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Theoretical and Experimental Studies on Some Anticancer derivatives: Electrochemical investigation

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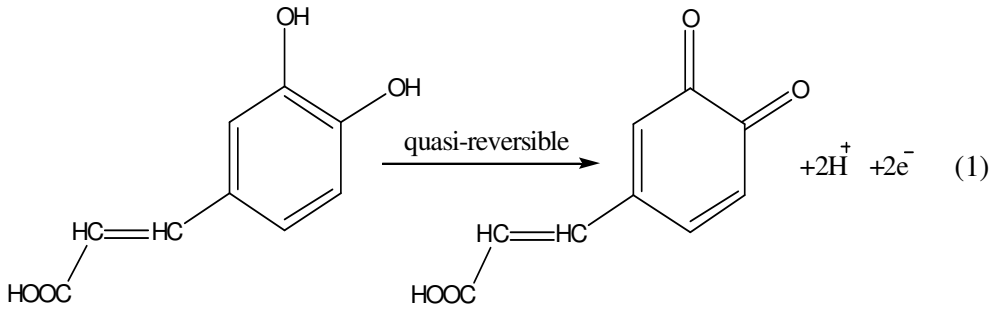
Electrode potential of caffeic acid and some *ortho*-dihydroxybenzene derivatives (anticancer derivatives), an important biological molecules that exhibit a wide variety of physiological and pharmacological properties, in aqueous solution is computed theoretically using Density Functional Theory (DFT) at the level of B3LYP and employing 6-31G(d,p) basis set, and also obtained experimental data with the aim of electrochemical technique (cyclic voltammetry). The theoretical and experimental values for the standard electrode potential of the studied *ortho*-dihydroxybenzene are in excellent agreement with each other and the average error of calculation of electrode potentials is less than 0.002 V between experiment and theory. The agreement mutually verifies the accuracy of experimental method and the validity of mathematical model. Analysis of correlation between experimental electrode potentials and calculated molecular descriptors has also been studied and notable relations have been found between electrode potentials and the eigenvalues of specific molecular orbital.

Keywords: Materials in Medicine; Cyclic voltammetry; DFT; Anticancer derivatives; Chemometrics

1. INTRODUCTION

Many chemicals of *ortho*-dihydroxybenzenes demonstrate an antioxidant activity and are able to prevent auto-oxidation via the radical formation inhibition [1], these compounds exhibit a wide variety of physiological and pharmacological properties. They participate in normal cell functions such

as neurotransmitters. Furthermore, natural compounds of this category extracted from plants (catechins and other polyphenols from green tea) have been found to illustrate anticancer properties [2]. In addition to, caffeic acid (3, 4-dihydroxy cinnamic acid) is ubiquitous in plants. As an early intermediate of phenylpropanoid metabolism, it is a precursor for structural polyphenols and many biologically active secondary compounds that are important in the defense chemistry of plants [3]. Many biological activities have been reported for free caffeic acid. In bioassay experiments, it inhibited the growth of plants [4,5], fungi [6-8], bacteria [9,10] and insects [11]. In several plant species, the levels of caffeic acid and other phenolics appear to be related to past resistance [12]. Caffeic acid is one of many phenolics considered to be an important part of the general defense mechanism of plants against infection predation [13,14]. For these reasons, knowledge of the redox properties of these compounds is important for a better understanding of their behavior in biological environments. Dihydroxybenzenes oxidation at glassy-carbon electrode in aqueous solutions is well documented [15,16] and involves a transfer of two electrons and two protons to provide the associated quinone. In the special case of caffeic acid this process is described by reaction (1).



(1)

Furthermore, accurate calculation of standard electrode potentials is advantageous especially where the experimental measurement is difficult due to complex chemical equilibria [17-22]. For molecules, the experimental redox potentials of which are not available, useful models for the prediction of these potentials would be helpful [23]. Accurate calculation of electrode potentials is advantageous in a number of different areas including the elucidation of electrochemical reaction mechanisms and the design of molecules with particular redox properties [24]. Therefore, it is essential to be able to predict the redox potentials. Quantum mechanical calculations in B3LYP levels of DFT theory have been extensively employed to the study of electrode potential and the results have been compared with the experimental values [25-31].

Since the solvation energy of organic molecules plays a critical role in their reactivity, calculations of solvation energies of studied molecules in water have been also of interest [32]. Different solvation algorithms have been recently introduced in order to calculate solvation energies [33-37]. These methods are different in many ways, one of which is the way they model the cavity created in the solvent into which the solute molecules are placed. In PCM models, the solvation energy is partitioned into four components from the electrostatic interaction (ΔG_{elec}), cavity term (ΔG_{cav}), dispersion (ΔG_{dis}) and repulsion energies (ΔG_{rep}), the last three terms form non-electrostatic interactions between solute and solvent.

In the PCM models, the variation of the free energy when going from vacuum to solution is composed of the work required to build a cavity in the solvent (cavitation energy) together with the electrostatic and non-electrostatic work dispersion and repulsion energy.

Now, we present the calculated electrode potentials of some *ortho*-dihydroxybenzene derivatives. The systems investigated here were: catechol (**1**), Caffeic acid (trans 3,4-dihydroxycinnamic acid) (**2**), Cis 3,4-dihydroxycinnamic acid (**3**) (only in theoretical studies), 4-tert-butylcatechol (**4**), 3,4-dihydroxybenzaldehyde (**5**) and 4-nitro catechol (**6**).

2. CALCULATION AND EXPERIMENTAL DETAILS

A mono-substituted (*Ortho*-quinone) form (Q) can be converted to its reduced *ortho*-dihydroxybenzene (H_2Q) using catechol (H_2Q') as a reference molecule according to the following isodesmic reaction:

$$Q_{(sol)} + H_2Q'_{(sol)} \longrightarrow H_2Q_{(sol)} + Q'_{(sol)} \qquad (2)$$

where the oxidized form of catechol (Q´) along with the reduced form of substituted *o*rtho-dihydroxybenzene are the products of reaction (2). The difference between the standard electrode potential of two species can be obtained from the change in Gibbs free energy of reaction (3):

$$\Delta G = -nF\,(E_Q - E_{Q'}) \qquad (3)$$

where n is number of electrons transferred (n = 2 in this case) and F is the Faraday constant [19,35]. In order to obtain standard electrode potential of molecule Q, the change of Gibbs free energy of reaction (2) is required along with the experimental value of electrode potential of the reference molecule, catechol. The change of standard Gibbs energy of reaction (2) can be computed using the thermodynamic cycle that is shown in Fig. 1 [36]. From this cycle, ΔG is computed by the following expression:

$$\Delta G = \Delta G_{gas} + \Delta G_{sol} \qquad (4)$$

where ΔG_{gas} is standard Gibbs energy of reaction (2) in the gas phase and ΔG_{sol} is the net solvation energy of reaction (2) and is defined as follows:

$$\Delta G_{sol} = \Delta G_{Q',sol} + \Delta G_{H_2Q} - \Delta G_{Q,sol} - \Delta G_{H_2Q',sol} \qquad (5)$$

The gas phase contribution to the Gibbs energy can be determined from ab initio calculations. These calculations have been performed at the B3LYP levels. The zero-point energies and thermal corrections together with entropies have been used to convert the internal energies to the Gibbs energies at 298.15 ^{o}K [37]. Different solvation algorithms have been introduced in order to calculate

solvation energies. Solvation energies, ΔG_{sol}, have been calculated using Polarisable Continuum Model (PCM) [34]. GAUSSIAN98 [38] have been employed for all DFT calculations.

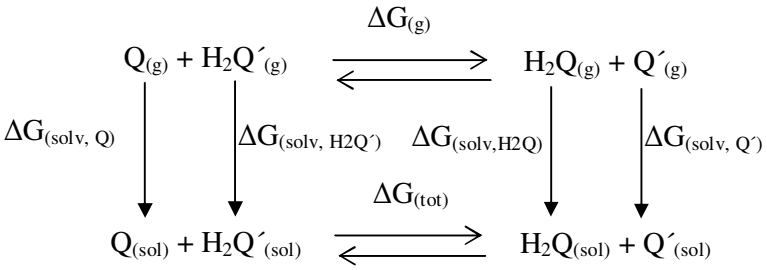


Figure 1. The thermodynamic cycle proposed to convert standard Gibbs energy of isodesmic redox reaction in the gas phase to the standard Gibbs energy of reaction in solution.

All of the cyclic voltammograms (CVs) were performed with the aid of a setup, comprising a PC PIII Pentium 300 MHz microcomputer equipped with a data acquisition board (PCL-818PG, PC-Labcard Co.) and a custom made potentiostat in aqueous media (H_2O) containing of 0.05 M phosphate buffer (pH = 7.0) as a supporting electrolyte. The working electrode (WE) used in the voltammetry experiment was a glassy carbon (GC, disc S = π mm^2). A platinum wire was used as the counter electrode (CE). The working electrode (WE) potentials were measured versus the Ag|AgCl|KCl, sat. as a reference electrode (all electrodes from AZAR electrode) [39].

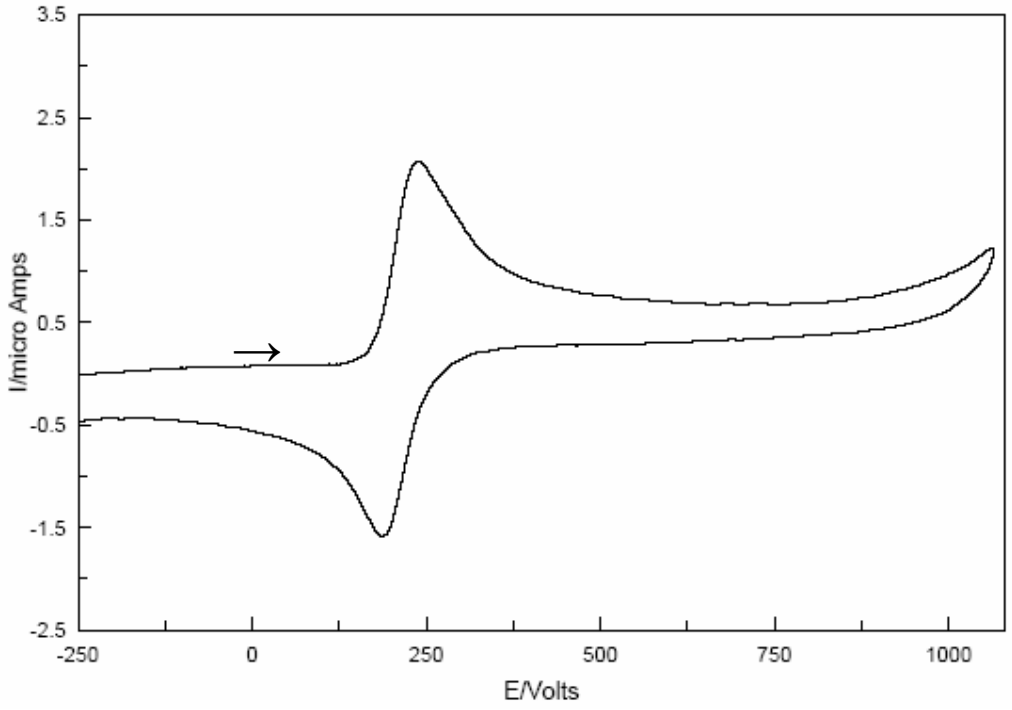


Figure 2. Cyclic voltammogram of 0.25 mM Caffeic acid

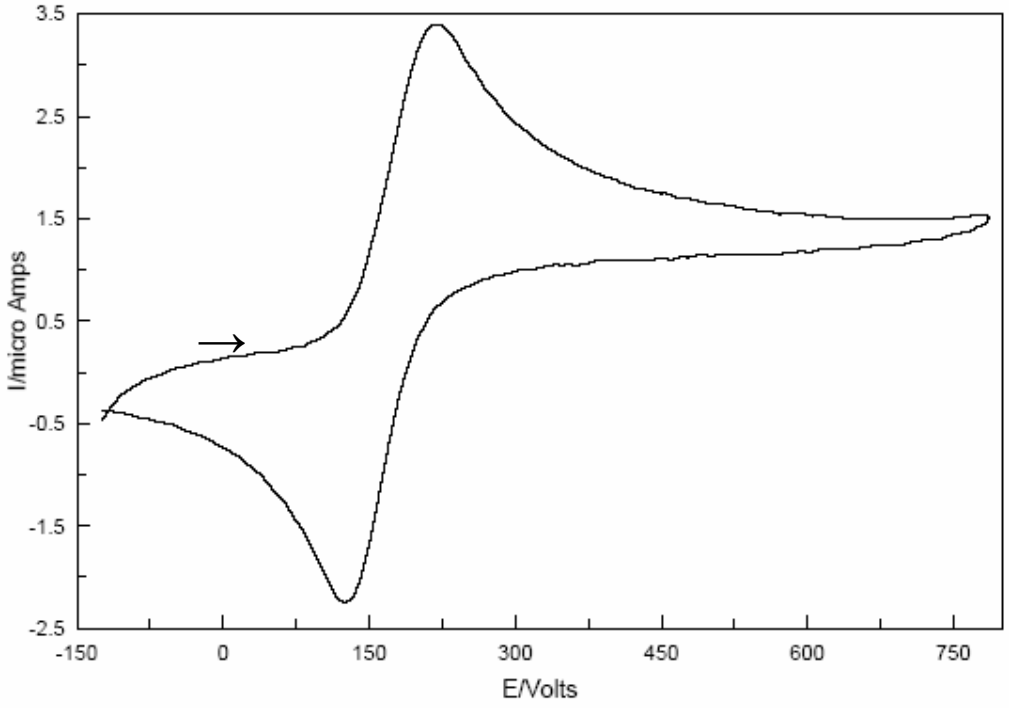


Figure 3. Cyclic voltammogram of 0.25 mM 4-*tert*-butylcatechol

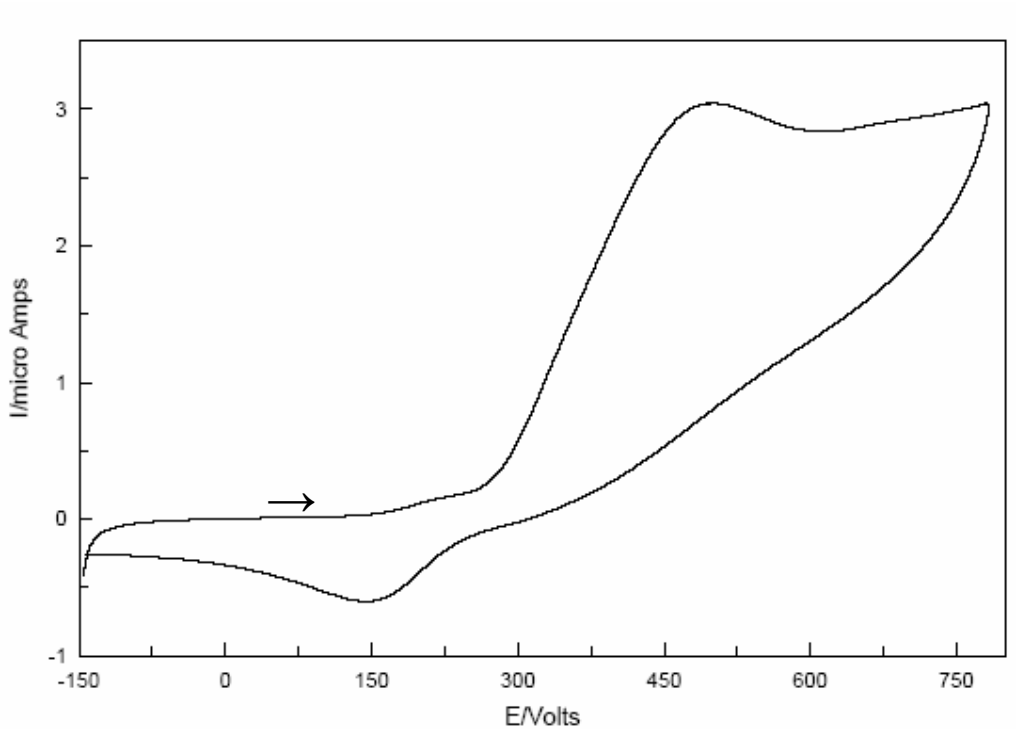


Figure 4. Cyclic voltammogram of 0.25 mM 3,4-dihydroxybenzaldehyde.

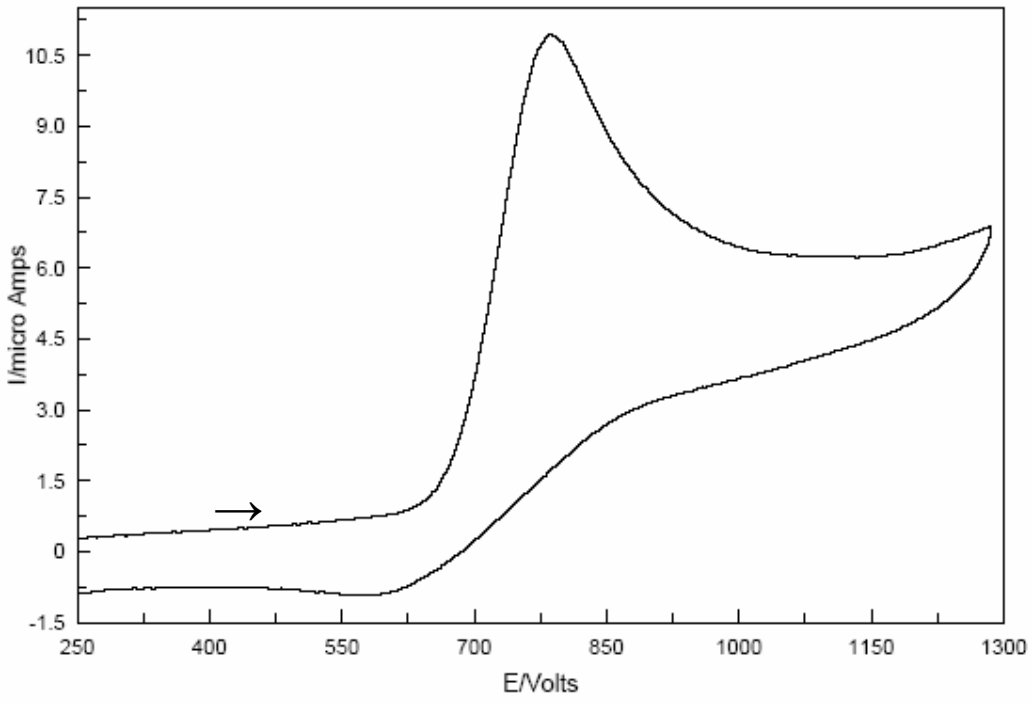


Figure 5. Cyclic voltammogram of 0.25 mM 4-nitrocatechol.

Furthermore, 3,4-dihydroxycinnamic acid, 4-*tert*-butylcatechol, 3,4-dihydroxy benzaldehyde and 4-nitro catechol were reagent-grade material and phosphate salts were of pro-analysis grade from E. Merck. These chemicals were used without further purification. The half-wave potentials ($E_{½}$) were calculated as the average of the anodic and cathodic peak potentials of the cyclic voltammograms ((E_{pa} + E_{pc})/2). Cyclic voltammograms were obtained at 25 $mV.s^{-1}$ (Figures 2-4) (except 4-nitrocatechol in 250 $mV.s^{-1}$, for appear the cathodic peak, Figure 5). All experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

It should also be mentioned that we have recently reported the application of different calculation methods in various areas [40-46]. We present the calculated electrode potentials of some *ortho*-dihydroxybenzene derivatives as shown in Fig. 6. The experimental electrode potentials of the studied molecules are in the range of 0.182 – 0.686 V. Table 1 shows the calculated Gibbs energy of molecules for both reduced and oxidized forms in the gas phase using DFT calculations at the B3LYP level of theory. The basis set of 6-31G (d, p) was chosen considering the size of studied molecules. Using frequency calculations, the zero-point energies and thermal corrections together with entropies have been calculated in order to convert the internal energies to the Gibbs energies at 298.15 ^{o}K. Solvation energies are computed in order to convert gas-phase energies to energies in solution phase. These solute-solvent interactions, ΔG_{sol}, which are calculated using PCM models of solvation, are shown in Table 1. The solvation energies are also computed at the same level of theory using the basis

set of 6-31G (d, p). This quantity is added to ΔG_{gas}, gas to give the change of Gibbs energy of each component in solution phase, ΔG, according to Eq. (4).

Table 1. The Gibbs free energy of studied molecules for both reduced (red.) and oxidised (ox.) in the gas phase and solution phase, along with the change of Gibbs free energy of reaction (1), ΔG_1, in both gas and solution phases

Mol.[a]	$\Delta G_{(gas)}$[b]		$\Delta G_{(sol.)}$[b]		ΔG_1(kJ/mol)	
	Red.	Ox.	Red.	Ox.	Gas	Solution
1[c]	-382.620818	-381.39224	-382.71608	-381.46134	0	0
2[c]	-648.56295	-647.3287	-648.71256	-647.45652	-14.92334	-3.42628
3[c]	-648.55017	-647.31883	-648.69942	-647.44293	-7.25951	-4.57887
4[c]	-539.78062	-538.55370	-539.98093	-538.72753	4.33733	3.50635
5[c]	-495.940332	-494.70691	-496.04791	-494.7840	-12.71792	-23.94193
6[c]	-587.11008	-585.87597	-587.21809	-585.94511	-14.54002	-47.91852

[a] See Fig. 6 for the list of studied molecules.
[b] These energies are in atomic units, Hartree (1 Hartree =2625.49975 kJ mol^{-1}[1])
[c]These energies have been calculated at B3LYP level using 6-31G(d,p) basis set.

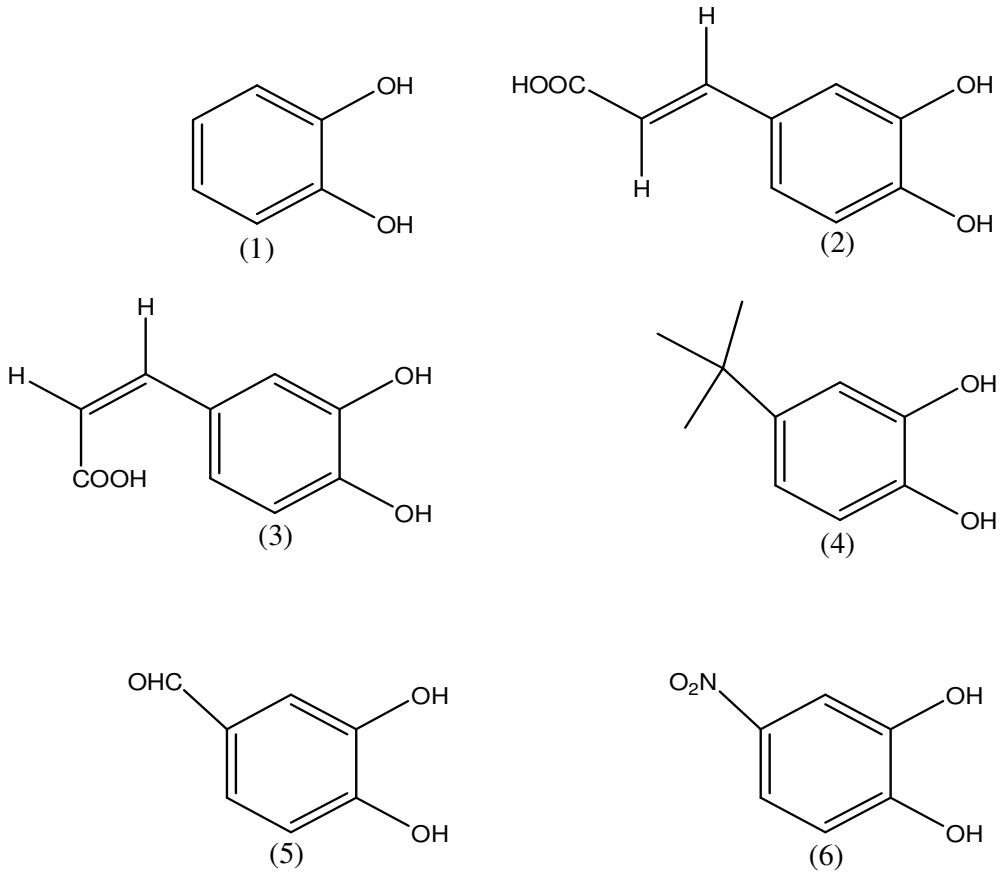


Figure 6. Reduced form of the studied molecules, catechol (**1**), Caffeic acid (trans 3,4-dihydroxycinnamic acid) (**2**), Cis 3,4-dihydroxycinnamic acid (**3**) (only in theoretical studies), 4-tert-butylcatechol (**4**), 3,4-dihydroxybenzaldehyde (**5**) and 4-nitro catechol (**6**).

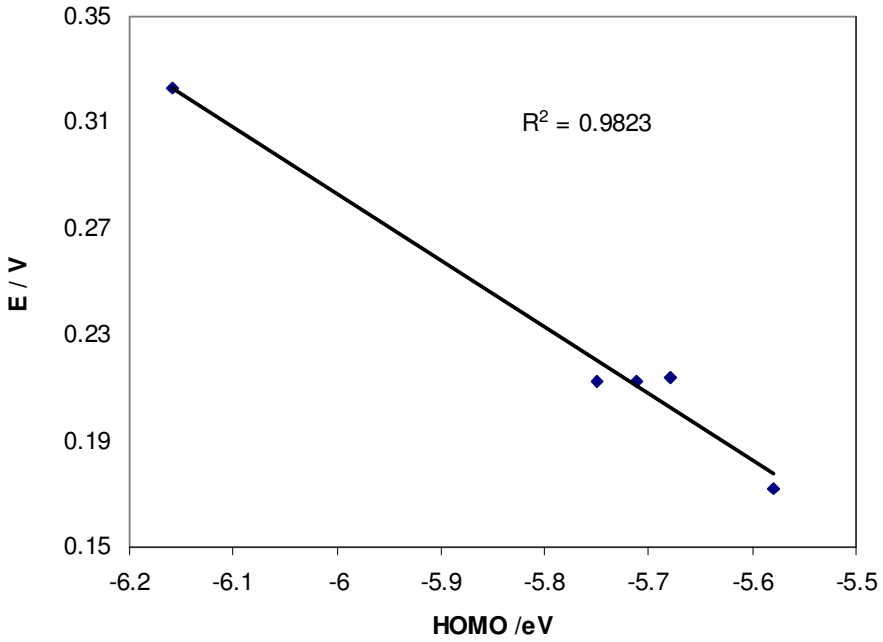


Figure 7. Electrode potentials of the studied *Ortho*-quinone derivatives (in V) vs. HOMO energies (in eV). (R^2 = 0.9823)

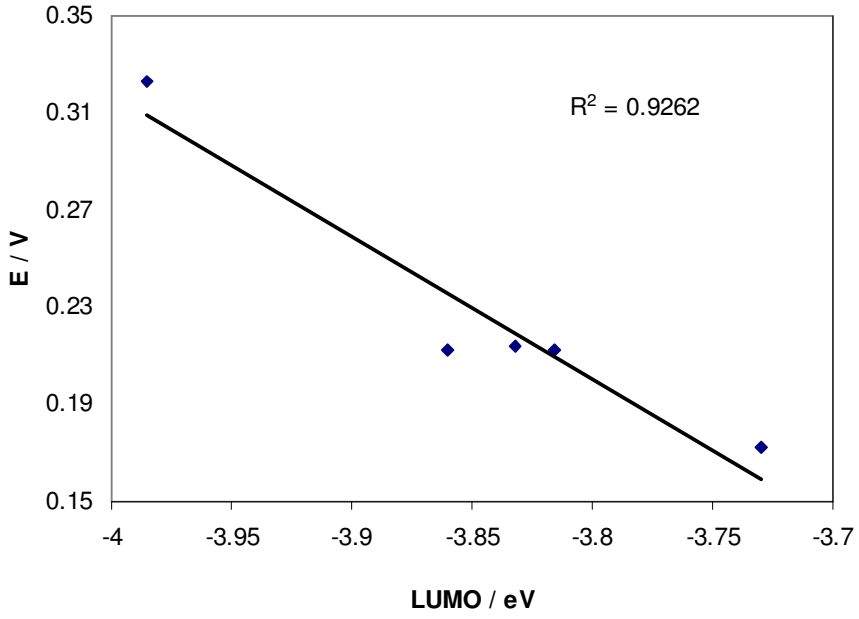


Figure 8. Electrode potentials of the studied *Ortho*-quinone derivatives (in V) vs. LUMO energies (in eV). (R^2 = 0.9262)

Following Sasaki et al. [47] and Saeva and Olin [48], the correlation between the calculated energies of the HOMO and LUMO and the electrode potentials of the molecules studied have been investigated. The energies of the HOMO and LUMO for the reduced and oxidized forms of the *Ortho*-

quinones studied are also calculated at the B3LYP level in the presence of solvent. Simple relations with the form of:

$$E/V = a + bE_{HOMO} \quad (6)$$

$$E/V = a + bE_{LUMO} \quad (7)$$

have been found between the electrode potentials, E, and energies of the HOMO of the reduced forms (E_{HOMO}) and energies of the LUMO of the oxidized forms (E_{LUMO}) (Table 2). The values of a and b are -1.2204 and -0.2506 for Eq. (6) and -2.0336 and -0.5880 for Eq. (7), respectively. These relations are also shown in Figs. 7 and 8. The relation between electrode potential and energy of the lowest unoccupied level of the molecule in the oxidized form is justified since the molecule accepts an electron to be converted to the reduced form. The relation between electrode potential and energy of the highest occupied molecular level of the molecule in the reduced form is also reasonable since the molecule in the reduced form has already gained an electron [48].

Table 2. Electrode potential of the studied molecules in water calculated at the level of B3LYP, compared with the experimental values. Differences (in V) between experimental and calculated values are shown.

Mol.[a]	$E_{½}$ (V)[b]	$E_{½}$ (V)[c]	$E_{½}$ (V)[c]	Exp.($E_{½}$ (V)[d])
1	0.214	0.203	0.219	0.214
2	0.232	0.211	0.236	0.2127
3	0.238	0.221	0.210	-
4	0.196	0.178	0.159	0.1822
5	0.338	0.323	0.309	0.3228
6	0.462	-	-	0.6858
r.m.s.[e]	0.002	0.0003	0.0009	-

[a] See Fig. 6 for the list of studied molecules.
[b] Electrode potentials calculated by Eq. (3) as explained in the text in B3LYP
[c] Electrode potentials calculated by Eqs. (6) and (7), respectively
[d] Experimental values.
[e] Root-mean-square errors (Calculated without number 6).

Table 3 also shows the calculated electrode potentials obtained by Eqs. (6) and (7). A significant improvement can be seen for all of the molecules and the root-mean-square of errors is decreased to less than 0.0003 V.

Standard electrode potentials of *ortho*-dihydroxybenzene derivatives can be obtained using the total Gibbs energies and the experimental value of the electrode potential of the reference molecule, catechol, in water (Eq. (3)). Table 3 presents the standard electrode potentials of the molecules studied together with the corresponding Gibbs energies of the redox reactions in water. The results of this work show that 1-6 oxidized in water to their respective *Ortho*-quinones with a quasi-reversible two-electron process. We calculated the value of $E_{1/2}$, not only for trans caffeic acid (2) but also for Cis-

caffeic acid (3). Although only $E_{1/2}$ for trans-caffeic acid in experimental has been obtained. According to the calculated value of $E_{1/2}$ (Table 3) for trans-caffeic acid(2) is less than that of the Cis-caffeic acid (3), because the steric effect in Cis-caffeic acid is more than the trans isomer and hence $E_{1/2}$ is larger as a for the Cis isomer. In 4-*tert*-butyl catechol having the maximum steric effect in this series, $E_{1/2}$ is minimum. According to table (3) type of substuated groups on the ring changes the $E_{1/2}$ value. Increasing the electron-withdrawing character at molecular ring causes an augmentation in $E_{1/2}$ value. The strength of the electron-withdrawing groups is: NO_2 > CHO >COOH-CH=CH >H > $C(CH_3)_3$ in 6 >5 >2>1>4 (Table 3).

Table 3. Eigenvalues of the molecular orbitals, HOMO and LUMO, for both reduced and oxidised forms of studied molecules

Mol.[a]	HOMO (eV)		LUMO (eV)	
	Red.	Ox.	Red.	Ox.
1	-5.67874	-7.03305	0.15783	-3.63190
2	-5.71167	-6.90571	-1.65400	-3.86048
3	-5.75004	-6.96122	-1.72956	-3.79898
4	-5.57000	-6.91741	0.15755	-3.59952
5	-6.15930	-7.14353	-1.45472	-4.000618
6	-6.07059	-7.35252	-2.21038	-4.01531

[a] See Fig. 6 for the list of studied molecules.

The error in 4-nitro catechol (6) which is the largest of all is a result of applying a high scan rate (250 mV/s) so as to be able to observe the cathodic peak. ($E_{1/2}$ reference compound (catechol) who obtained using 25 mV/s). Because of the large error in the case of 4-nitro catechol, its data are deleted from these used for drawing curves of E vs HOMO and LUMO energies (Fig. 7 and Fig. 8).

4. CONCLUSIONS

In the present work, DFT at level of B3LYP, has been employed in order to calculate the Gibbs free energies and electrode potentials. This relation can be used for calculation of electrode potential with an average error of 0.002 V. The optimization of geometry of molecules in the presence of solvent with the use of CPCM model of solvation at the same level of theory requires a considerable length of time of computations especially for very large molecules. Therefore, further refinement of theory should be carried out mainly in this regard. The theoretical and experimental determination of the electrode potentials of nitro compounds has always been problematic, and this can also be seen in this comparison.

In theoretical calculation of formal potentials, both anodic (oxidation) and cathodic (reduction) peaks are necessary. In about 4-Nitrocatechol because the NO_2 is a strong electron-withdrawing group, cathodic counterpart of anodic peak does not appear which is due to hydroxylation and dimerization reactions of related o-quinones and for this reason there was no report for the experimental and

theoretical formal potential of 4-Nitrocatechol, previousley. In this work we obtained this parameter in higher scan rates and reported.

Trans-caffeic acid is a natural compound while cis-caffeic acid is not in nature. However, we obtained the theoretical formal potential for cis-caffeic acid and compared it with that of trans form.

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