

Theoretical IR spectroscopic study of Copper Phthalocyanine (CuPc)

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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 H₂Pc. 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 (H₂Pc) 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 H₂Pc 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 be replaced by a wide range of metals like Cu [1,2]. The goal 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 valence electrons 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 a parametric function which contains numerical parameters obtained by fitting some experimental data, the calculations have been performed using MNDO-PM3 method 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 :-

$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$	1
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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 element's 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]:

$$V = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r' - r|} dr' \quad 2$$

The point r is the position of a positive probe charge. Z_A is the nuclear charge on atom A located at position R_A . The function $\rho(r')$ 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]:

$$\mu = \sum_i (-r_i) + \sum_A Z_A R_A \quad 3$$

where Z_A is the charge of the nuclear core and R_A 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/PM₃

method for vibrational bands and intensity for CuPc		
Vibrational number	Calculated position/ cm^{-1}	intensity
Stretching		
ν_{110}	1225	162
ν_{111}	1229	289
ν_{116}	1345	270
ν_{124}	1475	354
ν_{126}	1504	36
ν_{130}	1555	184
ν_{134}	1598	79
ν_{139}	1714	50
ν_{148}	1820	4.5
ν_{154}	3062	10
$\nu_{158/159}$	3071	20
ν_{162}	3077	34
$\nu_{164/165}$	3080	48
Bending		
ν_{25}	332	25
ν_{26}	331	12
ν_{32}	430	15
ν_{45}	588	44
ν_{53}	669	8
ν_{64}	780	33
ν_{66}	785	42
ν_{68}	802	73
ν_{71}	887	237
ν_{78}	957	369
ν_{79}	958	695
ν_{81}	965	24
ν_{98}	1108	24
ν_{100}	1145	561
ν_{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 (H_2Pc) 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 E_T , electronic energy E_e , core-core repulsion energy $E_{\text{core-core}}$, dipole moment μ , heat of formation ΔH_f , ionization potential I.P. and energy gap ΔE .

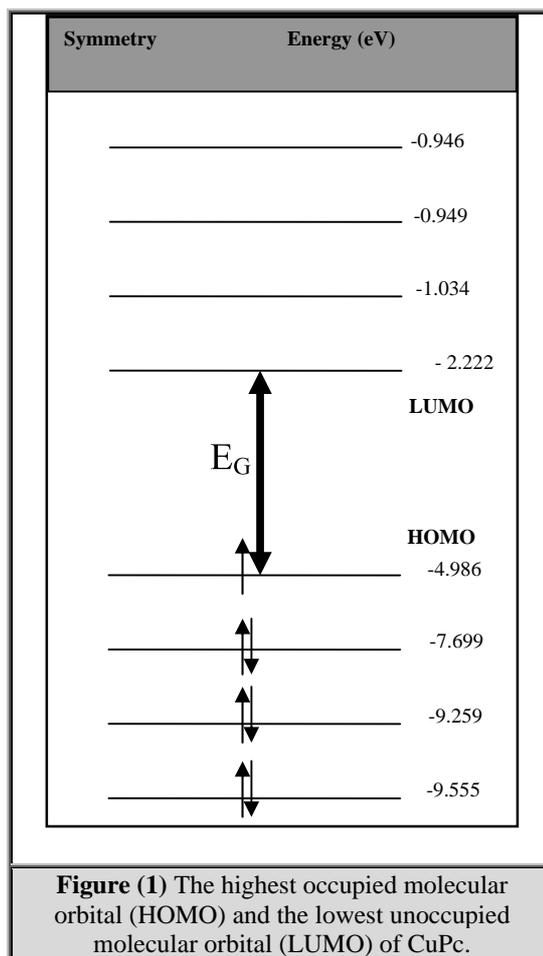
Table (2) Different parameters of CuPc and H_2Pc

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

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

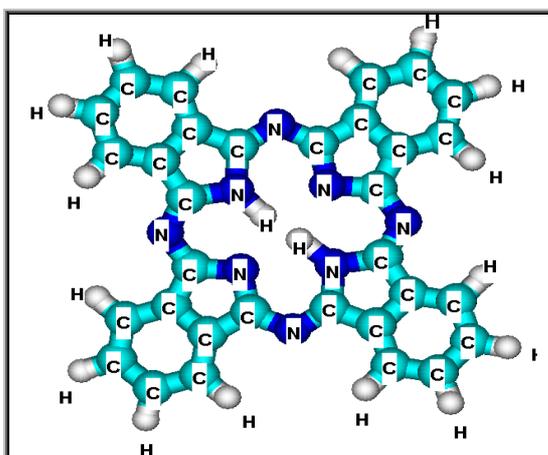
Fig.(3) and Fig(4) shows the electrostatic potential in two-dimensions and in three-dimensions respectively for CuPc molecule. A significant difference between CuPc and H2Pc appear to be in the relative values obtained and listed in table (1). It is apparent from the results that ET, Ee and μ and ΔH_f 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 bonding 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 Kobayashi et al [10] have supported this view that CuPc behaves somewhat 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.

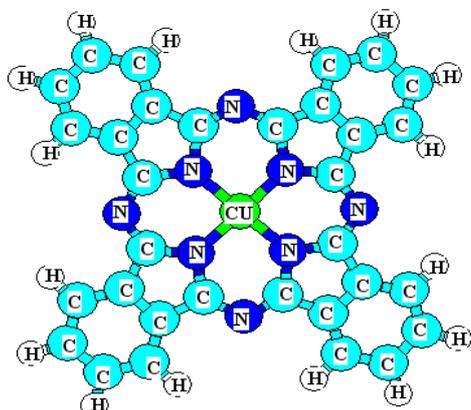


4. Conclusions:

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

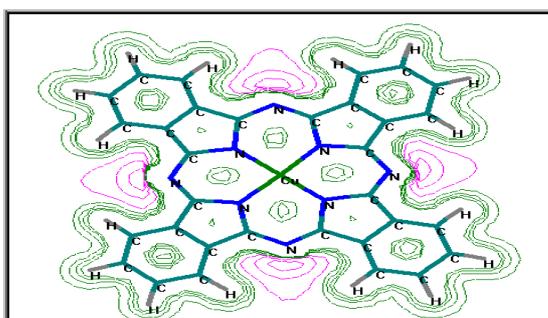


a. Structure formula of metal-free , Phthalocyanine (H_2Pc)



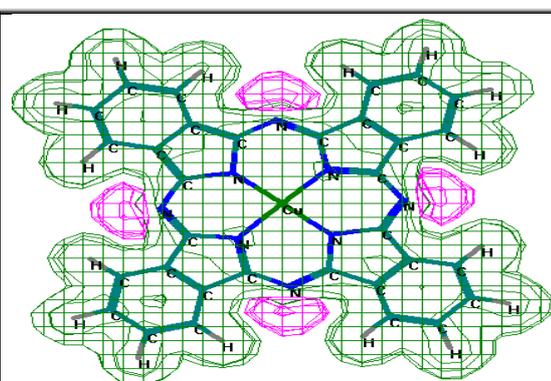
b. Structure formula of Cu- Phthalocyanine (CuPc)

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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