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Ab initio SCF-MO study of quinones of pyridine

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Abstract

Ab initio calculations at HF/6-31G** and B3LYP/6-31G** levels of theory for geometry optimization, MP2/6-31G**//HF/6-31G** and MP2/6-31G**//B3LYP/6-31G** for single point total energy calculations are reported for six quinones of pyridine and three benzoquinones. Among pyridoquinones, the 2,5-isomer is calculated to be the most stable geometry; the 2,3- and 3,4-isomers are 18.26 and 43.21 kJ mol^{-1} less stable, respectively.

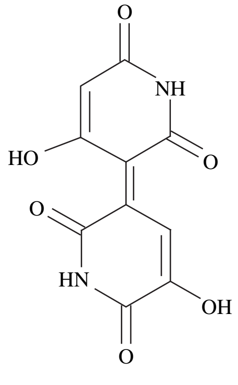
Keywords: Ab initio calculations; Molecular modelling; Pyridoquinones; Benzoquinones

1. Introduction

Quinones constitute an important class of naturally occurring compounds that are involved in many biological processes and have considerable synthetic and industrial applications [1]. An important class of heterocyclic quinones are pyridoquinones, which have become firmly established for a group of blue bacterial pigments [2]. Formally two aza-analogs of *o*-benzoquinone (2,3-PQ and 3,4-PQ), one aza-analog of *p*-benzoquinone (2,5-PQ), and three *m*-pyridoquinones (2,4-PQ, 2,6-PQ and 3,5-PQ) are possible (see Fig. 1). For ease of reference, abbreviated names rather than arbitrary numbers will be used for the benzoquinones and pyridoquinones. Thus, for example, *o*-benzoquinone and 2,3-pyridoquinone will be referred to simply as 1,2-BQ and 2,3-PQ, respectively (Fig. 1).

Even though some of the PQs are not presently available for more studies, it is possible to carry out *ab initio* calculations at the *Hartree–Fock* and DFT levels, from which many properties can be obtained with an accuracy that is competitive with experiment [3]. This study was undertaken to investigate the structural optimization of pyridoquinones shown in Fig. 1. Although theoretical studies have been reported for classical benzoquinones (1,2-BQ and 1,4-BQ), in order to compare PQs with BQs, we studied both the classical and non-classical (1,3-BQ) benzoquinones.

Pyridoquinones were first introduced by Kudernatsch, who reported that the oxidation of 2,3- or 2,5-pyridinediols provided compound **1** (Scheme 1) instead of 2,3-PQ or 2,5-PQ [4]. In fact, due to the facile solvation of the C=N bond in PQs, only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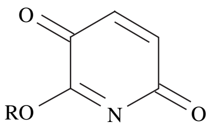
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Scheme 1.

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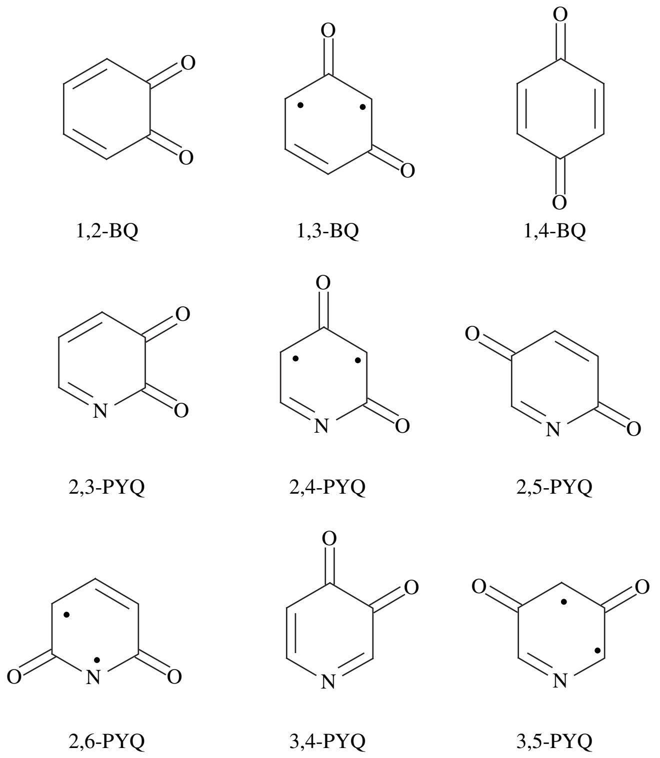

Fig. 1. Benzoquinones (BQs) and pyridoquinones (PQs).

azaquinones such as **2** are known [5]. Thermal rearrangement of 2,3-bis-azido-1,4-quinones provided the corresponding 1, 4-pyridoquinones. In contrast to 2,3- and 2,5-PQs, there are little literature reports on the isomeric 3,4-PQ [1].

2. Results and discussion

The results of *ab initio* calculations for benzoquinones (BQs) and pyridoquinones (PQs) are shown in Figs. 2 and 3 and Tables 1 and 2. According to these calculations, 1,4-BQ is the most stable isomer of benzoquinones in agreement with the experimental results [6]. 1,2-BQ is 28.83 kJ mol^{-1} less stable than the 1,4-isomer. This difference may be attributed to the dipolar repulsion between the adjacent electron pairs in 1,2-BQ (see Fig. 4). Both the classical benzoquinones are more stable than the non-classical *meta*-isomer (see Table 1).

For pyridoquinones, the 2,5-PQ is the most stable isomer by all methods. The 2,3-PQ is 18.26 kJ mol^{-1} less stable than 2,5-isomer due to the dipolar electron pair repulsions (Fig. 4). 3,4-PQ, which is 43.21 kJ mol^{-1} less stable than 2,5-PQ, is predicted to be the third stable isomer. As shown in Table 2, *m*-pyridoquinones are less stable than the classical isomers. Both HF and DFT methods predict the triplet (T) electronic configurations of the non-classical *meta*-benzoquinone and pyridoquinones to be more stable than the singlet (S) configurations, due to the higher multiplicity; however, predictions

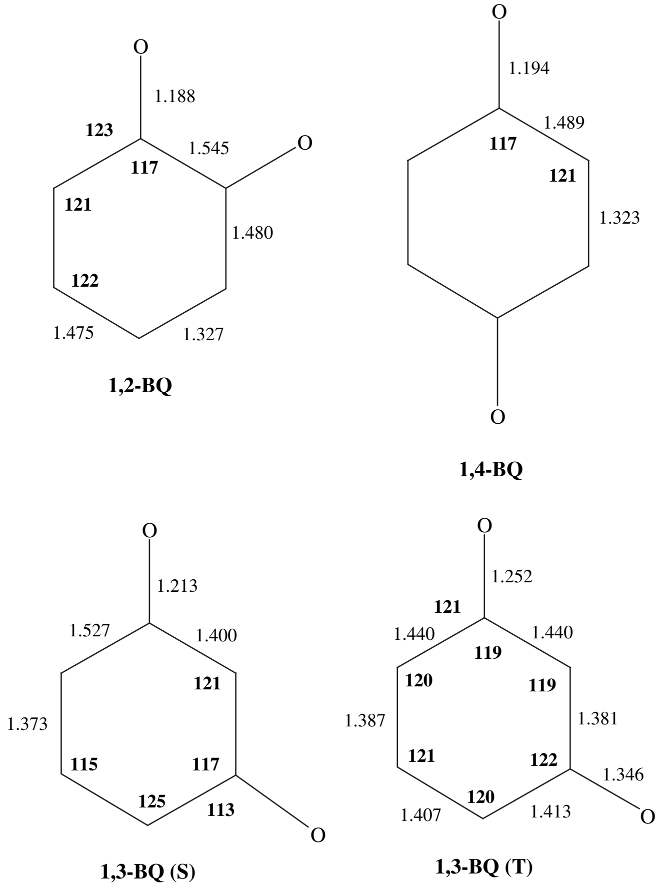

Fig. 2. Bond lengths (in Å) and bond angles (in °) in optimized geometries of benzoquinones (BQs).

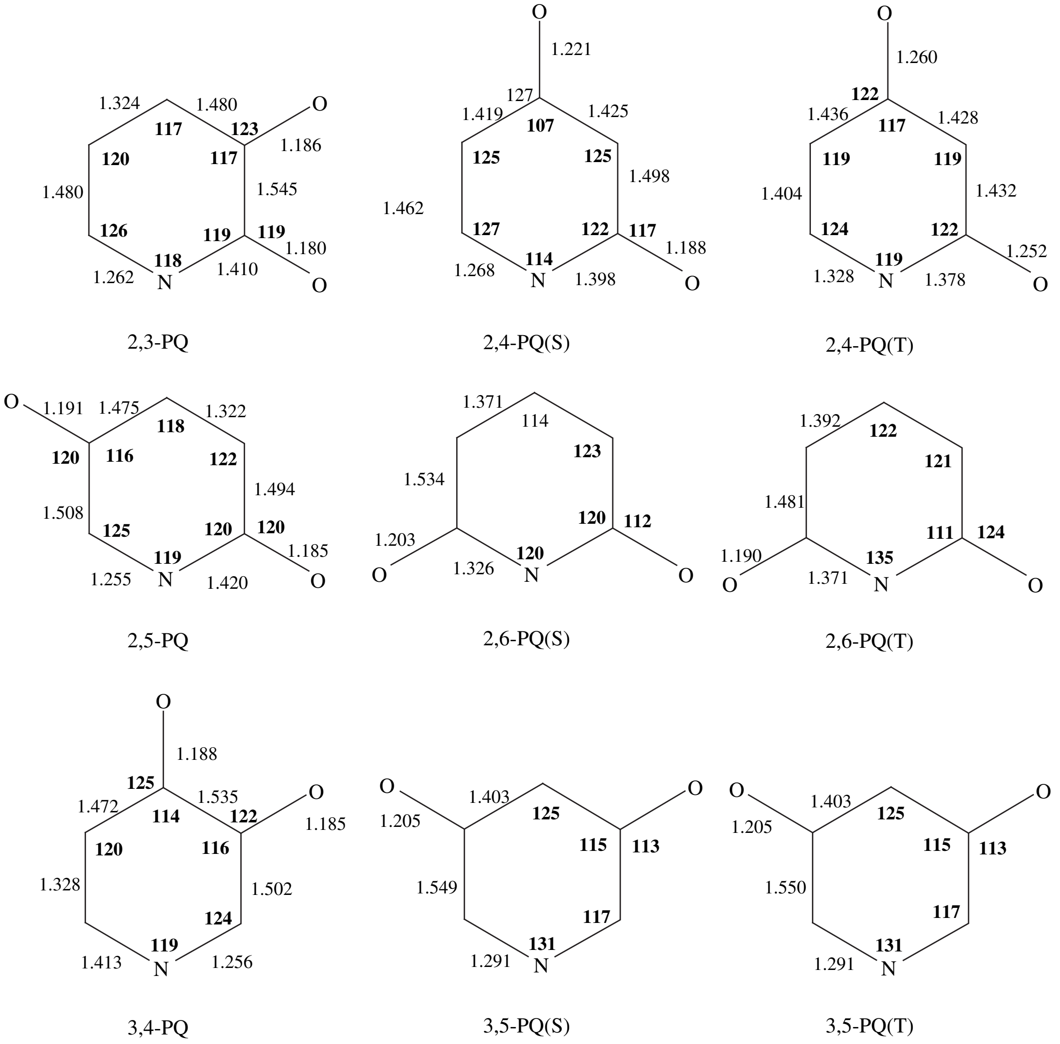

Fig. 3. Bond lengths (in Å) and bond angles (in °) in optimized geometries of pyridoquinones (PQs).

Table 1
Calculated total and zero-point vibrational energies (*Hartree*) and relative energies (including zero-point energy, kJ mol^{-1}, in parentheses) for benzoquinones (BQs)

Structure	1,4-BQ	1,2-BQ	1,3-BQ	
			(T)	(S)
HF/6-31G**	−379.24258 (0.00)	−379.22842 (37.07)	−379.21371 (65.81)	−379.13662 (270.37)
ZPE	0.0921	0.0921	0.08267	0.0889
B3LYP/6-31G**	−381.45774 (0.00)	−381.44666 (28.83)	−381.41242 (112.55)	−381.37267 (211.17)
ZPE	0.0852	0.0851	0.0827	0.0805
MP2/6-31G**//HF/6-31G**	−380.34966 (0.00)	−380.33864 (28.95)	−380.24740 (268.48)	−380.24722 (268.95)
MP2/6-31G**//B3LYP/6-31G**	−380.35600 (0.00)	−380.34527 (28.17)	−380.2527 (271.22)	−380.25412 (267.48)

Zero-point vibrational energy is scaled by a factor of 0.9135 for HF and 0.9804 for B3LYP methods to eliminate known errors in calculations.

Table 2
Calculated heats of formation (kJ mol^{-1}), total and zero-point vibrational energies (*Hartree*) and relative energies (including zero-point energy, kJ mol^{-1}, in parentheses) for pyridoquinones (PQs)

Structure	2,5-PQ	2,3-PQ	3,4-PQ	3,5-PQ		2,4-PQ		2,6-PQ	
				(T)	(S)	(T)	(S)	(T)	(S)
AM1	−42.31 (0.00)	−35.80 (6.51)	−11.69 (30.62)	19.90 (62.21)	174.85 (217.16)	46.66 (88.97)	226.55 (268.86)	148.74 (191.05)	213.59 (255.90)
HF/6-31G**	−395.23033 (0.00)	−395.22084 (24.96)	−395.21056 (51.73)	−395.10274 (311.28)	−394.98849 (461.08)	−395.20340 (57.70)	−395.11011 (307.57)	−395.19826 (72.86)	−395.14754 (211.38)
ZPE	0.0797	0.0797	0.07965	0.0698	0.0763	0.0743	0.0764	0.0750	0.0772
B3LYP/6-31G**	−397.48895 (0.00)	−397.48171 (18.85)	−397.47249 (43.21)	−397.43968 (129.35)	−397.40363 (210.22)	−397.43933 (123.26)	−397.39982 (234.59)	−397.42621 (154.93)	−397.42028 (171.14)
ZPE	0.0731	0.0730	0.0729	0.0708	0.0677	0.0704	0.07331	0.0693	0.695
MP2/6-31G**//HF/6-31G**	−396.36235 (0.00)	−396.35529 (18.52)	−396.34575 (43.58)	−396.23112 (344.53)	−396.23599 (331.74)	−396.25493 (282.02)	−396.26998 (242.50)	−396.26502 (255.52)	−396.27890 (219.08)
MP2/6-31G**//B3LYP/6-31G**	−396.36978 (0.00)	−396.36282 (18.26)	−396.35331 (43.24)	−396.25756 (294.62)	−396.26830 (266.42)	−396.25631 (279.9)	−396.27929 (273.56)	−396.26753 (268.44)	−396.28716 (216.91)

Zero-point vibrational energy is scaled by a factor of 0.9135 for HF and 0.9804 for B3LYP methods to eliminate known errors in calculations.

made by MP2 methods for the triplet and singlet configurations are reversed.

Selected geometrical data for benzoquinones and pyridoquinones are given in Figs. 2 and 3. According to all the methods employed, BQs and PQs are planar. The C=O bond lengths in the *meta*-isomer of PQs and BQs are longer than those calculated for the classical isomers. Carbon–carbon and carbon–nitrogen double bonds in classical BQs and PQs are shorter than the corresponding bonds in the non-classical *meta*-quinones. These results indicate that some other resonance structures such as those shown in Fig. 5 for 1,3-BQ and 2,4-PQ may become important in the resonance hybrides of *meta*-pyridoquinones.

In summary, *ab initio* calculations provide a picture of pyridoquinones from both structural and energetic points of view. 2,5-PQ is the most stable isomer of PQs. 2,3-PQ and 3,4-PQ are calculated to be 18.26 and 43.21 kJ mol^{-1} less stable than the 2,5-isomer. The singlet configurations of 3,5-PQ, 2,4-PQ, and 2,6-PQ are 6–50 kJ mol^{-1} more stable than the corresponding triplet configurations. It would be valuable, of course, to have direct structural data on pyridoquinones for comparison with the results of the *ab initio* calculations.

3. Calculations

Semiemprical calculations were carried out using AM1 method with MOPAC 7.0 program package [7,8]. Energy minimum geometries were located by minimizing energy, with respect to all geometrical coordinates, and without imposing any symmetry constrains. The AM1 results were used as input for the *ab initio* calculations, which were carried out using GUASSIAN 98 [9] at the HF/6-31G** and B3LYP/6-31G** levels of theory for geometry optimization, and MP2/6-31G**//HF/6-31G** and MP2/6-31G**//B3LYP/6-31G** for a single point total energy calculation. Vibrational frequencies were calculated at 6-31G** level for all geometries, which were confirmed to have zero imaginary frequency. The frequencies were scaled by a factor of 0.9135 for HF and 0.9804 for B3LYP methods and used for computation of the zero-point vibrational energies [10–13].

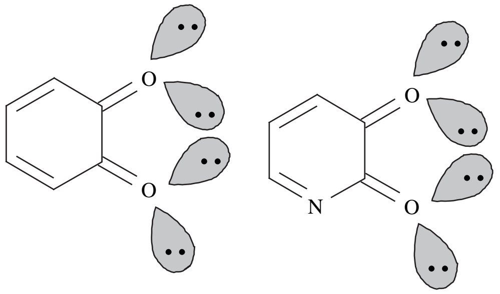

Fig. 4. Repulsive interactions of adjacent electron pairs in 1,2-BQ and 1,2-PQ.

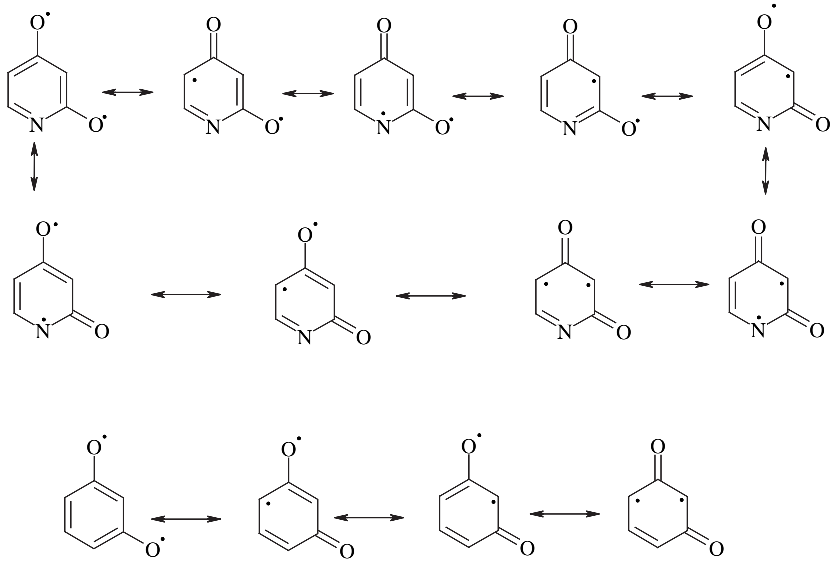

Fig. 5. Resonance structures for 1,3-BQ and 2,4-PQ.

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