

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

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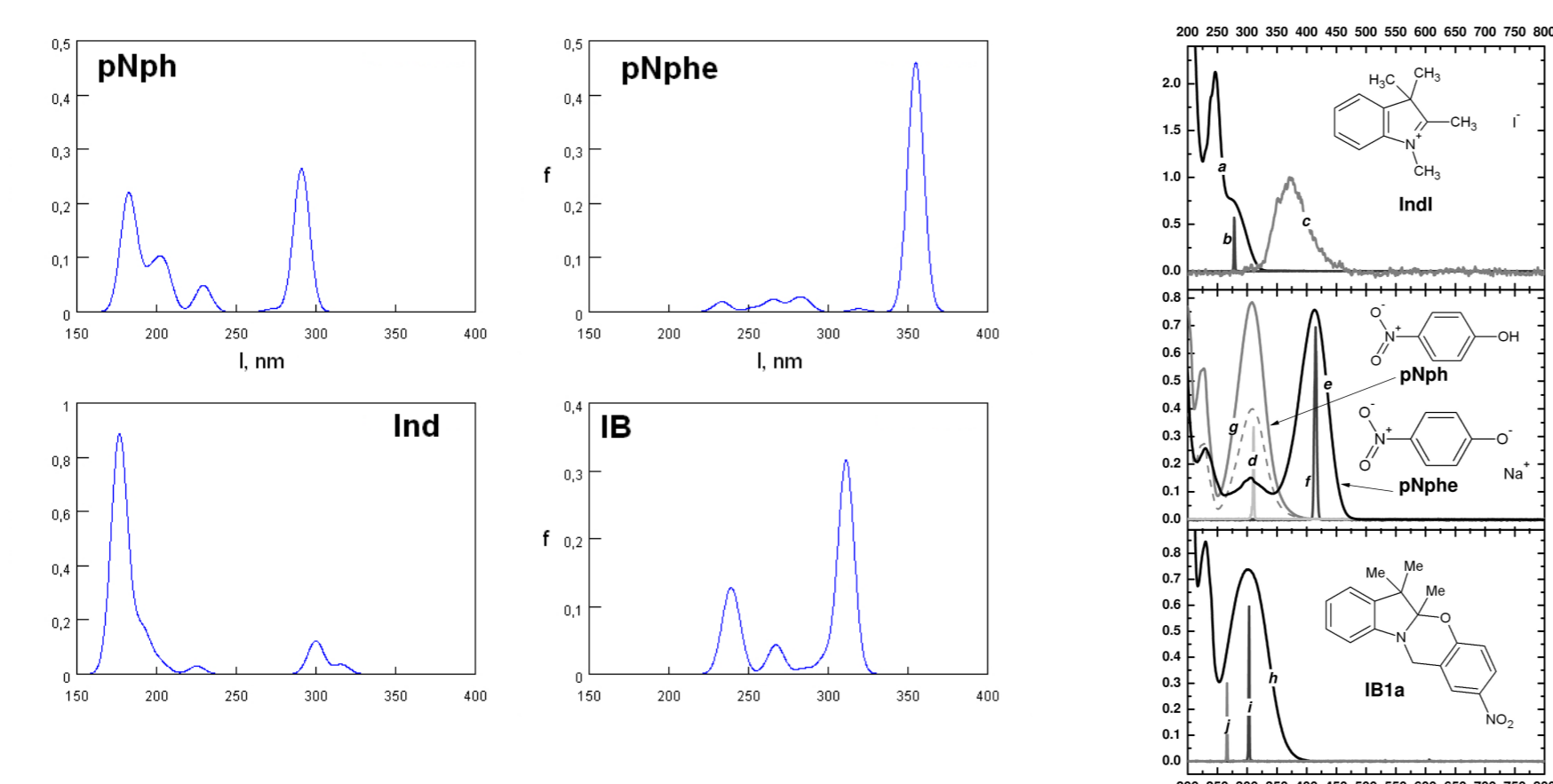
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Overview

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 [3]. 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 [4, 5]. 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, including time-dependent DFT (TD-DFT), ZINDO, unitary group approach (GUGA) and multiconfigurational perturbation theory (MCQDPT). The calculations were performed using Gaussian03 and GAMESS-US programs.

Absorption spectrum

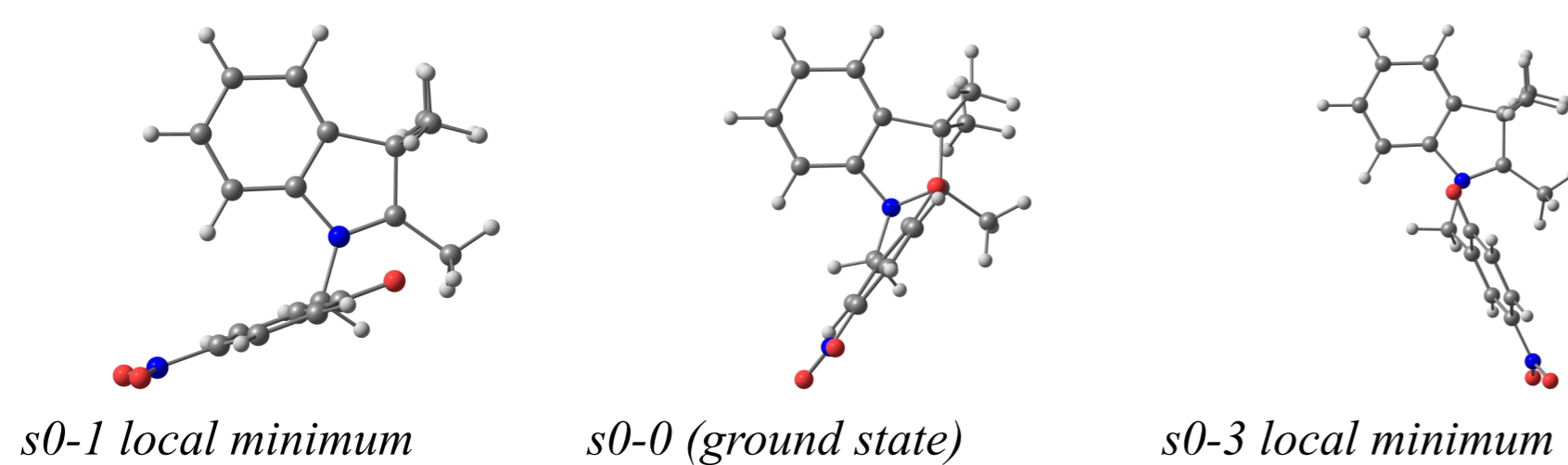


Absorption spectra of 5a,6-dihydro-12h-indolo[2,1-b][1,3]benzoxazine (indolo-benzoxazine, IB) compound and its molecular groups, 3H-indolium (Ind) and 4-nitrophenol/ 4-nitrophenolate (pNph/ pNphe). **Above:** theoretical absorption spectra based on TD-DFT calculations (B3LYP functional, 6-311++(2d,p) basis set, no solvent account) and experimental data from [4] (curves a, e, g and h). **Right:** Absorption peak wavelengths of IB compound and its molecular groups

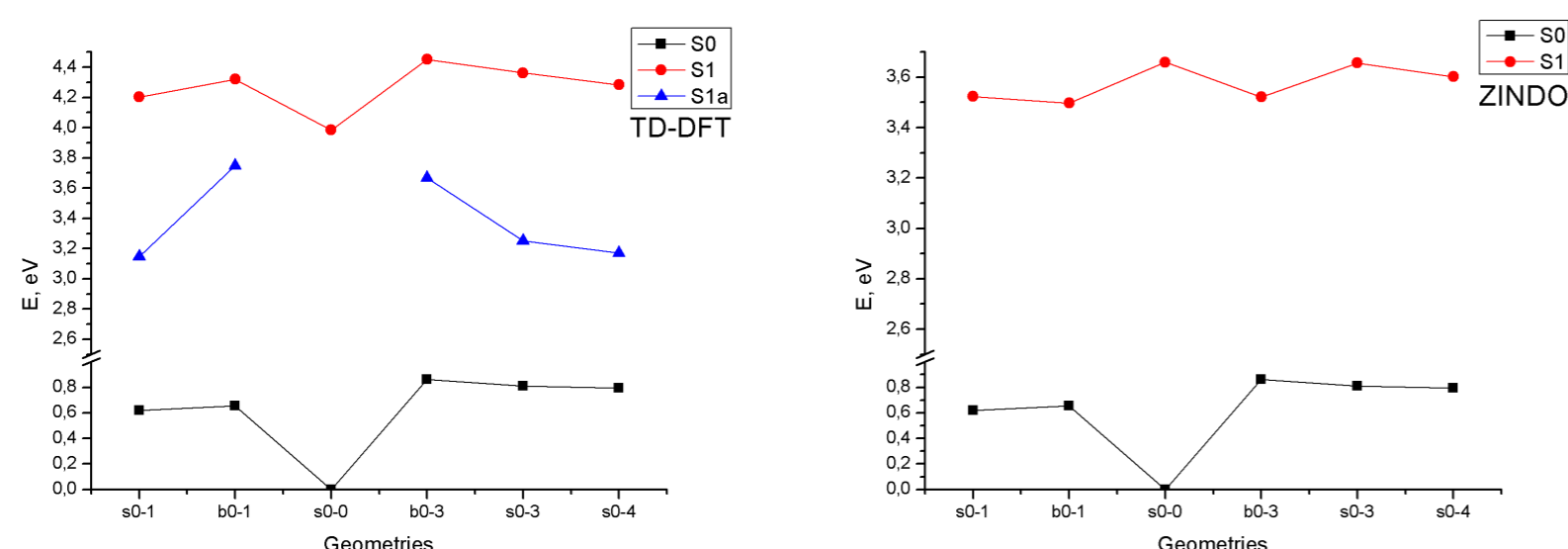
Compound	Experiment	TD-DFT
Ind(+)	278 nm 247 nm	300 nm ---
pNph	309 nm 225 nm	291 nm 182 nm
pNphe(-)	415 nm	355 nm
IB1a	302 nm 230 nm	311 nm ~240 nm

attributed to interaction with iodine

Energy surface of ground and lowest-lying excited states

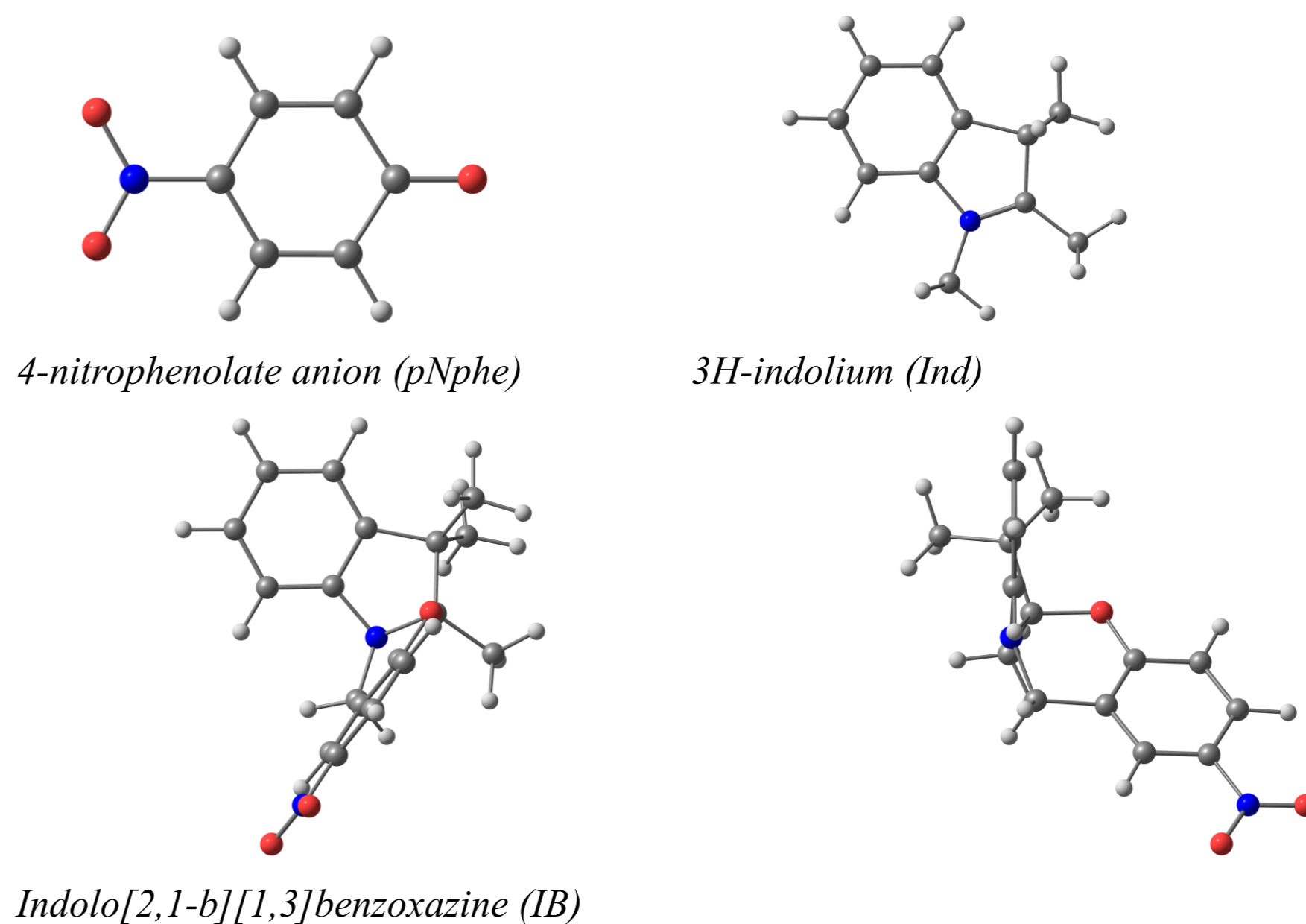


Molecular structure of IB compound in several minima of ground state energy. Global minimum (s0-0) corresponds to initial state of the compound, while the local minima (s0-1 and s0-3) exhibit the breaking of C-O bond and rotation of pNphe group that is suggested to occur during photoexcitation of the molecule.

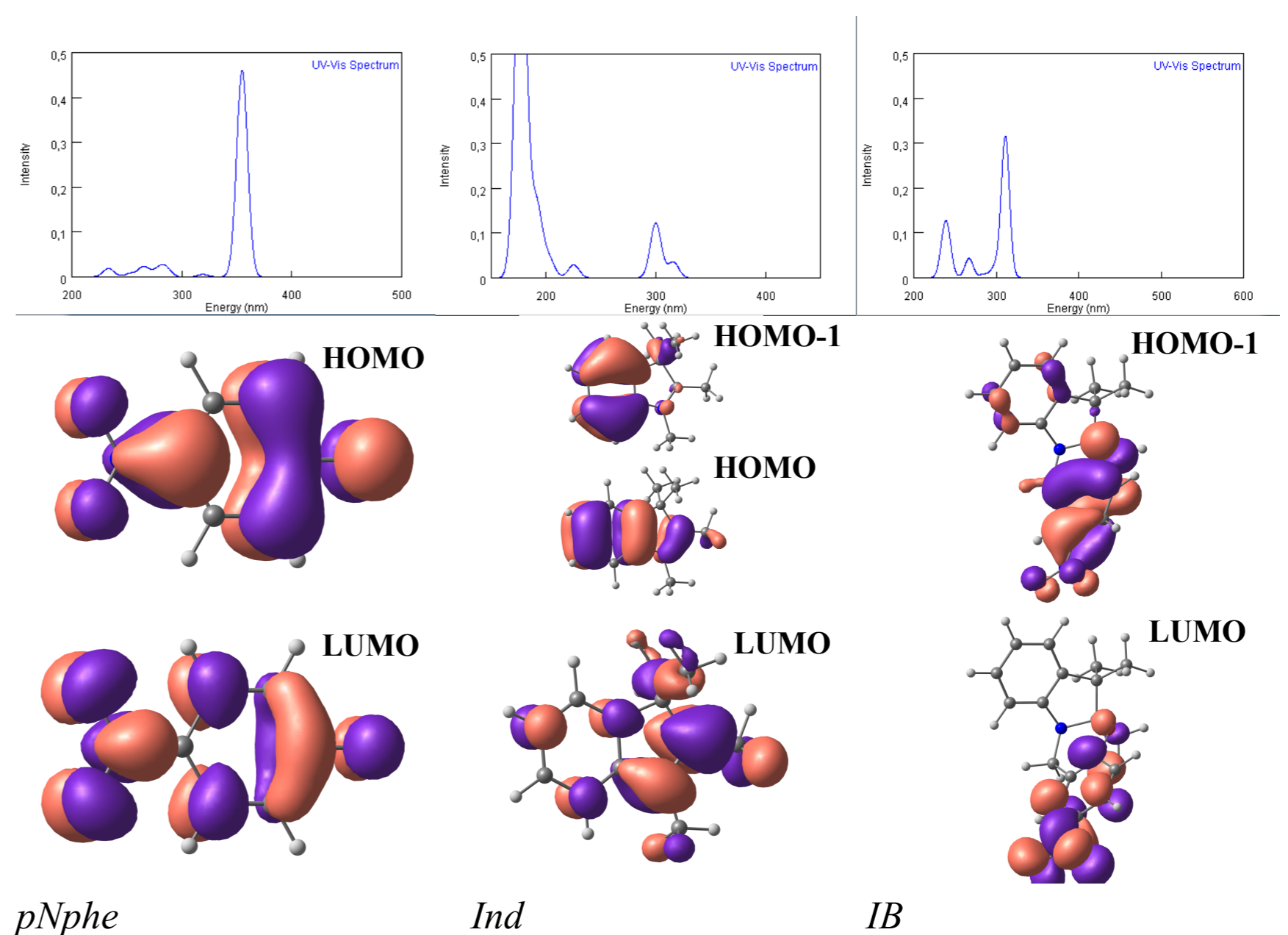


Energy values of ground (S0) and lowest-lying active excited states of various structures of IB compound, calculated using TD-DFT and ZINDO methods. s0-0 denotes global minimum, s0-1, s0-3, s0-4 – local minima, b0-1, b0-3 – transition structures

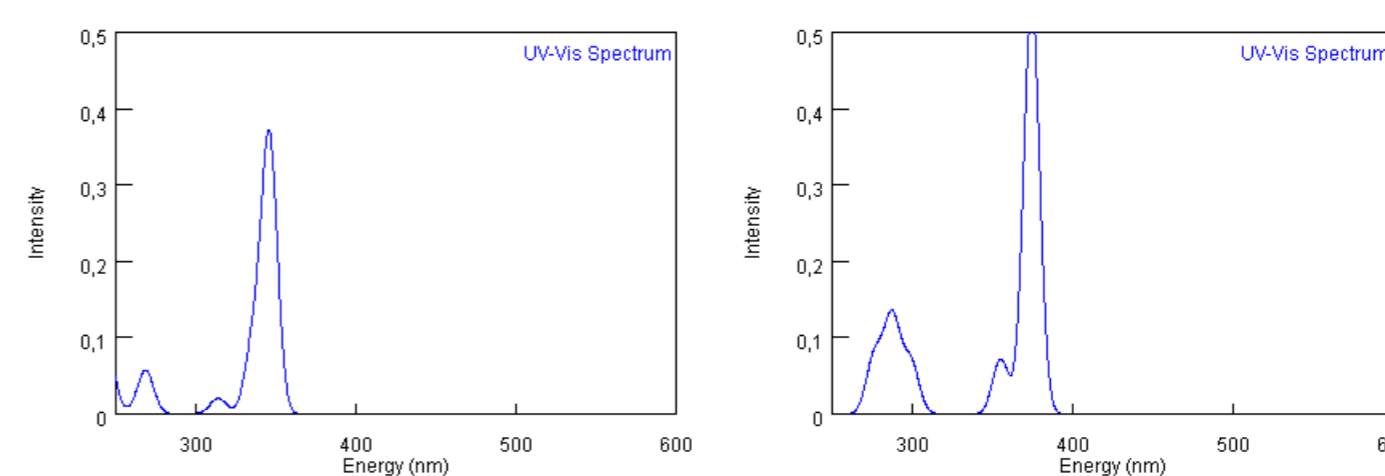
Molecular structure



Wavefunction character of photoexcitation



Absorption spectra (TD-DFT, solvent - acetonitrile) and molecular orbitals corresponding to the lowest active excitation of IB compound and its molecular groups.



Absorption spectrum (TD-DFT, solvent - acetonitrile) of ground state (s0-0, left) and s0-3 local minimum of IB compound

Results

In addition to the optimal ground state geometry three local energy minima of IB compound were located. Local minima represent variants of broken-up structure, formation of which during photoexcitation is suggested by the experiment. Most notable changes to the molecular structure outside the ground state are:

- breaking of the C-O bond between Ind and pNphe molecular groups;
- rotating of pNphe group around the C-C bond at the end of Ind methyl group;
- symmetrization of Ind group further away from ground state.

These changes split molecule into two loosely-connected groups, which affects absorption properties of the system. Relatively narrow spectrum of IB expands and starts exhibiting two distinct peaks around 400 nm and around 300 nm (see above). Molecular orbital analysis of IB compound and its molecular groups shows that lowest active excitation of the compound involves the same orbitals that are active during the excitation of separate groups.

Literature:

- [1] T. Hugel, N. B. Holland, H. E. Gaub, *Science*, **296**, 1103 (2002)
- [2] M. Irie, *Chem. Rev.*, **100**, 1683 (2000)
- [3] V. Amankavičienė, W. Holzer, S. J. Asadauskas, A. Šačkus, *Theses from International Conference on Organic Synthesis*, 58 (2006)
- [4] M. Barkauskas, V. Martynaitis, M. Vengris, *Lith. J. Phys.*, **48**, 231 (2008)
- [5] M. Tomasulo, S. Sortino, F. M. Raymo, *J. Org. Chem.* **73**(1), 118 (2008)

