

Specific features of 3, 6-bis (4-hydroxy phenyl)-piperazine-2, 5-dione (BHPPD) diphenolic monomer and compared with toxic industrial bisphenol-A (BPA): DFT calculation



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HIGHLIGHTS

- IR spectra, Mullikan charge analysis, molecular structures are calculated.
- Optimization energies, molecular masses, dipole moments, polarizations are obtained.
- Atomic electronic charges, HOMO and LUMO energies, hardness are calculated.
- DFT with the B3LYP method and 6-31G/6-311G* basis sets on BPA and BHPPD were used.

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ABSTRACT

In this study calculations of IR spectra, Mullikan charge analysis, molecular structures, energy optimization, molecular masses, dipole moments, polarizations, atomic electronic charges, HOMO and LUMO energies, gap energies, hardness, softness, electron affinities, chemical potentials and investigate of electro static potentials have been performed. The density functional theory (DFT) within the B3LYP method and 6-31G/6-311G* basis sets on BPA and BHPPD were used. A comprehensive comparison between the two methods was presented. The computations demonstrate that the 3, 6-bis (4-hydroxy phenyl)- piperazine-2, 5-dione (BHPPD) monomer can be viewed as another biodegradable diol which might be utilized as substitutes for the mechanically utilized poisonous diphenols, for example, bisphenol-A (BPA). BHPPD can be utilized as a part of the outline of biodegradable materials as grocery contact surface veneer coatings for jars, metal containers capping, defensive veneers and completions, vehicle parts, glues, aviation applications and as a covering for PVC tubes. The examination amongst BPA and BHPPD demonstrated that the novel nonpoisonous integrated fragrant diol has better physicochemical and poisonous properties contrasted with that of BPA.

1. Introduction

Bisphenols (BPs, for example, bisphenol-A (BPA, 2, 2-bis (4-hydroxydiphenyl) propane), are a class of chemical compounds which include of two phenolic rings attached each other through a crossing over carbon or other chemical combination [1]. BPA is an organic material which has been utilized as a material for the creation of phenol resinate, polyacrylates and polyesters however for the most part for the generation of epoxy resinate and polycarbonate plastics [2]. The epoxy

resins are used such grocery contact surface veneer coatings for jars, metal containers capping, defensive veneers and completions, vehicle parts, glues, aviation applications and as a covering for PVC tubes.

Recently, the production of BPA in the world has increased dramatically. D-4-hydroxyphenylglycine is the innate amino acid including an aromatic hydroxyl group. Visually active D-amino acids are generally utilized as a part of the pharmaceutical business as mediators for the production of semisynthetic antibiotics, pesticides, and new medicines [3,4]. Activated types of D-4-hydroxyphenylglycine are

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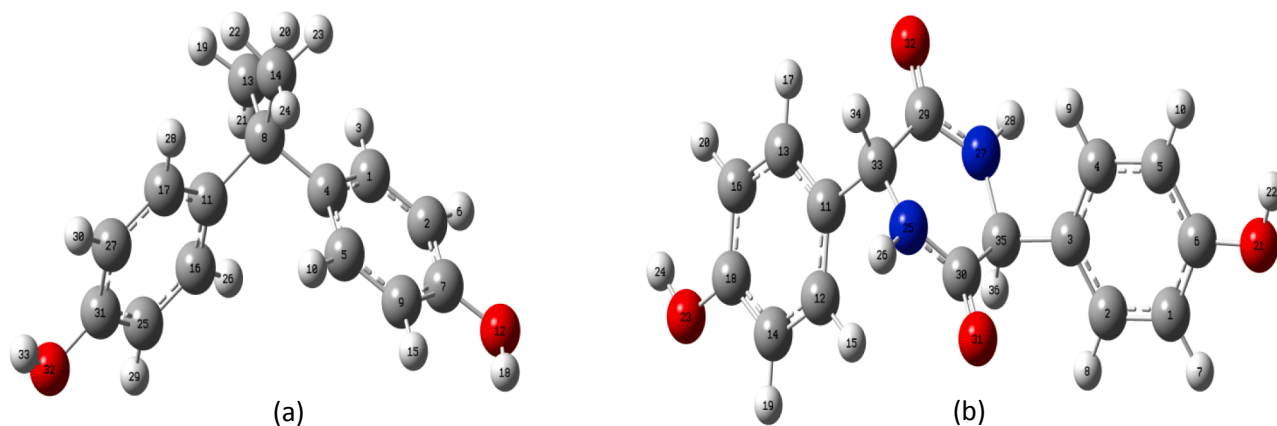


Fig. 1. Optimization molecular structure by using B3LYP method and 6-311G* basis set with numbering of atoms. BPA (a) and BHPPD (b).

additionally utilized in the enzymatic synthesis [5,6]. The other main problem in their use as biodegradable polyurethane in biomedical field is due to use of toxic conventional industrial used diphenolic monomer such as bisphenol-A as hard segment [7,8]. As noted above, a few analysts have concentrated on the poisonous quality of BPA, particularly its estrogenic action and numerous information are accessible at present [9, 10]. Tirgir et al. [11] synthesized bio degradable monomer and polymer that can be replaced of toxic BPA [11]. Density functional theory (DFT) methods fledged quantum chemistry a powerful gadget for the appointment electronic structure of molecules. In the DFT method [4] which contains electron correlation in a multiple way, the opportunity to carry out vibration analysis is relatively large organic molecules.

The purpose of this work is to investigate the molecular structure, optimization of the energy, IR spectroscopy, the high occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) analysis, determination of polarization, bond lengths, bond angles, electronic charge of atoms, softness and hardness, electron affinity and chemical potential of BPA and 3,6-bis(4-hydroxy phenyl)-piperazine-2,5-dione (BHPPD) [7] to compare with the results which were obtained using B3LYP method and 6-31G and 6-311G* basis sets. The optimized structures of BPA and BHPPD are shown in Fig. 1.

2. Details of calculation

In this study DFT calculations were carried out within Gaussian 09 W [12] software. Here we have used the B3LYP method and 6-31G, and 6-311G* basis sets. The structures of BPA and BHPPD were optimized using B3LYP/6-31G and B3LYP/6-311G*. By taking the differentiation of energy, the IR spectra is calculated. Determine the polarity of bond lengths, bond angles and the electric clouds around the atoms were performed within B3LYP/6-31G and B3LYP/6-311G*. Detection wave numbers were calculated with animation option of Gauss View 5.0 software that displays the shape of the vibration models [13].

3. Results and discussion

3.1. Molecular structure and DFT calculations

The calculations show that the symmetrical structure belongs to the C₂ point group. The molecular structure is optimized with B3LYP/6-311G* and the geometric parameters with B3LYP method and 6-31G/6-311G* basis sets as shown in Table A1 (see the Appendix). The obtained stoichiometry, optimization energy, heat capacity, molecular weight, dipole moment and polarization of the compound are given in Table A2 (see the Appendix). We found that the polarization increases with increasing the molecular weight while the dipole moment

decreases with increasing molecular weight. The obtained dipole moment of BPA and BHPPD respectively are 2.6777 and 2.3485 Debye. The dipole moment shows a molecular charge distribution as a vector in three dimensions. Therefore, it can be used as descriptors to describe the motion of electric charges around the molecules. The vector dipole moment of the molecule is depends on the center of positive and negative charges [14].

Table 1

The charge distribution calculated by the Mulliken (B3LYP/6-311G*) method of BPA and BHPPD.

Atoms	Atomic charges Of BPA	Atoms	Atomic charges Of BHPPD
c1	-0.182202	C1	-0.167303
c2	-0.1100974	C2	-0.108127
h3	0.124229	C3	-0.019338
C4	0.13695	C4	-0.065289
C5	-0.164634	C5	-0.188153
H6	0.13626	C6	0.259891
C7	0.24674	H7	0.172389
C8	-0.1211	H8	0.153881
C9	-0.138826	H9	0.164598
H10	0.1328	H10	0.153972
C11	0.13698	C11	-0.007057
O12	-0.6133	C12	-0.105487
C13	-0.39682	C13	-0.089886
C14	-0.3964	C14	-0.186188
H15	0.115385	H15	0.168788
C16	-0.166013	C16	-0.182986
C17	-0.182955	H17	0.176385
H18	0.367078	C18	0.263482
H19	0.13763	H19	0.171695
H20	0.13261	H20	0.156225
H21	0.1397	O21	-0.598188
H22	0.1313	H22	0.371280
H23	0.139	O23	-0.599667
H24	0.136659	H24	0.371851
C25	-0.10953	N25	-0.644780
H26	0.134176	H26	0.338352
C27	-0.1396	N27	-0.696894
H28	0.123782	H28	0.343039
H29	0.138322	C29	0.587505
H30	0.112721	C30	0.563554
C31	0.246226	O31	-0.375820
O32	-0.613148	O32	-0.392152
H33	0.367	C33	-0.270918
		H34	0.238850
		C35	-0.196851
		H36	0.239348

3.2. Electronic atomic charge

Mulliken and Natural Bond Orbital (NBO) are effective ways to study the internal and external molecular bonding and the interaction between them [17]. Also they are useful for study the transition of electronic charge or gynandries interaction in molecular system [15,16]. The obtained electronic charge calculated by B3LYP method and 6-311G* basis sets are shown in Table 1 and the plot is outlined in Fig. 2. The calculations show that the electronic charge in nitrogen atom related to BHPPD is topmost negative charge of the molecule which is about -0.696894 eV. The nitrogen (N27) atom is more electronegativity among the others and has nucleophilic property. Whereas the carbon (C29) atom has more positive charge (0.587505 eV).

3.3. The molecular orbital (HOMO-LUMO)

The HOMO and LUMO have strong determinative role in the chemical stability of molecules [18]. HOMO is illustrating the capability to give electron and LUMO is showing the capability to take electron [19]. The energy gap between HOMO and LUMO is determining the reactivity, polarization of light and chemical hardness and softness in the molecule [20]. Also the energy of HOMO is directly depending on the ionization potential while the energy of LUMO is directly affiliated to electron affinity [21]. The energy gap between HOMO and LUMO orbitals shown the high stability of molecule that means less reactivity in chemical reaction [22].

The 3D design of high occupied molecular orbital and low unoccupied molecular orbital of BPA and BHPPD using B3LYP/6-31G and B3LYP/6-311G* method and basis sets are shown in Fig. 3. The calculations show that the low unoccupied molecular orbitals in BHPPD are in

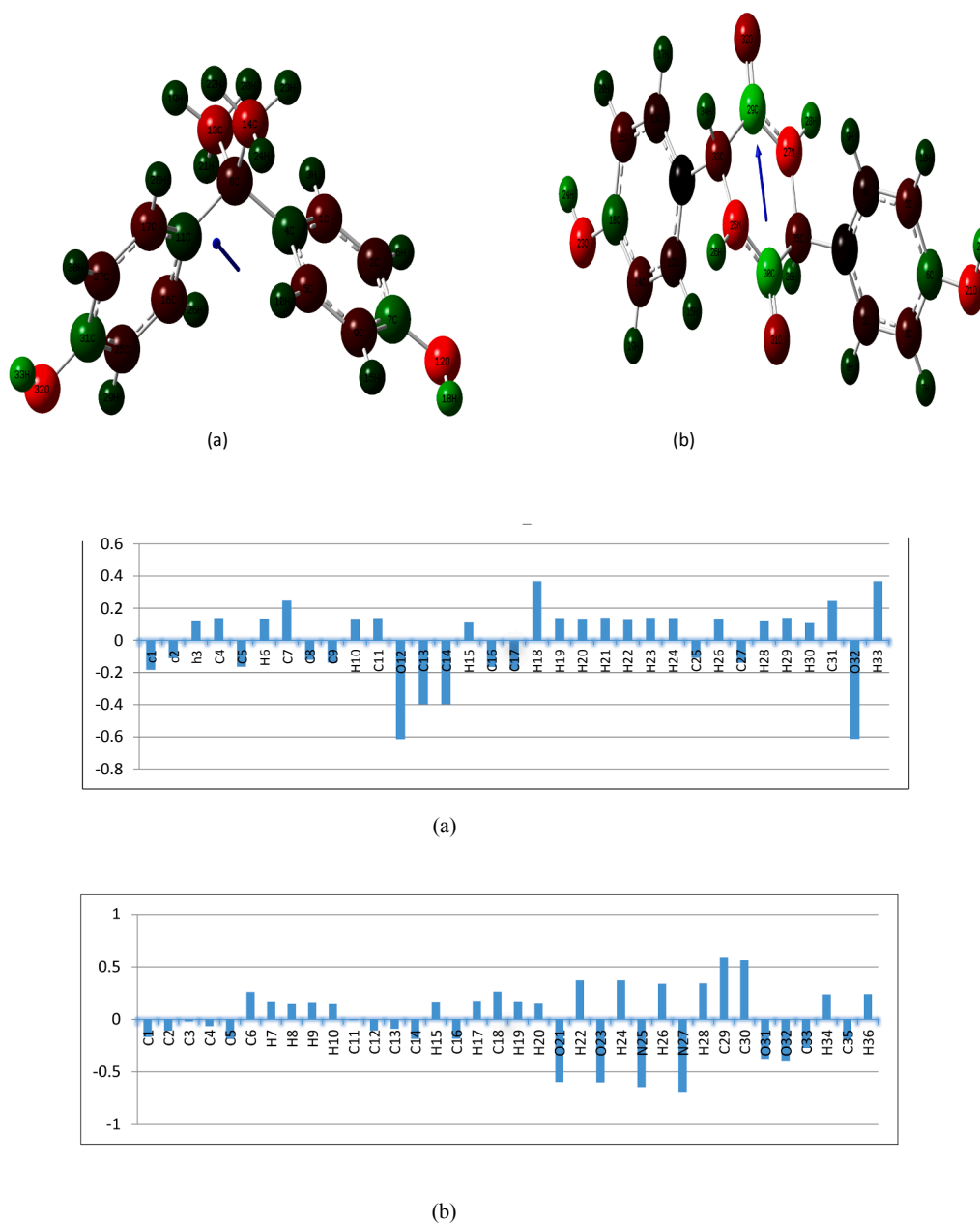


Fig. 2. Mulliken's plot and charge distribution for BPA (a) and BHPPD (b).

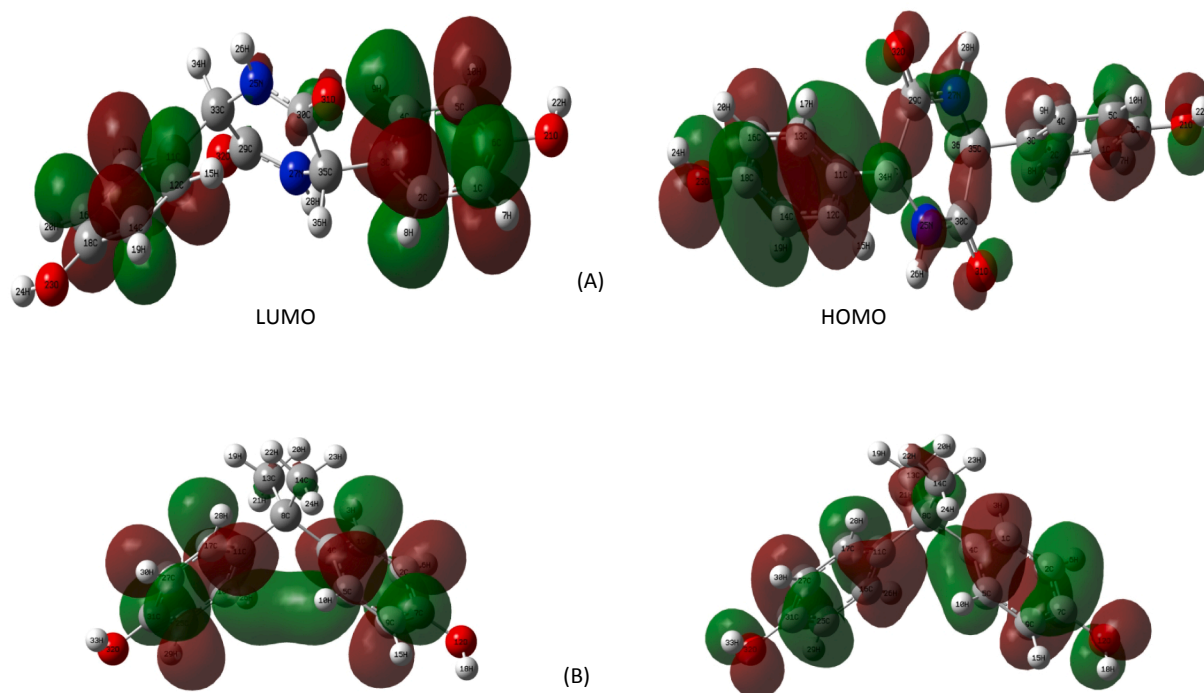


Fig. 3. The 3D design of HOMO and LUMO of BHPPD (A) and BPA (B).

Table 2

HOMO–LUMO energy values of BPA and BHPPD calculated at B3LYP method using 6-31G and 6-311G* basis sets.

Molecule Energies	BPA	BHPPD
E_{HOMO} energy (ev)	−0.20936	−0.23584
E_{LUMO} energy (ev)	−0.00215	−0.02535
E_{gap} energy gap (ev)	−0.20721	−0.21049
$E_{\text{HOMO}+1}$ (ev)	−0.22238	−0.23719
$E_{\text{LUMO}+1}$ (ev)	0.00604	−0.02127
$E_{\text{HOMO}+1} - \text{LUMO}+1$ energy gap (eV)	−0.22842	−0.21592

phenolic ring groups at the sides of this compound, while in BPA are in the center (hydrocarbon and phenolic groups). The density of the high occupied molecular orbitals in BHPPD are in the center of this compound then moved to the sides, whereas in BPA are situated at the sides because the density of HOMO moves from center to the sides at hydrogen atoms in phenolic ring groups. We noticed that the density of HOMO increases in the center of this compound, the energy gap (transfer HOMO to LUMO) from BPA to BHPPD as shown in Table 2. Variance of energy between HOMO and LUMO give the value of the energy gap. Increasing the energy gap between HOMO and LUMO led to increase the hardness [18].

3.4. Softness, hardness, electron affinity and chemical potential

The molecule with high energy gap known as hard molecules and the molecule with low energy gap known as soft molecules. The soft molecules are more polarize than the hard molecules because they need less energy for activation [23]. The η (reactive index) [24], μ (chemical potential) [22] and S (softness) [25] can be process as below:

$$[\eta = (I-A)/2]$$

$$[\mu = -(I + A)/2]$$

$$[S = 1/2\eta]$$

Where I and A are respectively, the ionization potential and electron affinity of the compound. According to Koopman theorem $I = -E_{\text{HOMO}}$

and $A = -E_{\text{LUMO}}$ and with a little bit approximation from Koopman theorem [26]:

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2 \quad \mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2$$

Parr et al. [27] reported a new description for the electron affinity in compounds as electron affinity index (ω), [$\omega = \mu^2/2\eta$].

The calculated softness, hardness, chemical potential and electron affinity within B3LYP/6-31G and B3LYP/6-311G* are shown in Table 3. We found that BPA has higher chemical potential and more softness in comparison to BHPPD. On other hand BHPPD has a higher electron affinity and more hardness in comparison to BPA.

3.5. IR spectroscopy

The IR spectra of BPA and BHPPD calculated by using B3LYP method and 6-31G\6-311G* basis sets are shown in Fig. 4. Aromatic nitro compounds have strong absorptions due to the asymmetric and symmetric stretching vibrations at 1570–1485 cm^{-1} and 1370–1320 cm^{-1} regions, respectively (Fig. 4a) [28]. After then, in this work the chemical structure of the BHPPD was carried out using elemental analysis, IR spectroscopy technique, by density functional theory (DFT) using B3LYP method and 6-311G* basis set. The characteristic peaks of secondary amine stretching ($-\text{NH}-$) in the range of 3000–3500 cm^{-1} which overlay with stretching of hydroxyl group ($-\text{OH}$) were evident in the spectrum. The amide carbonyl stretching [$\text{C}(\text{N})=\text{O}$] apparent at 1800 cm^{-1} calculated by DFT (B3LYP) theory and 6-31G\6-311G* basis sets (Fig. 4b).

Table 3

Hardness, Softness, chemical potential and electron affinity of BPA and BHPPD by using B3LYP method and 6-31G/6-311G* basis sets.

Molecule	Hardness [$\eta = (I-A)/2$] (eV)	chemical potential [$\mu = -(I + A)/2$] (eV)	Electron affinity [$\omega = \mu^2/2\eta$] (eV)	Softness [$S = 1/2\eta$] (eV^{-1})
BPA	0.103605	−0.105755	0.0539748	4.8216
BHPPD	0.105245	−0.130595	0.0810254	4.7508

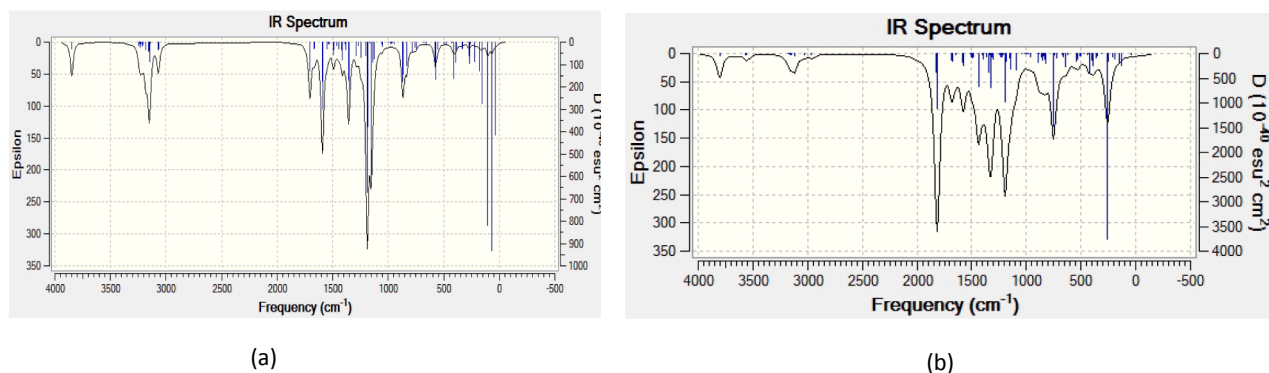


Fig. 4. The IR spectroscopy of BPA (a) and BHPPD (b) by using B3LYP method and 6-31G/6-311G* basis sets.

4. Conclusions

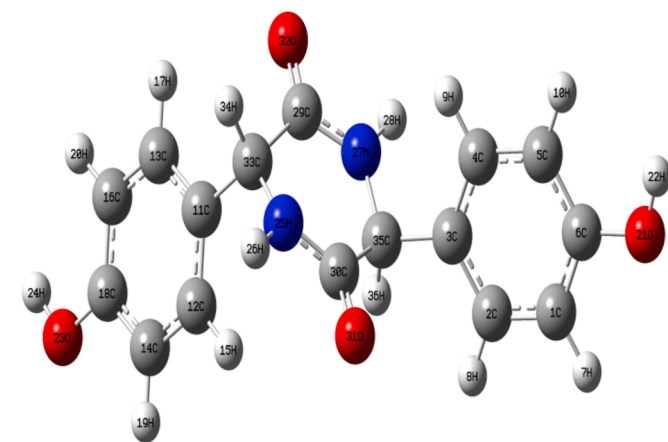
In this study calculations of molecular structures, energy optimization, molecular mass, dipole moments, polarizations, atomic electronic charges, HOMO and LUMO energies, band gap energies, hardness, softness, electron affinities, chemical potentials and the electrostatic potentials of BPA and BHPPD are performed using density functional theory based on B3LYP/6-31G and B3LYP/6-311G*. The calculations of the gap energies of HOMO and LUMO and 3D design of high occupied molecular orbitals and low unoccupied molecular orbitals are carried out. The obtained gap energies (variance between HOMO and LUMO) in BHPPD is higher than that of BPA. The calculations show that the high

occupied molecular orbitals in BHPPD are in phenolic ring groups and amide carbonyl at the side of this compound, on other hand in BPA are in central atoms (hydrocarbon groups) and density of the low unoccupied molecular orbitals in BHPPD are in central of phenolic ring groups which moved to the sides, while in BPA are in sides because density of LUMO moves from the center of benzene rings to sides at hydroxyl atoms in phenolic ring groups. We found that the density of the high occupied molecular orbitals are decreases in the center of BHPPD and BPA, the softness and chemical potential are decreases, whereas the electron affinities and hardness are increases. Also the calculated charges show more negative charge in nitrogen (N27) atom of BHPPD than that of BPA.

Appendix

Table A1

Optimized geometrical parameters for BHPPD molecule computed at B3LYP/6-31G* and B3LYP/6-311G* method and basis set. Bond length (Å) and bond angle (°).



Parameter	Method/basis set	
	B3LYP/6-311G*	B3LYP/6-31G*
<i>Bond lengths (Å)</i>		
R (1,6)	1.39628	1.39519
R (1,2)	1.38755	1.39311
R (1,7)	1.08401	1.07982
R (2,3)	1.39761	1.40092
R (2,8)	1.08520	1.08256
R (3,4)	1.39522	1.40109
R (3,35)	1.51924	1.51463

(continued on next page)

Table A1 (continued)

Parameter	Method/basis set	
	B3LYP/6-311G*	B3LYP/6-31G*
R (4,5)	1.39187	1.39371
R (4,9)	1.08500	1.08173
R (5,6)	1.39602	1.39846
R (5,10)	1.08748	1.08333
R (6,21)	1.36441	1.39257
R (11,33)	1.53196	1.53785
R (11,13)	1.39830	1.40300
R (11,12)	1.39729	1.40125
R (12,14)	1.39115	1.39509
R (12,15)	1.08450	1.08085
R (13,16)	1.38954	1.39412
R (13,17)	1.08415	1.08133
R (14,18)	1.39394	1.39450
R (14,19)	1.08413	1.08006
R (16,18)	1.39765	1.39828
R (16,20)	1.08757	1.08352
R (18,23)	1.36478	1.39367
R (21,22)	0.96401	0.97169
R (23,24)	0.96398	0.97169
R (25,26)	1.01218	1.00930
R (25,30)	1.36339	1.36706
R (25,33)	1.45674	1.46625
R (27,28)	1.01158	1.00953
R (27,35)	1.46039	1.47749
R (27,29)	1.35750	1.35945
R (29,33)	1.53398	1.53072
R (29,32)	1.21780	1.24985
R (30,31)	1.21469	1.24502
R (30,35)	1.54162	1.53797
R (33,34)	1.09306	1.09009
R (35,36)	1.09862	1.09708
<i>Bond angles (°)</i>		
A (6,21,22)	109.78651	112.13923
A (21,6,1)	117.48674	116.85867
A (21,6,5)	122.85484	122.77212
A (6,1,7)	118.88987	118.91166
A (6,5,10)	120.15243	120.29100
A (5,4,9)	119.23975	119.33622
A (4,5,10)	119.85968	120.06067
A (9,4,3)	119.90405	119.90228
A (4,3,35)	121.28517	120.86967
A (35,3,2)	120.17728	120.42224
A (3,2,8)	119.57861	119.66347
A (3,2,1)	121.19987	121.07485
A (8,2,1)	119.21927	119.26092
A (4,3,2)	118.50930	118.70798
A (2,1,7)	121.32257	121.64597
A (2,1,6)	119.78756	119.44224
A (20,16,18)	120.11968	120.31780
A (20,16,13)	119.77179	119.91085
A (16,13,11)	120.89353	120.69765
A (16,13,17)	119.59603	119.81583
A (17,13,11)	119.49245	119.47633
A (13,11,33)	119.31877	119.19756
A (13,11,12)	118.42352	118.76092
A (11,12,15)	120.29084	119.99144
A (11,12,14)	121.10713	120.86864
A (15,12,14)	118.59960	119.13734
A (12,14,19)	121.12027	121.42017
A (12,14,18)	119.93268	119.68668
A (19,14,18)	118.94691	118.89295
A (14,18,23)	117.65437	116.94332
A (14,18,16)	119.53437	120.21451
A (23,18,16)	122.81106	122.84214
A (18,23,24)	109.74522	112.04731
A (18,16,20)	120.11968	120.31780
A (18,16,13)	120.10847	119.77134
A (18,14,19)	118.94691	118.89295
A (16,13,17)	119.59603	119.81583
A (16,13,11)	120.89353	120.69765
A (11,33,34)	108.40287	108.74057
A (11,33,29)	110.25245	110.55933
A (11,33,25)	113.90876	114.02413

(continued on next page)

Table A1 (continued)

Parameter	Method/basis set	
	B3LYP/6-311G*	B3LYP/6-31G*
A (33,29,32)	120.65300	121.00869
A (33,29,27)	116.18057	115.72729
A (33,25,26)	116.99887	118.39823
A (33,25,30)	126.41894	126.03749
A (29,27,28)	114.70100	116.64836
A (29,27,35)	127.82240	125.56219
A (27,35,3)	110.95679	110.49401
A (27,35,30)	112.54803	110.08724
A (27,35,36)	109.61031	109.29407
A (27,29,32)	123.16615	123.25897
A (35,30,31)	120.81331	122.48963
A (35,30,25)	116.23913	115.09976
A (35,27,28)	117.07987	117.54391
A (31,30,25)	122.94656	122.38295

Table A2

The thermodynamic parameters of BPA and BHPPD calculated at B3LYP method using 6-31G* and 6-311G* basis sets.

Molecule	Total energy (thermal) E_{Thermal} (KCal/Mol)	Heat capacity C_v (Cal/Mol- Kelvin)	Entropy S (Cal/Mol- Kelvin)	Molecular weight (amu)	Dipole moment (Debye)	Polarization
BPA	182.132	56.022	$S_{\text{Total}} = 115.897$ $S_{\text{Translational}} = 42.176$ $S_{\text{Rotational}} = 33.100$ $S_{\text{Vibrational}} = 40.621$	228.11503	$\mu_x = -1.1978$ $\mu_y = 0.4375$ $\mu_z = 2.3546$ $\mu_{\text{total}} = 2.6777$	151.651
BHPPD	184.569	60.223	$S_{\text{Total}} = 115.953$ $S_{\text{Translational}} = 42.974$ $S_{\text{Rotational}} = 34.621$ $S_{\text{Vibrational}} = 38.358$	298.09536	$\mu_x = -0.8579$ $\mu_y = 2.1816$ $\mu_z = -0.1413$ $\mu_{\text{total}} = 2.3485$	180.212

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