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Calculation of the Electronic Properties Phthalocyanine (H_2Pc), Silicon Phthalocyanine (Sipc), Phosphorus Phthalocyanine (PPc) and Energy Gap by the AM_1 Method

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Abstract

Many semi-empirical methods are available in Gaussian 16. This patch enables analytical gradients and frequencies in addition to increasing efficiency by replacing the code from MOPAC open source, AM1 and PM3 technologies. In the case of a pure molecule, the values of total energy, bond energy, electronic energy, and nuclear energy (-170.893, -1496.855, -4332.708, 45) Kcal/mol have been successively added. After adding Si and P to the free Phthalocyanine molecule, the values transformed to (-133.30, -4987.486, -1294.027, 11.607) Kcal/mol. For the two resulting molecules (PcSi and PcP), the values became (-136.108, -4858.63, -9354.14, 79.930) Kcal/mol. Notably, the first number indicated an increase. Specifically, for total energy numbers, there was a decrease from -170.893 to -133.3 Kcal/mol when adding Si, and a decrease to -136.108 Kcal/mol when adding P. Overall, the energy value increased with both additions, but the bonding energy notably decreased with Si (-1496.855 to -4987.486 Kcal/mol) and P (-4858.63 Kcal/mol). Electronic energy increased from -4332.708 to -1294.027 Kcal/mol when Si was added. Nuclear energy decreased from 45.036 to 11.607 Kcal/mol when Si was added (increasing to 79.930 Kcal/mol with P). The Heat of Formation (H.o.F.) in Kcal/mol equaled 1565.04 when P was added, 1193.384 when Si was added, and 1531.528 when P was added again. The substantial impact of silicon on Phthalocyanine was evident. Furthermore, the dipole moment of the Phthalocyanine molecule, initially at D 3.687, decreased to D 2.093 and D 4.137 when Si was added first and P the second time, showcasing the significant impact of P due to its high atomic number. Determining the HOMO and LUMO and computing the values of Wavenumber, Wavelength, and Symmetry for the three molecules provided a clear illustration. The computation of electrical potential, electronic orbitals, and energy gap revealed an electronic density of 0.346 eV in the case of the free molecule H2Pc, 5.006 eV in the molecule PPc, and 5.660 eV in the case of SiPc. This offers a comprehensive understanding of the impact of adding P and Si to H2Pc.

1. Introduction

The photochemical, photophysical, optical, electrochemical, biological, and high stability features of phthalocyanine make it a very significant organic macrocycle with various uses,[1] including light-emitting diodes (LEDs) [2], solar cells [3,4], and field-effect transistors [5]. The polyaromatic ring, denoted by the abbreviation Pc for the phthalocyanato anion C32H16N8-2, can exist as a variety of derivatives, with hydrogen or transition metals (MPc or H2Pc) being the most frequent bonds [6]. Metal phthalocyanines (MPcs), which share structural similarities with the biological components chlorophyll and hemoglobin, are well-known dye pigments. These materials have displayed a variety of intriguing characteristics, such as the fact that they are organic semiconductors [7,8], are chemically and thermally highly stable [9,10], can readily form ordered thin films, and have photoconductivity [3,4]; demonstrate catalysis [11], etc. The most popular method for depositing MPc films is high vacuum evaporation [12,13]. Attempts have been made to employ these films as molecular components in a variety of electrical and optoelectronic devices [3,4,14]. The films' morphology, structural, electrical, and optical characteristics are essential for their technological applications. For instance, it is well known that more crystallinity enhances the conductivity, while smooth amorphous films provide better interactions. Ordering and direction are critical for the device's effectiveness, according to reports [15]. These molecules frequently exhibit anisotropic electrical transport features, which are brought on by the molecules' preferred orientation [15,16]. The molecular orientation of MPcs has recently been investigated for thin films formed under various experimental conditions on a variety of substrates, including conducting polymer [17], glass [20], quartz glass [18], silicon [12], gold [13,19], etc. This research has shown that the substrate, the deposition method, the heat-treatment temperatures, and the state of the substrates during film deposition all affect the grain orientation.

2. Phthalocyanine's minerals

STM has been used extensively to examine molecules on surfaces ever since it was developed. It proved to be the perfect instrument for the job because it provided access to both the molecule adsorbents' electrical structure and real space adsorption geometry. One of the first molecules examined was CuPc on polycrystalline silver as early as 1987 [1-3]. More MePc molecules have been studied recently on various metal surfaces (Me = Cu [22, 24-27], Co [27-29], Fe [30,31], Ni [32], Pd [33], Zn [34], Mn [35, 36], Sn [37], Si[38], P[39]). Typically, a single MePc molecule and its four isoindole groups (Fig.1) adsorb flat on the surface, are depicted in STM topography as a four-lobed cross form. The centre can be seen as a dip or a protrusion, depending on the properties of the metal ion's filled d states [40,41]. MePc self-assembles into highly structured clusters or layers as a result of interactions between molecules and their substrates as well as interactions between individual molecules. Ordered molecular domains may result from the substrate's symmetry in relation to the molecules' four-fold symmetry [42].

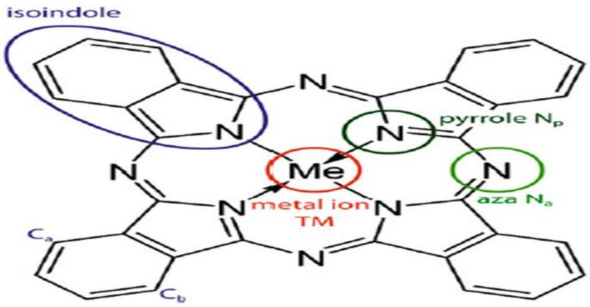


Figure (1): The metal phthalocyanine's Lewis structure. Four isoindole groups and four aza-bridging Nitrogen atoms make up the ligand. Na and NP are the labels given to the several varieties of nitrogen atoms. MePc can hold a wide range of metal ions. To detect chiral distortions, the two Carbone Ca and Cb atoms in the benzene rings are tagged.

(F. Wahab, and et al.., 2014) was able to produce a heterogeneous diode based on organic semiconductors Cobalt phthalocyanine (CoPc) with n-silicon. The Co Pc/n-Si junction's electrical characteristics can be seen through the photos that were captured and investigated using current and voltage (I-V) measurements. Atomic force microscopy (AFM) is used to investigate the Co Pc thin film's morphology. When biased Voltages are 3.6 V, the I-V, the link properties demonstrate behaviour correction with a correction rate of 145. The I-V characteristics were used to calculate the diode parameters idealization factor n, barrier height b, and series resistance Rs, which were then validated using the Cheung function.[43] (F. Roth, and et al.,2015) ,they studied the electronic properties of the manganese-phthalocyanine mixture and fullerene C60 (MnPc: C60) as a function of the concentration of the two components was studied using two complementary electron spectroscopy methods, photoemission spectroscopy (PES) as well as transmission electron energy loss (EELS) spectroscopy. The EELS investigated results showed that despite the rather small interface interaction the electronic excitation spectrum associated with MnPc is significantly changed by mixing C60 into MnPc thin films.[44] (G. appel1 and coauthors. 2002), They used solution pouring techniques to create layers of oligo-oxo silicon phthalocyanine tetrasulfonic acid and dihydroxy silicon phthalocyanine tetrasulfonic acid. With the help of optical X-ray emission Spectral analysis, the material's purity was verified. On the basis of the precise angle of the X-ray absorption spectrometer, an approximation of the substrate level is checked. The primary morphology of the deposit was amorphous, with some crystal structures having a substantial orientation and others having no orientation at all. This behaviour suggests that a number of preparation-related variables affect how the phthalocyanine crystallizes and is oriented.[45](T. L. Doane, 2013) Because of its distinct optical characteristics, they used phthalocyanine as a phototherapy (PDT). outstanding optical stability. They have been demonstrated to produce monooxygenase (1O2) effectively, which makes them particularly effective at treating cancer. The findings demonstrate that the water: lipid ratio and pH have significant influence on photophysics for the axial silicon phthalocyanine bound in the aqueous medium, eventually dictating their activities as PDT medicines. They recommended including it into the photophysics discussed as a cancer treatment. As required by PDT medicines, their functions. We propose that taking a closer look at the photophysics offered by PDT medications in aqueous solutions will provide direction for the development of more potent PDT agents in the future[46].

3. Search Molecules

Some important physical properties of three molecules, namely pure phthalocyanine(H2Pc) in figure(2) , Silicon-phthalocyanine(SiPc) in figure(3)and Phosphorus-phthalocyanine(PPc) in figure(4)

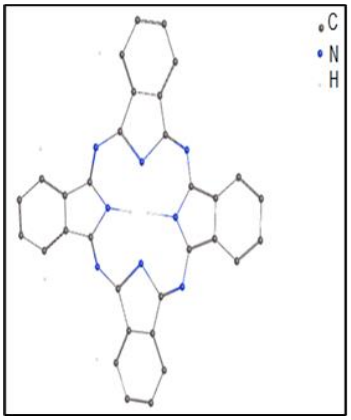


Figure (2): molecule of H_2Pc

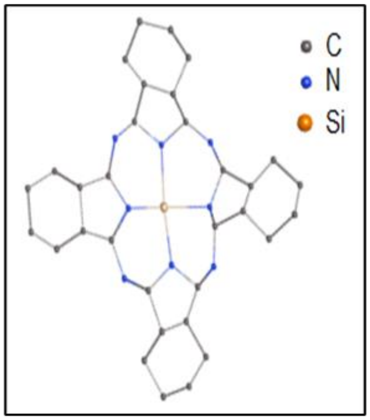


Figure (3): molecule of SiPc

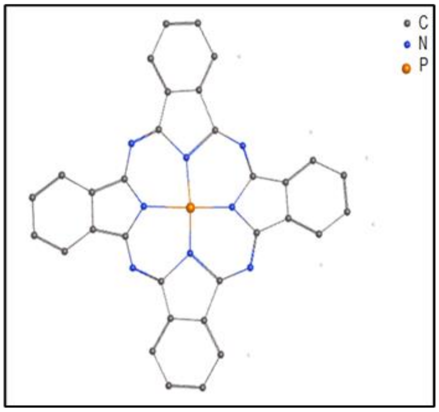


Figure (4): molecule of PPc

Some important physical properties were calculated, as shown in table (1)

Table (1): physical properties of three molecules

Feature	Molecule		
	H_2Pc	SiPc	PPc
Total Energy- Kcal/mol	-170.8937	-133.307.6	-136.108
Binding Energy- Kcal/mol	-1496.85.5	-4987.486	-4858.63
Electronic Energy- Kcal/mol	-4332.70.8	-1294.027	-9354.14
Nuclear Energy- Kcal/mol	45.03601	11.60719	79.93068

Also, the Heat of formation in unit (Kcal/mol) is calculated and Dipole moment in unit (Debey), which is the sum of the dipole moments of the three axes (x, y, z) in the molecule, and this moment is a measure of the polarity of the molecule, all of them are shown in table(2)

Table (2): the value of Heat of Formation and Dipole Moment for three molecules

Feature	Molecule		
	H_2Pc	SiPc	PPc
Heat of Formation(Kcal/mol)	1565.04	1193.384	1531.528
Dipole Moment(D)	3.687	2.093	4.137

3.1. Vibrational Spectrum

From table (3), we note that the:

- H2Pc molecule

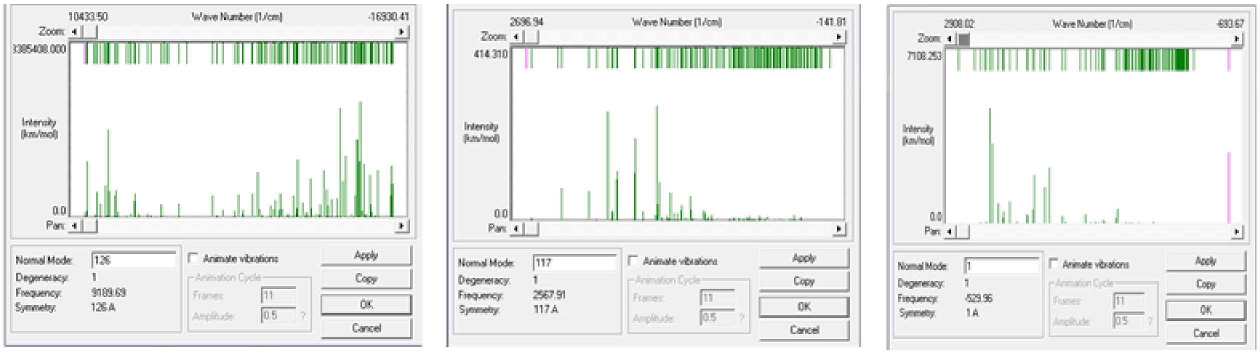
It has (126) vibrational patterns as follows (88) patterns with the negative value of the wavenumber from (-15686 to -1148.65)cm-1 and continues with negative values to orbit (89) [It is a natural issue as a result of the resistance shown by the molecule to the sudden change of energy in the zero energy level, and then returns the positive values of the vibrational frequencies as a result of the stability that occurs to it and this is what we notice in mode 89 and the next through the positive values of vibrational frequencies], from which positive values start to appear to the last orbit (126) and the values are confined between (980.55- 9189.69)cm-1 and wavelengths between (10880-1019)µm from symmetry (89A-126A).

- SiPc molecule

It has 117 vibrational patterns and one negative wave number with a value of (-12.78) cm-1 which is the first pattern and its symmetry is (1A), then the molecule is stable from pattern (2-117) and the frequency is between (62.5-5267.91) cm-1 wavelength between(159.97-1.89) µm , and the symmetry is from (2A-117A).

- PPc molecule

It has 117 vibrational modes and wave numbers with negative values of (-529.96)cm-1 to (-1.450) cm-1 from the first pattern to the ninth pattern and its symmetry (1A-9A), and then the molecule settles in the tenth pattern and its value is (3.91) cm-1 and its symmetry is (10A) and continues until the 117 pattern, so the frequency is between (3.91-2744.31) cm-1 and the wavelength is between (2557.54-0.364) µm and symmetry of (10A - 117A). And the Figure (5) shows the front interfaces of the program for calculating the vibrational frequencies of the three molecules



Normal Mode: 126
Degeneracy: 1
Frequency: 9189.69
Symmetry: 126 A

Normal Mode: 117
Degeneracy: 1
Frequency: 2567.91
Symmetry: 117 A

Normal Mode: 1
Degeneracy: 1
Frequency: -529.96
Symmetry: 1 A

A – H_2Pc B-SiPc C-PPc

Figure (5) : The interface of the Hyperchem program for calculating vibrational Frequencies A – H2Pc ,B-SiPc and C- PPc

Table (3) : The values of wavenumber ,wavelength and symmetry for three molecules

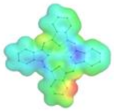
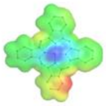
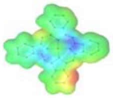
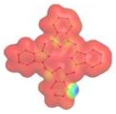
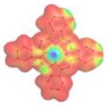
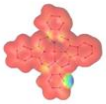
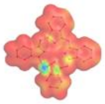
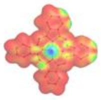
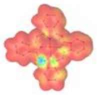
Molecule														
H_2Pc					SiPc					PPc				
No. M [(1)]	De.[(2)]	W.n.[(3)] V´ (cm^{-1})	W. l.[(4)] λ(µm)	Sy.[(5)]	No. M [(1)]	De.[(2)]	W.n.[(3)] V´ (cm^{-1})	W. l.[(4)] λ(µm)	Sy.[(5)]	No. M [(1)]	De.[(2)]	W.n.[(3)] V´ (cm^{-1})	W. l.[(4)] λ(µm)	Sy.[(5)]
1	2	-15686	----	1A	1	1	-12.78	------	1A	1	1	-529.96	----	1A
-	-	-	-	-	2	1	62.51	159.97	2A	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	9	1	-1.45	-	9A
-	-	-	-	-	-	-	-	-	-	10	3	3.91	2557.54	10A
88	1	-1148.65	----	88A	-	-	-	-	-	-	-	-	-	-
89	1	980.55	1019	89A	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	117	1	5267.91	1.89	117 A	117	1	2744.31	0.364	117A
-	-	-	-	-										
-	-	-	-	-										
126	1	9189.69	10880	126 A										

*No. M (1): Number of Mode, De (2): Degeneracy, W.n.(3):Wavenumber, W.l(4) Wavelength, Sy. (5): Symmetry

3.2. Calculation of some Electronic Properties

Some important electronic properties for (H2Pc, SiPc and PPc) molecules, such as Electron Density, Electron Potential, HOMO and LUMO, were calculated and as in the table (4) . Through the table (4) we notice that the cloud and the electronic distribution of the three molecules was very regular and in all parts of the molecules, the same thing applies to Electrostatic Potential, As well as the HOMO account, which represents the highest level of orbitals filled with electrons, and the LUMO account, which represents the lowest level of the orbitals not filled with electrons.

Table (4) : The values of Electron Density, Electron Potential, HOMO and LUMO for three molecules

Feature	H_2Pc	SiPc	PPc
1-Electron Density			
2-Electrostatic Potential			
3-HOMO			
4-LUMO			

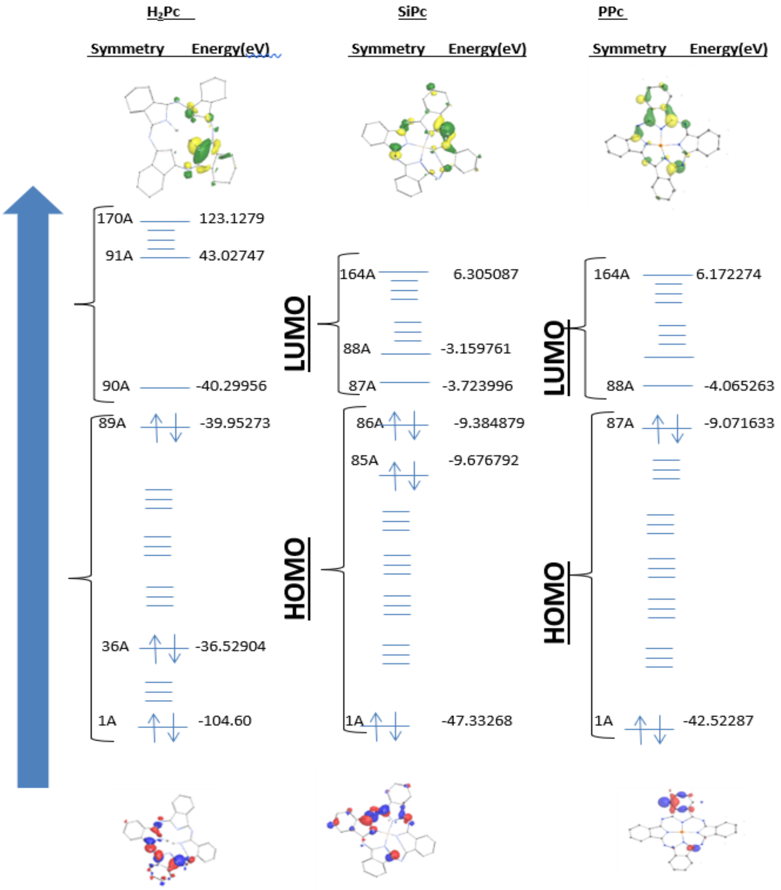


Figure (6) : represent the values of increasing Energy and Symmetry of H2Pc,SiPc and PPc

3.3 Energy Gap

The value of the energy gap was calculated for the three molecules and as in the table (5), we note that the energy gap is increased by adding phosphorus and silicon to the phthalocyanine, The addition of silicon led to a significant increase in the energy gap from the figure (7), We note that the Energy Gap of (SiPc) is greater than (H2Pc, PPc), and this is due to the synthesis of the element silicon, which has an electronegativity less.

Table (5) : The value of Energy Gap for three molecules

Energy Gap-eV ΔE(HOMO-LUMO)		
H_2Pc	**PPc**	**SiPc**
0.34683	**5.00637**	**5.660883**

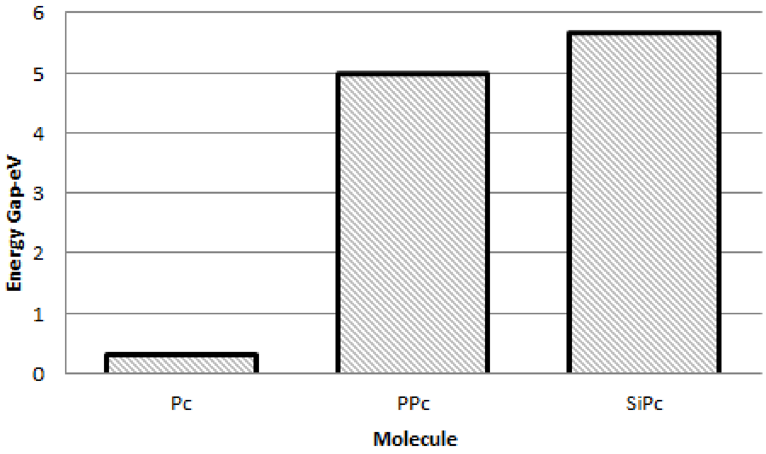


Figure (7): represent the Energy Gap and three molecules (H_2Pc, SiPc and PPc).

4. Conclusion

The phthalocyanine molecule has many properties and applications in medicine (cancer treatment), physics, chemistry and....,.the theoretical study showed that the addition of silicon and phosphorus to phthalocyanine led to an increase in the total energy value (-170.893,-133.3,-136.108) Kcal/mol sequentially, and reduced the Binding energy(from -1496.825 to -4987.486 and -4858.63) Kcal/mol sequentially , Silicon and phosphorus decreased the value of Electronic energy, (from -4332.708 to -1294.027and -9354.14) Kcal/mol sequentially , When calculating the value of Nuclear energy, we noticed that adding silicon and phosphorus to the free molecule leads to reducing its value to (11.607) Kcal/mol by adding silicon, while phosphorus increases its value to (79.930) Kcal/mol, the addition of silicon and phosphorus worked to reduce the value of the Heat of formation for Phthalocyanine (from 1565.04 to 1193.384 and 1531.528) Kcal/mol sequentially. The addition of silicon and phosphorus to phthalocyanine has reduced the number of negative values of vibrational frequencies from (88) negative frequencies to one negative frequency in the case of adding silicon and (9) negative frequencies in the case of adding phosphorus, which indicates the great effect of these additions to phthalocyanine, which gave it greater stability and balance after the addition. Through the calculations of the Electronic Density, it showed us the arrangement and the high regularity in the distribution of electrons, and this is clear through the electronic cloud around the atoms of the molecule. The Energy Gap has increased from (0.34683) eV to (5.00637)eV an increase of (6.9%) when adding phosphorus and to (5.660883) eV an increase of (6.11%) when adding silicon

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