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Molecular structure, Spectroscopy, and HOMO-LUMO of Ferrocene by quantum computing methods.

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Abstract

The main objective of this work is the application of different molecular modeling bases to predict the chemical reactivities and biological activities expected in this molecule. The structure of Ferrocene was optimized with the Gaussian 09 software by the DFT / B3LYP method and the bases set LanL2DZ. the efficiency of the bioinformatic methods used in the calculations of geometric parameters can be evaluated by comparing the results obtained with the experimental values (X-ray). the FT-IR, UV-VIS spectra theoretically predicted. The H1 and C13 NMR spectra were calculated by the gauge independent atomic orbital method (GIAO). A study of electronic properties, such as HOMO and LUMO energies, was performed using a time-dependent DFT (TD-DFT) approach.

Key words: N,N-dimethyl ferrocenyl methyl amin, molecular modeling, DFT.

1. Introduction

Organometallic chemistry and biochemistry have been merged in the last two decades into a new field: bioorganometallic chemistry. This new research area was devoted to the synthesis of new organometallic compounds and their biological and medical effects against some types of diseases, such as cancer and malaria. For several years, the use of ferrocene (Fig 1) in bioorganometallic chemistry has been growing rapidly, and several promising applications have been developed since ferrocene is a stable, nontoxic compound and has good redox properties.

This study focuses on finding the best basis set for DFT/B3LYP calculation in order to optimize ferrocene's derivatives. The results of this study can help scientists instead of synthesizing the derivatives without a previous knowledge of their effects in order to gain time, money and efforts.

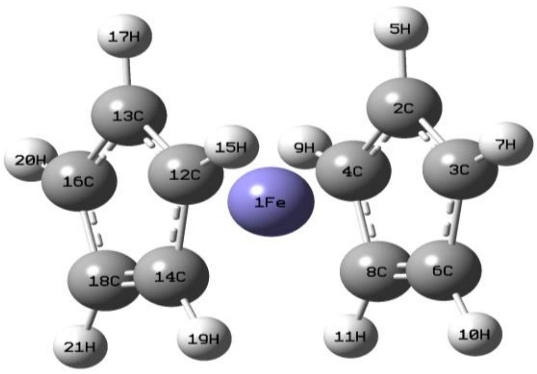


Figure 1. The structure of Ferrocene

2.Method

The optimization of the structure of Ferrocene was calculated using DFT/B3LYP calculation method with basis set: LanL2DZ. IR and RMN spectra were preformed using the same method. All the calculations are done using Gaussian 09.

3. Results and discussions

3.1. Molecular Geometry:

After the optimization the sandwich structure was confirmed as the structure that has the minimum stabilization energy. Theoretical bond lengths were compared with the experimental ones from literatures as it shown in the table bellow:

Table 1: *Comparison of the theoretical and experimental geometric parameters of Ferrocene.*

Parametres	Exp. [1]	B3LYP/LanL2DZ
	Length (A°)	
Fe-C	2.064	**2.1199**
C-C	1.440	**1.4433**
C-H	1.104	**1.0812**

The theoretical values of bond lengths are so close from the experimental ones and that confirms that B3LYP/Lanl2DZ is good at optimizing the geometric of ferrocene.

MESP maps have been determined by B3LYP/Lanl2DZ method. As it's shown below that the most electron rich regions (red and orange) are located on the middle of the cyclopentadienyl groups, which reflect the most electronegative regions.

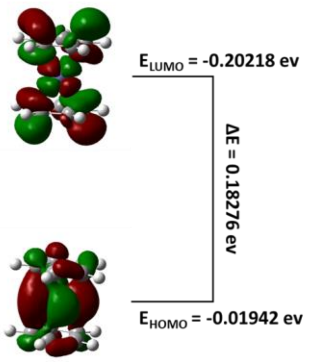


Figure 2. Frontier molecular orbitals of Ferrocene by DFT/B3LYP methods with Lanl2DZ

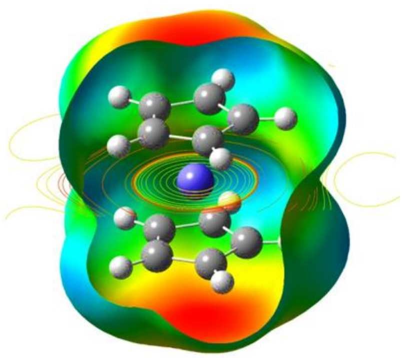


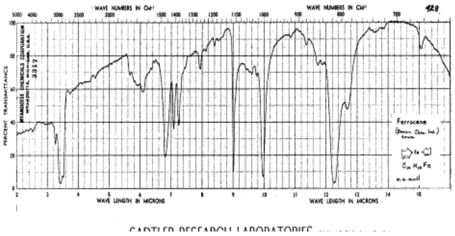
Figure 3. MESP Surface and contour map for Ferrocene

3.2. Spectroscopic analysis

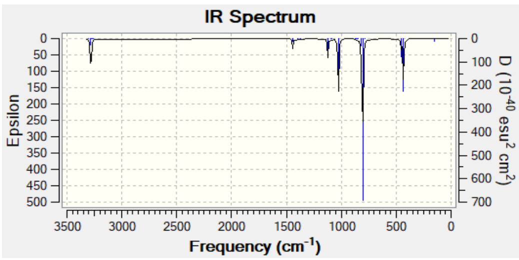
For more confident it must compare the theoretical spectrum of IR, UV-Vis and NMR with the experimental ones as it shown below.

3.2.1. IR analyses

The same method and basis was used to obtain the theoretical IR spectrum and it was compared with the experimental one as it shown in the following two figures.



IR Spectrum for ferrocene (Exp.) [2]



IR Spectrum for ferrocene (Theoretical)

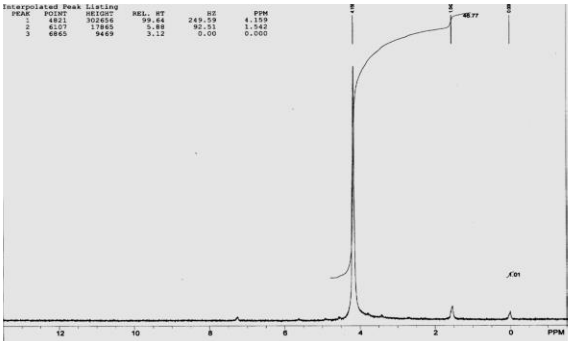
In the experimental and the theoretical IR spectrum there are 5 principal peaks looks similar to each other but there is a simple displacement in wavenumber values which is shown in the following table.

Table 2: *Comparative between experiment and theoretical values of IR spectrum.*

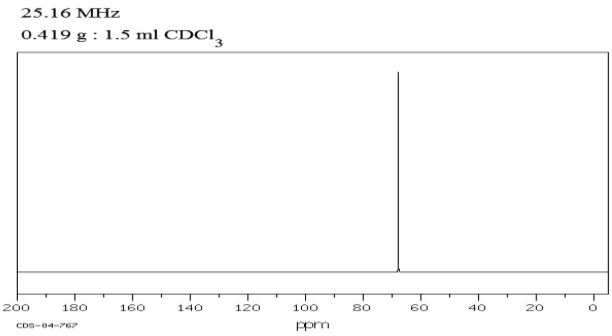
N	Experimental values (cm^{-1})	Theoretical values (cm^{-1})	Absolute value of displacement (cm^{-1})
01	806	805	1
02	1000	1026	26
03	1105	1123	18
04	1475	1443	32
05	2995	3281	286

3.2.2. NMR Analyses

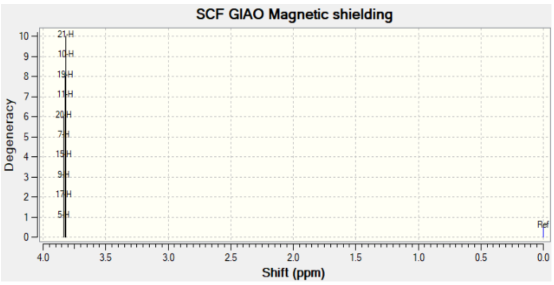
The same method and basis was used to obtain the theoretical NMR spectrum and it was compared with the experimental one as it shown in the following figures.



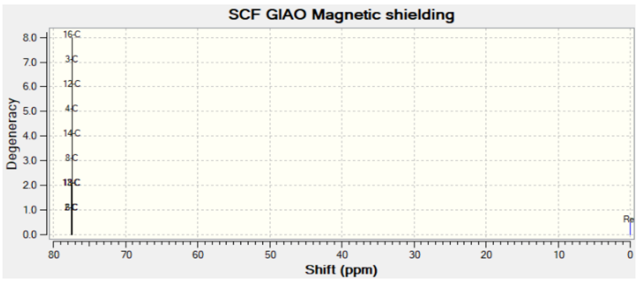
1H-NMR Spectrum for ferrocene (Exp.) [3]



13C-NMR Spectrum for ferrocene (Exp.) [4]



1H-NMR Spectrum for ferrocene (Theoretical)



13C-NMR Spectrum for ferrocene (Theoretical)

Figure 4. RMN spectrums of Ferrocene

There is no different between the theoretical and the experiment spectrum of both 1H-NMR and 13C-NMR. A simple displacement is shown in the next table.

Table 3: *Comparative between experiment and theoretical values of NMR spectrum.*

Type of spectrum	Experimental shift values (ppm)	Theoretical shift values (ppm)	Absolute value of displacement (ppm)
1H-NMR	4.15	3.58	0.57
13C-NMR	69	77.5	8.5

3.2.3. UV-Vis Analyses

The same method and basis was used to obtain the theoretical UV-Vis spectrum in ethanol as solvent and it was compared with the experimental values.

The ultraviolet and visible absorption spectra of ferrocene in ethanol are characterized mainly in the visible by a band centered at 440 nm [5], Outside the visible range, a weak peak occurs at 324 nm and several relatively weak but allowed absorptions are present between 265 nm and 230 nm. The strongest absorption of ferrocene is observed at 202 nm. [6]

The oscillator strength of this allowed absorption is 350 times stronger than that of the peak at 440 nm.

The theoretical spectrum is shown in figure below.

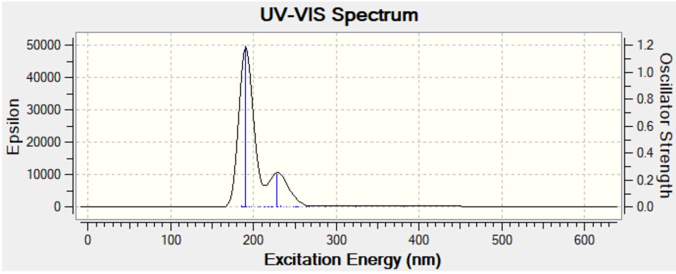


Figure 5. UV-Vis Spectrum for ferrocene (Theoretical)

4. Conclusion

The Lanl2DZ shows a good result of prediction the properties of Ferrocene. The geometric parameters showed a good agreement between the results obtained by quantum chemical calculations and the experiment values. The MESP map shows the most electron rich region (red and orange) which is located on the middle of the cyclopentadienyl groups, which reflect the most electronegative region. The low value of ΔE allows us to conclude that the studied molecule is reactive. Finally, IR, 13C NMR, 1H NMR spectra shows that the quantum chemical calculation is very good in prediction of the properties of Ferrocene and we can rely on these results in order to predict the effectiveness of the derivatives of this compound in many areas such as the therapeutic field

5. References

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