



Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Theoretical investigations of the structures and electronic spectra of 8-hydroxyquinoline derivatives



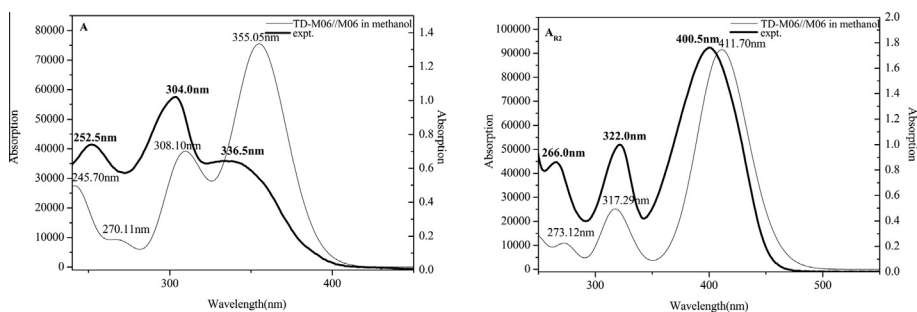
Pan Ning, Tiegang Ren, Yanxin Zhang, Jinglai Zhang*

Institute of Environmental and Analytical Sciences, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, China

HIGHLIGHTS

- The ground state of the two groups compounds were optimized based on 6-31G (d) basis set of B3LYP method.
- UV absorption spectra are simulated through TD-DFT method with PCM model.
- Explained the red shift behavior in the electronic spectra of products.
- The reaction products of two sets of experiments are confirmed reasonably with theoretical calculations.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 March 2013

Received in revised form 7 June 2013

Accepted 19 June 2013

Available online 1 July 2013

Keywords:

B3LYP

M06

8-Hydroxyquinoline

Electronic spectra

Red shift

ABSTRACT

The spectroscopic properties of 8-hydroxyquinoline derivatives are theoretically investigated by means of density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods. The target molecules are divided into two groups: group (I): (*E*)-2-(2-(3,5-dimethyl-1-phenyl-1*H*-pyrazol-4-yl)vinyl)quinolin-8-ol (A), together with corresponding potential reaction products of A with acetic acid, i.e., (*E*)-2-(2-(3,5-dimethyl-1-phenyl-1*H*-pyrazol-4-yl)vinyl)quinolin-8-yl acetate (A_{R1}), and (*E*)-2-(2-(3,5-dimethyl-1-phenyl-1*H*-pyrazol-4-yl)vinyl)-8-hydroxyquinolinium (A_{R2}); group (II): (*E*)-2-(2-(1-(4-chlorophenyl)-3,5-dimethyl-1*H*-pyrazol-4-yl)vinyl)quinolin-8-ol (B), as well as potential reaction products of B with acetic acid, i.e., (*E*)-2-(2-(1-(4-chlorophenyl)-3,5-dimethyl-1*H*-pyrazol-4-yl)vinyl)quinolin-8-yl acetate (B_{R1}), and (*E*)-2-(2-(1-(4-chlorophenyl)-3,5-dimethyl-1*H*-pyrazol-4-yl)vinyl)-8-hydroxyquinolinium (B_{R2}). The geometries are optimized by B3LYP and M06 methods. The results indicate that product molecules tend to be effectively planar compared with reactants. Subsequently, UV absorption spectra are simulated through TD-DFT method with PCM model to further confirm the reasonable products of two reactions. A_{R2} and B_{R2} are identified as the target molecules through the experimental spectra for the real products. It is worth noting that the maximum absorption wavelengths of compounds A_{R2} and B_{R2} present prominent red shift compared the initial reactants A and B, respectively, which should be ascribed to the enhance planarity of products that mentioned above and the decreased HOMO–LUMO energy gap. Geometric structures and optical properties for corresponding compounds are discussed in detail.

© 2013 Elsevier B.V. All rights reserved.

Introduction

As a family of very important quinoline compounds, 8-hydroxyquinoline derivatives have attracted considerable attention during

the past three decades. This should be ascribed to their diverse spectrum of industrial applications and biological activities. They are not only used as substructures for synthesis of effective HIV-1 integrase inhibitor or other bioactive compounds [1–4], but also have potential use in ion recognition for different metal ions [5–11] and emission and electron conduction layers in organic light emitting devices [12].

* Corresponding author. Tel./fax: +86 378 3881589.

E-mail address: zhangjinglai@henu.edu.cn (J. Zhang).

Previous experiments have reported that species and positions of substituent incorporated in the quinoline rings would make a difference in the bioactivities. Recently, a series of 8-hydroxyquinoline derivatives have synthesized by the author through incorporation of pyrazole group into different places. Interestingly, hyperchromicity was observed by the addition of acetic acid to two of the aforementioned derivatives (*E*)-2-(2-(3,5-dimethyl-1-phenyl-1*H*-pyrazol-4-yl)vinyl)quinolin-8-ol (A) and (*E*)-2-(2-(1-(4-chlorophenyl)-3,5-dimethyl-1*H*-pyrazol-4-yl)vinyl)quinolin-8-ol (B). This noteworthy phenomenon addresses two questions: (i) Can (A) or (B) react with acetic acid? (ii) What causes the red-shift in the absorption bands?

Because there is no definite experimental account for the two questions, we attempt to develop elucidation theoretically in this work. For clarity, a speculation is put forward that there exist two possible products in terms of reaction. (*E*)-2-(2-(3,5-dimethyl-1-phenyl-1*H*-pyrazol-4-yl)vinyl)quinolin-8-yl acetate (A_{R1}) and (*E*)-2-(2-(3,5-dimethyl-1-phenyl-1*H*-pyrazol-4-yl)vinyl)-8-hydroxyquinolinium (A_{R2}) are adopted as starting reactant A; (*E*)-2-(2-(1-(4-chlorophenyl)-3,5-dimethyl-1*H*-pyrazol-4-yl)vinyl)quinolin-8-yl acetate (B_{R1}), and (*E*)-2-(2-(1-(4-chlorophenyl)-3,5-dimethyl-1*H*-pyrazol-4-yl)vinyl)-8-hydroxyquinolinium (B_{R2}) are regarded as reactant B. Optimizations of the six above mentioned compounds are performed by the density functional theory (DFT) method. Next, time-dependent density functional theory (TD-DFT) method is employed to obtain the absorption spectra with the DFT-optimized structures. We will demonstrate that the theoretical investigation can help us to identify the reasonable reaction products of compounds A and B in acetic acid, and elucidate spectroscopic properties of product molecules.

Computational methods

Two quantum mechanical models based on DFT, namely, B3LYP [13–16] and M06 [17], are utilized to optimize the equilibrium geometries of two reactants, i.e., A and B, and four possible products, i.e., A_{R1} , A_{R2} , B_{R1} , and B_{R2} in the 1A electronic ground state. All geometry optimizations are performed without any symmetry constraints. 6-31G(d) [18,19] basis set is adopted in the geometry optimizations for all compounds. The computation of vibrational frequencies is undertaken at the same level to verify the nature of optimized stationary points. The nature of low-lying excited states is explored using time-dependent density functional theory

(TD-DFT) [20–22] with cc-pVDZ [23–25] basis set to obtain the absorption spectra. Considering that solvent effect plays an important role in spectroscopic properties of organic molecules, the polarized continuum model (PCM) [26,27] with methanol chosen from the available experiment has been employed to assess the solvent effects as implemented within the solvent reaction field using the optimized equilibrium structures in the gas phase. Applications of TD-DFT approaches in conjunction with PCM model for organic conjugated molecules have been reported and get considerable good results [28].

All theoretical calculations are carried out by using the Gaussian 09 [29] program package.

Results and discussion

Geometries and stabilities

The schematic structures of compounds in group (I) and group (II) are depicted in Fig. S1 (see Supplementary information). Primary geometric parameters (selected bonds lengths, angles and dihedral angles) optimized by B3LYP and M06 methods with 6-31G(d) basis set are tabulated in Tables 1 and 2, respectively.

As no experimental parameters for title compounds are available for direct comparison, two different functionals are selected to ensure the reliability of theoretical results. The maximum discrepancy between B3LYP and M06 calculations is within 0.02 Å for bond length and 2° for angle, which suggests that the selected DFT methods could reasonably describe the geometries.

According to the primary geometric parameters in Table 1, no significant changes are examined in product A_{R1} . While in terms of A_{R2} , it is interested that the bond lengths connecting the quinoline ring and the pyrazole ring are averaged with the double bond C11–C12 elongated by 0.021 Å and C8–C11 and C12–C13 shortened by 0.036 and 0.031 Å, respectively. Another remarkable variation with dihedral angle C11–C12–C13–C18 being 173.92° at M06 optimizations expands the delocalization of the conjugated systems, which is expected to contribute to the average tendency of related bond lengths. The same behavior takes place in group (II) compounds as displayed in Table 2, which will not be discussed in detail any more. The absence of single crystal for X-ray diffraction data brings about the challenge to verify the structures of products, thus spectroscopic properties are needed to be investigated further.

Table 1

Primary geometric parameters (bond lengths in Å, angles and dihedral angles in °) for compounds A, A_{R1} and A_{R2} in the ground state optimized at different levels of theory.

Atom number	A		A_{R1}		A_{R2}	
	B3LYP	M06	B3LYP	M06	B3LYP	M06
C3–C4	1.4342	1.4287	1.4264	1.4213	1.4121	1.4061
C3–O14	1.3602	1.3500	1.3878	1.3763	1.3630	1.3532
C4–C5	1.4307	1.4229	1.4300	1.4211	1.4140	1.4070
C4–N7	1.3556	1.3507	1.3563	1.3528	1.3779	1.3745
N7–C8	1.3313	1.3245	1.3315	1.3253	1.3576	1.3519
C8–C11	1.4643	1.4582	1.4635	1.4578	1.4282	1.4222
C11–C12	1.3526	1.3468	1.3529	1.3474	1.3733	1.3674
C12–C13	1.4497	1.4445	1.4487	1.4424	1.4185	1.4136
N16–N17	1.3688	1.3611	1.3688	1.3613	1.3795	1.3711
N16–C19	1.4215	1.4159	1.4221	1.4166	1.4312	1.4260
O14–C3–C4	116.96	116.91	119.08	118.19	115.16	115.22
C3–C4–N7	118.67	118.59	119.02	118.80	119.52	119.49
N7–C8–C11	115.15	115.38	115.30	115.82	117.70	117.43
C9–C8–C11	123.15	122.62	123.00	122.21	126.29	126.33
C12–C13–C18	125.13	125.80	125.18	125.19	124.45	125.04
C6–C5–C4–N7	–180.00	–179.73	–179.04	–178.99	–180.00	179.96
C8–C11–C12–C13	178.87	178.08	178.96	178.80	179.50	179.87
C11–C12–C13–C18	163.25	159.44	163.10	161.63	174.75	173.92
N17–N16–C19–C20	–139.25	–141.10	–138.79	–139.93	–130.94	–132.22

Download English Version:

<https://daneshyari.com/en/article/7673411>

Download Persian Version:

<https://daneshyari.com/article/7673411>

[Daneshyari.com](https://daneshyari.com)