THEORETICAL STUDY OF 1 AND 4 BENZOQUINONE AND DIFLUORO DERIVATIVES OF BENZOQUINONE ON ZINC OXIDE NANO PARTICLES BY DFT METHOD

Mohsen Oftadeh*, Bahman Barati

Chemistry Department, Payame Noor University, 19395-4697, Tehran, I. R. of Iran

ABSTRACT

This study investigates some aspects of interaction between 1 and 4 benzoquinone (BQ) and fluoro derivatives of 1, 4-BQ on surface of zinc oxide nanopatricles theoretically with using density functional method (B3LYP) and 6-31G as basis set. The significant quantities include HOMO, LUMO, chemistry potential, hardness and dipole moment have been computed and compared. The highest gap energy and the most hardness can be referred to the 1, 4- difluoro benzoquinone compared with two another derivatives, 2,5- and 2,6- difluoro benzoquinone. This interaction showed that these groups stabilize the rest of zinc oxide as blend.

Key words: gap energy, DFT, zinc oxide blend, benzoquinone, dipole moment, hardness

INTRODUCTION

With development of scientific programs and powerful computer programs many theoretical studies have been possibly done on the material sciences. These studies will communicate between mid-conductive metal oxide and other blends. These mid-conductive are important and they use as catalyst on photo catalytic systems, destroy environmental pollutions, transistors, and sunny cells [1-3]. For instance, the mid-conductive of zinc oxide (ZnO) is an ionic mid-conductive as grain color, energy wide band in 3.37 ev, and free energy in 60 MV in room's temperature and has important role on making industry catalyses systems [4-5]. Quinones are blends that can be coupled with DNA. Para benzoquinone has known and has been shown that it is anti aromatic [6]. Hydroquinone and specially its form oxide have poisoning effects on bio molecules [7]. Quantum chemistry obtains a lot of information about electronic structure and numeral frame. In this research, in order to do computations, we used density functional theory (DFT). High computational time for the large molecular systems was main motivation for using DFT. At present, DFT is a standard device for solution of quantum chemistry problems, especially in nano calculations [8, 9].

* e-mail: m_oftadeh@pnu.ac.ir

COMPUTATIONAL METHOD

Accordance to theoretical concepts, benzoquinone and difluoro derivatives are enough small and have tended to theoretical computations. In this research, the interaction of these compounds with the surface of zinc oxide $(ZnO)_n$ in wurtzite have been investigated by using Gaussian 03 program at B3LYP/6-31G** level of theory. The significance quantities, like as HOMO and LUMO energies, gap energies, chemical potentials (μ), hardness and dipole moments (P) were computed and compared.

RESULTS AND DISCUSSION

First 1, 4-BQ and Fluoro derivatives of 1, 4-BQ was studied at B3LYP/6-31G** level of theory. The results have been collected in *Table 1*.

Table 1 – HOMO, LUMO, gap energy, potential energy, hardness and dipole moment calculated at B3LYP/6-31G** level of theory in gas phase for 1,4-BQ and their fluro derivatives

Molecule	HOMO (Hartree)	LOMO (Hartree)	Gap energy (Hartree)	μ (Hartree)	η (Hartree)	P (Debye)
BQ	-0.2759	-0.1413	0.1346	-0.2086	0.0673	0.0007
2F BQ	-0.2899	-0.1519	0.1380	-0.2209	0.0690	1.7316
23DF BQ	-0.3050	-0.1623	0.1428	-0.2336	0.0714	2.8427
25DF BQ	-0.3057	-0.1617	0.1440	-0.2367	0.0720	0.0045
26DF BQ	-0.3007	-0.1626	0.1381	-0.2317	0.06901	1.0844
235 TF BQ	-0.3149	-0.1720	0.1429	-0.2435	0.0714	2.7600
FLORIN	-0.3194	-0.1819	0.1375	-0.2507	0.0688	0.0072

The results showed that 2, 3, 5, 6-tetrafluro-1, 4-BQ has the most variation in HOMO and LUMO compared with BQ. So the flurination of BQ leads to increase of the gap energy. Also they cause to increase the hardness and stabilize the BQ. 2, 3-difluro-1, 4-BQ has the highest dipole moment. The next step included the optimization of the $(ZnO)_{4n}$, n=1-3, clusters by using B3LYP/6-31G** method which the results have been showed in *table 2*. By attention to the results of table 2, it shows the HOMO and LUMO levels of energy decrease by increasing the size of ZnO cluster. The highest gap energy and stability are related to $(ZnO)_{12}$.

Table 2 – HOMO, LUMO, gap energy, potential energy, hardness and dipole moment calculated at B3LYP/6-31G** level of theory in gas phase for (ZnO)2n, n=1-3, clusters

$(ZnO)_{4n}$ n=1,2,3	HOMO (Hartree)	LOMO (Hartree)	Gap energy (Hartree)	μ (Hartree)	η (Hartree)	P (Debye)
$(ZnO)_4$	-0.2462	-0.1318	0.1144	-0.1890	0.0572	0.0262
$(ZnO)_8$	-0.2408	-0.1250	0.1158	-0.1829	0.0579	0.0154
$(ZnO)_{12}$	-0.2371	-0.1118	0.1252	-0.1745	0.0626	0.8476

This is the quantum size effect. $(ZnO)_{12}$ cluster has the lowest potential energy and it's stability is high. This cluster has the highest hardness and dipole moments.

The third step was the computing of these quantities for the 1, 4-BQ derivatives adsorbent on the $(ZnO)_8$ cluster by the method. *Table 3* showed these results for the combined systems.

Table 3 – HOMO, LUMO, gap energy, potential energy, hardness and dipole moment calculated at B3LYP/6-31G** level of theory in gas phase for combined 1, 4-BQ derivatives and $(ZnO)_8$ cluster systems

System	HOMO (Hartree)	LOMO (Hartree)	Gap energy (Hartree)	μ (Hartree)	η (Hartree)	P (Debye)
$(ZNO)_8$+BQ	-0.2230	-0.1803	0.0426	-0.2017	0.0213	7.1316
$(ZNO)_8$+2FBQ	-0.2270	-0.1878	0.0393	-0.2074	0.0196	4.7501
$(ZNO)_8$+23DF BQ	-0.2263	-0.1981	0.0282	-0.2122	0.0141	7.1735
$(ZNO)_8$+25DFBQ	-0.2391	-0.1667	0.0724	-0.2029	0.0362	7.6515
$(ZNO)_8$+26DFBQ	-0.2391	-0.1669	0.0722	-0.2030	0.0361	2.3461
$(ZNO)_8$+235TFBQ	-0.2314	-0.2062	0.0252	-0.2188	0.0126	3.4259
$(ZNO)_8$+FLORINE	-0.2312	-0.2009	0.0303	-0.2161	0.0151	0.7346

The flurination of the BQ cause to decrease the HOMO and to vary the LUMO compared to the BQ on the ZnO cluster. The highest HOMO is related to the 2, 6-difluro-1, 4-BQ, and the highest variation on the LUMO is related to 2, 3, 5-trifluro-1, 4-BQ. The lowest chemical potential energy and the highest hardness are related to 2, 3, 5, 6-tetrafluro-1, 4-BQ and 2, 5-difluro-1, 4-BQ, respectively. So the second system has the highest stabilize. Such trend was observed in dipole moments for the systems so that the highest value is related to 2, 5-difluro-1, 4-BQ.

Also, we observed that fluoro blends of 1, 4-BQ cause to be changing on (LUMO) and (HOMO) energy in comparison with 1, 4-BQ when they are absorbed on the surface of ZnO cluster. The quantities of the gap energy showed that 2 ,5-difluoro-1, 4-BQ has the highest hardness and stability in comparison with rest of zinc blends.

After absorption of 1, 4-BQ and fluoro derivatives on the surface of the zinc oxide blends, the HOMO and LUMO energies of zinc oxide blends decrease and increase, respectively. By attention to the gap energies and therefore to the hardness, 2 ,5-difluoro-1, 4-BQ and 2 ,6-difluoro-1 ,4-BQ cause to be more stability of zinc oxide in comparison with the rest of fluoro blends.

CONCLUSIONS

The stability of the blends affects on what ever the size of blends and it became greater the stability of blend when the size will be increased. Also, the results showed that the fluorine groups on the benzoquinone cause to be chang-

ing on LUMO and HOMO energy. The quantities of the gap energy and hardness for these blends showed that 2, 5- and 1,4-difluoro benzoquinone in comparison with rest of zinc blends, increased. After absorption of 1, 4- difluoro benzoquinone on the blends HOMO and LUMO decreases and increases compared with the rest of blends, respectively. The highest gap energy and the most hardness can be refer to the 1, 4- difluoro benzoquinone compared with two another derivatives, 2,5- and 2,6- difluoro benzoquinone. This interaction showed that these groups stabilize the rest of zinc oxide as blend.

REFERENCES

[1] Xueli Cheng, Feng Li and Yanyun Zhao, Journal of Molecular Structure: THEOCHEM 894 (2009) 121.
[2] J. Pollmann, P. KNger, M. Rohlfing, M. Sabisch and D. Vogel, Applied Surface Science 104/105 (1996) 1.
[3] S. Irrera, D. Costa, K. Ogle and P. Marcus, Superlattices and Microstructures 46 (2009) 19.
[4] A. Wander and N.M. Harrison, Surface Science 468 (2000) L851.
[5] A. Wander and N.M. Harrison, Surface Science 457 (2000) L342.
[6] . Aaron Rojas-Aguilar, Honorio Flores-Lara, Melchor Martinez-Herrera and Francisco Ginez-Carbajal, J. Chem. Thermodynamics 36 (2004) 453.
[7] Yuanzhi Song, Jimin Xie, Huoming Shu, Ganqing Zhao Xiaomeng Lv and Hongyan Cai, Bioorganic & Medicinal Chemistry 13 (2005) 5658.
[8] A. K. Rappe, ClJ. Casewit, K. S. Colwell and W. A. Goddard, J. phys. Chem., 94 (1990) 8897.
[9] M. Oftadeh, L. Tavakolizadeh, J. Nano Letters, 2011, in press.