

Malinee Promkatkaew 2009: Structural and Electronic Properties of Methoxy Substituted Cinnamates Based on Quantum Chemical Calculations. Master of Science (Chemistry), Major Field: Chemistry, Department of Chemistry. Thesis Advisor: Mr. Songwut Suramitr, Ph.D. 71 pages.

The structural and electronic properties of methoxy substituted cinnamates with five different substituted positions were investigated using the time-dependent density functional theory (TD-DFT) and symmetry-adapted cluster configuration interaction (SAC-CI) methods. These series included *cis*- and *trans*-isomers of ortho-(**1**), meta-(**2**), and para-(**3**)-monomethoxy and 2,4,5-(**4**) and 2,4,6-(**5**) trimethoxy substituted compounds. The ground state geometries were obtained at the B3LYP/6-31G(d) and B3LYP/6-311G(d) levels of theory, whereas, the excited state geometries were obtained at the CIS/D95(d) levels of theory. All the compounds were stable as *cis*- and *trans*-isomers in the planar structure in both the S_0 and S_1 states, except the 2,4,6-(**5**)-trimethoxy substituted compound. The TD-B3LYP/6-31G(d) and SAC-CI/D95(d) calculations reproduced the recently observed absorption and emission spectra satisfactorily. Three low-lying excited states were found to be relevant for the absorption in the UV blocking energy region. The calculated oscillator strengths of the *trans*-isomers were larger than the respective *cis*-isomers, which is in good agreement with the experimental data. In the ortho- and meta-monomethoxy substituted compounds, the most intense peak was assigned as the transition from next HOMO to LUMO, whereas in the para-monomethoxy substituted compound, it was assigned to the HOMO to LUMO transition. This feature was interpreted as being from the variation of the MOs due to the different substituted positions, and was used to explain the behavior of the excited states of the trimethoxy substituted compounds. The emission from the local minimum in the planar structure was calculated for the *cis*- and *trans*-isomers of the five compounds. The relaxation pathways which lead to the non-radiative decay were also investigated briefly. In the TD-DFT and SAC-CI calculations provide reliable results and a useful insight into the optical properties of these molecules, and therefore, provide a useful tool for developing UVB blocking compounds with regard to the tuning of the absorption.

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