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Electronic Structure of Substituted Benzoquinones and Quinonechloroimides

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The electronic structures of several halogen substituted bezoquinones and benzoquinoneimines have been studied by HeI/HeII photoelectron spectroscopy and Green's function calculations. The information on the electronic structure is discussed in the context of their electron-transfer properties and biological activity.

Introduction

The benzoquinone compounds (BQ) are very interesting because they exhibit a rich variety of chemical properties and biological activities. The chemically interesting behavior of BQ includes electron and proton-transfer processes. Benzoquinones undergo one- or two-electron reversible reduction processes. They can be attached to protein molecules and participate in electron and proton transfers in biological systems. For example, some BQ are involved in the generation of reactive oxygen species (superoxide anion radical $O_2^{\bullet -}$ or hydroperoxide radical $OOH^{\bullet}$). Such species are byproducts of energy generating processes in cell mitochondria.[1,2] The processes involve both electron transfer and stabilization of quinone−hydroquinone complexes by hydrogen bonding. The biological activity of benzoquinones had also been noted. It was known that halogenated benzoquinones are inhibitors of bacterial urease enzymes and thus can be used as antibacterial treatment for, e.g., stomach ulcers.[3] Benzoquinoneimines (BQI) have also been studied and found to metabolize seven times faster than BQ, producing superoxide radical anions and possessing growth-inhibiting, potential antitumor, activity.[4] It is therefore not surprising that biologically active benzoquinones have been studied extensively by electrochemical methods (measurement of reduction half-wave potentials).[5] In the context of biological activity, studies were made of substituted benzoquinones to explore the role of substituent effects on solvent partition coefficients.[6] Substituent effects were also investigated on a more fundamental level (i.e., without specific reference to biological activity).[7] A correlation of computational, density functional methods (DFT), and voltammetric half-wave potentials was investigated in order to establish the feasibility of utilizing substituent constant to describe substituted benzoquinones.[8] A study by Frontana et al.[8] showed that, while Hammett-derived substituent constants are not good descriptors for voltammetric data, the electron affinities are.

Since the general basis of BQ activity resides in reversible electron-transfer processes it is only natural that the electronic structure of many BQ had been studied by ultraviolet (UV) photoelectron spectroscopy (UPS). UPS provides very good insight into the electronic structure of gas-phase molecules, and the extensive work on the measurements and analysis of photoelectron spectra has been reviewed previously.[9] We wished to complement the previous UPS work in several ways. We present the variable photon energy measurements (HeI/HeII spectra) of several substituted BQ which has not been done previously. The use of variable photon energy measurements is very useful in view of the known difficulties of using Koopmans approximation to interpret the UPS of BQ.[9] Also, we present here the photoelectron spectra of several substituted BQ and BQI which have not been reported previously.

Theoretical Methods

The sample compounds **1**−**7** were purchased from Sigma-Aldrich and used without further purification after confirming their identity and purity by NMR spectroscopy (Scheme 1).

The HeI/HeII photoelectron spectra were recorded on the Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe or Ar gas which was added to the sample flow. The spectral resolution in HeI and HeII spectra was 25 and 70 meV, respectively, when measured as fwhm of the $3p^{-1}$ $^2P_{3/2}$ $Ar^+ \leftarrow Ar$ ($^1S_0$) line. The samples were recorded with the inlet probe heated in the range from 40−120 °C. The spectra obtained were reproducible and showed no signs of decomposition which was established by the measurement of the NMR spectrum of the sample residue (i.e., the sample left in the probe after the completion of the measurement).

The quantum chemical calculations were performed with the Gaussian 03 program.[10]

For the assignment of photoelectron spectra, full geometry optimization was performed first using the DFT method at the B3LYP/6-31G* level (no imaginary frequencies were detected). The basis sets for all atoms in **5** and **7** were of effective core potential type[11] (SDD basis set) in order to account for the relativistic effects of heavy halogens. Subsequently, a single-point Green's functions (GF) type calculation[12] (starting with DFT formalism and 6-311G** basis as indicated previously) was performed in order to obtain vertical ionization energies. The use of this method obviates the need to rely on Koopmans' approximation which was shown to be unsatisfactory for the interpretation of UPS of benzoquinones.[9,12]

The DFT geometries of some benzoquinones are compared in Table A (in the Supporting Information) with measured ones obtained by X-ray or electron diffraction.[13,14] The agreement

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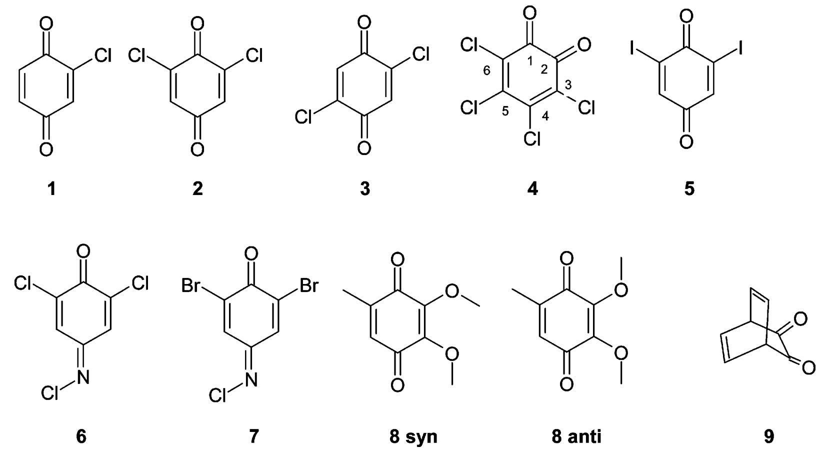
SCHEME 1



between experimental and calculated geometries is satisfactory thus validating our choice of computational method.

Results and Discussion

Photoelectron Spectra. The HeI/HeII photoelectron spectra of **1**−**8** are shown in Figures 1−8 (of the Supporting Information) and the relevant ionization energies and assignments summarized in Table 1. The interpretation of spectra is based on comparison with the assigned spectra of benzoquinone and related compounds[15−17] and on changes in relative band intensities on going from HeI to HeII radiation. The atomic photoionization cross-sections of outer np valence orbitals in C, N, O, Cl, Br, I differ significantly at HeI and HeII photon energies.[18] The HeII/HeI cross-section ratios for C, N, O, Cl, Br, and I are 0.31, 0.44, 0.64, 0.05, 0.06, and 0.09, respectively. This difference can be used as an assignment aid especially for bands corresponding to halogen lone pair ionizations. Thus we expect that bands corresponding to ionizations from benzoquinone π-orbitals or halogen lone pairs to show relative intensity decrease on going from HeI to HeII radiation.

Chloro-*p*-benzoquinones (1−3). We compared the spectra of **1**−**3** with the spectrum of *p*-benzoquinone whose definitive assignment has recently been published.[15] The set of four orbitals localized on BQ moiety in 10−11 eV region comprises linear combinations of in-plane oxygen lone pairs (n_o^+ and n_o^-) and π-type bonding orbitals (π^+, π^-) as shown in Scheme 2.

The oxygen localized and ring localized orbitals in this set can be distinguished by their relative band intensity changes in HeI and HeII spectra. The orbitals with oxygen character can be expected to show increase in relative band intensity vs ring localized orbitals. This is the consequence of atomic photoionization cross-sections for carbon and oxygen (see above). The orbital ionizations corresponding to BQ moiety in **1**−**3** can be expected to appear at higher energies than in the parent benzoquinone[15] due to the inductive effect of chlorine substituent. Indeed, a small inductive shift of 0.3 eV approximately, toward *higher* ionization energies is observed on going from BQ to **1**−**3** (Figures 1-3). The shift is not consistent with the spectra of tetrachloro-*p*-benzoquinone[19] where smaller shifts of 0.1−0.3 eV toward *lower* ionization energies had been measured. The decrease (rather than the expected increase) can be rationalized by noting that upon perchlorination the length of CO bond decreases (by 0.027 Å) and that of π-bond in BQ increases (by 0.02 Å).[14] This is an indication of reduced interaction between C=C and C=O moieties which can be related to the destabilization of pertinent orbitals, i.e., resonance and not only inductive bonding effects need to be considered.

The nature of HOMO ionizations in **1**−**3** can be ascertained by inspecting HeI/HeII band intensities (HOMO ionization band increases in intensity relative to three other benzoquinone bands) which suggest that HOMO has oxygen lone pair character and can on the basis of GF calculations be definitely attributed to the n_O^- type orbital. The bands at higher ionization energies show a very pronounced decrease in intensity on going from HeI to HeII radiation and can therefore be described as chlorine lone pairs (n_{Cl}). The detailed assignment of chlorine lone pairs is given in Table 1. We wish only to note that there are two types of n_{Cl} bands present in **1**−**3**: the sharper ones at lower ionization energies (corresponding to chlorine lone pair localized in the molecular plane $n_{Cl}^{||}$) and the broader ones at higher ionization energies (lone pair perpendicular to the molecular plane $n_{Cl}^{\perp}$). These two types of lone pairs also exhibit different degrees of interaction with BQ moiety. For example, in the spectrum of **3**, the $n_{Cl}^{||}$ bands at 12.1 eV are virtually degenerate which suggests their negligible interaction with BQ moiety. On the other hand, the separation between $n_{Cl}^{\perp}$ bands is much larger (0.6 eV). We can thus conclude that while not dominant in **1**−**3**, there is discernible resonance interaction between chlorine lone pairs and BQ core π-orbitals.

Tetrachloro-*o*-benzoquinone (4). The photoelectron spectra of **4** can be assigned by comparison with the spectrum of *o*-benzoquinone[20] which exhibits bands at 9.6, 9.99, 11.0, and 12.3 eV. These bands correspond to *o*-BQ localized orbitals: n, π, n, and π. Upon perchlorination, these bands experience small (0.2 eV) shifts in ionization energies. The small inductive shift in ionization energies can be related to small changes in the molecular structure of *o*-benzoquinone upon perchlorination.[21] For example, the changes in CC bond lengths are less than 0.01 Å.

The bands at 9.59 and 12.13 eV decrease in relative intensity on going from HeI to HeII which suggests that the BQ orbital manifold at 9.59, 10.15, 11.1, and 12.13 eV can be interpreted as originating from the ionizations of π, n, π, and n orbitals, respectively.

The bands at 11.7 and 12.6 eV (manifold of overlapping ionic states) show a very pronounced decrease in band intensity in HeII spectra and can be assigned to chlorine lone pair ionizations.

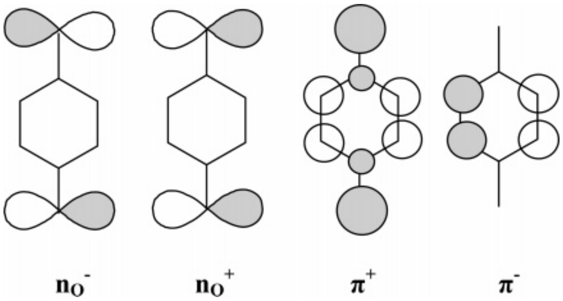
It is interesting to analyze possible through-space interactions between oxygen lone pairs of neighboring carbonyl groups in *o*-benzoquinone, **4** and **9**, on the basis of their previously assigned photoelectron spectra.[9,19,20,22] The energy splitting between n_O^- and n_O^+ (Δn) orbitals of benzoquinone moiety shall be used as an indicator of through-space interactions. The

TABLE 1: Experimental Vertical Ionization Energies (E_i/eV), Calculated Ionization Energies (GF/eV), Band Assignments, and Relative HeII/HeI Band Intensities for Substituted Benzoquinones[a,b]

molecule	band	E_i	GF	assignment	HeII/HeI
1 (C_s)	X	10.17	10.1	n_O^- (a′)	1.1
	A	10.53	10.8	n_O^+ (a′)	
	B	10.53	10.8	π^- (a″)	
	C	11.14	11.30	π^+ (a″)	1.0
	D	12.13	11.90	n_{Cl} (a′)	0.4
	E	13.15	12.94	n_{Cl} (a″)	0.5
2 (C_{2v})	X−A	10.35	10.10, 10.52	π (a_2), n_O(b_2)	1.0
	B−C	10.85	11.08, 11.47	n_O(b_2), p (b_1)	1.0
	D	12.10	12.08	n_{Cl} (a_1)	0.11
	E	12.38	12.12	n_{Cl} (b_2)	0.11
	F	12.9	12.83	n_{Cl} (b_1)	0.3
	G	13.6	13.45	n_{Cl} (a_2)	0.5
	H	13.9	14.46	π_{CO} (b_1)	0.5
3 (C_{2hv})	X−B	10.45	10.07, 10.55	n_O^-(a_g), n_O^+(b_u)	1.0
			11.14	π^- (b_g),	
	C	10.90	11.43	π^+ (a_u)	1.0
	D−E	12.10	11.97, 12.15	n_{Cl} (a_g), n_{Cl} (b_u)	0.14
	F	12.85	12.86	n_{Cl} (a_u)	0.39
	G	13.45	13.34	n_{Cl} (b_g)	0.34
	H	14.05	14.5	π_{CO} (b_g)	0.9
4 (C_{2v})	X	(9.43), 9.59	9.20	π (a_2)	1.0
	A	10.15	10.54	n_O(a_1)	2.7
	B	11.1	10.90	π (b_1),	0.6
	C	11.7	11.4	n_{Cl} (b_1)	0.2
	D	12.13	12.05	n_O (b_2)	0.4
	E−J	12.60	12.05,	n_{Cl} (b_2), n_{Cl} (a_1),	0.4
			12.43,12.50	n_{Cl} (a_2), n_{Cl} (b_2),	
			12.73,12.75	n_{Cl} (b_1), π (a_2)	
			12.80,13.3	n_{Cl} (a_1)	
5 (C_{2v})	X−A	9.49, 9.82	9.28, 9.54	n_I (a_2), n_I (b_1)	1.0
	B	10.27	9.70	n_I (b_2)	1.3
	C	10.51	9.90	n_I (a_1)	1.2
	D	10.69	10.87	n_O^- (b_2)	1.2
	E	11.47	11.33	n_O^+ (b_2)	1.5
	F	11.68	11.76	π^+ (b_1)	
	G	11.88	11.80	π^- (a_2)	1.5
6 (C_s)	X	9.9	9.4	π_{CN} (a″)	1.0
	A−C	10.25	9.9, 10.47,	n_N (a′), n_O (a′)	
			10.97	π_{CC} (a″)	1.0
	D−E	11.80	11.4, 11.73	n_{Cl} (a′), n_{ClN} (a″)	0.24
	F	12.1	11.95	n_{Cl} (a′)	0.24
	G−H	12.8	12.51, 12.66	n_{ClN} (a′), π_{CC} (a″)	0.50
	I	13.45	13.22	n_{Cl} (a″)	0.36
7 (C_s)	X−A	10.1	9.67, 9.97	n_O (a′), π_{CN} (a″)	1.0
	B	10.6	10.81	n_N (a′)	0.9
	C−D	11.25	11.04, 11.05	n_{Br} (a′), n_{Br} (a′)	0.4
	E−F	11.5	11.36, 11.66	n_{Br} (a″), n_{Br} (a″)	0.4
	G−H	12.15	12.16, 12.36	n_{Cl} (a″), n_{Cl} (a′)	0.8
	I	(*12.61*)	12.49	π_{CC} (a″)	
8 (C_s)	X	8.9	8.5	π_{CC}^- (a″)	1.0
	A	9.55	9.97	n_O^- (a′)	2.1
	B	10.3	10.15	n_O^- (a′)	1.3
	C	10.8	10.37	π_{CC}^+ (a”)	1.1
	D	11.8	11.7	n_{OMe}	
$(CH_3)_2CNCl$	X	10.25		n_N	
	A	10.25		$\pi_{CN\perp}$	
	B	11.80		n_{Cl}	
	C	12.85		$n_{Cl}^{\|\|}$	
p-BQ	X	10.05		n_O^-	
	A	10.23		n_O^+	
	B	10.97		π_{CC}^-	
	C	10.97		π_{CC}^+	

[a] Numbers in brackets represent adiabatic ionization energy; numbers in italic font represent band partially obscured by the water peak. [b] The molecular plane is the *yz* plane. [c] The pole strengths in OVGF calculations were >0.89 for all ionizations below 14 eV.

SCHEME 2



Δn values in the parent *p*-benzoquinone and its derivatives **1**−**3** fall in the range of 0−0.4 eV and this represents through-bond interaction only as discussed previosly.[22b] The corresponding Δn values in **4** and *o*-benzoquinone are much larger amounting to 1.4−2.0 eV. The larger splitting in *o*-benzoquinones compared to *p*-benzoquinones can be expected due to the spatial proximity of oxygen lone pairs which can interact in through-bond and through-space fashion. However, in **9** an even larger splitting of 3 eV was measured. The reason for the large splitting was attributed to interactions of n_O orbitals of keto group with π-orbital of the correct spatial orientation.[22a] Comparison of the spectra of *o*-benzoquinone and **4** reveals that perchlorination increases the Δn splitting by 0.6 eV. This can be rationalized by decrease of exocyclic ∠CCO angles upon perchlorination[21] which brings two oxygen atoms closer in space.

2,6-Diiodo-*p*-benzoquinone (5). The assignment of the spectra of **5** relies on the GF calculations and HeII/HeI intensity changes, bearing in mind that iodine lone pair orbital ionizations give rise to bands whose intensity falls off dramatically in the HeII spectra. Also, the n_O ionizations show relative intensity increase compared to π-orbitals. The detailed assignment is given in Table 1. Unlike chloro-substituted benzoquinones, the orbitals of BQ moiety in **5** are strongly shifted toward higher ionization energies by up to 0.8 eV. This suggests the presence of strong resonance interactions between BQ moiety and iodine substituents. This interaction destabilizes iodine lone pairs and stabilizes BQ localized π-orbitals.

2,6-Dichloroquinone-4-chloroimine (6) and 2,6-Dibromoquinone-4-chloroimine (7). The spectra of two chloroimines were assigned by comparison with the spectra of reference molecules: benzoquinone,[15] $(CH_3)_2C{=}NCl$[17] and by HeI/HeII intensity changes. The ionization energies of reference molecules together with detailed assignments for **6**−**7** are given in Table 1.

The relative intensity of bands corresponding to n_O and n_N ionizations can be expected to increase on going from HeI to HeII radiation. Some band manifolds in the spectra contain ionic states whose energy spacing is 0.4 eV or less and in such cases the proposed assignment is tentative. The most interesting observation regarding the electronic structure of the two chloroimines is that in **6** the electronic structure of the quinone-chloroimine core is mainly perturbed by inductive effect of chlorine substituents in 2,6 positions. Replacement of chlorine by bromine as in **7** leads to major changes in the electronic structure of the core with bromine $n_{Br}^{\perp}$ out-of-plane lone pairs contributing to the core π-orbitals. This can be deduced from the HeI/HeII intensity changes of manifold 9.9−10.25 eV in **6** vs manifold 10.1−10.6 eV in **7**. The former manifold exhibits larger HeII enhancement than the latter. This can be attributed to the fact that core π-orbitals in **7** contain more halogen lone pair character than π-orbitals in **6**. Since halogen lone pair character reduces HeII photoionization cross-section and band intensity, the manifold in **7** should have a smaller intensity enhancement as observed.

2,3-Dimethoxy-6-methyl-*p*-benzoquinone (8). The spectra are shown in Figure 8 and the assignment is again obtained from GF calculations and HeI/HeII intensity changes. The intensity changes allow a distinction to be made between oxygen lone pairs and ring π-orbitals. Two prominent characteristics of the spectra of **8** can be detected. First, is the existence of bands in the 8−11.5 eV region which are broader than in other benzoquinones. Second, is the pronounced shift of the first three bands toward lower ionization energies. The molecular structure of **8** does not deviate significantly from the geometry of the parent *p*-benzoquinone.[23] Nonetheless, the crystal structure study[23] has shown the existence of a single, flexible conformer in which the methoxy group in 3-position is twisted out of the ring plane in order to relieve the CH_3−O interaction between two vicinal methoxy groups. This may be one possible factor contributing to large bandwidths. We have also performed Green's functions calculation for the syn (methoxy groups facing each other) and *anti* (methoxy groups away from each other) conformers of **8** (Scheme 1). The average difference in ionization energies amounts to 0.15 eV. The existence of several conformers of **8** in the gas-phase whose ionization energies differ slightly is consistent with the observed band broadening in UPS. The energy shifts and bandwidths can also be rationalized by the electron donating inductive and resonance effects of the methoxy and methyl groups. The methyl group usually exerts destabilizing inductive effect only as can be seen from the comparison of the spectra of BQ and its tetramethyl derivative.[19] The bands in the former are uniformly shifted toward lower ionization energies by 0.8 eV. Methoxy group exerts resonance effect as well and in the process enhances delocalization of the first four orbitals leading to band broadening. DFT calculations highlighted the importance which conformal positions of methoxy groups in methoxy substituted *p*-benzoquinones have on their IR spectra and electrochemical properties.[24] The existence of two conformers separated by low rotational barrier is also consistent with our interpretation of the UPS data. Thus we demonstrate the existence of peculiarities in the UV photoelectron spectra also. The conformational characteristics of methoxy-*p*-benzoquinones (ubiquinones) are important for their biological activity.[24] These molecules play important role in electron-transfer processes in bacterial photosynthesis when bound to a protein. It was suggested that protein can adjust redox potential of ubiquinone by altering the orientation of two methoxy groups, i.e., by changing the molecular conformation of the benzoquinone center.

Electron-Transfer Properties. Benzoquinones are known to undergo one or two-electron reductions and this is the basis of their biological importance. The measurement of electron affinity (E_{ea}), i.e., the ability to accept additional electron can be performed by several methods and the results obtained by different methods show some discrepancies (Table 2). We prefer to use mass-spectrometric results for E_{ea} whenever available because these results refer to free molecules in the gas phase, as was the case in UPS method. The E_{ea} values show that the introduction of electron-withdrawing substituents, e.g., halogens increases electron affinity vs the respective parent benzoquinone. The introduction of electron donating alkyl substituents on the other hand decreases electron affinity. Most electron-transfer reactions of benzoquinones take place in solution so other effects (e.g., radical anion solvation) may influence the measured E_{ea} values. However, inductive substituent effects appear to be the most important. Nevertheless, the very small difference in E_{ea} between tetrafluro and tetrachloro-BQ derivatives suggests that other effects can determine the final electron affinity.

TABLE 2: Lowest Experimental Vertical Ionization Energies (E_i/eV), Electron Affinities (E_{ea}/eV) Obtained Using Mass-Spectrometry (MS), CT Spectral Analysis (CT) or G3 Calculations (calc) and ΔE/eV for Substituted Benzoquinones and Imines[a,b]

compound	E_i	E_{ea} (MS)	E_{ea} (CT)	ΔE	E_{ea} (calc)
p-benzoquinone (PBQ)	10.05	1.91	1.83	8.14	1.91
o-benzoquinone (OBQ)	9.6	1.90[c]		7.7	1.98
tetra-Cl-PBQ	9.90	2.78	2.48	7.12	2.78
tetra-F-PBQ	10.96	2.70	2.45	8.26	2.68
2,6-di-Cl-PBQ (**2**)	10.35	2.48	2.23	7.87	2.46
2,5-di-Cl-PBQ (**3**)	10.45	2.44	2.30	8.01	2.44
Cl-PBQ (**1**)	10.17		2.05	8.12	2.21
tetramethyl-PBQ	9.25	1.58	1.67	7.67	1.67
2,5-diMe-PBQ	9.60	1.76	1.73	7.84	1.76
tetra-Cl-OBQ (**4**)	9.43		2.57	6.86	2.86
2,3-Cl-5,6-CN-PBQ	10.58		3.13	7.45	
2,3-diMeO-6-MePBQ (**8**)	8.9	1.86		7.04	1.85
5	9.49			6.47	3.02
6	9.9			7.88	2.02
7	10.1			7.01	3.09

[a] The electron affinities were obtained from ref 25 and 26 and ionization energies from refs 9, 15, and 19. [b] The $\Delta E = E_i - E_{ea}$ values were obtained from MS data if available, otherwise E_{ea} (calc) was used. [c] Reference 29.

E_{ea} measures how strong oxidant the compound is, while the first ionization energy (E_i) measures how good reductant it is. Both processes refer to intermolecular electron transfer. In many biological processes the electron transfer is reversible so we can combine the two measures to obtain: $\Delta E = E_i - E_{ea}$. To determine this gap we used the experimental first ionization energy from UPS and electron affinities (E_{ea}) and other information about anionic states from mass spectrometry or electron-transmission spectroscopy[25−27] (Table 2). Small ΔE values indicate that the compound can readily reverse the direction of electron transfer. ΔE values are also representative of the HOMO−LUMO orbital gap which is relevant for intramolecular electron transfer. According to the results in Table 2, **8** is the strongest reductant and **2** and **3** are the strongest oxidants among substituted benzoquinones. In the compounds **4**, **5**, **7**, and **8**, the direction of electron transfer is most easily reversed.

The electron affinity of some benzoquinone derivatives has not been determined experimentally. We have therefore calculated the electron affinities of **1**−**8** by subtracting the total energy of the neutral molecule and its radical anion (charge = −1, spin state doublet). The total energies for both species were obtained using G3MP2/B3LYP method.[28] The calculated E_{ea} results (Table 2) exhibit excellent agreement with the experimental electron affinities determined by mass-spectrometry, but not with the values obtained from CT spectra.[25]

Summary

Our analysis of the photoelectron spectra of substituted benzoquinones and quinine-chloroimines demonstrates that the substitution of benzoquinone core has a significant effect on the electron-transfer capability. We have also demonstrated the important influence of conformers on the molecular and electronic structure of ubiquinone in the gas phase and not only in the solution as was previously thought. We have also deduced the magnitude of HOMO−LUMO energy separation from experimental data. This energy gap can be used as a measure of the propensity of particular benzoquinone to undergo reversible electron-transfer processes.

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Supporting Information Available: DFT energies, calculated and experimental geometries for benzoquinones, HeI/HeII photoelectron spectra and their analysis, and tabulated ionization energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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