



## 2,5-bis(2'-benzoxazolyl)hydroquinone (BBHQ), a dually fluorescent ESIPT system revisited: XRD analysis and supersonic jet studies of deuterated species

A. Vdovin <sup>a,1</sup>, E. Karpiuk <sup>b</sup>, J. Lipkowski <sup>c</sup>, A. Listkowski <sup>c</sup>, M. Kijak <sup>a</sup>, A. Grabowska <sup>a</sup>, J. Sepi $\text{ł}$  <sup>a,\*</sup>

<sup>a</sup> Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

<sup>b</sup> Institute of Physics, Polish Academy of Science, Warsaw, Poland

<sup>c</sup> Kardynał Wyszyński University, Warsaw, Poland

### ARTICLE INFO

#### Article history:

Received 15 March 2018

Received in revised form

6 June 2018

Accepted 11 June 2018

Available online 13 June 2018

#### Keywords:

ESIPT-Molecule

Dual emission

X-ray analysis

Mass selected spectroscopy

Deuterium substitution effect

### ABSTRACT

The new experimental results of the dually emitting ESIPT molecule, the 2,5-bis(2'-benzoxazolyl)hydroquinone (BBHQ) are presented. The results of the XRD analysis are the following: the unit cell of the monoclinic symmetry contains the perfectly planar BBHQ molecules, with two O-H...N intramolecular hydrogen bonds. There are two molecules in the asymmetric part of the cell, one – the single BBHQ structure and the other being superposition of the main component with the site occupation factor (sof) 77.4(6)% and the minor one: sof = 22.6(6)% - the same structure rotated by 180° along the long axis of the molecule. The remarkable agreement of the experimentally determined molecular structure with theoretical results reported in the literature, was observed. The dispersed fluorescence spectra of jet cooled molecule, covering two fluorescence bands were measured. It was observed that the intensity ratio of both emissions was dependent on excitation by subsequent quanta of the leading vibration of 114 cm<sup>-1</sup>. The height of the barrier separating the two emitting tautomers was estimated as ~340 cm<sup>-1</sup>. Moreover, the two independent experimental tools, the double-resonance fluorescence depletion (DFD) and mass selected two photon ionization (R2PI) techniques were applied to the partially deuterated jet cooled BBHQ enabling the separation and identification of four different deuterated species, some not known until now.

© 2018 Elsevier B.V. All rights reserved.

### 1. Introduction

The Excited State Intramolecular Proton Transfer (ESIPT) reactions have been studied for several decades becoming particularly fruitful branch of molecular spectroscopy. They belong to the fastest chemical reactions known in nature, studied from purely academic point of view [1–4] and also as subjects of numerous applications, like lasing systems [5], optical switches [6], ionic sensors [7], solar concentrators [8] or molecules used in photodynamic therapy [9].

The majority of ESIPT systems reported since the pioneering

work of A.Weller [10], have one intramolecular hydrogen bond “preparing” the molecule for an ultrafast phototautomerization reaction. The reacting system sends the signal of fluorescence emitted typically by the reaction product – a phototautomer. The ultrafast proton transfer reaction leaves no chance for the emission of the primary excited structure. The potential energy surfaces of the reactive S<sub>1</sub> states have in majority of systems only one stable minimum corresponding to the phototautomer which in the ground state (S<sub>0</sub>) does not exist as a chemical entity. This property has very important spectroscopical consequences: the typical absorption/emission spectrum of the ESIPT system is characterized by a very large Stokes shift reaching sometimes 6000–10000 cm<sup>-1</sup> of separation between absorption and phototautomeric emission spectra. It is obvious that in such molecules no reabsorption takes place.

Among the ESIPT molecules, there are however the dually fluorescent ones emitting the radiation of both phototautomers:

\* Corresponding author.

E-mail address: [jsepiol@ichf.edu.pl](mailto:jsepiol@ichf.edu.pl) (J. Sepi $\text{ł}$ ).

<sup>1</sup> Present address: Philips Lighting Res., High Tech. Campus 7, 5656 AE Eindhoven, The Netherlands.

the primary structure, and the product of ESIPT reaction.

One of the most studied families of dually fluorescent molecules are the derivatives of bis-benzoxazole. The “mother” compound of this family is the 2,5-bis(2'-benzoxazolyl)hydroquinone, BBHQ (Fig. 1). This molecule is a particularly interesting system. It was studied for many years from several points of view. Thus, the dual emission was observed in condensed phase [11,12] as well as in molecular jets [13,14], with the study of isotope effects of OH → OD substitution [13]; in solutions the ultrafast kinetics of ESIPT reaction and the equilibration of two  $S_1$  excited tautomers, the dienol and mono-keto form, was also reported [15,16].

BBHQ and related systems are still an object of continuous interest. Among others, the two papers on BBHQ deserve special attention. One [17] simulating the multiplet structure of the excitation spectrum of BBHQ observed at phototautomeric fluorescence in jet cooled system. The simulation suggests the contribution of the diketo-tautomer in the  $S_1$  state. The second publication [18] reports on the results of Zero Kinetic Energy (ZEKE) detection of photoelectrons. The two energy thresholds for ionization of jet cooled BBHQ were assigned to the excited enol and monoketo forms. Moreover, several papers on molecular modeling [19,20] and the new applications [21,22] appeared in the last years. Last but not least, the polarity dependent ultrafast kinetics, the calculation of the potential energy curves of the  $S_0$  and  $S_1$  states were published recently [23,24].

In the present work we report on the results of experiments illustrating new aspects of spectroscopy of BBHQ, e.g. the effect of breaking the symmetry of the molecule by the isotopic substitution and ESIPT reaction.

We also show for the first time the results of X-rays diffraction (XRD) experiments of BBHQ crystals. However, some X-rays data on the related structures can be found in the literature. Thus the 2-(2'-hydroxyphenyl)benzoxazole (HBO), a molecule structurally close to “one half” of BBHQ, was reported to exist in the solid state, as a 1:1 mixture of the two rotamers differing by the intramolecular H-bonds [25]. The next system whose XRD analysis was recently reported, is the symmetric ditertbutyl-derivative of BBHQ. Here, according to Ref. [20], the structure is composed of one rotamer with both, relatively short (1.888 Å) hydrogen bonds O-H...N.

## 2. Experimental

### 2.1. Materials and methods

BBHQ was synthesized and purified as in Ref. [26]. Crystallization of BBHQ was tried with the use of a variety of solvents, best results were obtained with benzene or acetylacetone. Seven crystals were used for X-ray experiments. The best crystal suitable for the structure analysis was obtained by slow evaporation of BBHQ solution in acetylacetone, at room temperature. The needle shaped specimen was mounted on the Bruker D8 single crystal diffractometer and diffraction data were collected at temperatures from 100 K to room temperature.

The experimental setup for the laser induced fluorescence in supersonic jets has been described previously [27]. BBHQ vapors mixed with helium carrier gas were expanded at 3 atm stagnation pressure into the vacuum chamber through the 0.5 mm pulsed

nozzle (General Valve Series 9). The sample was heated typically up to 540 K. Deuteration of BBHQ was achieved by adding  $D_2O$  or  $CH_3OD$  to the expansion mixture. Commercially available  $D_2O$  and  $CH_3OD$  (Dr. Glaser, AG Basel, isotopic purity 99.8 and 99.65%, respectively) were used. The partial vapor pressure of the solvent was kept typically between 0.2 and 4 torr. Under these conditions the relative abundance of the  $BBHQ_{(OH,OD)}$  and  $BBHQ_{(OD,OD)}$  in the beam was of the order of 25–35% for each of these isotopomers.

Fluorescence was excited by the home-built dye laser (pumped by the Nd-YAG laser) operating with Stilbene 3 dye, with  $0.3\text{ cm}^{-1}$  bandwidth and  $30\ \mu\text{J}$  pulse energy. Laser induced fluorescence excitation (LIFE) spectra were recorded with a photomultiplier (Hamamatsu R2949). The spectra of primarily excited enol form, resulting in “blue” emission (420–530 nm), and proton transferred keto form, resulting in “red” emission (550–700 nm) were measured using Schott UG11 and OG590 filters, respectively.

Dispersed fluorescence spectra were measured by a 0.275 m spectrograph (Spectra Pro 275, Acton Research), equipped with a 1200 groves/mm grating, and with a CCD camera (Princeton Instruments LN). The resulting spectral resolution was about  $30\text{ cm}^{-1}$ . The spectra covering broader spectral range, including emission from both tautomeric forms, were recorded with another grating (300 groves/mm) at the expense of spectral resolution ( $120\text{ cm}^{-1}$ ).

Double-resonance fluorescence depletion (DFD) technique was applied to reveal spectral features resulting from possible contributions of different conformers, isotopomers or impurities. A narrow band ( $<0.1\text{ cm}^{-1}$ ) optical parametric oscillator (OPO, Sunlite EX, Continuum) pumped by a Nd:YAG laser (Powerlite Precision 8000, Continuum) was used as a „probe“ laser, with pulses delayed by ~ 150 ns in respect to dye laser used as a „pump“.

Mass-selected resonant two-photon ionization spectra were measured with the instrumentation described previously [28]. Several modifications were introduced to the time-of-flight (TOF) laser mass spectrometer to improve its mass resolution. With a 50 cm long flight tube of mass spectrometer the achieved mass resolution ( $M/\Delta M$ ) was 600 without implementing a reflectron stage. This resolution was sufficient to resolve H/D isotopomers of BBHQ molecule (mass 342.30 amu). Supersonic beam was produced with Ne as a carrier gas. The tunable nanosecond dye laser pulses were used to excite the molecules to the first excited electronic state. The OPO pulses doubled in KDP crystal (280,3 nm after doubling) were applied to ionize the molecules. The typical energies of excitation and ionization pulses were  $30\ \mu\text{J}$  and  $60\ \mu\text{J}$ , respectively. The temporal jitter of the time delay between the two laser pulses was typically less than 1 ns.

## 3. Results

### 3.1. X-ray analysis

The immediate symmetry displayed on diffraction patterns is  $2_1$ . However, both unit cell parameters and the molecular structure which appeared after solution, may be indicative of higher symmetry. Thus, the structure determination procedure adopted was a two step process: structure solution in the orthorhombic symmetry and structure refinement in the monoclinic space group  $P2_1$ .

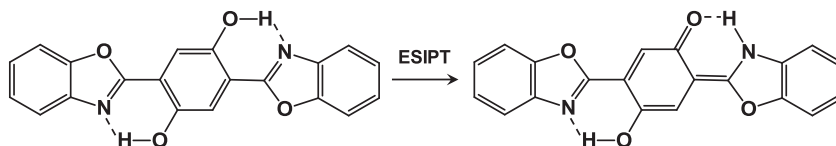


Fig. 1. ESIPT reaction in BBHQ on the level of the  $S_1$  state.

Download English Version:

<https://daneshyari.com/en/article/7807009>

Download Persian Version:

<https://daneshyari.com/article/7807009>

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