1713 | 6849 |
| | C2-O$_1$ | 1757 | 3938 |
| | | 2120 | 1572 |
| | C≡O | 2175 | 1295 |
| | | 2245 | 1266 |
| 3-Me | N-C$_7$ | 1285 | 3906 |
| | N=C$_{11}$ | 1734 | 1307 |
| | C$_9$-C$_{10}$ | 1746 | 4193 |
| | | 2122 | 1640 |
| | C≡O | 2175 | 1306 |
| | | 2244 | 1286 |
| 4-Me | N-C$_7$ | 1298 | 3667 |
| | N=C$_{11}$ | 1718 | 5700 |
| | C$_7$-C$_8$ | 1750 | 1374 |
| | | 2122 | 1638 |
| | C≡O | 2174 | 1307 |
| | | 2244 | 1285 |

the strongest infra-red absorption peaks and their intensities are displayed in TABLE 4. The simulated IR spectra of the derivatives is calculated by replacing one of its Hydrogen with methyl group. On replacing the hydrogen with methyl group, the total vibrations increase from 99 to 108.

## CONCLUSION

The C1 symmetry point group resulting from nuclophilic addition of pyridine and its substituted derivatives to the 1,5-η-2-methoxycyclohexadienyl iron tricarbonyl to form new pyridino-1,4-η-2-methoxy-cyclohexa-1,3-diene irontricarbonyl complexes have been calculated using Semi-empirical PM3. Properties investigated include optimized geometries, dipole moments, electronic structure, thermodynamic parameters and vibrational frequencies. Semi-empirical calculations reveal that all the complexes are thermodynamically stable. The HOMO – LUMO energy gaps of these complexes are about equal with no significant changes. The dipole moment decreases in the order H > 2-Me > 3-Me > 4-Me (TABLE 2). It is however interesting to note that the use of computation has given us the opportunity to take a critical look at these complexes at the molecular level to produce results which are otherwise inaccessible by conventional experimental conditions. Appart from the infra-red spectra data, there are no experimental or theoretical data on the organometallics investigated.

Our result may therefore form the basis for reference for further experimental and theoretical work.

## ACKNOWLEDGEMENT

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