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Employment of Electrodonating Capacity as an Index of Reactive Modulation by Substituent Effects: Application for Electron-Transfer-Controlled Hydrogen Bonding

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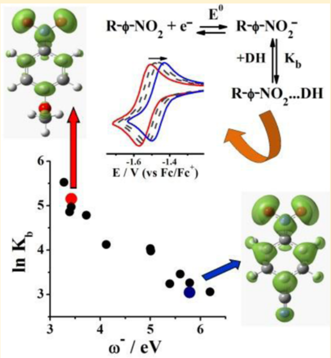
S *Supporting Information*

ABSTRACT: Evaluation of the substituent effect in reaction series is an issue of interest, as it is fundamental for controlling chemical reactivity in molecules. Within the framework of density functional theory, employment of the chemical potential, μ, and the chemical hardness, η, leads to the calculation of properties of common use, such as the electrodonating (ω^-) and electroaccepting (ω^+) powers, in many chemical systems. In order to examine the predictive character of the substituent effect by these indexes, a comparison between these and experimental binding constants (K_b) for binding of a series of radical anions from *para*- and *ortho*-substituted nitrobenzenes with 1,3-diethylurea in acetonitrile was performed, and fair correlations were obtained; furthermore, this strategy was suitable for all of the studied compounds, even those for which empirical approximations, such as Hammett's model, are not valid. Visual representations of substituent effects are presented by considering the local electrodonating power $\omega^-(\boldsymbol{r})$.



1. INTRODUCTION

Hydrogen bonding is a fundamental interaction for stabilizing structures in many systems of biological importance, such as DNA and the secondary structures of proteins and peptide systems.[1] Because of its directional character, this interaction has been used extensively for building molecular aggregates,[2,3] which have found many applications.[4−6] It is well-known that changing the charge of the molecules involved in the ensemble can enhance the degree of affinity by hydrogen bonding.[7,8] An interesting effect provoked by this process occurs in electron transfer reactions, where a change in the oxidation or reduction potentials of the latter molecules to more negative or positive values, respectively, is observed when the amount of the hydrogen-bond donor is increased; this phenomenon is known as Electrochemically Controlled Hydrogen Bonding, or, in a more specific way, as electron-transfer-controlled hydrogen bonding (ETCHB), as electron uptake or withdrawal determines the strength of the hydrogen bond.[7] Because of its strength and directionality, ETCHB has been used for designing electronics devices,[9] molecular machines,[6,9,10] sensors,[11−13] and systems for anion recognition.[14−18]

This simple reactive system can be represented with the well-known case of the interaction between substituted radical anions electrogenerated from aromatic nitro compounds ($\text{R}{-}\phi{-}\text{NO}_2^{\bullet-}$) and urea as the hydrogen-bond donor (DH):[7]

$$\text{R}{-}\phi{-}\text{NO}_2 + \text{e}^- \overset{E_{1/2}}{\rightleftarrows} \text{R}{-}\phi{-}\text{NO}_2^{\bullet-} \qquad (1)$$

$$\text{R}{-}\phi{-}\text{NO}_2^{\bullet-} + \text{DH} \overset{K_b}{\rightleftarrows} \text{R}{-}\phi{-}\text{NO}_2^{\bullet-}\cdots\text{DH}] \qquad (2)$$

The magnitude of the affinity constant (K_b, eq 2) is the key parameter for describing reactivity in these systems; also, K_b determines the extent of the above-mentioned shift in potential values. Concerning substituent effects, Smith and co-workers found that using substituents with different electron-donor/acceptor abilities produced changes in both half-wave potential values of the corresponding nitrobenzene ($E_{1/2}$) and a shift in the half-wave potential ($\Delta E_{1/2}$) with concentration:[14] the results showed that substituents with higher electron-donor capacity (characterized by more negative $E_{1/2}$ values) lead to an enhancement in the complex stability ($\Delta E_{1/2}$ increases). Similar effects occurred for ETCHB between substituted radical anions from tetramethyl-1,4-benzoquinone or tetrachloro-1,4-benzoquinone and methanol as the hydrogen-bond donor; in this case, the former compound, bearing an electrodonating substituent, presented a higher binding constant ($K_b = 3.5 \times 10^2$), whereas the latter, which has on its structure an electrowithdrawing group, showed the opposite behavior ($K_b = 1.71 \times 10^1$).[19] Substituent effects were also discussed by Cheng and colleagues,[20] concerning the interaction between radical cations of substituted triarylamines and imidazoles, revealing that electrodonating amino groups in the triarylamine structure increased the stability of the radical cations, thus shifting the oxidation potential of these species toward less positive values.

In all of the previously discussed results, substituent effects have invariably been related with electrodonating or electro-

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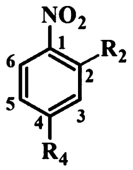
withdrawing capacities as presented in the Hammett and Taft model.[21] From a general chemical perspective, there are certain limitations of this model, as its definition relies on the corresponding empirical parameters (σ_x), which are valid for the x substituent in a relative position respect to the reactive center. σ_x values take into account only electronic effects referred to specific reactions (e.g., dissociation of benzoic acid).[21,22] Also, the amount of available σ_x data is limited. Finally, mixed substituent effects (e.g., considering both inductive properties and field effects for a specific group) cannot be employed in a general context, as specific interactions between the reactive group and the substituent tend to vary for each reaction series.[23]

In order to avoid the use of the Hammett and Taft model, a valuable and general strategy for addressing substituent effect comes from the use of quantum-chemical descriptors, which are properties calculated from electronic structure calculations on either a global or local scale for the reactive species. Cheng employed DFT methods to analyze variations in the charge distribution of the central nitrogen atom and concluded that this distribution is related to changes in acidity of the electrogenerated radical cation.[20] In other work, Galano and co-workers employed a linear combination of quantum-chemical indexes (ionization energies, electron affinities, and charges of oxygen atoms) to describe the experimental values for the interaction of quinone radical anions with methanol.[24] This latter result is interesting, as no single index (such as electrodonating or electroaccepting power, electrophilicity, or electronegativity) was correlated with the experimental results. In order to test the validity of the proposed theoretical scheme based on variations of electronic distribution by the substituent effect, the association processes of a series of radical anions electrogenerated from *ortho*- and *para*-substituted nitrobenzenes (Table 1) with the hydrogen-bond donor 1,3-diethylurea were employed, and the measured K_b values were correlated with calculated quantum-chemical indexes. The results of this analysis are presented and discussed in this work.

Table 1. General Structure of the Nitrobenzene Derivatives Studied



compound	R_2	R_4
1	H	H
2	OCH_3	H
3	CH_3	H
4	$CONH_2$	H
5	$COCH_3$	H
6	COH	H
7	CN	H
8	H	OCH_3
9	H	CH_3
10	H	$CONH_2$
11	H	$COCH_3$
12	H	COH
13	H	CN

2. RESULTS AND DISCUSSION

2.1. Electrochemical Analysis of ETCHB in Substituted Nitrobenzene Compounds. Cyclic voltammetry experiments were performed on solutions of the studied substituted nitrobenzenes in the presence of increasing concentrations of the hydrogen-bond donor 1,3-diethylurea ([DH] = 0−0.13 mol L^{-1}). For example, the experimental voltammograms obtained for unsubstituted nitrobenzene (**1**) are shown in Figure 1.

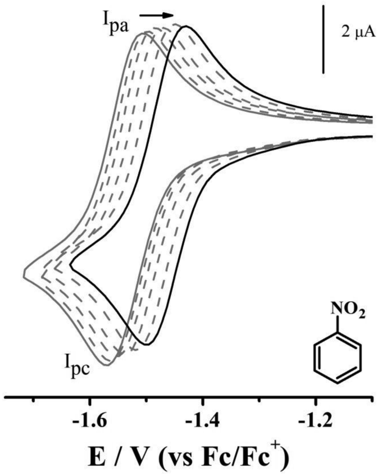


Figure 1. Cyclic voltammograms for 0.001 mol L^{-1} nitrobenzene (**1**) in CH_3CN/0.1 mol L^{-1} n-Bu_4NPF_6 [scan rate (v) = 100 mV s^{-1}; glassy carbon (GC) working electrode (WE), area = 0.0079 cm^2] with different amounts of added 1,3-diethylurea (DH): gray line, [DH] = 0 mol L^{-1}; black line, [DH] = 0.13 mol L^{-1}; dashed lines show voltammograms obtained at intermediate DH concentrations (0.004, 0.013, 0.032, and 0.068 mol L^{-1}).

The voltammograms showed a reversible electron transfer process associated with the formation of a radical anion (Figure 1, peaks I_{pc} and I_{pa}). With increasing DH concentration, a shift toward less negative potential values occurred (Figure 1); all of the studied compounds presented this behavior regardless of the chemical nature of the substituent in the structure and its relative position (*ortho* or *para*) with respect to the nitro group, as exemplified by the cyclic voltammograms of 2-methylnitrobenzene (**3**) (Figure 2), 4-methylnitrobenzene (**9**) (Figure 2), 2-nitrobenzonitrile (**7**) (Figure 3), and 4-nitrobenzonitrile (**13**) (Figure 3) with increasing amounts of DH (the rest of the voltammograms are presented in the Supporting Information). It should be noticed that the voltammetric signals in the absence of DH appear at different potential values. This effect has been studied previously by comparing experimental reduction potential values and data obtained from electronic structure calculations[22] to analyze the influence of the substituent; in the present work, no further discussion of this result will be presented.

This behavior is consistent with the mechanism described above (eqs 1 and 2) and indicates specific interactions between the electrogenerated radical anion of the nitro compound and DH via ETCHB. For the range of DH concentrations studied, the potential shifts were used to determine the corresponding binding constants K_b in order to measure the stability of the formed complex. For this purpose, the model suggested by Gómez and co-workers[25] was employed, wherein the association between the redox species $R{-}\phi{-}NO_2^{\bullet -}$ and DH occurs by successive equilibrium steps, dependent on the DH

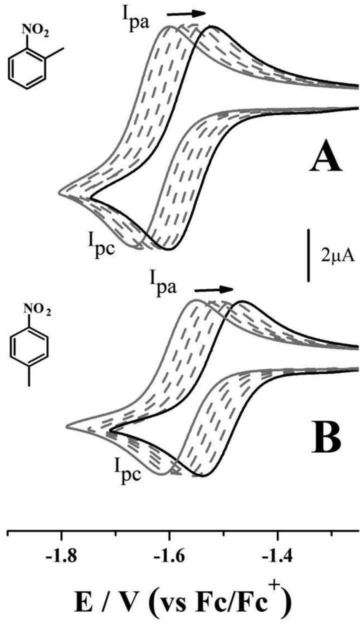


Figure 2. Cyclic voltammograms for 0.001 mol L^{-1} (A) 2-methylnitrobenzene (**3**) and (B) 4-methylnitrobenzene (**9**) in CH_3CN/0.1 mol L^{-1} n-Bu_4NPF_6 (ν = 100 mV s^{-1}; GC WE, 0.0079 cm^2) with different amounts of added 1,3-diethylurea (DH): gray line, [DH] = 0 mol L^{-1}; black line, [DH] = 0.13 mol L^{-1}; dashed lines show voltammograms obtained with intermediate DH concentrations [(A) 0.013, 0.032, 0.059, and 0.093 mol L^{-1}; (B) 0.010, 0.022, 0.041, and 0.076 mol L^{-1}]. Arrows indicate the direction of the shift of the voltammetric signals.

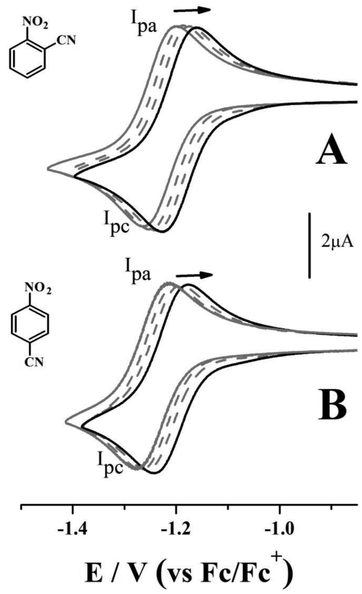


Figure 3. Cyclic voltammograms for 0.001 mol L^{-1} (A) 2-nitrobenzonitrile (**7**) and (B) 4-nitrobenzonitrile (**13**) in CH_3CN/0.1 mol L^{-1} n-Bu_4NPF_6 (ν = 100 mV s^{-1}; GC WE, 0.0079 cm^2) with different amounts of added 1,3-diethylurea (DH): gray line, [DH] = 0 mol L^{-1}; black line, [DH] = 0.13 mol L^{-1}; dashed lines show voltammograms obtained with intermediate DH concentrations [(A) 0.027 and 0.068 mol L^{-1}; (B) 0.019 and 0.059 mol L^{-1}] . Arrows indicate the direction of shift of the voltammetric signals.

concentration. Therefore, for the successive association of n guest molecules with the reduction product acting as a single host, experimental variations of $E_{1/2}$ as a function of [DH] can be fitted using the following equation:[25]

$$E_{1/2} = E^0 + \left(\frac{RT}{F}\right)\ln(1 + \beta_1[\mathrm{DH}] + \cdots + \beta_n[\mathrm{DH}]^n) \quad (3)$$

where the β_n are the corresponding global association constants, defined by

$$\beta_n = \prod_{i=1}^{n} K_I \quad (4)$$

where K_i is the binding constant for the ith binding step. Figure 4 shows some examples of nonlinear fitting of experimental $E_{1/2}$ values measured at different DH concentrations employing eq 3 with n = 1; the values obtained for the whole series of studied compounds are presented in Table 2.

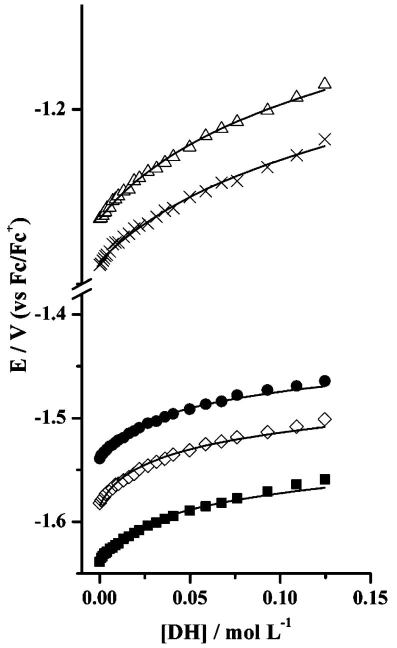


Figure 4. Variations of $E_{1/2}$ as a function of added 1,3-diethylurea (DH) for 0.001 mol L^{-1} solutions of substituted nitrobenzene derivatives: (×) 4-nitrobenzonitrile; (△) 2-nitrobenzonitrile; (●) nitrobenzene; (◇) 4-methylnitrobenzene; (■) 2-methylnitrobenzene. Solid lines are fits of the experimental values to the equation $E_{1/2} = E^0 + (RT/F)\ln(1 + \beta_1[\mathrm{DH}])$.

The data presented in Table 2 considered an association model involving 1:1 stoichiometry and therefore $K_b = \beta_1$, which has been reported by Smith for ETCHB involving nitrobenzene derivatives and aryl ureas,[14] and this model afforded a fair fit with the experimental $E_{1/2}$ variations (Figures 1−3). An overview of the obtained values indicates that larger K_b values were obtained for systems bearing substituents with known electrodonating abilities (OCH_3/CH_3), while lower K_b values were obtained when electrowithdrawing groups were present in the structure ($CONH_2/COCH_3/COH/CN$). These observations are in concordance with the trends suggested by Smith, where the stability of the complex increased as the $E_{1/2}$ value of the substituted nitrobenzene become more negative.[14] In order to analyze systematically the effect of the substituents, the Hammett model was employed. As a result of comparing both σ_X and log K_b for the latter compounds (Figure 5), a linear

Table 2. Values of E^0 and Binding Constants ($K_b = \beta_1$) for the Studied ETCHB between Radical Anions of Substituted Nitrobenzenes and 1,3-Diethylurea

compound	$E_{1/2}$/V vs Fc/Fc$^+$	$K_b \times 10^{-2}$
1	−1.539	1.20 ± 0.07
2	−1.684	2.50 ± 0.35
3	−1.638	1.29 ± 0.13
4	−1.484	0.56 ± 0.01
5	−1.406	0.62 ± 0.02
6	−1.301	0.26 ± 0.01
7	−1.231	0.26 ± 0.01
8	−1.644	1.72 ± 0.19
9	−1.582	1.44 ± 0.10
10	−1.390	0.54 ± 0.02
11	−1.319	0.32 ± 0.01
12	−1.254	0.21 ± 0.01
13	−1.245	0.21 ± 0.01

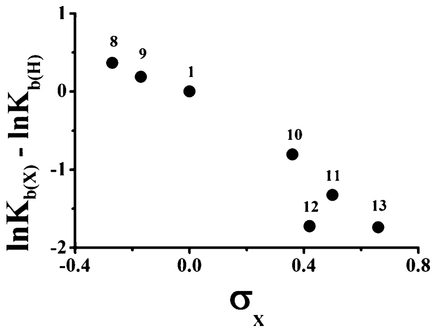


Figure 5. Correlation between σ_X and experimental log K_b for compounds **8**−**13**. X represents the *para* substituent.

correlation was obtained, consistent with the behavior described above. However, σ_X data are available only for *para*-substituted compounds (compounds **8**−**13**),[26] thus preventing a generalization of this approach for the whole series of compounds studied. Also, compound **12** did not fit in the relationship, suggesting that the Hammett description is unable to take into account specific electronic properties of this substituent (CHO), and therefore, derivatives bearing CHO in their structures would not be parametrized by this model. Instead of σ_X as a chemical descriptor, other properties obtained by quantum-chemical analysis could provide information on how the substituent modifies the electron density in the radical anion to explain the experimental results.

2.2. Employment of Quantum-Chemical Indexes To Describe the Reactivity in ETCHB. In order to analyze how the chemical structure determines the changes in binding constants observed experimentally (Table 2), a description based on reactivity indexes from quantum-chemical calculations was employed. In this context, density functional theory affords a chemically useful framework.[27−31] This arises from identifying two main properties in the reactive system: the chemical potential (μ) and the chemical hardness (η),[32,33] defined as the first and second derivatives of the energy of the system, E, with respect to the number of electrons, N, respectively, at a constant external potential $\upsilon(r)$,

$$\mu^{\pm} = \left(\frac{\partial E}{\partial N}\right)^{\pm}_{\upsilon(r)} \tag{5}$$

$$\eta^{\pm} = \left(\frac{\partial^2 E}{\partial N^2}\right)^{\pm}_{\upsilon(r)} = \left(\frac{\partial \mu}{\partial N}\right)^{\pm}_{\upsilon(r)} \tag{6}$$

The corresponding signs (+ or −), consider that the right and left derivatives are different when evaluated at a given integer value of N. Parr presented an extension of the approach by defining the electrophilicity index (ω) as

$$\omega \equiv \mu^2/2\eta \tag{7}$$

To calculate this index, it is necessary to evaluate the variations of the energy change (ΔE) for a system in which electron transfer is occurring. In this case, a second-order Taylor series expansion gives the following expression for ΔE:

$$\Delta E = \mu \Delta N + \frac{1}{2}\eta(\Delta N)^2 \tag{8}$$

By finite differences, both μ and η can be related to the energy for accepting one electron from a given donor [i.e., the electron affinity (A)] and also to the energy related to the inverse process, namely, donating one electron [i.e., the ionization potential (I)], as follows:

$$\mu = -\frac{I + A}{2}$$

$$\eta = I - A \tag{9}$$

With these considerations, the electrophilicity becomes approximately

$$\omega \approx \frac{(I + A)^2}{8(I - A)} \tag{10}$$

Gázquez and co-workers reported that when the direction in which the charge is flowing in a given system is considered, it is possible to identify the chemical potential for the charge donation process (μ^-) and that for the charge acceptance process (μ^+), defined by[34]

$$\mu^- = \frac{1}{4}(3I + A)$$

$$\mu^+ = \frac{1}{4}(I + 3A) \tag{11}$$

As the changes in chemical potential, μ, are more significant for the electron uptake/removal steps compared with the chemical hardness, η, the latter index becomes

$$\eta = \frac{1}{2}(I - A) \tag{12}$$

With this new set of equations, it is possible to define an index called electrodonating power (ω^-) that is associated with charge donation and one called electroaccepting power (ω^+) that is associated with charge acceptance as follows:

$$\omega^- \equiv \frac{(\mu^-)^2}{2\eta} \approx \frac{(3I + A)^2}{16(I - A)} \tag{13}$$

$$\omega^+ \equiv \frac{(\mu^+)^2}{2\eta} \approx \frac{(I + 3A)^2}{16(I - A)} \tag{14}$$

These indexes have been employed to describe electron transfer processes in several compounds[35−37] and have also been used to analyze ETCHB processes,[24] though in the latter case they were of little use as no significant direct correlation with the experimental data was found. For comparison with the experimental results in this work, values of *I*, *A*, ω^+, and ω^-, were calculated for the species involved in the association step (eq 2), namely, the radical anions of the nitro compounds R−ϕ−$NO_2^{\bullet -}$, and the results are shown in Table 3.

Table 3. Calculated Vertical Ionization Potentials (*I*), Vertical Electron Affinities (A), Electroaccepting Powers (ω^+), and Electrodonating Powers (ω^-) for the Radical Anions of the Studied Nitro Compounds[a]

compound	I/eV	A/eV	ω^+/eV	ω^-/eV
1	3.519	1.200	1.365	3.725
2	3.296	1.025	1.117	3.277
3	3.388	1.062	1.162	3.387
4	3.915	1.667	2.209	5.000
5	3.666	1.353	1.613	4.122
6	3.843	1.896	2.916	5.786
7	3.870	1.788	2.561	5.390
8	3.462	1.066	1.157	3.421
9	3.430	1.071	1.169	3.419
10	3.701	1.666	2.325	5.009
11	3.746	1.837	2.806	5.597
12	3.811	1.992	3.290	6.191
13	3.839	1.895	2.916	5.783

[a] For all of the calculated data, the solvent effects were considered using the Cramer and Truhlar model;[30,31] the data were calculated at the BHandHLYP/6-311++G(2d,2p) level.

Analysis of the binding process (eq 2) suggests that the electron-rich molecule (i.e., the radical anion R−ϕ−$NO_2^{\bullet -}$) is associated with the electrophilic hydrogen bond donor, DH; therefore, there should be a direct relationship between the binding constant (Table 2) and the electrodonating power, as shown in Figure 6.

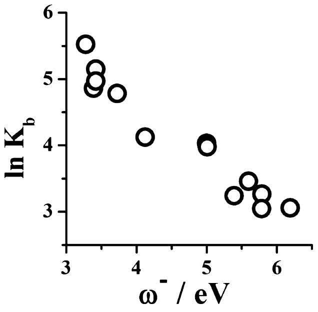


Figure 6. Relationship between experimental binding constants (K_b) and electrodonating powers (ω^-).

It should be commented that by the definition of ω^-, a smaller value of this parameter is related to a larger capability for charge donation,[34] as is expected to occur in molecules where electrodonating groups are present (e.g., compounds **3** and **9**), and vice versa for molecules bearing electrowithdrawing substituents (e.g., compounds **7** and **13**). It should also be noticed that electroaccepting power values present a fair relationship with the experimental K_b data; however, the rationale for comparing this parameter with the binding constant suggests that the hydrogen-bond donor would behave as an electron donor, which is inconsistent with experimental observations where the proton is the species being transferred.[38] In conclusion, the binding process can be systematically explained by analyzing the variation of the electrodonating power as a global reactivity index for the studied compounds.

In order to visualize how these changes in electrodonating capacity modify, on a local scale, the charge transfer ability of the studied radical anions, one can use the local electrodonating power, defined as[34]

$$\omega^-(\mathbf{r}) = \frac{(\mu^-)^2}{2\eta^-} f^-[\rho_{N_0};\mathbf{r}] = \omega^- f^-[\rho_{N_0};\mathbf{r}] \tag{15}$$

where $f^-[\rho_{N_0};\mathbf{r}]$ is the Fukui function, which is related to the differential change in electron density due to an infinitesimal change in the number of electrons,[39] in this case, for the process involving the loss of one charge by the radical anion or its ionization potential (*I*); as presented above, this latter quantity is the one that determines the electrodonating capacity of the molecule (eq 13). The required Fukui index can therefore be approximately calculated by employing the side derivative:

$$f^-(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)^-_{\nu(\mathbf{r})} \approx \rho_{\nu,N}(\mathbf{r}) - \rho_{\nu,N-1}(\mathbf{r}) \tag{16}$$

The local electrodonating power $\omega^-(\mathbf{r})$ becomes a representation of the scaling of the corresponding Fukui function for the ionization process of the radical anion. Figure 7 shows the changes in local electrodonating power for the radical anions of compounds **9** and **13** as examples.

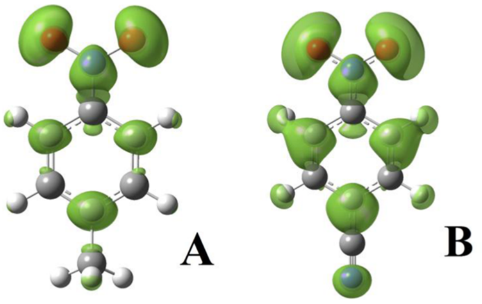


Figure 7. Local electrodonating power $\omega^-(\mathbf{r})$ for the radical anion of (A) 4-methylnitrobenzene (**9**) and (B) 4-nitrobenzonitrile (**13**).Isosurfaces are represented at 0.008 Å^{-3}.

Visual evaluation of the $\omega^-(\mathbf{r})$ plots presented in Figure 7 indicates that for the compound bearing the electrodonating substituent $-CH_3$, the condensed values are lower in the region of the NO_2 function compared with those shown for the compound containing the electrowithdrawing substituent −CN, so the former substituent is a better charge-donating agent and thus could promote higher binding constants, as was experimentally observed. It should be noticed that this analysis can be extended to the whole series of studied compounds, regardless of the position of the substituent (*ortho* or *para*) with respect to the nitro function, so this descriptor provides a good alternative for analyzing the changes in density provoked by a given substituent.

As commented above, employment of these single indexes individually was not useful for describing trends in the behavior of quinones,[24] though in that case the effects were addressed to a linear combination of *I*, *A*, charge on the O atom of the quinone dianion, and a remaining index that is not directly associated with a given calculated parameter. Even though the charge of the O atom is likely to be associated with the binding process, the presence of both I and A in the definition presented by these authors for analyzing trends in variations of the binding constant is not clear. Interestingly, the coefficient multiplying I is higher than the one multiplying A, which is consistent with the employment of the electrodonating power ω^- as presented here (eq 13). Further extensions of this analysis are planned to be performed for cases where the binding process competes with proton transfer, such as in the case of dinitrobenzene derivatives.[40]

3. CONCLUSIONS

This electrochemical and theoretical study of electrochemically controlled hydrogen bonding in systems formed by radical anions of *para*- and *ortho*-substituted nitrobenzenes with 1,3-diethylurea in acetonitrile has shown that the binding constant (K_b) for the formation of the 1:1 complex depends on the nature of the substituent, although this effect could not be fully parametrized by the classical Hammett model considering simple electrodonating or electrowithdrawing effects. The use of chemical descriptors based on the analysis of the chemical potential, μ, and the chemical hardness, η, leads to a fair correlation of the experimental K_b value with the electrodonating power (ω^-) for each substituted compound independent of the relative position of the substituent (*ortho* or *para*) with respect to the nitro function. This parameter is also conceptually related to the nature of the binding process, as the studied radical anions act experimentally as electrodonating agents for the electrophilic hydrogen-bond donor (DH). From the visual representation of these modifications provided by the local electrodonating power $\omega^-(\mathbf{r})$, experimental differences are related to local decreases in this value at the nitro function, thus leading to higher K_b values for compounds bearing electrodonating groups and vice versa. Further extensions of this approach to analyze competitive hydrogen bonding and proton transfer are currently under study.

4. EXPERIMENTAL AND THEORETICAL SECTION

4.1. Chemicals. Electrochemical studies were carried out using 0.001 mol L^{-1} solutions of nitrobenzene (**1**), 2-methoxynitrobenzene (**2**), 2-methylnitrobenzene (**3**), 2-nitrobenzamide (**4**), 2-nitroacetophenone (**5**), 2-nitrobenzaldehyde (**6**), 2-nitrobenzonitrile (**7**), 4-methoxynitrobenzene (**8**), 4-methylnitrobenzene (**9**), 4-nitrobenzamide (**10**), 4-nitroacetophenone (**11**), 4-nitrobenzaldehyde (**12**), and 4-nitrobenzonitrile (**13**) dissolved in acetonitrile (dried over molecular sieves); these solutions contained 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6, dried the night before use at 105 °C) as the supporting electrolyte. All of the solutions were maintained under an inert atmosphere by saturation with high-purity nitrogen (grade 5.0) at room temperature (approximately 20 °C). 1,3-diethylurea solutions (0.5 mol L^{-1}) were prepared in CH_3CN/0.1 mol L^{-1} n-Bu_4NPF_6 containing the corresponding substituted nitrobenzenes (0.001 mol L^{-1}) to avoid dilution during titration experiments.

4.2. Instrumentation. Cyclic voltammetry experiments were performed using an AUTOLAB PGSTAT 302N potentiostat/galvanostat interfaced with a personal computer at a scan rate of 0.1 V s^{-1} and applying IR drop compensation with R_u values determined from positive feedback measurements (R_u = 550 Ω).[41,42] A glassy carbon disk electrode (0.0079 cm^2) was used as the working electrode; the surface was polished with 0.05 μm diamond powder and rinsed successively with acetone and acetonitrile before each voltammetric run. A nonaqueous commercial reference electrode (Ag/0.01 mol L^{-1} $AgNO_3$ + 0.1 mol L^{-1} n-Bu_4NClO_4 in acetonitrile) and a platinum wire were used as the reference and auxiliary electrodes, respectively. Potential values obtained are referred to the ferrocene/ferrocenium (Fc/Fc^+) couple as recommended by IUPAC.[43]

4.3. Theoretical Procedures. Geometry optimization and frequency calculations on the neutral and radical anion structures of the studied compounds were carried out with the program Gaussian 09, revision B.01,[44] using the approach of the density functional theory. The BHandHLYP functional was employed, as described in the Gaussian manual,[45] with a 6-311++G(2d,2p) basis set. Optimized structures were obtained by considering the solvent effect using the Truhlar model.[46,47] Frequency analyses for all the structures were performed after full geometry optimizations and revealed the absence of negative frequencies, thus indicating the structures to be minimum-energy conformers. Also, for the radical anions, optimizations were performed considering annihilation of spin contaminants. With these results, vertical ionization potentials and electron affinities for the radical anions were obtained that are more accurate than those found using the eigenvalues of the HOMO and LUMO, respectively, when employing approximate functionals in DFT.[48]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Voltammograms for the studied compounds with different added amounts of 1,3-diethylurea, local electrodonating capacity indexes, and geometrical properties of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245−255.

(2) Lehn, J. M., *Supramolecular Chemistry: Concepts and Perspectives*; Wiley-VCH: Weinheim, Germany, 1995.

(3) Lehn, J. M. *Eur. Rev.* **2009**, *17*, 263−280.

(4) Nijhuis, C. A.; Ravoo, B. J.; Huskens, J.; Reinhoudt, D. N. *Coord. Chem. Rev.* **2007**, *251*, 1761−1780.

(5) *Physical Supramolecular Chemistry*, 1st ed.; Echegoyen, L., Kaifer, A. E., Eds.; Springer: New York, 1996.

(6) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Venturi, M. *Acc. Chem. Res.* **2001**, *34*, 445−455.

(7) Smith, D. K.. Electrochemically Controlled H-Bonding. In *Electrochemistry of Functional Supramolecular Systems*; Ceroni, P., Credi, A., Venturi, M., Eds.; John Wiley & Sons: Hoboken, NJ, 2010; Chapter 1, pp 1−32.

(8) Boulas, P. R.; Gómez-Kaifer, M.; Echegoyen, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 216−247.

(9) Shipway, A. N.; Willner, I. *Acc. Chem. Res.* **2001**, *34*, 421−432.

(10) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72−191.

(11) Shinkai, S.; Ikeda, M.; Sugasaki, A.; Takeuchi, M. *Acc. Chem. Res.* **2001**, *34*, 494−503.

(12) Goldberg, L. M.; Bryce, M. R.; Petty, M. C. *J. Mater. Chem.* **1999**, *9*, 1957−1974.

(13) Ge, Y.; Smith, D. K. *Anal. Chem.* **2000**, *72*, 1860−1865.

(14) Bu, J.; Lilienthal, N. D.; Woods, J. E.; Nohrden, C. E.; Hoang, K. T.; Truong, D.; Smith, D. K. *J. Am. Chem. Soc.* **2005**, *27*, 6423−6429.

(15) Breinlinger, E. C.; Niemz, A.; Rotello, V. M. *J. Am. Chem. Soc.* **1995**, *117*, 5379−5380.

(16) Gray, M.; Cuello, A. O.; Cooke, G.; Rotello, V. M. *J. Am. Chem. Soc.* **2003**, *125*, 7882−7888.

(17) Jordan, B. J.; Pollier, M. A.; Miller, L. A.; Tiernan, C.; Clavier, G.; Audebert, P.; Rotello, V. M. *Org. Lett.* **2007**, *9*, 2835−2838.

(18) Carr, J. D.; Coles, S. J.; Hursthouse, M. B.; Light, M. E.; Tucker, J. H. R.; Westwood, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3296−3299.

(19) Gómez, M.; González, F. J.; González, I. *J. Electrochem. Soc.* **2003**, *150*, E527−E534.

(20) Cheng, H.-C.; Chiu, K. Y.; Tu, Y.-J.; Yang, T.-F.; Su, Y. O. *Org. Lett.* **2013**, *15*, 3868−3871.

(21) (a) Hammett, L. P. *Chem. Rev.* **1935**, *17*, 125. (b) Hammett, L. P. *Physical Organic Chemistry*; McGraw-Hill: New York, 1940; p 184. (c) Jaffé, H. H. *Chem. Rev.* **1953**, *53*, 192. (d) Taft, R. W., Jr. Separation of Polar, Steric and Resonance Effects in Reactivity. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; John Wiley & Sons: New York, 1956.

(22) Frontana, C.; Vázquez-Mayagoitia, A.; Garza, J.; Vargas, R.; González, I. *J. Phys. Chem. A* **2006**, *110*, 9411−9419.

(23) Zuman, P. *Substituent Effects in Organic Polarography*; Plenum Press: New York, 1967.

(24) Galano, A.; Gómez, M.; González, F. J.; González, I. *J. Phys. Chem. A* **2012**, *116*, 10638−10645.

(25) Gómez, M.; González, F. J.; González, I. *Electroanalysis* **2003**, *15*, 635−645.

(26) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(27) Parr, R. G.; Yang, W. T. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(28) Chermette, H. *J. Comput. Chem.* **1999**, *20*, 129−154.

(29) Geerlings, P.; De Proft, F.; Langenaeker, W. *Chem. Rev.* **2003**, *103*, 1793−1873.

(30) Chattaraj, P. K.; Sarkar, U.; Roy, D. R. *Chem. Rev.* **2006**, *106*, 2065−2091.

(31) Gázquez, J. L. *J. Mex. Chem. Soc.* **2008**, *52*, 3−10.

(32) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801−3807.

(33) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512−7516.

(34) Gázquez, J. L.; Cedillo, A.; Vela, A. *J. Phys. Chem. A* **2007**, *111*, 1966−1970.

(35) Cerezo, J.; Zúñiga, J.; Bastida, A.; Requena, A. *J. Phys. Chem. A* **2012**, *116*, 3496−3506.

(36) Martínez, A. *J. Phys. Chem. B* **2009**, *113*, 4915−4921.

(37) Jaramillo, P.; Pérez, P.; Fuentealba, P. *J. Phys. Chem. A* **2009**, *113*, 6812−6817.

(38) Bonin, J.; Constentin, C.; Robert, M.; Saveant, J.-M.; Tard, C. *Acc. Chem. Res.* **2012**, *45*, 372−381.

(39) Parr, R. G.; Yang, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 4049−4050.

(40) Chan-Leonor, C.; Martin, S. L.; Smith, D. K. *J. Org. Chem.* **2005**, *70*, 10817−10822.

(41) Roe, D. K. Overcoming Solution Resistance with Stability and Grace in Potentiostatic Circuits. In *Laboratory Techniques in Electroanalytical Chemistry*; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1996.

(42) He, P.; Faulkner, L. R. *Anal. Chem.* **1986**, *58*, 517−523.

(43) Gritzner, G.; Küta, J. *Pure Appl. Chem.* **1984**, *4*, 461−466.

(44) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2010.

(45) Used as defined in the Gaussian 09 manual: $0.5E_X^{HF} + 0.5E_X^{LSDA} + 0.5E_X^{Becke88} + E_C^{LYP}$.

(46) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378−6396.

(47) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364−382.

(48) Zhan, C.-G.; Nichols, J. A.; Dixon, D. A. *J. Phys. Chem. A* **2003**, *107*, 4184−4195.