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THEORETICAL MODELING OF TWO-PHOTON ABSORPTION OF BENZOXAZOLES EXHIBITING EXCITED STATE PROTON TRANSFER

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Two-photon absorption spectra of 2-(2'-hydroxyphenyl)benzoxazole, 2,5-bis(2-benzoxazolyl)phenol and 2,5-bis(2-benzoxazolyl)hydroquinone are modeled by time-dependent density functional theory calculations. In contrast to the linear absorption, where the transitions to the two lowest excited states are leading, the two-photon absorption cross sections are significant for the transitions to higher states which are weak in one-photon absorption spectra. The 2,5-bis(2-benzoxazolyl)phenol and 2,5-bis(2-benzoxazolyl)hydroquinone demonstrate the maximum cross section of about ten times larger than that of 2-(2'-hydroxyphenyl)benzoxazole. The largest value of the cross section is calculated for 2,5-bis(2-benzoxazolyl)hydroquinone to be about 1500 units of Goeppert-Mayer for excitation at 600 nm.

Keywords: two-photon absorption, excited state proton transfer, benzoxazole derivatives, molecular modeling.

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1. Introduction

Two-photon absorption (TPA), a simultaneous absorption of two photons, — is a non-linear optical process with intensity depending on the square of incoming light. The TPA process has been gaining greater interest in a number of areas, particularly in the fields of two-photon fluorescent microscopy and imaging, three-dimensional microstructure optical data storage, optical switching, optical power limiting, photodynamic therapy [1]. 2-(2'-hydroxyphenyl)benzoxazole (HBO), 2,5-bis(2-benzoxazolyl)phenol (DBP) and 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) (Fig. 1) are benzoxazole derivatives with single and double hydrogen bonds undergoing photoinduced excited state intramolecular proton transfer (ESIPT). The ESIPT converts enol structure of the molecules with the OH…N hydrogen bonds into keto structure with the O…HN hydrogen bonds and causes appearance of fluorescence with an anomalously large Stokes shift. For the compound HBO TPA has been studied in solution in cyclohexane with excitation at wavelength of 532 nm (photon energy of 2.33 eV). The value of TPA cross section is estimated to be $9.38\cdot10^{-21}$ cm^4/GW [2]. In this paper we describe a theoretical study on TPA of HBO, DBP and BBHQ aiming evaluation of the substances as efficient media for two-photon absorption.

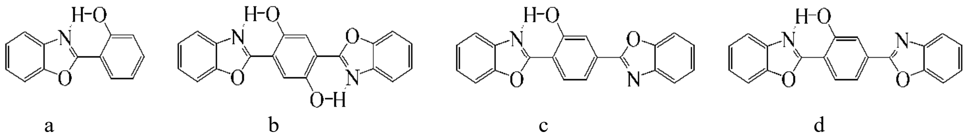

Fig. 1. Molecular structure of HBO (a), BBHQ (b) and two conformations of DBP (c, d).

2. Calculations details

One-photon absorption (OPA) transitions are described by an oscillator strength given by expression

$$\delta^{OPA} = \frac{2\omega_f}{3}\sum_{\alpha}\left|\langle 0|\mu_\alpha|f\rangle\right|^2 \qquad (1)$$

where ω_f is excitation energy of the transition from the ground state $\langle 0|$ to the excited state $|f\rangle$; μ_α is the dipole moment operator for a certain Cartesian component *α*.

Transition matrix for two-photon transition is given by the sum-over-states formula:

$$S_{\alpha\beta} = \sum_n \frac{\langle 0|\mu_\alpha|n\rangle\langle n|\mu_\beta|f\rangle}{\omega_n - \dfrac{\omega_f}{2}} + \frac{\langle 0|\mu_\beta|n\rangle\langle n|\mu_\alpha|f\rangle}{\omega_n - \dfrac{\omega_f}{2}}, \tag{2}$$

where *α*, *β* are Cartesian coordinates *x, y, z*; summation by *n* takes into account all states including ground and final ones. In the case of linear polarization of the incident light the transition moment δ^{TPA} averaged by all orientations of the molecules is expressed by

$$\delta^{TPA} = \sum_{\alpha\beta} \left(S_{\alpha\alpha} S^*_{\beta\beta} + 2 S_{\alpha\beta} S^*_{\alpha\beta} \right). \tag{3}$$

Two-photon absorption cross-section σ^{TPA} describes the attenuation of the incident light with the intensity *I* propagating along the coordinate *z*:

$$\frac{dI}{dz} = \frac{\sigma^{TPA}}{\omega_i} N_g I^2 . \tag{4}$$

where ω_i is energy of an incident photon; N_g is the number of molecules per unit volume in the ground state; it equals

$$\sigma^{TPA} = \frac{4\pi^2 a_0^5 \alpha}{15c} \frac{\omega_f}{\Gamma} \delta^{TPA} \tag{5}$$

where a_0 is the Bohr radius, α is the fine structure constant, *c* is speed of light, Γ is lifetime broadening. The value of Γ is supposed to be 0.1 eV. The molecular two-photon cross section is usually expressed in the units of Goeppert-Mayer (GM, 1 GM = 10^{-50} cm^4 s photon^{-1}) [1, 3].

All calculations are performed with the DALTON program [4,5]. Oscillator strength and two-photon absorption cross section are obtained by linear and quadratic response TDDFT methods implemented in DALTON using the Becke three-parameter Lee-Yang-Parr (B3LYP) functional [6] and 6-31G(d,p) basis set. The photons are supposed to have the same energy.

3. Results and discussion

The structure of molecules is obtained by the optimization of atom coordinates in relation to the minimum of energy using the B3LYP functional and 6-31G(d,p) basis set. The most stable conformations of the molecules are considered. The molecule of DBP can exist as two conformations which have close values of energy; they are formed by the rotation of the non-hydrogen-bonded moieties [7], the most stable structure is shown in Fig. 1c. Results of calculations for the one-photon and two-photon transitions are summarized in Table 1. The one-photon absorption spectra are dominated by the transitions to the lowest excited states S_1 and S_2 for all three compounds studied. The energy and oscillator strength of the one-photon transitions agree with the results obtained earlier [7]. The two-photon cross-section is leading for transitions to the states S_4 and S_5 in the case of HBO, to S_4 and S_6 in the case of DBP, and to S_3 in the case of BBHQ. The magnitudes of the TPA cross section of the DBP rotamer *d* are similar to ones of the most stable structure *c* except the transitions to the states S_3, S_9, and S_{12} which exhibit substantially lower TPA cross sections for the rotamer *d* than for rotamer *c*. The largest two-photon absorption cross-sections of DBP and BBHQ are about 10 times as much as the largest TPA cross section of HBO. The value for TPA cross section of S_0–S_3 transition of a BBHQ molecule is calculated to be 1520 GM. Due to the centrosymmeric structure of the molecule of BBHQ there are strict selection rules for OPA and TPA: transitions that are active in OPA are inactive in TPA and vice versa. The transition S_0–S_{12} of a BBHQ molecule is predicted to have TPA cross section of 875 GM, however, the excitation by two photons with the same frequency requires the energy of 2.76 eV that is near the first one-photon absorption band (the energy of the vertical transition S_0–S_1 is 2.94 eV). This causes small value of the denominators in the formula (2) for n = 1 but leads to the appearance of one-photon absorption.

Table 1

Calculated one-photon (OPA) and two-photon absorption (TPA) parameters for excited singlet states of HBO, DBP and BBHQ

Compound	State	Symmetry	Energy, eV	δ^{OPA}	δ^{TPA}, a.u.	σ^{TPA}, GM
HBO	S_1	A'	3.92	0.37	164	2
	S_2	A'	4.49	0.35	976	14
	S_3	A'	4.76	0.03	305	5
	S_4	A'	5.19	0.01	7010	138
	S_5	A'	5.43	0.03	5550	120
	S_6	A"	5.61	0.00	2	0
	S_7	A'	5.65	0.01	1240	29
	S_8	A'	5.67	0.02	1070	25
	S_9	A'	5.86	0.06	85	2
DBP rotamer c / rotamer d	S_1	A'	3.44 / 3.46	1.13 / 1.14	199 / 269	2 / 2
	S_2	A'	3.86 / 3.80	0.30 / 0.27	12200 / 12000	134 / 127
	S_3	A'	4.15 / 4.17	0.01 / 0.02	10400 / 269	131 / 3
	S_4	A'	4.28 / 4.28	0.03 / 0.03	86400 / 94100	1160 / 1260
	S_5	A'	4.40 / 4.40	0.01 / 0.01	451 / 418	6 / 6
	S_6	A'	4.76 / 4.78	0.01 / 0.02	25300 / 24900	420 / 418
	S_7	A"	4.95 / 4.93	0.00 / 0.00	8 / 8	0 / 0
	S_8	A'	5.10 / 5.06	0.05 / 0.11	2610 / 4720	50 / 88
	S_9	A'	5.16 / 5.16	0.02 / 0.00	1120 / 335	22 / 7
	S_{10}	A'	5.25 / 5.25	0.03 / 0.04	1160 / 1080	24 / 22
	S_{11}	A"	5.35 / 5.33	0.00 / 0.00	9 / 7	0 / 0
	S_{12}	A'	5.36 / 5.32	0.01 / 0.00	509 / 113	11 / 2
BBHQ	S_1	B_u	2.94	0.46	0	0
	S_2	B_u	3.76	0.98	0	0
	S_3	A_g	4.12	0.00	122000	1520
	S_4	A_g	4.30	0.00	7330	99.2
	S_5	B_u	4.31	0.02	0	0
	S_6	A_g	4.32	0.00	1170	16
	S_7	B_u	4.77	0.01	0	0
	S_8	A_g	4.92	0.00	985	17.5
	S_9	A_g	5.05	0.00	8910	167
	S_{10}	B_u	5.11	0.01	0	0
	S_{11}	A_u	5.20	0.00	0	0
	S_{12}	B_g	5.30	0.00	55	1
	S_{13}	B_u	5.30	0.03	0	0
	S_{14}	B_u	5.36	0.06	0	0
	S_{15}	A_g	5.53	0.00	39100	875

The excitation energy for the transitions with the largest TPA cross section of HBO and BBHQ is close to the energy of vertical transitions for the keto structures in the excited states which correspond to the maxima of fluorescence bands with an anomalously large Stokes shift. The calculated values for the vertical transitions of the keto structures reported in [7] are 2.67 eV for HBO and 1.97 eV for BBHQ. The corresponding values of excitation energy $\omega_f/2$ are 2.60 and 2.06 eV. In the case of DBP the energies of excitation and fluorescence transition are 2.66 eV [7] and 2.14 eV.

4. Conclusions

Theoretical modeling of two-photon absorption is performed for three benzoxazoles exhibiting excited state intramolecular proton transfer. Molecules that possess two beznoxazole fragments are predicted to be more efficient in two-photon absorption than 2-(2'-hydroxyphenyl)benzoxazole. Transitions with large two-photon absorption cross section have higher energy than the lowest transitions that demonstrate large oscillator strength for one-photon absorption. Nevertheless, it is possible to excite these transitions by the two-photon absorption with photons, which energy is substantially below the edge of the one-photon absorption.

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