

## CALCULATIONS OF MOLECULAR PROPERTIES OF 2-(2'-HYDROXYPHENYL)BENZOXAZOLE BY SEMI-EMPIRICAL TIGHT-BINDING METHODS

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The semi-empirical tight-binding methods GFN1-xTB and GFN2-xTB are applied to calculations of structure, energy and normal vibrations of the molecule of 2-(2'-hydroxyphenyl)benzoxazole undergoing excited state intramolecular proton transfer. The results are compared with ones obtained by the density-functional tight-binding methods with hydrogen interaction corrections and density functional theory. The GFN2-xTB method is found to provide good correspondence to the results obtained by more accurate but much slower density functional theory method for geometrical parameters of hydrogen bond, relative energy of molecular conformations and potential energy surface.

**Keywords:** excited state intramolecular proton transfer, modeling, molecular vibrations, semi-empirical methods, density functional tight-binding theory.

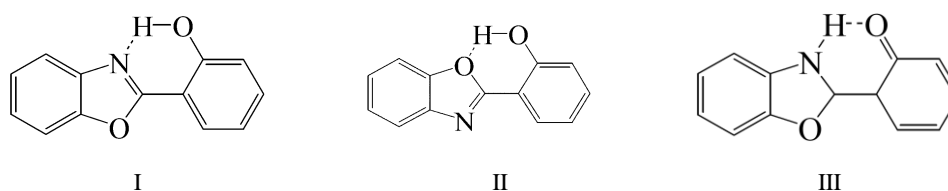
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### 1. Introduction

2-(2'-hydroxyphenyl)benzoxazole (HBO) is an organic substance that demonstrates excited state intramolecular proton transfer (ESIPT). HBO has been studied for several decades to elucidate microscopic mechanism of this photochemical reaction and tested as possible luminescent substance for a number of applications. HBO has been studied in the solid state [1, 2], incorporated into polymer chains [3], proteins, lipids, DNA [4] and used as a ligand in complexes with metals [5].

The semi-empirical tight-binding methods GFN-xTB have been proposed for calculating the structures, vibrational frequencies, and non-covalent interactions of molecules. They can be applied to large molecular system and solids due to their two orders of magnitude faster performance than more accurate density functional theory methods. The methods are parameterized for all spd-elements and the lanthanides up to atomic number 86 [6].

In the ground state the most stable structure of the molecule of HBO is enol form I with an intramolecular hydrogen bond OH...N (Fig. 1). In the first excited state keto form III with an O...HN hydrogen bond has energy lower than the enol form. The ESIPT leads to the keto structure formation and causes luminescence with an anomalously large Stokes shift. Another internally H-bonded structure with an OH...O hydrogen bond is possible (structure II in Fig. 1), which causes luminescence with usual Stokes shift. HBO forms molecular crystals by weak van der Waals interaction [1, 2, 7].



**Fig. 1. Molecular structures of HBO (I – enol with an intramolecular OH...N hydrogen bond, II – enol with an intramolecular OH...O hydrogen bond, III – keto).**

In the present paper we calculate energy, structures, and vibrational frequencies of a molecule of HBO by the semi-empirical tight-binding methods. The study aim is the assessment of this approach accuracy in the case of a molecule with internal hydrogen bond undergoing the ESIPT.

## 2. Calculations details

Semi-empirical tight-binding calculations of structure, energy and vibrations of a molecule of HBO were performed using the GFN1-xTB and GFN2-xTB methods [6]. The density-functional based tight-binding (DFTB) calculations were done with the third order correction (DFTB3) [8] and with hydrogen interaction corrections. The hydrogen interaction corrections are damping method [8, 9] and the H5 correction with additional D3 dispersion correction (DFTB3-H5D3) [10, 11]. The DFTB and GFN-xTB calculations were performed by the DFTB+ program package with default parameters [12]. Vibrations of isolated molecules were calculated in harmonic approximation. The results are compared with the values obtained by the density functional theory (DFT) method using the B3LYP functional and 6-31G(d,p) basis set. The DFT calculations were performed with the GAMESS program suit [13, 14]. Comparison of the normal vibrations was done by the expansion of eigenvectors in terms of the eigenvectors of normal modes obtained by the DFT method under condition that the principal axes of inertia were the same for both structures.

## 3. Results and discussion

All methods predict that the minimum energy structure is enol form I. The values of the bond OH length in this structure differ from the DFT value within 0.021 Å, maximum deviation is found for the GFN1-xTB method. The GFN2-xTB method, in its turn, demonstrates the closest value (Table 1). For the distances NH (hydrogen bond) and NO (the distance between heavy atoms forming the hydrogen bond) deviations are more pronounced: within 0.14 and 0.11 Å (DFTB3-D3H5) correspondingly; the best agreement is provided by GFN2-xTB as well. For the hydrogen bond OH...O in structure II where the ESIPT is not possible the deviations are noticeably less: the largest difference is 0.015 Å (DFTB3-D3H5) found for the O...H distance (see Table 1). The values of energy obtained by DFTB3, DFTB3 with damping correction, and GFN-xTB methods are lower than the value obtained by the DFT calculations, the least difference is found for GFN2-xTB (0.06 eV). The D3H5 correction yields the value of energy of structure II larger than DFT by about 0.05 eV.

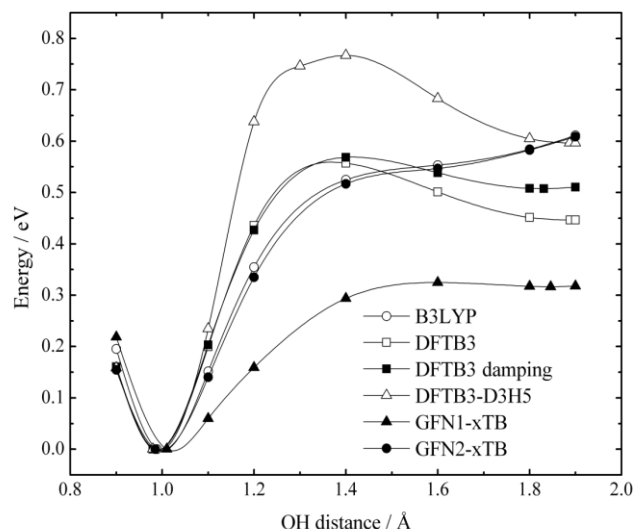
Table 1

**Geometrical parameters of hydrogen bonding, energy of structure II, and frequency deviations of normal vibrations of the structure I of an HBO molecule in the ground state calculated by various methods**

Parameter	DFT (B3LYP)	DFTB3	DFTB3 damping	DFTB3- D3H5	GFN1- xTB	GFN2- xTB
O-H length, Å	0.989	0.982	0.980	0.980	1.010	0.985
N...H distance, Å	1.778	1.898	1.882	1.917	1.644	1.768
NO distance, Å	2.659	2.759	2.742	2.769	2.562	2.641
Energy of structure II, eV	0.27	0.17	0.14	0.32	0.19	0.21
O-H length, Å	0.974	0.973	0.972	0.973	0.974	0.968
O...H distance, Å	1.865	1.867	1.852	1.880	1.865	1.872
OO distance, Å	2.696	2.707	2.689	2.716	2.696	2.705
RMS frequency deviation, cm <sup>-1</sup>	0	80	79	80	78	61
Max frequency deviation, cm <sup>-1</sup>	0	196	197	195	493	263

Scan of the potential energy surface along the distance OH minimizing the molecule energy demonstrates that there is no local minimum for keto structure III in the ground state in the cases of DFT and GFN2-xTB calculations (Fig. 1). Other methods yield local minima of different depth. The existence of these local minima is confirmed by harmonic vibration calculations yielding real frequencies for the points with zero gradients. The minimum energy path along the distance OH calculated with GFN2-xTB is very close to

the curve obtained by DFT (see Fig. 1). The largest deviations from the DFT results are demonstrated by GFN1-xTB underestimating the value of energy of the keto structure and DFTB3-D3H5 in the region of the energy barrier between the enol and keto structures.



**Fig. 2.** The minimum energy path along the distance OH calculated with various methods: density functional theory method with B3LYP functional and 6-31G(d,p) basis set (B3LYP), density functional-based tight-binding method (DFTB3), density functional-based tight-binding method with hydrogen correction by damping (DFTB3 damping), density functional-based tight-binding methods with the H5 correction and an D3 dispersion correction (DFTB3-D3H5), semi-empirical methods with extended tight-binding Hamiltonians (GFN1-xTB and GFN2-xTB).

The normal modes calculated with the GFN-xTB method demonstrate less root-mean-square deviation from the frequencies of vibrations obtained by DFT with the largest contribution into the expansion than the modes calculated by the considered DFTB variants (see Table 1). The GFN-xTB methods improve correspondence of the eigenvectors of two twisting modes with the lowest frequencies. The expansion coefficients are 0.78 for the DFTB3-D3H5 and 0.99 for the GFN1-xTB methods. In crystalline state, the low-frequency molecular modes are mixed with external motions of the molecules in the lattice [2]. The GFN1-xTB method yields 6 modes with significant difference in the eigenvectors (square of the largest expansion coefficient is less than 0.5) against 10-11 for other methods. However, in contrast to the DFTB methods, the GFN-xTB methods underestimate the frequency of the OH stretching vibration by 493 and 263  $\text{cm}^{-1}$  so that the frequency of the OH stretching vibration is calculated to be less than the frequency of the CH stretching vibrations.

#### 4. Conclusions

The accuracy of semi-empirical tight-binding methods GFN1-xTB and GFN2-xTB is considered for calculating the structure, energy and normal vibrations of a molecule of photoreactive substance undergoing the excited state intramolecular proton transfer. It is found that the GFN2-xTB method provides good correspondence to the results obtained by the more accurate but much slower DFT method for geometrical parameters of hydrogen bond, relative energy of molecular conformations, and relaxed potential energy surface scan along the distance OH. The accuracy of the calculations of normal vibrations by the GFN-xTB methods is like that of the DFTB calculations; at the same time, the frequency of the OH stretching mode is significantly underestimated.

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