Lee-Yang-Parr (B3LYP) Density Functional Theory Calculations of Di-Cyano Naphthalene Molecules Group

Mohsin K. AL-Khaykanee
College of Science – Babylon University – Hilla - Iraq
*Email- mohsin_7704@yahoo.com

Abstract

The electronic properties of cyanonaphthalene molecules group were investigated depending on the B3LYP density functional theory. The best geometry for the structures of the studied molecules was investigated by using 6-31G** basis set. Total energies, electronic states, energy gaps, ionization potentials and electron affinities were calculated. As a result, the total energy for naphthalene was decrease linearly with the number of side group added to the ring. The forbidden energy gap was reduced and 1,3dicyanonaphthalene molecule has the smallest value.

Keywords: DFT, Lee-Yang-Parr, Ionization potential, Electron affinity, Electrophilic index

1. Introduction

Aromatic compounds are important in industry and play key roles in the biochemistry of all living things [1]. The organic semiconductor materials, such as, conjugated organic molecules have been widely used as active materials for optoelectronic devices such as light emitting diodes[2-5], field effect transistor[6-9], and photovoltaic and solar cells[10,11]. The organic thin film transistors are one type of the so called organic devices, in which they fabricated by using the organic semiconductors [12]. These materials have advantages of easy fabrication, mechanical flexibility and low cost. There are many organic materials show useful field effect transistor performance, which can be characterized by their carrier mobility and on/off current ratios [13, 14].

Many studies on cyclic oligomers have been reported both experimentally and theoretically [15, 16], in [17] the substituent effects of oligomers such as oligothiophene, oligopyrrole and oligofuran are discussed in terms of reorganization energy. Also, [18] studied the geometric and electronic properties for cyanothiophene oligomers as a prototype of an organic conducting polymer using ab initio and density functional theory, and they showed that the cyano group generally reduced the band gap with variation of the substitution position.

In present work, density functional theory has been performed to study the electronic properties of the dicyanoaromatic molecules to determine the effects of the substituent position.

2. Computational details

Chart 1 represents the molecules under study. The optimization of molecular geometries and analyses of vibration frequencies have been done by employing Gaussian 03[19] package of programs at the density functional theory level by using three parameters Lee-Yang-Parr (B3LYP) functional with 6-31G basis sets. The hybrid functional B3LYP has shown to be highly successful for calculation the electronic properties such as ionization potentials, electronic states and energy gaps [20-22].
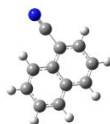
According to B3LYP functional, the exchange correlation energy E_{xc}^{B3LYP} is given by [23, 24]:

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0 \left(E_x^{HF} - E_x^{LDA} \right) + a_x \left(E_x^{GGA} - E_x^{LDA} \right) + a_c \left(E_c^{GGA} - E_c^{LDA} \right)$$

Where the three parameters $a_0=0.20$, $a_x=0.27$ and $a_c=0.81$
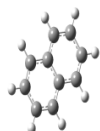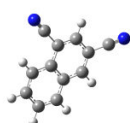

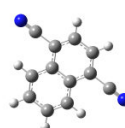Naphthalene   1, monocyano-naphthalene   1, 2, dicyano-naphthalene

1, 3, dicyano-naphthalene   1,4dicyano-naphthalene

Chart. 1: The structures of studied molecules

3. Results and discussion

Table (1) represents the results of the total energy and electronic states for the analyzed structures of the studied molecules. It is clear that from table (1), the total energy for all new molecules depends on the number of side groups adding to the ring. The total energy is decreasing with the increase of the radicals number as a linear relationship, this indicates that the addition give the molecule more stability. In the other hand, the total energy for all dicyanonaphthalene molecules is approximately the same in which this refer to that the total energy is independent on the position of the dicyano radical in the ring, as we see in figure (1).

B3LYP functional used in this study has a high efficient to calculate the electronic properties for the organic studied molecules, such as ionization potentials(IP), electron affinities(EA), electronic chemical potentials(k), hardness(η), electrophilicities(w) and energy gaps(E_g). Figure (2) declare that the ionization potential for the cyan naphthalene molecules group is greater than that for the naphthalene molecule, but the 1,4dicyanonaphthalene molecule has the largest value of ionization potential, this indicates that the naphthalene molecule needs small energy to become cation comparing with the others. Adding the radical to the ring leads to increasing the ability of the electron affinity for the molecule, the electron affinity for 1,3dicyanonaphthalene molecule is the largest, as we see in figure (3). The results in figure (3) mean that these cyan naphthalene molecules group need large energy to become anion in comparing with naphthalene.

Figures (4) and (5) represent the behavior of chemical potential and hardness for the studied molecules as a function of side groups' number, respectively. It is obvious from these figures that the   group molecules have chemical potential and hardness less than these for the original ring, adding the radicals give the molecule more softness.

The electrophilicity for studied molecules as a function of side groups' number is shown in figure (6). The substitution of the side groups reduced the population in the high occupied molecular orbital, and this led to a decrease in the energy gap for the original ring, this effect of the side group was the largest in 1,3dicyanonaphthalene molecule in which it has energy gap of (4.076 eV), as shown in figure (7).

4. Conclusions

In order to elucidate the positional preference in cyano side groups on naphthalene molecule, we have estimated total energy of cyan naphthalene molecules at the basis of B3LYP/6-31G**. The total energy for the naphthalene ring were reduced linearly with the number of adding side groups, and the origin of the reduction was attributed to the electron localization on the side group in the highest occupied molecular orbital. This ionization led the molecules have reduced energy.

The electronic chemical potential for cyan naphthalene molecules are lowers values comparing with the original ring. A hard molecule has a large energy gap and a soft molecule has a small energy gap. The cyanonaphthalene molecules are soft with small energy gaps. Therefore, the electron densities for these molecules are changing more easily than for naphthalene, thus these molecules may be more active compared with naphthalene.

The decreasing of the forbidden energy gap for the cyan naphthalene molecules group compared with the original ring comes from the effect of the side group added to the ring, a small energy gap means small excitation energies of manifold of the excited states.

References:

1. K. J. Denniston, J. Topping and T. M. Dwyer", General Organic and Biochemistry", 5th Edition, Towson University, 2007.

2. C. Tang, S. A. VanSlyke, Appl. Phys. Lett, 51, 913, 1987.

3. J. H. Burroughes, D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, Nature (London), 347, 539, 1990.

4. J. R. Sheats, H. Antoniadis, M. hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman and A. Stocking, science, 273, 884, 1996.

5. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, Nature (London), 397, 121, 1999.

6. F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava, Science, 265, 1648, 1994.

7. G. Horowitz, D. Fichou, X. Z. Peng, Z. G. Xu, F. Gamier, Solid State Commun, 72, 381, 1989.

8. G. Horowitz, Adv. Mater, 10, 365, 1998.

9. H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y. Y. Lin, A. Dodabalapur, Nature (London), 404, 478, 2000.

10. G. Yu, J. Wang, J. Mc Elvain, A. Heeger, Adv. Mater, 10, 1431, 1998.

11. C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, Adv. Funct. Mater, 11, 15, 2001.

12. H. E. Katz, J. Mater. Chem, 7, 369, 1997.

13. H. Klauk, D. J. Gundlach, M. Bonses, C. C. Kuo, T. Jackson, Appl. Phys. Lett, 76, 1692, 2000.

14. T. W. Kelley, D. V. Muyres, P. F. Baude, T. P. Smith, T. P. Jones, Mater. Res. Soc. Symp. Proc, 771, 169, 2003.

15. M. D. Curtis, J. Cao, J. W. Kampf, J. Am. Chem. Soc, 126, 4318, 2004.

16. S. E. Koh, C. Risko, D. A. de Silva Filho, O. Kwon, A. Facchefti, J. L. Bredas, T. J. Marks, M. A. Ratner, Adv. Funct. Mater, 18, 332, 2008.

17. G. R. Hutchison, M. A. Ratner, T. J. Marks, J. Am. Chem. Soc, 127, 2339, 2005.

18. M. A. De Oliveira, H. F. Dos Santos, W. B. De Almeida, In. J. Quan. Chem, 90, 603, 2002.
19. M. J. Frisch and J. A. Pople, Gaussian 03, Inc. Pittsburgh PA, (2003).

20. J. Engelberts, R. Havenith, J. Van Lenthe, L. Jenneskens, P. Fowler, Inorg. Chem, 44, 52266, 2005.
21. J. C. Santos, W. Tiznado, R. Contreras, P. Fuentealba, J. Chem. Phys, 120, 1670, 2004.
22. J. C. Santos, J. Andres, A. Aizman, P. Fuentealba, J. Chem. Theory Comput, 1, 83, 2005.
23. H. Dorsett and A. White, " Overview of Molecular and Ab Initio Molecular Orbital Methods Suitable For Use With Energetic Materials", Aeronautical ana Maritime Research Laboratory, Australia, 2000.
24. G. E. Scuseria and V. N. Staroverov, " Progress in the development of exchange-correlation functional ", Elsevier, Amsterdam, 2005.

Table (1): Total energy and electronic states for molecules

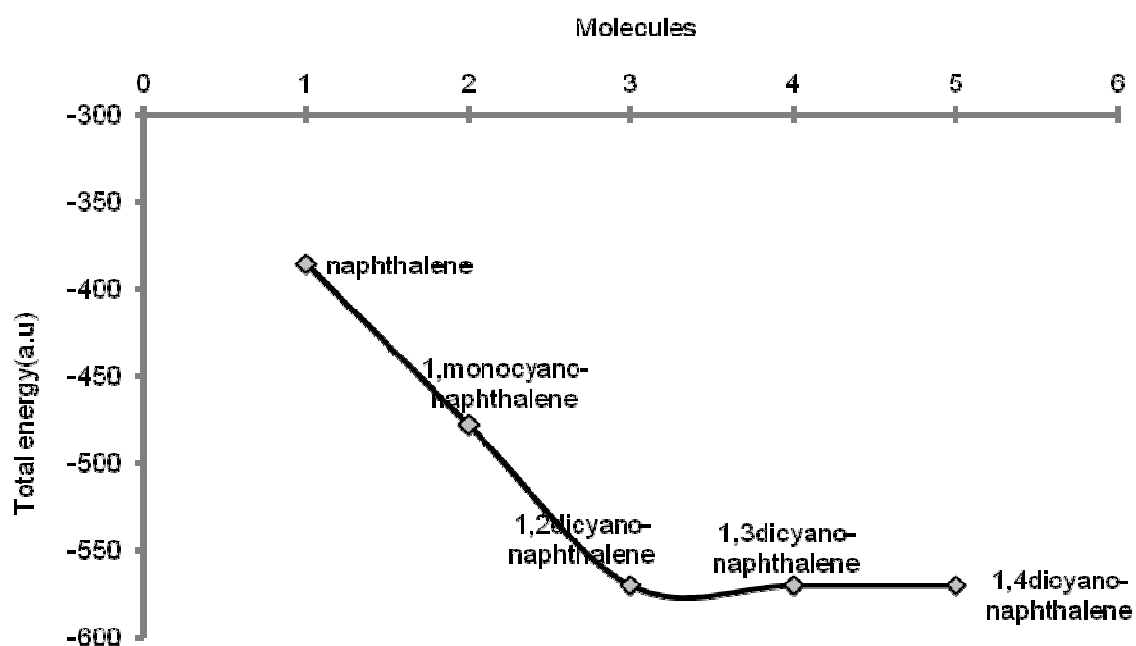| structure	symbol	energy(a.u)	electronic states(eV)	
			HOMO	LUMO
naphthalene	1	-385.8076	-0.96187	-5.82512
1,monocyano naphthalene	2	-478.0192	-1.90007	-6.37204
1,2dicyano-naphthalene	3	-570.2239	-2.67365	-6.86263
1,3dicyano-naphthalene	4	-570.2272	-2.78113	-6.85774
1,4dicyano-naphthalene	5	-570.2280	-2.57434	-6.96304

www.iiste.org

IISTE

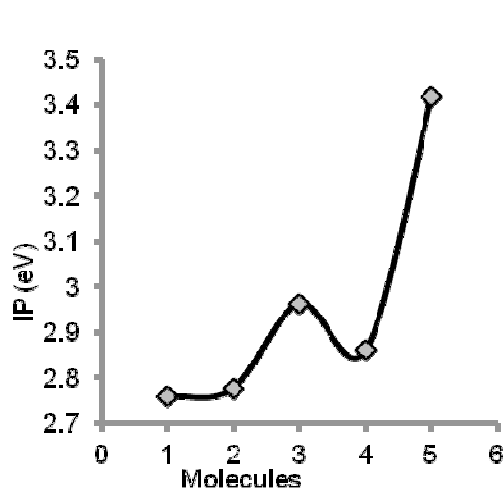Figure (1): Total energy as a function of radicals' number

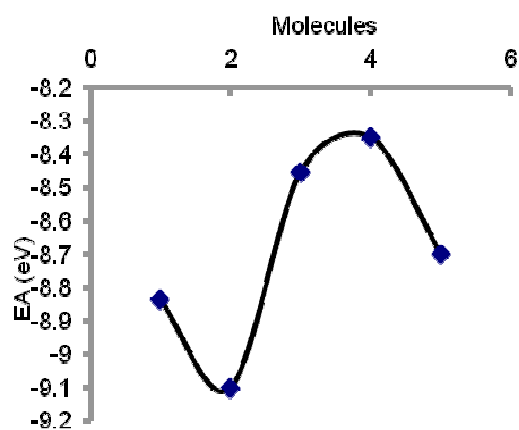Figure (2): The ionization potential for studied molecules

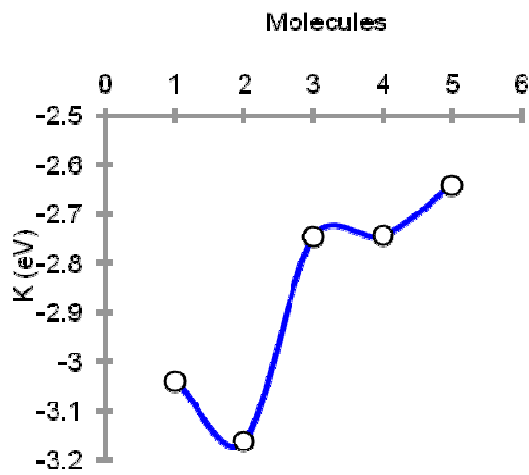Figure (3): The electron affinity for studied molecules

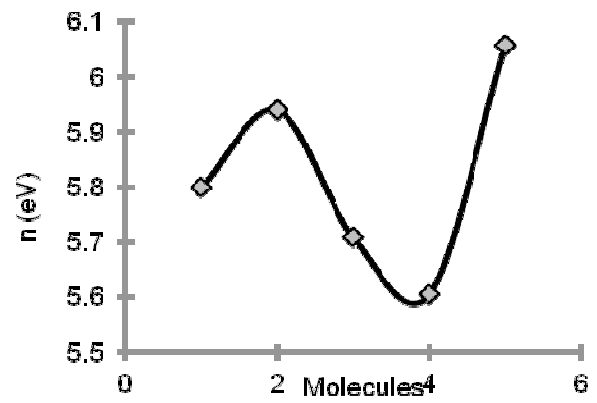Figure (4): The chemical potential for studied molecules
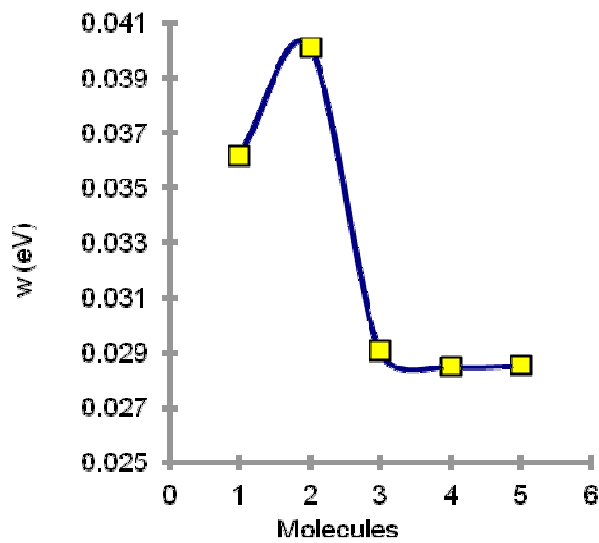

Figure (5): The hardness for studied molecules

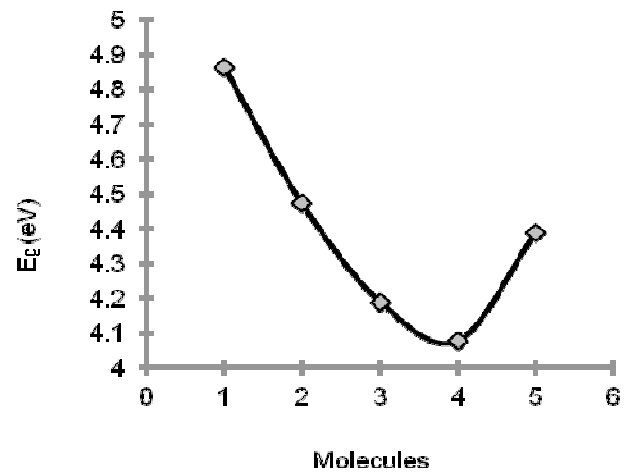Figure (6): The electrophilicity for studied molecules

Figure (7): The forbidden energy gap for studied molecules

CALL FOR PAPERS

The IISTE is currently hosting more than 30 peer-reviewed academic journals and collaborating with academic institutions around the world. There's no deadline for submission. **Prospective authors of IISTE journals can find the submission instruction on the following page:** http://www.iiste.org/Journals/

The IISTE editorial team promises to the review and publish all the qualified submissions in a **fast** manner. All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Printed version of the journals is also available upon request of readers and authors.

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar