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Quantum Chemical Characterization of the Vertical Electron Affinities of Didehydroquinolinium and Didehydroisoquinolinium Cations

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Vertical electron affinities (EA) are predicted for the lowest energy singlet states of the 21 didehydroquinolinium cation isomers and the 21 didehydroisoquinolinium cation isomers, as well as the doublet states of the seven dehydroquinolinium cation isomers, the seven dehydroisoquinolinium cation isomers, the seven *N*-methyldehydroquinolinium cations, and the seven *N*-methyldehydroisoquinolinium cations, by using density functional theory. For the monoradicals, the calculated EA of the radical site depends only on the distance from the (formally charged) nitrogen atom, and is reduced by 0.14−0.24 eV when the NH^+ group is replaced with an NCH_3^+ group. Nearly all of the calculated EAs for the ortho biradicals are lower (by 0.04−0.72 eV) than those for either of the corresponding monoradicals. For the meta biradicals, the calculated EAs lie either between the EAs of the corresponding monoradicals or higher (by 0.07−0.58 eV), and they are extremely sensitive to the separation (distance) between the two dehydrocarbon atoms. For the biradicals that do not have either an ortho or meta relationship the calculated EAs are all higher (by 0.02−1.93 eV) than those for either of the corresponding monoradicals. The EAs are examined to gain insight into the nature of inductive/field and resonance effects that influence the electrophilicity of the radical site(s), which is a major factor controlling the reactivity of these types of (bi)radicals.

Introduction

Organic molecules having one (monoradicals), two (biradicals), or more (polyradicals) unpaired spins are thought to play an important role in a variety of fields, including organic synthesis, development of new organic materials, and the biological activity of organic compounds.[1,2] Therefore, these species have attracted significant interest over the years. Aromatic carbon-centered σ,σ-biradicals (didehydroarenes) have received especially intense attention since the discovery that 1,4-didehydroarenes are the biologically active intermediates of the enediyne class of antitumor antibiotics.[3] This type of biradical can cleave double-stranded DNA via abstraction of hydrogen atoms from each DNA strand. Reactivity studies on these biradicals are hindered by their high reactivities and short lifetimes in solution.[1,4] However, information on the factors that might control their reactivity is highly desirable for the development of better DNA-cleaving drugs.

To improve the understanding of the properties of didehydroarenes, computations have been employed to explore various factors that might control their reactivity (e.g., singlet−triplet (S−T) gap, radical site separation, substituents, heteroatoms, charge).[4,5] The reactivity-controlling role of the S−T gap for biradicals that have a singlet ground state (which is the case for most didehydroarenes) appears to be generally accepted by the scientific community.[4,5a,6] However, our preliminary experimental studies on didehydro(iso)quinolinium cations have led to the surprising conclusion that electronic effects (due to the S−T gap) can be completely offset by polar effects in radical reactions of didehydroarenes.[7] In fact, due to greater polarity, some singlet biradicals have been shown to be more reactive than related monoradicals.[7] Prior to this research, nothing was known about polar effects on the reactions of organic biradicals, although these effects have been known[8] for a long time to be very important in controlling the reactivity of (polar) monoradicals. While Donahue and Anderson's ionic avoided curve crossing model[9] provides a simple way to rationalize the influence of the polarity of a radical on its reactivity (expressed as the electron affinity, EA; the energy released when an electron is added to the radical), further studies are still needed to understand the influence of polarity and other factors on the chemical properties of didehydroarenes.

As a first step toward a thorough investigation of the properties of didehydro(iso)quinolinium cations, we recently carried out a computational study on the S−T gaps of all 42 isomers of these molecules.[10] We report here the results obtained in the second step of this series of investigations—a computational examination of the vertical EAs for the 42 isomers of the didehydro(iso)quinolinium cations and related monoradicals.

Computational Methods

Molecular geometries for the *N*-methylquinolinium cation, the *N*-methylisoquinolinium cation, and the 14 isomeric *N*-methyldehydro(iso)quinolinium cations (MeD(I)Qs) were optimized at the multiconfigurational self-consistent field (MC-SCF) and density functional (DFT) levels of theory using the

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correlation-consistent polarized valence-double-ζ (cc-pVDZ[11]) basis set.[12] For all molecules, calculations were carried out using C_s point group symmetry. The MCSCF calculations were of the complete active space (CASSCF) variety[13] and included (in the active space) the full π-space for each molecule and, for each of the monoradicals, the nonbonding σ orbital. The DFT calculations were of two types. Both used the gradient-corrected exchange functional of Becke,[14] which was combined either with the gradient-corrected correlation functional of Lee, Yang, and Parr[15] (BLYP) or that of Perdew et al.[16] (BPW91). All DFT geometries were verified to be local minima by computation of analytic vibrational frequencies, and these (unscaled) frequencies were used to compute zero-point vibrational energies (ZPVE) and 298 K thermal contributions ($H_{298} - E_0$) for all species. DFT calculations for doublet states of monoradicals employed an unrestricted formalism; total spin expectation values for Slater determinants formed from the optimized Kohn−Sham orbitals did not exceed 0.76.

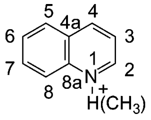
Single-point calculations were also carried out for the ground states of the 14 isomeric dehydro(iso)quinolinium cations (D(I)-Qs), the 14 isomeric *N*-methyldehydro(iso)quinolinium cations (MeD(I)Qs), and the singlet states of the 42 isomeric didehydro(iso)quinolinium cations (DD(I)Qs),[17] using the augmented, correlation-consistent polarized valence-double-ζ (aug-cc-pVDZ[18]) basis set. In almost all cases, these calculations were carried out for the UBLYP/cc-pVDZ optimized geometries. However, for a few of the meta biradicals,[19] it was necessary to use the MCSCF/cc-pVDZ geometries because the UBLYP/cc-pVDZ structures were bicyclic. In general, then, these electronic energies are of either the UBLYP/aug-cc-pVDZ//UBLYP/cc-pVDZ or UBLYP/aug-cc-pVDZ//MCSCF/cc-pVDZ variety.

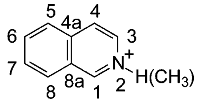
To compute vertical EAs for the monoradicals and biradicals, single-point calculations ((U)BLYP/aug-cc-pVDZ), using the optimized geometry for each monoradical or biradical, were also carried out for the states that are produced when a single electron is added to the nonbonding σ orbital (or one of the two such orbitals) of each molecule.[20] Thus, for the monoradicals (doublet ground states) these calculations were carried out for (zwitterionic) *singlet* states, whereas (zwitterionic) *doublet* states were computed for each of the biradicals (singlet initial states).[21] Finally, RBLYP/aug-cc-pVDZ single-point calculations were also carried out for the singlet states of the D(I)Qs (only) using the optimized (RBLYP/cc-pVDZ) geometries in order to compute adiabatic EAs for these molecules.

All MCSCF and DFT calculations were carried out with the MOLCAS[22] and Gaussian 98[23] electronic structure program suites, respectively.

Results

Geometries. Geometric information for the *N*-methyl(iso)-quinolinium cations, the ground states of the *N*-methyldehydro(iso)quinolinium cations, and the (zwitterionic) singlet states of the dehydro(iso)quinolinium cations, obtained using the (U)-BPW91, (U)BLYP, and MCSCF methods, is provided in the Supporting Information. For all quinolinium and isoquinolinium cations, the atom numbering scheme is indicated as follows:





In general, the (U)BLYP geometries for *N*-methylquinolinium cation, *N*-methylisoquinolinium cation, and the doublet states of the MeDQs and MeDIQs, are characterized by slightly longer bond lengths than the (U)BPW91 geometries, although the bond angles obtained using the two methods are about the same. The MCSCF geometries show shorter C−H bond lengths and slightly smaller bond angles about dehydrocarbon atoms than either of the DFT methods, but all other bond angles are about the same as those obtained using either DFT method. The MCSCF geometries also show greater localization of the aromatic π bonds. These geometric differences are similar to those noted[17] previously for didehydro(iso)quinolinium cations.

TABLE 1: Adiabatic and Vertical Electron Affinities (eV) for *m*-Dehydroquinolinium Cations and *N*-Methyl-*m*-dehydroquinolinium Cations[a]

	2	3	4	5	6	7	8
			m-Dehydroquinolinium Cations				
adiabatic	6.78	6.22[b]	6.05	5.63[b]	5.31	5.44	6.04
vertical	6.31	5.77	5.59	5.19	4.90	5.02	5.60
	(6.35)	(5.79)	(5.63)	(5.19)	(4.91)	(5.03)	(5.63)
			N-Methyl-*m*-dehydroquinolinium Cations				
vertical	6.07	5.60	5.45	5.03	4.76	4.87	5.37

[a] Calculated at the (U)BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ level of theory. Values in parentheses calculated at the (U)BLYP/aug-cc-pVDZ//MCSCF(11,11)/cc-pVDZ level of theory. [b] At the (U)BLYP/cc-pVDZ level, the C_s structure for the (zwitterionic) singlet state has one imaginary frequency; a (lower energy) C_1 stationary point was used instead.

The high quality of (U)BPW91/cc-pVDZ geometries, in general, has been noted before[5c,d,g,24] and derives in part from canceling errors associated with the approximate functional and the relatively modest basis set size.[25] This favorable cancellation of errors makes (U)BPW91/cc-pVDZ a very economical choice for computing aromatic monoradical structures. However, the (U)BLYP/cc-pVDZ geometries are of nearly the same quality,[5v,26] and we will focus any discussion of geometrical data primarily on results obtained at the (U)BLYP level because this method has been shown to provide values for EAs that are in good agreement with experimentally determined values (vide infra).

Geometries for the (zwitterionic) singlet states of the D(I)Qs were optimized at the RBLYP level only. Interestingly, minimum energy structures for six of the 14 D(I)Q singlet states (i.e., 3-DQ, 5-DQ, 5-DIQ, 6-DIQ, 7-DIQ, and 8-DIQ) were found to be nonplanar. A careful analysis of the geometries of these molecules provides no insight into why some of the singlet states are nonplanar and others are planar. However, an analysis of the partial atomic charges for these molecules suggests that the deviation from planarity permits mixing of the σ and π orbitals and thus allows the contribution of a resonance structure where the dehydrocarbon atom is a carbene, and the charge on nitrogen is annihilated. Even then, it is not clear why this is the case for only 6 of the 14 D(I)Qs, but the difference in energy between the nonplanar and planar structures is quite small (<2.5 kcal/mol) in each case.

Thermochemical Data. Electronic energies and selected thermochemical quantities were computed for the seven isomeric MeDQs, the seven isomeric MeDIQs, the *N*-methylquinolinium cation, and the *N*-methylisoquinolinium cation, using the (U)-BLYP and (U)BPW91 density functional models in conjunction with the cc-pVDZ basis set. Zero-point vibrational energies (ZPVEs) and 298 K thermal contributions to the enthalpy were computed for each molecule from the unscaled vibrational frequencies determined at either the (U)BPW91 or the (U)BLYP level. ZPVEs and 298 K thermal contributions are provided as Supporting Information.

Tables 1 and 2 list the vertical EAs, given by [E_0(monoradical; doublet state)] − [E_0(monoradical + electron; singlet state)],

TABLE 2: Adiabatic and Vertical Electron Affinities (eV) for *m*-Dehydroisoquinolinium Cations and *N*-Methyl-*m*-dehydroisoquinolinium Cations[a]

	1	3	4	5	6	7	8
	m-Dehydroisoquinolinium Cations						
adiabatic	6.84	6.62	6.13	5.52[b]	5.37[b]	5.47[b]	5.65[b]
vertical	6.35	6.15	5.72	5.04	4.84	4.85	5.18
	(6.38)	(6.19)	(5.77)	(5.05)	(4.85)	(4.86)	(5.20)
	N-Methyl-*m*-dehydroisoquinolinium Cations						
vertical	6.14	5.96	5.55	4.89	4.70	4.70	5.04

[a] Calculated at the (U)BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ level of theory. Values in parentheses calculated at the (U)BLYP/aug-cc-pVDZ//MCSCF(11,11)/cc-pVDZ level of theory. [b] At the (U)BLYP/cc-pVDZ level, the C_s structure for the (zwitterionic) singlet state has one imaginary frequency; a (lower energy) C_1 stationary point was used instead.

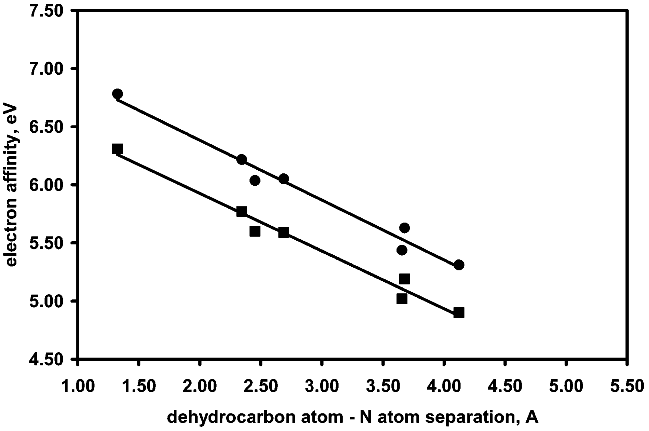


Figure 1. (U)BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ adiabatic (- -●- -) and vertical (- -■- -) electron affinities (eV) vs dehydrocarbon atom − N atom separation (Å) for *m*-dehydroquinolinium cations (2-DQ, 3-DQ, 8-DQ, 4-DQ, 7-DQ, 5-DQ, and 6-DQ, from left to right, respectively).

obtained at the (U)BLYP/aug-cc-pVDZ level of theory, for the 14 isomeric D(I)Qs[17] and the 14 isomeric MeD(I)Qs. Note that because these are *vertical* EAs, zero-point vibrational energies (ZPVEs) and 298 K thermal contributions to the enthalpy are necessarily not included. Also included in Tables 1 and 2 are the adiabatic EAs for the 14 isomeric D(I)Qs, given by [E_0(monoradical; doublet state) + ($H_{298} - E_0$)] − [E_0(monoradical + electron; singlet state) + ($H_{298} - E_0$)].

Plots of the (U)BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ adiabatic and vertical EAs vs the dehydrocarbon atom−N atom separations for the DQs and the DIQs are shown in Figures 1 and 2, respectively. A plot of the (U)BLYP/aug-cc-pVDZ//(U)-BLYP/cc-pVDZ vertical EAs vs the LUMO energies for the D(I)Qs and MeD(I)Qs is shown in Figure 3.

Finally, Tables 3 and 4 list the vertical EAs, given by [E_0(biradical; singlet state)] − [E_0(biradical + electron; doublet state)], obtained at the (U)BLYP/aug-cc-pVDZ level of theory, for the 21 isomeric DDQs and the 21 isomeric DDIQs.[17] For comparison, calculated vertical EAs for the three dehydropyridinium cations (DPs), and the six didehydropyridinium cations (DDPs) are provided in Table 5.

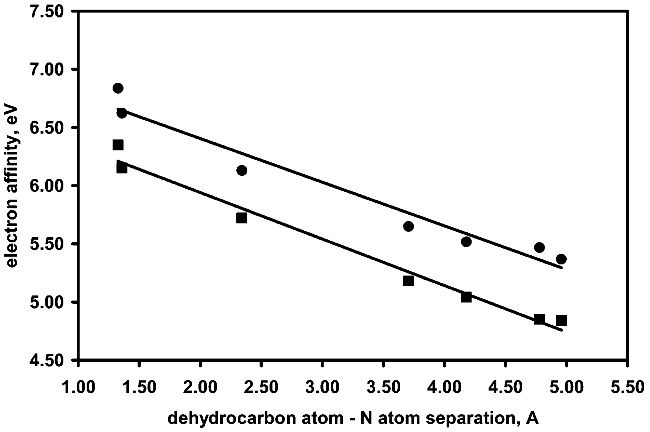


Figure 2. (U)BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ adiabatic (- -●- -) and vertical (- -■- -) electron affinities (eV) vs dehydrocarbon atom − N atom separation (Å) for *m*-dehydroisoquinolinium cations (1-DIQ, 3-DIQ, 4-DIQ, 8-DIQ, 5-DIQ, 7-DIQ, and 6-DIQ, from left to right, respectively).

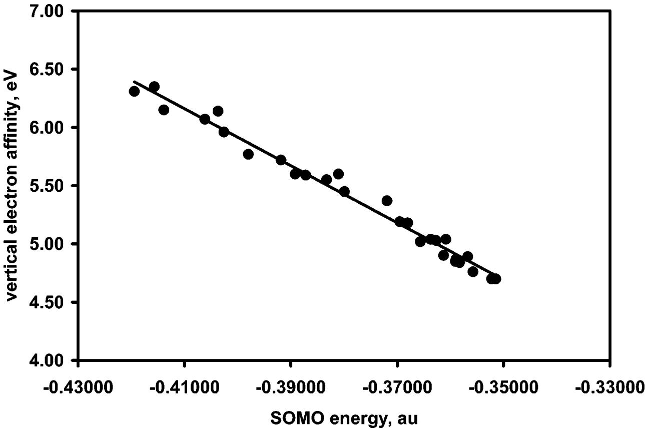


Figure 3. (U)BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ vertical electron affinities (eV) vs singly occupied molecular orbital (SOMO) energies (au) for D(I)Qs and MeD(I)Qs.

Discussion

Our goal here is to use the computed EAs for the various monoradicals and biradicals in order to gain insight into the nature of inductive/field effects that influence the electrophilicity of the radical site(s). The (relative) electrophilicity of the radical site(s) in a monoradical or biradical is likely to play an important role in determining its *reactivity*. That is, monoradicals and biradicals that have high EAs (e.g., high electrophilicities) might be expected to be more reactive than those that have low EAs.

Quality of Predicted EAs. The (U)BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ level of theory was used for all of the EA calculations because this method has been shown to provide quite good agreement with experimentally determined (adiabatic) EAs for a series of small molecules (for the molecules in the test set, the average absolute error is 0.15 eV).[27] To evaluate the accuracy of this method for estimating EAs of aromatic monoradicals and biradicals similar to those studied here, adiabatic EAs for *o*-benzyne, *m*-benzyne, *p*-benzyne, phenyl radical, and 1-naphthyl radical were also computed at the (U)-BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ level of theory. The adiabatic EAs for *o*-benzyne, *m*-benzyne, *p*-benzyne, phenyl radical, and 1-naphthyl radical are calculated to be 0.74, 1.06, 1.49, 1.03, and 1.32 eV, respectively. These values differ from the known values for *o*-benzyne, *m*-benzyne, *p*-benzyne, phenyl radical, and 1-naphthyl radical (0.564,[28] 0.852,[27,29] 1.265,[27] 1.096,[30] and 1.403 eV,[31] respectively) by 0.18, 0.21, 0.23, 0.07, and 0.08 eV, respectively. The agreement between the calculated and experimental EA values is quite good for the monoradicals, but is only fair for the benzynes. The larger deviations for the benzynes are likely to be a result of the fact that the EAs for these molecules correspond to addition of an electron to (neutral) molecules that have significant closed-shell character (to produce open-shell anions).[26,32] Nevertheless, the computational method

TABLE 3: Vertical Electron Affinities (eV) for *m,n*-Didehydroquinolinium Cations[a]

2,3	2,4	2,5	2,6	2,7	2,8	3,4	3,5	3,6	3,7	3,8	4,5	4,6	4,7	4,8	5,6	5,7	5,8	6,7	6,8	7,8
5.92	*6.11*	6.47	6.46	6.95	6.65	5.29	6.10	6.19	6.10	6.23	5.88	5.91	5.88	6.43	4.71	*5.26*	6.00	4.61	*5.48*	4.88

[a] Calculated at the UBLYP/aug-cc-pVDZ//UBLYP/cc-pVDZ level of theory; values in italics calculated at the UBLYP/aug-cc-pVDZ//MCSCF(12,12)/cc-pVDZ level of theory.

TABLE 4: Vertical Electron Affinities (eV) for *m,n*-Didehydroisoquinolinium Cations[a]

1,3	1,4	1,5	1,6	1,7	1,8	3,4	3,5	3,6	3,7	3,8	4,5	4,6	4,7	4,8	5,6	5,7	5,8	6,7	6,8	7,8
6.73	6.72	6.37	6.47	6.52	6.46	5.68	6.39	6.45	6.32	6.34	5.93	5.99	5.90	6.28	4.58	*5.21*	5.73	4.49	*5.16*	4.64

[a] Calculated at the UBLYP/aug-cc-pVDZ//UBLYP/cc-pVDZ level of theory; values in italics calculated at the UBLYP/aug-cc-pVDZ//MCSCF(12,12)/cc-pVDZ level of theory.

TABLE 5: Vertical Electron Affinities (eV) for *m*-Dehydropyridinium Cations and *m,n*-Didehydropyridinium Cations[a]

m-dehydropyridinium cations	2	3	4			
	6.59	6.08	5.84			
m,n-didehydropyridinium cations	2,3	2,4	2,5	2,6	3,4	3,5
	6.23	*6.46*	7.11	7.15	5.64	*6.30*

[a] Calculated at the (U)BLYP/aug-cc-pVDZ//(U)BLYP/cc-pVDZ level of theory. Values in italics calculated at the (U)BLYP/aug-cc-pVDZ//MCSCF(8,8)/cc-pVDZ level of theory.

does reproduce the trend in EAs quite well. Thus, because we are primarily interested in relative values, rather than absolute values, of EAs for the monoradicals and biradicals, we believe this computational method is adequate for estimating the EAs of these species.

Trends in EAs for Dehydro(iso)quinolinium Cations. Interestingly, both the adiabatic and vertical EAs for the D(I)Qs show a linear dependence on the distance between the dehydrocarbon atom and the (formally charged) N atom (Figures 1 and 2). For the DQs, the regression equation for the adiabatic EAs ($R^2 = 0.98$, 7 data points) is

$$(\text{EA, eV}) = -0.52 \times (\text{C}_{\text{dehydro}}\text{−N distance, Å}) + 7.42 \quad (1)$$

whereas for the vertical EAs ($R^2 = 0.98$, 7 data points) the correlating equation is

$$(\text{EA, eV}) = -0.50 \times (\text{C}_{\text{dehydro}}\text{−N distance, Å}) + 6.92 \quad (2)$$

Similarly, for the DIQs, the regression equation for the adiabatic EAs ($R^2 = 0.96$, 7 data points) is

$$(\text{EA, eV}) = -0.38 \times (\text{C}_{\text{dehydro}}\text{−N distance, Å}) + 7.16 \quad (3)$$

whereas for the vertical EAs ($R^2 = 0.98$, 7 data points) the correlating equation is

$$(\text{EA, eV}) = -0.40 \times (\text{C}_{\text{dehydro}}\text{−N distance, Å}) + 6.74 \quad (4)$$

For the DQs (eq 1 and 2) and the DIQs (eq 3 and 4), the slopes of the lines show that both the adiabatic and vertical EAs decrease by about 0.5 and 0.4 eV, respectively, per 1 Å increase in the dehydrocarbon atom−N atom separation. This is to be expected since the EA, and therefore the electrophilicity, of the radical site should decrease as the separation between the dehydrocarbon atom and the *electron-withdrawing* NH^+ group increases. Finally, note that the *y*-intercepts of the regression equations in some sense correspond to the EA of the (formally charged) N atom, i.e., a dehydrocarbon atom−N atom separation of zero Å.

Similar trends are observed for the vertical EAs of the MeD(I)Qs (Tables 1 and 2). For the MeDQs, the regression equation for the vertical EAs ($R^2 = 0.97$, 7 data points) is

$$(\text{EA, eV}) = -0.46 \times (\text{C}_{\text{dehydro}}\text{−N distance, Å}) + 6.64 \quad (5)$$

whereas for the MeDIQs ($R^2 = 0.98$, 7 data points) the correlating equation is

$$(\text{EA, eV}) = -0.38 \times (\text{C}_{\text{dehydro}}\text{−N distance, Å}) + 6.52 \quad (6)$$

Note that the slopes of the lines for the MeDQs (eq 5) and the MeDIQs (eq 6) are smaller than those for the DQs (eq 2) and the DIQs (eq 4) by 0.04 and 0.02 eV, respectively. Clearly, methylation of the N atom (i.e., to produce an NCH_3^+ group) reduces somewhat the dependence of the EA on the dehydrocarbon atom − N atom separation. This is likely due to the (weak) electron donating ability of the methyl group, which causes a slight reduction in the electron-withdrawing ability compared to the NH^+ group. Thus, methylation of the N atom for the DQs and DIQs reduces (compared to the protonated molecules) the vertical EAs by 0.14−0.24 eV (Table 1) and 0.14−0.21 eV (Table 2), respectively.

An examination of the energies of the singly occupied molecular orbitals (SOMOs) of the ground states for the D(I)Qs and MeD(I)Qs (i.e., the nonbonding σ orbital in each case) indicates that there is also a direct relationship between the SOMO energies and the calculated (vertical) EAs (Figure 3). This relationship is perhaps not surprising considering the fact that the calculated EAs are based on the addition of an electron to the SOMOs of these molecules.[20] The regression equation for the vertical EAs for the D(I)Qs and MeD(I)Qs ($R^2 = 0.98$, 28 data points) is

$$(\text{EA, eV}) = -24.49 \times (\text{SOMO energy, au}) - 3.88 \quad (7)$$

Thus, for the monoradicals, the EA, and therefore the electrophilicity, of the radical site depends only on the distance between the radical site and the formally charged N atom, which is also reflected in the SOMO energies of the ground states of these species. It seems likely that a combination of inductive and field effects[33] (caused by the (formally charged) N atom) are responsible for the distance dependence of the EAs (i.e., both effects are distance-dependent). However, we will not attempt to separate the two effects for the molecules studied here.

Trends in EAs for ortho Didehydro(iso)quinolinium Cations. With the exception of 2,3-DDQ, the calculated EAs for the ortho isomers are all lower (by 0.04−0.72 eV) than those for either of the corresponding monoradicals generated by "capping" one of the two biradical sites with a hydrogen atom. This is perhaps not surprising since the (zwitterionic) doublet states for these isomers have an electron in a strongly antibonding (π^*-type) orbital. Indeed, there is also a direct (linear) relationship between the calculated vertical EA for each ortho isomer and the energy of the lowest unoccupied molecular orbital (LUMO) for the ground (singlet) state; the regression equation for the vertical EAs ($R^2 = 0.99$, 9 data points) is

$$(\text{EA, eV}) = -25.36 \times (\text{LUMO energy, au}) - 2.30 \quad (8)$$

Moreover, for the ortho isomers, the magnitude of the LUMO energy (and, consequently, the magnitude of the EA for the biradical) does not appear to depend on the singlet−triplet (S−T) splitting for the biradical. For example, the calculated S−T splittings for 3,4-DDQ and 5,6-DDQ are identical (−34.8 kcal/mol[10]), but the vertical EAs for these two biradicals differ by 0.58 eV (5.29 and 4.71 eV, respectively; Table 3). The higher EA for 3,4-DDQ is a result of the fact that the EAs for the corresponding monoradicals, 3-DQ and 4-DQ, (5.77 and 5.59 eV, respectively; Table 1) are much greater than those for 5-DQ and 6-DQ (5.19 and 4.90 eV, respectively; Table 1). Again, it appears that inductive/electric field effects also have a direct influence on the LUMO energies (and EAs) of the ortho isomers of these molecules. Finally, the calculated EA for 2,3-DDQ (5.92 eV) is greater than that for 3-DQ (5.77 eV), but less than that for 2-DQ (6.31 eV). For this molecule, it appears that the close proximity of the ortho benzyne group to the (formally charged) N atom provides significant charge stabilization in the (zwitterionic) doublet state. Similar effects have been noted before for the 2,3-didehydropyridinium cation[5d] and the 2,3-didehydroquinolinium cation[10] and are thought to result from inductive effects in the aromatic ring system. Interestingly, one might also expect this to be the case for 3,4-DDIQ (i.e., this molecule also has the ortho benzyne group adjacent to the N atom). However, in naphthalene-like systems, there is a significant degree of bond alternation,[5h,10] and as a result, the 2,3-bond in 2,3-DDQ is calculated to be longer (1.270 Å) than the 3,4-bond in 3,4-DDIQ (1.257 Å). Thus, the π^*-type LUMO for 3,4-DDIQ is significantly higher in energy than that for 2,3-DDQ, and this leads to an EA for this molecule (5.68 eV) that is lower than either of the corresponding monoradicals (6.15 and 5.72 eV for 3-DIQ and 4-DIQ, respectively; Table 2).

Trends in EAs for meta Didehydro(iso)quinolinium Cations. For all but two of the meta isomers (e.g., 6,8-DDQ and 1,3-DDIQ), the minimum energy structures obtained for the (ground) singlet states using either the UBLYP/cc-pVDZ or UBPW91/cc-pVDZ levels of theory are tricyclic.[17] For these isomers, then, we will examine EAs calculated using the minimum energy structures obtained at the MCSCF/cc-pVDZ level of theory[34] because this method does not give tricyclic structures for any of these isomers, and the (calculated) separation between the dehydrocarbon atoms is approximately the same for each molecule (ca. 2.16−2.24 Å). Furthermore, because the computed bond angles about dehydrocarbon atoms are somewhat smaller at the MCSCF/cc-pVDZ level than at either DFT level (vide supra), we compare the calculated EAs for the biradicals with those for the corresponding monoradicals also obtained[17] using MCSCF/cc-pVDZ optimized geometries (Tables 1 and 2).

Like the ortho isomers, the (zwitterionic) doublet states for the meta isomers have an electron in an antibonding (σ^*-type) orbital, although the antibonding interaction is expected to be significantly weaker for these isomers. Thus, for 2,4-DDQ, 6,8-DDQ, and 6,8-DDIQ, the calculated (vertical) EAs lie between the EAs of the corresponding monoradicals, whereas the EAs for 5,7-DDQ, 1,3-DDIQ, and 5,7-DDIQ are all higher (by 0.07−0.58 eV) than those for either of the corresponding monoradicals. For 5,7-DDQ, 1,3-DDIQ, and 5,7-DDIQ, the distances between the (formally charged) N atom and each of the two radical sites is approximately the same. However, this is not the case for 2,4-DDQ, 6,8-DDQ, and 6,8-DDIQ. It appears that when the two radical sites are approximately equidistant from the N atom, then it is more favorable (i.e., higher EA) to add an electron to the biradical since the antibonding (σ^*-type) orbital has greater amplitude between the two radical sites (and, thus, closer to the N atom) than is found for either of the corresponding monoradicals. In contrast, when the biradical has one radical site that is significantly closer to the N atom than the other, the electron density associated with the added electron is greater at the radical site closer to the N atom (instead of between the two radical sites), which leads to EAs for these biradicals that lie between those of the corresponding monoradicals.

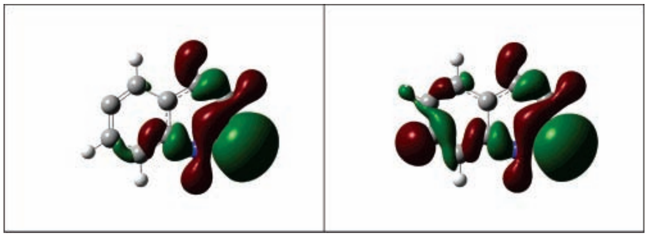


Figure 4. Highest occupied molecular orbitals (HOMOs) for the (zwitterionic) doublet states of 2,6-DDQ (left) and 2,7-DDQ (right).

It is also noteworthy that the calculated EAs for the meta isomers, in particular, are extremely sensitive to the separation between the two dehydrocarbon atoms. For example, at the UBLYP/cc-pVDZ level of theory, the calculated dehydrocarbon atom separation for the (singlet) ground state of 6,8-DDQ is 1.98 Å, whereas at the MCSCF/cc-pVDZ level the calculated dehydrocarbon atom separation is 2.20 Å. This relatively small difference (0.22 Å) in dehydrocarbon atom separations corresponds to a difference of 1.15 eV in the calculated EAs using the two different geometries![35]

Finally, the calculated vertical EAs for the meta isomers are also linearly dependent on the LUMO energies for the ground (singlet) states; the regression equation for the vertical EAs ($R^2 = 0.99$, 6 data points) is

$$(\text{EA, eV}) = -34.33 \times (\text{LUMO energy, au}) - 4.81 \quad (9)$$

Like the ortho isomers, the magnitude of the LUMO energy (and, consequently, the magnitude of the EA for the biradical) does not appear to depend on the S−T splitting for the biradical.

Trends in EAs for Other Didehydro(iso)quinolinium Cations. For all of the other biradicals (i.e., those biradicals that do not have either an ortho or meta relationship), the calculated vertical EAs are all higher (by 0.02−1.93 eV) than either of the corresponding monoradicals. The higher EAs for these biradicals appear to derive from two effects. First, each radical site in the biradical acts like an electron-withdrawing “substituent” for the second radical site. This increases the electrophilicity (and EA) of each radical site, and, as a result, the EA for the biradical is greater than either of the (isolated) monoradicals. Second, unlike the ortho and meta isomers, the EAs for these isomers do also depend on the S−T splitting. For example, the calculated EA for 2,7-DDQ (6.95 eV; Table 3) is 0.49 eV greater than that for 2,6-DDQ (6.46 eV), even though the EAs for the corresponding monoradicals for each molecule are about the same (Table 1). The calculated S−T splittings (CASPT2/cc-pVDZ//UBLYP/cc-pVDZ) for 2,7-DDQ and 2,6-DDQ are −2.7 and −0.4 kcal/mol,[10] respectively. Thus, the (weak) coupling between the radical sites in 2,7-DDQ provides a greater degree of charge delocalization in the (zwitterionic) doublet state (compared to 2,6-DDQ), which leads to a higher EA for this molecule (Figure 4).

For all of the biradicals studied here, there are, in principle, two (zwitterionic) doublet states to consider (i.e., addition of an electron to either of the two nominally nonbonding molecular orbitals). However, in all cases, we have calculated the EA for the lowest energy doublet state (only). For the ortho and meta isomers, the two doublet states should have significantly different energies as a result of the strong coupling between the two radical sites in these molecules. For the more weakly interacting systems, though, these states should lie much closer in energy. An examination of the highest occupied molecular orbitals (HOMOs) for the lowest energy doublet states for these molecules shows that, in all cases, the electron density is greater at the radical site closest to the formally charged N atom. This is undoubtedly a result of the greater (Coulombic) charge stabilization that derives from the close proximity of the opposite formal charges. For example, for the lowest energy doublet state of 2,6-DDQ (a biradical in which there is little to no interaction between the two radical sites), the electron density in the HOMO is virtually completely localized at the 2-position, rather than the 6-position (Figure 4).

For the weakly interacting biradicals (i.e., those having neither an ortho nor a meta relationship), there is no obvious correlation between the EAs and the LUMO energies of the singlet initial states. However, because these biradicals require broken-symmetry solutions to the Kohn−Sham self-consistent field equations, the definition of the singlet LUMO is problematic and it is not clear that any particular conclusion should be drawn in this instance.

Comparison to (Di)dehydropyridinium Cations ((D)DPs). While only a few comparisons between the (D)DPs and the (D)D(I)Qs are possible, such comparisons are useful to evaluate the effect(s) on the EAs due to the presence of the additional, fused aromatic ring. For the monoradicals, the calculated vertical EAs for the DPs (Table 5) are all higher than those for the D(I)Q analogues (2-DP, 2-DQ and 3-DIQ; 3-DP, 3-DQ and 4-DIQ; 4-DP, 4-DQ) by 0.25−0.44 eV. Clearly, the additional, fused aromatic ring in the D(I)Qs provides greater charge delocalization (of the (formally charged) N atom) than exists in the pyridinium ring system, and this results in lower EAs for the D(I)Qs (this is also true in every case for the DD(I)Qs). However, like the D(I)Qs, the EAs for the DPs are also linearly dependent on the distance between the (formally charged) N atom and the radical site.

Interestingly, the trends in EAs noted above for the DD(I)Qs are also present for the six DDPs. For example, the calculated EA for 2,3-DDP (ortho isomer) lies between those for 2-DP and 3-DP (like 2,3-DDQ), while the calculated EA for 3,4-DDP (also an ortho isomer) is lower than that for either 3-DP or 4-DP (like 3,4-DDQ). For the meta DDPs, the calculated EA for 2,4-DDP lies between those for 2-DP and 4-DP, whereas the calculated EAs for 2,6-DDP and 3,5-DDP are both higher than either of the corresponding monoradicals. This trend in EAs for the meta DDPs is also entirely consistent with that noted above for the meta DD(I)Qs. As expected, the calculated EA for 2,5-DDP (a biradical that has neither an ortho nor a meta relationship) is higher than that for either 2-DDP or 5-DDP.

Finally, the extreme sensitivity of the EAs to the separation between the two dehydrocarbon atoms noted above for meta DD(I)Qs also manifests in the meta DDPs. For example, at the (U)BLYP/cc-pVDZ level of theory, the calculated dehydrocarbon atom separation for the (singlet) ground state of 2,4-DDP is 2.00 Å, whereas at the MCSCF/cc-pVDZ level the calculated dehydrocarbon atom separation is 2.17 Å. In this case, the difference of 0.17 Å in the dehydrocarbon atom separations for the two different geometries corresponds to a difference of 0.98 eV in the calculated EAs.

Conclusions

For the monoradicals studied here, the EA, and therefore the electrophilicity, of the radical site depends only on the distance between the radical site and the (formally charged) N atom, which is also reflected in the SOMO energies of the ground states of these species. In addition, methylation of the nitrogen atom (i.e., to produce an NCH_3^+ group) reduces somewhat the dependence of the EA on the dehydrocarbon atom − N atom separation. This is likely due to the (weak) electron donating ability of the methyl group, which causes a slight reduction in the electron-withdrawing ability compared to the NH^+ group. Thus, methylation of the N atom reduces (compared to the protonated molecules) the vertical EAs for the DQs and DIQs by 0.14−0.24 eV and 0.14−0.21 eV, respectively.

With only one exception, the calculated EAs for the ortho isomers are all lower (by 0.04−0.72 eV) than those for either of the corresponding monoradicals. The lower EAs for the ortho isomers is a result of adding an electron to a strongly antibonding (π^*-type) orbital. In addition, the calculated EAs for the ortho isomers linearly correlate with the LUMO energies for the ground (singlet) states (but not the S−T splittings). It appears that inductive/electric field effects are responsible for the trend in the LUMO energies (and EAs) of the ortho isomers of these molecules.

For the meta isomers, the calculated EAs lie either between the EAs of the corresponding monoradicals, or higher (by 0.07−0.58 eV) than either of the corresponding monoradicals. For these isomers, in particular, the calculated EA seems to be extremely sensitive to the separation (distance) between the two dehydrocarbon atoms. A relatively small change in this distance leads to a large change in the calculated EA. For example, changing the dehydrocarbon atom separation by only 0.22 Å causes the calculated EA to change by 1.15 eV! Like the ortho isomers, the calculated EAs for the meta isomers linearly correlate with the LUMO energies for the ground (singlet) states (but not the S−T splittings).

For those biradicals that do not have either an ortho or meta relationship, the calculated vertical EAs are all higher (by 0.02−1.93 eV) than either of the corresponding monoradicals. The higher EAs for these biradicals appear to derive from two effects. First, each radical site in the biradical acts like an electron-withdrawing “substituent” for the second radical site. This increases the electrophilicity (and EA) of each radical site, and as a result, the EA for the biradical is greater than either of the (isolated) monoradicals. Second, unlike the ortho and meta isomers, the EAs for these isomers do also depend on the S−T splitting; (weak) coupling between the radical sites provides a greater degree of charge delocalization in the (zwitterionic) doublet state, which leads to an increased EA. An examination of the highest occupied molecular orbitals (HOMOs) for the lowest energy doublet states for these molecules shows that, in all cases, the electron density is greater at the radical site closest to the (formally charged) N atom. This is undoubtedly a result of the greater (Coulombic) charge stabilization that derives from the close proximity of the opposite formal charges. Finally, unlike the monoradicals, and the biradicals having either an ortho or meta relationship, there is no obvious correlation between the EAs and the LUMO energies of the singlet initial states. This appears to be an artifact of the computational method employed here.

Finally, the additional, fused aromatic ring in the D(I)Qs and DD(I)Qs (compared to the DPs and DDPs) provides greater charge delocalization (of the (formally charged) N atom), which results in lower EAs for the D(I)Qs and DD(I)Qs. In addition, the same trends in EAs noted for the DD(I)Qs are also present for the DDPs.

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Supporting Information Available: Tables of Cartesian coordinates, zero-point vibrational energies, and 298 K thermal contributions for the ground states of the MeD(I)Qs, and the (zwitterionic) singlet states of the D(I)Qs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Note that, for these calculations, we are computing the electron affinity of the radical site *not* the electron affinity of the *molecule*.

(21) Because the monoradicals and biradicals studied here contain a formal positive charge on the nitrogen atom, the states that are produced when an electron is added to the nonbonding orbital of either a monoradical or a biradical are formally zwitterionic, i.e., they contain localized positive (π) and negative (σ) charges.

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