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Electronic Structure and Optical Properties of Conjugated Molecules: SAC-CI Study

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Abstract. Electronic structure and optical properties of some organic conjugated molecules, chelating hetero-atomic conjugated ligands and some derivatives of the UVB blocking cinnamates, have been investigated by the SAC-CI method. The absorption and emission spectra of these molecules have been reproduced in high accuracy. The excited-state geometry relaxation was interpret based on the electrostatic force theory. The present work provides a useful basis for the theoretical design predicting the optical properties of the molecules.

Keywords: SAC-CI, optical properties, hetero-atomic conjugated molecule, UVB blocking
PACS: 31.15.ag, 31.15.bw, 31.15vq

INTRODUCTION

Chelating heteroatomic conjugated molecules, such as pyridine, benzoxazole, and benzothiazole derivatives, are technologically important compounds. An increasing research focus for heteroatomic conjugate molecules is their application in the area of organic optoelectronic materials, such as photoconducting materials, liquid crystals, and fluorophores. Heteroatomic conjugate molecules have also been widely used as cyclometalated ligands in heavy metal complexes because of their strong chelating capability and their characteristic optical properties based on π-conjugation. Heavy metal complexes, such as Ir(III) and Pt(II) complexes, have been proven to be excellent phosphorescent dyes for the organic light-emitting diodes.

Cinnamates also have received much attention, as they are the most widely used UVB blocking compounds among the various cosmetic sunscreen agents. Cinnamates achieve UVB blocking from a ππ* absorption followed by a *cis–trans* isomerization at the propenyl double bond in the S_1 state and a relaxation to the ground state involving nonradiative decay. As a UVB blocking compound, the optical properties, in particular the photoabsorption efficiency in the UVB energy region (290–320 nm) is an important factor. In order to achieve the favorable optical properties, molecular design using the variation of the substituents has been extensively performed.

The SAC–CI (symmetry-adapted cluster-configuration interaction) method[1] has been shown to be reliable and useful for investigating a wide variety of molecular spectroscopic properties in many successful applications.[2] In this work, we have systematically investigated the electronic structure and optical properties of some conjugated molecules. The first group belongs to the chelating hetero-atomic conjugate molecules that are widely used for developing iridium (III) complexes, including 2-phenyl pyridine (PPY), 2-phenyl quinoline (PQ), and bonzo[h]quinoline (BZQ).[3] The second group is the methoxy substituted cinnamates, which show excellent UVB blocking performace.[4] The target molecules are ortho-(**1**), meta-(**2**), and para-(**3**) monomethoxy substituted cinnamates, and 2,4,5-(**4**) and 2,4,6-(**5**) trimethoxy cinnamates in both *cis*- and *trans*- isomers. The difference in electronic transitions among these molecules and the effect of methoxy substitution at the ortho-, meta-, and para-positions were analyzed.

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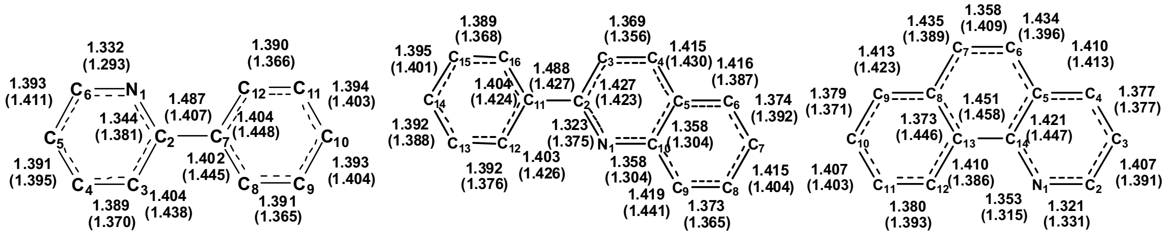
RESULTS AND DISCUSSION

chelating hetero-atomic conjugated molecules

We studied the electronic structure and optical properties of the 13 chelating hetero-atomic conjugated molecules,[3] categolized into three group: I) PPY, PQ, and BZQ; II) DPO, BO, BON, and OP; and III) BT BTP, αBSN, βBSN THP, and BTTH, based on the heteroatoms in their molecular structures. In this article, we present the results of the molecules in group I.

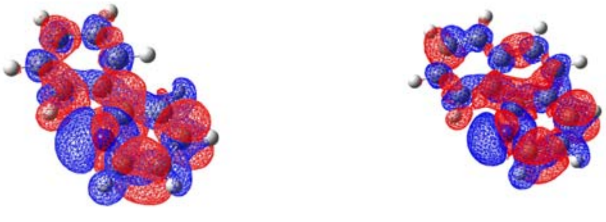
Each compound in this group contains one N atom in the conjugated ring. Figure 1 illustrates the calculated geometries of PPY, PQ and BZQ in the ground state (S_0) and the lowest $\pi\pi^*$ excited state (S_1) with the CC bond lengths. In the S_0 state of PPY, a non-planar structure is most stable with the torsion angle of 20.4°; the energy difference between planar and non-planar structure is about 0.2 kcal/mol. The PQ also has non-planar geometry at the S_0 state with =21.0°. These molecules becomes planar from a non-planar structure by the S_0-S_1 excitation. For PPY, the inter-ring CC bond distance is 1.488Å in S_0 and the bond shrinks significantly to 1.407Å in S_1. The bonds in the pyridyl and phenyl rings also become elongated or shorten alternatively by the S_0–S_1 excitation. The same trend was also found in PQ.



(a) PPY (b) PQ (c) BZQ

FIGURE 1. Geometries of PPY, PQ, and BZQ in the S_0 and S_1 states. Values are bond lengths of the S_0 (S_1) states.

The geometry relaxation in the excited state can be interpreted using the electrostatic force (ESF) theory. As an example, we discuss the geometric changes in the S_1 state of PPY. In ESF theory, geometry relaxation in the excited state is due to the force acting on nuclei caused by changes in electron distribution. The differences in the SAC–CI electron density between the S_0 and S_1 states in PPY and BZQ are shown in Figure 2. In PPY, the electron density in the C–C (C_2–C_3, C_7–C_{12}, C_7–C_8) and C_2=N_1 bonds in the phenyl ring and pyridyl ring decrease, while the density of the inter-ring C_2–C_7 bond significantly increases. The EC force along bonds including the C_2=N_1 and C_2–C_3 bonds decreases because of the decrement of electron density, whereas the EC force is enhanced along the C_2–C_7, C_6–N_1, and C_3–C_4 bonds. Consequently, the former bond lengths increase, and the latter bond lengths decrease. This geometry change enhance the conjugation between two rings and the S_1 structure of PPY becomes planar.



(a) PPY (b) BZQ

FIGURE 2. The SAC–CI electron density difference between the S_0 and S_1 states of PPY and BZQ. The region in the blue range has a decrement of electron density and that in the red range has an increment of electron density when a molecule is excited.

The experimental and theoretical absorption spectra of PPY and PQ are compared in Figure 3. The calculated spectra satisfactorily reproduced the position of the observed absorption peaks for these molecules. Based on the SAC–CI calculations, we assign the broad peak around 4.49eV (276 nm) as the second and third transitions calculated as 4.49eV and 4.69eV. The peak around 5.14eV (242nm) is assigned as the transition with a vertical excitation energy of 5.15eV. These transitions are mainly due to ππ* transitions. The SAC–CI calculation for PQ shows that the strongest transition occurs at an energy of 5.22eV. The experimental spectrum gives a strong indication that the absorption is very strong above 4.76eV (260nm). The absorption energies of 3.87eV and 4.49eV in our calculations are consistent with the structures at 3.87eV (320nm) and 4.35eV (285nm) in the experimental absorption spectra.

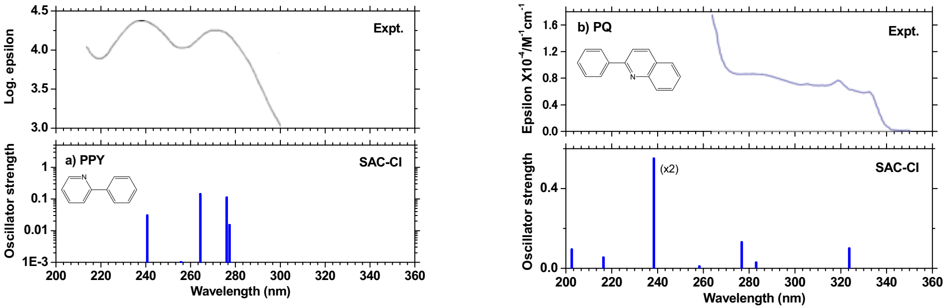
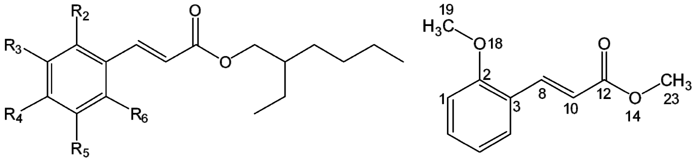


FIGURE 3. Theoretical absorption spectra of (a) PPY and (b) PQ compared with the experimental spectra.

UVB blocking cinnamates

The electronic structure and optical properties of the *cis*- and *trans*-isomers of methoxy substituted cinnamates have been investigated using the SAC-CI method.[4] The molecules are ortho-(**1**), meta-(**2**), and para-(**3**) monomethoxy substituted cinnamates, and 2,4,5-(**4**) and 2,4,6-(**5**) trimethoxy cinnamates as shown in Figure 4. In this article, we focus on the results of the *trans* isomers of the compounds **1**, **2**, and **3**. The trend of *cis*-isomers are similar to those of *trans*-isomers and the results of tri methoxy derivatives are referred to ref. [4].



Mol.	R_2	R_3	R_4	R_5	R_6
1	OCH_3	H	H	H	H
2	H	OCH_3	H	H	H
3	H	H	OCH_3	H	H
4	OCH_3	H	OCH_3	OCH_3	H
5	OCH_3	H	OCH_3	H	OCH_3

FIGURE 4. Chemical structures of 2-ethylhexyl-cinnamate derivatives and the calculated model compounds of trans-isomers.

The S_0 and S_1 state geometries of the *trans*-isomers of ortho-(**1**), meta-(**2**), and para-(**3**) methoxy substituted compounds were shown in Figure 5. All the compounds, except for the *cis*-**5** compound, had local minima in the coplanar structure of the *cis*- and *trans*-isomers in both the S_0 and S_1 states due to π-conjugation. In the S_0 state, the rotational energy barrier of the methoxy group is very low, although the planar structure is the most stable structure. The global minimum of the S_1 state is in the form of a nonplanar structure, but local minimum exist in the planar structure. The emission was observed from this local minimum in the planar structure, and in particular, a strong emission was observed for compound **2**.[5]

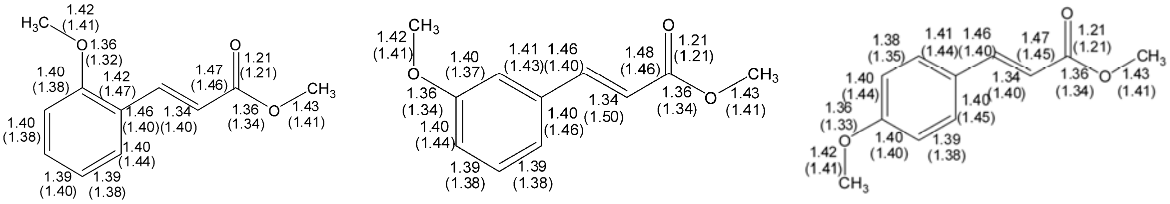


FIGURE 5. CC and CO bond length of the S_0 and S_1 states (in parentheses) of *trans*-**1**, *trans*-**2**, and *trans*-**3**.

It was found that the C_1–C_2, C_3–C_8, C_{10}–C_{12}, C_{12}–O_{14}, and O_{14}–C_{23} bond lengths decrease and the length of the other bonds increases. In the S_0 state, the carbon–carbon bond alternation exists for both the single and double bonds, but this bond alternation relaxes in the S_1 state. Since the excitation is relatively localized in the central unit, the prominent changes occur in the vinylene unit. For example, in the *trans*-**1** compound, the change in bond length is

Δr = +0.048, –0.060, and +0.057 Å for C_2–C_3, C_3–C_8, and C_8–C_{10}, respectively, while the other changes in bond length are within 0.022 Å.

The absorption spectra of the methoxy substituted cinnamates were calculated. The SAC-CI excitation spectra for the monomethoxy substituted molecules are compared with the experimental absorption spectra in Figure 6. For the monomethoxy substituted compounds, the excited states that contribute to the absorption have a different character that depends on the methoxy substituted position. In the case of the ortho-(*trans*-**1**) and meta-(*trans*-**2**) compounds, the S_3 state has the highest transition probability, and is characterized as being the transition from the next HOMO to LUMO (nH–L) transition, whereas, the highest transition possibility of the para-(*trans*-**3**) compound was calculated for the $S_0 \rightarrow S_1$ transition, and the excitation character is a HOMO–LUMO (H–L) transition. The agreement with the experimental values was satisfactory; the deviations were within about 10 nm.

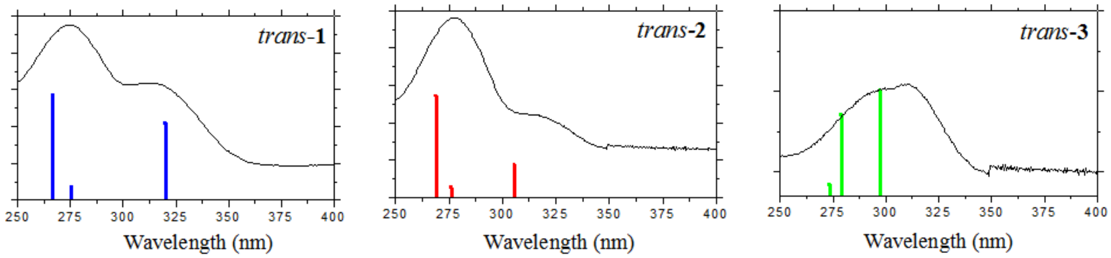


FIGURE 6. SAC-CI absorption spectra of trans-**1**, **2** and **3** compounds compared with the experimental spectra.[5]

The emission energies of these molecules have also been calculated using the SAC-CI method. The stable geometries of the S_1 state were located using CIS followed by the SAC-CI calculations of the vertical emission energies. The calculated emission energies are in good agreement with the experimental data as shown in Table 1.

TABLE 1. Emission energy (ΔE), emission wavelength (λ_{max}), oscillator strength (f) calculated using the SAC-CI method. Experimental values are cited from Ref. 5.

Mol.	**SAC-CI**			**Expt.**
	ΔE (eV)	λ_{max} (nm)	f	λ_{max} (nm) in hexane
trans-**1**	3.37	367	0.44	359
trans-**2**	3.62	343	0.29	350
trans-**3**	3.52	352	0.61	351

SUMMARY

Electronic structure and optical properties of chelating hetero-atomic conjugated ligands and some derivatives of the UVB blocking cinnamates have been investigated by the SAC-CI method. The absorption and emission spectra of these molecules have been reproduced in high accuracy. The present work provides a useful basis for the theoretical design predicting the optical properties of the molecules.

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