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Synthesis, Spectroscopic and TD-DFT Quantum Mechanical Study of Azo-Azomethine Dyes. A Laser Induced *Trans-Cis-Trans* Photoisomerization Cycle

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Abstract

This paper describes the synthesis, spectroscopic characterization and quantum mechanical calculations of three azo-azomethine dyes. The dyes were synthesized via condensation reaction between 4-(dimethylamino)benzaldehyde and three different 4-aminobenzene azo dyes. Quantum chemical calculations on the optimized molecular geometry and electron densities of the *trans (E)* and *cis (Z)* isomers and their vibrational frequencies have been computed by using DFT/B3LYP density-functional theory with 6-311++G(d,p) basis set in vacuo. The thermodynamic parameters such as total electronic energy *E (RB3LYP)*, enthalpy H_{298} (sum of electronic and thermal enthalpies), free Gibbs energy G_{298} (sum of electronic and thermal free Gibbs energies) and dipole moment μ were computed for *trans (E)* and *cis (Z)* isomers in order to estimate the $\Delta E_{trans\rightarrow cis}$, $\Delta\mu_{trans\rightarrow cis}$, $\Delta H_{trans\rightarrow cis}$, $\Delta G_{trans\rightarrow cis}$ and $\Delta S_{trans\rightarrow cis}$ values. After molecular geometry optimization the electronic spectra have been obtained by TD-DFT calculations at same basis set and correlated with the spectra of vapour deposited nanosized films of the dyes. The NBO analysis was performed in order to understand the intramolecular charge transfer and energy of resonance stabilization. Solvatochromism was investigated by UV-VIS spectroscopy in five different organic solvents with increasing polarity. The dynamic photoisomerization experiments have been performed in DMF by pump lasers λ = 355 nm (mostly E→Z) and λ = 491 nm (mostly Z→E) in spectral region 300 nm – 800 nm at equal concentrations and times of illumination in order to investigate the photodynamical *trans-cis-trans* properties of the -CH=N- and –N=N- chromophore groups of the dyes.

Keywords: azo-azomethine dyes; Schiff bases; azobenzene dyes; DFT quantum chemical calculations; trans-cis-trans photoisomerization; solvatochromism; photochromism.