

Study of The Effects of Some Organic Monomers on The Electronic Structure For C₂₀ Cage Fullerene

C₂₀ دراسة تأثير بعض المونومرات العضوية على التركيب الالكتروني للفولورين

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فيزياء نظرية

Abstract:

Three parameters Lee-Yang-Parr B3LYP density functional theory calculations are applied for C₂₀ cage fullerene some organic monomers included thiophene, furan, vinyle and pyrrole are used to interact on C₂₀ cage. The computations are carried out the large 6-31G(d,p) basis sets.

The results declare that the used monomers all have large band gap, and the monomers – fullerene composites have narrow band gap of these composites can lead to materials that can absorb solar radiation.

الخلاصة:

تم في هذا العمل تطبيق حسابات دالة الكثافة للمعاملات الثلاثة في المستوى Lee-Yang-Parr B3LYP على الفوليرين حجم C₂₀ ، بعد ربط بعض المونوميرات العضوية والتي اشتملت الثايوفين، الفيوران، الفينيل والبييرول بجزيئة الفوليرين C₂₀ حيث أجريت جميع الحسابات باستعمال الدوال الأساس 6-31G الكبيرة.

توضح النتائج إن جميع المونوميرات المستعملة كانت ذات حزمة فجوة كبيرة، بينما كانت مركبات المونومير - فوليرين ذات حزمة فجوة ضعيفة وان هذه الفجوة الواطنة لهذه المركبات يمكن أن يقود إلى مواد يمكنها من امتصاص الإشعاع الشمسي.

Introduction

The C₂₀ is the smallest possible of fullerene family, it is without hexagonal rings, it contains just twenty pentagons. The stable isomers of C₂₀ clusters consist of ring, bowl and fullerene structures, and these structures are all can be experimentally produced under suitable reaction conditions[1]. The C₂₀ cluster has been extensively studied theoretically [2].

In molecular orbital theory calculations, The C₂₀ has fourfold degenerate highest occupied molecular orbital HOMO in which there are only two electrons are populated into these orbitals [2,3].

Each carbon atom in C₂₀ cage is bonded to three others with a bond angle of 180°. Which is close to the tetrahedral bond angle. The discovery of carbon fullerene have been intense efforts towards finding or designing fullerene structures of other materials to have a better control over material properties [4].The C₂₀ can be considered as a layer of graphene that is rolled up into a small sphere.

In graphite, the carbon atoms from sheets, within a sheet there are sp²-orbitals pointing to three neighbors, forming hexagons with strong σ -bonds. The fourth valence electron in a p_z-orbital perpendicular to the sheet becomes delocalized in a weak π -bond[5].

In this study, B3LYP/6-31G(d, p) calculations on C₂₀ cage fullerene and the monomer-fullerene composites have been performed. The reaction activity of the most stable fullerene with the addition of monomers has been explored.

Method and computational details

All the computational studies were carried out using the density functional theory (DFT) methods implemented in the Gaussian 09 suite of programs [6]. The molecular properties of the compounds have been computed by DFT using the standard 6-31G(d, p) basis sets. In the DFT calculations the Lee, Yang and Parr correlation functional [7] is used together with Becke's three parameters[8]exchange functional B3LYP. Conformational analysis of the molecules has been performed to have an idea about the lowest energy structures of the species.

The geometry optimization was performed at the B3LYP density functional theory with the same basis set [6, 9]. Harmonic vibration frequencies were computed at the same level of theory. The hybrid functional B3LYP has shown to be highly successful for calculation the electronic properties such as ionization potentials, electronic states and energy gaps [10-12].The DFT partitions the electronic energy as $E = E_T + E_V + E_J + E_{XC}$, where E_T , E_V , and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively. The electron correlation is taken into account in DFT via the exchange correlation term E_{XC} , which includes the exchange energy arising from the anti-symmetry of the quantum mechanical wave function and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional HF procedure [13].

The geometry optimized structures are obtained without any symmetry restriction, and vibrational analysis for each structure does not yield any imaginary frequencies, which indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface [14].

The ionization potential is calculated as the energy difference between the energy of the molecule derived from electron-transfer (radical cation) and the respective neutral molecule; $IP_v = E_{\text{cation}} - E_n$. The EA was computed as the energy difference between the neutral molecule and the anion molecule: $EA = E_n - E_{\text{anion}}$ [15]. The high occupied molecular orbital energy HOMO and the lowest unoccupied molecular orbital energy LUMO energy was also used to estimate the ionization potential IP and the electron affinity EA in the framework of Koopmans' theorem: $IP = -\epsilon_{HOMO}$ and $EA = -\epsilon_{LUMO}$ [16].

One of the other global properties is the electric dipole polarizability, which is a measure of the linear response of the electron density in the presence of an infinitesimal electric field, F, and represents a second-order variation in the energy, viz.[17] :

$$\alpha = - \left(\frac{\partial^2 E}{\partial F_a \partial F_b} \right)_{a,b = x, y, z}$$

If some of applied molecules are planar and some are not, it will be useful to report polarizability quantities that are invariant to the choice of coordinate system. One of them is the mean polarizability $\langle \alpha \rangle$ is evaluated using the equation [18].

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

Where $\alpha_{xx} \leq \alpha_{yy} \leq \alpha_{zz}$ are the eigenvalues of the polarizability tensor.

Results and discussion

Table 1 shows the total energy, symmetry and imaginary frequency numbers for C₂₀ fullerene, thiophene, furan, vinyl and pyrrol structures computed at B3LYP density functional theory done by Gaussian 09 package of programs. It is clear from table 1 that all the monomers have not imaginary frequency, that mean a good geometry was done by the used method and the structure of each molecule

corresponds to at least a local minimum on the potential energy surface. The large thiophene monomer has the small value of total energy in which it contain sulfur atom in its structure.

Table 1 : Total energy and the symmetry of structures

Structure	Total energy (a.u)	symmetry	No. of imaginary frequency
C20 fullerene	-92.831	I _h	0
Thiophene	-548.473	C _{2v}	0
Furan	-227.350	C _{2v}	0
Vinyl	-77.600	D _{2h}	0
pyrrole	-207.647	C _{2v}	0

Table 2 shows the results of conduction band, valence band and energy gab for the studied structures. It is shown that negative values were results for the valence of all C₂₀ and monomers. Which it conduction bands have different positive and negative values depend on the distribution of energy levels of the structure. All monomers that interact to C₂₀ fullerene have large band gaps, they are have the order of vinyle > thiophene > pyrrol > furan. Each one of used monomers has a wide band gap, means (E_g > 5 ev), this is a major character for these monomers. The hypolarizability of used monomers in this study was illustrated in table 3, the thiophene has the largest value of polarizability and it has more reactive to interact with fullerene.

Table 2 : Valence band , conduction band and energy gap for structures

Monomer	α_{xx} (a.u)	α_{yy} (a.u)	α_{zz} (a.u)	α_{ave} (a.u)
Thiophene	62.328	54.221	16.519	44.356
Furan	42.196	41.795	11.481	31.824
Vinyl	30.746	18.487	5.792	18.341
Pyrrole	45.943	47.727	11.908	35.192

Table 3 : Average polarizability for studied monomers

Structure	Value band (eV)	Conduction band (eV)	Energy gap (eV)
C20 fullerene	-2.645	-2.410	0.235
Thiophene	-9.303	-3.534	5.769
Furan	-5.986	0.382	6.368
Vinyle	-10.312	-4.571	6.741
pyrrole	-5.298	1.295	6.593

The results of monomers-fullerene composites are illustrated in table 4. The monomers-fullerene composites have narrow band gap . The feature that a polymer that could capture all of the solar photons down to 1.0 eV would allow absorption of approximately 75% of all the solar photons. This feature expanding by shifting the polymer absorption spectrum into the near-infrared region.

Table 4: Binding energy, valence band, conduction band and energy gap for monomers – fullerene composites

composite	Binding energy (a.u)	Valence band (eV)	Conduction band (eV)	Energy gap(eV)
Thiophene- fullerene	-5.18	-4.125	-3.386	0.739
Furan - fullerene	-4.45	-3.438	-3.015	0.423
Vinyle- fullerene	-3.98	-5.021	-4.226	0.795
Pyrrole- fullerene	20.25	-3.596	-3.288	0.308

This is initially achieved through the use of small band gap energy polymers, this lead to efficiencies approach to high as 3.5% in polymer – fullerene composites solar cells. The small band gap polymers is the solution of this problem.

From table 4, the band gap of all monomers – fullerene is below 1.5 eV. All monomers – fullerene composites have narrow band gap, these composites-fullerene have the order of pyrrole–fullerene < furan–fullerene < thiophene–fullerene < vinyl- fullerene.

Conclusions

B3LYP density functional theory calculations were employed to calculate the monomers – fullerene composites structures. One can conclude that:

- 1- The geometry optimization for the used monomers is a good at 6-31G (d,p) basis sets.
- 2- A best choice of the monomers in which they are all have large band gap can be interact with C₂₀ cage fullerene.
- 3- Thiophene has the smallest band gap compared with other used monomers, and it has the largest polarizability. Thiophene-fullerene composite has small binding energy, this may leads to feature work about the polymer-fullerene composites.
- 3-The main feature for this study is that the band gap for monomers - fullerene composites is below 1.5 eV. This open a new field to design new structures of polymer – fullerene composites can be allow to absorption approximately 75% of all the solar photon.

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