

Influence of methyl substitution and bond length alternation on the lowest excited states of linear polyenes

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Due to their central role in biophysical photo-processes and technical applications, linear polyenes are frequent targets of experimental and theoretical research. However, the understanding of the nature of their lowest excited electronic states still poses a challenging task. Here the influence of methyl substitution on the vertical excitation energies and excited state geometries of linear polyenes and the influence of bond length alternation strongly affecting computed vertical excitation energies have been investigated.

The performance of various levels of theory in the description of the electronic ground state geometry of linear polyenes is studied in detail. In addition, the algebraic diagrammatic construction (ADC)^[2] scheme is used to calculate vertical excitation energies. The results obtained are compared with experimental absorption and fluorescence data, which have recently been published for 1,1'-dimethylpolyenes^[1]. The best agreement is achieved when B3LYP/cc-pVTZ equilibrium structures are used, most likely due to most fortuitous cancellation of error. Moreover, the vertical excitation energies of methyl substituted linear polyenes strongly depend on the position and the rotational conformation of the methyl groups. While butadiene and the two isomers of dimethyl-butadiene were used to study the effect of different substitution schemes in detail, longer polyenes with up to seven double bonds are also included in our theoretical investigation.

Literature:

[1] R. L. Christensen et al, *Journal of Physical Chemistry* 112 (2008) 12629-12636

[2] J. Schirmer, *Physical Review A* 26 (1982) 2395