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Dyes and Pigments 75 (2007) 474–478
DYES and PIGMENTS
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Ab initio SCF-MO study of quinones of pyridine

Issa Yavari [a,b,*], Nader Zabarjad-Shiraz [b,c]

[a] *Department of Chemistry, Tarbiat Modarres University, PO Box 14115-175, Tehran, Iran*
[b] *Chemistry Department, Science and Research Campus, Islamic Azad University, Ponak, Tehran, Iran*
[c] *Department of Chemistry, Islamic Azad University, Central Tehran Branch, Tehran, Iran*

Received 19 June 2006; accepted 22 June 2006
Available online 28 August 2006

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.

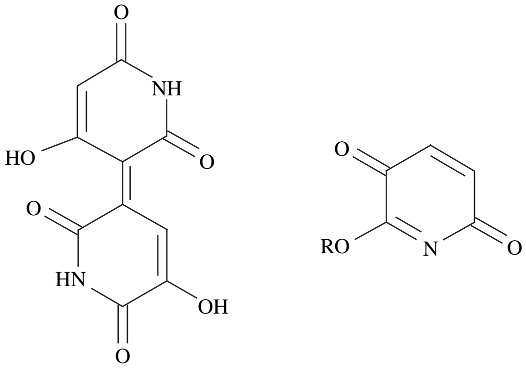
Keywords: Ab initio calculations; Molecular modelling; Pyridoquinones; Benzoquinones

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



1 **2**

Scheme 1.

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* Corresponding author. Department of Chemistry, Tarbiat Modarres University, PO Box 14115-175, Tehran, Iran. Tel.: +98 21 88006631; fax: +98 21 88006544.

E-mail address: yavarisa@modares.ac.ir (I. Yavari).

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doi:10.1016/j.dyepig.2006.06.024

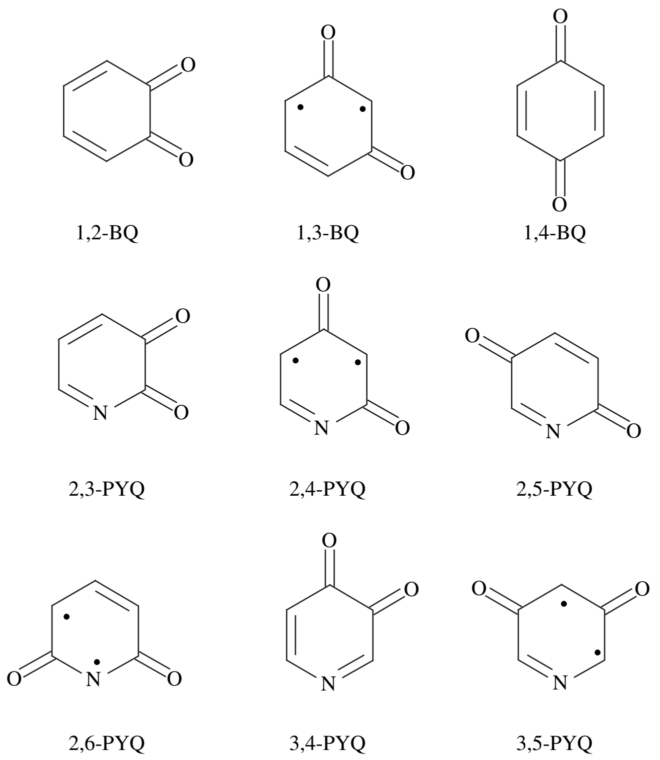

1,2-BQ 1,3-BQ 1,4-BQ
2,3-PYQ 2,4-PYQ 2,5-PYQ
2,6-PYQ 3,4-PYQ 3,5-PYQ

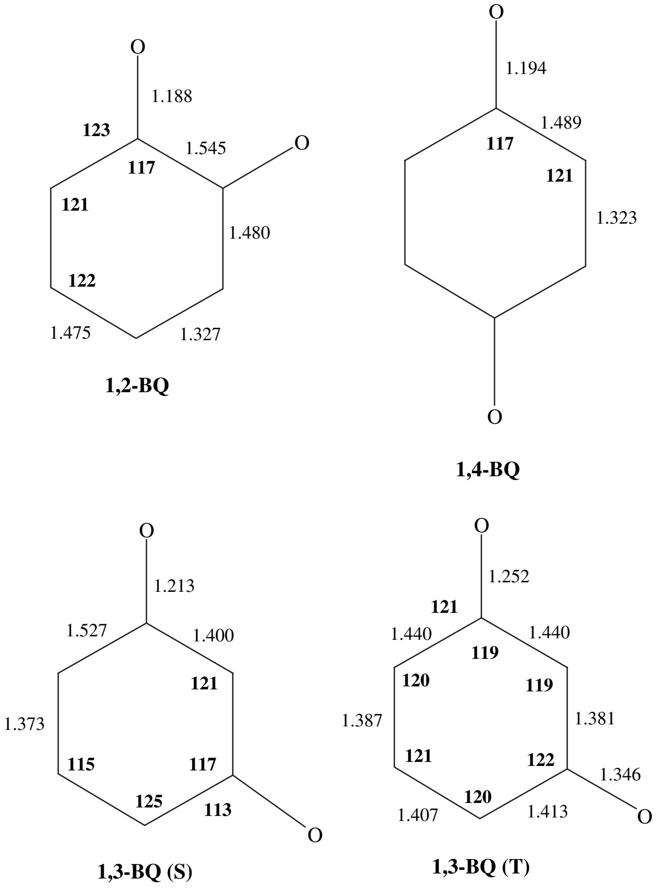
Fig. 1. Benzoquinones (BQs) and pyridoquinones (PQs).

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



1,2-BQ **1,4-BQ**
1,3-BQ (S) **1,3-BQ (T)**

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