Research Article

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Computational studies on electronic and optical properties of dopamine derivatives structure: A DFT study**

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Abstract: Dopamine is considered an important molecule that plays several essential roles in the human body, and herein lies the key to this paper on the electronic and optical properties of dopamine and its derivatives, such as quinone and L-dihydroxyphenylalanine (L-DOPA), using DFT and TD-DFT methods, respectively. Our findings show that dopamine has a dielectric behavior, whereas quinone and L-DOPA have semiconductor behaviors in the ground and excited states. By computing the optical properties, we disclose that the electronic transition spectrum of dopamine, quinone and L-DOPA are observed in the ultraviolet region, visible spectrum, and (ultraviolet and visible regions), respectively. Other properties, such as ionization potential, electronic affinity, hardness and softness are also calculated due to their importance in sensor applications and sensing.

Keywords: DFT; TD-DFT; dopamine; quinone; L-DOPA; energy gap

1 Introduction

Organic electronic and optical properties are enabling significant advances in the fields of materials science, handling the creation of potential materials of inexpensive produce and straightforward for much of devices, such as solar photovoltaic or light-emitting diodes (LEDs) [1–3].

Dopamine (3,4-Dihydroxyphenethylamine) might be considered one of the hormone and generality essential neurotransmitters that work as a messenger with regard to synaptic transmission in the brain and body. Additionally, it represents a major trait in learning, motor control, motivation, attention, etc. [4–7]. Naturally, dopamine can cause serious mental disorders because of its several functions within the human body. Particular examples are the addictions to drug, computer game, social media, and gambling. In general, the addictions are associated to the immoderate amounts release of dopamine. These addictions can be attributed to the repetition of such behaviors that lead to dopamine release [8–10]. In recent decades, some researchers have indicated that Dihydroxyphenethylamine ($C_8H_{11}NO_2$) is associated with attention deficit / hyperactivity disorder [11, 12]. Furthermore, Parkinson's disease can be traced to dopamine deficiency. Unfortunately, dopamine cannot be administered therapeutically since it cannot penetrate the blood brain barrier. However, L-DOPA is considered a precursor to dopamine in that it can be employed to extend the concentration of the material of $C_8H_{11}NO_2$ in the medicament of Parkinson's illness due to its capability to pass through the barrier [13]. Of course, the ability to monitor both dopamine ($C_8H_{11}NO_2$) and L-DOPA ($C_9H_{11}NO_4$) concentrations are of considerable biological importance [14]. That notwithstanding, it is significant within the brain and body, but it is difficult to discover the presence of $C_8H_{11}NO_2$. Hence, the cyclic voltammetry (CV) is usually utilized to defect whether dopamine exists [15]. This method is utilized experimentally whereas dopamine ($C_8H_{11}NO_2$) is oxidized to become dopamine o-quinone ($C_8H_9NO_2$) [16].

The major purpose of this study is to enhance some electronic and optical properties of the dopamine and its aforementioned derivatives. Then, we can utilize these systems in the optoelectronic applications such as photovoltaic and solar cells, LED, and sensors.

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2 Computational details

In this study, we begin by optimizing dopamine, quinone, and L-DOPA using DFT method, which is implemented in the Gaussian (09W) package with the 6-31G basis set [17] in its ground state. Depending on the first principle of DFT computations, the energy gaps (E_g), frontier orbital distributions (HOMO and LUMO), and IR spectra are computed to all these systems. The energy gap can be computed from this formula [18–22]:

$$E_g = E_{LUMO} - E_{HOMO} \quad (1)$$

Based on the DFT method and Koopmans' theorem, we study the reactivity of these structures. The description of the reactivity would include the ionization potential ($I.P$), electron affinity ($E.A$), electronegativity (χ), chemical hardness (η) and chemical softness (σ) which are calculated by using the following parameters [23–25]:

$$\left. \begin{aligned} I.P &= -E_{HOMO} \\ E.A &= -E_{LUMO} \end{aligned} \right\} \quad (2)$$

$$\chi = \frac{I.P + E.A}{2} \quad (3)$$

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial^2 N} \right)_{V(r)} \quad (4)$$

$$\eta = \frac{I.P - E.A}{2} \quad (5)$$

$$\sigma = \frac{1}{2\eta} \quad (6)$$

DFT using Becke exchange [26] functional and Lee-Yang-Parr correlation functional [27], with the 6-31G mention basis set [28] were applied in the quantum-chemical evaluation [29–31]. Later, the optical properties of these structures

are calculated via the TD-DFT method that also carried out in the 09W package. Both electronic excitation energies and oscillator strengths are evaluated as perpendicular excitations of the lower ground state of systems via TD-DFT approach in space. Eventually, the TD-DFT absorption spectra evaluations are realized employing B3LYP with 6-31G(d) basis set [21, 22].

3 Results and discussions

Dopamine has an amine group and a catechol ring at the termination of a linear hydrocarbon. Hence, dopamine has a number of isomers that depends on the location of two Hydroxyl groups. In this work, we shall investigate different properties of three molecular systems.

The expression energy optimization involves an attempt to satisfy the configuration at the lowest-energy of molecules. Such a technique is used to find the wave function and estimate the energy at starting geometry. Later, we come to identify a new geometry with lower energy by means of running duplicate processes until we obtain the lowest-energy geometry. Finally, the energy optimization of these structures along with the force resultant between all atoms should be equal to zero. Obviously, the optimization process will stop when it reaches a stationary point, as shown in Figure 1.

The first step in this search is started by optimizing the dopamine derivatives in order to generate specimens of dopamine, dopamine o-quinone and L-DOPA, without symmetry constraint. We find out that these structures are located at the minimum energy state. These results are obtained without imaginary frequency, which means the results are correct and accurate. The geometrical optimization of these structures are shown in Figure 2.

Figure 1: The different steps are utilized to treat and select a best geometry optimization of structures: (a) dopamine, (b) L-DOPA, (c) quinone.

Figure 2: Geometrical optimization of the dopamine (a), L-DOPA (b), and quinone (c). The white, gray, red, and blue colours indicate Hydrogen, Carbon, Oxygen, and Nitrogen, respectively. The length of the bonds are also clarified.

Figure 3: Infrared spectra each of the dopamine (a), L-DOPA (b), and quinone (c).

Figure 3 represents the infrared spectrum diagram of the dopamine derivatives. This result is in agreement with the previous studies [32, 33]. This Figure also shows the number of peaks, which represent the bonding bonds between two carbon atoms in the range of (800–1300) cm^{-1} region. It is referred to the single bonds (C-C) compounds. Besides, the values at 1550 cm^{-1} region approximately represent the double bonds (C=C) vibration aromatic compounds. The characteristic absorbance peak at 3100 cm^{-1} corresponds to the (C-H) vibration aliphatic hydrogens. Therefore, these values of peaks are tremendously in agreement with the previous reference [34]. Besides fundamentals, there are some other bands in absorption spectrum, called overtones or combinations, which may also provide evidence for a relatively weak intensity.

Figure 4 shows the schematic of the HOMO and LUMO surfaces. The resulting orbitals may be interpreted as per molecular orbital theory, which considers molecular orbitals a linear combination of the atomic orbitals. The band

Figure 4: The values of LUMO (in the top), HOMO (in the bottom) and energy gap for dopamine derivatives at two states (ground and excited state).

gap is defined as the difference between the upper region of the valence band and the lower region of the conduction band. From this Figure, we can observe that the dopamine has a highest apex at the ground state (0.358 eV). The en-

Table 1: The values of ionization potential (I.P), electron affinity (E.A), Mulliken electronegativity (χ), hardness (η), and softness (σ).

System	I.P (eV)	E.A (eV)	χ (eV)	η (eV)	σ (eV) ⁻¹
Dopamine	5.3783	-0.3581	2.5101	2.868	0.1743
L-DOPA	5.4665	-0.3216	2.5724	2.894	0.1727
Quinone	6.6572	3.3474	5.0022	1.655	0.3021

Table 2: The values of wavelength of maximum emission (λ_{max}), vertical excited of energy (ΩA), oscillator strength (f), and major electronic transition of the dopamine, L-DOPA, and quinone with TD-DFT method.

System	λ_{max} (nm)	ΩA (eV)	Os. S.(f)	Electronic transition
Dopamine	243.69	5.0877	0.0525	H-2->L+1 (22%)
L-DOPA	544.85	2.2756	0.0055	HOMO->LUMO (93%)
Quinone	520.02	2.3842	0.0131	HOMO->LUMO (94%)

ergy gaps of all system are expanded from semiconductor to insulator. Yet, while the energy gap of the quinone in the ground and excited states occurs within the energy gap for semiconductor materials (3.309 and 2.882 eV), the values of the energy gap to relative the dopamine and L-DOPA occur within insulator region. These parameters are considered very significant because the value of the energy gap is represented as a gauge to determine whether can be used it in applications of electronic. In other words, the semiconductor devices of electronic can be used depending on the value of energy gap.

In Table 1, all values are calculated by using the expression in Eqs. (1–6). In fact, the ionization potential and electron affinity are very important because they can be utilized to predict the strength of chemical bonds. Additionally, they can be used as measures of whether an atom or molecule will become an electron donor or an electron acceptor. We detect that the quinone structure has a higher energy to become cation due to its higher value of the *I.P.*, which is (6.6572 eV) compared with other structures. However, the dopamine structure requires a smaller energy to become cation due to its lower value of the *I.P.* (5.3783 eV) compared with other structures.

The negative *E.A.* is required to obtain efficient cathodes that can supply electrons to the vacuum with little energy loss. Furthermore, both *I.P.* and *E.A.* are represented as primary bases to predict and obtain other properties, and so they can be used as sensors devices.

For the electronegativity, we find out that the quinone structure has a higher value (5.0022 eV), which means this structure has a greater force to attract the shared electrons while the dopamine structure has a smaller value. So, it is equal 2.5101 eV.

Drawing on previous equations and Table 1, we can see that the energy gap is a function of the chemical hardness

and softness. When the structure has a higher value of the hardness, it means it has a large value of the energy gap. For instance, the L-DOPA structure has value of the hardness and energy gap (at ground state), which are equal to (2.894 and 5.788 eV), respectively. Softness is equal to the inverse of the hardness, which leads to the largest value of hardness corresponding to the smallest value of softness and vice versa. The hardness and softness are parameters that are so important that they can be used to test both the performance and sensitivity of explosive molecules [35].

In this section, the absorption wavelength (λ_{max}), vertical excited singlet states or excitation energy (ΩA), and oscillator strength (f) along with the main excitation configuration of the dopamine derivatives are studied by applying TD-DFT method. From Table 2 and Figure 5, all structures reveal a strong absorption band in UV-VIS regions, which is around 243.69 nm for dopamine while the L-DOPA and quinone shift toward the VIS region. It is, therefore, evident that the absorbed wavelengths of these structures increase as shown (dopamine < quinone < L-DOPA). This property is very interesting because the results of maximum wavelength of structure as aforementioned in Table 2 and Figure 5 is in complete agreement with the results obtained by using the mathematical equation ($E = 1240/\lambda_{max}$ nm) [36–38]. In so doing, the energy (E) in eV points out that the perpendicular excited singlet states is relative to the samples studied. Moreover, the calculated wavelength values of absorption are inversely proportional to the excitation energy. That means the highest values of vertical excited energy (ΩA) corresponds to the shortest wavelength of maximum emission (λ_{max}), as shown in Table 2. These values of wavelengths are very useful in LEDs applications, optical fibers and solar cell. The values of oscillator strengths occur between (0.0525 and 0.0055). Thus, these results are in

Figure 5: The UV-VIS spectra each of (a) dopamine, (b) L-DOPA, and (c) quinone.

good agreement with references to the oscillator strengths ranging at (0 and 1) [39].

4 Conclusion

In this paper, the electronic and optical properties of dopamine and its derivatives have been studied using DFT / B3LYP technique / 6-311G (d,p) level of theory. According to the energy gap, we have detected that the dopamine and quinone have insulator and semiconductor behaviors while L-DOPA exhibited a dielectric behavior in the ground state and a semiconductor behavior in the excited state. Finally, the electronic transition spectrum of the dopamine have appeared in the ultraviolet region, while the resulting spectrum of the L-DOPA have occurred in the ultra violet and visible regions, respectively, and the quinone have been within the visible spectrum.

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