تاثير مجاميع ثنائي امينو على الخواص التركيبية والالكترونية لجزيئة الازولين باستخدام نظرية دالة الكثافة

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The effect of substitution groups (di-amino) on structural and electronic properties of azulene molecular by DFT method.

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Abstract

The effect of substitution groups (di-amino) on structural and electronic properties of azulene molecular is studied theoretically using density functional theory DFT. Based on B3LYP with 6-31(d, p) basis set was used to investigate the effect on the structure and electronic properties for the positional variation of the amino substituent in the azulene by performing Gaussian 09 program. The optimized structures, total energies, electronic states (HOMO-LUMO), energy gaps, electron density and electrostatic potential surfaces ionization potentials, electron affinities, global hardness, softness and dipole moment were calculated.

Keywords: B3LYP/DFT calculations, azulene molecule, di-amino group, energy gap, Ionization potential.

الخلاصة

دراسة تاثير مجاميع ثنائي امينو على الخواص التركيبية والالكترونية لجزيئة الازولين دراسة نظرية عن طريق استخدام نظرية دالة الكثافة، بالاعتماد على دالة لي-ينك-بار ذات المعاملات الثلاث مع مجموعة أساس 6-31(d, p) ، حيث تم استخدام مجموعة الاساس هذه لمعرفة مدى تاثر الخواص التركيبية والالكترونية لجزيئة الازولين عندما توضع مجاميع ثنائي امينو في مواضع مختلفة في جزيئة الازولين عن طريق استخدام برنامج كاوس 09. تم حساب التراكيب المثلى، الطاقات الكلية، الحالات الالكترونية، فجوات الطاقة، سطوح الكثافة الالكترونية والجهد الكهروستاتيكي، الجهود الايونية، الالفة الالكترونية والصلابة ، الليونة وعزم ثنائي القطب.

الكلمات المفتاحية: حسابات نظرية دالة الكثافة، جزيئة الازولين، مجاميع تنائي امينو، فجوة الطاقة، الجهد الايوني.

1. Introduction

Azulene is a bicyclic,nonbenzenoid aromatic hydrocarbon as shown in figure (1) and is an isomer of naphthalene. Azulenes have long been of interest to chemists due to their striking colours, interesting chemistry and unusual electronic properties. Azulene derivatives may be used as advanced materials for optoelectronic [Kurotobi K et al, 2006, Murai M et al, 2017] and electrochromic [Ito.S et al, 2009] devices, charge-transport [Yamaguchi Y et al, 2016, Wang F et al, 2004] nonlinear optics and chemical sensing [Lopez-Alled CM et al, 2017] some recent reviews serve to summaris these areas [Xin H et al,2017, Dong J-X et al, 2016]. Some azulene derivatives have also been shown to have anti-inflammatory [Ramadan M et al, 2006, Rekka E et al, 2002] antiulcer [Zhang L-Y et al, 2011, Yanagisawa T et al, 1988] anticancer [Sekine T et al, 2007,

Ishihara M et al, 2011] and anti-HIV [Peet J et al, 2016] properties. In theoretical chemistry ; the fundamental laws of the physics are combined with mathematical methods to study progressions of chemical relevance. Computational chemistry, also called molecular modeling, is important and basic that is applied in the molecular science research [D. Young, 2001].The molecular modeling methods and physicians are now pervasive used to investigate computationally many properties such as energies of molecules,molecular geometries, electronic structure, electron and charge distributions, infrared(IR), ultra-violet (UV), nuclear magnetic resonance (NMR) spectra, and the physical properties of the biological, inorganic, organometallic, polymeric, catalysis drug and other molecular systems [Y. Wang, 2014, D. D. Fitts, 2002, A. Hamid, 2004]. In this paper, we studied the electronic structure of azulene compound by using Density Functional Theory (DFT) employing Gaussian 09 suite of programs [Frisch M. J et al, 2009]. The aim of this work is the theoretical investigation of the effect of substitution groups (di-amino) on structural and electronic properties and the reactivity of azulene molecular by DFT method

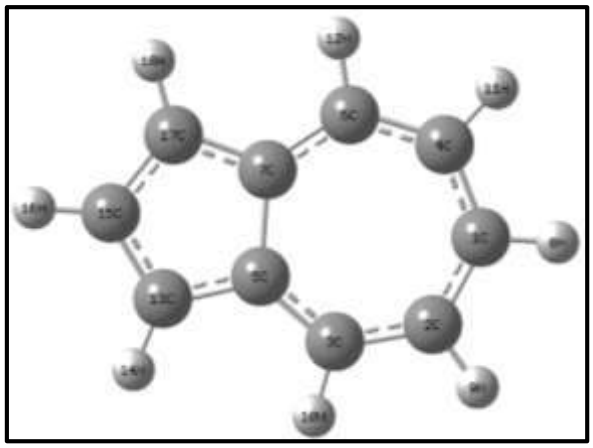

*Figure **1. Azulene structure estimated by DFT/B3LYP/6-31G* calculations.***

2. Theory

The effect of substitution groups (di-amino) on structural and electronic properties of azulene molecular has been studied by Density Functional Theory (DFT). Three parameters B3LYP density functional theory with 6-31G (d, p) basis set [R. Jeffrey Reimers, 2011, R. O. Jones, 2015, V. Sahni, 2010, P. J. Stephens, 1994] are used in this paper to perform the ground state calculations. Full geometry optimizations of azulene molecule was drawn on Gauss View 5.0.8 [D.D. Roy et al, 2009] and relax using the Gaussian 09 package of programs [Frisch M. J et al, 2009] as shown in figure (2). The hybrid exchange-correlation functional B3LYP is very effective for computation the electronic properties of azulene molecule such as the total energy, energy of highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbital (LUMO), energy gap, ionization potential (IP), electron affinity (EA), hardness (H) and softness (S) [C. Zhan et al, 2003, Y. Karzazi et al, 2016, A. Hinchliffe, 2003].

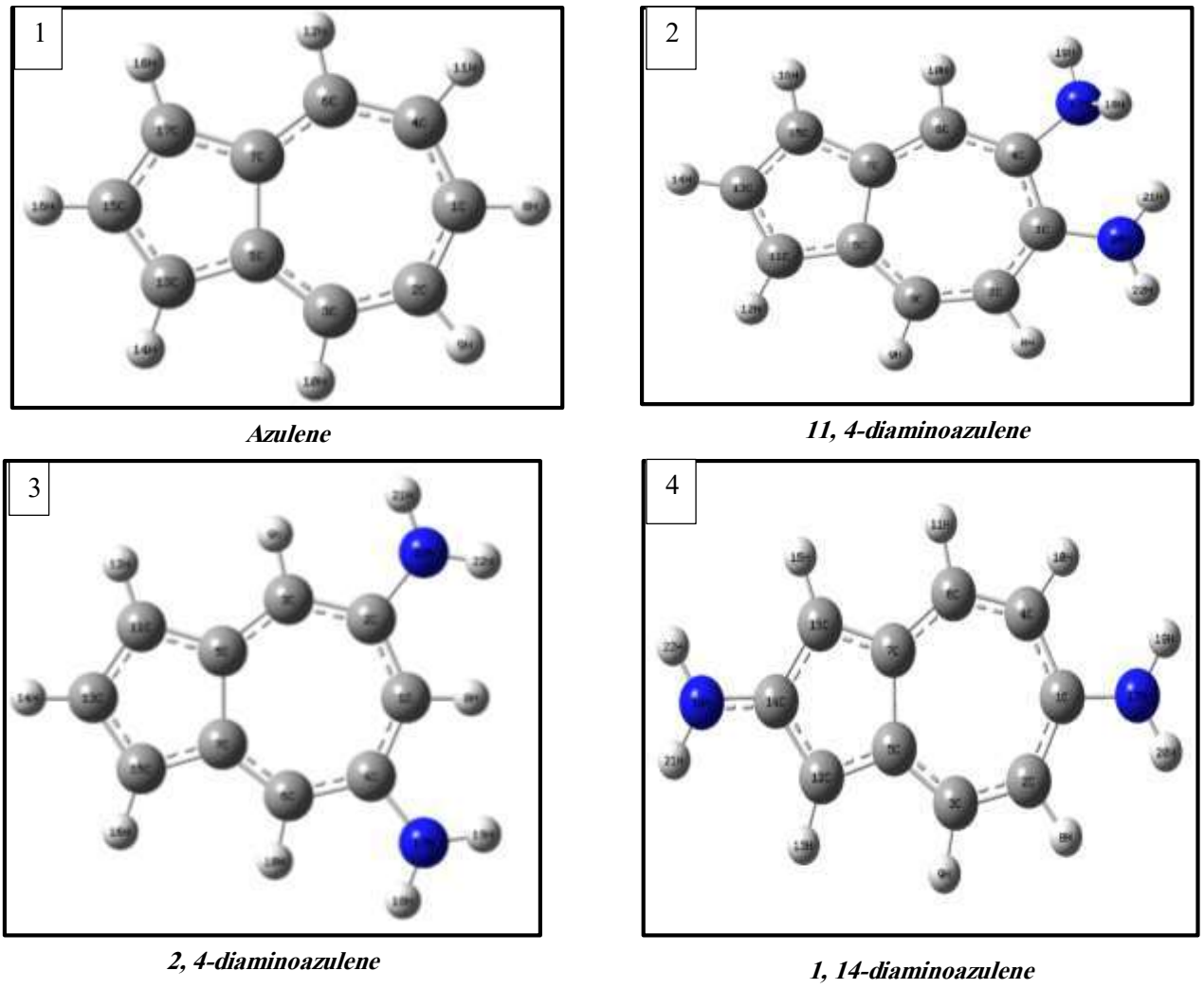

Figure 2. The optimized structures of azulene molecule and its derivatives with Nitro groups in different positions.

3. **Results and discussion**

The computational results of the electronic structure and the properties of the azulene compound are presented in this section. Table (1) illustrates total energies and the symmetry of structures the energy gaps, electronic states such as the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for molecules studied

Table 1. Total Energy, symmetry, HOMO – LUMO and energy gaps for molecules.

Mol.	Total Energy (a.u)	Symmetry	HOMO (eV)	LUMO (eV)	HOMO (eV) Ref.[ ]	LUMO (eV) Ref.[ ]	Energy gap (eV)	Energy gap (eV) Ref. [ ]
1	-385.745	C_1	-5.19621	-1.83293	-6.72	-2.44	3.36328	4.28
2	-496.341	C_1	-4.56737	-1.15347	----	----	3.413892	-----
3	-496.386	C_1	-4.03022	-1.37633	------	-----	2.653889	-----
4	-496.307	C_1	-4.29716	-0.68735	-----	-----	3.609811	----

From table (1), we can see that structural and electronic properties and the reactivity of azulene molecular are affected by addition (di-amino) groups, where that the total energy, energy gap, HOMO and LUMO energy, decreasing compared with the original molecule as shown in figures (3-5) respectively. Decrease the energy gaps improves the conductivities and also increases the solubilities of these molecules.

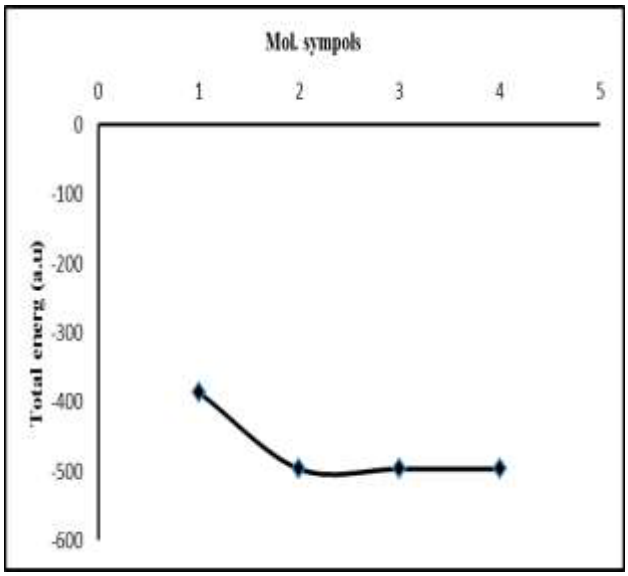

Figure 3. ***The calculated total energy for molecules studied.***

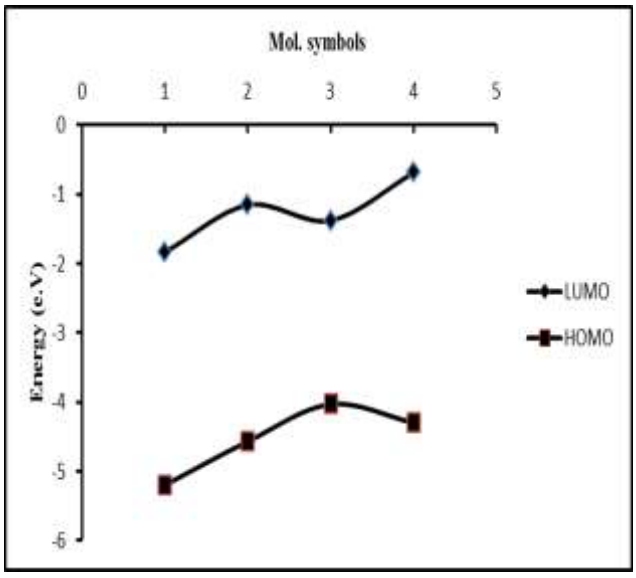

Figure 4 ***The HOMO and LUMO energies for molecules studied.***

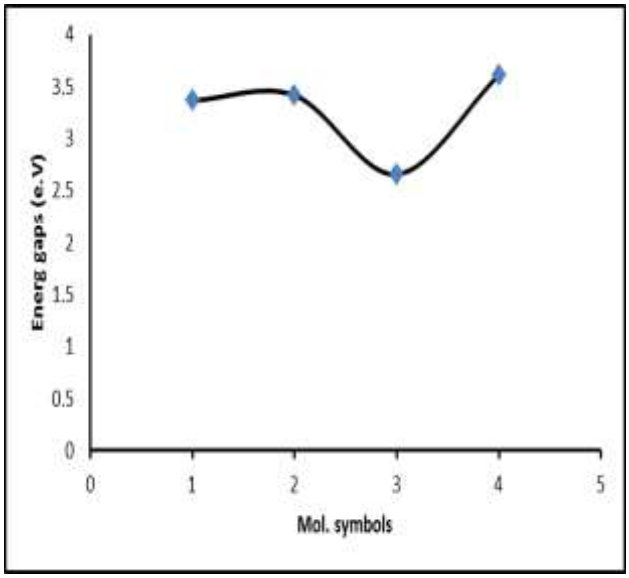

Figure 5. ***The calculated energy gaps for molecules studied.***

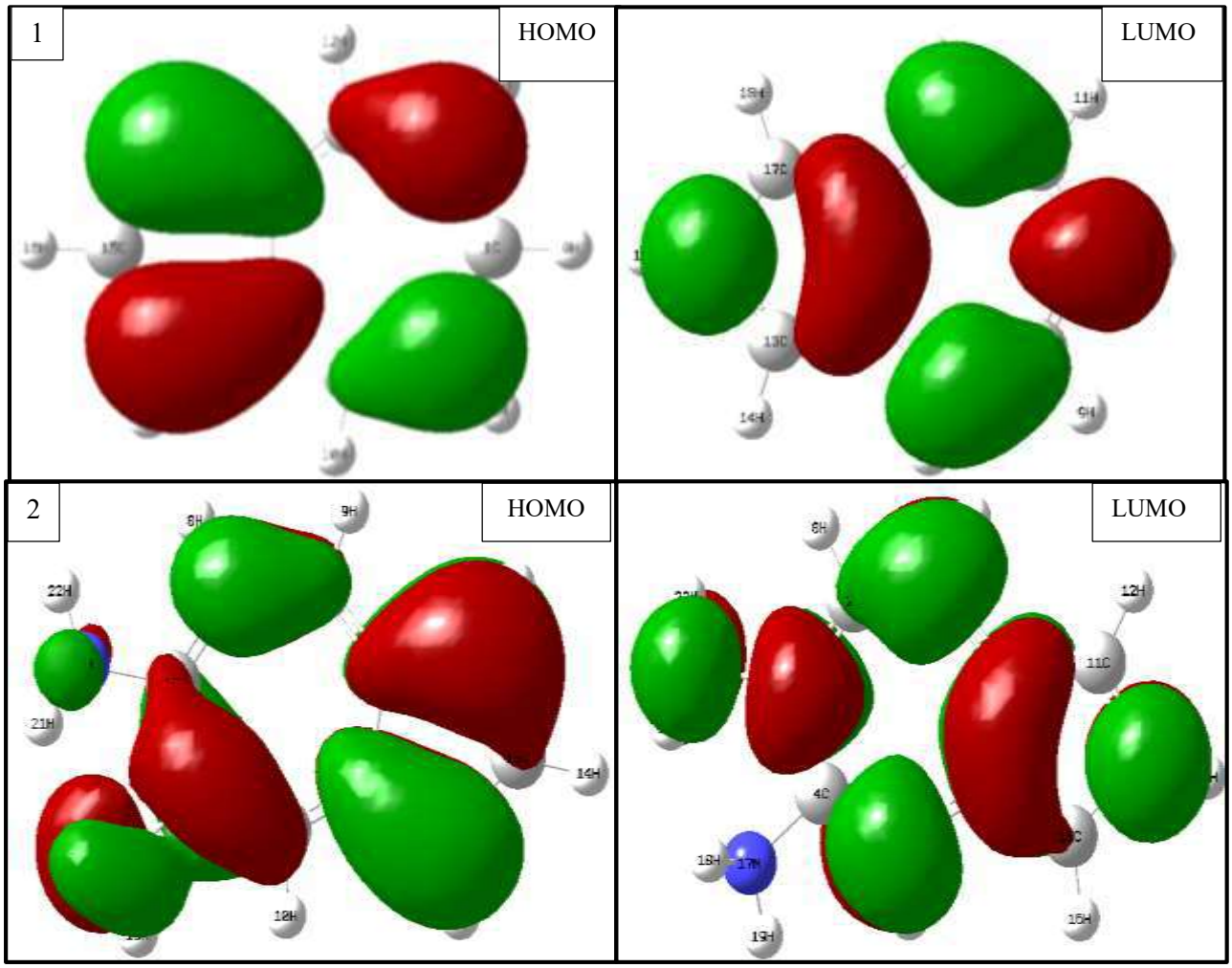

Figure (6) illustratese the 3-D distribution of HOMOs and LUMOs for the studied molecules.

Table (2) illustratese that the ionization potentials (IP),electron affinities(EA), softness (S) and hardness (H) values decreasing compared with the original molecule. Also from table (2), we can see that the electronic properties for all diaminoazulene molecules are approximately the same which this indicate to that, the electronic properties depend on the number of radicals added to the ring and independent on the position of the di-amino radical in the ring. Addition di-amino groups leads to variety the symmetrical distribution of the electronic structure of the molecule therefore, change the dipole moment, as shown in table (2).

Table 2. The electronic properties of azulene and diaminoazulene.

Mol.	IP (eV)	EA(eV)	H (eV)	S (eV)	μ
1	5.196213	1.832933	4.279746	2.139873	1.1794
2	4.567366	1.153474	3.990629	1.995315	4.3486
3	4.030221	1.376332	3.342055	1.671028	4.5409
4	4.297161	0.68735	3.953486	1.976743	1.0566

Electron Density and Electrostatic Potential Surfaces

Figure (7) illustrates the three dimensional shape of electron density and electrostatic potential distribution surfaces of azulene and diaminoazulene molecules. From this figure, it can be seen

that the electron density distribution surface for studied moleculs is asymmetric, where that the electron density is dragged towards the atoms of high electronegativity. Figure (7) explain the distribution of electrostatic potential depends on the negative and positive charges and depends also on the electronegativity of the atoms in the azulene and diaminoazulene molecules. In general, the electrostatic potential surfaces are dragged toward atoms of high electronegativity.

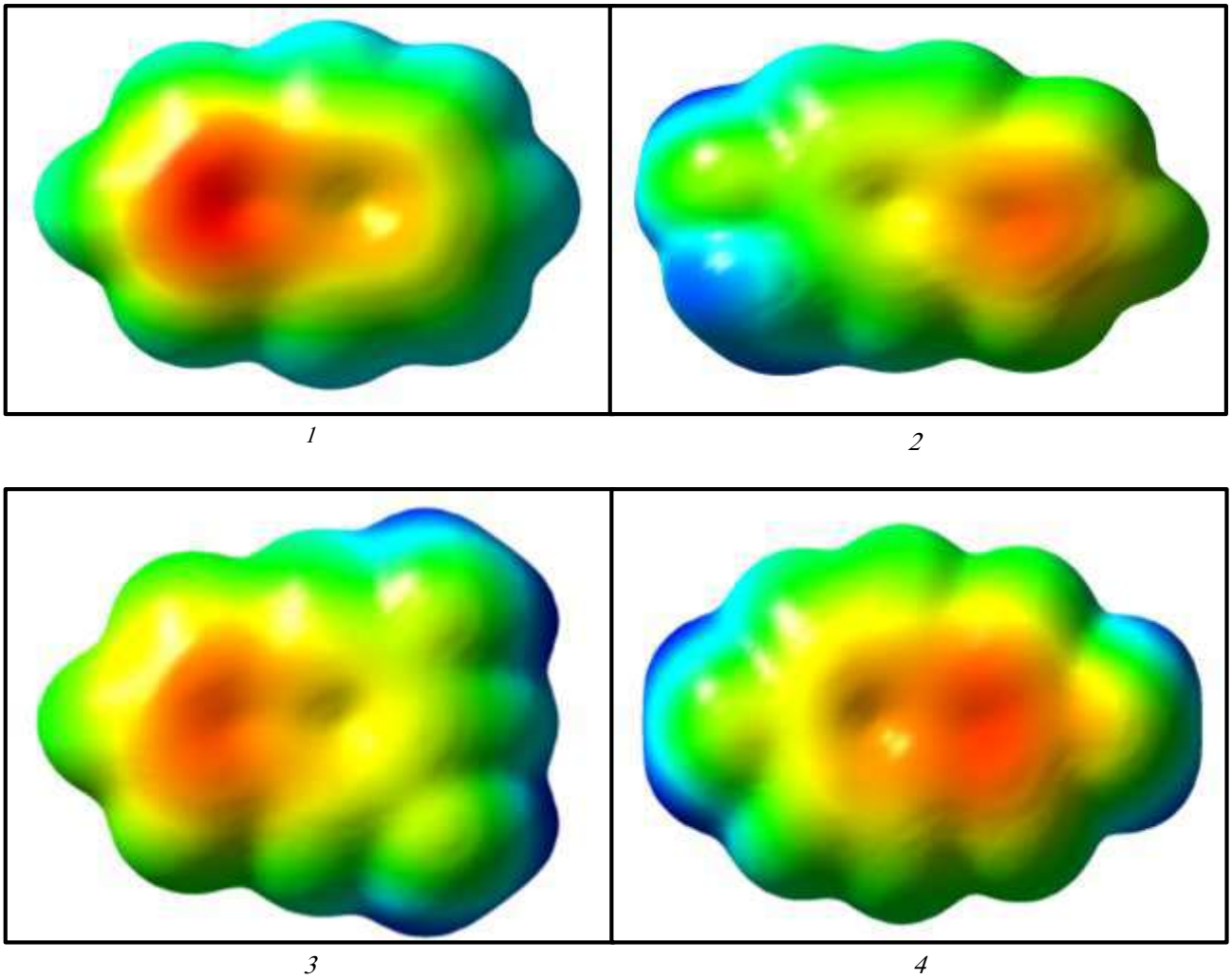

Figure 7. ***Electron Density and Electrostatic Potential Surfaces of azulene and diaminoazulene estimated by DFT/B3LYP/6-311G* calculations.***

Conclusions

1. Full geometry optimizations of azulene compound have been computed by density functional theory (DFT) based on the hybrid function of three parameters Lee-Yang-Parr (B3LYP) with 6-31 (d, p) basis set.
2. The structural and electronic properties and the reactivity of azulene molecular are affected by addition (di-amino) groups.
3. The ionization potentials (IP),electron affinities(EA), softness (S) and hardness (H) values decreasing compared with the original molecule.
4. The electrostatic potential and electron density surfaces are dragged toward atoms of high electronegativity.

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