Unveiling electrostatic portraits of quinones in reduction and protonation states

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Abstract. Quinones are known to perform diverse functions in a variety of biological and chemical processes as well as molecular electronics owing to their redox and protonation properties. Electrostatics chiefly governs intermolecular interaction behaviour of quinone states in such processes. The electronic distribution of a prototypical quinone, *viz.*, *p*-benzoquinone, with its reduction and protonation states (BQS) is explored by molecular electrostatic potential (MESP) mapping using density functional theory. The reorganization of electronic distribution of BQS and their interaction with electrophiles are assessed for understanding the movement of ubiquinone in bacterial photosynthetic reaction centre, by calculating their binding energy with a model electrophile *viz.*, lithium cation (Li^+) at B3LYP/6-311+G(d,p) level of theory. The changes in the values of the MESP minima of BQS states alter their interacting behaviour towards Li^+ . A good correlation is found between the value of MESP minimum of BQS and the Li^+ binding strength at the respective site. To acquire more realistic picture of the proton transfer process to quinone with respect to its reduction state in the photosynthetic reaction center, interaction of BQS with model protonated motifs of serine, histidine as well as NH_4^+ is explored. Further, the electronic conjugation of the reduced states of 9,10-anthraquinone is probed through MESP for understanding the switching nature of their electronic conductivity.

Keywords. Quinones; redox; molecular electrostatic potential; molecular conjugation; cation binding.

1. Introduction

Quinones are a widely recognized class of organic compounds, ubiquitously found in the nature, with wide applications in a variety of disciplines such as electrochemistry, biology, medicinal chemistry, synthetic chemistry and nanotechnology. The quinone-hydroquinone redox couple serves as a prototypical example of the organic redox electrode used in pH measurements as it shows the change in potentiometric or polarographic potential with the change in pH.^{1,2} The reduction of quinone to hydroquinone is a single-step two-proton two-electron reaction in the acidic pH and only a two-electron one in the alkaline medium.¹ However, it is either two-electron one-proton or only two-electron reaction¹ in the neutral pH.

The applicability of quinones in various fields, mainly in biological energy transduction processes such as photosynthesis and respiration, is a consequence of their ability to undergo sequentially reversible proton and electron transfer reactions for the interconversion of quinones to the respective quinol forms.³ Ubiquinones are found in the mitochondrial respiratory chain complexes *viz.*, Complex I (NADH:ubiquinone oxidoreductase), Complex II (succinate:quinone oxidoreductase) and Complex III (ubiquinol:cytochrome c oxidoreductase), wherein electron transfer from NADH to O_2 is executed by quinone-to-quinol redox reactions.⁴ In symmetric photosynthetic type II reaction center, *viz.*, PSII, of plant and bacterial reaction centers (RCs), photoexcited electrons are transferred through various acceptors of the side A to quinone Q_A (ubiquinone or plastoquinone) and then to quinone Q_B , at the side B.⁵⁻⁷ Further, by accepting two electrons and two protons, Q_B transforms into quinol $\text{Q}_\text{B}\text{H}_2$ via various reduction

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and protonation states. Then Q_BH_2 passes into the membrane, guided by the weak intermolecular interactions such as hydrogen bonding (H-bonding), and releases electrons and protons to get re-oxidized. This transfer of protons generates a proton gradient around the cell membrane which is responsible for the ATP synthesis.⁷ Extensive experimental and theoretical research has been done for understanding the mechanism of the key steps in the photosynthetic process, viz., binding of Q_B in the protein pockets and its transformation to Q_BH_2 . Various X-ray crystallographic and site-directed mutagenesis studies suggest that structural and functional features of amino acid residues are involved in the binding⁸ and migration of Q_B .^{6,9} Stowell *et al.*,¹⁰ analysed the crystal structures of bacterial photosynthetic RC of *Rhodobacter sphaeroid* under light illumination and in the dark. They observed that in the dark-adapted structure, ubiquinone Q_B is situated at distal site (away from non-haem iron) with the particular framework of H-bonds formed between its carbonyl oxygens and surrounding amino acid viz., His-L190. However, in the light-adapted structure, with electron transfer, the Q_B have been found to have undergone a displacement of ~ 4.5 Å towards proximal site (closest to non-haem iron) with 180° propeller twist showing H-bonding interaction with His-L190 and Ser-L223 from where it receives the protons through various pathways.^{10,11} Such type of migration of Q_B was also observed by Lancaster and Michel¹² in the RC of another bacterial species *Rhodospseudomonas viridis*. They noticed hydrogen bonding interaction of Q_B with similar bonding interaction as observed by Stowell *et al.*,¹⁰ at proximal site. Further, it was suggested^{6,13} that the Q_B is observed in different redox states viz., neutral, semiquinone anion (Q_B^- and Q_BH^-) and as fully protonated dihydroquinone (QH_2) in crystal structures of RCs. According to the crystal structure reported by Stowell *et al.*,¹⁰ anionic $QB^{\bullet-}$ exists in the proximal site. On the other hand, the neutral quinone state was reported to be at the proximal site in the X-ray crystal structure given by Lancaster *et al.*¹² Breton *et al.*,¹⁴ performed FTIR vibrational spectroscopic study to gain insights of distinct Q_B interactions at the two different binding sites in Pro-L209 $\rightarrow$ Tyr mutant RC and concluded that the proximal binding site is dominant for neutral Q_B . With the mutagenesis and kinetic investigation of electron transfer in the RC of *Rhodobacter sphaeroid*, Takahashi *et al.*,¹⁵ suggested that electrostatics plays a crucial role in the interaction of quinone states with the surrounding amino acids. Special attention has also been drawn to the importance of binding affinities of the different states of ubiquinone for performing their functions in the RC. Manojkumar *et al.*,¹⁶ have studied the structural, electronic and spectral properties of H-

bonded complexes of BQ and its anionic forms, viz., $BQ^{\bullet-}$ and BQ^{2-} with one- and two water molecules for examining the effect of H-bonding on the complexes in different electronic states of BQ using varied levels of theoretical methods. They observed that the interaction energies of $BQ^{\bullet-}$ and BQ^{2-} -water monomer/dimer complexes are more favourable than the respective neutral BQ complexes by ~ 2.6 and ~ 6.0 kcal mol⁻¹ due to the increase in H-bond strength (by ~ 2 kcal mol⁻¹) in the reduced species. Nepal *et al.*,¹⁷ recently studied, using the DFT method, the H-bonding interactions of *o*-quinone and its radical semiquinone anion with several proton donor molecules viz., dimethylamine, methanol, ethanol, dimethylurea and a strong cationic species, viz., $CNH_2(NHCH_3)_2^+$. They visualized the MESP regions and qualitatively assessed the H-bonding ability of *o*-quinone substituted with the electron-donating NH_2 and electron-withdrawing Cl groups. The study revealed that the cationic proton donor species $CNH_2(NHCH_3)_2^+$ forms more stabilized multi H-bonded complexes with *o*-quinone and its radical semiquinone anion than with the other species. In particular, they observed a remarkable increase in binding energies for the complexes of cationic H-bonded donor $CNH_2(NHCH_3)_2^+$ with *o*-semiquinone radical anion than complexes with neutral *o*-quinone by a factor of 4.3.

Quinones also have potential applications in the emerging field of molecular electronics devices such as single molecular switches.¹⁸⁻²⁰ Molecular switch is a device that alters the conductance on or off by changing its molecular states in response to external stimuli such as electric field, temperature, light, *etc.*²¹ Markussen *et al.*,²² analysed theoretically the switching mechanism in anthraquinone (AQ)/hydroanthraquinone (AQH_2) redox couple. They calculated molecular electronic conductance of a molecule containing central 9,10-anthraquinone π -conjugated with ethyne as a main spacer unit and phenylsulfanyl at both the ends as a linker group to the electrode using *ab-initio* non-equilibrium Green-functions (DFT-GF) method. Smaller electronic conductance observed in AQ than in AQH_2 has been attributed to presence of destructive interference in the former one. In line with this, Seidel *et al.*,²³ synthesized and characterized the 9,10-anthraquinone spacer unit as used by Markussen *et al.*,²² but using thienyl linkers to investigate their application as redox-active switches. Cyclic voltammetry measurements performed by Seidel *et al.*,²³ showed the occurrence of two fully reversible reduction waves confirming that the compound can be switched electrochemically between AQ and AQH_2 states. They also calculated the electron transport characteristics of AQ and AQH_2 forms of spacer unit using DFT-GF

approach and observed ~ 4 times higher conductance for AQH₂ than AQ. Furthermore, Darwish *et al.*,¹⁸ developed AQ/AQH₂ redox couple-based norbornyl-ogous bridge tetrathiol single molecular switch and showed experimentally that the low conducting AQ moiety can be switched electrochemically and reversibly to high conducting AQH₂ one using scanning tunnelling microscopy (STM) break junction technique. A redox-mediated on/off fluorescence-based switching mechanism has recently been observed by Greene *et al.*,²⁴ with 2,3-dimethoxy-1,4-benzoquinone linked to boron-dipyrromethene fluorophore segment. For this molecule, the intramolecular photoinduced electron transfer (PeT) has been observed with quenching in its fluorescence activity when quinone is present in its oxidized form. However, the reduction of quinone to quinol form deactivates the intramolecular PeT and the molecule shows fluorescence emission. With these findings, Greene *et al.*,²⁴ anticipated that this redox mediated reversible quinone/quinol off/on couple can be applied to understand and monitor complex redox processes without disturbing the system and to develop probes which sensitively monitor electron transfer in biological cellular respiration systems such as mitochondria.

In summary, it seems that the mechanism of binding, migration of secondary electron acceptor Q_B (in its various redox states) and further reduction to quinol in the protein binding pockets is yet not completely clear.¹³ Furthermore, it seems that quinone in its reduced states conduct electronic charge differently, which makes quinone as a potential candidate for molecular electronic switch. Can one explain the mechanism in a simple way using the concept of electronic conjugation?

For the characteristic functioning of quinone (Q) in the above mentioned areas of research, Q should be present in its specific state. Quinone is capable of adopting different reduction and protonation states (*cf.* Figure 1).²⁵ Of these states, QH⁺, QH₂²⁺ and QH₂^{•+} are generated only under extreme conditions. However, the other intermediate states *viz.*, quinone radical anion (Q^{•-}), semiquinone radical (QH[•]), semiquinone anion (QH⁻) and hydroquinone (QH₂) states manifest their characteristic roles in quinone electrochemistry and biological processes.²⁵

Reduction or protonation reactions interconvert² one quinone state to other (*cf.* Figure 1). Such conversions alter the non-covalent (such as H-bonding and cation binding) intermolecular interaction behaviour, which controls the functions of quinones in the respective redox biological centres and molecular electronic switches.^{26–28} Much of the previous work has focused on the comparison of geometries, vibrational spectra and spin properties of the reduction and protonation

Figure 1. Possible reduction and protonation states of quinone (Q). See text and Reference 34 for details.

states of *p*-benzoquinone (BQS), a prototype of class of quinones.^{2,16,29–31} These BQS states (depicted in Figure 1) were employed by Nonella²⁵ and Zhao *et al.*,³² for providing basic data for the analysis of the vibrational spectra of biological quinones. Manojkumar *et al.*,¹⁶ studied the structures, energetics and spectra of hydrated BQ and the corresponding anions for examining the effect of H-bonding on these properties of the BQS.

Electrostatics is known to play a key role in the non-covalent interactions.^{11,33–43} In view of this, obtaining a complete picture of the electrostatic nature of all the possible reduction and protonation states of quinone and correlating its effect on their cation-binding behaviour seems worthwhile. Especially, the understanding of non-covalent interactions involving metal ion binding is expected to provide valuable insights for structural and functional properties of molecular systems.⁴⁴ Particularly, the site of metal cation binding confirms the electron localization in the corresponding region of a molecular system.⁴⁰

Molecular electrostatic potential (MESP) is a scalar field, used extensively^{38,45–47} in the literature for exploring reactivity patterns of molecules and their non-covalent interactions. Particularly, it is a well-recognized property for investigating the sites for electrophilic attack.^{33–43} Gadre *et al.*,⁴¹ studied the H-bonded complexes of HF with some molecules and established the relationship between the H-bond length and position of the most negative MESP minimum of H-bonded complexes with a remarkable correlation coefficient of 0.96. They also developed^{37,38b,c} a model showing a good correlation between MESP topographical features

and binding patterns in weakly bonded complexes. Furthermore, Pingale⁴⁸ successfully employed the MESP topography as a quantitative measure of strength of electronic conjugation of some organic π -conjugated systems such as dimers of ethylene, benzene, furan, *etc.*, by means of MESP values of conjugation critical points (CCPs), which connect the two molecular electron localized regions. Deep negative MESP value at the CCP (V_{CCP}) indicates a large extent of conjugation in the respective molecular electronic regions.⁴⁸

Though the quinone moieties in various reduction and protonation states play crucial role in the processes of various disciplines,^{3,7,18} we focus on photosynthesis and molecular switches in the present study. For both the processes, i.e. movement of Q_B moiety and its protonation based on electrostatic interactions of specific reduction or protonation states of quinone with surrounding amino acids in RC and varied amount of electron/charge transfer through Q to QH_2 states, the electronic distribution of each quinone state is key parameter for understanding their mechanisms. In the present work, three-dimensional mapping of MESP of the quinone states is employed with a view to understand the mechanism of the above processes.

2. Computational details

The geometries of BQS and $BQS \cdots Li^+$ systems are optimized at the B3LYP/6-311+G(d,p) (for closed shell states) and UB3LYP/6-311+G(d,p) (for open shell states) levels of theory in gas phase using GAUSSIAN09 package.⁴⁹

The electrostatic nature and regions of electron localization of BQS are explored by MESP analysis. The MESP, $V(\mathbf{r})$, a measure of an interaction with a unit positive charge, at a point $\mathbf{r}$ is defined as:

$$V(\mathbf{r}) = \sum_A^N \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3\mathbf{r}' \quad (1)$$

where, Z_A denotes the charge of the nucleus A located at $\mathbf{R}_A$ and $\rho(\mathbf{r})$ is the molecular electronic charge density. The first and second terms on the r.h.s. of the equation Eq. (1) represent the nuclear and electronic contributions respectively. Three-dimensional information regarding a scalar field is provided by its topographical analysis.⁵⁰ MESP calculations and topographical analysis of all the BQS and related molecules have been carried out by employing the optimized gas phase geometries through the INDPROP⁵⁰ program. The present level of theory is known to be adequate for MESP topographical analysis.^{51–53} The deep negative-valued MESP minima of BQS, representing the strongest electron localization regions, are considered as anchoring points for the Li^+ cation. Frequency calculations are done for all the optimized geometries of BQS and $BQS \cdots Li^+$ complexes for confirming the minimal nature of optimized geometries on

the potential energy surfaces. The contribution of functions corresponding to higher multiplicity states (expectation values $\langle S^2 \rangle$), was found to be negligible for all the open shell (radicals) BQS studied in this work. The binding energy (ΔE) of a BQS is calculated as per the usual definition, *viz.*,

$$\Delta E = E(BQS \cdots Li^+) - [E(BQS) + E(Li^+)] \quad (2)$$

where, $E(BQS \cdots Li^+)$, $E(BQS)$ are the energies of fully optimized $BQS \cdots Li^+$ complex, BQS, respectively, and $E(Li^+)$ is the energy of the Li^+ ion. MESP features of BQS and optimized geometries of $BQS \cdots Li^+$ complexes are visualized using UNIVIS⁵⁴ and GuassView 5.0 packages, respectively. The basis set superposition error (BSSE)-corrected binding energies are also calculated using counterpoise correction method.⁵⁵

To obtain a more realistic picture of the process of proton transfer to quinone as a function of its reduced state in bacterial photosynthetic reaction center, interaction of the reduced states of BQS with motifs of protonated Serine (SER) and Histidine (HIS) as well as with NH_4^+ are explored. The binding energies are calculated at the optimized complex geometries of BQS with SER, HIS and NH_4^+ with frozen monomers, i.e., at the geometries in the optimized complex. Furthermore, BSSE-corrected binding energies are also calculated. The role of dispersion forces in complex formation is explored by employing M06-2X functional.⁵⁶

Further, the electron conductivity switching behavior through the 9,10-benzoanthraquinone and its reduced and protonated state *viz.*, QH_2 calculated by Seidel *et al.*,²³ is analyzed *via* the MESP topographical study. The CCP, i.e. a (3, +1) saddle point connecting the negative MESP regions engulfing the minima, is explored for understanding the conductivity pattern.

3. Results and Discussion

The MESP features of BQ with its different reduction and protonation states are presented by the selected negative and positive MESP isosurfaces displayed in Figure 2. MESP minima, which are marked as dark blue dots, highlight the electron localization regions for these states. In Figure 2, a positive-valued meshwire isosurface is also shown for highlighting the nuclear framework.

p-Benzoquinone (BQ): The three MESP isosurfaces of values -25.1 (blue), 3.1 (yellow) and 431.7 (red meshwire) kcal mol⁻¹ for BQ are shown in Figure 2(a). Here, the negative-valued regions indicate prominent electronic charge localization around the oxygen atoms. The MESP value of four (symmetric) minima, which are engulfed by blue isosurfaces is -38.8 kcal mol⁻¹. These minima are situated in the molecular plane, about 1.37

Figure 2. The MESP features of BQ in different reduction and protonation states with the selected negative and positive MESP isosurfaces (blue (B), yellow (Y) and red (R)). The values of MESP minima are denoted in italics. MESP values are in kcal mol⁻¹. See text for details.

Å away from the respective oxygen atoms. These minima are also seen in the two dimensional (2D) contour diagram of BQ in molecular plane given in Figure 3(a).

***p*-Benzoquinone radical anion (BQ^{•-}):** Figure 2(b) reveals the negative regions of BQ^{•-} to be much more negative than those of BQ. The complete molecule of BQ^{•-} is covered by a negative-valued MESP sheath. The MESP minima of the oxygens at UB3LYP calculation exhibit a large reduction in the value, *viz.*, -152.1 kcal mol⁻¹, approximately 3.9 times those for BQ and located at 1.23 Å away from the oxygen (*cf.* Figure 3(b) for 2D contours). The MESP values of C=C bond minima present above the ring of BQ^{•-} (as seen in Figure 2(b)) are -103.4 kcal mol⁻¹ and they are located about 1.62 Å above the ring plane in the respective C=C bond region.

***p*-Benzoquinone dianion (Q²⁻):** The highly negative character of BQ²⁻ compared to BQ and BQ^{•-} is conspicuous from Figure 2(c). The MESP minima values of oxygen and C=C bond show a dramatic reduction and turn out to be -263.5 and -214.5 kcal mol⁻¹, about 1.17 Å away from the oxygen atom and 1.47 Å at a perpendicular distance above the ring plane, respectively.

It is also reflected in Figure 3(c) that depicts the 2D MESP contours in molecular plane of BQ²⁻. The oxygen MESP minimum value of BQ²⁻ is 6.79 times that for BQ.

***p*-Benzoquinone cation (BQH⁺):** The characteristic MESP distribution of BQH⁺ is shown in Figure 2(d) wherein the complete molecule is covered with a positive-valued MESP isosurface. Only one positive valued (*i.e.*, 49.2 kcal mol⁻¹) MESP minimum is observed for this state at a distance of 1.78 Å from the carbonyl oxygen. These observations emphasize the electrophilic nature of BQH⁺ state, as may be intuitively expected from its cationic nature.

***p*-Benzoquinone radical (BQH[•]):** This molecule shows negative-valued MESP patches around it (*cf.* Figure 2(e)). More negative charge is localized near the carbonyl oxygen region than the hydroxyl oxygen region. The hydroxyl oxygen MESP minimum is -22.2 kcal mol⁻¹ located about 1.32 Å from it. MESP minima of carbonyl oxygen are deeper than those of neutral BQ possessing values of -57.1 and -56.8 kcal mol⁻¹ at a distance of 1.33 Å from the oxygen atom. The MESP minima of carbonyl oxygen region

Figure 3. 2D MESP contours (values are given from inside out and in kcal mol^{-1}) (R:red contours are positive and B:blue are negative) of, (a) BQ (R: 947.54, 455.57, 152.48, 45.18 and B: -35.77, -29.49, -20.71, -15.06); (b) $\text{BQ}^{\bullet-}$ (R: 673.32, 263.55, 58.36 and B: -148.09, -133.66, -101.03, -71.54, -64.01); and (c) BQ^{2-} (R: 480.04, 208.33, 5.65 and B: -257.28, -240.34, -196.41, -173.19, -149.35). The respective oxygen minima are shown by blue dots.

are deeper by a factor of ~ 2.6 than those of hydroxyl oxygen.

***p*-Benzoquinone anion (BQH^-):** The observed MESP values here are deeper than those for $\text{BQH}^\bullet$ (cf. Figure 2(f)). The MESP minima of carbonyl and hydroxyl oxygens are -177.9 and $-121.9 \text{ kcal mol}^{-1}$, respectively, and are located 1.16 and $1.23 \text{ \AA}$ away from them. This shows that the carbonyl oxygen of BQH^- is more nucleophilic than the hydroxyl one. Minima of the carbonyl and hydroxyl oxygens in BQH^- are about 3.13 and 5.49 times more pronounced as compared with their counterparts in $\text{BQH}^\bullet$.

Hydroquinone dication (BQH_2^{2+}): The negative MESP region is conspicuous by its absence for BQH_2^{2+} (cf. Figure 2(g)) and not a single negative MESP minimum is found for this cationic species. This highlights highly electrophilic behavior of BQH_2^{2+} molecule.

Hydroquinone radical cation ($\text{BQH}_2^{\bullet+}$): For this state also, no negative-valued MESP region is noticed (cf. Figure 2(h)).

Hydroquinone (BQH_2): This state shows negative MESP islands, along with a pair of MESP minima

for each oxygen (see Figure 2(i)) at $-39.3 \text{ kcal mol}^{-1}$ situated about $1.28 \text{ \AA}$ away from it. On the other hand, the minima, above and below the ring plane and perpendicular to $\text{C}=\text{C}$ bonds possessing a value of $-14.3 \text{ kcal mol}^{-1}$, lie $1.87 \text{ \AA}$ above the ring plane. Thus, the MESP distributions of BQ and BQH_2 are seen to differ to some extent.

In summary, the carbonyl or hydroxyl oxygen regions of all the non-cationic states possess pronounced negative MESP values. These values become more negative with the trends observed in going from $\text{BQ} \rightarrow \text{BQ}^{\bullet-} \rightarrow \text{BQ}^{2-}$, $\text{BQH}^+ \rightarrow \text{BQH}^\bullet \rightarrow \text{BQH}^-$ and $\text{BQH}_2^{2+} \rightarrow \text{BQH}_2^{\bullet+} \rightarrow \text{BQH}_2$ with the addition of an electron in each step. A noteworthy observation is that the carbonyl oxygen regions for the singly protonated states, $\text{BQH}^\bullet$ and BQH^- , are more electron rich than the respective hydroxyl counterparts. It is also noticed that the cationic states viz., BQH^+ , $\text{BQH}_2^{\bullet+}$ and BQH_2^{2+} have only positive MESP around them, establishing their electrophilic identity. On the other hand, anionic states, viz., BQ^{2-} , $\text{BQ}^{\bullet-}$ and BQH^- are engulfed by a negative MESP sheath around them showing their nucleophilic nature. These observations are in accordance with the theorem proved by Pathak and Gadre⁵⁷ regarding the zero flux

Figure 4. MESP isosurfaces (blue (B), yellow (Y) and red (R)) and minima of *o*-BQ and *o*-BQ^{•-}. The values of MESP minima are denoted in italics. MESP values are in kcal mol⁻¹ (See text for details.)

surface for anions. Another significant observation is that the protonation of a particular BQ state increases the MESP values of the regions more positive making it less nucleophilic or more electrophilic moiety. This behavior is observed for $\text{BQ} \rightarrow \text{BQH}^+ \rightarrow \text{BQH}_2^{2+}$, $\text{BQ}^{\bullet-} \rightarrow \text{BQH}^{\bullet} \rightarrow \text{BQH}_2^{\bullet+}$ and $\text{BQ}^{2-} \rightarrow \text{BQH}^- \rightarrow \text{BQH}_2$ states.

We have also performed MESP topographical analysis on a topological isomer of *para*-BQ i.e. *ortho*-benzoquinone (*o*-BQ) and its radical semiquinone anion (*o*-BQ^{•-}), as another test case that has been studied by Nepal *et al.*¹⁷ The MESP isosurfaces with respective minima of *o*-BQ and *o*-BQ^{•-} are shown in the Figure 4(a) and (b), respectively. The most negative MESP minimum is observed near carbonyl oxygen of *o*-BQ having value $-51.3 \text{ kcal mol}^{-1}$, indicating the more electron localization (see Figure 4(a)). However, in the case of *o*-BQ^{•-} the most negative MESP minimum also observed in carbonyl oxygen region shows the value of $-170.7 \text{ kcal mol}^{-1}$ which is deeper by a factor of about 3.3 than that observed for *o*-BQ.

As shown by Nepal *et al.*,¹⁷ a cationic species viz., $\text{CNH}_2(\text{NHCH}_3)_2^+$ forms a complex with *o*-BQ. The deeper negative electronic region of *o*-BQ^{•-}, around the oxygen atom, than that in *o*-BQ supports the reported higher binding energy (~ 2.1 times) of cationic species with *o*-BQ^{•-} than the latter one. We have verified this by the calculation of ΔE via Eq. (2) for electrophilic Li⁺ binding.

These cation binding interactions may be considered as a prototype for the aforementioned interactions of ubiquinone redox states with the surrounding protonated amino acids in the photosynthetic RC.

Negative MESP minima are used as the binding sites for Li⁺. The ΔE value (via Eq. (2)) for *o*-BQ $\cdots$ Li⁺ complex is observed at $-60.97 \text{ kcal mol}^{-1}$, when Li⁺ is placed in the vicinity of the carbonyl oxygen lone pair. However, the ΔE value turns out to be

$-172.67 \text{ kcal mol}^{-1}$, for *o*-BQ^{•-} $\cdots$ Li⁺ (Li⁺ bonded at carbonyl oxygen binding site) complex which is 2.8 times more favourable than *o*-BQ $\cdots$ Li⁺. This increase in ΔE value for the complex of *o*-BQ^{•-} state with Li⁺ is also reflected in cation binding energies to this anionic state than *o*-BQ (4.3 times) noticed by Nepal *et al.*¹⁷

Keeping the above in mind, a complete picture of the electronic distribution in reduction and protonation states of BQ is further confirmed with the interaction of a test electrophile, viz., Li⁺, in terms of the respective binding energies, ΔE . The corresponding optimized structures along with their Li⁺ binding distances are shown in Figure 5. The calculated ΔE s of these fully optimized BQS $\cdots$ Li⁺ complexes are reported in Table 1. The negative MESP minima are observed near the C=C, carbonyl as well as the hydroxyl oxygen regions of BQS indicating stronger electron localization. These features are utilized for generating the initial guess structures of BQS $\cdots$ Li⁺ complexes. As BQH⁺, BQH₂²⁺ and BQH₂^{•+} are immersed in positive MESP isosurfaces with no negative MESP minima, these BQS are not considered for calculation of binding energies with Li⁺. The ΔE values of Li⁺ with BQ are observed as $-43.83 \text{ kcal mol}^{-1}$ at carbonyl oxygen binding site (Figure 5a) and $-9.17 \text{ kcal mol}^{-1}$ above the ring plane (Figure 5b). The MESP minimum for BQ^{•-} is substantially more negative and as a consequence, ΔE of BQ^{•-} $\cdots$ Li⁺ complex is observed to be more favourable. The values for ΔE s of BQ^{•-} $\cdots$ Li⁺ complex are $-139.58 \text{ kcal mol}^{-1}$ at carbonyl oxygen binding site and $-126.15 \text{ kcal mol}^{-1}$ above the ring plane. It can also be noticed that the ΔE values observed for *o*-BQ $\cdots$ Li⁺ and *o*-BQ^{•-} $\cdots$ Li⁺ are more prominent than those observed for BQ $\cdots$ Li⁺ and BQ^{•-} $\cdots$ Li⁺, in line with more negative values of the respective MESP minima for the *o*-benzoquinone states

Figure 5. The minimum energy structures of BQS...Li⁺ complexes. The values in brackets are respective binding energies of BQS...Li⁺ complexes in kcal mol^{−1}. The values near to the dotted lines are distances of Li⁺ from respective position in Å. See text and Table 1 for details.

Table 1. Calculated binding energies with full optimized monomers (ΔE), binding energy at the optimized complex geometry with frozen monomers (ΔE^{FM}) and BSSE-corrected binding energies (ΔE^{BSSE}), V_{min} and distances of Li⁺ from respective positions of different reduction and protonation states of *p*-benzoquinone with Li⁺ using B3LYP/6-311+G(d,p) level of theory.

State	Position ^a	V_{min} (kcal mol ^{−1})	d_{min} (Å)	d_{Li^+} (Å)	ΔE (kcal mol ^{−1})	ΔE^{FM} (kcal mol ^{−1})	ΔE^{BSSE} (kcal mol ^{−1})
BQ	−O	−38.86	1.37	1.74	−43.83	−44.81	−44.20
	ARP	—	—	2.14	−9.17	−9.70	−8.91
BQ ^{•−}	−O	−152.08	1.23	1.63	−139.58	−141.02	−140.44
	ARP	−103.41	1.61	1.76	−126.15	−126.70	−125.89
BQ ^{2−}	−O	−263.47	1.17	1.63	−237.80	−240.46	−216.40
	ARP	−214.52	1.47	1.61	−241.43	−243.11	−224.32
BQH [•]	−O	−57.12	1.33	1.71	−58.44	−59.26	−58.67
		−56.77					
	−OH	−22.19	1.32	1.85	−25.31	−26.88	−26.06
	ARP	−4.28	2.09	1.96	−24.55	−25.29	−24.53
BQH [−]	−O	−177.9	1.16	1.61	−159.26	−161.86	−161.26
	ARP	−118.04	1.62	1.71	−142.23	−143.61	−142.79
BQH ₂	−OH	−39.29	1.23	1.80	−39.59	−43.52	−42.57
	ARP	−14.26	1.87	1.85	−39.08	−40.31	−39.55

^a−O: Carbonyl oxygen, −OH: hydroxyl oxygen and ARP: from the ring plane (See Figure 4 for details).

V_{min} : Most negative valued MESP minimum.

d_{min} : Distance of MESP minimum from the carboxyl/hydroxyl oxygen or above the ring plane.

d_{Li^+} : Perpendicular distance of Li⁺ from the ring centre.

than those of *p*-benzoquinone. Addition of another electron to BQ^{•−} further deepens the MESP minimum values as a result of more electron localisation at carbonyl oxygen as well as C=C regions and it is

reflected in more favourable ΔE than the BQ having values at −237.80 kcal mol^{−1} at carbonyl oxygen and −241.43 kcal mol^{−1} above the ring plane (cf. Table 1)

Figure 6. Correlation between value of most negative MESP minimum $V_{\min}$ and the corresponding Li^+ binding energy (ΔE) of BQS. See text for details.

Further, it is observed that addition of an electron and a proton to BQ, i.e., $\text{BQH}^\bullet$ state follows the trend going from more negative than the BQ one MESP minimum values at carbonyl (which is having most negative MESP minimum value) towards more positive side at the hydroxyl oxygen and then above the ring in $\text{C}=\text{C}$ regions. The respective calculated ΔE s are -58.44 , -25.31 and -24.55 kcal mol⁻¹ for $\text{BQH}^\bullet \cdots \text{Li}^+$ complexes. However, for the reduced state $\text{BQH}^- \cdots \text{Li}^+$, the ΔE is more enhanced to -159.26 kcal mol⁻¹ at carbonyl oxygen position and then above the ring in $\text{C}=\text{C}$ region (-142.23 kcal mol⁻¹). For $\text{BQH}_2 \cdots \text{Li}^+$ complexes, ΔE s are observed to be -39.59 and -39.08 kcal mol⁻¹ at hydroxyl oxygen and above the ring site respectively. From calculated ΔE of $\text{BQS} \cdots \text{Li}^+$ complexes, it is noticed that the carbonyl oxygen is the more favourable site for Li^+ binding and it is also reflected from respective MESP minima values. A remarkable correlation between the MESP minimum values and the respective Li^+ binding energies of all the non-cationic BQS is observed as given in Figure 6, with a correlation coefficient (R^2) of 0.998. The BSSE corrected binding energies (cf. Table 1) also turn out to be in good agreement with ΔE and show correlation coefficient 0.995 with MESP minimum values.

Furthermore, we have assessed the interactions of BQ and its reduction states $\text{BQ}^{\bullet-}$ and BQ^{2-} with two model systems, viz., SER and HIS, mimicking the realistic interacting systems observed in photosynthetic reaction centre interacting with the ubiquinone for proton transfer processes.¹⁰ More electron localized regions of the states near the oxygen lone pair obtained with deepest MESP minima are chosen to assess these interactions.⁵⁸ The minimum energy structures of the complexes $\text{BQS} \cdots \text{SER}$ and $\text{BQS} \cdots \text{HIS}$ are depicted in Figure 7.

The binding energies for SER with BQ and $\text{BQ}^{\bullet-}$, respectively, (see Table 2) are -5.66 and -14.30 kcal mol⁻¹, where the proton transfer from SER to BQ is not observed. However, the proton transfer is observed from SER to carbonyl oxygen of BQ^{2-} in the $\text{BQ}^{2-} \cdots \text{SER}$ complex formation (cf. Figure 7) with the binding energy -111.71 kcal mol⁻¹. The noticeably higher binding energy of BQ^{2-} with SER than that of BQ and $\text{BQ}^{\bullet-}$ is attributed to the proton transfer in the complex. Similarly BQ and $\text{BQ}^{\bullet-}$ interacting with HIS show binding energies of -4.62 and -20.52 kcal mol⁻¹, respectively, without proton transfer. In this case also, the proton transfer is observed in doubly reduced state of BQ from HIS to carbonyl oxygen of BQ^{2-} in $\text{BQ}^{2-} \cdots \text{HIS}$ complex formation (see Figure 7) with binding energy -166.54 kcal mol⁻¹. This suggests that only single reduction of BQ is not sufficient to transfer a proton from the amino acids. However, with the source of higher H^+ population connected through proton transfer pathways through protonated amino acids and hydronium ions to the quinone moiety in photosynthetic reaction center may transfer the proton to singly reduced state, $\text{BQ}^{\bullet-}$. To verify the latter conjecture, the interaction of a highly proton donating cation, i.e. NH_4^+ with BQ systems is also studied.

The neutral state, BQ shows -24.89 kcal mol⁻¹ binding energy with NH_4^+ complex. The remarkable observation is that in case of $\text{BQ}^{\bullet-} \cdots \text{NH}_4^+$ and $\text{BQ}^{2-} \cdots \text{NH}_4^+$ complexes, proton transfer take place from NH_4^+ to the carbonyl oxygen of $\text{BQ}^{\bullet-}$ and BQ^{2-} with binding energies -215.87 and -397.96 kcal mol⁻¹, respectively. The BSSE correction in binding energies is negligible for the complexes of BQ, $\text{BQ}^{\bullet-}$ with SER, HIS and NH_4^+ , whereas it is somewhat larger for the respective BQ^{2-} complexes (see Table 2). However, the same increasing binding energy trend is observed with BSSE correction for all the above complexes (cf. Table 2) as that with uncorrected ones. The impact of dispersion effect on the binding energies calculated by employing M06-2X functional is observed to be less prominent but shows consistent increasing trend with B3LYP functional.

The study shows that the SER and HIS interact with carbonyl oxygen of BQ, the neutral state, via weak intermolecular H-bonding and similar kinds of features are also observed for anionic $\text{BQ}^{\bullet-}$ state. When BQ accepts two electron and becomes dianion i.e. BQ^{2-} , the negative MESP at its carbonyl oxygen becomes more susceptible to accept proton from HIS as well as SER. But in case of $\text{BQS} \cdots \text{NH}_4^+$ complexes, BQ shows hydrogen bonding interaction with NH_4^+ , however, anionic $\text{BQ}^{\bullet-}$ and BQ^{2-} states abstract protons from donor NH_4^+ .

Figure 7. The minimum energy structures of, I) BQS $\cdots$ SER II) BQS $\cdots$ HIS and III) BQS $\cdots$ NH $_4^+$ complexes. The respective H-bond lengths are given in Å and values in the brackets are binding energies. i.e., ΔE^{FM} values of respective complex.

Table 2. Calculated binding energies (ΔE^{FM}) in kcal mol $^{-1}$ of optimized geometries of complexes of SER, HIS and NH $_4^+$ with reduction states of *p*-benzoquinone viz., BQ, BQ $\bullet^-$ and BQ $^{2-}$ using B3LYP/6-311+G(d,p) level of theory. The ΔE values calculated using M06-2X are shown in parentheses. ΔE^{BSSE} is the BSSE-corrected binding energy.

State	SER		HIS		NH $_4^+$	
	ΔE^{FM}	ΔE^{BSSE}	ΔE^{FM}	ΔE^{BSSE}	ΔE^{FM}	ΔE^{BSSE}
BQ	-5.66 (-7.27)	-5.31	-4.62 (-5.20)	-4.32	-24.89 (-24.31)	-24.57
BQ $\bullet^-$	-14.30 (-16.41)	-13.77	-20.52 (-22.42)	-20.08	-215.87 (-219.14)	-215.51
BQ $^{2-}$	-111.71 (-94.39)	-106.29	-166.54 (-175.07)	-154.97	-397.96 (-387.36)	-370.14

As mentioned earlier, the AQ/AQH $_2$ redox couple (Scheme 1) has proved to be promising component in molecular switches.¹⁸ Hence, it is important to analyse their electronic delocalization/conjugation as it plays an important role in electron conduction.²¹ As conjectured by Pingale,⁴⁸ the V_{CCP} values provide a quantitative measure for electronic conjugation present in a molecule. Here, we also correlate the quantitative strength of the conjugation represented by V_{CCP} between the rings of the AQ and AQH $_2$ states with their molecular electronic conductivity responsible for the switching mechanism.²¹ The MESP calculations are

performed on AQ and AQH $_2$ states of 9,10-anthraquinone π -conjugated with ethyne (see Scheme 1); i.e. the main spacer unit in redox active switches studied by Seidel *et al.*²³

The MESP topographical features of AQ and AQH $_2$ are shown in Figure 8. In AQ, each carbonyl oxygen (see Figure 8(a)) possess more negative MESP minima of values -38.6 and -38.3 kcal mol $^{-1}$ than its other regions. Moreover, the ethyne parts show ring-like isosurfaces containing four minima above and below the molecular plane of value -12.0 kcal mol $^{-1}$ connecting the minima of carbonyl oxygen through

Scheme 1. Redox reaction of AQ to AQH₂ spacer units.

Figure 8. The selected MESP isosurfaces (blue (B), yellow (Y) and red (R)) of (a) AQ and (b) AQH₂. The values of V_{CCP} are denoted in italics. MESP values are in kcal mol⁻¹. See text for details.

CCPs of value -2.8 kcal mol⁻¹. Four minima (values -1.4 kcal mol⁻¹) are observed near π -regions of C=C bond of the side rings are ~ 27 times less negative than the minimum of the carbonyl oxygen and it suggests the large electronic localization of oxygen lone pairs. The C=C bond minima are connected with the minima of carbonyl oxygen lone pairs through (3, +1) saddle points of value -1.3 kcal mol⁻¹ (*cf.* Figure 8(a)). In case of AQH₂, the carbonyl oxygen atoms possess two MESP minima of values -29.9 and -26.4 kcal mol⁻¹ (see Figure 8(b)).

Two minima of values, -10.6 and -10.3 kcal mol⁻¹ which are typically 7 times deeper than the corresponding minimum of AQ are present above and below the side rings. These side ring minima are connected with the ones of carbonyl oxygen lone pair electrons by (3, +1) saddles of values -7.8 and -6.1 kcal mol⁻¹ that are ~ 6 times deeper than those of AQ, which are absent in AQ (*cf.* Figure 8(a) and (b)). The presence of central MESP CCPs is a signature of conjugation between π -regions of side rings of AQH₂ (constructive interference) and attributed to its more electron conducting behaviour. The absence of central quinoid ring CCP connecting π -regions of side rings signifies

lack of a π -conjugation (destructive interference) and consequently non-conducting nature in AQ. These features are in agreement with the switching mechanism of AQ/AQH₂ couple observed by Seidel *et al.*²³

4. Conclusions

In the present study, an attempt has been made to understand the fundamental electrostatic nature of all possible reduction and protonation states of quinone, which may create attractive and repulsive forces with their receptors to fulfill their role in various processes. Moreover, it has been shown that quinones can act as molecular switch in their quinoidal and quinol states. That makes them potential candidates to control electronic conductivity through a molecular switch in molecular electronic devices.

In this paper, the three-dimensional MESP mapping of different reduction and protonation states of *p*-benzoquinone, is employed as a probe for exploring the electron distribution and its influence on the reactivity in the form of interactions with a model electrophile *viz.*, Li⁺. A good correlation has been found between

the MESP features and the corresponding pronounced Li^+ cation bonding strength. The salient feature of the present work is that under the impact of pronounced negative MESP values, reduced *p*-benzoquinone states, viz., $\text{BQ}^{\bullet-}$ and BQ^{2-} interact strongly with an electrophile as modelled by Li^+ in comparison with neutral BQ. The study also suggests that the singly reduced state of quinone shows H-bonding with protonated amino acids, viz., SER and HIS without having a possibility of proton transfer process. When protons are readily available, such as in the case of NH_4^+ , the proton transfer may occur from donor to singly reduced state of quinones. However, the dianion state of quinone can abstract the protons from protonated amino acids HIS and SER moieties. This gives an intuitive picture of the movement of reduced ubiquinone species towards the protonated amino acids in the photosynthetic RC, with major contribution from electrostatic interactions. Due to the analogous geometrical nature of the oxygen regions, we expect similar MESP features of other substituted quinone state of interest which are significant in various important biochemical and other chemical processes. It is hence hoped that the present work provides a first step towards understanding detailed mechanisms of quinone activity (such as its interactions with side chains and other electrophiles in RC) in these processes. Furthermore, the MESP topographical features of quinone states support the understanding of electron conductivity switching mechanism in AQ/AQH₂ redox system.²² The presence of conjugation between the rings of the AQH₂ by means of central CCPs reveals their higher molecular electronic conductivity than AQ and consequently the switching mechanism. It illustrates the importance of roles of quinone redox states and their characteristic MESP features in modern molecular electronics.

Supplementary Information (SI)

Cartesian co-ordinates and energies of the optimized geometries of BQS (SI) and the complexes viz., $\text{BQS} \cdots \text{Li}^+$ (SII), $\text{BQS} \cdots \text{NH}_4^+$ (SIII), $\text{BQS} \cdots \text{SER}$ (SIV) and $\text{BQS} \cdots \text{HIS}$ (SV) at B3LYP/6-311+G(d,p) (for closed shell states) and UB3LYP/6-311+G(d,p) (for open shell states) levels of theory are provided in the Supplementary Information, which is available at www.ias.ac.in/chemsci.

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References

1. Heffner J E, Raber J C, Moe O A and Wigal C T 1998 Using cyclic voltammetry and molecular modelling to determine substituent effects in the one-electron reduction of benzoquinones *J. Chem. Educ.* **75** 365
2. Guin P S, Das S and Mandal P C 2011 Electrochemical reduction of quinones in different media: a review *Int. J. Electrochem.* **2011** 1
3. Ernster L and Dallner G 1995 Biochemical physiological and medical aspects of ubiquinone function *Biochim. Biophys. Acta* **1271** 195
4. Marreiros B C, Calisto F, Castro P J, Duarte A M, Sena F V, Silva A F, Sousa F M, Teixeira M, Refojo P N and Pereira M M 2016 Exploring membrane respiratory chains *Biochim. Biophys. Acta* **1857** 1039
5. Kato Y, Nagao R and Noguchi T 2016 Redox potential of the terminal quinone electron acceptor Q_b in photosystem II reveals the mechanism of electron transfer regulation *Proc. Natl. Acad. Sci. (U. S. A.)* **113** 620
6. Okamura M Y, Paddock M L, Graige M S and Feher G 2000 Proton and electron transfer in bacterial reaction centres *Biochim. Biophys. Acta* **1458** 148
7. Feher G, Allen J C, Okamura M Y and Rees D C 1989 Structure and function of bacterial photosynthetic reaction centres *Nature* **339** 111
8. Nabadryk E and Breton J 2008 Coupling of electron transfer to proton uptake at the Q_B site of the bacterial reaction center: A perspective from FTIR difference spectroscopy *Biochim. Biophys. Acta* **1777** 1229
9. Fyfe P K and Jones M R 2000 Re-emerging structures: continuing crystallography of the bacterial reaction centre *Biochim. Biophys. Acta* **1459** 413
10. Stowell M H B, McPhillips T M, Rees D C, Soltis S M, Abresch E and Feher G 1997 Light-induced structural changes in photosynthetic reaction center: implications for mechanism of electron-proton transfer *Science* **276** 812
11. Walden S E and Wheeler R A 2002 Protein conformational gate controlling binding site preference and migration for ubiquinone-b in the photosynthetic reaction center of *Rhodobacter sphaeroides* *J. Phys. Chem. B* **106** 3001
12. Lancaster C R D and Michel H 1997 The coupling of light-induced electron transfer and proton uptake as derived from crystal structures of reaction centres from *Rhodospseudomonas viridis* modified at the binding site of the secondary quinone, Q_B *Structure* **5** 1339
13. Zhu Z and Gunner M R 2005 Energetics of Quinone-Dependent Electron and Proton Transfers in *Rhodobacter sphaeroides* Photosynthetic Reaction Centers *Biochemistry* **44** 82
14. Breton J, Boullais C, Mioskowski C, Sebban P, Baciou L and Nabadryk E 2002 Vibrational spectroscopy favors a unique Q_B binding site at the proximal position in wild-type reaction centers and in the Pro-L209 → Tyr Mutant from *Rhodobacter sphaeroides* *Biochemistry* **41** 12921
15. Takahashi E and Wraight C A 1996 Potentiation of proton transfer function by electrostatic interactions in photosynthetic reaction centers from *Rhodobacter sphaeroides*: first results from site-directed mutation of the H subunit *Proc. Natl. Acad. Sci. U. S. A.* **93** 2640

16. Manojkumar T K, Choi H S, Tarakeshwar P and Kim K S 2003 *Ab initio* studies of neutral and anionic *p*-benzoquinone-water clusters *J. Chem. Phys.* **118** 8681
17. Nepal B and Scheiner S 2016 Enhancing the reduction potential of quinones *via* complex formation *J. Org. Chem.* **81** 4316
18. Darwish N, Díez-Pérez I, Da Silva P, Tao N, Gooding J J and Paddon-Row M N 2012 Observation of electrochemically controlled quantum interference in a single anthraquinone-based norbornylogous bridge molecule *Angew. Chem. Int. Edit.* **51** 3203
19. Baghernejad M, Zhao X, Ørnsø K B, Füeg M, Moreno-García P, Rudnev A V, Kaliginedi V, Vesztergom S, Huang C, Hong W, Broekmann P, Wandlowski T, Thygesen K S and Bryce M R 2014 Electrochemical control of single-molecule conductance by fermi level tuning and conjugation switching *J. Am. Chem. Soc.* **136** 17922
20. van Dijk E H, Myles D J T, van der Veen M H and Hummelen J C 2006 Synthesis and properties of an anthraquinone-based redox switch for molecular electronics *Org. Lett.* **8** 2333
21. Xiang D, Wang X, Jia C, Lee T and Guo X 2016 Molecular-scale electronics: from concept to function *Chem. Rev.* **116** 4318
22. Markussen T, Schiøtz J and Thygesen K S 2010 Electrochemical control of quantum interference in anthraquinone-based molecular switches *J. Chem. Phys.* **132** 224104
23. Seidel N, Hahn T, Liebing S, Seichter W, Jens K and Weber E 2013 Synthesis and properties of new 9,10-anthraquinone derived compounds for molecular electronics *New J. Chem.* **37** 601
24. Greene L E, Godin R and Cosa G 2016 Fluorogenic ubiquinone analogue for monitoring chemical and biological redox processes *J. Am. Chem. Soc.* **138** 11327
25. Nonella M 1997 Structures and vibrational spectra of *p*-benzoquinone in different oxidation and protonation states: a density functional study *J. Phys. Chem. B* **101** 1235
26. Boesch S E and Wheeler R A 1997 π -Donor substituent effects on calculated structures spin properties and vibrations of radical anions of *p*-chloranil *p*-fluoranil and *p*-benzoquinone *J. Phys. Chem. A* **101** 8351
27. Brandt U and Trumpower B L 1994 The protonmotive Q cycle in mitochondria and bacteria *Crit. Rev. Biochem.* **29** 165
28. Trumpower B L and Gennis R B 1994 Energy transduction by cytochrome complexes in mitochondrial and bacterial respiration: the enzymology of coupling electron transfer reactions to transmembrane proton translocation *Annu. Rev. Biochem.* **63** 675
29. O'Malley P J 1997 A density functional study of the effect of reduction on the geometry and electron affinity of hydrogen bonded 1,4-benzoquinone implications for quinone reduction and protonation in photosynthetic reaction centres *Chem. Phys. Lett.* **274** 251
30. Nonella M, Mathias G and Tavan P 2003 Infrared spectrum of *p*-benzoquinone in water obtained from a QM/MM hybrid molecular dynamics simulation *J. Phys. Chem. A* **107** 8638
31. Pou-Amérigo R, Merchán M and Ortí E 1999 Theoretical study of the electronic spectrum of *p*-benzoquinone *J. Chem. Phys.* **110** 9536
32. Zhao X, Imahori H, Zhan C-G, Sakata Y, Iwata S and Kitagawa T 1997 Resonance Raman and FTIR spectra of isotope-labeled reduced 1,4-benzoquinone and its protonated forms in solutions *J. Phys. Chem. A* **101** 622
33. Politzer P and Truhlar D G 1981 In *Chemical applications of atomic and molecular electrostatic potentials* (New York: Plenum)
34. Politzer P, Landry S J and Wärmhelm T J 1982 Proposed procedure for using electrostatic potentials to predict and interpret nucleophilic processes *J. Phys. Chem.* **86** 4767
35. Sjöberg P and Politzer P 1990 Use of the electrostatic potential at the molecular surface to interpret and predict nucleophilic processes *J. Phys. Chem.* **94** 3959
36. Tomasi J, Bonaccorsi R and Cammi R 1990 In: *Theoretical methods of chemical bonding, Part 3* Maksic Z B (Ed.) (New York: Springer) and references therein
37. Gadre S R, Pundlik S S and Shrivastava I H 1994 A "Critical" appraisal of electrostatic charge models for molecules *Proc. Ind. Acad. Sci. (J. Chem. Sci.)* **106** 303
38. (a) Orozco M and Luque J 1996 in *Molecular electrostatic potentials concepts and applications Vol. 3*. J S Murray and K D Sen (Eds.) (Amsterdam: Elsevier) and references therein; (b) Gadre S R, Bhadane P K, Pundlik S S and Pingale S S 1996 In *Molecular electrostatic potentials concepts and applications Vol. 3*. J S Murray and K D Sen (Eds.) (Amsterdam: Elsevier) and references therein; (c) Roy D K, Balanarayan P and Gadre S R 2009 Signatures of molecular recognition from the topography of electrostatic potential *J. Chem. Sci.* **121** 815
39. Gejji S P, Suresh C H, Bartolotti L J and Gadre S R 1997 Electrostatic potential as a harbinger of cation coordination: CF_3SO_3^- ion as a model example *J. Phys. Chem.* **101** 5678
40. Pingale S S, Gadre S R and Bartolotti L J 1998 Electrostatic insights into the molecular hydration process: a case study of crown ethers *J. Phys. Chem. A* **102** 9987
41. Gadre S R and Bhadane P K 1997 Patterns in hydrogen bonding via electrostatic potential topography *J. Chem. Phys.* **107** 5625
42. Gadre S R and Pundlik S S 1997 Complementary electrostatics for the study of DNA base-pair interactions *J. Phys. Chem. B* **101** 3298
43. Lancaster C R D 2003 The role of electrostatics in proton-conducting membrane protein complexes *FEBS Lett.* **545** 52
44. Sharma B, Neela Y I and Sastry G N 2016 Structures and energetics of complexation of metal ions with ammonia water and benzene: a computational study *J. Comp. Chem.* **37** 992
45. Bhattacharjee A K, Pundlik S S and Gadre S R 1997 Conformational and electrostatic properties of naphthazarin, juglone and naphthoquinone: an *ab initio* theoretical study *Cancer. Invest.* **15** 531
46. Abroshan H, Dhumal N R, Shimb Y and Kim H J 2016 Theoretical study of interactions of a $\text{Li}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ion pair with $\text{CR}_3(\text{OCR}_2\text{CR}_2)_n\text{OCR}_3$ ($R = \text{H}$ or F) *J. Phys. Chem. Chem. Phys.* **18** 6754

47. Gadre S R and Bhadane P K 1998 Complexes of ammonia with propane and cyclopropane: electrostatic guidelines for *ab initio* treatment *Theor. Chem. Acc.* **100** 300
48. Pingale S S 2011 Molecular electrostatic potential for exploring π -conjugation: a density-functional investigation *Phys. Chem. Chem. Phys.* **13** 15158
49. Gaussian 09 Revision A 02 Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Petersson G A, Nakatsuji H, Li X, Caricato M, Marenich AV, Bloino J, Janesko B G, Gomperts R, Mennucci B, Hratchian H P, Ortiz J V, Izmaylov A F, Sonnenberg J L, Williams-Young D, Ding F, Lipparini F, Egidi F, Goings J, Peng B, Petrone A, Henderson T, Ranasinghe D, Zakrzewski V G, Gao J, Rega N, Zheng G, Liang W, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Throssell K, Montgomery J A Jr, Peralta J E, Ogliaro F, Bearpark M J, Heyd J J, Brothers E N, Kudin K N, Staroverov V N, Keith T A, Kobayashi R, Normand J, Raghavachari K, Rendell A P, Burant J C, Iyengar S S, Tomasi J, Cossi M, Millam J M, Klene M, Adamo C, Cammi R, Ochterski J W, Martin R L, Morokuma K, Farkas O, Foresman J B and Fox D J 2009 Gaussian Inc, Wallingford CT.
50. The topographical analysis is brought out in term of characterizing the critical points (CPs) where the first order partial derivatives of this field vanish. The CPs are represented by a notation (rank, signature) where rank is the number of nonzero eigenvalues of the Hessian matrix and signature is the algebraic sum of the signs of these eigenvalues. The non-degenerate CPs are further characterized viz., minimum (3, +3), maximum (3, -3) or saddles of types (3, +1) and (3, -1).
51. Shirsat R N, Bapat S V and Gadre S R 1992 Molecular electrostatics: a comprehensive topographical approach *Chem. Phys. Lett.* **200** 373
52. Kulkarni S A 1996 Electron correlation effects on the topography of molecular electrostatic potentials *Chem. Phys. Lett.* **254** 268
53. Gadre S R, Kulkarni S A, Suresh C H and Strivastava I H 1995 Basis set dependence of the molecular electrostatic potential topography a case study of substituted benzenes *Chem. Phys. Lett.* **239** 273
54. Limaye A C and Gadre S R 2001 UNIVIS-2000: An indigenously developed comprehensive visualization package *Curr. Sci. (India)* **80** 1296
55. Boys S F and Bernardi F 1970 The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors *Mol. Phys.* **19** 553
56. Zhao Y and Truhlar D G 2008 The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals *Theor. Chem. Acc.* **120**, 215
57. Pathak R K and Gadre S R 1990 Maximal and minimal characteristics of molecular electrostatic potentials *J. Chem. Phys.* **93** 1770
58. Bijina P V, Suresh C H and Gadre S R 2018 Electrostatics for probing lone pairs and their interactions *J. Comput. Chem.* **39** 488