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Theoretical and Electrochemical Study of the Quinone–Benzoic Acid Adduct Linked by Hydrogen Bonds

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Received: April 25, 2003; In Final Form: August 13, 2003

Electronic structure calculations were carried out to prove the stability of the 1,4-benzoquinone–benzoic acid adduct, Q(HBz), linked by hydrogen bonds. The Q(HBz) geometry was optimized using the density functional theory (DFT), with gradient-corrected and hybrid exchange-correlation functionals, and Møller–Plesset perturbation theory (MP2) with DZP plus diffuse functions and TZVP basis sets; the fitting approach on the electron density was tested for DFT calculations with the TZVP/A2 basis set. Two stable planar conformers Q(HBz) were determined and confirmed by a frequency analysis. Conformer **1** has two hydrogen bonds, one O–H···O_Q and one weak C_Q–H···O, where O_Q is a quinone oxygen and C_Q corresponds to a quinone α -carbon. In the conformer **2** the Q(HBz) adduct is stabilized also with two hydrogen bonds, one is C_Q–H···O like the conformer **1**, and the other one is a C_B–H···O bond, where C_B is a carbon that belongs to the ring of the benzoic acid. Binding energies for both conformers are reported, a good agreement between DFT and MP2 results was obtained only when the basis set superposition error is included. Furthermore this agreement is better between DFT with a hybrid exchange-correlation functional and the MP2 method. The binding energy at our best level of theory was -7.7 kcal/mol for conformer **1** and -3.7 kcal/mol for conformer **2**. Additionally to the theoretical study, a novel electrochemical method is proposed to characterize the Q(HBz) adduct. The electrochemical characterization of the neutral–neutral association by hydrogen bonds was performed in DMSO, on the basis of voltammetric current measurements. The method stems from the fact that the diffusion coefficient of the electroactive compound is modified by effect of the association, of Q with HBz, which provokes significant variations in the voltammetric current peak. By using this variation, it was determined that the Q and HBz are associated with a 1:1 stoichiometry with a conditional association constant of 12 M^{-1} . This electrochemical approach represents an alternative tool to evaluate association constants involving neutral species, in conditions where the spectroscopic techniques are difficult to apply.

I. Introduction

The hydrogen bond topic has received, for a long time, large attention by experimental and theoretical groups; this interest is obvious because this contact is relevant in biological systems.^{1,2} The characterization of such interaction has been around geometrical parameters and the strength exhibited by the link X–H···O, where X represents a donor atom of the hydrogen involved in the short contact. Recently, it has been shown that the C–H···O contact must be considered as an important stabilizer of some systems. In this way, weak directional C–H···O interactions became, in recent years, one of the main topics of hydrogen bond research.³ In this field, electronic structure calculations can play an important role, mainly to supply binding energy estimations that are difficult to know by studying structural and spectroscopy data alone. Additionally, it has been established that this hydrogen bond is weak and several considerations must be taken into account to evaluate the strength of such contact by quantum chemical methods.⁴

Because quinones are very important redox species that take part in important biological process,^{5–8} the study of weak

C–H···O hydrogen bond interactions in this kind of molecules is relevant. In a recent short communication, a C–H···O hydrogen bond was observed in a system built with quinone (Q) and benzoic acid (HBz).⁹ By performing high-level ab initio calculations, it was found that the Q(HBz) adduct is stabilized by two different hydrogen bonds. Two levels of theory were reported: with the Møller–Plesset perturbation theory (MP2),¹⁰ with an augmented polarized double- ξ (DZP+diff) basis set,¹¹ the Q(HBz) adduct geometry shows O–H···O and C–H···O hydrogen bonds, which stabilize the adduct by -7.7 kcal/mol, with the basis set superposition error (BSSE) included.¹² At the density functional theory (DFT) level,¹³ using a gradient-corrected exchange-correlation functional, and a polarized triple- ξ basis set (TZVP) with an auxiliary basis set (A2),¹⁴ the same hydrogen bonds as in the MP2/DZP+diff method were observed. A binding energy just 0.17 kcal/mol higher than the MP2/DZP+diff method was obtained, but without considering the BSSE. However, there is still controversy in the literature about the reliability of DFT in the description of weak hydrogen bonds.¹⁵ For this reason, our theoretical study of the Q(HBz) system was extended to report, in this paper, a more detailed discussion about the performance of different basis sets and theoretical methods in the description on O–H···O and C–H···O hydrogen bond interactions.

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Additionally to the theoretical study we present, in this work, an electrochemical approach that permits characterization of the hydrogen bond in neutral systems such as the Q(HBz) system. It is well-known that this kind of system represents a challenge to be studied by electrochemical methods.^{16,17} Techniques such as optical and magnetic resonance or spectroelectrochemistry have been focused to study hydrogen bond interactions between *charged molecules* and proton donors.^{18–20} However, the association between neutral molecules by hydrogen bond interactions in solutions shows difficulties to be studied by these methods.^{16,17,21} The variation of the redox potential due to this interaction is not easily measurable and additional complications could be presented when the protonation of reduction products occurs.²² In this context it is better to focus on apparent diffusion coefficients; because the complex should have a smaller diffusion coefficient and consequently a current variation must be observed.¹⁷ In a previous paper we report a method based on the diffusion coefficient.⁹ Thus, in this paper we discuss in detail the electrochemical approach that supports the formation of the neutral adduct Q(HBz) and the strategy to elucidate its stoichiometry and its conditional association constant.

We present in section II details of quantum chemical methods applied on Q(HBz) adduct; results and discussion about hydrogen bonds involved in this system are also presented. In Section III the electrochemical approach is discussed in detail and it is applied on the Q(HBz) system. Finally, in section IV some general conclusions are addressed.

II. Electronic Structure of the Quinone–Benzoic Acid Adduct

II.a. Quantum Chemical Methods. Recently there has been large interest in applying DFT in the study of the electronic structure of biochemical systems where hydrogen bonds are relevant.²³ Thus, in this work, the performance of this theory with gradient-corrected (BLYP)^{24,25} and hybrid (B3LYP)^{25,26} exchange-correlation functionals, on the description of hydrogen bonds in two Q(HBz) conformers, is presented. Although there must be several conformers in this adduct, because there are several possibilities of X–H···O contact, we considered the conformers where more stable contacts can be given. The basis sets used were the DZP+diff and the TZVP without and with an auxiliary basis set TZVP/A2. We compare the DFT results with those obtained with the MP2 method; in this case the basis sets used were the DZP+diff and the TZVP. The BSSE was estimated by the counterpoise procedure¹² for all methods with the DZP+diff and TZVP basis sets. In this work all calculations were done using the NWChem program.²⁷ For all methods considered in this work the geometries were optimized. A frequency analysis was done, with the two exchange-correlation functionals used in this work and the basis sets DZP+diff and TZVP/A2, and no imaginary frequency was observed in both conformers.

II.b. Geometrical Parameters of Hydrogen Bonds. The geometries of the two conformers Q(HBz) studied here are depicted in Figure 1. Both structures were optimized using the theoretical methods describe above. As can be observed in Figure 1, conformer **1** has two hydrogen bonds, one O–H···O and one weak C–H···O. In the last one, the donor atom is a C atom of the 1,4-benzoquinone ring; this hydrogen bond will be denoted as C_Q–H···O. Conformer **2** also has two hydrogen bonds, in this case the Q(HBz) adduct is stabilized with two C–H···O hydrogen bonds, one is a C_Q–H···O like the conformer **1**, and the other one will be denoted as C_B–H···O, because the C donor is in the benzoic acid ring. It is worth

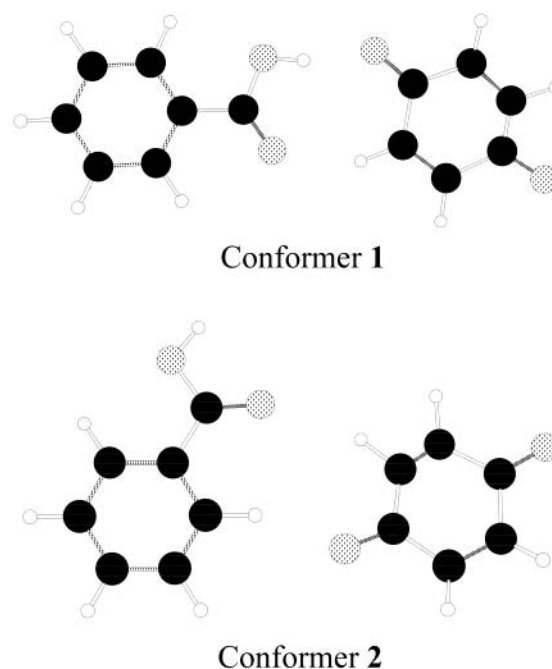


Figure 1. Geometries of conformers **1** and **2** of the Q(HBz) adduct at the MP2/TZVP level of theory.

noting that both conformers exhibit planar structures. Other possible nonplanar conformers were searched for conformer **1**, by scanning a dihedral angle, until the C–H···O bond was broken; no minimum was found. A further optimization was done in a planar conformer where the O–H···O is the only contact of the Q(HBz) adduct using the B3LYP/TZVP/A2 method; however, an imaginary frequency was found. This result is not in agreement with semiempirical methods that predict a nonplanar structure of this adduct. Additional studies must be performed to establish the reasons of such disagreement. In this work we considered only stable conformers and consequently the adduct with just the contact O–H···O was not included.

The structural parameters for hydrogen bonds described in this work for both conformers and for all methods used are reported in Table 1. We considered in this work the basis set TZVP/A2 to test the performance of the fitting approach on the electron density, to approximate the coulomb contribution, on the description of O–H···O and C–H···O contacts. From Table 1 it is evident that the basis set TZVP/A2 with BLYP and B3LYP functionals gives geometrical parameters similar to those of the basis set TZVP. It is an important result because, when the fitting approach is used, the computing times are considerably reduced; this is relevant in the study of large systems. A survey of the structural features in C–H···O hydrogen bonds, similar to those found recently in 1,4-benzoquinone dimers by Steiner et al.,²⁸ reveals that the distribution of hydrogen bond H···O distances has mean values of 2.47 Å, donor–acceptor distances (C···O) of about 3.53 Å on average, and C–H···O angles of 165.7°. As seen in Table 1, for the C_Q–H···O hydrogen bond present in conformer **1**, all levels of theory considered in this work predict shorter H···O and C···O distances than the average reported in ref 28. It is important to point out that among the basis sets used in this work the DZP+diff basis set gives for all methods the shortest distances H···O and C···O. Of course, we expect this fact will be mapped in the magnitude of binding energies. With respect to the C_Q–H···O angle, all predictions are close to the average of 165.7°, the MP2/DZP+diff method gives the largest difference with 8° less linear. Another feature observed for

TABLE 1: Hydrogen Bond Geometrical Parameters for Conformers 1 and 2 of the Q(HBz) Adduct^a

Conformer 1						
method	C _Q –H···O			O–H···O		
	<i>d</i> (O–H)	<i>d</i> (C _Q –O)	<i>A</i> (C _Q HO)	<i>d</i> (O–H)	<i>d</i> (O–O)	<i>A</i> (OHO)
BLYP/DZP+diff	2.23	3.28	158.9	1.78	2.77	169.6
BLYP/TZVP	2.26	3.31	160.0	1.82	2.80	168.8
BLYP/TZVP/A2	2.26	3.31	160.2	1.82	2.81	168.6
B3LYP/DZP+diff	2.21	3.25	158.1	1.78	2.76	171.2
B3LYP/TZVP	2.23	3.27	159.2	1.80	1.80	170.4
B3LYP/TZVP/A2	2.24	3.28	159.4	1.80	1.80	170.2
MP2/DZP+diff	2.20	3.23	157.6	1.79	2.77	171.5
MP2/TZVP	2.22	3.25	158.9	1.80	2.78	169.3

Conformer 2						
method	C _Q –H···O			C _B –H···O		
	<i>d</i> (O–H)	<i>d</i> (C _Q –O)	<i>A</i> (C _Q HO)	<i>d</i> (O–H)	<i>d</i> (C _B –O)	<i>A</i> (C _B HO)
BLYP/DZP+diff	2.27	3.37	177.4	2.49	3.53	158.9
BLYP/TZVP	2.34	3.43	179.0	2.59	3.62	156.7
BLYP/TZVP/A2	2.34	3.43	178.7	2.60	3.63	156.9
B3LYP/DZP+diff	2.25	3.34	176.7	2.44	3.47	158.5
B3LYP/TZVP	2.29	3.38	179.5	2.52	3.54	156.4
B3LYP/TZVP/A2	2.29	3.38	179.2	2.53	3.55	156.6
MP2/DZP+diff	2.23	3.31	178.7	2.34	3.32	150.3
MP2/TZVP	2.27	3.35	176.5	2.42	3.40	150.2

^aDistances are in angstroms and angles in degrees. See text for the definition of C_Q and C_B.

TABLE 2: Hydrogen Bond Binding Energies, with and without the Basis Set Superposition Error (BSSE), and ΔH for Conformers 1 and 2^a

method	conformer 1			conformer 2		
	ΔE w/o BSSE	ΔE w/BSSE	ΔH^b	ΔE w/o BSSE	ΔE w/BSSE	ΔH^b
BLYP/TZVP/A2	−7.90			−2.75		
BLYP/TZVP	−7.84	−7.35	−6.61	−2.75	−2.49	−2.23
BLYP/DZP+diff	−8.87	−7.49	−6.62	−3.76	−2.55	−1.88
B3LYP/TZVP/A2	−8.72			−3.32		
B3LYP/TZVP	−8.68	−8.24	−6.97	−3.33	−3.10	−2.32
B3LYP/DZP+diff	−9.59	−8.33	−7.34	−4.21	−3.15	−1.90
MP2/TZVP	−9.95	−8.05	−6.77	−5.12	−3.89	−3.11
MP2/DZP+diff	−12.16	−7.73	−6.74	−7.18	−3.70	−3.04

^a All quantities are in kcal/mol. ^b $\Delta H(0\text{ K}) = \Delta E + \text{BSSE} + \Delta(\text{ZPE})$. The B3LYP zero point energies were used in MP2 method.

conformer **1** is that any method in this work yields more linear O–H···O hydrogen bonds with respect to the C_Q–H···O contact; this observation stems from the fact that the O–H···O is a more directional hydrogen bond than the C_Q–H···O. However, the DZP+diff basis set indicates this with a decrement of the C_Q–H···O angle.

Comparing the C_Q–H···O hydrogen bonds in conformers **1** and **2**, it is clear that this contact is optimal in conformer **1** because the hydrogen bond distances are shorter. However, the C_Q–H···O angle is more linear in conformer **2**; in fact, this angle is the largest observed with any method, even comparing it with the O–H···O angle of conformer **1**. In conformer **2**, geometrical parameters for the C_Q–H···O hydrogen bond are more favorable in the sense that all methods give shorter distances and more linear angles than the C_B–H···O hydrogen bond. This result suggests that the H atom of the benzoic acid ring is less acidic than the H atom of the quinone ring, in accord with the well-known chemical behavior of these systems. Furthermore, this finding is in agreement with the experimental observations of the influence of the α hydrogen on the association of hydroquinone dianion with aliphatic alcohols.²⁹

II.c. Strength of the C–H···O Hydrogen Bond. Binding energies for both conformers are reported in Table 2. From this table, it can be observed that the DZP+diff basis set for all methods without BSSE corrections yields the highest binding

energy, in agreement with the results obtained in the geometrical parameters where the contact distances are the shortest. Comparing the binding energies with and without BSSE corrections, it is clear that the BSSE is larger with the DZP+diff basis set than the TZVP basis set, but this error is more significant with the MP2 approach. For example, from Table 2 with the DZP+diff basis set, the estimated BSSE for conformer **1** using MP2 is 4.4 kcal/mol whereas the mean value for DFT is 1.3 kcal/mol. These corrections represent, with respect to the corrected binding energy, 57% for MP2 and 17% in average for the DFT methods used here. However, for conformer **2**, the BSSE is more important because it represents 94% for the MP2 method and, on average, 41% for the BLYP and B3LYP methods. Another interesting feature to observe in Table 2 is that BSSE for a given basis set is always bigger in MP2 than in DFT calculations. The BSSE for **1** in MP2/TZVP is 1.9 kcal/mol whereas in BLYP/TZVP it is just 0.49 kcal/mol; in this case the BSSE correction is about 24% and 7%, respectively. With the same TZVP basis set, for conformer **2** the BSSE represents 32% for MP2 and 10% for BLYP. Curiously, the B3LYP method with the TZVP presents the smallest BSSE corrections with only 5% for **1** and 7% for **2**. There is no significant difference in the estimation of binding energies for both conformers when auxiliary basis set are or are not used in DFT calculations. It is clear that the TZVP/A2 basis set gives

an overestimation of the binding energy with respect to the TZVP and BSSE correction. For the BLYP method there is a difference of 7% for **1** and 10% for **2** whereas that for B3LYP these differences are 6% for **1** and 7% for **2**. Comparing DFT and MP2 results, it is worth noting that when the BSSE correction is taken into account, the binding energy is consistent with both theories; however, there is a better agreement between B3LYP and MP2 methods. These results show that the BSSE corrections must be included in the estimation of binding energies presenting hydrogen bond contacts. Additional to the BSSE corrections, in Table 2 the zero point energy (ZPE) is included through the ΔH . It is well-known that the ZPE reduces the stabilization of the systems. From Table 2 it is clear that the ΔH shows that the hydrogen bonds studied in this work are relevant in the formation of the Q(HBz) adduct.

As expected, all calculations agree that **1** is more stable than **2** because the O—H \cdots O hydrogen bond present in conformer **1** stabilizes this structure more and conformer **2** is only stabilized by two weak hydrogen bonds. Furthermore, we found another conformer with C—H \cdots O contacts exclusively, but the binding energy associated with this conformer was so small that it cannot compete with conformers **1** and **2** and it is not discussed here. Dividing the BSSE and ZPE corrected binding energies by the number of C—H \cdots O interactions in conformer **2** yields an estimation of the strength of the C—H \cdots O hydrogen bonds in Q(HBz) adduct. The resulting value for MP2/TZVP is -1.56 kcal/mol and for B3LYP/TZVP -1.16 kcal/mol; Steiner et al.²⁸ gave an estimation of -1.4 kcal/mol for the strength of the C—H \cdots O hydrogen bond in a 1,4-benzoquinone dimer model, very close to our estimations with both methods. Considering that the strength of the C—H \cdots O hydrogen bond is the same in both conformers, it is possible to estimate the contribution to the stability of the O—H \cdots O hydrogen bond in conformer **1**. In this way MP2/TZVP yields -5.21 kcal/mol for the strength of the O—H \cdots O hydrogen bond and B3LYP/TZVP, -5.81 kcal/mol. Thus, it is clear that both theories, MP2 and DFT, including the BSSE correction and the ZPE give similar estimations for binding energies and hydrogen bonds strengths.

It is not possible at this moment to give an estimation for the equilibrium constant because this is directly related to the free energy changes; however, it is known that thermal corrections and solvent effects may decrease the binding energies reported in this work. In this way, our estimations are an upper limit of the strength of these kinds of interactions.

III. Electrochemical Approach Based on Diffusion Coefficient

III.a. Voltammetric Behavior. The theoretical characterization of hydrogen bonding between the 1,4-benzoquinone and benzoic acid, which are neutral species, has shown that the adduct Q(HBz) stabilized by hydrogen bonds is thermodynamically viable. An experimental characterization of these hydrogen bond interactions in hydrogen donor solvents is a challenge, because it requires a high host–guest concentration ratio. In a previous communication, a voltammetric method has been proposed to evaluate the magnitude of the equilibrium constant under this type of extreme condition.⁹ This method is based on the voltammetric behavior of the reduction processes of Q, when association processes are in competition with protonation reactions, and on the current peak measurements when the neutral–neutral association mode is present. Some of the hypotheses stated in the application of this method are supported by our theoretical study and are widely discussed below.

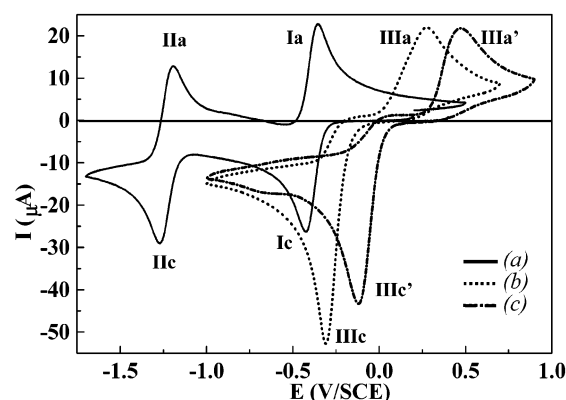


Figure 2. Typical cyclic voltammetry of 2.0 mM 1,4-benzoquinone, in DMSO + 0.2 M Bu₄NPF₆, on glassy carbon electrodes (o.d. = 3 mm) at 0.1 V s⁻¹. Several concentrations of benzoic acid were used: (a) 0.0 M; (b) 0.03 M; (c) 1.00 M.

Figure 2 shows the voltammetric behavior of the reduction process of Q for several concentrations of HBz, in DMSO as solvent.

Voltammogram a, in Figure 2, shows the typical behavior of the reduction of Q in DMSO without HBz. The reversible redox signal Ic and IIc corresponds respectively to the formation of semiquinone Q^{•-} and the dianion Q²⁻.^{22,30} Voltammogram b shows the reduction of Q in the presence of HBz (30 mM) in DMSO. In contrast with (a), it can be observed that the waves IIc, IIa, and Ia disappear and two new waves arise (IIIc and IIIa). The modification in the voltammetric behavior is basically a consequence of the protonation of semiquinone Q^{•-} and the fast reduction of the protonated semiquinone QH[•].^{22,31} Therefore the signal IIIc represents an overall two-electron reduction mechanism, which can be considered to occur following an ECE or DISP1 mechanism,³² and wave IIIa corresponds to the oxidation of the protonated dianion QH⁻. Finally, voltammogram c shows the reduction of Q in DMSO with a large concentration of HBz (1.0 M). At this concentration, it is observed that the current peak IIIc' is significantly lower than the current peak IIIc observed in (b). The decrease of current peak IIIc, corresponding to an apparent two-electron mechanism, with the increment of concentration of the donor proton, cannot be only explained by electron transfer and protonation reactions. Thus, to understand the effect of the high concentration of HBz on the electrochemical behavior of Q, it can be considered that the current peaks I_{Pic} and I_{PIIIc} are respectively described by the current peak equations for a reversible one-electron process,

$$I_{P_{Ic}} = I_{P_Q} = 0.446FSC_Q D_Q^{1/2} (Fv/RT)^{1/2} \quad (1)$$

and for a two-electron ECE-DISP1 mechanism^{33,34}

$$I_{P_{IIIc}} = I_{P_{Q+HBz}} = 0.992FSC_Q D_{Q+HBz}^{1/2} (Fv/RT)^{1/2} \quad (2)$$

In eqs 1 and 2, F is the Faraday constant, S is the electrode area, R is the ideal gas constant, T is the temperature, v is the potential sweep rate, and C_Q and D are respectively the concentration and diffusion coefficient of the electroactive species.

On the basis of eqs 1 and 2, important information can be obtained from the apparent electron number, $n_{app} = I_{P_{IIIc}}/I_{P_{Ic}}$, which corresponds to the current peak of wave IIIc ($I_{P_{IIIc}}$) normalized with respect to the current peak of the reversible one-electron reduction of Q in aprotic media ($I_{P_{Ic}}$).³⁴

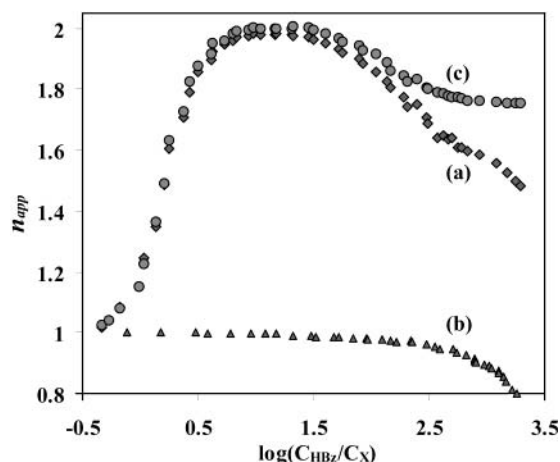


Figure 3. Apparent electron number, n_{app} , as a function of $\log(C_{HBz}/C_X)$: (a) 1,4-benzoquinone (X) + HBz without correction; (b) ferrocene (X) + HBz; (c) 1,4-benzoquinone (X) + HBz corrected with respect to ferrocene.

Thus, it is obtained that

$$n_{app} = \frac{0.992FSC_Q D_{Q+HBz}^{1/2} (Fv/RT)^{1/2}}{0.446FSC_Q D_Q^{1/2} (Fv/RT)^{1/2}} \quad (3)$$

In aprotic medium as well as in the presence of HBz, the parameters C_Q , D , F , S , R , and T are equal in all the experiments. In this way, eq 3 indicates that the value for the standardized current $n_{app} = I_{PQ+HBz}/I_{PQ}$ should be described by

$$n_{app} = 2.2 \frac{D_{Q+HBz}^{1/2}}{D_Q^{1/2}} \quad (4)$$

If the diffusion coefficient D_Q in aprotic medium does not vary from the diffusion coefficient D_{Q+HBz} in the presence of HBz, the maximum value expected for n_{app} should be close to 2.2.

The variation of n_{app} with respect to the concentration of HBz is depicted in Figure 3. In this figure curve a corresponds to the values of n_{app} for Q as a function of HBz. In the range $C_{HBz}/C_Q < 100$, it is observed that the value of n_{app} varies from 1.0 to a maximum value close to 2.0, but it does not reach 2.2, as predicted by eq 4. At higher concentrations of HBz, $C_{HBz}/C_Q > 100$, it is observed that the values of n_{app} do not remain constant, and they begin to diminish.

According to eq 4, the decrement of n_{app} as a function of HBz concentration suggests that the diffusion coefficient D_{Q+HBz} is lower than the diffusion coefficient D_Q in aprotic medium. Such variation should be influenced by the increase of the viscosity of the solution. Thus, to correct this effect, a standard curve with ferrocene in the presence of increasing HBz concentrations was constructed, and it is presented in curve b. The decrement of the percentage for the standardized current of ferrocene as a function of the concentration of HBz was then evaluated and used to correct the n_{app} value for Q. The corrected values of n_{app} are represented in curve c of Figure 3. It is observed that the maximum value of n_{app} is about 2.0. Once the viscosity effect was corrected, it is observed, however, that n_{app} decreases even when the HBz concentration is increased and remains constant to a value of 1.79 at concentrations of HBz greater than 1 M.

Considering that the effect of the solution viscosity was indeed corrected, the behavior observed for n_{app} with HBz (curve c) can be only interpreted by a decrement of the diffusion

coefficient of the electroactive species from the aprotic to the acidic medium. Such diminution is basically attributed to the intervention of quinone species associated by hydrogen bonds with HBz, as concluded in the theoretical study. Considering that the volume of the associated quinone is greater than the volume of the free quinone, this proposal falls in line with the fact that the diffusion coefficient of the associated quinone is lower than that corresponding to the free quinone, which provokes the diminution of the current peak observed. It is necessary to point out here that this is the main statement for the quantitative analysis of the association process.

Although the formation of benzoic acid dimers has been proposed,^{35,36} we have assumed that in DMSO, as solvent, it is not important.³⁷ In the range of benzoic acid concentration, used to detect the formation of the Q(HBz) adduct (1 M), the concentration ratio (DMSO/HBz = 14.08) overshoot the HBz concentration, consequently, it can be assumed that in DMSO (coordinating solvent), the benzoic acid solvation must be preferred to the dimer formation. Furthermore, considering that the benzoic acid to quinone concentration ratio (HBz/Q) is higher than 1000, the association of neutral Q should be then the preferred one. Additionally, Q, HBz, and Q(HBz) are solvated by the DMSO. This fact is taken in account implicitly in the experimental association constant evaluated in this work; thus we must refer to it as a conditional association constant of the adduct.

From the point of view of the protonation processes of the quinone anions, the only effect of a dimer must be the modification in the reactivity toward the proton transfer, which must be, consequently, manifested on the peak potential measurements. Considering that the benzoic acid is highly concentrated, the simultaneous presence of free benzoic acid and a dimer do not interfere with the current peak measurement, which depends of the diffusion of the electroactive quinone and not on the diffusion of the donor protons.

III.b. Evaluation of Coefficient of Diffusion and Stoichiometry (n) of $Q(HBz)_n$. Considering that the n_{app} parameter presents a limit that depends on the concentration of HBz, it can be proposed that at high concentrations of HBz the current peak of the reduction process must be determined by the transport properties of the associated complex $Q(HBz)_n$. Thus, the limit values of n_{app} can be used to determine both the stoichiometry and the diffusion coefficient of the associated species $Q(HBz)_n$. Taking into account that the diffusion coefficient of the free quinone can be easily obtained, the calculation of the diffusion coefficient of the associated species $Q(HBz)_n$ can be carried out by considering that D_{Q+HBz} in eq 4 corresponds to $D_{Q(HBz)_n}$.

The diffusion coefficient of Q ($D_Q = 6.04 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) was obtained by single potential step chronoamperometry using 1,4-benzoquinone in aprotic media on a glassy carbon electrode. From the limit value $n_{app}(HBz) = 1.79$, the estimated value for the diffusion coefficient of the associated complex was $D_{Q(HBz)_n} = 3.92 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The determination of the stoichiometry of the complexes from the calculated diffusion coefficient cannot be directly obtained from these measurements. In this way, an empirical correlation between the diffusion coefficient and the molecular weight (FW) of a series of quinones is proposed to estimate both the molecular weight and the stoichiometry of the complex. Such correlation is possible because the interactions between these quinones and the solvent are essentially the same. Thus the diffusion coefficient of a family of quinones was evaluated in DMSO by chronoamperometry. Figure 4 shows a linear relationship between the diffusion coefficient, of seven

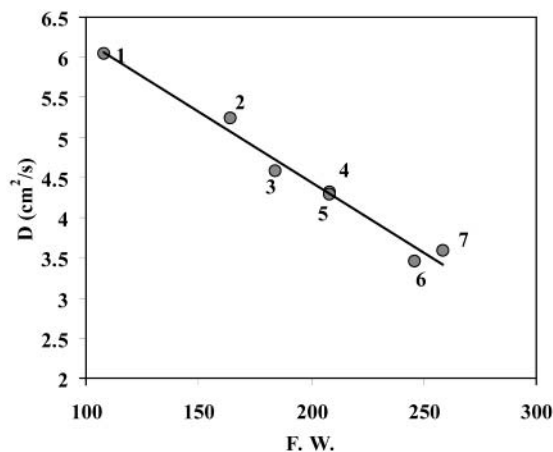


Figure 4. Diffusion coefficient as a function of molecular weight (FW) for seven quinones: (1) 1,4-benzoquinone; (2) tetramethyl-1,4-benzoquinone; (3) phenyl-1,4-benzoquinone; (4) phenanthrenequinone; (5) anthraquinone; (6) 5,12-naphthacenequinone; (7) tetrachloro-1,4-benzoquinone.

quinones, and their molecular weight. It is found that

$$D_Q [\text{cm}^2 \text{s}^{-1}] = -1.81 \times 10^{-8} \text{FW} + 8.06 \times 10^{-6} \quad (5)$$

Considering that the association complex $Q(\text{HBz})_n$ presents the same transport properties as the quinones used to construct Figure 4, the eq 5 can be used to estimate the formula weight of the complex and consequently their stoichiometry. Thus, the molecular weight estimated for the associated complex of $Q(\text{HBz})_n$ was 229 ± 19 . This value is comparable to the addition of the molecular weight of $Q + \text{HBz}$ (230), which indicates that the association occurs according to a 1:1 stoichiometry. Although other complexes, presenting different stoichiometries, could be present, their contribution can be disregarded by considering that the corresponding successive association constants are even smaller than that corresponding to the complex 1:1.

III.c. Evaluation of the Association Equilibrium Constant of the $Q(\text{HBz})$ Adduct. Once that the stoichiometry of the $Q(\text{HBz})$ adduct was determined, the association constant K can be estimated. The method here described is an alternative to that reported in a previous communication.⁹ This method considers that the total current peak is an additive contribution of the reduction of the free quinone (Q) and the associated quinone $Q(\text{HBz})$:

$$I_p = I_{p_Q} + I_{p_{Q(\text{HBz})}} = 0.992FS(Fv/RT)^{1/2}(C_Q D_Q^{1/2} + C_{Q(\text{HBz})} D_{Q(\text{HBz})}^{1/2}) \quad (6)$$

This equation is valid when the reduction of both species follows an ECE-DISP1 mechanism. In the case of the systems studied here, this condition is generally attained for a concentration ratio of $C_{\text{HBz}}/C_Q > 30$. Scheme 1 shows the mechanism of reaction considering only the ECE pathway.

Sequence “a” in Scheme 1 corresponds to the reduction of Q , and sequence “b” to the reduction of the complex $Q(\text{HBz})$. Both ECE pathways are parallel and are connected through an association equilibrium involving Q and HBz . Equation 6 describes then the passage from pathway “a” to pathway “b” by increasing the concentration of HBz .

The diffusion coefficient for the free quinone D_Q and the associated quinone $D_{Q(\text{HBz})}$ in all the range of HBz concentration

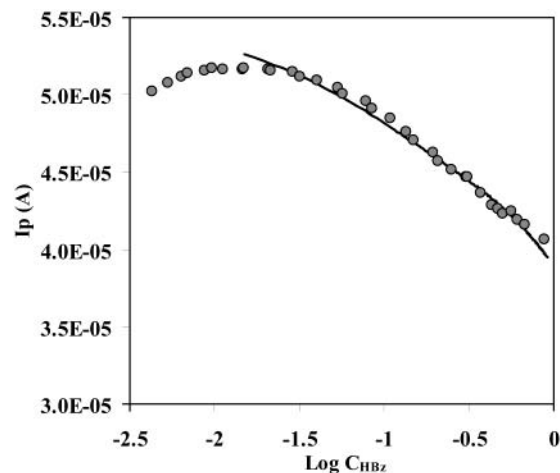
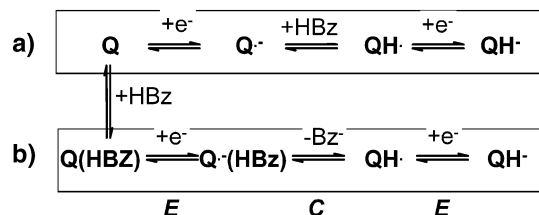


Figure 5. Current peak potential, I_p , without correction for 1,4-benzoquinone + HBz as a function of $\log(C_{\text{HBz}})$, the continuous line represents the best fitting using eq 6, $K = 12 \text{ M}^{-1}$ for $Q(\text{HBz})$.

SCHEME 1: Mechanism of the 1,4-Benzoquinone (Q) Reduction in the Presence of Different Quantities of Benzoic Acid (HBz): (a) Low Concentration and (b) High Concentration



were evaluated from equations

$$D_Q [\text{cm}^2 \text{s}^{-1}] = D_Q^0 (1 - mC_{\text{HBz}}) \quad (7)$$

$$D_{Q(\text{HBz})} [\text{cm}^2 \text{s}^{-1}] = D_{Q(\text{HBz})}^0 (1 - mC_{\text{HBz}}) \quad (8)$$

According to a linear approximation between the diffusion coefficient of ferrocene and the concentration of HBz , the factor $m = 0.2535$ was determined and used as input in eqs 7 and 8. These equations consider that both diffusion coefficients vary in the same way as the diffusion coefficient of ferrocene with the chemical composition of solution (i.e., viscosity). The ferrocene was selected to obtain eqs 7 and 8 because its one-electron oxidation process is not affected by the presence of HBz in all the range of concentration.

The diffusion coefficients D_Q^0 and $D_{Q(\text{HBz})}^0$ required in eqs 7 and 8 were obtained from experimental results. $D_Q^0 = 6 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ was obtained by chronoamperometry, and the diffusion coefficient, $D_{Q(\text{HBz})} = 3.92 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ was obtained from the convergence limit curve c in Figure 3.

On the other hand, the concentration of free quinone, C_Q , and the associated quinone, $C_{Q(\text{HBz})}$, at each HBz concentration, was directly obtained from the equilibrium constant K ,

$$K = \frac{C_{Q(\text{HBz})}}{C_Q C_{\text{HBz}}} = \frac{C_{Q(\text{HBz})}}{(C_Q^0 - C_{Q(\text{HBz})})(C_{\text{HBz}}^0 - C_{Q(\text{HBz})})} \quad (9)$$

The fitting of the experimental data of current peak as a function of $\log(C_{Q(\text{HBz})})$ was carried out by the iteration method using eq 6 and it is shown in Figure 5 with a continuous line. The best fitting was obtained for an equilibrium constant of $K = 12$

M^{-1} . This value is close to that obtained with the method previously reported ($K = 10\text{--}15\text{ M}^{-1}$).⁹

The binding constant determined by the electrochemical method for the Q(HBz) adduct corresponds to a free energy of complex formation of ca. -1.6 kcal/mol . Obviously this value cannot be related directly with the binding energy estimation given in section II.c; as mentioned before, other corrections are needed and our group is working now in this direction.

IV. Conclusions

In this work the 1,4-benzoquinone–benzoic acid adduct was studied by theoretical and electrochemical approaches. It was found by theoretical methods two planar conformers of the Q(HBz) adduct, both stabilized by two hydrogen bonds. Conformer **1** exhibits one $O\cdots H\cdots O_Q$ and one weak $C_Q\cdots H\cdots O$ bond. On the other hand, it is found that conformer **2** also exhibits two hydrogen bonds: one is $C_Q\cdots H\cdots O$ like **1**, and the other one is a $C_B\cdots H\cdots O$ bond. Comparing geometrical parameters for the $C_Q\cdots H\cdots O$ hydrogen bond in conformer **1** and conformer **2**, it is found that this is more favorable in the former because the distances obtained are shorter. Besides, these parameters show that the hydrogen α in Q is more acidic than an H atom in the HBz ring, in agreement with previous experimental results. Large discrepancies are found in the binding energies for DFT with respect to the MP2 method; however, there is good agreement between these methods if the basis set superposition error is included. Thus this correction is mandatory for this kind of system, as has been suggested in other systems,³⁸ in addition to MP2 calculations where the BSSE is larger. The agreement is better between B3LYP and MP2 calculations when the BSSE is included. The binding energy at our best level of theory was -7.7 kcal/mol for conformer **1** and -3.7 kcal/mol for conformer **2**. Because the solvent and thermal effects are not considered, these values represent an upper estimation of the binding energy. Consequently, it is expected that experimental techniques give smaller values depending of the solvent used.

The electrochemical characterization of the neutral–neutral association by hydrogen bonds is reliable when the voltammetric current peak measurements are considered. The method stems from the fact that the diffusion coefficient of the electroactive compound is dependent on the stoichiometry of the association complex. It is worth noting that the concentration of the donor proton is important to determine the adduct stoichiometry. Because the current peak description is based on an additive contribution of the reduction of both free and associated species, the variation of the total current peak as a function of the donor proton concentration can be directly related to the conditional association constant. Using this novel strategy, in this work it was determined that the Q and HBz are associated with a 1:1 stoichiometry and a conditional association constant of 12 M^{-1} . Although the Q(HBz) adduct was studied here, this methodology can be applied to other types of systems presenting the neutral–neutral association mode. This approach is an important and complementary tool in chemistry to evaluate association constants in systems where it is hard to use spectroscopical techniques.

V. Experimental Section

1,4-Benzoquinone 99%, benzoic acid 99%, ferrocene 97%, and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) 98% were Aldrich chemicals. The 1,4-benzoquinone was previously purified by sublimation under reduced pressure. Dimethyl sulfoxide spectrophotometric grade, containing less than 0.1%

water, was used as the solvent. The solutions of 1,4-benzoquinone were deoxygenated by dry argon bubbling, and an inert atmosphere was maintained over the solutions during each experimental run. The added solutions of acid contained 1,4-benzoquinone + 0.2 M Bu_4NPF_6 to avoid the dilution.

The electrochemical apparatus consisted of a potentiostat RADIOMETER DEA332 with positive feedback resistance compensation. The experiments were carried out at $25\text{ }^\circ\text{C}$ on a conventional three-electrode cell. The work electrode was a 3 mm diameter glassy carbon disk (Sigradur G from HTW, Germany). This electrode was polished with $1\text{ }\mu\text{m}$ alumina powder and ultrasonically rinsed with ethanol before each run. The counter electrode was a platinum screen and the reference electrode an aqueous saturated calomel electrode (SCE).

Acknowledgment. Financial support for J.G., R.V., and F.J.G. was provided by CONACYT, México, through projects J33153-E, C01-39621, and G32710-E, respectively.

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