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Elucidating the conformational change and electronic absorption spectrum of *p*-dimethylamino-cinnamaldehyde merocyanine across different solvent polarities

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We present a theoretical study on the structural and electronic properties of the *p*-dimethylamino-cinnamaldehyde (DMACA) merocyanine molecule in solvents of different polarities by combining the free energy gradient and the average solvent electrostatic configuration methods via an iterative procedure based on the sequential quantum mechanics/molecular mechanics hybrid methodology. Studying such a system in solution is a crucial step for understanding the solvent effects on its properties, which can have implications in fields such as optoelectronics and biophysics. We found that the DMACA molecule presents different geometries in nonpolar and polar solvents, changing from a polyene-like structure with a pyramidal dimethylamino group (in gas phase or nonpolar solvents) to a cyanine-like structure with a planar dimethylamino group in water due to the stabilizing effect of hydrogen bonds between DMACA and water. The molecular absorption spectrum showed a significant change, increasing solvent polarity with a large shift of the lower energy band, while the other two low lying bands did not shift significantly. The study accurately described the solvatochromic shift of the lowest-energy band and analyzed the structure of the excited states in terms of the one-electron transition density matrix, which showed that the dominant excited state (associated with the first lower energy band) is characterized by a local excitation on the benzene ring with charge transfer character to the carbon conjugated segment.

Topics

Quantum mechanical/molecular mechanical calculations, Molecular geometry, Absorption spectroscopy, Fluorescent dye, Solvent effect

Supplementary Material

Supplementary materials- zip file