MODELLING OF PHOTOCHROMIC PROPERTIES OF BENZOXAZINE COMPOUND BY MEANS OF QUANTUM CHEMICAL METHODS

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Photochromic compounds are light-sensitive molecular systems which exhibit changes of absorption properties during photoinduced processes. Changes in absorption spectrum indicate energy transfer and structural transformations of the system [1], which are reversible (by thermal dissipation or by photoexcitation of a different wavelength) in most cases. Possible applications of such compounds include molecular-scale electronics and high density data storage [2].

Here are presented the results of quantum chemical calculations of structural and electronic properties of photochromic indolo[2,1-b][1,3]benzoxazine compound. Spectral measurements upon the excitation of this compound show the presence of two distinct chromophoric groups in the system, which are created by breaking C-O bond of the oxazine ring in the initial complex [3]. Within few hundred nanoseconds system reverts back to the ground state. Molecular structure and excitation properties of the complex and its subgroups are determined using several quantum chemical methods. The calculations were performed using Gaussian03 and GAMESS-US programs.

Structure optimization of benzoxazine compound was performed using density functional theory (DFT) with B3LYP functional and two different basis sets (6-31G(d) and 6-311G(2d,p)). In addition to the optimal ground state geometry three local minima (representing variants of broken-up structure, see Fig. 1) were located, as well as transition points in the ground state potential surface. Geometric structure of molecular subgroups in the system – 3H-indolium and 4-nitrophenolate anion – was optimized using the same method and basis sets. Electron-energy states for all compounds were obtained using several methods, including time dependent DFT (TD-DFT), GUGA-CIS and ZINDO. Calculation results in vacuum and using polarization continuum solvent model (PCM), with acetonitrile acting as solvent, were also compared. Theoretical absorption spectra of the initial compound and its subgroups in ground state, based on TD-DFT calculations, agree fairly well with experimental observations.

Optimal geometry of benzoxazine compound in lowest active excited state was calculated using CIS method and 6-311++(2d,p) basis set; it was found to be similar to the geometric structure of the complex in first local ground state energy minimum. Changes to absorption spectrum caused by the deformation of the complex approaching the excited state energy minimum were shown to be in correspondence with experiment results in time range of 200 fs to 725 fs.

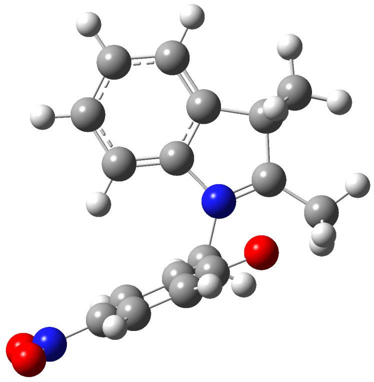

Figure 1. Structure of indolo[2,1-b][1,3]benzoxazine compound with open oxazine ring

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