

Quantum-Chemical Studies of Electron Transitions of Merocyanine Derivatives of Cyclohexadienon

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Neutral merocyanines are donor-acceptor substituted polymethine molecules, and as such, they represent an important class of organic chromophores with other linear conjugated system, e.g. polymethinic dyes, squaraines, cyanine bases and polyenes.

In this report presented the results of quantum chemical investigation of the electron structure and nature of electron transitions of merocyanine derivatives of the cyclohexadienon with variable donor residues Het.

The chemical constitution of variable donor terminal groups to have an important influence on the electronic structure of merocyanine molecules and their electron transitions. In the Gaussian 03 software package performed molecule modeling, quantum chemical calculations of molecular geometry and distribution of the electron density in the main and excited states. Quantum-chemical calculations of optimized molecular geometry were performed using the DFT/CAM-B3LYP//6-31G(d, p) method; electron transition characteristics were calculated using the TD-DFT/CAM-B3LYP//6-31G(d, p) method and the semi-empirical ZINDO method. Of course, calculated and experimental data do not match perfectly, which is typical for quantum-chemical estimations, however, the correlation is sufficient to correctly analyze the nature of electron transitions.

The dependence of atomic charge alternation on the chemical constitution of the donor terminal group is estimated by

$$\Delta q_{\mu} = |q_{\mu+1} - q_{\mu}|,$$

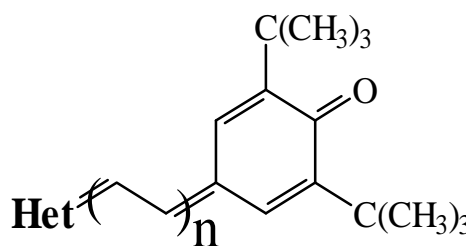
where q_{μ} is the charge at the μ -th atom. A simple quantum-chemical approximation showed that BLA bonds (bond length alternation) can have a positive or a negative value, depending on the donor and/or acceptor strengths of the terminal groups.

The degree of bond alternation is calculated by the following formulas:

$$\Delta l_{\nu} = (-1)^{-\nu} (l_{\nu+1} - l_{\nu}),$$

where l_{ν} is the length of the ν -th bond.

The mutual dispositions of delocalized MOs and local π -orbitals as well as n-MO depend on the donor properties of the variable terminal residues, Het; calculated energies of the frontier and several nearest levels of the merocyanines.



- [1] N. Tyutulkov, J. Fabian, A. Mehlhorn, F. Dietz, A. Tatjer, *Polymethine Dyes. Structure and properties*, St. Kliment Ohridski University Press, Sofia, 1991.