Journal of Chemical Reactivity and Synthesis 2022: 12(1) 1-17

Research Article

Theoretical study of the para chlorophenol adsorption on phosphorus-doped polypyrrole with DFT

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ARTICLE INFO:

Received:
5 January 2022

Accepted:
28 February 2022

Available online:
15 March 2022

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ABSTRACT

In this study, the adsorption of para-chlorophenol on phosphorus-doped polypyrrole was investigated using density functional theory (DFT). Calculations are performed at two levels b3lyp/6-31+G(d, p) and wb97xd/6-31+G(d, p), for two orientations of adsorbate molecules. The correlation-exchange function wb97xd shows more negative adsorption energy for the adsorption of these compounds. Evaluation of energy level changes of HOMO and LUMO orbitals, hardness, chemical potential, softness, electrophilicity, diploe moment, charge transfer by Molliken method and natural bond orbitals (NBO), adsorption energy, the density of states (DOS) diagrams, molecular electrostatic potential (MEP), Intermolecular distances and analysis of non-covalent interactions (NCI) have been performed. Analysis of non-covalent interactions shows more van der Waals interactions between adsorbent and adsorbate in the wb97xd correlation-exchange function compared to b3lyp.

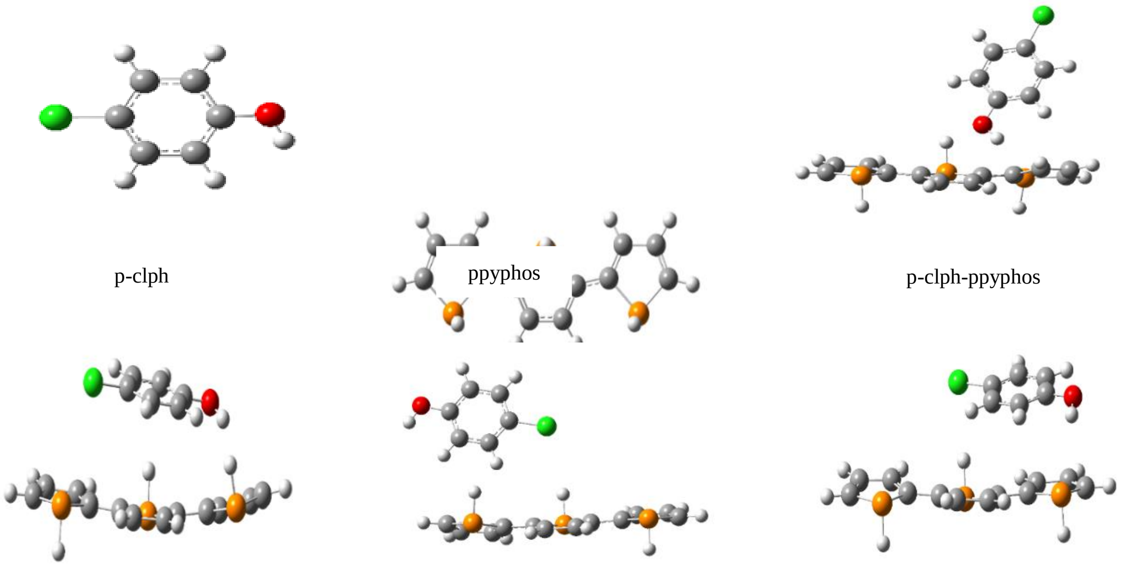
Keywords: Adsorption, para chlorophenol, phosphorus-doped polypyrrole, Density functional theory (DFT)

1. Introduction

Phenolic compounds are one of the most widely used and abundant classes of ionizable organic acid compounds [1]. their high solubility in water and carcinogenic properties make them one of the most hazardous compounds for the environment. Phenolic compounds are the prerequisites and raw materials for the production of many drugs and industrial materials, so these materials are present in many industrial effluents such as petrochemical, pharmaceutical and textile, and pesticides [2-4]. Most Environmental Protection agencies (EPA) have listed phenolic compounds and their derivatives as hazardous and harmful to humans and the environment. The united states environmental protection agency (USEPA), the Central Pollution Control board (CPCB), and the European Union (EU) set the standard amount for phenol and aniline in industrial and agricultural effluents, at 1.0 mg/L [5-7]. These substances can be transmitted to the human body and other organisms through respiration, skin, and drinking water. Exposure to phenolic compounds can damage organs such as the kidneys, spleen, and pancreas. Causes poisoning and disorders of the gastrointestinal tract, lung disorders, and even seizures [8]. For this reason, phenolic compounds are among the most dangerous compounds for humans, other living organisms, and the environment, so the need to eliminate these compounds is increasingly felt. There are several methods for removing these materials, the most important of which are their adsorption on a suitable adsorbent and advanced oxidation processes [9-15]. Many studies have been done on adsorption phenolic compounds in theory [16-23]. Conductive polymers such as polypyrrole, polyaniline, and polythiophene have recently received much attention for their use as adsorbents due to their good adsorption, easy preparation, low cost for preparation, and suitable mechanical and chemical properties. [24-38]. These conductive polymers have also recently been widely used in drug delivery systems [39], fuel cells [40], and sensors [41]. In this work, the adsorption of para chlorophenol on phosphorus-doped polypyrrole using the density functional theory (DFT) at two levels of B3LYP/6-31+G (d,p) and WB97XD/6-31+G (d,p) was investigated. In this study The lowest molecular orbital energy (LUMO), the highest molecular orbital energy (HOMO), band gap (E_g), dipole moment (μ_d), reactivity parameters including chemical potential (μ), hardness (η), electrophilicity (ω) and softness (σ), adsorption energy (E_{ads}), minimum distance Between adsorbent and adsorbates (d), charge transfer by natural population analysis (Q_{NBO}) and Mulliken charge analysis ($Q_{mulliken}$), the density of states (DOS), molecular electrostatic potential (MEP), and non-covalent interaction analysis (NCI) were analyzed.

2. Computational method

All calculations were performed using Gaussian 09 software package. The output files of the molecules were analyzed using the GaussView 06 software. Calculations were performed in gas phases at level B3LYP/6-31+G (d,p) [42] and WB97XD/6-31+G (d,p) level of theory. The effect of orientation was investigated for cases where the adsorbates approach the adsorbent from both sides. Mode (1) is used to approach para-chlorophenol by Cl. To study the effect of the correlation-exchange function, the B3LYP correlation-exchange function was changed to WB97XD [43,44] and a significant improvement in adsorption results was observed. we replaced the nitrogen atom with the phosphorus atom in polypyrrole (ppyphos) and saw good results. [46-48]. the energy of lowest unoccupied molecular orbital (LUMO), the energy of highest occupied molecular orbital (HOMO), band gap (Eg), moment dipole (μ), adsorption energy (E_{ads}), charge transfer by natural population analysis (NBO), and Mulliken analysis, minimum distance Between adsorbent and adsorbates (d), analysis of the density of states (DOS) and molecular electrostatic potential (MEP) was performed. Non-covalent interaction (NCI) analysis was performed to investigate the nature of intermolecular interactions at the level of the theory mentioned above using multiwfn and VMD software. GaussSum 3.0 was used to plot the density of states. A set of symbols is used to distinguish between optimized structures. For para-chlorophenol from the p-clph. To perform calculations at the level of wb97xd/6-31+G (d,p), a w is added to the end of each structure, and not using it means calculating at the level of b3lyp.



p-clph ppyphos p-clph-ppyphos

p-clph-ppyphosw p-clph-ppyphos1 p-clph-ppyphos1w

Fig. 1. The optimized structure of the p-clph and ppyphos, at B3LYP/6-31+G (d,p) levelof theory in the gas phase. adsorption of p-clph on ppyphos in gas and at B3LYP/6-31+G (d,p)and WB97XD/6-31+G (d,p) level of theory

The adsorption energies E_{ads} between adsorbates (phenolic compound) and adsorbents were obtained from the following equation:

$$\boldsymbol{E_{ads} = E(adsorbent - adsorbate) - E(adsorbent) + E(adsorbate)} \qquad \mathbf{(1)}$$

Where $E(adsorbent - adsorbate)$ is related to the energy of the adsorbent (ppy)-adsorbate (p-clph) complex. E (adsorbent) is the energy of polypyrrole as the adsorbent and E (adsorbate) is the energy of the p-clph.

The charge transfer between the adsorbent and the adsorbent during adsorption is obtained by the difference between the polypyrrole adsorbent charge before and after adsorption by the following equation

$$\Delta q = q_{ppy\ before\ adsorption} - q_{ppy\ after\ adsorption} \qquad (2)$$

where $q_{ppy\ before\ adsorption}$ and $q_{ppy\ after\ adsorption}$ are total structure charges of the ppy before and after adsorption, respectively. We computed the electrophilicity index (ω). This index indicates the direction of charge transfer. A higher value of ω indicates the higher electrophilic power of the structure [45].

$$\omega = \frac{\mu^2}{2\eta} \qquad (3)$$

$$\mu = \frac{(E_{HOMO} + E_{LUMO})}{2} \qquad (4)$$

$$\eta = \frac{(-E_{HOMO} + E_{LUMO})}{2} \qquad (5)$$

Where μ is electronic chemical potential, and η is the chemical hardness of the ground state [46-49].

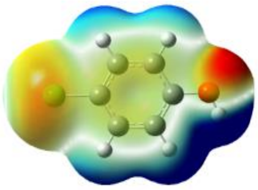
Result and discussion

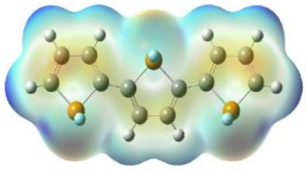
3.1. Optimized structure

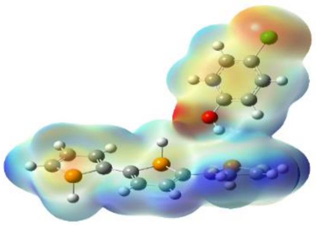
The optimized structure of para chlorophenol (p-clph) in the gas phase at B3LYP/6-31+G (d,p) level of theory, Phosphorus-doped polypyrrole (ppyphos) at B3LYP/6-31+G (d,p) level of theory in the gas phase, adsorption of the p-clph on ppyphos in two orientations at b3lyp and wb97xd functional in gas phase illustrated in Fig 1. Mode (1) is used to approach para chlorophenol by Cl. We used three pyrrole monomers for phosphorus-doped polypyrrole.

3.2. intermolecular distances and dipole moment

For adsorption of the pclph on ppypphos The distance between the adsorbent and the adsorbate is the minimum distance between oxygen or chlorine in the adsorbed p-clph with hydrogen atoms attached to phosphorus in the ppyphos adsorbent. (Table 2). The indicated distances are in the range of intermolecular forces and physical absorption. dipole moment is less in the wb97xd correlation-exchange function, which means less charge separation, and this can be a measure of stability. The change in the moment dipole of the adsorbent-adsorbed complex compared to isolated adsorbent and adsorbent indicates an interaction.







3.3. Molecular electrostatic potential (MEP)

Molecular electrostatic potential (MEP) gives important information than reactive electrophilic and nucleophilic sites. MEP surfaces of the pclph, ppyphos and, adsorption of the pclph on this adsorbent were calculated and illustrated in Fig. 2. MEP was calculated for pclph from $-3.045e^{-2}\ a.u.$ to $-3.045e^{+2}\ a.u.$ These potentials are often identified by a color scheme. Red indicates the most negative potential values, and blue indicates the most positive potential values. The results show that the oxygen and chlorine atoms of the p-clph have a higher electron density (negative) and a red color [50]. The density of electrons on the oxygen atom of the hydroxy group is higher than the chlorine atom. This suggests that these groups may be considered nuclear attack sites. In contrast, modified ppy amine functional groups lead to high positive electron density. This indicates that amine groups are the electrophilic attack sites for ppyphos. MEP was calculated for modified polypyrrole from $-2.700e^{-2}\ a.u.$ to $-2.700e^{+2}\ a.u.$ According to these results, the mechanism of adsorption of pclph on ppyphos can be done through electron density transfers between nuclear and electrophilic groups of adsorbents and adsorbates. In general, at the wb97xd correlation-exchange function for all phenolic compounds adsorption structures on phosphorus-doped polypyrrole, there is better interaction between electrophilic and nucleophilic groups compared to level b3lyp correlation-exchange function, which leads to more negative adsorption energy in this function. MEP was calculated for adsorption of the pclph on modified polypyrrole from $-3.045e^{-2}$ a.u. to $-3.045e^{+2}\ a.u.$

3.4. natural bond orbital analysis (NBO)

electron charge transfer was investigated by NBO and Mulliken methods. Electron charge transfer is defined as the difference between the absorbent charge before and after absorption. NBO analysis is more accurate than the Mulliken method [51] because Mulliken arbitrarily divides electrons between base functions and ignores electronegative and hybridizing effects as well as Pauli effects. NBO is the eigen state of the density matrix operator. Table 2 shows charge transfer of adsorption of the pclph on ppyphos. Transfer charges often indicate physical absorption. transfer size is a measure of adsorption power. In general, the higher the charge transfer, the more negative the absorption energy. For example, it can be seen that for most cases, the charge transfer in the correlation-exchange function of the wb97xd is greater than the b3lyp and its adsorption energy is also higher. The difference in the size and sign of the charge transfer in the two methods of Mulliken and NBO is due to their different formalism in charge calculation. The slight irregularities observed in the transfer of loads are due to different optimized structures and the approach of the approaching groups.

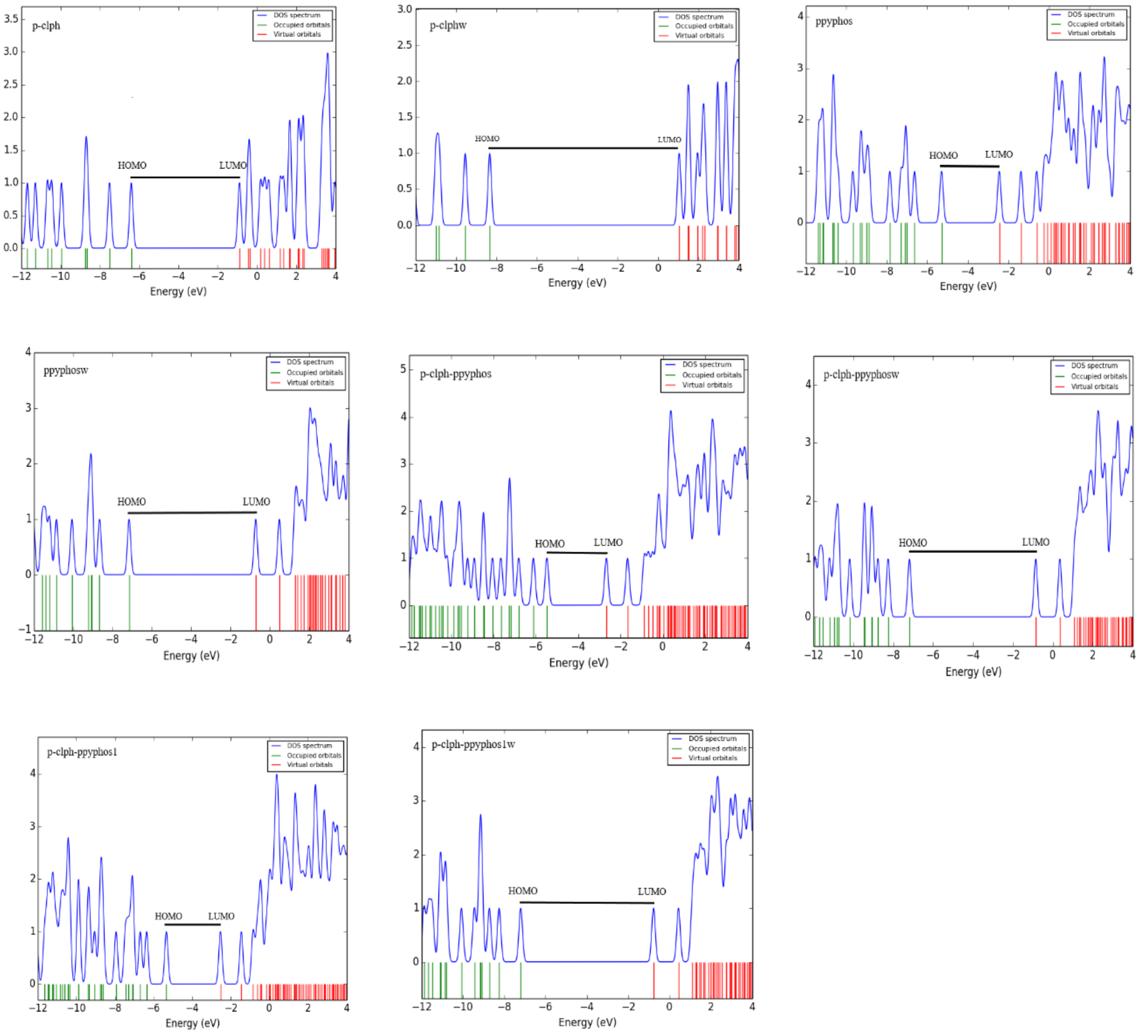


Fig. 3. DOS diagrams of pclph, ppyphos and adsorption of pclph on ppyphos in the gas phase at b3lyp and wb97xd functional.

3.5. natural bond orbital analysis (NBO)

For understanding the electronic properties of structures, DOS was calculated for the isolated adsorbents and adsorbate and adsorbate-adsorbent complexes [52]. Figure 3 shows the dos diagrams and the LUMO and HOMO energy levels are marked on them. Changes in HOMO and LUMO energy levels in the complex compared to adsorbents and isolated adsorbates indicate interaction. More bandgap makes greater kinetic stability. The bandgap in the wb97xd correlation exchange function is greater for the corresponding structures than the b3lyp correlation exchange function. This is in agreement with the more negative energy absorption in this exchange-correlation function. Mirror symmetry (Coulson-Rashbrook rule) isobserved for orbitals [53].

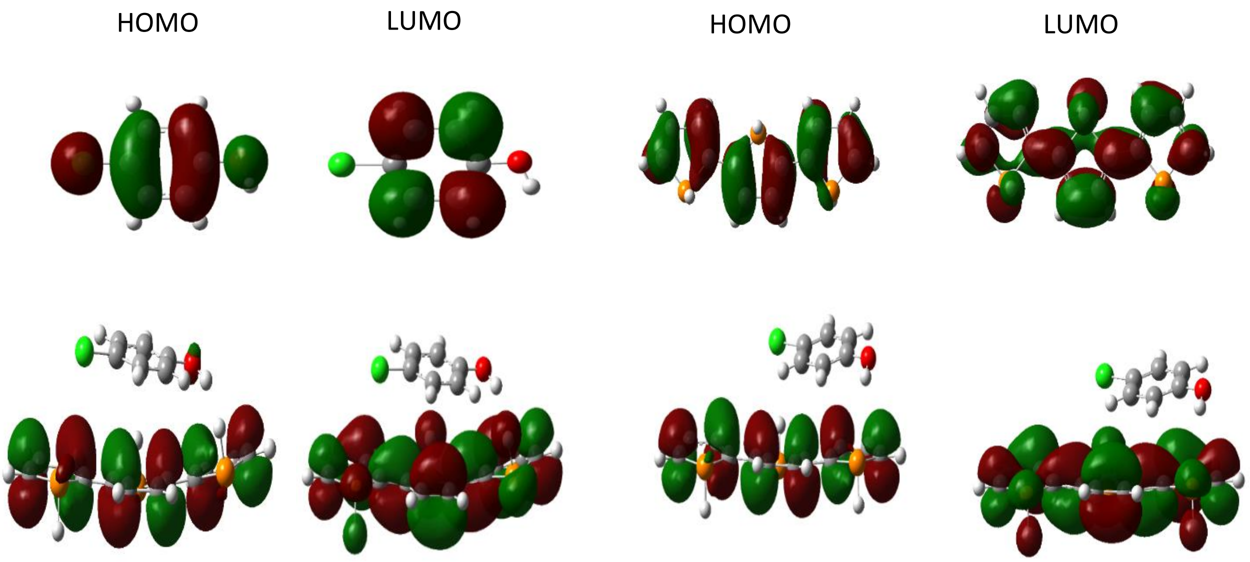


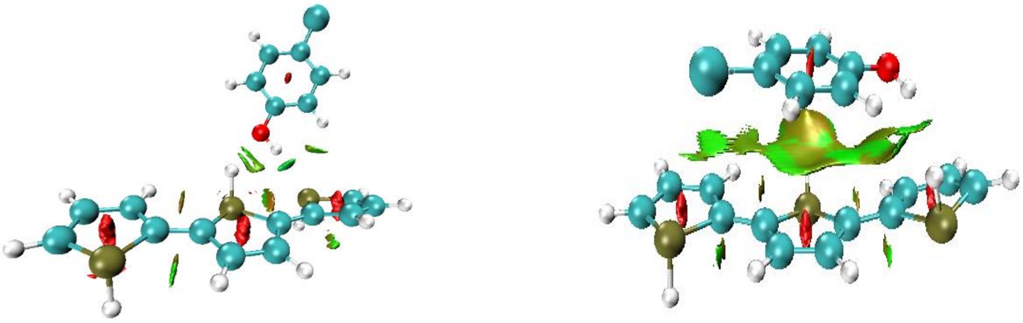
Fig .4. the molecular orbitals of HOMO and LUMO for para chlorophenol, ppyphos, and adsorption of p-clph on this adsorbent.

3.6. Non-covalent interaction (NCI) analysis

Non-covalent interactions are a method used to understand the nature of the intermolecular force involved between molecules. The NCI indices rely on the electron density and the reduced density gradient (s), as shown in equation

$$s = \frac{1}{2(3\pi^2)^{\frac{1}{3}}} \frac{\nabla\rho}{\rho^{\frac{4}{3}}} \qquad (6)$$

This analysis can be used to determine intermolecular forces such as hydrogen bonding, van der Waals interactions, and repulsive steric interactions. Usually, two methods are used to make this analysis. In the first method, a graph is used that is generated with the plots of the reduced density gradient (s) versus (sign λ_2)ρ, where (sign λ_2)ρ is the electron density multiplied by the sign of the second Hessian eigenvalue (λ_2). The value of (sign λ_2)ρ is useful to predict the nature of interaction [54,55]. In the second method, intermolecular interactions in the NCI method can be visualized by gradient isosurface in the real space of the molecules. In the 3D visualization of NCI isosurface, Green color is used for van der Waals interaction, Blue color for hydrogen bonding, red color is used for repulsive steric interactions. Fig 5 shows NCI analysis. We used the second method in this project. To investigate intermolecular interactions and use non-covalent interaction analysis, adsorption of pclph on polypyrrole doped with phosphor in the gas phase was used in both wb97xd and b3lyp exchange correlations and only one orientation. To adsorb para chlorophenol on phosphorus-doped polypyrrole in the wb97xd correlation exchange function der Waals interactions is greater than the wb97xd correlation function



p-clph-ppyphos

p-clph-ppyphosw

Fig. 5. Reduced density gradient isosurfaces are depicting non-covalent interaction (NCI) regions for adsorption of p-clph on ppyphos at b3lyp and wb97xd functional. The isosurfaces were constructed with RDG 0.5 au. and the colors scaling from -0. 04 < $(\text{sign}\ \lambda_2)\rho$ < 0.02 au.

3.7. Adsorption energy

In the calculations performed in this project, the adsorption energy for the correlation-exchange function wb97xd is more negative than b3lyp. The reason for this is the specific formalism of these correlation-exchange functions, which, as we saw in NCI analysis, the wb97xd functional involve intermolecular forces well and leads to appropriate optimized structures.

Table 1. The energy of the HOMO (E_{HOMO}) and LUMO (E_{LUMO}) orbitals, band gap energy (E_g), Dipole moment (μ_d), and for para chlorophenol in phase gas t at B3LYP/6-31+G (d,p) and WB97XD/6-31+G(d,p) level of theory, ppyphos adsorbent and adsorption energy (E_{ads}) for adsorption of p-clph on ppyphos in phase gas at B3LYP/6-31+G (d,p) and WB97XD/6-31+G(d,p) level of theory.

System	$E_{(HOMO)}(eV)$	$E_{(LUMO)}(eV)$	$E_g(eV)$	$\mu_D(Debye)$	$E_{ads}(\frac{kJ}{mol})$
p-clph	-6.397	-0.887	5.510	2.330	-
p-clphw	-8.332	1.038	9.371	2.361	-
ppyphos	-5.299	-2.449	2.850	1.455	-
ppyphosw	-7.158	-0.722	6.436	0.856	-
p-clph-ppyphos	-5.481	-2.670	2.811	4.206	0.669
p-clph-ppyphosw	-7.188	-0.859	6.329	1.388	-37.213
p-clph-ppyphos1	-5.338	-2.532	2.806	1.728	7.582
p-clph-ppyphos1w	-7.203	-0.776	6.427	1.577	-30.500

3.8. Reactivity parameters

In this study, reactivity parameters including hardness (η), chemical potential (μ), softness (σ) and electrophilicity (ω) were also investigated. Chemical potential is a measure of the stability of a system and indicates the degree to which the system tends to remain in that state. The standard definition of chemical potential for a particle is defined as the change in Gibbs free energy relative to its mole. But it is shown that for an N electron system with total electron energy E and an external potential V (r) the chemical potential is as follows.

$$\mu = (\frac{\partial E}{\partial N})_{V(r)} \qquad (7)$$

Hardness is a quantity that depends on the charge and polarizability of the system. Polarization includes the concept of the excitability of electrons and orbital and energy changes. By these definitions, hardness seems to be related to electronic energy. This concept was introduced by Pearson

$$\eta = -(\frac{\partial^2 E}{\partial N^2})_{V(r)} = -(\frac{\partial \mu}{\partial N})_{V(r)} \qquad (8)$$

Kopman's theory, which is an approximate theory, calculates chemical potential and hardness as follows.

$$\mu = -\frac{(\mathrm{IP} + \mathrm{EA})}{2} = \frac{(\mathrm{E}_{LUMO} + \mathrm{E}_{HOMO})}{2}$$

$$\eta = \frac{(\mathrm{IP} - \mathrm{EA})}{2} = \frac{(\mathrm{E}_{LUMO} - \mathrm{E}_{HOMO})}{2}$$

That IP ionization energy is approximately equal to -E_{HOMO} - and EA is electron-affinity energy and approximately equal to -E_{LUMO}. They introduced a quantity called electrophilicity, which is a measure of the tendency of a compound to pull an electron cloud from the environment toward it. The exchange-correlation function of the wb97xd has more hardness, which is in agreement with the less dipole moment. For the wb97xd functional, the electrophilicity values are lower, which is in agreement with the negative chemical potential and more hardness.

Table 2. Reactivity parameters include hardness (η), chemical potential (μ), softness (σ) and electrophilicity (ω) for adsorbate, ppyphos adsorbent, and adsorption of this adsorbate on ppyphos. Calculated charge transfer by Mulliken charge analysis ($Q_{mulliken}$), and natural population analysis (Q_{NBO}) and intermolecular distance for adsorption p-clph on ppyphos at B3LYP/6-31+G (d,p) and WB97XD/6-31+G (d,p) level of theory.

System	$\eta(eV)$	$\mu(eV)$	$\sigma(eV^{-1})$	$\omega(eV)$	$d(A^{\circ})$	$Q_{NBO}(e)$	$Q_{mulliken}(e)$
p-clph	2.755	-3.642	0.362	2.407	-	-	-
p-clphw	4.685	-3.647	0.213	1.419	-	-	-
ppyphos	1.425	-3.874	0.701	5.265	-	-	-
ppyphosw	3.218	-3.940	0.310	2.411	-	-	-
p-clph-ppyphos	1.405	-4.075	1.975	5.908	2.55	-0.029	-0.046
p-clph-ppyphosw	3.164	-4.023	0.316	2.557	2.52	+0.00019	+0.123
p-clph-ppyphos1	1.403	-3.935	0.712	5.518	3.26	+0.00029	-0.07
p-clph-ppyphos1w	3.213	-3.989	0.311	2.476	2.82	+0.00118	+0.057

4. Conclusion

The calculations show that the WB97XD correlation-exchange function has more negative absorption energy than B3LYP, which could be related to the involvement of the dispersion forces in this correlation-exchange function. The more negative absorption energy almost always increases the bandgap and this leads to the stability of the system.

Acknowledgment

The author appreciates the chemistry department of the Sharif University of Technology.

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