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Theoretical IR spectroscopic study of Copper Phthalocyanine (CuPc)

M. T. Hussein
University of Baghdad, College of Science,
Physics Department
e.mail MmohammedTaki18@yahoo.com

Abstract

The mobile π electron of Phthalocyanine can serve as current carries and provide the basis for semiconductor properties and to increase the current carries by substituting with Copper metal. The modes of vibration recorded for CuPc were (165) with vibrational frequencies recorded in the region (15- 3080)cm^{-1},intensity and symmetry for each mode were interpreted on the basis of using HyperChem 6.0 semi-empirical molecular orbital of self consistent field of MNDO method (Modified Neglected of Differential Overlap) of parameterization PM3 involving a quantum mechanical semi-empirical Hamiltonian with restricted and unrestricted Hartree-Fock approximation. The high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) were (-4.986 and -2.222)eV respectively. The energy gap calculation (ΔE) was (2.764) eV, the ionization potential (I.P.) was (4.986) eV and electron affinity (E.A.) was (2.222)eV . Other characteristic such as dipole moment, the charge density and electrostatic potential were plotted with a contour diagram, using both two and three dimensions. The results suggest that CuPc has anomalous behavior than metal-free phthalocyanine H_2Pc. Such behavior was ascribed to the bonding nature of the central Cu ion differing from that of other metal derivatives. We can suggest that CuPc has attracted much attention as a potential candidate for device applications.

Keyword: *spectroscopic study of Copper Phthalocyanine*

1.Introduction

Phthalocyanines (H_2Pc) have many unique properties which make them useable in different fields. Strong color, high stability and very suitable as coloring agents. The mobile π electrons phthalocyanines can serve as current carriers and provide the basis for semiconductor properties and photovoltaic effects.

The H_2Pc molecule consists of an inner porphyrin ring with four benzene rings located symmetrically at the four corners. At the center of the molecule is a pair of hydrogen atoms. The two central hydrogen atoms of H2Pc can replaced by a wide range of metals like Cu [1,2] The goals of this study is to obtain the spectroscopic properties, potential energy, dipole moment of this very heavy semi planar molecule . The semi-empirical quantum mechanical method MNDO/PM3 has been used to calculate the theoretical parameters underlying the studied compounds [3-6]. In this method only valance electron are considered explicitly and they are assumed to move in a fixed core framework formed by the nuclei and inner shell electrons. Valence electrons are treated using a minimum basis set simplified by neglecting some electron repulsion integrals involving differential overlap. The remaining integrals are then equated to parametric function which contain numerical parameters obtained by fitting some experimental data, the calculations have been performed using MNDO-PM3 method is implemented in an improved version of HyperChem 6.0. program.[7]

2. Theory

According to Fischer and Herriksson [8] the energy gap ΔE between HOMO (high occupied molecular orbital) and LUMO (low unoccupied molecular orbital) is defined as :-

$$\Delta E = E_{LUMO} - E_{HOMO} \qquad (1)$$

This term can be used as a characteristic quantity for metallic complexes. Cherry et al [9] have been used the concept of HOMO-LUMO gap in developing a theoretical model that is capable for qualitative explanation of the structure stability and conformation barriers in many molecular systems. An elements ability to act as an electron donor or acceptor is related to its ionization potential (I.P.), but there seems to be no formal relationship. It was observed that, small values of I.P. act as active electron donors while high values of I.P. act as active electron acceptors. The absolute values of the last EHOMO represent the ionization potential.

The results of electrostatic potential calculation can be used to predict initial attack positions of protons (or other ions) during a reaction. The contour plot dialog box to request a plot of the contour map of the electrostatic potential of a molecular system can be used after done by a semi-empirical calculation using following expression [7]:

$$V=\sum_{A}\frac{Z_A}{|R_A-r|}-\int\frac{\rho(r')}{|r'-r|}\,dr' \qquad (2)$$

The point r is the position of a positive probe charge. ZA is the nuclear charge on atom A located at position RA. The function ρ(r') is the electronic density. In the above equation, the first term represents the contribution of the nuclei to the electrostatic potential and the second term is the electronic contribution.

In the quantum mechanical description of dipole moment, the charge is a continuous distribution that is a function of r, and the dipole moment is an average over the wave function of the dipole moment operator µ which is calculated using the following expression [7]:

$$\mu=\sum_{i}(-r_i)+\sum_{A}Z_A R_A \qquad (3)$$

where ZA is the charge of the nuclear core and RA is the distance between the origin and nucleus A. Note that the sign convention used in the quantum mechanical calculation of dipoles is opposite to that used in molecular mechanics dipole calculations; this reflects the differing sign conventions of physics and chemistry.

3. Results and Discussion

The theoretical vibrational frequencies of CuPc using Hyperchem program with method MNDO/PM3 Semi-empirical illustrated (3N-6=165) modes , with vibrational frequencies recorded in the region (15-3080) cm-1 . The stretching bonds (N-1) were equal 56 modes while the bending bonds (2N-5) were equal 109 modes . The highest intensities of these modes are shown in Table (1) .

Table (1) Data calculated by MNDO/PM_3 method for vibrational bands and intensity for CuPc

Vibrational number	**Calculated position/cm^{-1}**	**intensity**
Stretching		
υ_{110}	**1225**	**162**
υ_{111}	**1229**	**289**
υ_{116}	**1345**	**270**
υ_{124}	**1475**	**354**
υ_{126}	**1504**	**36**
υ_{130}	**1555**	**184**
υ_{134}	**1598**	**79**
υ_{139}	**1714**	**50**
υ_{148}	**1820**	**4.5**
υ_{154}	**3062**	**10**
$\upsilon_{158/159}$	**3071**	**20**
υ_{162}	**3077**	**34**
$\upsilon_{164/165}$	**3080**	**48**
Bending		
υ_{25}	**332**	**25**
υ_{26}	**331**	**12**
υ_{32}	**430**	**15**
υ_{45}	**588**	**44**
υ_{53}	**669**	**8**
υ_{64}	**780**	**33**
υ_{66}	**785**	**42**
υ_{68}	**802**	**73**
υ_{71}	**887**	**237**
υ_{78}	**957**	**369**
υ_{79}	**958**	**695**
υ_{81}	**965**	**24**
υ_{98}	**1108**	**24**
υ_{100}	**1145**	**561**
υ_{108}	**1185**	**8**

The energy gap (ΔE) and Ionization potential (I.P.) for Cu-phthalocyanine molecule is shown in Fig.(1). The ground state equilibrium geometry properties of metal-free phthalocyanine (H2Pc) molecule and Cu-phthalocyanine after substituting Cu-metal were calculated and is shown in Fig.(2a) and Fig.(2b) respectively. Table (2) represent the total energy ET , electronic energy Ee, core-core repulsion energy Ecore , dipole moment µ , heat of formation ΔHf , ionization potential I.P. and energy gap ΔE.

Table (2) Different parameters of CuPc and H_2Pc

Compound	CuPc	H_2Pc
E_T Kcal/mol	-150329.327	-123603.324
E_e Kcal/mol	-1420634.73	-1239072.76
$E_{core-core}$ Kcal/mol	1270305.402	1115469.442
µ Deby	0.34770 D	1.173
ΔH_f	149.367	293.86

Kcal/mol		
I.P. Kcal/mol	4.986eV	1.2121
ΔE eV	2.764	2.418

Fig.(3) and Fig(4) shows the electrostatic potential in two-dimensions and in three-dimensions respectively for CuPc molecule. A significant difference between CuPc and H2Pc appear to be in the relative values obtained and listed in table (1). It is apparent from the results that ET, Ee and µ and ΔHf decreases while Ecore-core increase . This may be attributed to the anomalous behaviour of CuPc. Such behaviour was ascribed to the bounding nature of the central Cu ion differing from that of other metal derivatives. In CuPc the metal ion is co-ordinated by the four inner nitrogen atoms of macro cyclic ring to form a square planar configuration. In general, the electrons in the fully filled 3d orbital cannot contribute to covalent bounding in a divalent Cu ion. Thus, most 4-fold Cu ion complexes tend to form a semi-plane using a d s p2 hybrid. For CuPc however, the Cu ion is forced into a square planar to fit the rigid macro cycle ring. To do this the outer 3d orbital is used for 4s0 4p1 hybridization forming an outer orbital complex. Infrared spectral data by Kobyashi et al [10] have supported this view that CuPc behaves some what differently than other Pc's. It apparent from the results above that, the term energy gap can be used as a characteristic quantity for metallic complexes. Cherry et al [9] have used the concept of HOMO-LUMO gap in developing a theoretical model that is capable for quantitative explanation of the structure ability to act as an electron donor or acceptor is related to its ionization potential but there seems to be no formal relationship. It was observed that small value of ionization potential as active electron-donor while high values of I.P. as active electron acceptors. Moreover, the measured HOMO and LUMO levels can indeed be considered as relevant for the estimation of a charge transfer from one molecule to another. The energy gap of CuPc is (2.764)eV and (2.418)eV for H2Pc is approximately in a good agreement with the vales reported by Gao W. and Kahn A. [11].

In the present work the difference between H2Pc and CuPc appear to be in the relative value at electron distribution governs the electrostatic potential describes the interaction of energy of the molecular system with a positive point charge. Electrostatic potential is useful for finding sites of reaction in a molecule positively charged species tend to attack where the static potential is strongly negative.

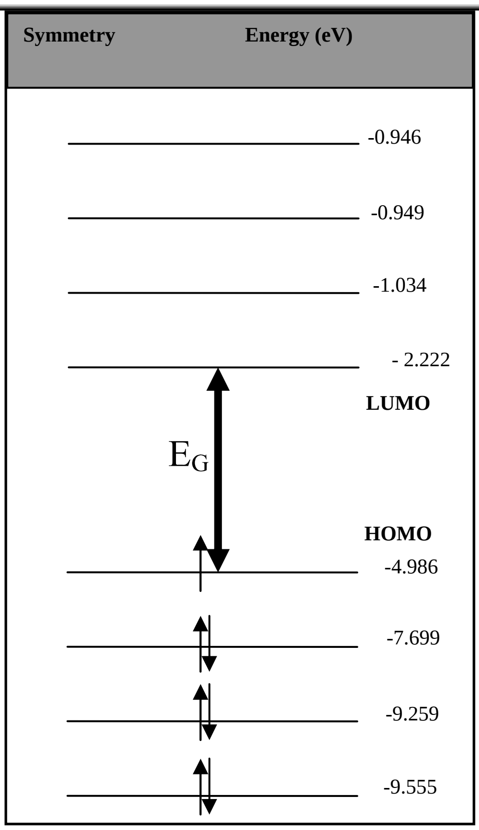
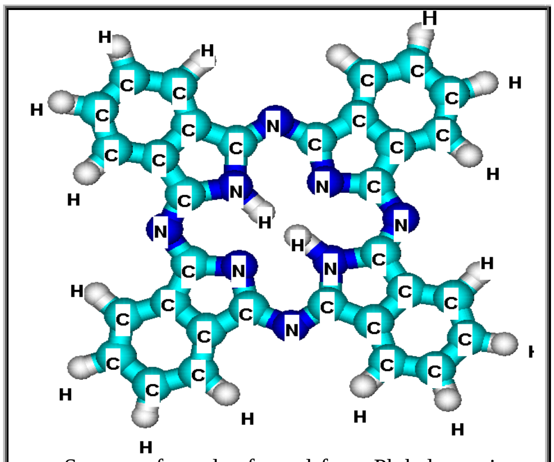


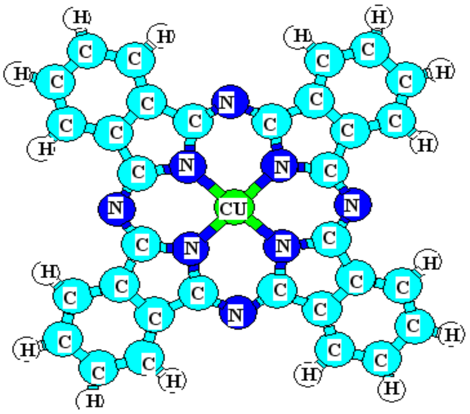
Figure (1) The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of CuPc.

4. Conclusions:

The copper atom can behave as a donor located at the centre of molecules while Phthalocyanine molecule exerts as an acceptor , to form Semi-Planar CuPc molecule

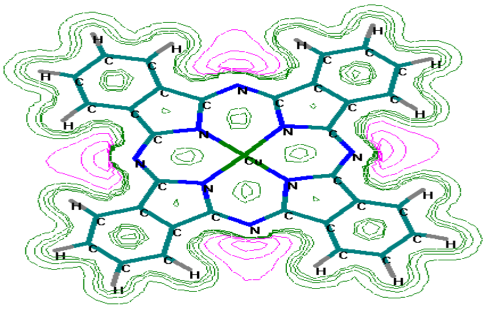


a. Structure formula of metal-free , Phthalocyanine (H_2Pc)



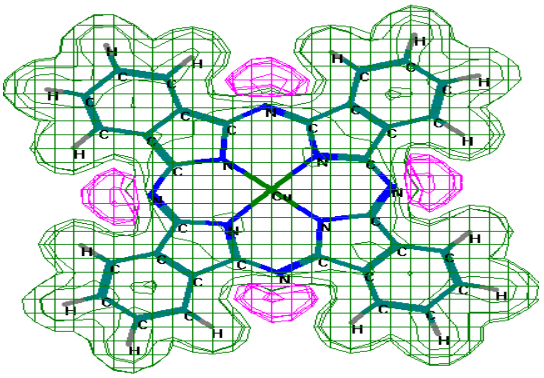
b. Structure formula of Cu- Phthalocyanine (CuPc)

Figure (2)



Electrostatic Potential -2D

Figure (3) Electrostatic Potential in two-dimensions of CuPc



Electrostatic Potential -3D

Figure (4) Electrostatic Potential in three-dimensions of CuPc

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