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Substituent Effect on a Family of Quinones in Aprotic Solvents: An Experimental and Theoretical Approach

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In this work a comparison between redox potentials, obtained by constructing current−potential plots from chronoamperometric measurements, and the parameter σ_x, as proposed by Zuman in terms of the Hammett substituent parameters, was performed for several quinone compounds. This study shows the limitations of this approach and proves that methods based on quantum chemistry can be used to study the substituent effect in quinone systems. By using the Density Functional Theory, in the Kohn−Sham context with three exchange-correlation functionals, BLYP, B3LYP, and BHLYP, it was found that the electron affinity is good enough to give a useful relationship with experimental redox potentials of quinone systems. This conclusion is reached when the basis set functions involve diffuse functions, and also when the Hartree−Fock exchange energy is included in the exchange-correlation functional. The Fukui function, to describe preferential sites involved at initial stages of a system that bind an electron, is analyzed when electron donor and electron acceptor groups are present as substituents in quinone systems. The methods applied in this work are valid for any kind of quinone compound and will be used in further analysis of the electron reorganization in semiquinone species.

I. Introduction

The experimental and theoretical characterization of the quinone, or systems where this functional group is involved, is very important since these systems have an important role in biological processes.[1] This is relevant, considering that a large part of the biological activity of quinonoid systems is related to its capacity to generate free radicals via redox reactions. The electrogenerated radical anion species (semiquinone) have long half-life periods and lead to Reactive Oxygen Species (ROS, e.g., superoxide anion radical and H_2O_2) in biological systems.[2] Therefore, there are many research groups that have tried to find functional relationships between the chemical reactivity and molecular structure for this type of compounds. It is well recognized that such kind of studies are important, especially when the modulation of the chemical reactivity of different molecules is commanded by the substituent effect.

The Hammett and Taft model[3] has proven to be a useful tool to give reactivity−structure relationships for some systems. This proposal is based on the estimation of the empiric parameter σ_x, which is defined through the relationship between the acidity constant, K_a, of an X-substituted benzoic acid ($K_a^{X-C_6H_4COOH}$) with respect to the unsubstituted benzoic acid ($K_a^{C_6H_5COOH}$) according to the equation

$$\log \frac{K_a^{X-C_6H_4COOH}}{K_a^{C_6H_5COOH}} = \rho\sigma_x \qquad (1)$$

The parameter ρ, or reaction constant, is related to the nature of the chemical reaction under a given set of conditions. For the case of X-substituted benzoic acids $\rho = 1$. The magnitude of this parameter measures the susceptibility of a reaction to electrical effects.[4] To obtain σ_x values in a correct way, it is necessary to define a system property sensitive to the substituent effect. For electrochemical reactions, Zuman[5] applied the Hammett formalism to establish relationships between the halfwave potentials ($E_{1/2}$) and the substituent effect employing the corresponding values of σ_x. In general terms, both quantities can be related when an excess free energy is expressed by comparing the $E_{1/2}$ values with that obtained for the hydrogen-substituted compound. Thus, a relationship is established between $\Delta E_{1/2}$ and the σ_x values to obtain

$$\Delta E_{1/2} = \rho_{\pi,k}\sigma_x \qquad (2)$$

The reaction constant, $\rho_{\pi,k}$, takes into account the substituent effect for a given electrochemical reaction, in a similar fashion as ρ in eq 1. Different forms of eq 2 have led to a systematic evaluation of the excess free energy in systems substituted with a great variety of functional groups, these equations are known as the Hammett−Zuman relationships.[6] The main problem with the Hammett−Zuman approach is that even when this model gives good predictions of shifts in $E_{1/2}$ values for several reaction series,[7] it is not possible to use this approach for most compounds.[8] Taking as an example the first reduction process of quinones in aprotic medium, and in order to apply eq 2, benzoquinones, naphthoquinones, and anthraquinones must be classified in different groups, even when the electrochemical reaction pathway is similar for all of them.[6] It means that each group has an assigned $\rho_{\pi,k}$, giving a dependence of this quantity with respect to the chemical structure.[5]

The Hammett−Zuman approach is reliable just if a large number of substances is considered to evaluate steric or

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mesomeric effects related to the presence of a given substituent. This is an important restriction since in many cases the system set is small.[5] Additionally, from electrochemical information it has been found that a substituent can change the total rate of the electron-transfer reaction, or even induce the presence of different mechanisms when very reactive species are formed at the electrode, such as occurs during the self-protonation processes.[7] Although the Hammett−Zuman model presents a practical way to describe the substituent effect on a reaction set, it depends on empirical relationships that sometimes do not work in a general way.

From the previous discussion, it is clear that an approach independent of the studied systems is necessary and that stems directly from molecular properties. For this purpose, quantum chemistry methods have been used to study the electron structure of some quinone systems.[9−31] The Kohn−Sham (KS) method[32] has been principally used since it can be applied to systems of medium or large size.[18−29,31] Several approaches have been considered to estimate redox potentials or to relate these quantities to some molecular properties. To simulate protic and aprotic solvents, in recent works the redox potential was estimated by computing the total energy of the neutral and anion systems inside a cavity surrounded by a continuum dielectric.[22−26,31] Assuming that the Koopmans' theorem keeps its validity within the KS model, in some works the redox potential has been related to the orbital energy corresponding to the lowest unoccupied molecular orbital (LUMO).[23,33,34] Some facts should be mentioned that must be taken into account to ensure the success of these approaches: (1) To give a good estimation of the energy difference between anion and neutral species it is important to use basis set functions that represent correctly the electron density in the asymptotic region.[35] (2) The Koopmans' theorem is valid within the Hartree−Fock (HF) theory,[36] although there are several reports where removal energies are related to the KS orbital energies.[37,38] (3) The KS LUMO cannot be considered as an approximation to the electron affinity since its physical meaning is related to vertical excitation energies.[39]

In the redox process of quinone systems, the electron density of the system bears important changes and these will be different depending on the involved substituent. To evaluate the primary stages of the reduction processes and how they are affected by a given substituent, it is useful to analyze the Fukui function.[40] Within the reactivity framework of the density functional theory (DFT)[41] this function is defined as[40]

$$f^{\pm}(\mathbf{r}) = \left(\frac{\partial n(\mathbf{r})}{\partial N}\right)_{v} \tag{3}$$

By definition this quantity gives local information of changes in the electron density, $n(\mathbf{r})$, when the number of electrons, N, is changed at a fixed external potential, $v(\mathbf{r})$. Since derivatives with respect to the number of electrons are discontinuous, it is important to define the path to evaluate the Fukui functions. The plus sign in eq 3 is used when the system is gaining electrons and the minus sign when it is losing electrons. For the redox process, the derivative must be evaluated in the direction where the neutral system gains electrons. However, in the redox process N and the spin number, $N_s = N_\alpha - N_\beta$, are changing simultaneously. Instead of the $\{N, N_s\}$ representation, in this report the $\{N_\alpha, N_\beta\}$ representation will be used since, in this case, the number of electrons with spin α, N_α, is changing and the number of electrons with spin β, N_β, is constant.[42]

In this work we show that the Hammett−Zuman approach is a limited proposal and that the redox potentials of some of the quinone systems can be related to the electron affinity obtained from quantum chemistry methods. Two approaches are considered for the analysis. First, experimental redox potentials of some quinone families are reported and the Hammett−Zuman approach is revisited to evaluate its applicability to these systems. Second, within the KS method, three exchange-correlation functionals are tested to estimate electron affinities and they are related to experimental redox potentials. Finally, we explore the usefulness of the Fukui function to describe initial stages of the redox process when a substituent is changed.

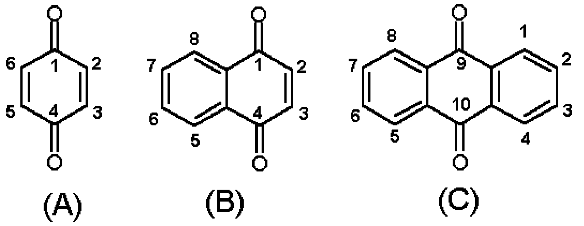

Figure 1. Chemical structures of the quinone families considered in this work: (A) 1,4-benzoquinone, (B) 1,4-naphthoquinone, and (C) 9,10-anthraquinone.

The chemical structures of the quinone families considered in this work are depicted in Figure 1. The numbers in the figure indicate the relative positions of the substituents in the analyzed compounds. This work is organized as follows: in Section II and Section III details about the experimental and theoretical methods are given. The results and discussion are presented in Section IV and the concluding remarks in Section V.

II. Experimental Details

IIa. Compounds, Solvent, and Supporting Electrolyte. The halfwave potentials, $E_{1/2}$, for the first monoelectronic reduction were determined in acetonitrile for three quinone families—benzoquinones: 1,4-benzoquinone [BQ], 2-methyl-1,4-benzoquinone [MeBQ], 2-tertbutyl-1,4-benzoquinone [TButBQ], 2-phenyl-1,4-benzoquinone [PhBQ], 2-chloro-1,4-benzoquinone [ClBQ], 2,5-dimethyl-1,4-benzoquinone [25MeBQ], 2,6-dimethyl-1,4-benzoquinone [26MeBQ], 2,5-dichloro-1,4-benzoquinone [25ClBQ], 2,6-dichloro-1,4-benzoquinone [26ClBQ], 2,5-ditertbutyl-1,4-benzoquinone [25TButBQ], 2,6-ditertbutyl-1,4-benzoquinone [26TButBQ], 2,6-dimethoxy-1,4-benzoquinone [26MeOBQ], 5-methyl-2,3-dimethoxy-1,4-benzoquinone [Q0], tetramethyl-1,4-benzoquinone [TMeBQ], tetrafluoro-1,4-benzoquinone [TFBQ], tetrachloro-1,4-benzoquinone [TClBQ]; naphthoquinones: 1,4-naphthoquinone [NQ], 2-methyl-1,4-naphthoquinone [MeNQ], 2-methoxy-1,4-naphthoquinone [MeONQ], 2-bromo-1,4-naphthoquinone [BrNQ]; and anthraquinones: 9,10-anthraquinone [AQ], 2-methyl-9,10-anthraquinone [MeAQ], 2-ethyl-9,10-anthraquinone [EtAQ], 2-tertbutyl-9,10-anthraquinone [TButAQ], 2-chloro-9,10-anthraquinone [2ClAQ], 2-hydroxymethyl-9,10-anthraquinone [CH_2OHAQ].

Benzoquinones and 1, 4-naphthoquinone (NQ) were resublimed prior to their use, the other compounds were A. R. quality grade and they were used without further purification. All the substances were obtained from Aldrich except for 25MeBQ, which was obtained from Fluka Chemika.

Anhydrous Acetonitrile (CH_3CN, Aldrich 98%) was dried overnight with P_2O_5, and distilled prior to use. The distillate was received over oven-activated 3 Å molecular sieve (Merck) and kept in a desiccator. The method is useful to obtain dry acetonitrile, characterized by the absence of OH bands in IR spectra. The supporting electrolyte was made with tetraethylammonium tetrafluoroborate (Fluka Chemika, Electrochemical grade, Et_4NBF_4). A night before of the experiments the salt of

Et_4NBF_4 was dried at 90 °C and solutions with concentration 0.1 mol L^{-1} were used.

IIb. Electrochemical Determinations. Cyclic voltammetry and chronoamperometry (employed to build sampled current voltammetric curves) were performed with an AUTOLAB PGSTAT 30 potentiostat/galvanostat. IR drop correction was performed during all the experiments, using R_u values (82 Ohms) obtained with the positive feedback technique, and employing the "High Speed" mode of the potentiostat. A conventional three-electrode cell was used to carry out these experiments, employing as the working electrode a platinum microelectrode (BAS, surface: 0.025 cm^2), polished with 0.05 μm alumina (Büehler), sonicated in distilled water for 10 min, and rinsed with acetone prior to use. The polishing process was performed after the electrochemical study of each compound. Between each chronoamperometric or voltammetric run for the electrochemical study of each compound, the electrode was rinsed with acetone. These procedures allowed reproducibility in the experimental results. A platinum mesh was used as the counter electrode (surface: 0.6 cm^2). The potential values were obtained against the reference (Bioanalytical Systems, BAS) of Ag/0.01 mol L^{-1} of $AgNO_3$ + 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile, separated from the medium by a Vycor membrane. Potential values are reported versus the ferricinium/ferrocene couple (Fc^+/Fc), according to the IUPAC recommendation.[43] The potential of the Fc^+/Fc couple was measured for each separate compound to avoid changes in potential due to modifications caused by the membrane aging.

Electrochemical experiments were carried out as follows: Solutions of the studied quinones in the range of 1 to 10 mmol L^{-1} were dissolved in the 0.1 mol L^{-1} solutions of Et_4NBF_4 in acetonitrile. With these prepared solutions, sampled current voltammetry curves were built up employing the methodology described by Bard.[44] Thus for each substance the response of several chronoamperograms at different potential values in the negative direction was recorded obtaining plots such as those presented in Figure 2A. Then, sampling of the current at different sampling times allowed the construction of pseudostationary current−potential, $i-E$, curves represented in Figure 2B. From Figure 2B the halfwave potential ($E_{1/2}$) was determined by plotting the function

$$E = E_{1/2} + \frac{0.06V}{n}\log\left(\frac{i_d(\tau) - i(\tau)}{i(\tau)}\right) \qquad (4)$$

where i_d is the limiting current obtained for each curve.[45] Periodic pulse experiments were employed rather than single chronoamperometric experiments, since capacitive current effects are corrected in a more effective manner.[46] This procedure led to reproducible curves on the time scale of 0.5 to 500 ms. For all the curves a pseudostationary state was reached. All the obtained potentials are referred to the Fc^+/Fc couple as recommended by the IUPAC.[43]

III. Theoretical Details

The electronic structure of some quinone compounds was obtained by using the KS model. In this context three exchange-correlation functionals were employed: BLYP,[47] B3LYP,[48] and BHLYP.[49] With these methods the electron affinity, EA, was computed as the total energy difference EA = $E^{\mathrm{Neutral}} - E^{\mathrm{Anion}}$. To explore the reliability of the basis set functions, three different basis sets were tested: 6-31G**,[50] 6-31++G**,[51] and TZVP.[52] For these calculations, the geometry of the anion system was also optimized. Minima in the potential energy surface were found since a frequency analysis was performed for each method on each molecular structure. Thus, vertical, EA_v, and adiabatic, EA_a, electron affinities are reported. In the case of the Fukui functions a single point calculation was carried out on the neutral geometry, and in this way the external potential was fixed. All calculations were made with the NWChem code v4.5.[53]

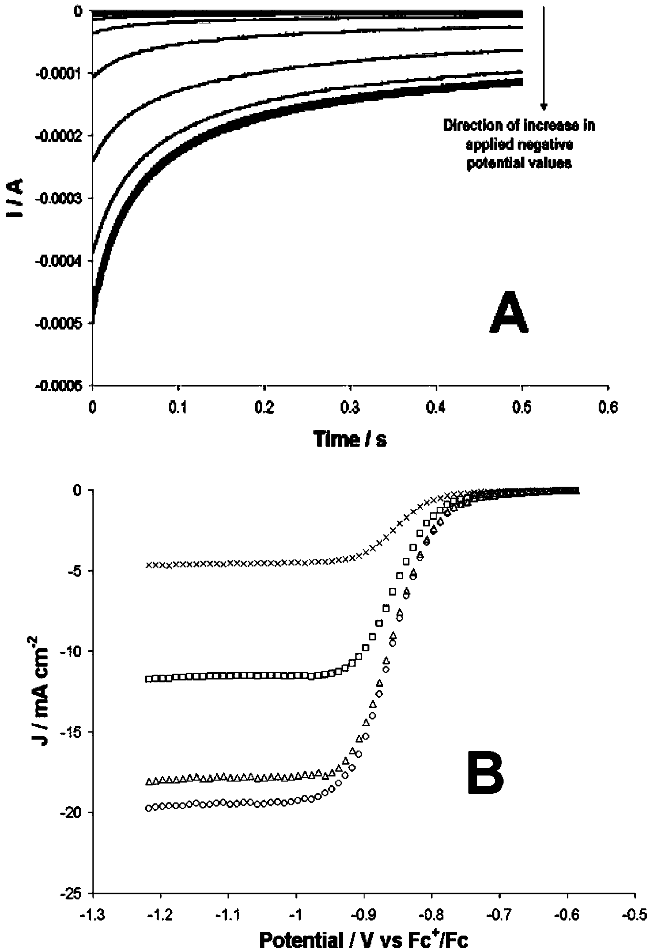

Figure 2. (A) Typical chronoamperograms at different potentials in the negative direction for a solution of 0.01 mol L^{-1} BQ in 0.1 mol L^{-1} Et_4NBF_4/CH_3CN. (B) Typical sampled current voltammograms obtained for 0.01 mol L^{-1} BQ in 0.1 mol L^{-1} Et_4NBF_4/CH_3CN for different sampling times: (×) 0.5, (□) 0.05, (△) 0.005, and (○) 0.0005 s.

IV. Results and Discussion

IVa. Inconsistencies of the Hammett−Zuman Model for the Prediction of Electrochemical Behavior of Quinones. The experimental $E_{1/2}$ values obtained in this work are reported in Table 1. For convenience the quinone compounds were classified in families according to the number of fused aromatic rings that constitute the main structure, i.e., benzoquinones are analyzed independently of naphthoquinones and anthraquinones. We can see from this table that, within the benzoquinone family, the TClBQ shows the highest $E_{1/2}$ value and the TMeBQ the lowest one. Thus, electron-withdrawing substituents induce more positive $E_{1/2}$ values with respect to that of the nonsubstituted system, whereas the electron-donating substituent induces negative $E_{1/2}$ values. Similar behavior is presented for naphthoquinones and anthraquinones, as can be seen in Table 1.

In Table 1 the σ_x parameter is also presented. For polysubstituted compounds the Peover's suggestion was used to obtain

TABLE 1: Values for $E_{1/2}$ and σ_x of the Studied Quinone Compounds

	$E_{1/2}$/V vs Fc$^+$/Fc	σ_x
substituted-1,4-benzoquinones		
TClBQ	−0.340	0.92
TFBQ	−0.358	0.24
26ClBQ	−0.516	0.46
25ClBQ	−0.535	0.46
ClBQ	−0.602	0.23
PhBQ	−0.842	−0.01
BQ	−0.851	0
MeBQ	−0.928	−0.17
TButBQ	−0.958	−0.2
Q0	−0.990	−0.71
25MeBQ	−1.002	−0.34
26MeBQ	−1.010	−0.34
26MeOBQ	−1.050	−0.71
25TButBQ	−1.059	−0.40
26TButBQ	−1.074	−0.40
TMeBQ	−1.175	−0.68
2-substituted-1,4-naphthoquinones		
BrNQ	−0.920	0.23
NQ	−1.029	0
MeNQ	−1.113	−0.17
MeONQ	−1.163	−0.27
2-substituted-1,4-anthraquinones		
ClAQ	−1.184	0.23
AQ	−1.259	0
CH_2OHAQ	−1.283	0
EtAQ	−1.298	−0.15
TButAQ	−1.300	−0.20
MeAQ	−1.316	−0.17

TABLE 2: Linear Relationship $\Delta E_{1/2} = \rho_{\pi,k}\sigma_x + b^a$

family	$\rho_{\pi,k}$/V	b/V	r^2
2-X-1,4-benzoquinones	0.55	0.0300	0.9827
2-X-1,4-naphthoquinones	0.48	0.0045	0.9999
2-X-9,10-anthraquinones	0.28	0.0004	0.9146

[a] $\Delta E_{1/2} = E_{1/2}$(X-substituted quinone) − $E_{1/2}$(H-substituted quinone).

σ_x.[54] A linear relationship is found when σ_x is contrasted, within each quinone family, with the $E_{1/2}$ values. The linear parameters of such a relationship are presented in Table 2.

From Table 2 it is clear that a good linearity is obtained for the relationship $\Delta E_{1/2} = f(\sigma_x)$ for the substituted benzoquinones. However, it is important to mention that the data for two compounds were not included in this relationship: TFBQ and Q0. It has been presumed that the fluorine atoms have a strong interaction with the quinone system via resonant effects,[5] and this effect induces changes in the $E_{1/2}$ value for its corresponding quinone. For Q0, the size and asymmetry of the substituents in the molecule induce steric effects that can be associated with the failure of the Hammett−Zuman model for this compound. In fact, the linear relationship is not kept when such compounds are included. Clearly this empirical approach is not satisfactory since it cannot take into account the effect of any substituent.

Additionally, from Table 2, we should remark the difference of the reaction constant $\rho_{\pi,k}$ (eq 2) for each quinone family. It is well-known that changes in reaction constants usually imply a difference in the electrochemical reaction pathway,[4] which does not occur within the experimental setup employed in this work since all the compounds present the same reaction mechanism. This is an additional evidence of the nonapplicability of the Hammett−Zuman model.

In conclusion, although the Hammett−Zuman model sometimes allows predictions of $E_{1/2}$ values when the substituent is changed, in this work we have shown that this empirical approach is unable to predict redox potentials for any quinone system. Thus, its applicability is restricted to analyze quinone systems grouped by families. Therefore, a different model is necessary to achieve an appropriate description of the electrochemical reactivity of any quinone compound.

IVb. The Lowest Unoccupied Molecular Orbital Energy and the Electron Affinity. There are several works where the $E_{1/2}$ is estimated by using the KS model or other theoretical methods where the system size allows it. Evidently, the size of some quinone systems does not allow large basis sets in a KS calculation and for that reason in several works limited basis sets have been used.[22−26] This approach is well justified; however, there must be a “minimal” basis set to use in this kind of compounds. For some quinone systems reported in Table 1 the vertical and adiabatic electron affinities were obtained in this work employing different basis sets; the results are reported in Tables 3, 4, and 5. Additionally, the negative value of the LUMO energy, $-\epsilon_{\mathrm{LUMO}}$, for each compound is included in the same tables. The compounds are sorted according to the experimental information available ($E_{1/2}$ values) and no distinction of families was made for this case. Although we are not estimating the EA for all the compounds considered experimentally, we have studied some of them considering the whole range of experimental redox potentials.

We can see from Tables 3−5 that for any of the considered methods in this work ϵ_{LUMO} is negative. This result is relevant since if one wants to use the Koopmans’ theorem, the negative of ϵ_{LUMO} must be taken. In several works the LUMO and HOMO energies are related to redox potentials. However, and strictly speaking, the negative of the LUMO energy of the neutral system must be related just to EA_v. In Figure 3 we present EA_v and EA_a as a function of $-\epsilon_{\mathrm{LUMO}}$, and in Table 6 the linear parameters found for the relationship EA vs $-\epsilon_{\mathrm{LUMO}}$ are reported. From these results it is clear that the linear relationship is improved when the basis set functions contain diffuse functions. Furthermore, we can see that the relationship is improved if an important contribution of HF exchange energy is used. The corresponding part of the HF exchange energy is weighted by a different factor: 0.0 for BLYP, 0.2 for B3LYP,[48] and 0.5 for BHLYP.[49] Thus, diffuse functions and an important contribution of the HF exchange energy in the exchange-correlation functional give a good correlation between electron affinity and $-\epsilon_{\mathrm{LUMO}}$. Surprisingly EA_a gives a better relationship with $-\epsilon_{\mathrm{LUMO}}$ than the EA_v. This result is not justified and we cannot expect that for other systems it will be preserved, since the Koopmans’ theorem is not valid for this situation.

Because the vertical and adiabatic electron affinities have a relationship with $-\epsilon_{\mathrm{LUMO}}$ then we can deduce that there is a relationship between them. The linear parameters found for EA_a vs EA_v, with the basis set 6-31++G**, are reported in Table 7. It is clear from this table that there is a strong correlation between EA_a and EA_v. Curiously such a relationship is not new since in other processes it is also observed.[55] This result does not imply small geometry relaxation changes, and we can see from Table 8 that these changes represent a percent relative deviation of 7.9 to 13.1 for BLYP/6-31++G**, 8.8 to 14.7 for B3LYP/6-31++G**, and 11.5 to 20.7 BHLYP/6-31++G**—clearly the largest deviations are obtained for the exchange-correlation functional with the biggest part of the HF exchange energy. The strong relationship between adiabatic and vertical EAs justifies the relationship between adiabatic EA and the LUMO energy. In other situations such a relationship is not expected. This fortuitous fact supports the validity of the use of LUMO energies for the estimation of electron affinities in this type of compounds.

TABLE 3: Adiabatic (EA$_a$) and Vertical (EA$_v$) Electron Affinities and Minus the LUMO Energy, $-\epsilon_{LUMO}$, Obtained with BLYP and the Basis Sets 6-31G, 6-31++G**, and TZVP**[a]

	6-31G**			6-31++G**			TZVP		
	EA$_v$	EA$_a$	$-\epsilon_{LUMO}$	EA$_v$	EA$_a$	$-\epsilon_{LUMO}$	EA$_v$	EA$_a$	$-\epsilon_{LUMO}$
TClBQ	2.1779	**2.3978**	4.6944	2.6172	**2.8402**	5.0205	2.5685	**2.8013**	5.0136
TFBQ	1.7074	**1.9942**	4.6061	2.5375	**2.8354**	5.2819	2.4936	**2.7986**	5.2700
25ClBQ	1.8004	**2.0359**	4.4831	2.3235	**2.5636**	4.8665	2.2694	**2.5187**	4.8570
PhBQ	1.3586	**1.5552**	3.9057	1.9266	**2.1268**	4.3473	1.8849	**2.0915**	4.3466
BQ	−1.3850	**1.3693**	4.0703	1.8159	**2.0384**	4.5432	−0.6780	**−0.5002**	4.5381
MeBQ	1.0862	**1.2955**	3.9102	1.7149	**1.9376**	4.3696	1.6591	**1.8856**	4.3616
TButBQ	1.1766	**1.4027**	3.8886	1.7491	**1.9798**	4.3137	1.7014	**1.9362**	4.3069
25MeBQ	1.0082	**1.2179**	3.7490	1.6146	**1.8353**	4.1954	−0.9886	**1.7818**	4.1838
26MeBQ	1.0131	**1.2244**	3.7592	1.6203	**1.8429**	4.2057	1.5629	**1.7915**	4.1957
NQ	1.1165	**1.2954**	3.6738	1.6981	**1.8855**	4.1138	1.6607	**1.8523**	4.1163
25TButBQ	1.1858	**1.4231**	3.7237	1.6883	**1.9243**	4.1053	1.6454	**1.8863**	4.0971
26TButBQ	1.1872	**1.4297**	3.7289	1.6963	**1.9342**	4.1144	1.6505	**1.8930**	4.1038
MeNQ	1.0386	**1.2139**	3.5214	1.6048	**1.7878**	3.9533	1.5656	**1.7532**	3.9533
TMeBQ	0.9529	**1.1699**	3.5597	1.4760	**1.6992**	3.9517	1.4313	**1.6605**	3.9473
AQ	1.0078	**1.1368**	3.2599	1.5438	**1.6775**	3.6814	0.5991	**0.6739**	3.6896
MeAQ	0.9727	**1.0996**	3.1855	1.4975	**1.6290**	3.6011	1.4710	**1.6071**	3.6080

[a] All quantities are in eV.

TABLE 4: Adiabatic (EA$_a$) and Vertical (EA$_v$) Electron Affinities and Minus the LUMO Energy, $-\epsilon_{LUMO}$, Obtained with B3LYP and the Basis Sets 6-31G, 6-31++G**, and TZVP**[a]

	6-31G**			6-31++G**			TZVP		
	EA$_v$	EA$_a$	$-\epsilon_{LUMO}$	EA$_v$	EA$_a$	$-\epsilon_{LUMO}$	EA$_v$	EA$_a$	$-\epsilon_{LUMO}$
TClBQ	−0.2234	**2.6636**	4.2764	2.7698	**3.0369**	4.5506	0.0972	**2.0126**	4.5455
TFBQ	1.9874	**2.3291**	4.2037	2.6841	**3.0344**	4.7657	2.6459	**3.0042**	4.7484
25ClBQ	1.9951	**2.2745**	4.0129	2.4424	**2.7273**	4.3413	2.4026	**2.6971**	4.3341
PhBQ	1.5119	**1.7601**	3.4268	2.0085	**2.2627**	3.8112	1.9772	**2.2370**	3.8073
BQ	1.3352	**1.5895**	3.5403	1.8990	**2.1690**	3.9511	1.8599	**2.1341**	3.9467
MeBQ	1.2567	**1.5139**	3.3903	1.7986	**2.0685**	3.7877	1.7577	**2.0326**	3.7797
TButBQ	1.3404	**1.6138**	3.3710	1.8315	**2.1099**	3.7359	1.7973	**2.0807**	3.7290
25MeBQ	1.1769	**1.4343**	3.2381	1.6977	**1.9660**	3.6233	1.6540	**1.9280**	3.6115
26MeBQ	1.8228	**1.4414**	3.2474	1.7040	**1.9741**	3.6326	1.6619	**1.9376**	3.6223
NQ	1.2563	**1.4829**	3.1761	1.7642	**1.9978**	3.5639	1.7392	**1.9779**	3.5666
25TButBQ	1.3425	**1.6266**	3.2162	1.7702	**2.0532**	3.5405	1.7388	**2.0279**	3.5306
26TButBQ	1.3462	**1.6350**	3.2211	1.7777	**2.0639**	3.5472	1.7431	**2.0354**	3.5349
MeNQ	1.1783	**1.3992**	3.0351	1.6715	**1.8991**	3.4149	1.6436	**1.8770**	3.4132
TMeBQ	1.1171	**1.3812**	3.0572	1.5653	**1.8359**	3.3956	1.5325	**1.8102**	3.3896
AQ	1.1174	**1.2843**	2.7989	1.5908	**1.7610**	3.1761	1.5757	**1.7513**	3.1837
MeAQ	1.0841	**1.2485**	2.7317	1.5458	**1.7135**	3.1022	1.5286	**1.7023**	3.1076

[a] All quantities are in eV.

TABLE 5: Adiabatic (EA$_a$) and Vertical (EA$_v$) Electron Affinities and Minus the LUMO Energy, $-\epsilon_{LUMO}$, Obtained with BHLYP and the Basis Sets 6-31G, 6-31++G**, and TZVP**[a]

	6-31G**			6-31++G**			TZVP		
	EA$_v$	EA$_a$	$-\epsilon_{LUMO}$	EA$_v$	EA$_a$	$-\epsilon_{LUMO}$	EA$_v$	EA$_a$	$-\epsilon_{LUMO}$
TClBQ	3.1205	2.2836	2.6179	2.5868	**2.9241**	3.3521	2.5569	**2.9077**	3.3360
TFBQ	3.0422	1.9313	2.3561	2.4947	**2.9243**	3.4992	2.4554	**2.8953**	3.4664
25ClBQ	2.7934	1.8459	2.1941	2.2203	**2.5739**	3.0777	2.1870	**2.5520**	3.0604
PhBQ	2.1827	1.3049	1.6283	1.7346	**2.0648**	2.5218	1.7092	**2.0453**	2.5087
BQ	2.2483	1.1485	1.4742	1.6297	**1.9697**	2.6091	1.5985	**1.9445**	2.5971
MeBQ	2.1091	1.0691	1.3979	1.5296	**1.8696**	2.4581	1.4959	**1.8427**	2.4413
TButBQ	2.0891	1.1427	1.4875	1.5563	**1.9065**	2.4048	1.5296	**1.8844**	2.3903
25MeBQ	1.9683	0.9878	1.3165	1.4285	**1.7662**	2.3063	1.3911	**1.7366**	2.2834
26MeBQ	1.9751	0.9936	1.3245	1.4354	**1.7750**	2.3146	1.3986	**1.7463**	2.4061
NQ	1.9371	1.0327	1.3329	1.4743	**1.7789**	2.2891	1.4548	**1.7670**	2.2826
25TbutBQ	1.9443	1.1354	1.4898	1.4917	**1.8446**	2.2213	1.4654	**1.8249**	2.2011
26TbutBQ	1.9493	1.1416	1.5018	1.4999	**1.8565**	2.2276	1.4706	**1.8341**	2.2053
MeNQ	1.8089	0.9536	1.2465	1.3809	**1.6771**	2.1532	1.3574	**1.6627**	2.1414
TmeBQ	1.8010	0.9260	1.2596	1.3026	**1.6420**	2.0971	1.1838	**1.5908**	1.9959
AQ	1.6253	0.8574	1.0863	1.2766	**1.5064**	1.9766	1.2650	**1.5028**	1.9743
MeAQ	1.5674	0.8271	1.0537	1.2336	**1.4616**	1.9100	1.2204	**1.4570**	1.9048

[a] All quantities are in eV.

We can see also the importance of the diffuse functions in the prediction of electron affinities, since the BLYP method predicts negative electron affinities for BQ with the basis sets 6-31G** and TZVP, and for the 25MeBQ with the basis set TZVP. With the B3LYP/6-31G** method, the vertical electron affinity is negative for the TClBQ. Contrary to this behavior, the three exchange-correlation functionals tested in this work predict positive electron affinities with the basis set 6-31++G**,

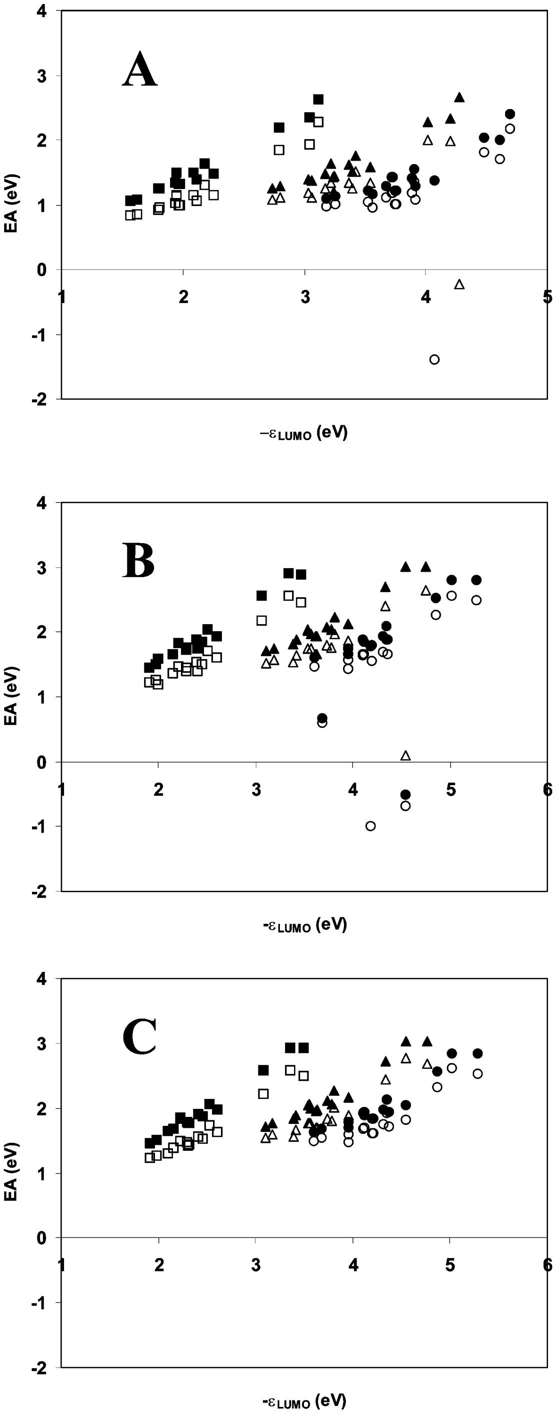

Figure 3. Vertical and adiabatic electron affinities compared with the negative of the LUMO energy. Solids points correspond to adiabatic EA and blank points to the vertical EA: (A) 6-31G**, (B) TZVP, and (C) 6-31++G**; (○) BLYP, (△) B3LYP, and (□) BHLYP.

TABLE 6: Linear Parameters for the Relationship EA = $m(-\epsilon_{LUMO}) + b$ Considering All the Compounds of Tables 3−5[a]

method	m	b	R^2
	vertical		
BLYP/6-31G**	0.5272	−0.9458	0.0933
BLYP/TZVP	0.7894	−1.9780	0.1301
BLYP/6-31++G**	0.7276	−1.3023	0.8637
B3LYP/6-31G**	0.0077	1.2243	0.0001
B3LYP/TZVP	0.1187	1.2659	0.0107
B3LYP/6-31++G**	0.7944	−1.0686	0.9166
BHLYP/6-31G**	0.8865	−0.6689	0.9456
BHLYP/TZVP	0.8841	−0.5570	0.9519
BHLYP/6-31++G**	0.8846	−0.5370	0.9635
	adiabatic		
BLYP/6-31G**	0.7893	−1.5908	0.8453
BLYP/TZVP	0.7840	−1.5841	0.2028
BLYP/6-31++G**	0.7969	−1.3864	0.9068
B3LYP/6-31G**	0.8619	−1.2385	0.9132
B3LYP/TZVP	0.8645	−1.0933	0.9427
B3LYP/6-31++G**	0.8646	−1.0719	0.9479
BHLYP/6-31G**	0.9543	−0.4895	0.9612
BHLYP/TZVP	0.9474	−0.3713	0.9638
BHLYP/6-31++G**	0.9546	−0.3806	0.9756

[a] Electron affinities and LUMO energies are in eV.

TABLE 7: Parameters of the Linear Relationship $EA_a = mEA_v + b$[a]

method	m	b	R^2
BLYP/6-31++G**	1.0648	0.0953	0.9924
B3LYP/6-31++G**	1.0660	0.1336	0.9922
BHLYP/6-31++G**	1.0685	0.2167	0.9925

[a] Electron affinities are expressed in eV.

TABLE 8: Percent Relative Deviation, $100(EA_a - EA_v)/EA_a$, for BLYP, B3LYP, and BHLYP Methods by using the 6-31++G Basis Set**

	BLYP	B3LYP	BHLYP
TClBQ	7.9	8.8	11.5
TFBQ	10.5	11.5	14.7
25ClBQ	9.4	10.4	13.7
PhBQ	9.4	11.2	16.0
BQ	10.9	12.4	17.3
MeBQ	11.5	13.1	18.2
TButBQ	11.7	13.2	18.4
25MeBQ	12.0	13.6	19.1
26MeBQ	12.1	13.7	19.1
NQ	9.9	11.7	17.1
25TButBQ	12.3	13.8	19.1
26TButBQ	12.3	13.9	19.2
MeNQ	10.2	12.0	17.7
TMeBQ	13.1	14.7	20.7
AQ	8.0	9.7	15.3
MeAQ	8.1	9.8	15.6

and this result shows the importance of the diffuse functions in the basis set and that the considered quinone systems are able to bind an electron in the gas phase. A comparison can be performed between the EAs predicted in this work and experimental data previously reported in the literature[56,57] for some of the compounds analyzed here. A linear relationship was found between the experimental EAs and the theoretical values of EA_a ($R^2 = 0.9918$ for BLYP, $R^2 = 0.9922$ for B3LYP, and $R^2 = 0.9911$ for BHLYP).

Because we found linear relationships between the adiabatic EAs obtained with BLYP, B3LYP, and BHLYP and those obtained experimentally, it is reasonable to think that there are relationships between these methods. Thus, we tried to correlate the adiabatic EAs obtained with these methods. We found that $EA_{BHLYP} = 1.1757EA_{BLYP} - 0.4196$ with $R^2 = 0.9966$ and $EA_{BHLYP} = 1.0928EA_{B3LYP} - 0.3969$ with $R^2 = 0.9992$; these results show that the BHLYP method gives an overestimation of EA with respect to BLYP and B3LYP methods. This result is important since in other systems, where singlet−triplet excitation energies are evaluated, such a relationship also has been found.[58]

Although there are several works where the solvent is considered explicitly to give a theoretical estimation of the experimental redox potentials, there is evidence that for some quinone systems the solvent has no effect on the first redox potential.[59] Assuming that this observation is applicable to the systems studied in this work, in Table 9 we are reporting the

TABLE 9: Parameters of the Linear Relationship $\Delta E_{1/2} = m(-\mathrm{EA_a}) + b^a$

method	m	B	R^2
BLYP/6-31++G**	−0.7470	−2.4473	0.9678
B3LYP/6-31++G**	−0.6948	−2.4337	0.9715
BHLYP/6-31++G**	−0.6363	−2.1823	0.9738

[a] Electron affinities are expressed in eV and half-wave potentials in V.

linear parameters obtained when the experimental redox potentials of Table 1 are correlated with the negative of the theoretical adiabatic EAs reported in Tables 3−5. From Table 9 it is evident that there is a linear relationship between the redox potentials and the electron affinities, independent of either the involved substituents or the number of fused rings in the quinone system. The linear relationship is improved when the contribution of the HF exchange is increased in the exchange-correlation functional. From these results it is clear that by using hybrid functionals and diffuse functions the $\mathrm{EA_a}$ is a good predictor of redox potentials. It is worth noting that the solvent does not play an important role in these systems.

IVc. The Fukui Function as a Predictor of Preferential Sites To Bind an Electron in Quinone Systems. As we mentioned in the Introduction, we are interested in the process where a system is binding an additional electron. Thus, the changes in the electron density will be measured by

$$\Delta n(\mathbf{r}) = \left(\frac{\partial n(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta,v} \Delta N_\alpha = \left\{\left(\frac{\partial n_\alpha(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta,v} + \left(\frac{\partial n_\beta(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta,v}\right\}\Delta N_\alpha \quad (5)$$

where the total density is defined as

$$n(\mathbf{r}) = n_\alpha(\mathbf{r}) + n_\beta(\mathbf{r}) \quad (6)$$

The derivatives involved in eq 5 are identified as the generalized Fukui functions

$$f^{+}_{\alpha\alpha}(\mathbf{r}) = \left(\frac{\partial n_\alpha(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta,v} \quad (7)$$

and

$$f^{+}_{\beta\alpha}(\mathbf{r}) = \left(\frac{\partial n_\beta(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta,v} \quad (8)$$

For the redox process it is clear that the derivative must be evaluated in the direction where the neutral system gains electrons with $\Delta N_\alpha = N_\alpha{}^0 + 1 - N_\alpha{}^0 = 1$. In this way the change in the electron density is

$$\Delta n(\mathbf{r}) = f^{+}_{\alpha\alpha}(\mathbf{r}) + f^{+}_{\beta\alpha}(\mathbf{r}) \quad (9)$$

Basically there are two approximations to evaluate the derivative

$$f^{+}_{\sigma\alpha}(\mathbf{r}) = \left(\frac{\partial n_\sigma(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta,v} \quad (10)$$

One is, by using the finite differences approximation,

$$f^{+}_{\sigma\alpha}(\mathbf{r}) \cong n_\sigma^{\mathrm{Anion}}(\mathbf{r}) - n_\sigma^{\mathrm{Neutral}}(\mathbf{r}) \quad (11)$$

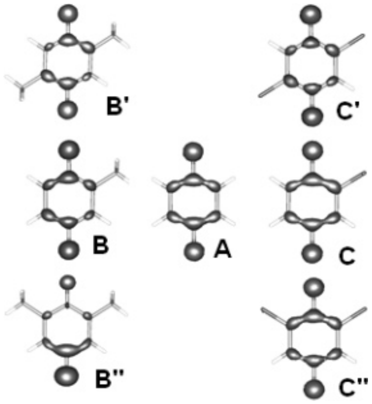

Figure 4. Fukui function $f^{+}_{\alpha\alpha}$ for the benzoquinone and some of its derivatives. Derivatives with chlorine as subtuituent are in the right column. Derivatives with methyl groups as substituent are in the left column. Positive isosurface at 0.006.

and the other one is obtained if the orbitals do not show relaxation, named frozen core approximation

$$f^{+}_{\alpha\alpha}(\mathbf{r}) \cong n_{\alpha,\mathrm{LUMO}}(\mathbf{r}) \quad (12)$$

with

$$f^{+}_{\beta\alpha}(\mathbf{r}) \cong 0 \quad (13)$$

Thus within this last, the Fukui function $f^{+}_{\alpha\alpha}$ can be estimated by the LUMO density, $n_{\alpha,\mathrm{LUMO}}(\mathbf{r})$. The cross term (eq 13) is zero because within this approximation the β electron density does not suffer changes. In this work, eq 11 is used, since there is evidence that the frozen core approximation cannot be applied in a general way.[42] Therefore on the neutral molecule geometry, the density components are computed for the neutral and anion systems.

The positive contribution of the Fukui function $f^{+}_{\alpha\alpha}$ for BQ, MeBQ, 25MeBQ, 26MeBQ, ClBQ, 25ClBQ, and 26ClBQ is depicted in Figure 4. The positive contribution of this quantity represents the excess of the α electron density of the anion system with respect to the neutral one. For the mentioned compounds, the positive contribution was always larger than the corresponding negative one. Furthermore, the contribution of the $f^{+}_{\beta\alpha}$ Fukui function was appreciably less than the $f^{+}_{\alpha\alpha}$ and for that reason their pictures are not presented.

Starting with BQ, it can be seen from Figure 4A that the preferential sites to receive an electron are the oxygen and the carbon atoms, although the dominant part is on the oxygen atoms. It also can be deduced, from the same figure, that the bonds C1−C2, C1−C6, C4−C3, and C4−C5 (see Figure 1 for numbering) have an important contribution to $f^{+}_{\alpha\alpha}$. The effect of the methyl group in BQ is depicted in Figure 4B,B′,B″. Clearly, when the methyl group appears as a substituent (Figure 4B), the contribution to the Fukui function is diminished on the C1−C2 bond and on the C2 atom, while a higher decrease of this function is observed on the C3 atom. Contrary to this behavior, there is a slight increment of this function on atom C5.

An additional methyl group in the system will drastically change the response of $f^{+}_{\alpha\alpha}$ depending on the carbon atom where it is added. For example, if a methyl group is added to the C5 atom the result is shown in Figure 4B′. This picture is in accord with the previous discussion, since a reduction of $f^{+}_{\alpha\alpha}$ is expected on atom C5, an appreciable diminishment on the C6 atom, and an increment in the effects of the methyl group on the C2 atom. When the net changes are considered, this function shows an important contribution on the C2 and C5 atoms. When the second methyl group is substituted on the C6 atom (Figure 4B″), the response is drastically different from the previous case since the new methyl group must increase $f^{+}_{\alpha\alpha}$ on the C3 atom and diminish it on C5. By adding these effects with those induced by the methyl on C2, the function $f^{+}_{\alpha\alpha}$ presents the behavior depicted in Figure 4B″. From this picture we can see that there is an increment on C3, C4, and C5 atoms and their respective bonds, but the most interesting result is that observed on the oxygen of the C5 atom, where $f^{+}_{\alpha\alpha}$ is higher than that obtained for the other oxygen atom. Thus, two methyl groups on the same side induce that the opposite site becomes a preferential site to bind an electron.

An electronegative substituent such as the chlorine induces different effects on the $f^{+}_{\alpha\alpha}$, with respect to those observed for the methyl group; these are depicted in Figure 4C,C′,C″. Chlorine substitution induces as a preferential site, to bind an electron, the carbon atom where it is bonded. This fact implies that, at some point, the carbon−chlorine bond can be reduced in a parallel electron-transfer process by the quinone reduction step. Some authors have presented evidence of this type of coupled chemical reactions.[60] When two chlorines are on the same side of the ring where oxygen is present, the preferential site to bind an electron is precisely the carbon atoms bearing the chlorine substituents (Figure 4C″). When the chlorine atoms are in opposite sides, the carbon atoms attached with the chlorine substituent present an increase in the function $f^{+}_{\alpha\alpha}$, which is also well localized (Figure 4C′). In summary, in the process to bind an electron for BQ the oxygen atoms will always be the preferential sites to bind an electron. In addition to these sites, the electron in excess will prefer the carbon atoms and bonds between them. When a substituent is present, then the carbon atoms will show different behavior depending on the nature of the substituent. If the substituent is an electron donor then the additional electron in the redox process will be located on the opposite side of the substituent. When the substituent is an electron-withdrawing group, then the additional electron will bind on the side where the substituent is present. Our analysis was made for the isolated BQ and the redox process implies necessarily more complex steps. However, according to the relationship between EAs and experimental redox potentials, the Fukui function can give a good idea about the initial stages of the redox process.

V. Concluding Remarks

It was found that the Hammett−Zuman approach for quinone compounds, even though it is useful for the prediction of $E_{1/2}$ values in some systems, is not able to describe the chemical properties of the quinones studied here, since the analysis should be performed by grouping the quinone compounds into arbitrary families (benzoquinone, naphthoquinone, and antraquinone). Instead of using such an empirical approach, the electron affinity ($\mathrm{EA} = E^{\mathrm{Neutral}} - E^{\mathrm{Anion}}$) of the studied compounds was calculated by quantum chemistry methods. This parameter proved to be good enough to correlate with the experimental redox potential, when diffuse functions and a contribution from the Hartree−Fock exchange energy is included in the exchange-correlation functional. The negative of the LUMO energy gives a good correlation with vertical and adiabatic electron affinities, particularly for the adiabatic one, but such a correlation has no physical rationalization and therefore is not recommended. Finally, we found that the generalized Fukui function is a good predictor of preferential sites to bind an electron for the analyzed quinone systems when different substituents were changed in the system.

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