Theoretical and experimental studies for different compounds to calculate: electronic transfer, energy gap and NLO properties

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Abstract
This work involves theoretical and experimental studies for seven compounds to calculate the electrons spectrum and NLO properties. The theoretical study is done by employing the Time Depending Density Functional Theory TD-DFT and B3LYP/high basis set 6-311++G (2d,2p), using Gaussian program 09. Experimental study by UV/VIS spectrophotometer device to prove the theoretical study. Theoretical and experimental results were applicable in spectrum and energy gap values, in addition to convergence theoretically the energy gap results from $\Delta E_{HOMO\text{-}LUMO}$ and UV/VIS. spectrum. Consider the theoretical method very appropriate to compounds that absorb in vacuum UV.

Keywords: TD-DFT, UV-VIS, NLO, Eg

Introduction
        Quantum mechanics calculation is the theory of calculations equations include various programming languages. considered the semiempirical theory (PM3) developed by Dewar and coworkers [1-4] succeeded In molecular cloning energies, repeat molecular structures, and interpret the chemical reaction the either important to TD-DFT suggested the atomic weight, vibration of bonds and energy of atoms, and electronic ionization [5-8]. The energy gap represents the distance between equivalent band and conductance band in semiconductor, with in other materials the different between MO [9]. The two different spectra forms emission spectroscopy are a molecule that is exposed to a transition from high energy to low energy levels releasing excess energy as the photon. Radiation losses due to the absorption of these wavelengths are detected by absorption spectroscopy. The energy of the photon emitted or absorbed [10].

There was an important limit known as selection rule, the first type, and spin selection rule during the electronic transition, no change in spin inversion, the second type, Laporte selection rule, related to molecules that have a center of symmetry. [11,12,13]. The structure molecule in the excited state different from that in the ground state, the Franck–Condon basis is a semi stated an transition of electronic is almost take place changes not occur in the positions of the nuclei in structure [14].

The transferred from a gas phase to a solvent the wavelength and intensity of absorption are affected. These were related to asymmetric disorder of the excited and ground states of the molecule. These depending on the state of the reactions between solvent and solute at these states. But the absorption of spectra by non-polar solvents keep almost the same characters of the gas phase spectra [15,16]. The aim of this work is to study the UV/VIS. spectra and energy gap by using quantum mechanical calculations done by DFT method and compare with experimental results to prove this method a powerful to study UV/VIS. spectra and its properties.

Calculations methods

The construction of the compounds was build using Gaussian View program. Then, equilibrium geometries were calculated by using Gaussian 09 package [17], their corresponding geometries in the gas phase were calculated by (TD_DFT) was done utilizing Beckes three-parameter utilitarian and the connection useful of Lee, Yang and Parr (B3LYP) with a 6-311++G (2d,2p) level of hypothesis [18-20]. Non-linear optical (NLO) properties were calculated in vacuum, the biological activity calculated in water as a solvent, both by HF/321G. The calculated descriptors involve; the energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), ionization energy (IE), electron affinity (EA), energy gap (E_{GAP}), absolute hardness (η), absolute softness (S), optical softness (So), absolute electronegativity (χ), chemical potential (CP), electrophilicity index (ω), nucleophilicity index (N), additional electronic charges (N_{Max}), polarizability (α), the first hyperpolarizability (β_o) and dipole moment (μ), Equations (1-13). Urea was used as a standard in the determination of NLO properties [21-23].

$$IE \text{ (Ionization potential)}= -E_{HOMO} \tag{1}$$

$$EA \text{ (Electron affinity)}= -E_{LUMO} \tag{2}$$

$$E_{gap}= E_{LUMO}-E_{HOMO} \tag{3}$$

$$\eta \text{ (Hardness)}= (\partial^2 E/\partial N^2)\nu(r) \quad \eta= (IE-EA)/2 \tag{4}$$

$$S \text{ (global softness)}= 1/\eta \tag{5}$$

$$So= 1/E_{gap} \tag{6}$$

$$\chi \text{ (Electronegativity)}= -\mu= -(\partial E/\partial\Lambda)\nu(\rho) = (IE+EA)/2 \tag{7}$$

$$CP= -\chi \tag{8}$$

$$\text{Global electrophilicity index } (\omega)= (-x)^2/2\eta = \mu^2/2\eta \tag{9}$$

$$N_{Max}= -CP/\eta \tag{10}$$

$$N= 1/\omega \tag{11}$$

α (Polarizability)= $1/3(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$ (12)

β_o (hyperpolarizability)= $[(\beta_{xxx}+\beta_{xyy}+\beta_{xzz})^2+(\beta_{yyy}+\beta_{yzz}+\beta_{yxx})^2+(\beta_{zzz}+\beta_{zxx}+\beta_{zyy})^2$ (13)

Where the αxx= polarizability in the x-axis direction, αyy= polarizability in the y-axis direction, αzz= polarizability in the z-axis direction. The βxxx, βyyy, βzzz= hyperpolarizability in x, y, z-axis, respectively.

Experimental part

Seven compounds measured there spectra in spectrophotometer device type (sp-3000 nano). Four compounds in liquid state (acetone, acetic acid, aniline, and ethanol) and three in solid state (naphthalene, benzoic acid, and alpha-naphthol). The solid-state compounds treated with suitable solvents. The order was introduced to device like the range of wavelength scan (190-800 nm) and to extract the greater wavelength with the spectra figure for each compound.

Results and discussion

In this work, seven electronic transitions are done by Time-Dependent Density Functional Theory method (TD-DFT) [24]. These analyses discussed from lowest energy structures (optimized) in the gas phase. Quantum chemical computations are employed to investigate the electronic properties for the studied compounds. The calculations contain the electronic absorption spectra (UV-Visible), such as HOMO and LUMO orbital energies to calculate the energy gap in equation 1:

$E_g = E_{LUMO} - E_{HOMO}$

Moreover, from spectra by using equation 2: $E=hC/\lambda$

Where (h= blank constant, c= speed of light, λ= greater wavelength) with absorption wavelengths (λ max), and oscillator strengths (*f*) based on the optimized geometry in gas phase, **table 1** [25]. Theoretically and experimentally spectra for all compounds were discussed, benzoic acid in **figure 1** showed two peaks first at (215.6, 220 nm) for π-π*, and second for n- π* at (264.9, 270 nm) respectively predict and experiment value, while the energy gap equal to (5.7, 5.6 eV), acetic acid wave length (164, - nm) in **figure 2** for π -π* and (191, - nm) for n-π* respectively, while the energy gap (6.8, - eV), **figure 3** showed acetone wave length for π-π* equal to (173.17, - nm) and n-π* equal to (213.42, 210 nm) respectively, in addition to energy gap value (6.2, 5.9 eV), aniline structure showed absorb at (227.14, 220 nm) expected for π-π* as shown in **figure 4** and (247.84, 242 nm) for n-π* respectively, when the energy gap equal to (5.7, 5.6 eV). α-Naphthol present one peak at (286.9, 278 nm) respectively for π-π* with (298.8, 320 nm) for n- π* and energy gap (5.4, 4.4 eV) as present in **figure 5**, ethanol showed peak at (167.6 nm) for n-π* respectively and (7.2 eV) for energy gap can observe in **figure 6**, and naphthalene showed absorb at (288, 286 nm) respectively due to π-π* as showed in **figure 7**, and energy gap (4.6, 4.3 eV). Results showed the converge between theoretical (ΔE_theo.) and experimental (ΔE_exp.) measurement as shown in **figure 8**, this results can indicate possibility to dependent TD-DFT method.

More errors present in vacuum UV (150-200) in use spectrophotometer device, because interfere the spectra of medium, so theatrical method consider the right way, although the value characterized with dash mean in vacuum area can't be good value. Energy gap values in **table 1** are approximate relatively, this can be the theoretical method reference for all compounds syntheses and novel.

The oscillator strength (f) represent probability to absorb energy and transform to other excite state when its value more than (0.0003), and increase this value the absorption increase. The results obtained the optimizing structures and the electrons density as showed in **table 2**. Different in energy ($\Delta E_{HOMO-LUMO}$) calculated theoretically could dependent to characterize the lambda max in more charts by compare ($\Delta E_{HOMO-LUMO}$) with (E) value that funded from λ.

Table 1: Theoretical and experimental results for the compounds studied.

| Com. Name	Theoretical Results					Experimental Results		
	π-π^*	n- π^*	$\Delta E_{LUMO\text{-}HOMO}$	E= hc/λ	f	π-π^*	n- π^*	E= hc/λ
Benzoic acid	215.6	264.9	5.770	5.7674	0.0187	220	270	5.6363
Acetic acid	164	191	6.83597	6.77959	0.004	-	-	-
Acetone	173.17	213.42	6.22782	5.81013	0.0273	-	210	5.9047
Aniline	227.14	247.84	5.78539	5.46255	0.0113	220	242	5.6363
α-Naphthol	286.9	298.8	4.5838	4.3220	0.0664	278	320	4.4604
Ethanol	-	167.6	7.20385	7.1971	0.0108	-	-	-
Naphthalene	288	-	4.6608	4.2779	0.0597	286	-	4.3356
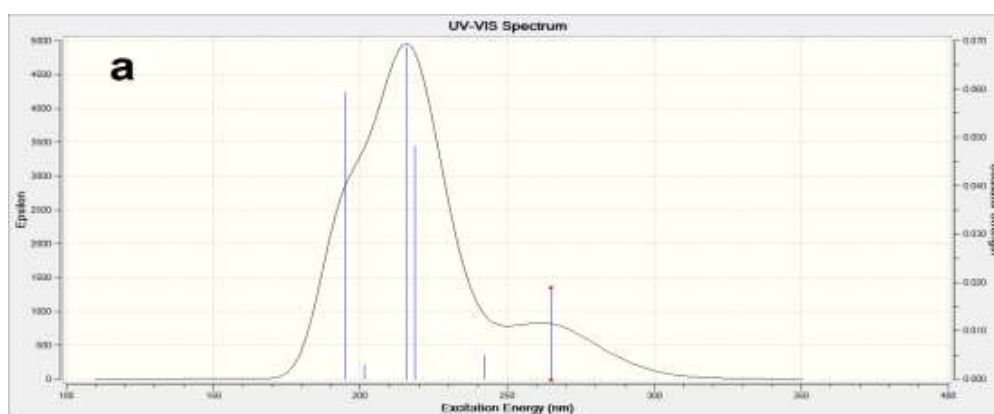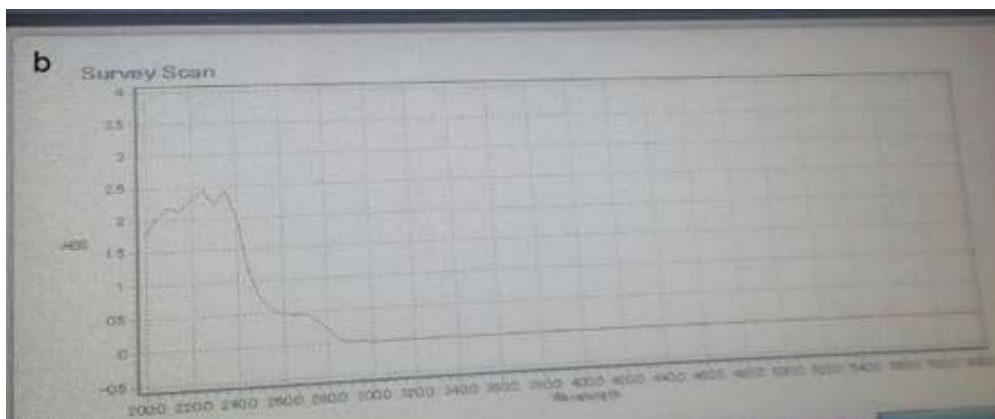
Figure 1: Charts showing lambda max and other absorption for benzoic acid a-
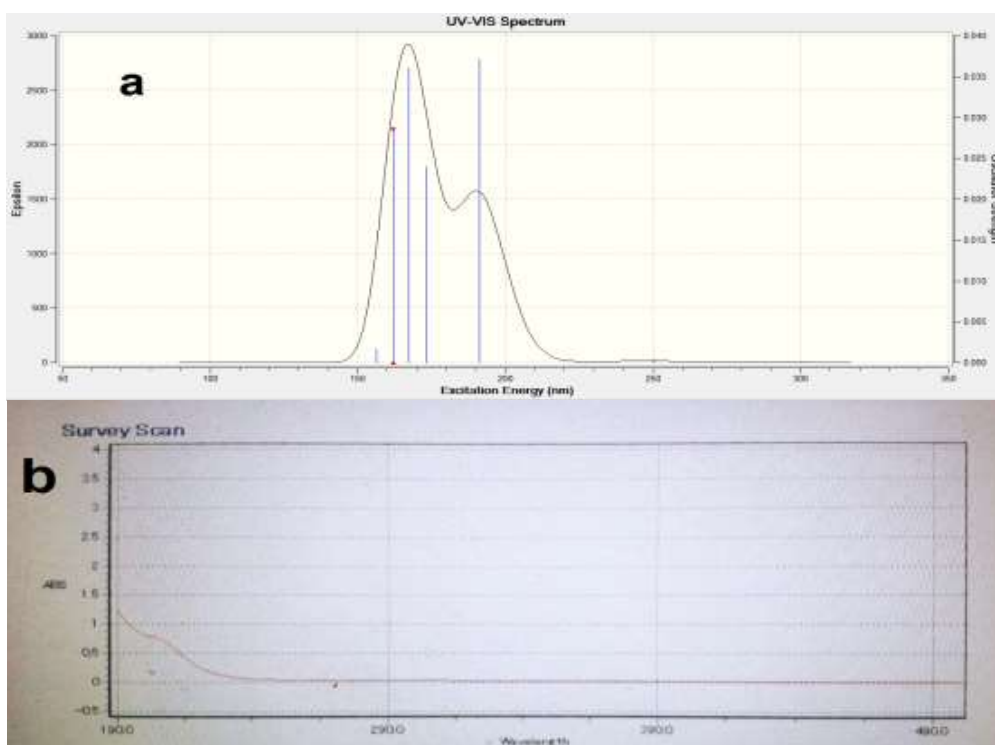Theoretically by (TD-DFT) b- Experimentally.

Figure 2: Charts showing lambda max and other absorption for acetic acid a-
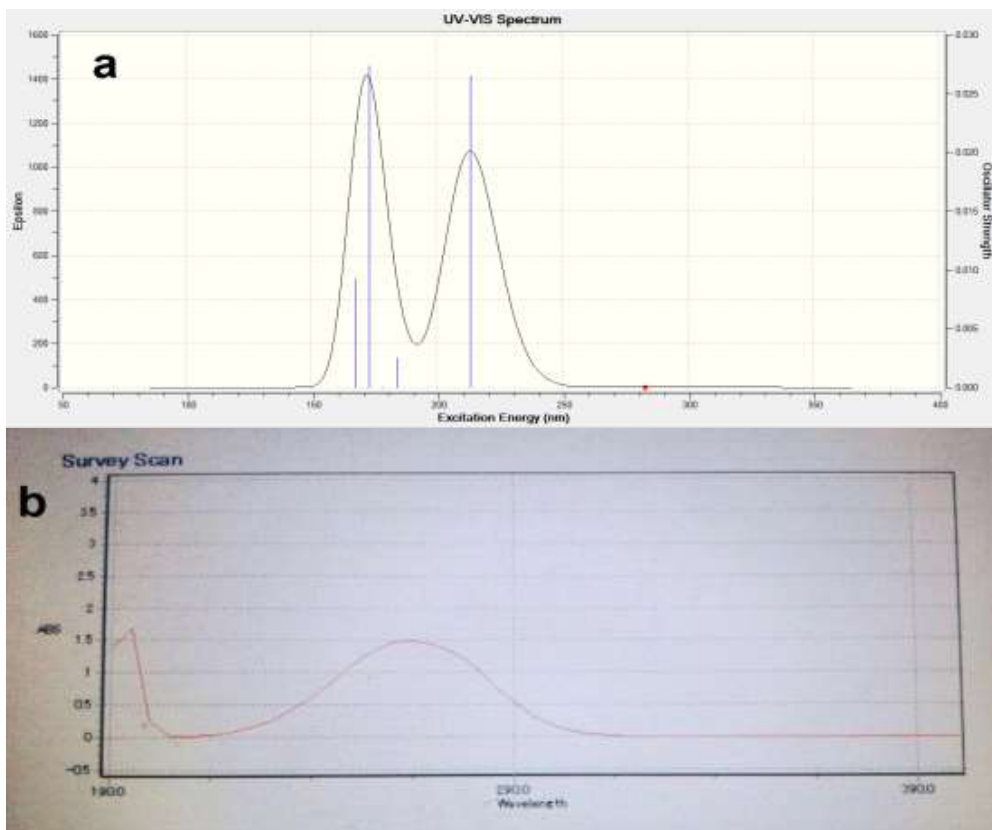Theoretically by (TD-DFT)   b- Experimentally.

Figure 3: Charts showing lambda max and other absorption for acetone a-
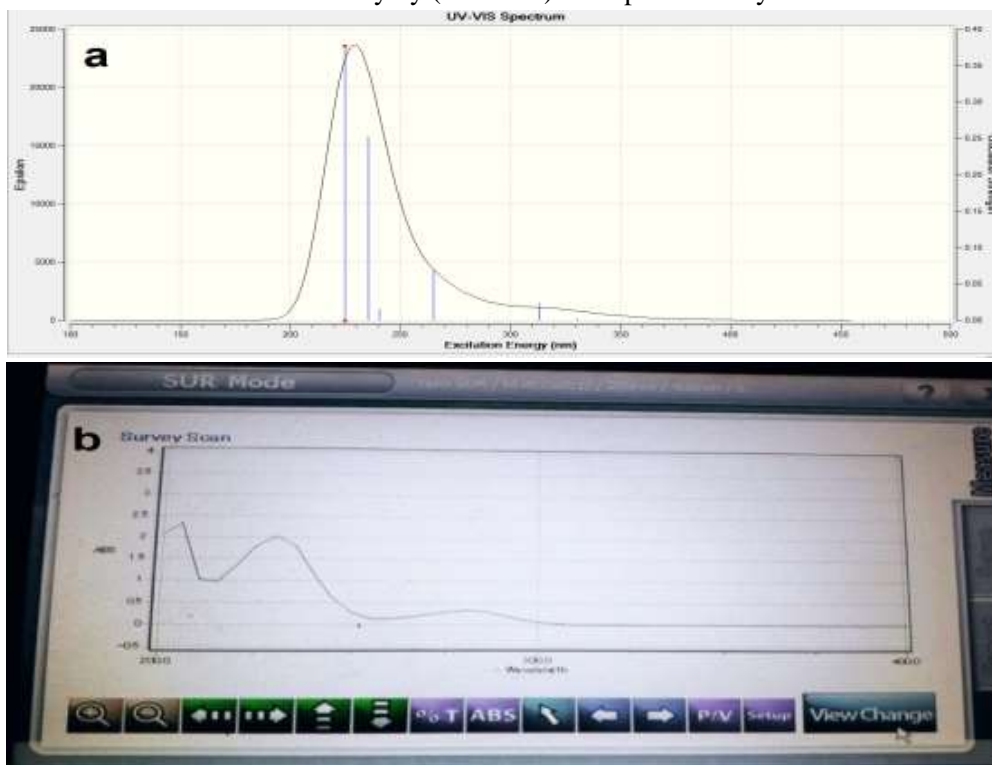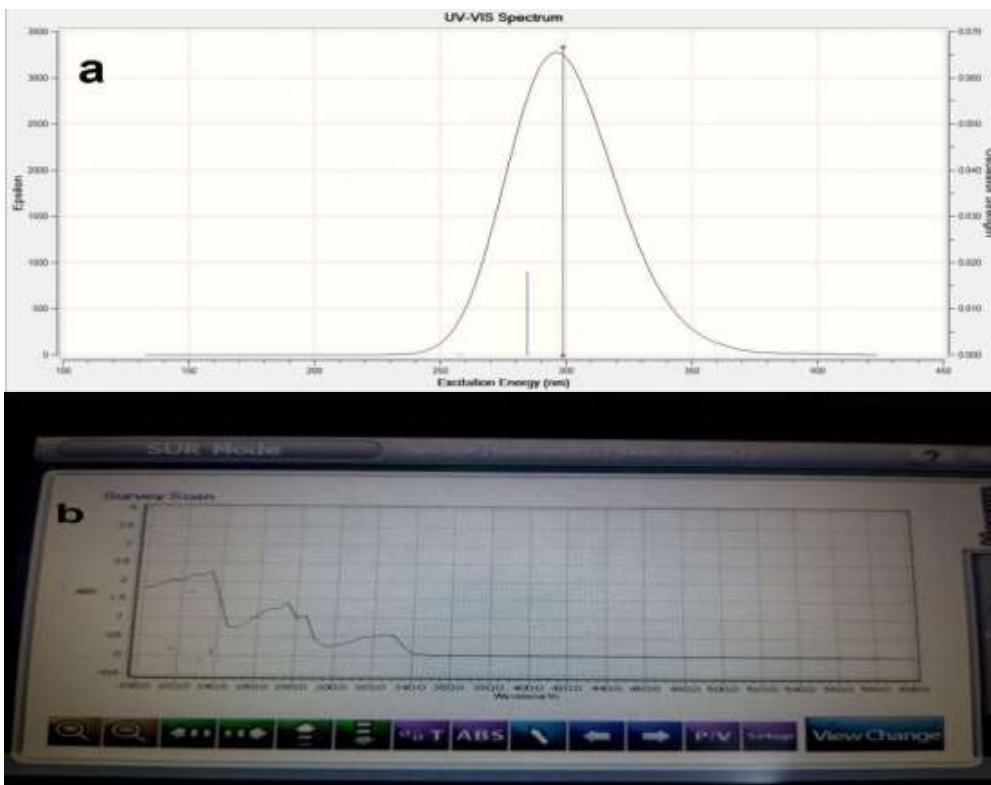Theoretically by (TD-DFT) b- Experimentally.

Figure 4: Charts showing lambda max and other absorption for aniline a-
Theoretically by (TD-DFT) b- Experimentally.

Figure 5: Charts showing lambda max and other absorption for carbon α-Naphthol a-Theoretically by (TD-DFT) b- Experimentally.
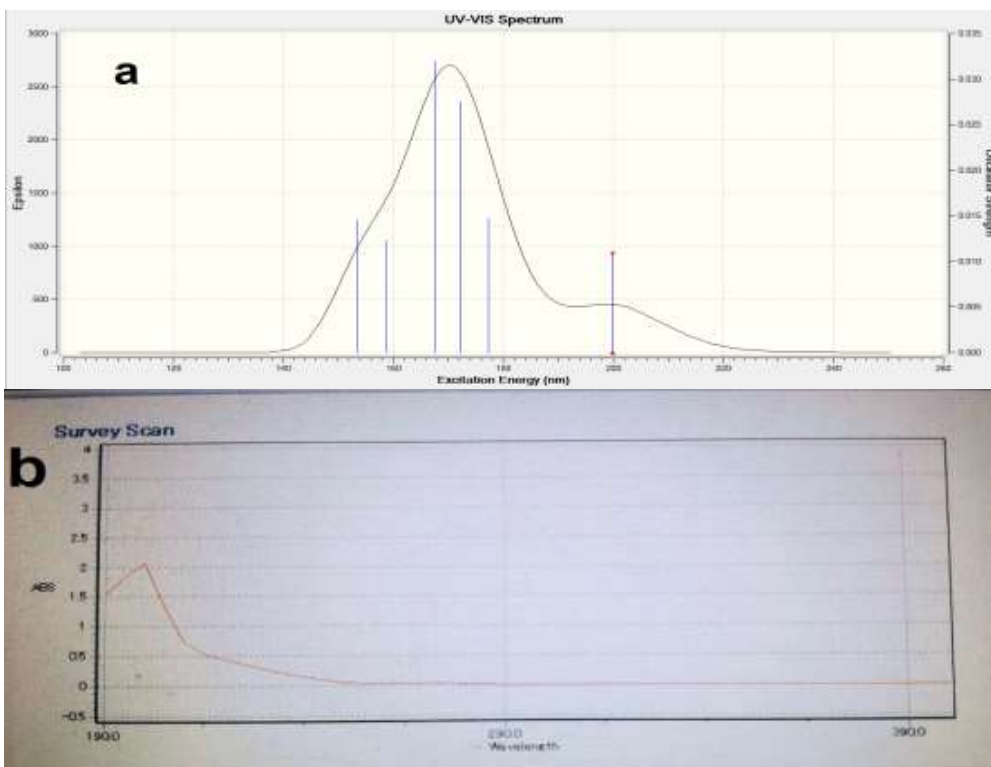

Figure 6: Charts showing lambda max and other absorption for ethanol a-Theoretically by (TD-DFT) b-Experimentally.
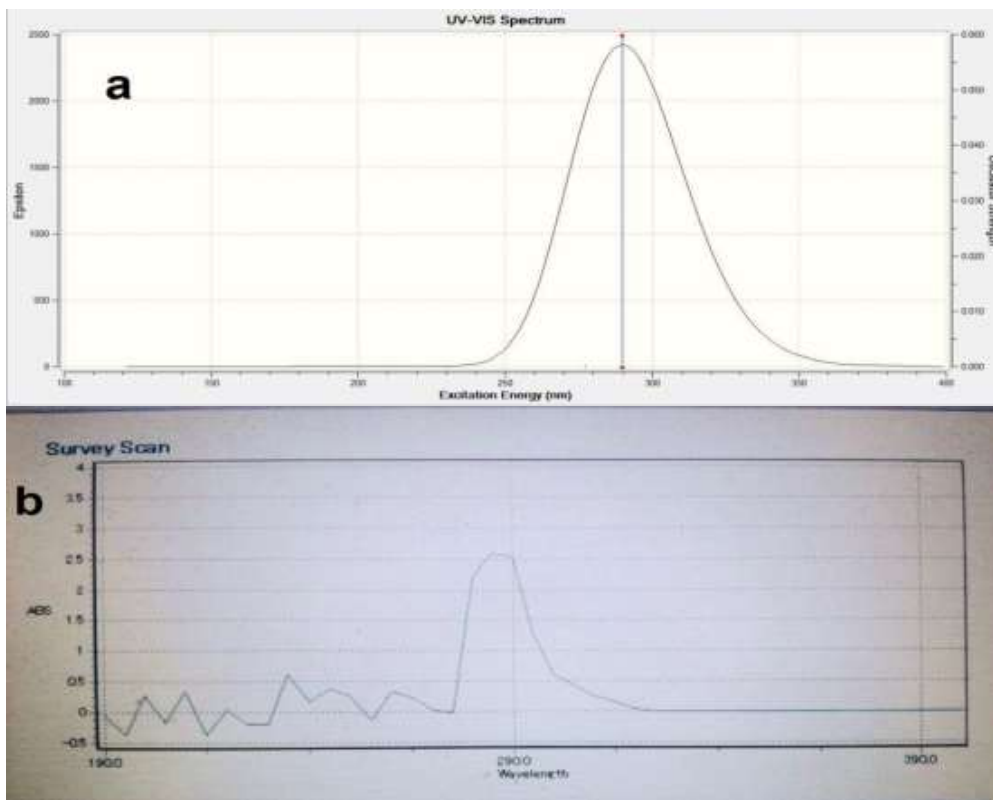
Figure 7: Charts showing lambda max and other absorption for naphthalene a-Theoretically by (TD-DFT) b-Experimentally.
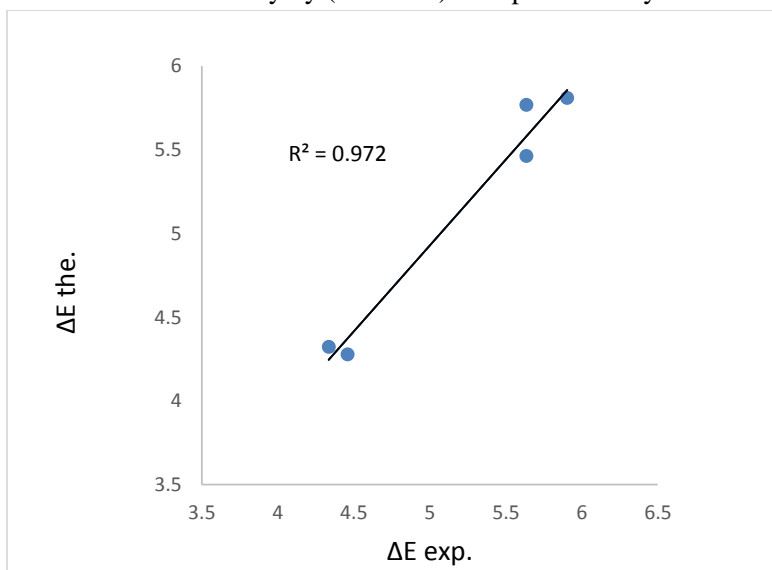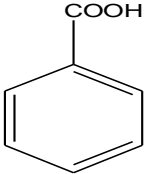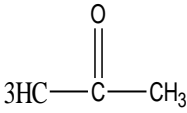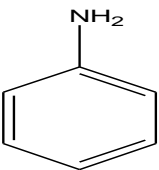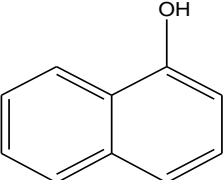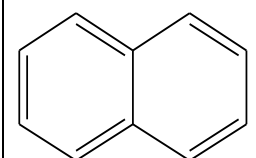

Figure 8: Predicted values and experimental values and there coefficient determination.

Table 2: The Frontier molecule orbital density distributions of the compounds in optimization as calculations using TD-DFT method. Red color indicates the negatively charged lobe; green color indicates the positive charge lobe.

Com. Name	Structure	Optimized structure by TD-DFT
Benzoic acid		
Acetic acid	CH3COOH	
Acetone		
Aniline		
α-Naphthol		

Ethanol	CH3CH2OH	
Naphthalene		

Information from (NLO)

The important of (NLO) properties present in telecommunications and optical practical. The delocalization of π electrons and the molecules planarity increase the NLO properties to molecules. The NLO properties investigated using computational techniques in easily. Nonetheless, when assessing the NLO properties, vacuum measurement should be taken into consideration. Several quantum chemical descriptors (QCDs) are determined to estimate the NLO properties and to indicate the best. The QCDs of NLO properties as shown in Table 3. The urea is generally used as a reference in the investigations of NLO properties [26-30]. Therefore, urea as reference at the same level of calculation.

Table 3: Some quantum chemical descriptors of NLO properties for calculated prodrugs in the vacuum.

Comp.	$E_{HOMO}{}^a$	$E_{LUMO}{}^a$	IE^a	EA^a	$E_{gap}{}^a$	η^a
Benzoic acid	-7.511	-1.662	7.511	1.662	5.848	2.924
Acetic acid	-7.854	-1.018	7.854	1.018	6.836	3.418
Acetone	-7.053	-0.824	7.053	0.824	6.228	3.114
Aniline	-6.470	-0.576	6.470	0.576	5.894	2.947
α-Naphthol	-8.543	-0.355	8.543	0.355	8.188	4.094
Ethanol	-7.560	-0.355	7.560	0.355	7.204	3.602
Naphthalene	-5.842	-1.749	5.842	1.749	4.093	2.046
Urea	-6.727	1.559	9.522	-1.559	8.286	2.633
Comp.	χ^a	CP^a	S^b	$S_o{}^b$	N_{Max}	ω
Benzoic acid	4.586	-4.586	0.341	0.170	1.568	3.597
Acetic acid	4.436	-4.436	0.292	0.146	1.297	2.879
Acetone	3.938	-3.938	0.321	0.160	1.264	2.491
Aniline	3.523	-3.523	0.339	0.169	1.195	2.106

α-Naphthol	4.449	-4.449	0.244	0.122	1.086	2.417
Ethanol	3.958	-3.958	0.277	0.138	1.098	2.174
Naphthalene	3.796	-3.796	0.488	0.244	1.854	3.520
Urea	6.889	-6.889	0.380	0.121	2.616	0.805

a: in eV, b: in eV^{-1}, c: in Å^3, d: in cm^5/esu.

These parameters only give suggestion about the molecules. The favorite QCDs of NLO properties that should be available in the active compounds are describe in the following:

- E_{HOMO}; if the energy level of HOMO is high, NLO properties of molecules increase with the increasing the energy level of HOMO.
Naph.>Ani.>Urea>Acet.>Benz.>Eth.>Acetic.>α-Naph.
- E_{LUMO}; the decreasing of energy gap means increasing of electron mobility and this supports the increase of NLO property
α-Naph.= Eth.>Ani.>Acet.>Acetic> Benz.>Urea>Naph.
- IE; low values meaning high NLO property
Naph.>Ani.>Acet.>Benz.>Eth.>Eth.>Acetic>α-Naph.>Urea
- EA; high values meaning low NLO property
Urea>Naph.= Eth>Ani.>Acet.>Acetic>Benz.>α-Naph.>
- E_g; the decreasing of energy gap means increasing of electron mobility and this supports the increase of NLO property.
Naph.>Benz.>Ani.>Acet.>Acetic>Eth.>α-Naph.>Urea
- η; the decreasing of hardness means the increasing of NLO properties.
Naph.>Urea>Benz.>Ani>Acet.>Acetic>Eth.>α-Naph.
- S; the increasing of softness means the increasing of NLO properties.
Naph.>Urea>Benz.>Ani>Acet.>Acetic>Eth.>α-Naph.
- S_o; the increasing of optical softness means the increasing of NLO properties.
Naph.>Benz.>Ani>Acet.>Acetic>Eth.>α-Naph.>Urea
- χ; electron delocalization increases with decreasing of the absolute electronegativity.
Ani.>Naph.>Acet.>Eth.>Acetic>α-Naph.>Benz.>Urea
- Chemical potential (CP) and nucleophilicity indexes (ω). The increasing in the (CP) and (ω), lead to an increase in the NLO properties of the prodrug.
Ani.>Naph.>Acet.>Eth.>Acetic>α-Naph.>Benz.>Urea
Benz.>Naph.>Acetic>Acet.>α-Naph.>Eth.>Ani.>Urea
- NMAX; the higher value is the more active in NLO applications.
Urea>Naph.>Benz.>Acetic>Acet.>Ani.>Eth.>α-Naph
The net order of correlation for the activity of the studied prodrugs with NLO properties are: Naph.>Benz.>Ani. >Acet.>Acetic> Eth.>α-Naph.

Conclusion

The quantum mechanics calculation presents the electrons transmutation, NLO properties, lambda max, and oscillator strength and energy gap by UV/VIS. In addition to spectra and (HUMO, LUMO) values. The compounds measured experimentally by spectrophotometer device, where described the electrons transmutation and lambda max. The comparison between theoretical and experimental results showed by coefficient determination value (R^2= 0.972), the convergence and the possibility to

choice the grater wavelength by $\Delta E_{HOMO\text{-}LUMO}$. The measurement experimentally in vacuum area is difficult and with some error, so TD-DFT calculation considers the true method. The NLO properties showed the order of compound activity as follow Naph.>Benz.>Ani. >Acet.>Acetic> Eth.>α-Naph.

Acknowledgments

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