

# TDDFT Calculations of Electronic Spectra of Benzoxazoles Undergoing Excited State Proton Transfer

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**Abstract** Energies and oscillator strengths of vertical transitions for various rotameric and tautomeric species of 2-(2'-hydroxyphenyl)benzoxazole (HBO), 2,5-bis(2-benzoxazolyl)phenol (DBP) and 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) have been calculated in the ground and first excited states with the use of TDDFT methods. The TDDFT results demonstrate good correspondence to the frequencies of absorption and fluorescence bands of the benzoxazoles reported for measurements in supersonic jets and solution, but fail to predict relative energies of the enol and keto tautomers of DBP and BBHQ in the excited state. Low intensity of the fluorescence bands attributed to the conformations of HBO and DBP that do not undergo excited state proton transfer is shown to be caused by low concentrations of the conformations in the ground state. For the three compounds large-amplitude twisting of the keto tautomer is found to be one of radiationless processes resulting in decrease of the fluorescence with a large Stokes shift.

**Keywords** Density functional theory · Excited state proton transfer · Benzoxazole derivatives · Fluorescence · Absorption · Radiationless transitions

## Introduction

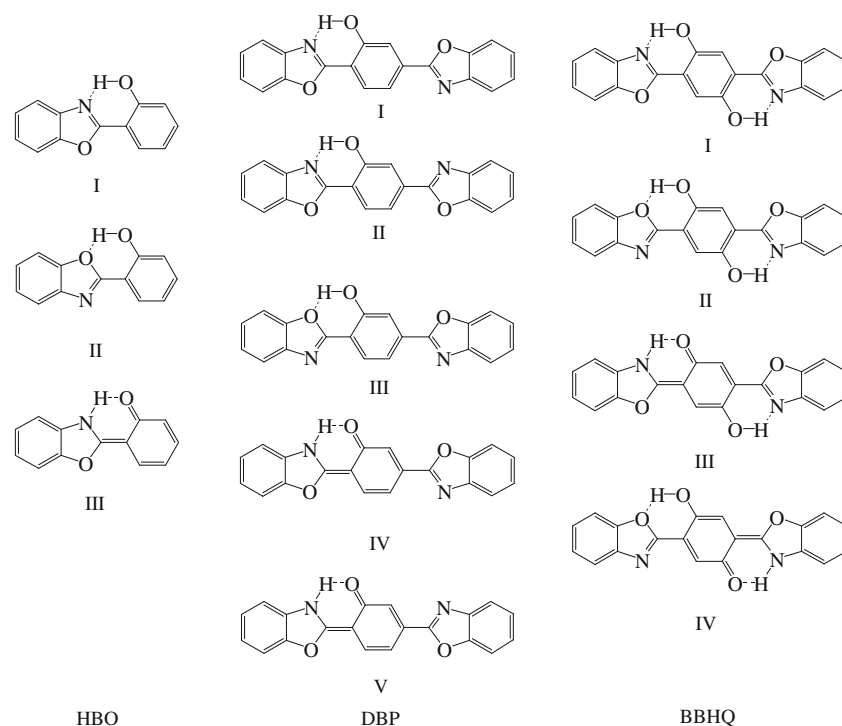
Excited state proton transfer (ESIPT) has been extensively studied both experimentally and theoretically regarding its importance as a photochemical reaction as well as its relevance for various applications [1–7]. 2-(2'-hydroxyphenyl)benzoxazole (HBO), 2,5-bis(2-benzoxazolyl)phenol (DBP)

and 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) are benzoxazole derivatives that exhibit ESIPT from the phenolic hydroxy group to nitrogen atom, the tautomers are enol and keto structures [1, 8]. In the ground state the benzoxazoles possess intramolecular hydrogen bonds and can form rotamers with OH...N and OH...O H-bonds. Only the conformations with OH...N hydrogen bonds undergo ESIPT and show fluorescence with an anomalously large Stokes shift, the OH...O conformers of HBO and DBP have been supposed to be responsible for emission with a normal Stokes shift [9–13]. BBHQ has been found to have enol and keto structures that are in equilibrium in the excited state, the enol tautomer exhibits fluorescence with a normal Stokes shift [14–17]. Despite the presence of two identical hydrogen bonding sites in the molecule, only transfer of one proton has been identified to occur in the excited state of BBHQ [18, 19]. Some tautomeric and rotameric structures of molecules of HBO, DBP and BBHQ are shown in Fig. 1.

Quantum yield of tautomeric fluorescence of HBO in solution is strongly dependent on the viscosity of the solvent and temperature. The radiationless decay of the excited state has been attributed to large-amplitude twisting around the bond linking the phenol and benzoxazole moieties of the keto tautomer [20, 21]. A radiationless process with activation energy similar to the value found in HBO (about 0.15 eV) has been revealed for BBHQ in solution [14] and supersonic jets [16] but decay of the excited enol state has been proposed for explanation of the observations [14]. DBP demonstrates a high quantum yield (0.48) in solution [8] while a threshold of about 0.05 eV that triggers decrease of intensity of the keto fluorescence has been determined in supersonic jet conditions [13].

Quantum chemical description of ESIPT requires multireference methods involving dynamical electron correlation such as CASPT2 and MRCI because the excited states are expected to have crossing of potential energy surfaces (PES)

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**Fig. 1** Rotameric and tautomeric species of 2-(2'-hydroxyphenyl)benzoxazole (HBO), 2,5-bis(2-benzoxazolyl)phenol (DBP) and 2,5-bis(2-benzoxazolyl)phenol (BBHQ)

or conical intersections, however, time-dependent density functional theory (TDDFT) has been successfully applied to the calculation of excited state properties, PES and molecular dynamics simulations for the molecules of some substances undergoing the proton transfer in the excited state [22–24].

Theoretical studies on ESIP in HBO have been performed at semi-empirical and *ab initio* configuration interaction with single excitations (CIS) levels of theory. Semi-empirical calculations predict two minima that correspond to enol and keto tautomeric structures of HBO separated by a barrier both in the ground and excited state [25–29]. *Ab initio* Hartree-Fock and CIS calculations also yield two-well potential energy surfaces in the ground and excited state, but taking into account electron correlation by the MP2 perturbation method eliminates the barrier for back proton transfer in the ground state [30]. One minimum that corresponds to enol structure has been determined by DFT calculations performed for HBO, DBP and BBHQ in the ground state [31]. A TDDFT study of electronic absorption spectra of a number of benzazole derivatives, which include HBO, demonstrates good agreement of the calculated absorption and fluorescence wavelength with the experimental values, although the excited state structures of the molecules have not been optimized with TDDFT [32]. Semi-empirical calculations on BBHQ predict double-well PES and non-planar (skewed) structure of the keto tautomer, similar to the structure yielded by MNDO/H calculations on HBO [17, 33]. Theoretical modeling of ESIP in DBP has not been reported yet, but TDDFT calculations of the frequencies of absorption

bands of several related benzoxazolylphenoles demonstrate good correspondence to the measured values [34].

Rotamerism of HBO, DBP and BBHQ has been studied by quantum chemical calculations mainly in the ground state. It has been shown that the enol structures with OH...N hydrogen bonds are more stable by about 0.25 eV than the structures with OH...O hydrogen bonds [25, 30, 31, 34], excluding the AM1 results reported for HBO, which yield close values for the energies of conformations I and II [27, 28]. Rotation of the non-hydrogen-bridged benzoxazole moiety of DBP leads to structure II that has been found to be only by 0.01 eV less stable than structure I [31, 34]. In the excited state the AM1 semi-empirical calculations predict that rotamer II of HBO is less stable by about 0.07 eV than rotamer I while in the ground state the energy difference is 0.006 eV [28]. The CNDO/SCI calculations of the S<sub>1</sub> state of HBO predict a barrier of about 0.57 eV for the structure II to structure I conversion which is much higher than the barrier of 0.11 eV obtained with the AM1 method in the ground state. It has been concluded that the high value of the barrier in the excited state provides that the interconversion is too slow to occur within the lifetime of S<sub>1</sub> [27].

In the present paper we describe quantum chemical calculations of structure, potential energy surfaces and vertical transitions of molecules of HBO, DBP and BBHQ in the ground and first excited states with TDDFT methods. The purpose of the work is to describe theoretically observed features of the absorption and fluorescence spectra that are

caused by the existence of various tautomeric and rotameric species of the benzoxazole derivatives and to find out possible radiationless channels of decay of the excited state.

### Computational Details

All calculations have been performed with the use of the GAMESS [35, 36] program package employing the 6-31G (d,p) basis set and B3LYP functional. Optimization of structure and calculations of properties in the excited state have been performed with the TDDFT method.

The potential energy profile for ESIPT has been studied along the OH distance of the phenolic hydroxy moiety; remaining coordinates have been optimized for a given value of the OH stretching coordinate. Optimization of structure and calculation of the minimum energy path for ESIPT have been carried out under assumption of  $C_s$  symmetry of the molecules. The potential energy profiles for rotation around the inter-ring CC bond have been calculated taking the averaged value of the four dihedral CCCO and CCCN angles as a driving coordinate. Vibrational frequencies have been calculated for the optimized planar structures of HBO in the ground and excited states.

### Results and Discussion

Relative energies and dipole moments of the different planar rotameric and tautomeric structures (Fig. 1) optimized in the ground and first excited ( $\pi\pi^*$ ) states along with energies and oscillator strengths of the vertical transitions are collected in Tables 1, 2 and 3. In the ground state only a minimum that corresponds to the enol structure has been determined for all three compounds (Fig. 2). The enol structures with OH...O intramolecular hydrogen bond (Fig. 1, structures II of HBO and BBHQ, structure III of DBP) are predicted to have energy about 0.27 eV (0.26 eV with zero-point vibrational energy correction) above the most stable OH...N rotamers (structures I). This relation of the energies agrees with the results of the DFT calculations performed for HBO, DBP and BBHQ molecules [31], and MP2 calculations for HBO [30]. Hence, in thermodynamic equilibrium the number of OH...O molecules is expected to be small even at room temperature in comparison with that of OH...N rotamers. Intensity of the corresponding fluorescence bands is expected to be low due to low concentrations of the OH...O conformations in the ground state. This agrees with experimental results that for the molecules of HBO and DBP cooled in supersonic jets only the keto fluorescence has been observed [13, 25], and, in non-polar solvents, the normal Stokes shifted fluorescence has low intensity at room temperature [9–11]. The  $S_0$ – $S_1$  transition of the OH...O conformer is blue-shifted by about

0.11 eV while the energies of the  $S_0$ – $S_2$  transitions of OH...N and OH...O forms differ only by 0.02 eV. In the  $S_1$  state the energy difference between the enol OH...N and OH...O conformers is larger than in the ground state, the values are 0.58 eV for HBO, 0.29 eV for DBP and 0.36 eV for BBHQ.

The planar enol conformation of the molecule of DBP with the rotated non-hydrogen-bridged moiety (structure II) has the energy only 0.01 eV above the most stable structure I that implies the significant number of these species in the ground state. The calculated shift of the  $S_0$ – $S_1$  transition of rotamer II toward higher frequencies is in good agreement with the fluorescence excitation spectra measurements in supersonic jets [13]. The energy of the  $S_0$ – $S_2$  transition of structure II is predicted to be lower by about 0.03 eV than that of structure I.

The energy of the  $S_0$ – $S_1$  transition of structure II of BBHQ is shifted to the higher value by about 0.09 eV, while the  $S_0$ – $S_2$  transition is slightly (0.03 eV) red-shifted. The  $S_0$ – $S_3$  and  $S_0$ – $S_4$  transitions are dipole-forbidden for symmetry reasons, enol structure I of BBHQ optimized in the ground and excited state is very near the structure with  $C_{2h}$  symmetry.

Absorption of the enol species (both OH...N and OH...O) of the three compounds is strongly allowed for the transitions to the two lowest excited states  $S_1$  and  $S_2$ , which are  $\pi\pi^*$  states. The energies of the vertical transitions calculated with TDDFT are in good agreement with the measured energies of the absorption bands. The energies of the vertical  $S_1$ – $S_0$  transitions calculated for the enol structures of HBO and DBP with OH...O hydrogen bonds optimized in the  $S_1$  state are in good agreement with the frequencies of the fluorescence bands that demonstrate a normal Stokes shift in solution. The energies of the  $S_1$ – $S_0$  transitions of the enol structures with OH...N hydrogen bonds are calculated to be lower by 0.16 eV than those of the OH...O rotamers of HBO. For the BBHQ molecule the difference is 0.11 eV, for DBP the energies of the transitions are almost equal. The conformations with the OH...N hydrogen bonds can undergo ESIPT forming keto tautomers.

In the case of HBO, it has been found that the TDDFT calculations predict two minima that correspond to the enol and keto structures separated by a low barrier (Fig. 2). We have located a transition state for ESIPT by unconstrained search for the saddle point. The energy of the transition state is 0.02 eV above the  $S_1$  enol minimum and geometry is planar with OH distance of 1.182 Å. Although the minimum energy path along the OH distance is not an exact reaction coordinate the corresponding point on the potential energy profile has energy that deviate less than  $10^{-3}$  eV from the value of energy of the saddle point. The keto form (Fig. 1, structure III) is determined to be more stable, the energy difference is 0.19 eV. Consideration of harmonic zero-point vibrational energy gives a value of 0.18 eV. The dipole

**Table 1** Calculated values of relative energy (E), dipole moment ( $\mu$ ), energy of vertical transitions ( $\Delta E$ ), oscillator strength (f) and experimental values of energy of transitions ( $\Delta E_{\text{exp}}$ ) of different planar rotameric and tautomeric structures of HBO

Geometry	State	E / eV	$\mu$ / D	$\Delta E$ / eV	f	$\Delta E_{\text{exp}}$ / eV
Enol with OH...N hydrogen bond (structure I)						
S <sub>0</sub>	S <sub>0</sub>	0	2.13			
	S <sub>1</sub>	3.92		3.92	0.37	3.71 <sup>a,e</sup> 3.70 <sup>b</sup> 3.65 <sup>c</sup> 3.67 <sup>d</sup>
	S <sub>2</sub>	4.49		4.49	0.35	4.23 <sup>e</sup>
	S <sub>3</sub>	4.76		4.76	0.03	4.56 <sup>e</sup>
S <sub>1</sub>	S <sub>0</sub>	0.22				
	S <sub>1</sub>	3.72	2.94	3.5	0.29	
Keto with O...HN hydrogen bond (structure III)						
S <sub>1</sub>	S <sub>0</sub>	0.86				
	S <sub>1</sub>	3.53	2.09	2.67		2.46 <sup>a</sup> 2.48 <sup>f</sup> 2.51 <sup>b</sup>
Enol with OH...O hydrogen bond (structure II)						
S <sub>0</sub>	S <sub>0</sub>	0.27	1.1			
	S <sub>1</sub>	4.3		4.03	0.42	3.89 <sup>a</sup>
	S <sub>2</sub>	4.74		4.47	0.33	
	S <sub>3</sub>	5.02		4.75	0.02	
S <sub>1</sub>	S <sub>0</sub>	0.52				
	S <sub>1</sub>	4.11	1.22	3.66	0.52	3.40 <sup>a</sup> 3.44 <sup>f</sup>

<sup>a</sup>In cyclohexane [11]

<sup>b</sup>In Ar matrix [25]

<sup>c</sup>0-0 in Ar matrix [25]

<sup>d</sup>0-0 in supersonic jet [25]

<sup>e</sup>In cyclohexane [9]

<sup>f</sup>In acetonitrile [11]

**Table 2** Calculated values of relative energy (E), dipole moment ( $\mu$ ), energy of vertical transitions ( $\Delta E$ ), oscillator strength (f) and experimental values of energy of transitions ( $\Delta E_{\text{exp}}$ ) of different rotameric and tautomeric structures of DBP

Geometry	State	E / eV	$\mu$ / D	$\Delta E$ / eV	f	$\Delta E_{\text{exp}}$ / eV	
Enol with OH...N (structure I)							
S <sub>0</sub>	S <sub>0</sub>	0	1.67				
	S <sub>1</sub>	3.44		3.44	1.14	3.49 <sup>a</sup> 3.64 <sup>b</sup> 3.52 <sup>c</sup> 3.45 <sup>d</sup>	
	S <sub>2</sub>	3.86		3.86	0.29		
	S <sub>3</sub>	4.16		4.16	0.01		
S <sub>1</sub>	S <sub>0</sub>	0.18					
	S <sub>1</sub>	3.25	2.42	3.07	1.33		
Keto with O...HN hydrogen bond (structure IV)							
S <sub>1</sub>	S <sub>0</sub>	0.71					
	S <sub>1</sub>	3.36	6.58	2.66	0.29	2.50 <sup>a</sup>	
Enol with OH...N hydrogen bond (structure II)							
S <sub>0</sub>	S <sub>0</sub>	0.01	3.18				
	S <sub>1</sub>	3.48		3.46	1.14	3.46 <sup>d</sup>	
	S <sub>2</sub>	3.82		3.8	0.27		
	S <sub>3</sub>	4.18		4.17	0.02		
Keto with O...HN hydrogen bond (structure V)							
S <sub>1</sub>	S <sub>0</sub>	0.76					
	S <sub>1</sub>	3.39	6.31	2.63	0.2		
Enol with OH...O hydrogen bond (structure III)							
S <sub>0</sub>	S <sub>0</sub>	0.27	1.95				
	S <sub>1</sub>	3.75		3.48	1.28		
	S <sub>2</sub>	4.19		3.92	0.18		
	S <sub>3</sub>	4.43		4.17	0.01		
	S <sub>1</sub>	S <sub>0</sub>	0.47				
		S <sub>1</sub>	3.54	2.82	3.07	1.47	3.25 <sup>d</sup>

<sup>a</sup>In toluene [8]

<sup>b</sup>Vapor [13]

<sup>c</sup>In 3-methylpentane [13]

<sup>d</sup>0-0 in supersonic jet [13]

**Table 3** Calculated values of relative energy (E), dipole moment ( $\mu$ ), energy of vertical transitions ( $\Delta E$ ), oscillator strength (f) and experimental values of energy of transitions ( $\Delta E_{\text{exp}}$ ) of different planar rotameric and tautomeric structures of BBHQ

Geometry	State	E / eV	$\mu$ / D	$\Delta E$ / eV	f	$\Delta E_{\text{exp}}$ / eV
Enol with two OH...N hydrogen bonds (structure I)						
S <sub>0</sub>	S <sub>0</sub>	0	0			
	S <sub>1</sub>	2.95		2.95	0.47	3.04 <sup>a</sup> 2.97 <sup>b</sup> 2.98 <sup>c</sup>
	S <sub>2</sub>	3.76		3.76	0.98	3.73 <sup>c</sup>
	S <sub>3</sub>	4.13		4.13	0	
	S <sub>4</sub>	4.3		4.3	0	
S <sub>1</sub>	S <sub>5</sub>	4.31		4.31	0.02	4.38 <sup>c</sup>
	S <sub>0</sub>	0.19				
S <sub>1</sub>	S <sub>1</sub>	2.76	0	2.57	0.4	2.76 <sup>d</sup> 2.60 <sup>c</sup>
	Enol with OH...N and OH...O hydrogen bonds (structure II)					
S <sub>0</sub>	S <sub>0</sub>	0.27	2.09			
	S <sub>1</sub>	3.3		3.04	0.49	
	S <sub>2</sub>	4		3.73	0.94	
	S <sub>3</sub>	4.42		4.15	0.01	
S <sub>1</sub>	S <sub>0</sub>	0.45				
	S <sub>1</sub>	3.12	2.25	2.68	0.42	
Keto with O...HN and OH...N hydrogen bonds (structure III)						
S <sub>1</sub>	S <sub>0</sub>	0.83				
	S <sub>1</sub>	2.8	5.29	1.97	0.23	2.10 <sup>a</sup> 2.12 <sup>c</sup>
Keto with O...HN and OH...O hydrogen bonds (structure IV)						
S <sub>1</sub>	S <sub>0</sub>	1.08				
	S <sub>1</sub>	3.18	6.35	2.11	0.23	

<sup>a</sup>In toluene [8]

<sup>b</sup>0–0 in supersonic jet [17]

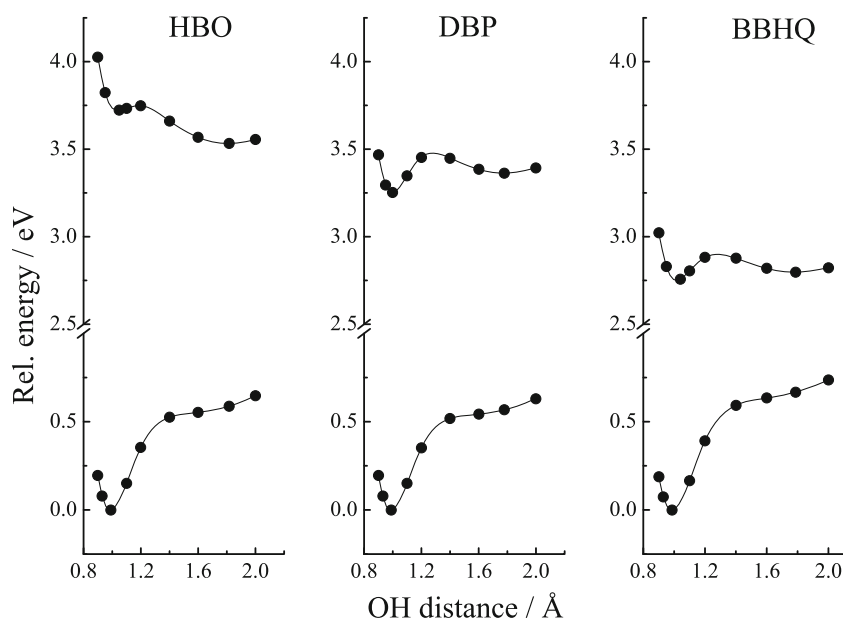
<sup>c</sup>In Ar matrix [17]

<sup>d</sup>In supersonic jet [16]

moment of the molecule of HBO does not change significantly upon ESIPT, the dipole moment of the keto structure is less than that of enol one in the excited state. For DBP and BBHQ, the calculations predict that the enol structure is more stable than the planar keto by 0.11 (DBP) and

0.04 eV (BBHQ). ESIPT in DBP and BBHQ increases the dipole moments of the molecules significantly that lower the energy of the excited keto structures in solution. However, an experimental study of DBP performed in supersonic jets [13] has detected only keto fluorescence. In jet experiments,

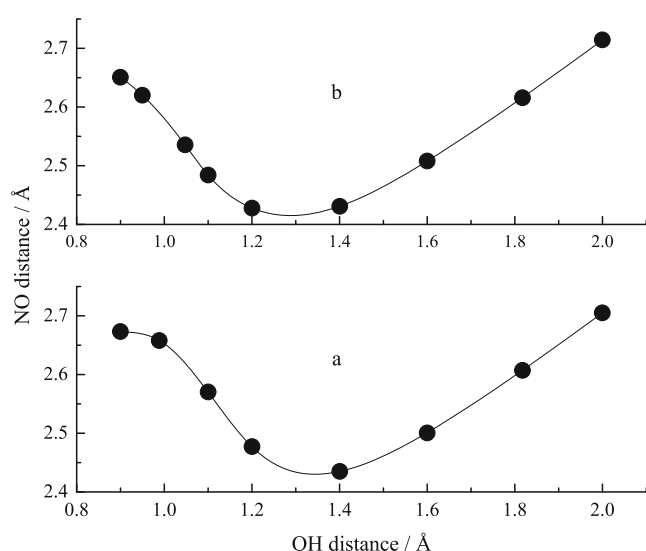
**Fig. 2** Potential energy profiles along the OH stretching coordinate in the ground and excited states of HBO, DBP and BBHQ



excitation of fluorescence of BBHQ with moderate excess of energy above the origin also leads to predominance of keto fluorescence [16, 17] implying that the keto structures of DBP and BBHQ responsible for the fluorescence are more stable than the enol. In non-polar solvent, the keto fluorescence of BBHQ predominates as well; the energy difference between the enol and keto tautomers has been estimated to be 0.02 eV [14]. Thus, the TDDFT calculations with the B3LYP functional overestimate stability of the enol structures in comparison with the planar keto structures for DBP and BBHQ. Calculations performed with the Coulomb-attenuated CAM-B3LYP exchange-correlation functional also predict energy of the enol structure lower than keto for DBP and BBHQ, whereas they overestimate energy of the vertical transitions by about 0.4 eV relatively to those obtained with the B3LYP functional. The energies of the vertical transitions calculated with the B3LYP functional for the optimized excited state structures of the keto forms are quite close to the energies of the observed fluorescence bands.

The potential energy profile for proton transfer is affected by the distance between the heavy atoms (oxygen and hydrogen) that constitute the hydrogen bonding site. In Fig. 3 dependence of the ON distance on the OH distance is shown for the minimum energy path calculated with the OH bond as a driving coordinate in the molecule of HBO. The dependencies are similar for the three substances both in the ground and excited states, the barrier for proton transfer decreases when the oxygen and nitrogen atoms are getting into proximity.

Unconstrained optimization of geometry of the enol species lead to the planar structures both in the ground and first excited state for all three compounds even started from non-planar molecules. The potential energy profiles for the



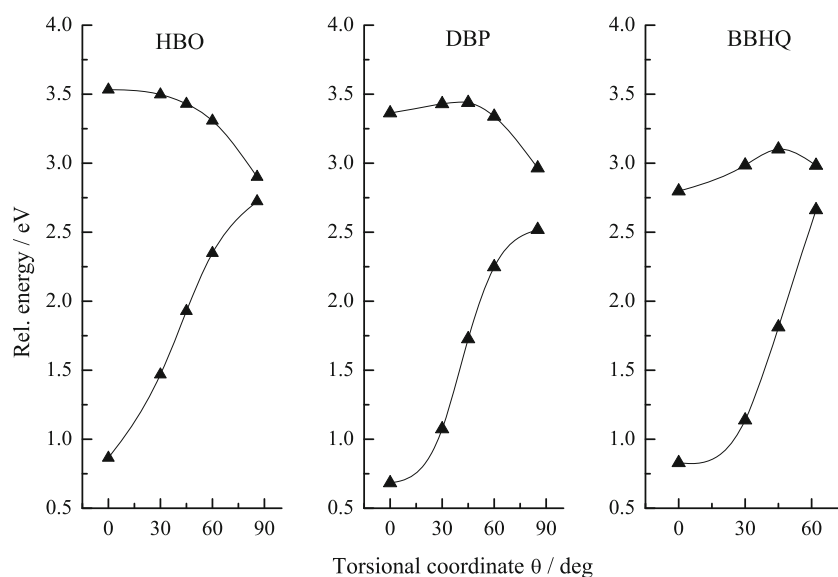
**Fig. 3** Dependence of the ON distance corresponding to the minimum energy on the OH distance for the ground (a) and excited (b) states of HBO

rotation of benzoxazole and phenolic moieties of the keto species are shown in Fig. 4. Unconstrained optimization of the twisted keto structure of HBO in the first excited state converges to the geometry where the phenolic and benzoxazole moieties are almost perpendicular and the molecule undergo slight pyramidization at the carbon atom of the benzoxazole moiety (Fig. 5). In the molecule of HBO the CCCN dihedral angle is 74.9° and CCCO dihedral angle is 83.1°. Optimization of the twisted keto structure of DBP predicts the planar keto conformation if the initial geometry is not far from planar. If the initial structure is taken from the region of the large torsional coordinate  $\theta$  then the optimization results in the twisted structure similar to that of HBO. In the molecule of DBP the CCCN and CCCO angles are 73.2° and 81.9°, the non-hydrogen-bridged benzoxazole moiety is coplanar with the phenolic ring. The twisting of the molecules of all three compounds is accompanied by decrease of the gap between the ground and first excited state, in BBHQ the gap becomes too small and the TDDFT calculations stop to converge. The magnitudes of the gap between the  $S_1$  and  $S_0$  states in the minima of the TDDFT potential energy surfaces are 0.20 eV (HBO) and 0.28 eV (DBP). Analysis of the orbitals along the potential energy profiles shows that the  $S_1$  state is a  $\pi\pi^*$  state at all points. The potential energy profile demonstrates that the planar structure of the keto species of HBO in the  $S_1$   $\pi\pi^*$  state is a transition state in relation to the rotation rather than a minimum. Normal-mode calculations under assumption of  $C_s$  symmetry, predicting an out-of-plane vibration with one imaginary frequency of 34  $\text{cm}^{-1}$ , confirm that the planar keto structure is a transition state. The barrier for rotation of the keto species estimated from the potential energy curves increases from DBP to BBHQ (0.08 and 0.36 eV correspondingly). The decrease of the gap between the  $S_1$  and  $S_0$  states points to the possibility of intersection of PES of the ground and first excited states in the vicinity of the minimum energy path upon the rotation which is a radiationless channel for decay of the excited keto state, however, in the molecules of HBO and DBP the intersection does not lie on the minimum energy path. Our results for BBHQ demonstrate that a radiationless process with activation energy comparable with that found experimentally (about 0.15 eV) [14, 16] can be related to large-amplitude twisting of the keto species. The estimation of the barrier for DBP is close to the value of 0.05 eV of the threshold found for DBP in the supersonic jet study [13].

The energy of the  $S_1$ – $S_0$  transition of the keto tautomer of DBP with the rotated non-hydrogen-bridged benzoxazole moiety (structure V) is predicted to be red-shifted by about 0.03 eV in comparison with the transition of structure IV. The energy of the  $S_1$ – $S_0$  transition of the keto rotamer III of BBHQ is expected to be blue-shifted by 0.14 eV, while the  $S_1$ – $S_0$  transition of corresponding enol conformer II is red-



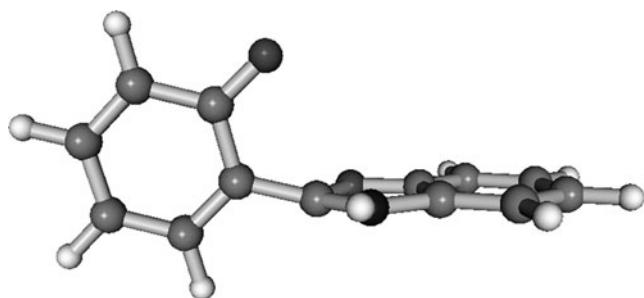
**Fig. 4** Potential energy profiles for rotation of the protonated benzoxazole moiety of the keto structures of HBO, DBP and BBHQ in the excited state. The energy of the ground state is shown for the geometry optimized in the excited state



shifted by approximately the same value. The relation of the energies of enol and keto tautomers II and III in the excited state is similar to the results for conformations I and IV described above. It should be noted that there is no reports on the structures V of DBP and III of BBHQ detected experimentally. The planar diketo structure of BBHQ with two transferred protons has been found to be less stable than planar keto structure III in the  $S_1$  state by 0.08 eV so that single proton transfer is preferable. The calculated energy of the  $S_1$ – $S_0$  vertical transition of the diketo tautomer of BBHQ is significantly less than that of the keto structure (1.2 and 1.97 eV correspondingly). Our calculations support assignment of the fluorescence band with a large Stokes shift to the keto rather than diketo structure of the molecule.

## Conclusion

Time-dependent density functional theory has been applied to the calculations of structure and electronic transitions of rotameric and tautomeric species of the benzoxazoles that



**Fig. 5** The twisted keto structure of HBO corresponding to the minimum of the potential energy surface in the first excited state

undergo excited state proton transfer. In the ground state the predominating species are enol with OH...N hydrogen bonds, the potential energy profiles for proton transfer are strongly asymmetric with one minimum. The number of molecules with OH...O hydrogen bonds is predicted to be small even at room temperature. The enol conformations with OH...O hydrogen bonds of the compounds studied have been found to demonstrate blue shift of the first absorption transitions in relation to those of the most stable enol structures. The enol rotamers with OH...N hydrogen bonds of the three substances show ESIPT resulting in the keto structures. In the excited state of HBO the keto structure is predicted by TDDFT to be more stable than enol with a low barrier between the tautomers, whereas in the case of DBP and BBHQ the enol structures is predicted to be more stable than the planar keto structures. The relation of energies of the tautomers of DBP and BBHQ in the excited state is in contradiction with the experimental results. The calculated energies and oscillator strengths of the vertical electronic transitions of the planar structures are in good agreement with the observed absorption and fluorescence spectra for all three benzoxazoles. Twisting of the keto species around the bond linking the benzoxazole and phenolic or hydroquinone moieties leads to decrease of the gap between the excited and ground state that indicate the possibility of intersection which is a radiationless process of decay of the excited state but exploration of the potential energy surfaces in the close vicinity of the intersection needs multireference methods.

For more accurate modeling of the absorption and fluorescence spectra vibrational energy should be taken into account, however, in the case of the considered benzoxazoles the motion of the transferring proton cannot be treated as harmonic vibration because of shallow or no minima corresponding to some tautomers on the potential energy surfaces.

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