Studying Stability of Fluorographene with DFT Method

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ABSTRACT: Graphene is the monolayer, honeycomb lattice of carbon atoms and has zero band gap. There are different methods for band gap creation in graphene. One of them is graphene fluorinated. We investigate fluorographene properties, because fluorographene has stability more than other halogenated graphenes and chair configuration due to the more stability than other configuration. In this paper, first fluorographene stability as compared with pure graphene with density functional theory is investigated. Then we consider increase rings influence in fluorographene molecule. Here, all of simulation and calculations is done by DFT method and 6-31g basic sets in gaussian 09 software. In this article, we will show the stability three rings fluorographene is lesser than pure graphene and we can increase stability by increasing number of rings in fluorographene molecule. We will survey on three rings fluorographene and six rings fluorographene by using of five quantity dipole moment, hardness, the total energy of the system, polarizability, the distance between levels of energy lumo and homo orbitals.

Keywords: Stability, Fluorographene, Graphene, Density Functional Theory, Basic sets

INTRODUCTION

Graphene includes a layer of sp² carbon atoms which has been arranged in honeycomb lattice (Karlicky, 2013). Graphene has been regarded as millions of layer in the form of graphite which has been usually made on tip of pen until its discovery in 2004. In 2004, Andre Geim and Konstantin Novoselov from University of Manchester successfully produced this substance (Lu, 1999). Since primary isolation of graphene in 2004, many studies have shown that this carbon substance with atomic thickness has unique mechanical power, very considerable thermal and electrical conductions, high surface area and gas impenetrability (Novoselov, 2012). Graphene is the smallest effective mass (zero) and can pass long micrometer distances (in micrometer) without scattering at room temperature. Density of graphene flow is six times as much as the copper (Lu, 1999). Graphene causes to be very interesting for different applications due to high quality of its crystal samples and its miraculous electric properties in addition to other desirable properties. Graphene is one of the important candidates of substance for the next generation of the electric substances due to mobility of charge carrier (Novoselov, 2012). But graphene lacks band gap in fermi levels and this challenges its application in unique electronics (Schwertz, 2010). There are several ways for creation of band gap. The finite band gap can be created by entrapping electrons in nanopipes with application of potential difference on two layers of graphene (McCann, 2006). Change of chemical specifications of graphene is another new way for creation of band gap (Cheng, 2010). It has been shown that electric conduction considerably changes by adding chemical impurity to pure graphene (Lu, 1999). Zero band gap of graphene is opened by hydrogenation and halogenation and strongly depends on chemical compound of mixed graphene halides (Karlicky, 2012). When radicals such as oxygen, hydrogen or atoms of fluorine are absorbed on surface of graphene, they make covalent bonds with atoms of carbon. Hybridization of these atoms of carbon changes from sp² to sp³ which leads to opening of band gap (such as diamond) (Leenaerts, 2010). Stability of graphene halides is reduced with increasing size of halogen atom (Karlicky, 2012). Relative theoretical calculations on a set of hypothetical graphene derivatives (graphene and fluoride, chloride, bromide and graphene iodide) mention that thermodynamic stability of halogen layers is much higher than that of other graphene derivatives. Difference in thermodynamic stability between graphene halides can show many applications (Zbor’il, 2010). Fluorographene is stable in case graphene iodide is decomposed automatically. Several functions have predicted that graphene band gap is more than fluorographene. Calculation of GGADFT shows that graphene is a matter which has direct band
gap and estimates that if band gap is about 3.5 electronvolts. GW calculations have suggested different values of band gap (Lu, 1999). Theoretical calculations of high level of the recent optical properties have been performed with BSE and computation for electron-hole and electron-electron correlations and exciton effects have shown that the first peak of exciton has occurred in graphene absorption spectrum of 3.8 electronvolts. Values of the reported band gap for fluorographene are controversial. The experimental measurements have shown that the insulated fluorographene with band gap of 3 electronvolt (from optical spectrum) and resistance of more than $10^{12}$ ohms (Karlický, 2012).

Theoretically, studies of the first principles of fluorographene have started in 1993 based on accessible tests on monofluoridographite (Leenaerts, 2010). Testers and theorists have studied hydrogenated and halogenated graphene derivatives due to extensive potential applications with stoichiometric method. Several new two-dimensional crystals have been recently prepared based on graphene, hydrogenated graphene (graphene, CH) and fluorinated graphene (fluorographene, CF or fluoride graphene) (Geim, 2007). The studied type of halogenated graphene was comparable with experimental formula $C_aX_2Y_4(c=a + b; X = H, F; Y = F, Cl, Br, I; I \neq X)$. Four different forms of fluorographene, armchair, boat, zigzag and furniture. In all cases, the primary assumed model is armchair because it has been shown that it is the most stable form for graphene and fluorographene. The assumed model is infinite two-dimensional structural model with the smallest possible supercell under periodical border conditions (PBC). The infinite structures were modeled with DFT linear scale with Gaussian orbitals and periodical border conditions (PBC). These calculations were performed with Gaussian 09 which is a suitable tool for application of hybrid functions. For comparison, computations on the simplest systems had been performed with basic set of flat wave. HSE06, m06L, PBE, BLYP, BPW91, TPSS and LDA functions were tested with large basic set which produce almost equal band gaps and geometries such as basic set of flat wave and include effective nuclear potential for heavy elements.

Generally, Density functional theory (DFT) has been used in most computations of electrical structures of solid state matters (Kummel, 2008). Density functional theory (DFT) is the exception which allow electron density and its cumulative computational form to replace complex electron N wave function and continuous Schrödinger Equation. What Tomas and Fermi found in 1964 was that statistical hypotheses can be used for approximation of electrons scattering in an atom. The hypotheses which have been mentioned by Thomas in 1927 are that: electrons are uniformly scattered in six-dimensional phase space for second order electron motion in each volume of $\hbar^3$ and that there is effective potential field which has been determined with nuclear load and electrons distribution (Parr, 1989). In this paper, we study two-dimensional crystals based on graphene, fluorographene. To study electrical and structural properties, we investigate it with density functional theory (DFT). This method is performed with Gaussian software 09 and with B3LYP base function. Fluorographene is considered as armchair and its stability is studied. We obtain five quantities of dipole moment, hardness, total energy of the system, polarization, distance between molecular orbitals of Homo and Lumo with output of Gaussian computation output and study stability of 20-cyclic graphene systems, tricyclic graphene systems and six-cyclic fluorographene.

**Properties of fluorographene**

Properties of fluorographene in terms of band gap and stability: $C_2FBr$ and $C_2HBr$ derivatives seem to be suitable material for application in optoelectrics because their band gaps are similar to these conventional semiconductors and are expected to remain stable under environmental conditions. Results show that other fluorinated compounds ($C_2H_2F_2$, $C_2F_2Cl$, $Y=Cl, Br, I$) are stable insulators (Karlický, 2012). The obtained layered fluorographene shows strong insulating behavior at room temperature with resistance of more than 1 Tesla/ohm. At high temperature with stability of above 400˚C, almost all Raman Graphene peaks disappear when accumulating with the areas which are not fully fluorinated (Leenaerts, 2010). Anyway, it can show the presence of defects in the sample, for example, a small part of carbon atoms may not have bond with fluorinated atoms. They experimentally found that fluorographene has Young's modulus of 100 newton/ meter and optical measurements suggest band gap of 3 electronvolts. Probability of one-way absorption has been studied and it yields crystalline structure of $C_2F$ with large band gap. With computations of density functional theory (DFT), shape of fluorographene armchair is seriously more desirable than other shapes. With local density approximation (LDA) for exchange correlation function, direct band gap of 3.5 electronvolts has been calculated for shape of armchair. The DFT estimations have shown band gap well. Recent computations use more accurate GW computations and obtained larger band gap of 7.4 electronvolts for armchair of monofluoridographene. This theoretical value is twice as much as the experimental value obtained for fluorographene which is 3 electronvolts. The experimental value for Young's modulus is half of the model which has been recently obtained from the first principle calculations (228 Newton/m) for armchair of fluorographene. Theoretical and experimental values of Young's modulus differ only in small percentage (Karlický,
Theoretical predictions of electrical properties of fluorographene focus on a band structure called band gap. Despite many research works, there are many problems about band structure of fluorographene. The band gap has been usually assumed for armchair of fluorographene with unit cell including 4 atoms. The conventional local density approximation (LDA) or generalized gradient approximation (GGADFT) predicts that fluorographene has direct band gap: the bottom of conduction band and top of the valence band are located in the first Brillouin Zone. Top of the valence band is degenerated twice. The minimum direct band gap of fluorographene i.e. 3.1 electronvolts from the predicted GGADFT shows that fluorographene has insulating properties in agreement with fluridegraphe calculations. Band gap values of other fluorographene forms are seldom above 4.2 electronvolts for armchair (Karlicky, 2013).

Photoluminescence measurements have identified emitted peak of 3.8 electronvolts in fluorographene scattering in the acetone, which determine band to band, electron and free hole. Theoretical calculations of fluorographene band gap have suggested values of 3.1 electronvolts with GGADFT (similar to values for fluridegraphe). Agreement between values of band gap may be accidental because high level theoretical calculations predict about 7.5 electronvolts with band gap GW. Finally, optical spectrum calculation with BSE on GW predicts start of spectrum in approximately 7.5 electronvolts. This value was assumed to be in good agreement with the experimental values (3 and 3.8 electronvolts for optical measurements). Optical band gap of fluorographene is about 3.8 electronvolts which is almost enough for optoelectrical applications in UV zone.

We separately introduce optical, vibrational and thermodynamic properties of fluorographene. Studies of absorption spectrum of the graphene which has been partially or wholly fluorinated clearly show that they show different optical properties. The absorption spectrum of the graphene shows that it is relatively uniform for optical energies of below 2.5 electronvolts but strongly increases in blue light zone and has absorption peak in UV spectrum (4.6 electronvolts). In comparison, the partially fluorinated graphene shows more transparency while fluorographene shows transparent visible frequencies and light absorption starts only in blue zone. This shows that fluorographene is semiconductive with broad gap or insulator with band gap of larger than or equal to 3 electronvolts.

Theoretical experiment of the vibrational modes can provide valuable information about infrared spectrum and experimental Raman of fluorographene. Particularly, one can compare the observed peaks with the calculated Raman active modes by transferring information of Raman spectrum on special structure. Theoretical experiment has shown that phonon spectrum and density of states (DOS) don’t show phonon groups for the most stable form i.e. armchair. Important role of acoustic modes has been attributed to fluorine atoms while high frequency modes have about 1200 cm\(^{-1}\) of clear carbon property.

Graphene and derivatives of graphene and fluorographene can be separated and made in free mixed membranes. It allows measurement of elastic constants of these matters from nanoindentation with atomic force microscope. The experimental elastic constants can be compared with the first principle calculations and by giving information about purity and structural crystallinity of the experimental samples (Karlicky, 2013).

The corresponding structures with energy minimums are coordinated with general optimization and lengths of the criterion unit cell are used for default convergence in Gaussian. Total energies calculated for the best structures determine strength of the relative type of graphene by calculating difference of total energies of \(\Delta E'^{\text{rel}}\). Pyrite band gap has been shown with BLYP unit vector which is twice as much as the experimental value. Finite short functions seems to be an effective way for standard hybrid functions like Heyd, Scuseria and HSE hybrid functions. HSE functions carefully predict electrical properties of low dimension carbon matters and optical transitions in both of them, semi-conductive and metal single-walled carbon nanotubes. Therefore, we expect HSE function calculations to be useful for careful description of electrical structure of the assumed systems in our study (Karlicky, 2012).

We reported the theoretical calculations of two different computational models, armchair of graphene (CH) and on halogenated systems (CX, X=F, Cl, Br, I). The first model (model A) includes perhydrocoronene and halogen, for example, C\(_{24}\)X\(_{24}\)so that X= H, F, Cl, Br. The second model (model B) includes infinite two-dimensional structure with the smallest possible unit cell, C\(_{2x}\)X\(_{2x}\) trans under periodical border conditions (PBC). All calculations have been done with Gaussian 09. Infinite structures were determined with Density functional theory (DFT) with Gaussian orbitals PBC9 more than the basic set of wave plane which had been modeled in solid state calculations. Becke-Lee-Yang-Parr function (BLYP) combined with basic set of LANL2DZ and nuclear potential had been applied in most discussed Harrin calculations. All electron calculations had been performed with small basic set of 3-21G for comparison. Corresponding structures with minimum energy had been obtained by optimizing all coordinates (and lengths of unit cell in model B) with default convergence criterion in Gaussian. K-point network from ten points in ten points of Brillouin Zone in distance of 20 a.u. in any direction when cells started working. This was useful for obtaining convergence accuracy of \(10^{-6}\) a.u. For total energies and \(10^{-5}\) ev for band gaps for...
CH, CF and CCl. For CBr, it was necessary to use 40 points in 40 points to obtain k-point sample with the same convergence accuracy for total energies and accuracy of 10^{-8} ev for band gaps (Zbor'il, 2010).

**COMPUTATIONAL METHOD**

In this paper, DFT theory has been used for calculation of band structure and we try computational methods for two-dimensional crystal of graphene and fluorographene based on DFT and orbital basic set and compare results of calculation with the accessible criterion information. Generalized gradient approximation and local density approximation (LDA) functions were regarded negligible with Kohn–Sham finite band gap method compared with the experimental finite values while they were estimated with Hartree-Fock (HF) finite method.

Space is divided into very small cubes (cells). Each length of L and volume of $\Delta V = L^3$ include fixed number of electrons (which may have different values for different cells) and it is assumed that electrons act independently of each other like independent fermions at temperature of 0 Kelvins in each cell with independent cells. Energy levels of a particle are given in three-dimensional space with the following formula:

$$\varepsilon(n_x, n_y, n_z) = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2}{8mL^2} R^2$$

(1)

So, $n_x, n_y, n_z = 1, 2, 3, ...$ and the second equality determines R quantity. For high quantum numbers for large R, the number of given energy levels with energy of below $\varepsilon$ is approximated with $\frac{1}{8}$ of a sphere with radius of R in space of $(n_x, n_y, n_z)$. These energy levels are below $\varepsilon$:

$$g(\varepsilon)\Delta \varepsilon = \phi(\varepsilon + \delta \varepsilon) - \phi(\varepsilon) = \frac{\pi}{4} \left(\frac{8mL^2}{\hbar^2}\right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} \delta \varepsilon + O((\delta \varepsilon)^2)$$

(2) So, function $g(\varepsilon)$ is density of states in energy $\varepsilon$.

To calculate total energy for cell with $\Delta N$ electron, we need probability of the state with the occupied energy $\varepsilon$ which is called $f(\varepsilon)$. This scattering is Fermi–Dirac.

$$f(\varepsilon) = \frac{1}{1 + e^{\beta (\varepsilon - \mu)}}$$

(3)

Now, we obtain total energy of electrons in this cell with sum of dispersions from different energy states.

$$\Delta E = 2 \int g(\varepsilon) f(\varepsilon) d\varepsilon = 4\pi \left(\frac{2m}{\hbar^2}\right) \frac{3}{2} L^3 \int_{0}^{\infty} \varepsilon^{\frac{3}{2}} d\varepsilon = \frac{8\pi}{5} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} L^3 \varepsilon_f^{\frac{5}{2}}$$

(4)

Fermi energy $\varepsilon_f$ relating to the number of electrons $\Delta N$ in the cell is obtained:

$$\Delta N = 2 \int f(\varepsilon) g(\varepsilon) d\varepsilon = \frac{8\pi}{3} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} L^3 \varepsilon_f^{\frac{3}{2}}$$

(5)

By calculating shares of all cells (sum of share of all cells), total kinetic energy is obtained.

**DISCUSSION OF SIMULATION RESULTS**

Fluorographene has insulating properties and direct band gap of fluorographene has been calculated 3.1 ev but direct band gap of 3.5 ev has been obtained for armchair of the fluorographene. Acoustic mode has been attributed to fluorine atoms and high frequency mode has clear carbon characteristic. In the performed calculations, it has been shown that phonon spectrum and density of states don’t show phonon for armchair (Karlicky, 2013). To study electrical and structural properties of fluorographene, we study them with density functional theory method. We have simulated and optimized armchair of fluorographene molecule with DFT method with Gussian 09 software with B3LYP basic function.
Blue tubes are fluorine atoms and gray tubes are carbon atoms in each hexagonal corner and bond between carbon-carbon atoms and carbon–fluorine atoms has been marked with dark gray tube. Form of bond between fluorine and carbon atoms is that each carbon atom is connected to fluorine atom from top of the plane or at the bottom of the plane so that if fluorine atom is connected from the bottom of the plane to carbon atom, neighbor atoms are connected from top of the graphene plane to fluorine atom and vice versa. Each fluorine atom makes approximate angle of 90 degrees with graphene plane.

Armchair of the fluorographene along with basic vectors and high symmetry points $\Gamma$, $M$ and $\kappa$ is shown in Figure 2.

We first study graphene. We have shown Homo and Lumo molecular orbitals for 20 cyclic graphene in Figure 3.

Energy levels of 20 cyclic graphene are shown in Figure 4. We can observe orbital energies of Homo and Lumo orbitals in this Figure.
Theoretical calculations show that electrical properties of graphene derivatives such as band gap can be changed by changing impure compounds. DFT calculations of electronic structure of graphene and halogenated graphene derivatives (fluorographene and other comparable graphene halides) show that basic set of orbital limited to a zone can be successfully and effectively used for such two-dimensional matters. For this purpose, we fluorinate the graphene to open its band gap and use electrical properties of fluorinated graphene.

Homo and Lumo molecular orbitals and energy levels for tricyclic fluorographene are shown in Figures 5 and 6.

Comparison of graphene and tricyclic fluorographene energy levels shows that graphene has full Homo orbital and tricyclic fluorographene has half-filled Homo orbital. Since half-filled orbital weakens stability (full Homo orbital indicates stability of molecule and half-filled orbital reduces stability of molecule). We conclude that fluorographene is less stable than graphene due to having half-filled Homo orbital (on the contrary, graphene has higher stability due to having full Homo orbital). In molecular orbitals 96 and 97 (in both spin orbitals), many energy
changes occur (for example, in spin orbital $\beta$, we reach from -0.32ev in molecular orbital 96 to -0.2 in molecular orbital 97). This shows intensive increase of orbital energy and as a result, we see considerable decrease of stability. Hence, we conclude that although band gap of graphene is opened (for electrical applications) by fluorinating the graphene, stability of graphene molecule is considerably reduced through fluorination. It is necessary to note that the reason that two energy levels have been considered for tricyclic fluorographene is that energy level of the right side relates to spin orbital $\beta$ and energy level of the left side relates to spin orbital $\alpha$ and Lumo and Homo molecular orbitals are different for each one of the spin orbitals because the last orbital of the molecule is half-filled as shown in Figure 6.

Now, we increase the number of cycles to study effect of cycles increase (or enlargement of molecule) on stability of molecule. Lumo and Homo molecular orbitals and energy level for six cyclic fluorographene are shown in Figures 7 and 8.

By observing energy levels of six cyclic fluorographene, we find that Homo molecular orbital of six cyclic fluorographene is full. We also see small mutation of energy from molecular orbital 162 to molecular orbital 163 and smaller mutation of energy from molecular orbital 163 to molecular orbital 164 but we don’t see sudden increase of orbital energy level which we observed in tricyclic fluorographene. In general, stability of the six cyclic fluorographene is higher than that of tricyclic fluorographene molecule (due to paired Homo orbital and mutation with less mutation than the tricyclic molecule). Effect of the number of cycles on specifications of the structure is that when the number of cycles increases, the number of energy levels increases and as a result, the number of Lumo and Homo orbitals increases. To study stability of five quantities of polarizability, hardness, dipole moment and total energy of system and energy difference, we calculate Lumo and Homo orbitals for each one of the molecules of 20 cyclic graphene, tricyclic fluorographene and six-cyclic fluorographene and study effect of these quantities on stability of these molecules and finally compare systems with each other in terms of stability.

We first study 20 cyclic molecule of graphene. Total energy of the system and dipole moment of the system are obtained from output of Gaussian energy calculations:
E(RB3LYP)= -2322/55683071 A.U. Dipole moment= 2/0067 debye

The more the dipole moment of the system, the more stable the molecule and the less the system energy, the more stable the molecule will be. We calculate polarizability of molecule with the following formula:

$$\alpha = \frac{XX + YY + ZZ}{3}$$

(6)

Where XX, YY and ZZ are dipole moment almond axes x, y and z and $\alpha$ is polarizability of molecule. The less the polarizability of molecule, the more stable the molecule will be (Kataraj and San Gopta, 1996). With formula 6, we obtain for the 20 cyclic molecule of graphene:

$$\alpha = 0/32656$$ debye

We obtain energy of Lumo and Homo orbitals from Gaussian output:

$E_{\text{Homo}}$= -0/29598 ev , $E_{\text{Lumo}}$= -0/29249 ev

From energy difference of Lumo and Homo orbitals, we have:

$$E_{\text{Lumo}} - E_{\text{Homo}} = 0/00349$$ ev

The less the energy difference of Lumo and Homo orbitals, the softer and the less stable the molecule will be and vice versa. In other words, the larger the distance between Lumo and Homo molecular orbitals, the harder and more stable the molecule will be.

We now calculate hardness but briefly introduce it. Hardness is measurement of resistance of different types of solid matter against stable deformation when a force is applied. Macroscopic hardness has been specified with strong intermolecular bonds but behavior of solid matter under force is complex. Hardness depends on ductility, plasticity, strain, strength etc. here, we calculate hardness of molecule more carefully with hardness formula. To obtain hardness, we first calculate electron affinity (IP) and ionization potential (EA):

$$IP = E_{\text{Homo}} , \quad EA = -E_{\text{Lumo}}$$

(7)

$$\text{hardness} = \frac{IP - EA}{2}$$

(8)

(Chattaraj, 1996). For hardness of molecule, we have 20-cyclic graphene:

$$\text{hardness} = 0/001745$$ ev

We now study tricyclic fluorographene molecule. Dipole moment and total energy of the related system are as follows:

E(RB3LYP)= -1792/56961537 A.U. Dipole moment= 1/1103 debye

By comparing these results with 20-cyclic graphene molecule, we conclude that dipole moment of 20-cyclic molecule of graphene is much higher than tricyclic molecule of fluorographene and this makes 20-cyclic graphene molecule more stable than tricyclic fluorographene molecule. Total energy of graphene system is less than total energy of tricyclic fluorographene system and this leads to more stability of 20-cyclic graphene molecule than tricyclic fluorographene.

We calculate polarizability and distance between Lumo and Homo orbitals and hardness of tricyclic fluorographene molecule:

With formula 6 for polarizability, we have:

$$\alpha = -0/3978$$ debye

We see that polarizability of tricyclic fluorographene molecule is less than polarizability of 20-cyclic graphene molecule and as a result, it increases stability of tricyclic fluorographene.

Since we have two spin orbitals $\alpha$ and $\beta$, we separately calculate hardness of molecules considering each one of the spin orbitals $\alpha$ and $\beta$.

We calculate orbital energy difference and hardness for spin orbital $\alpha$ and $\beta$:

$E_{\alpha\text{Homo}}$= -0/21771 ev , $E_{\alpha\text{Lumo}}$= -0/1969 ev

$E_{\alpha\text{Lumo}} - E_{\alpha\text{Homo}} = 0/02602$ ev

$$\text{hardness}_{\alpha} = \frac{-E_{\text{Homo}} + E_{\text{Lumo}}}{2} = \frac{+0/21771 - 0/1969}{2} = \frac{0/02602}{2} = 0/01301$$ ev

$E_{\beta\text{Homo}}$= -0/21774 ev , $E_{\beta\text{Lumo}}$= -0/21771 ev

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\[ E_{\beta\text{Lumo}} - E_{\beta\text{Homo}} = 0/00003 \text{ ev} \]
\[ \text{hardness}_S = \frac{-E_{\text{Homo}} + E_{\text{Lumo}}}{2} = \frac{+0/21774 - 0/21771}{2} = 0/00003 = 0/00015 \text{ ev} \]

We said that the harder the molecule the more stable the molecule will be. The obtained hardness of graphene molecule is higher than the calculated hardness for tricyclic fluorographene for both spin orbitals \( \alpha \) and \( \beta \) and as a result, stability of the graphene molecule is higher than that of tricyclic fluorographene molecule and this confirms the previous results in study of molecular orbitals. The larger the distance between Lumo and Homo molecular orbitals, the harder and more stable the molecule will be. Difference of orbital energies relating to spin orbital \( \alpha \) of tricyclic fluorographene molecule is higher than difference of orbital energies of 20-cyclic graphene but difference of orbital energies relating to spin orbital \( \beta \) of tricyclic fluorographene molecule is much lower than difference of orbital energies of 20-cyclic graphene. We conclude that more hardness, lower system energy, higher dipole moment and larger difference of Lumo and Homo molecular orbitals in spin orbital \( \beta \) make 20-cyclic graphene molecule more stable than tricyclic fluorographene molecule and these results confirm the previous results obtained from comparison of energy levels of these two molecules.

Now, we study six-cyclic fluorographene molecule. The quantities are obtained as discussed in the previous sections.

\[ E(\text{RB3LYP}) = -3030/43111373 \text{ A.U.} \]

Dipole moment = 0/1514 debye
\[ \alpha = -0/0444 \text{ debye} \]
\[ E_{\text{Homo}} = -0/22134 \text{ ev}, \quad E_{\text{Lumo}} = -0/20624 \text{ ev} \]
\[ E_{\text{Homo}} = 0/01510 \text{ ev} - E_{\text{Lumo}} \]
\[ \text{hardness} = 0/00755 \text{ ev} \]

By comparing these results with results of tricyclic fluorographene, we conclude that energy of six-cyclic fluorographene molecule is lower and more stable. Six-cyclic dipole moment is lower than tricyclic dipole moment and as a result, it decreases stability of six-cyclic fluorographene molecule. Polarizability of six-cyclic fluorographene molecule is less than that of tricyclic graphene molecule and as a result, it makes six-cyclic fluorographene molecule more stable. Energy difference of Lumo and Homo orbitals in six-cyclic graphene molecule shows energy difference of molecular orbitals of tricyclic fluorographene molecule and spin orbitals of \( \alpha \) and \( \beta \). Hardness of six-cyclic fluorographene molecule shows the difference between hardness of tricyclic fluorographene molecule for spin orbitals \( \alpha \) and hardness of tricyclic fluorographene for spin orbital \( \beta \). We conclude that low polarizability, low energy, high hardness and large distance between Lumo and Homo orbitals in orbital \( \alpha \) of this molecule increase stability of six-cyclic fluorographene molecule. Only low dipole moment decreases stability of fluorographene which has no considerable effect and we conclude that stability of six-cyclic fluorographene molecule is higher than that of tricyclic fluorographene molecule which confirms the obtained results for comparison of the molecular orbitals of these two molecules.

**CONCLUSION**

In this paper, we studied two-dimensional crystals based on graphene, fluorographene. To study electrical and structural properties, we studied it with density functional theory method. This method has been performed with Gaussian software and B3LYP base function. In this paper, we considered fluorographene as armchair and studied its stability with DFT method and with base set of 6-31G. It has been shown that tricyclic fluorographene molecule is less stable than graphene and with increasing the number of cycles and enlarging molecule of fluorographene, its stability also increases. Homo orbital is full in graphene and fluorographene and half-filled in tricyclic fluorographene. Energy rate of orbitals in energy level of graphene uniformly increases while there is sudden mutation from orbital 96 to orbital 97 in tricyclic fluorographene. We studied stability of 20-cyclic graphene systems, tricyclic fluorographene and six-cyclic fluorographene with five quantities of polarizability, hardness, dipole moment and total energy of system and distance between Lumo and Homo molecular orbitals and confirm the obtained results for stability of molecules for study of molecular orbitals.
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