

## VIBRONIC STRUCTURE OF ABSORPTION SPECTRUM OF 2,5-DI-(2-BENZOXAZOLYL)PHENOL

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Vibronic structure of the absorption spectrum of 2,5-di-(2-benzoxazolyl)phenol is calculated using the Franck-Condon approximation and harmonic model for vibrations. 2,5-di-(2-benzoxazolyl)phenol is an organic compound that exhibits excited-state intramolecular proton transfer. It is found that the use of normal modes and values of energy of the electronic states calculated with the B3LYP density functional provides good agreement with the experimental spectrum in terms of the position of intense bands. The largest intensity of vibronic transitions is found for deformation vibrations changing the distance between the oxygen and nitrogen atoms of the hydrogen bond, a deformation vibration of the phenol ring, stretching vibrations of the benzoxazole moieties.

**Keywords:** excited state intramolecular proton transfer, absorption, density functional theory, electronic and vibrational states.

Received 21.11.2023; Received in revised form 09.12.2023; Accepted 15.12.2023

### 1. Introduction

An organic compound 2,5-di-(2-benzoxazolyl)phenol (DBP) is an organic compound that undergoes excited-state intramolecular proton transfer (ESIPT) [1-4]. The most stable molecular structure in the ground state  $S_0$  is the enol form I with a hydrogen bond OH...N (Fig. 1). Another structure II formed by the rotation of a non-hydrogen-bonded benzoxazole moiety is calculated to be less stable by about 0.01 eV [3]. DBP demonstrates two bands in the fluorescence spectrum: the first with normal Stokes shift and the second with anomalously large Stokes shift. The fluorescence with the large Stokes shift is attributed to the transitions in the keto structure formed by ESIPT. At least a part of the fluorescence with the usual Stokes shift is attributed to the transitions in the structure due to difference in the fluorescence excitation spectra [1-3]. The absorption spectrum of DBP in solution (Fig. 2), as well as the spectrum of the related compound 2,5-bis(6-methyl-2-benzoxazolyl)phenol [4,5], exhibit sharp vibronic bands at room temperature. The spectra of the transitions to the first  $S_1$  and second  $S_2$  excited states are overlapping [3,5].

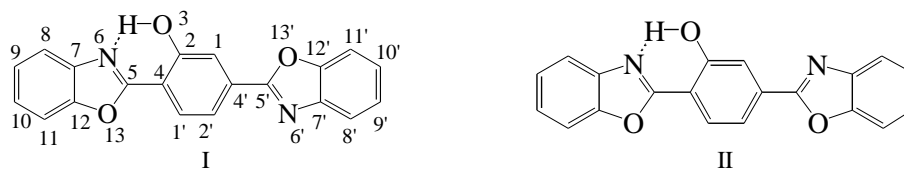


Fig. 1. Enol structures of a DBP molecule with the atomic numbering scheme.

In this work we perform theoretical modeling of the absorption of DBP in order to find out the molecular vibrations, which are manifested in the spectrum.

### 2. Calculations details

The calculations of structure and vibrations were performed for an isolated molecule by the DFT and TDDFT methods with the B3LYP functional and def2-SVP basis set using the RIJCOSX approximation implemented in the ORCA software package [6-8]. The vibrations were calculated in harmonic approximation. Vibronic structure of the absorption spectra was calculated with the FCclasses3 code [9,10] using the time-dependent [11] and time-independent methods [12-15] in the Franck-Condon approximation. The time-dependent method allows calculating the spectrum but does not allow considering each vibronic transition separately. Normal coordinates in the ground and excited states were supposed to

be related by the Duschinsky transformation [16]. The spectra were simulated using Gaussian lines with HWHM of 0.045 eV and 0.035 eV for the  $S_0$ - $S_1$  and  $S_0$ - $S_2$  transitions, correspondingly. The experimental absorption spectrum of DBP was obtained by the Shimadzu UV-3100 spectrophotometer in  $CCl_4$  solution at room temperature with resolution 1 nm.

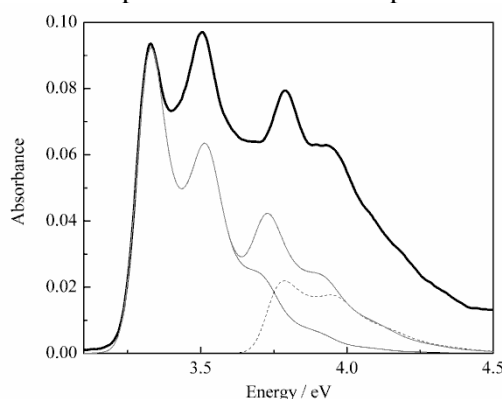
### 3. Results and discussion

The enol structures I and II of the molecule of DBP are calculated to be planar. The difference in energy between the structures I and II is about 0.014 eV that implies the ratio about 0.6 for the numbers of the rotamers in thermodynamic equilibrium according to the Boltzmann distribution.

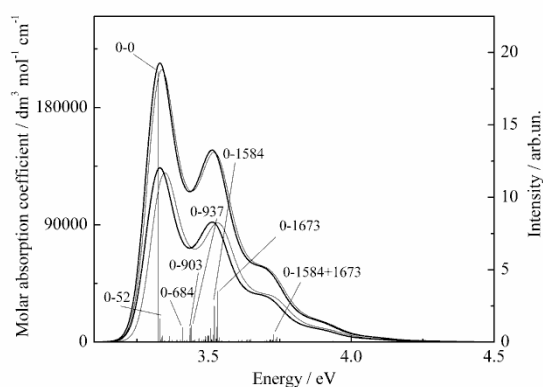
The largest changes in lengths of bonds between the heavy atoms in the state  $S_1$  in comparison with the state  $S_0$  are found for the bonds  $C_2$ - $C_4$  and  $C_2$ - $C_4'$  of the phenol moiety, for the bonds  $C_4$ - $C_5$  and  $C_4$ - $C_5'$  linking the benzoxazoles and phenol moieties, and for the bonds  $C_5$ - $N_6$ ,  $C_5$ - $N_6'$ ,  $N_6$ - $C_7$ ,  $N_6$ - $C_7'$  and  $C_{12}$ - $C_7$ ,  $C_{12}$ - $C_7'$  in the oxazole rings. The valence angles are  $C_4$ - $C_2$ - $O_3$ ,  $C_1$ - $C_2$ - $C_4$ ,  $C_2$ - $C_4$ - $C_1$ ,  $C_1$ - $C_2$ - $C_4$ ,  $C_2$ - $C_4$ - $C_1$  and  $O_{13}$ - $C_5$ - $N_6$ . The structure II demonstrates similar changes in structural parameters. In the state  $S_2$  the changes are  $C_4$ - $C_5$ ,  $C_4$ - $C_5'$ ,  $C_5$ - $N_6$ ,  $C_5$ - $N_6'$ ,  $N_6$ - $C_7$ ,  $N_6$ - $C_7'$ ,  $C_{12}$ - $C_7$  for bond lengths and  $C_4$ - $C_2$ - $O_3$ ,  $C_1$ - $C_2$ - $C_4$ ,  $C_2$ - $C_4$ - $C_1$ ,  $C_1$ - $C_2$ - $C_4$ ,  $C_2$ - $C_4$ - $C_1$ ,  $C_4$ - $C_5$ - $N_6$ ,  $C_2$ - $C_4$ - $C_5$  for valence angles.

The spectrum calculated for the isolated structure I demonstrates good correspondence to the experimental spectrum measured in  $CCl_4$  for the position of the intense vibronic components of the  $S_0$ - $S_1$  and  $S_0$ - $S_2$  transitions but significantly overestimates the intensity of the first vibronic band (Fig. 2). The spectrum of the structure II is calculated to be similar to the spectrum of the structure I and cannot be distinguished in the case of the assumed inhomogeneous broadening value (Fig. 3). The calculated value of energy for the 0-0 transition  $S_0$ - $S_1$  is 3.31 eV for the structure I that is lower by 0.14 eV than the value of 3.45 eV obtained by high-resolution fluorescence excitation spectra measurements for jet-cooled molecules [1].

Molecules of DBP have 105 normal vibrations; the lowest frequency in the ground state is  $30\text{ cm}^{-1}$  so that the low-frequency vibrational energy levels are populated by thermal excitation. This leads to the large number of transitions and we calculate the transitions with the time-independent method at temperature 0 K to simplify the analysis (Fig. 4).

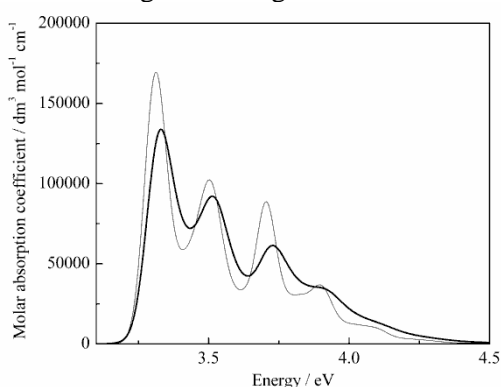


**Fig. 2. Experimental absorption spectrum of DBP dissolved in  $CCl_4$  (bold line) and spectra calculated with the time-dependent method (grey line) for the structure I. Thin black and dashed lines denote spectra formed by the  $S_0$ - $S_1$  and  $S_0$ - $S_2$  transitions.**

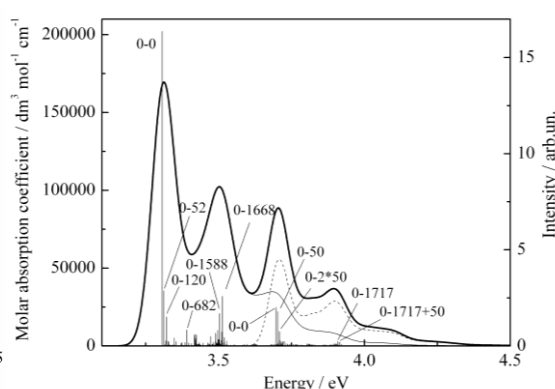


**Fig. 3. Absorption spectrum for the  $S_0$ - $S_1$  transitions modeled for the structures I (bold line) and II (grey line) with the time-dependent method at room temperature along with the spectra for pure I (upper black) and mixture of the I and II (upper grey) species. The stick spectrum represents vibronic transitions in the structure II at 0 K.**

The largest intensities of the transitions are found for the vibrations of the structure I with calculated frequencies 52, 120, 682, 1588, 1668  $\text{cm}^{-1}$  in the state  $S_1$  and 50, 1717  $\text{cm}^{-1}$  in the state  $S_2$  (Fig. 5). For the structure II the normal modes are 52, 684, 903, 937, 1584 and 1673  $\text{cm}^{-1}$  in the state  $S_1$  (see Fig. 3). The vibrations 1588, 1668, 1717, 903, 937, 1584 and 1673  $\text{cm}^{-1}$  demonstrate noticeable contribution of several modes of the ground state to the Duschinsky transformation but can be related to the corresponding ground state vibrations by the largest element of the matrix. The vibrations with frequencies 52 and 50  $\text{cm}^{-1}$  correspond to the modes with frequency 52  $\text{cm}^{-1}$  in the ground state which is in-plane deformation vibration that changes the angles  $C_2-C_4-C_5$  and  $C_2-C_4-C_5$ . The vibration 120  $\text{cm}^{-1}$  corresponds to the mode 123  $\text{cm}^{-1}$  in the state  $S_0$ ; this vibration is deformation that changes the angles  $C_4-C_5-N_6$  and  $C_4-C_5-N_6$ . These low-frequency vibrations affect the distance between the atoms O and N forming the hydrogen bond. The vibration 682  $\text{cm}^{-1}$  corresponds to the mode 711  $\text{cm}^{-1}$  in the state  $S_0$ ; this vibration is in-plane deformation of the phenol ring. The vibration 1588  $\text{cm}^{-1}$  is related to the mode 1631  $\text{cm}^{-1}$  in the state  $S_0$ , this mode is a stretching vibration of phenol and oxazole rings. The vibrations 1668 and 1717  $\text{cm}^{-1}$  correspond to the mode 1691  $\text{cm}^{-1}$  in the state  $S_0$ , which is a stretching vibration of phenol and oxazole rings involving the  $C_4-C_5$  and  $C_4-C_5$  bonds.



**Fig. 4.** Absorption spectrum modeled with the time-dependent method at room temperature (bold line) and time-independent method at temperature 0 K (grey line) for the structure I.



**Fig. 5.** Absorption spectrum modeled with the time-independent method at temperature 0 K (black line). Grey and dashed lines denote spectra formed by the  $S_0-S_1$  and  $S_0-S_2$  transitions. The stick spectrum represents vibronic transitions.

The calculated spectrum does not demonstrate long progressions formed by the low-frequency vibrations. This pattern corresponds to the experimental high-resolution fluorescence excitation spectra measured in supersonic jets. Experimental values of frequencies of vibrations are 52 and 115  $\text{cm}^{-1}$  in the state  $S_1$  [1].

#### 4. Conclusions

Calculations of the vibronic structure of the  $S_0-S_1$  and  $S_0-S_2$  absorption bands of 2,5-di-(2-benzoxazolyl)phenol assuming the harmonic vibrational movement of the nuclei obtained with the B3LYP density functional reproduce energy of sharp intense vibronic components observed in experiments but predict large relative intensity of the 0-0 transition to the first excited state.

#### References

1. **Vdovin, A.** Excited state proton transfer in jet-cooled 2,5-di-(2-benzoxazolyl)phenol / A. Vdovin, J. Sepioł, J. Jasny, J. M. Kauffman, A. Mordzinski // Chem. Phys. Lett. – 1998. – Vol. 296. – P. 557–565.

2. **Kauffman, J. M.** Synthesis and photophysical properties of fluorescent 2,5-dibenzoxazolylphenols and related-compounds with excited-state proton-transfer / J.M. Kauffman, G.S. Bajwa, // *J. Heterocycl. Chem.* – 1993. – Vol. 30. – P. 1613–919.
3. **Syetov, Y.** Optical absorption and luminescence spectra of 2,5-di-(2-benzoxazolyl) phenol in the solid state/ Y. Syetov // *Ukr. J. Phys. Opt.* – 2017. – Vol. 18(3). – P. 139–142.
4. **Luzina, E.** Effect of alkyl substituents on excited state intramolecular proton transfer dynamics of jet-cooled bis(benzoxazolyl)phenoles/ E. Luzina, J. Sepioł, Y. N. Svartsov, A. Grabowska // *J. Chem. Phys.* – 2007. – Vol. 126. – P. 194308-7.
5. **Dobkowski, J.** Solving the Puzzle of Unusual Excited-State Proton Transfer in 2,5-Bis(6-methyl-2-benzoxazolyl)phenol / J. Dobkowski, M. Kijak, S. Gawinkowski, E. Karpiuk, M. Pietrzak, I. V. Sazanovich, J. Waluk // *J. Phys. Chem. A* – 2022. – Vol. 126. – P. 1823–1836.
6. **Neese, F.** The ORCA program system / F. Neese // *WIREs Comput. Mol. Sci.* – 2012. – Vol. 2. – P. 73–78.
7. **Neese, F.** Software update: the ORCA program system, version 4.0, / F. Neese // *WIREs Comput. Mol. Sci.* – 2017. – Vol. 8. – P. e1327–6.
8. **Neese, F.** Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A ‘chain-of-spheres’ algorithm for the Hartree–Fock exchange / F. Neese, F. Wennmo, A. Hansen, U. Becker // *Chem. Phys.* – 2017. – Vol. 356. – P. 98–109.
9. **Santoro F., Cerezo J.** FCclasses3, A code for vibronic calculations. Version 3.0.3, 2023. Visit <http://www.iccom.cnr.it/en/fcclasses>.
10. **Cerezo, J.** FCclasses3: Vibrationally-resolved spectra simulated at the edge of the harmonic approximation / J. Cerezo, F. Santoro, *J. Comput. Chem.* – 2023. – Vol. 44. – P. 626–643.
11. **Ávila Ferrer, F.J.** First principle computation of absorption and fluorescence spectra in solution accounting for vibronic structure, temperature effects and solvent inhomogeneous broadening / F. J. Ávila Ferrer, J. Cerezo, J. Soto, R. Improta, F. Santoro // *Comput. Theoret. Chem.* – 2014. – Vol. 1040-1041. – P. 328–337.
12. **Santoro, F.** Effective method to compute Franck-Condon integrals for optical spectra of large molecules in solution / F. Santoro, R. Improta, A. Lami, J. Bloino, V. Barone // *J. Chem. Phys.* – 2007. – Vol. 126. – P. 084509-13.
13. **Santoro, F.** Effective method to compute vibrationally resolved optical spectra of large molecules at finite temperature in the gas phase and in solution / F. Santoro, R. Improta, A. Lami, V. Barone // *J. Chem. Phys.* – 2007. – Vol. 126. – P. 184102–11.
14. **Santoro, F.** Effective method for the computation of optical spectra of large molecules at finite temperature including the Duschinsky and Herzberg–Teller effect: The Q<sub>x</sub> band of porphyrin as a case study / F. Santoro, R. Improta, A. Lami, J. Bloino, V. Barone // *J. Chem. Phys.* – 2008. – Vol. 128. – P. 224311–17.
15. **Santoro, F.** Computational approach to the study of the line-shape of absorption and electronic circular dichroism spectra / F. Santoro, V. Barone // *Int. J. Quantum Chem.* – 2010. – Vol. 110. – P. 476–486.
16. **Ávila Ferrer, F.J.** Comparison of vertical and adiabatic harmonic approaches for the calculation of the vibrational structure of electronic spectra / F.J. Ávila Ferrer, F. Santoro // *Phys. Chem. Chem. Phys.* – 2012. – Vol. 14. – P. 13549–13563.