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Outperformance of CAM-B3LYP than M062X Density Functional in Mixed Transition of Local Excitation and Charge Transfer

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Abstract. A balance between the local excitation (LE) and charge-transfer (CT) transitions is an important issue of a density functional. In this work, we compare the performance between the global hybrid functional M062X and long-range separated functional CAM-B3LYP when they calculate the absorption energies of visible light photoswitches hemithioindigo (HTI) Z1, Z2, Z4, Z5 and Z7. The electronic excitations of HTI Z1 and Z2 are mixtures of LE and CT transitions. CAM-B3LYP succeeds to predict the same absorption energy sequence of the five compounds as the experimental results while M062X predicts a wrong sequence of HTI Z1 and Z2. Another global hybrid functional M06 is also employed for a comparison. Finally, we suggest CAM-B3LYP rather than M062X when dealing with mixed electronic transtions.

Keywords: Photoswitches, Hemithioindigo, Vertical Excitation Energy, Density Functional.

1. Introduction

Photoisomerization induced by double bond twisting plays a central role in applications of molecular motors and photoswitches [1-4]. Hemithioindigo (HTI) is a class of emerging visible light photoswitches that is composed of a thioindigo fragment and a stilbenze part connected by a C=C double bond [5, 6], as shown in Figure 1. In our very recent study, we have used M06, M062X, B3LYP and BMK functionals to study the excited-state properties of a series of HTI derivatives (HTIs), including Z1, Z2, Z4, Z5 and Z7 [7]. Their molecular structures are shown in Figure 1. We find that none of these density functionals predict a correct absorption energy sequence of these HTIs. This is induced by that the involved electronic transitions in HTIs are a mixture of local excitation (LE) and charge-transfer (CT) excitation. It is well-known that the exact exchange-correlation (XC) functional is unavailable and thus the available density functionals are approximate functionals. A single pure density functional is unable to deal with CT states owing to the delocalization error [8]. In contrast, Hartree-Fock (HF) approximation suffers from localization error. Thus, inclusion of HF exchange in pure functionals provides a way to cancel the errors, which is the principle of hybrid functionals. The inclusion percent of HF exchange is denoted as X, which is a constant in global hybrids, such as M06, M062X, B3LYP and BMK. Another kind of hybrid functionals is that the HF exchange fraction is a function of interelectronic separation r_{12}, that is, the range-separated hybrids or named as the long-range corrected functionals, such as the CAM-B3LYP functional [9].

In range-separated hybrids, the electronic-electronic Coulomb interaction term is divided into two or more terms by using the complementary error function (erfc) and the error function (erf). Thus, the Coulomb operator can be written as follows:

$$\frac{1}{r_{12}} = \frac{\mathrm{erf}\,(\omega r_{12})}{r_{12}} + \frac{\mathrm{erfc}\,(\omega r_{12})}{r_{12}}$$

where erfc=1-erf. The first and second terms correspond to long-range and short-range, respectively. The adjustable parameter ω determines the range over which the separation occurs. Obviously, when ω equals to zero, the long-range term is zero, and when $\omega \to \infty$ the short-range term is zero. In the CAM-B3LYP functional, the HF exchange fraction increases from 19 to 65 percent from short-range to long-range interelectronic separation. Note that the HF exchange fraction of M06 and M062X is 27 and 54, respectively.

In order to compare the performance of long-range corrected hybrid functional and global functionals, we calculate the absorption energies of HTIs Z1, Z2, Z4, Z5 and Z7 in dichloromethane (DCM) by CAM-B3LYP functional. The absorption energies of these HTIs by M06 and M062X functional have been calculated in our recent study, which turns out that neither of these two functionals could predict the correct energy sequence [7].
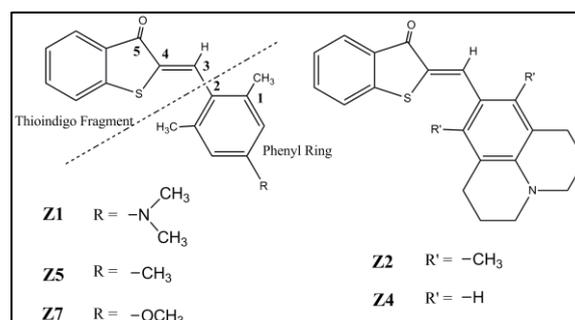
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Figure 1. The chemical structures of Hemithioindigo Z1, Z2, Z4, Z5 and Z7.

2. Computational Details

In all calculations, the long-ranged corrected CAM-B3LYP functional in cooperation with the 6-31+g(d, p) basis set was used. Polarized continuum model (PCM) was used to simulate the bulk DCM solvent. Because DCM is aprotic, the solvent-solute hydrogen bonding effect could be ignored. Ground-state geometries were optimized and then checked by frequency calculations where no imaginary frequency was found. Electronic absorption energies were calculated using the linear-response PCM (LR-PCM). It turned out that the lowest excited state (S_1) was the absorption state for all HTIs. In order to analyze the CT characters in electronic transitions, the natural orbital charges (NBO) in ground state (S_0) and S_1 were calculated. The atomic NBO charges of thioindigo fragment in S_0 and S_1 were summed, respectively. Their difference was the amount of transferred charge (in unit a.u.)

3. Results and discussion

The optimized S_0 geometries of HTIs Z1, Z2, Z4, Z5 and Z7 are shown in **Figure 2**. Inspection of **Figure 2** obviously shows that except HTI Z4 is a planar geometry, other HTIs exhibit pre-twisting geometries where the thioindigo and phenyl planes are not coplanar. These geometrical characteristics are in agreement with the equilibrium geometries optimized by M06 and M062X functionals [7]. Based on these equilibrium S_0 geometries, the vertical excitation energies are calculated.

Table 1 collects the two lowest excited state (S_1, S_2) transition energies and their corresponding transition orbitals and oscillator strengths. Obviously, for all studied HTIs, the S_1 possesses significant oscillator strength while the oscillator strength of the S_2 is very small. The transition energy of the S_2 is much higher than the S_1. The S_1 state contributes to the experimental first UV-visible absorption peak. Note that neither M06 nor M062X predicts the correct absorption energy sequence of the HTIs Z1, Z2, Z4, Z5, Z7.[7] Experiment determines the absorption energy sequence is Z5 > Z7 > Z1 > Z2 > Z4 [10]. However, M06 predicts the absorption energy of
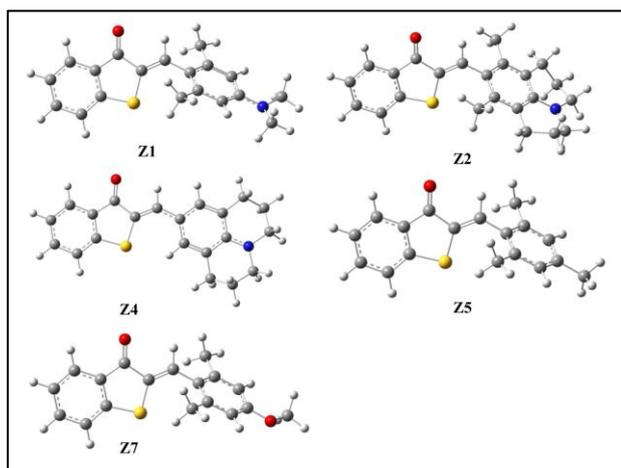
Z2 lower than Z4 while M062X predicts the absorption energy of Z1 lower than Z2 [7]. Inspection of Table 1 clearly indicates that CAM-B3LYP predicts the same absorption energy sequence as experimental results. Therefore, CAM-B3LYP outperforms M06 and M062X on calculating the absorption energies of HTIs.

Table 2 shows the amount of transferred NBO charge in S1 transition calculated by M062X, M06 and CAM-B3LYP. For each HTI, M06 predicts significantly larger CT character than M062X and CAM-B3LYP, while the latter two functionals predict nearly the same CT character. It is well-determined that functionals with smaller X overestimate the stability of CT states.[11] The hybrid functional M06 has smaller X than M062X (27 vs. 54). In CAM-B3LYP, X is not a constant and increases from 19 to 65 as interelectronic separation increases. Only CAM-B3LYP predicts the same absorption energy sequence indicates this long-range corrected functional combines the advantages of M06 and M062X.

Because many theoretical studies employ M062X to explore the excited-state properties [12-14], we focus on discussing the difference between these two functionals. Both the two functionals are hybrid functionals, but the HF exchange fraction in M062X is a constant (54%) while that in CAM-B3LYP is a function of interelectronic distance (19~65%). In the long interelectronic distance where the CT state plays a major role, the two functionals involve a similar HF exchange fraction, making both of them avoiding the overestimation of CT stability, which is a serious problem in B3LYP and M06 functionals. However, when the local excitation character in an electronic transition is obvious, the M062X functional overestimates the transition energy due to its involvement of large HF exchange fraction. Note that the pure functional without any HF exchange fraction gives better performance on LE states than hybrid functionals. As a result, in the short interelectronic distance where the LE character is predominant, the CAM-B3LYP outperforms than M062X. The 19% HF exchange of CAM-B3LYP in in short interelectronic distance is near to the 27% HF exchange of M06. Given that the M06

Figure 1: The optimized ground-state geometries in DCM at the PCM-B3LYP/6-31+g(d, p) calculation level.

Table 1. Vertical excitation energies (ΔE, in eV) of the two lowest excited states (S_1, S_2) and oscillator strengths (f), as well as the experimental absorption energies from ref [10]

$\Delta E(f)$	Z1	Z2	Z4	Z5	Z7
S_1	3.15(0.54)	2.98(0.43)	2.90(1.08)	3.44(0.17)	3.40(0.24)
S_2	3.64(0.02)	3.58(0.02)	3.78(0.10)	3.71(0.00)	3.69(0.01)
Exp.	2.70	2.56	2.41	2.95	2.92

Table 2. The amount of transferred NBO charges (in unit a.u.) from phenyl ring to the thioindigo fragment in the S1 calculated by M062X, M06 and CAM-B3LYP.

ΔQ	Z1	Z2	Z4	Z5	Z7
M06[a]	0.56	0.74	0.98	0.21	0.31
M062X[a]	0.40	0.56	0.29	0.03	0.10
CAM-B3LYP	0.38	0.58	0.28	0.00	0.06