Electronic and Spectral Properties of (PMMA-C102) by Using DFT

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Abstract. In this research, the electronic and spectral properties of PMMA with coumarin dye were studied. The suggested compounds are designed at the Gauss View 5.0.8 program and then relaxed by performing the three parameters Lee-Yang-Parr B3LYP hybrid functional density functional theory DFT method together with SDD basis sets at the Gaussian 09 package of programs to study of their ground state and spectroscopic properties. The electronic properties study included the ionization potential, electronic affinity, hardness, and electrophilicity, while the spectral properties included studying the IR spectra of the suggested compounds.

Keywords: DFT, PMMA, Dyes, electronic properties.

1. Introduction

Natural and synthetic dyes are compounds of great interest since they play an important role in our everyday life. The broad variety of technical and industrial applications, which includes “classical” utilizations like dyeing of textiles and other consumer goods as well as rather new usages such as laser dyes and dyes for organic light emitting diodes (OLEDs), liquid crystal (LC) displays, optical data storage and fluorescent labeling, has produced a great deal of research in this field. The main driving force is the constant demand for improved dyeing efficiency [1,2], or photochemical/photophysical properties [3,4], while also focusing on eco-friendly procedures [5,6], reduced toxicity [7,8], and decreased production costs [9]. A promising approach to fulfilling these requirements is the combination of dyes and polymeric materials, which will be highlighted in this review. The great advantage of such systems is the controllability of many features like solubility, stability, and toxicity through appropriate choice of polymeric material.
2. Computational methods

In the present study, we focus on considerable attention on the application of DFT to the (PMMA- C102). All the computational studies were carried out by using DFT method at B3LYP/SDD levels of theory. This study of (PMMA- C102). has been carried out by using the Gaussian 09 code and Gauss-View molecular visualization program package on the personal computer.

The computation of molecular properties in this study are carried out by Koopmans theorem (KT) as shown in the following description.

In quantum physics and chemistry, HOMO and LUMO are two most significant of molecular orbitals, where the HOMOs denotes highest occupied molecular orbitals and the LUMOs represents lowest unoccupied molecular orbitals. These orbitals are called “Frontier molecular orbitals (FMOs)” and as they lie at the outmost boundaries of the electrons of the molecules. The HOMO, which is the highest energy (outermost) orbital containing electrons, is the orbital acting as an electron donor. Contrariwise the LUMO is the lowest energy (innermost) orbital having space to accept electrons. The energy gap regards the difference of the energies between the HOMO and LUMO levels as in the following [10]:

\[ E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \] (1)

Here \( E_{\text{gap}} \) indicates the energy gap, \( E_{\text{LUMO}} \) and \( E_{\text{HOMO}} \) denoted the energies of HOMO and LUMO in consecution. FMOs and their resulting energy gap did not only decide the path the molecule interacts with other species, but their energy gap helps to describe the chemical reactivity and kinetic stability of the molecules such as in metal complexes [11].

The total energy (\( E_T \)) represented the sum of total kinetic and potential energy of the system, at the optimized structure where the total energy of the molecule must be at the lowest value because the molecule is at the equilibrium position, which means the resultant of the effective forces is zero [12].

The ionization potential (\( I_E \)) for a molecule is the quantity of energy necessary to remove an electron from an isolated atom or molecule and expressed as the energy difference between the positive charged energy (\( E_+ \)) and the neutral (\( E_n \)) as the relation: \( I_E = E_+ - E_n \). In addition, the HOMO energy was also used to compute \( I_E \) in the framework of Koopmans theorem as in the following form [13]:

\[ I_E = -E_{\text{HOMO}} \] (2)

The electron affinity (\( E_A \)) of a molecule or atom is the energy change when an electron added to the neutral atom to form a negative ion and expressed as the energy difference between the neutral energy (\( E_n \)) and the negative charged energy (\( E_- \)) according to the relation: \( E_A = E_n - E_- \). Furthermore, the LUMO energy was also used to calculate \( E_A \) according to Koopmans theorem as in the following [13]:

\[ E_A = -E_{\text{LUMO}} \] (3)

The hardness (H) is a measurement of molecule resistance to the change or deformation and defined as the form [14]:

\[ H = \frac{1}{2} \left( \frac{\partial^2 U}{\partial N^2} \right) \nu(\gamma) \] (4)

In terms of \( I_E \) and \( E_A \), the hardness is half of the energy gap between two frontier orbitals as in the following [15]:

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\[
H = \frac{I_E - E_A}{2}
\]  

(5)

The hard molecule has a large energy gap. The theoretical definition of chemical hardness has been provided by the DFT as the second derivative of electronic energy with respect to the number of electrons \( N \), for a constant external potential \( V(\vec{r}) \) as in the Eq. (6) [14]:

\[
H = \frac{1}{2} \frac{\partial^2 E}{\partial N^2} \left[ V(\vec{r}) \right] = \frac{1}{2} \left[ \frac{\partial \mu}{\partial N} \right] \left[ V(\vec{r}) \right]
\]

(6)

The electrophilicity index (\( \omega \)) is a measure of energy lowering due to maximal electron flow between donor and acceptor. In which the electrophilicity index given as follow [16]:

\[
\omega = \frac{\mu^2}{2H}
\]

(7)

Electrophilicity is built up from the electronic structure of molecules, independent of the nucleophilic. The electrophiles are species that stabilize upon receiving on additional amount of electronic charge from the environment [17].

3. RESULTS AND DISCUSSION

In Figure 1, it exposes that the dye rings at the sides of polymer is clear and the \( \pi \)-electron delocalization between the molecule units and aromatic rings is also clear. The effect of adding subgroups in dye rings are studied. In order to examine the effect of asymmetry in comparison with the corresponding symmetry compounds, some compounds of different subgroups are designed. The effect of the electron accepting and electron donating groups are studied. All the geometrical parameters have been calculated by employing the B3LYP hybrid function together with SDD basis sets at the Gaussian 09 program.

![Figure 1](image)

Figure 1. The relax structures of (PMMA- C102) compound.
The total energy $E_T$ in a. u for the studied compounds was calculated and listed in Table 1. As seen from mentioned Table, the $E_T$ is approximately independent on the position of the same subgroups in the compounds but depends only on the number of electrons in the compounds, this a sign to that the total energy is a reflection of the binding energy for each compound. $E_T$ is inversely proportional with the number of electrons, it decreased with increasing the number of electrons in the compound. Figure 2 shows the $E_T$ for the studied compounds. In other hand, the corresponding calculated values of viral ratio (-V/T) for the studied compounds in Table 1 showed they lie in the same range for such compounds, in which the experimental value for hydrogen atom (-V/T=2.0032) [18].

![Figure 2. Total energy of the compounds.](image)

**Table 1: The total energy $E_T$ and (-V/T) for the compounds.**

| Compound | $E_T$ a. u | -V/T |
|----------|------------|------|
| 1        | -810.628   | 2.0056 |
| 2        | -1230.20   | 2.0055 |
| 3        | -1640.53   | 2.0053 |
| 4        | -2108.51   | 2.0054 |
| 5        | -2567.34   | 2.0054 |
| 6        | -3042.67   | 2.0087 |

![Figure 3. Energy gaps of the compounds.](image)
Figure 3 shows the $E_g$ for the studied compounds we show that the energy gap is decreasing with increasing the dye ring to the polymer.

The values of IE and EA for the studied compounds are drawn in figure 4. The results showed, compound 6 has the lower IE in comparison with the other compounds, this indicates that compound 6 has high ability to donating an electron to becomes action in comparison with the others.

Figure 4. IE and EA of the compounds.

Figure 5 shows the calculated values of the electrophilicity $\omega$ and the electrochemical hardness $H$. As seen, the maximum value of $\omega$ is 5.7427 eV for compound 6 and the minimum value is 1.9424 eV for compound 3. This result is due to the difference of the configuration of the compounds under study. High Electrophilicity gave the compound high ability to donating/accepting an electron to from the surrounding species. Low $H$ indicates easily to an electron transfer from the valence to conduction band in the compound. Above result is a reflection to small band gap that the compound has.

Figure 5. hardness and electrophilicity of the compounds.
Figure 6 shows the infrared IR spectra of studied compounds analyzed from the B3LYP/DFT calculations. For compound 1, the spectrum showed the stretching C-H bonds was observed at (3028.73-3238.41) cm$^{-1}$ corresponding to low intensities equal to 49.89 km/mol and 0.111 Km/mol, respectively, the stretching C-C bonds lies at (1548.71-1675.24) cm$^{-1}$ with maximum intensity equals 70.597 Km/mol corresponding to 1617.63 cm$^{-1}$. The bending C-H bonds was observed at (1412.08-1530.23) cm$^{-1}$, the stretching C-O bond was observed at 1270.5 cm$^{-1}$.

For compound 2, the stretching C-H bonds lies in the range (3037.62-3241.25) cm$^{-1}$ with maximum intensity equals 122.68 Km/mol, these calculated values are agree with those in phenyl compounds from experimental studies [19]. The bending C-H bonds was observed at (1482.45-1527.35) cm$^{-1}$ while the stretching C-O was observed at 1281.77 cm$^{-1}$ corresponding to high intensity 490.167 Km/mol.

For the other compounds, the results showed the stretching C-H bonds lies in the range (3024.14-3238.6) cm$^{-1}$, in which refers to good relaxation was obtained for the studied compounds. The bending C-H bonds for these compounds was observed at the range (1205.15-1520.95) cm$^{-1}$. Above results are agree with the experimental data for cyclic carbon compounds [18].

![Figure 6. IR-Spectra of the compounds.](image-url)
4. Conclusions

Good relaxation was obtained for the studied compounds by using the B3LYP-DFT with a suitable SDD basis set. The calculated values of geometrical parameters and virial ratio of the compounds are in a good agreement with experimental data and other theoretical studies. The total energy is independent on the position of the same subgroup in the compounds, it depends only on the number of electrons in each compound. Approximately, all the studied compounds show destabilization of LUMO and stabilization of HOMO, they both changed importantly to propose different structures play significant roles in electronic properties. The effect of symmetry and distribution of dye rings has an influence on the calculation of HOMO and LUMO.

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