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论文

用PCM-TDDFT 研究螺吡喃、螺恶嗪类光致变色化合物的UV-vis光谱

林兵, 蔡敏, 李伟

武汉科技学院化学工程学院, 武汉 430073

摘要:

用包含有溶剂化效应的含时密度泛函理论(PCM-TDDFT), 选用PBE0和B3LYP 两种杂化函数在6-31+G(*d*) 基组水平上计算了21种螺吡喃和螺恶嗪的开、闭环的紫外吸收光谱. 通过计算光谱与实验光谱比较发现, B3LYP/6-31+G(*d*) 和PBE0/6-31+G(*d*) 能非常好地预测闭环态的最大吸收波长, 其平均绝对偏差(MAE)分别为0.20和0.16 eV, 计算光谱与实验光谱之间有较好的线性相关性(R分别为0.967和0.978). 对于开环态, 计算的最大吸收比实验谱峰高0.22 eV(B3LYP)和0.28 eV(PBE0). 通过对主要吸收谱峰的激发组态的分析发现, 主要的吸收谱峰主要源于最前线轨道HOMO, HOMO-1 和LUMO,LUMO+1间的$\pi\rightarrow\pi^*$ 电子跃迁.

关键词: 螺吡喃; 螺噁嗪; 紫外-可见吸收光谱; PCM-TDDFT

PCM-TDDFT Study of the UV-Vis Spectra of Photochromic Spirooxazine and Spiropyran Compound

LIN Bing, CAI Ming , LI Wei*

College of Chemical Engineering, Wuhan Unviersity of Science and Engineering, Wuhan 430073, China

Abstract:

Photochromic compounds and polymer are new functional materials, which can be widely used in optical information storage, optical conversion devices, optical switches and other fields. In this paper, the electronic absorption spectra of 21 spriooxazine and spiropyran derivatives in close and open-ring states were investigated in the framework of time-dependent density functional theory(TDDFT) with polariable continuum model(PCM) including solvent effect. The B3LYP and PBE0 hybrid functionals together with 6-31+G(*d*) basis set were selected to calculate the excitation energies of 8—30 lowest-lying singlet excited states. In close-ring states, both PBE0 and B3LYP functional well reproduce the experimental values, and the mean absolute error(MAE) are 0.16 and 0.20 eV, respectively. The mainly absorption bands mainly raise from the $\pi\rightarrow\pi^*$ transition from HOMO-1, HOMO to LUMO, LUMO+1. In open-ring states, both PBE0 and B3LYP overestimate the experimental excitation energies by 0.08—0.40 eV, and the MAE is 0.28 and 0.22 eV, respectively. Calculations reveal that the maximum absorption bands mainly result from the transition from HOMO or HOMO-1 to LUMO, and have $\pi\rightarrow\pi^*$ characters.

Keywords: Spriooxazine; Spiropyran; UV-Vis absorption spectrum; Polarizable continaum model (PCM)-time dependent density furctional theory(TDDFT)

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通讯作者: 李伟, 男, 博士, 教授, 主要从事分子模拟与光谱分析研究. E-mail: liwei_whu@sohu.com

作者简介:

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