

Aromaticity Investigation of Redox and Protonation States of *p*-Benzoquinone: A DFT Study

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Abstract

*Quinone/hydroquinone redox active couples are well known haematotoxic and carcinogenic pollutants in environment. Structure, stability and activity governed by aromaticity of quinones are the important aspects of the research in redox chemistry as they accept two electrons and two protons to become hydroquinones. Here we studied aromaticity of all possible redox and protonation states of *p*-benzoquinone (BQS), a parent compound of quinone family, by exploring harmonic oscillator model of aromaticity (HOMA) criterion with density functional theory at B3LYP/6-311+G(d,p) level. It is observed that addition of electron and proton separately in a BQS increases its ring aromaticity. However, with simultaneous addition, more enhancement in aromaticity is observed. These aspects further may be utilized to understand quinone chemistry for removal of quinone based toxicity.*

Keywords: Aromaticity, DFT, HOMA, Redox and Protonation States.

Introduction

Quinones, highly redox-active compounds, are ubiquitous in the nature including plants and animal tissues.[1] Due to their ability of accepting two electrons and two protons to become hydroquinone and *vice-versa*, quinones have an important role in electron and proton transport chains in photosynthesis and respiration reactions. Also a quinone compound *viz.* vitamin K plays vital role in blood coagulation, bone metabolism and growth. α -tocopherol (vitamin E) and pyrroloquinoline are biologically important vitamins.

Along with biological abundance, quinones, especially anthraquinones have been used in clinical treatments due to their antibiotic, immune suppressive and anti-inflammatory actions as well as in dyes and pigments for industrial applications.[1,2] *p*-Benzoquinone, a major benzene metabolite can be used as a potential candidate for developing photography, dye intermediate stabilizers in paints, varnishes oil and motor fuels.[2] It is also an important ingredient in cosmetic formulations of products for coating finger nails and hair dyes.

Biomedical applications and industrial developments are responsible for a huge increase in the release of quinone, hydroquinone compounds into the atmosphere, water bodies and soils. These are well-known haematotoxic and carcinogenic agents which are a subject of research in public health problem.

Study of quinone to hydroquinone transformation and *vice-versa* is crucial to understand their role in the bioreaction such as photosynthesis, to develop solar energy harvesting devices *viz.* solar cells.[3] Furthermore, degradation of quinone to hydroquinone pollutant is also important. In these

processes the detailed study of the stability and reactivity of quinone, quinol and the intermediate redox and protonation states is crucial.[4]

Aromaticity, a cyclic π -electron delocalization, one of the most important phenomena in organic, inorganic as well as in organometallic chemistry served as a parameter to understand the structure, stability and reactivity of the ring compounds.[5-8] Highly aromatic compounds possess more stability. The harmonic oscillator model of aromaticity (HOMA) is a widely used geometry based criterion to measure the ring aromaticity of a molecular system.[5]

The HOMA is defined as, [5-6]

$$HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^n (R_{opt} - R_i)^2$$

where, n = number of bonds in the ring, α = constant which is a 257.7 for C-C bond, to set a value of HOMA = 0 for non-aromatic or HOMA=1 for fully aromatic systems. R_i and R_{opt} stands for individual and optimal bond length of the ring respectively.[6]

In the present work, aromaticity of all the possible oxidation and protonation states of *p*-benzoquinone (BQS) as a prototypical example of quinone to quinol conversion, is studied by using HOMA indices.

Methodology

The geometries of all possible BQS are optimized at B3LYP/6-311+G(d, p) (for closed shell states) and UB3LYP/6-311+G(d, p) (for open shell states) levels of density functional theory (DFT). Frequency calculations are performed for all the optimized geometries of BQ to confirm their minimal nature on the potential energy surfaces. The quantification of aromaticity of all possible redox states of BQ is done by calculating HOMA index with reference to benzene molecule. All calculations are performed using GAUSSIAN09 package.[9]

Results and Discussions

The possible BQS by addition of electron and proton respectively are as shown in the Figure-1. The HOMA values of different BQS are calculated at B3LYP/6-311+G(d, p) and UB3LYP/6-311+G(d, p) levels.

Figure-1 represents BQS with their respective HOMA aromaticity indices. The HOMA value for benzene is observed as 1.000 which is a fully aromatic system. For *p*-benzoquinone i.e. BQ the obtained HOMA value is -0.6849 which is deeply negative showing its highly antiaromatic nature. For the horizontal schemes, one electron reduction of BQ results into $BQ^{\bullet-}$ redox state, for which HOMA index is observed to be 0.4313 showing its enhanced aromaticity features. This shows increase in aromaticity upon addition of electrons. The HOMA index further increased up to 0.7559 for doubly reduced BQ^{2-} state. While considering vertical schemes, addition of single H^+ to BQ converts it into BQH^+ state and its HOMA value is observed to be -0.2317 which is higher by 0.4532 than that of BQ. Further, addition of two protons to BQ raised its HOMA index from -0.6849 to -0.1928 for BQH_2^{2+} state i.e. higher by 0.0389 than BQH^+ one. Hence, the protonation of BQ also elevate the HOMA values and consequently aromaticity in corresponding redox states. The protonation of $BQ^{\bullet-}$ also shows rise in the HOMA value than that are observed for BQH^{\bullet} (0.6416) and for $BQH_2^{\bullet+}$ (0.7529). Similar increasing trend is observed in HOMA index for the addition of single and double electrons in BQH^+

having values 0.6416 (BQH^{\bullet}) and 0.7923 (BQH^{\ominus}) respectively. The HOMA values observed for BQH^{\ominus} and BQH_2 are at 0.7923 and 0.9994 respectively. Same increasing trend in HOMA index is observed for the BQ states obtained by sequential addition of protons to $BQ^{\ominus\ominus}$ i.e. 0.7923 (BQH^{\ominus}) and 0.9994 (BQH_2) (cf. Figure-1).

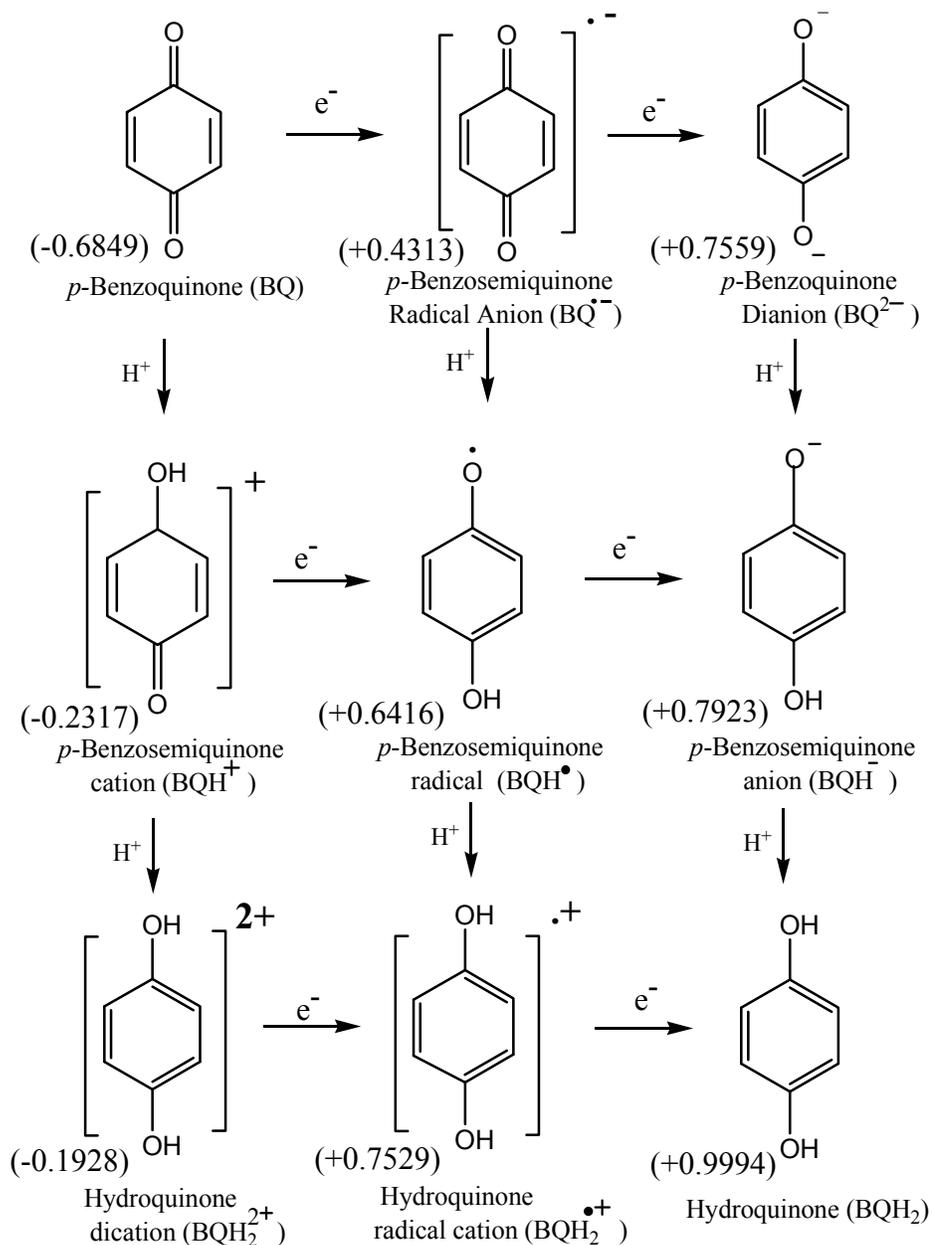


Figure-1. Possible redox and protonation states of a p -benzoquinone. The values shown within bracket represent HOMA values of respective states.

The simultaneous addition of electron and proton in BQ (cf. diagonal schemes in Figure-1) results into the increase in HOMA value of BQH^{\bullet} state (0.6416) by the factor of 1.3265 than BQ. It gets further increased by 1.6843 for another electron and proton addition for BQH_2 state i.e. 0.9994 which is quietly

closer to HOMA value of benzene. It is observed that BQH₂ possesses highest aromaticity features in all BQS. The same increasing trends in HOMA values are observed for the simultaneous addition of electron and proton into BQ²⁻ and BQH⁺ states see Figure-1. These observations implies that the aromatic character of BQ increases in greater extent upon simultaneous electron and proton addition than their individual separate addition.

Conclusions

Quinone/hydroquinone couples are ubiquitous chemicals in the environment due to their natural occurrence, human drugs as well as industrial activities. Their haematotoxicity and carcinogenicity make them environmental pollutants. Due to their redox properties they are present in various redox and protonation states. Structure, stability and reactivity of these states depend on ring aromaticity of the quinone moiety. In the present study, aromaticity of all the possible redox and protonation states of *p*-benzoquinones is analyzed based on HOMA criterion. It is observed that *p*-benzoquinone is the most anti-aromatic state and hydroquinone or quinol (BQH₂) is the most aromatic one in all BQS. In both cases i.e. addition of electron and proton the aromaticity of the state enhances. Furthermore, simultaneous addition of electron and proton enhances aromaticity more than their separate addition. This study may help to remove the quinone based pollutant from the environment with transformation through suitable BQS.

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References

- [1] N. Kishikawa and N. Kuroda “Analytical techniques for the determination of biologically active quinones in biological and environmental samples” *J. Pharm. Biomed. Anal.* vol. 87, pp. 261– 270, 2014.
- [2] F. J. Enguita and A. L. Leitão “Hydroquinone: Environmental Pollution, Toxicity, and Microbial Answers” *BioMed Research International* vol. 2013, Article ID 542168, pp.1-14 , 2014.
- [3] E. J. Son, J. H. Kim, K. Kim and C. B. Park, “Quinone and its derivatives for energy harvesting and storage materials” *J. Mater. Chem. A*, vol.4, pp. 11179–11202, 2016.
- [4] M. Nonella, “Structures and Vibrational Spectra of *p*-Benzoquinone in Different Oxidation and Protonation States: A Density Functional Study” *J. Phys. Chem. B*, vol. 101, pp. 1235-1246, 1997.
- [5] T. M. Krygowski and B. T. Steüpien, “Sigma- and Pi-Electron Delocalization: Focus on Substituent Effects” *Chem. Rev.* vol. 105, pp. 3482-3512, 2005.
- [6] H. Szatyłowicz et. al. “Why 1,2-quinone derivatives are more stable than their 2,3-analogues?” *Theor. Chem. Acc.* Vol.134, pp.1-14, 2015.
- [7] C. H. Suresh and N. Koga, “An isodesmic reaction based approach to aromaticity of a large spectrum of molecules” *Chem. Phys. Lett.* vol. 419, pp. 550-556, 2006.
- [8] A.T. Balaban, P. v. R. Schleyer and H. S. Rzepa, “Crocker, Not Armit and Robinson, Begat the Six Aromatic Electrons” *Chem. Rev.* vol.105, pp. 3436-3447, 2005.
- [9] M. J. Frisch *et al.* Gaussian09, Revision A.1, Gaussian Inc., Wallingford C.T. (2009).