

A new guiding principle towards the spectral design of organic functional molecules

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Abstract A molecular orbital (MO) study on organic functional molecules was presented. The thermal stability of diarylethene and spironaphthoxazine was investigated. Then the optical properties, absorption wavelengths and intensities, of functional dyes were examined. The role of configuration mixing was emphasized. Finally, unexpected dependence of quantum yield on the wavelength was studied in the photochemical ring opening reaction of diarylethene.

Introduction

Organic functional materials such as photochromic systems and near-IR absorbing organic dyes have a considerable potentiality for various applications. For the future development, an understanding on a molecular level is of crucial importance, since the substantial optical functions of the devices are often dependent on the single molecule rather than aggregate. Therefore these molecules provide an unique opportunity to study the mechanism by utilizing MO method. We present in this paper the results of the ab initio and semiempirical MO studies, concerning (i) the thermal stability, (ii) absorption spectral properties, and (iii) quantum yield in the ring opening reaction. It is emphasized that the language of configuration mixing can be used for the design of the shift as well as the shape of spectra. The mechanism of the dependency of quantum yield on wavelength is also discussed.

Thermal Stability

The thermal stability of the closed form of diarylethene derivatives is an important requirement for many applications. By using MNDO method, we obtained the state correlation diagram of a conrotatory reaction path and a disrotatory reaction path for 1,2-diphenylethene and 1,2-di(3-furyl)ethene. The photocyclization reaction proceeds in the conrotatory mode. Not the steric hindrance but electronic property controlled the thermal stability, the closed ring form was found to depend on the difference of aromaticity in open and closed forms (1).

Spironaphthoxazine exhibits a deep blue color by UV irradiation. The exact structure of the open form which was responsible for the deep blue color was unknown for a long time. The most stable structure was determined among various possible isomers by ab initio calculation. The result was confirmed by ¹H NMR NOE spectroscopy (2).

Absorption Spectral Properties

Kubo and collaborators reported that naphthoquinone methide dyes had non planar geometry with established X-ray structures (3). The absorption spectra was in near-IR region of ~772nm. These molecules were counter-example against a conventional guiding

principle for the design of bathochromic shift. Because the conventional principle required the extended π -conjugation for bathochromic shift, where the structure must be necessarily planar. Based on the ZINDO calculation, we have shown that owing to the configuration mixing, as shown in Figure 1, the bathochromic shift was possible at the expense of planarity (4,5).

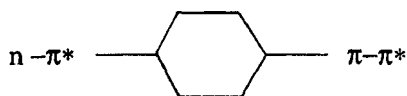


Fig. 1. Bathochromic shift through the configuration mixing.

A new blue dye of $\text{Ni}(\text{C}_{11}\text{N}_7\text{H}_2)_2$ shows extraordinarily similar spectral pattern with $\text{Ni}(\text{II})$ phthalocyanin. The understanding of this interesting similarity of the spectral pattern, not simply wavelength and intensity, provides the challenging opportunity for the future design of the functional dyes, since it is of fundamental importance for the industrial applications such as organic photo conductor, pigments and so on. On the basis of the four orbital model, which contains two configuration mixing, we have explained the source of the similarity. The swichover of the orbital symmetry was the origin of large intensity of Q band (6). The direction of the transition moment was confirmed experimentally by polarized absorption (7).

These two examples have demonstrated that the language of configuration mixing is as important as well established language of orbital.

Quantum Yield

The diarylethene shows unexpected dependence of quantum yield on the wavelength, in the ring opening photochemical reaction (8). We executed the ab initio MRSDCI calculation on the conrotatory ring opening path: 1,3-cyclohexadiene to cis-hexatriene. The property of Franck-Condon state on S_1 of cyclohexadiene ($\text{C}-\text{C}=1.54\text{\AA}$ for optimized structure of S_0) is described mainly by HOMO-LUMO configuration having a diffused Rydberg feature. This property is still retained at 1.75\AA . However, at 2.00\AA , before the transition state of S_0 , two electron excited configuration appears to be dominant rather than HOMO-LUMO configuration. Although we have not yet examined other factors such as the vibronic interaction, the present result indicates the intervention of the two electron excited state which could be the reason for the wavelength dependence (9).

The quantum yield of diarylethene derivatives in the photochemical ring opening reaction shows also the dependency on temperature, the dependency increases as the size of conjugation increases. A preliminary Natural Orbital analysis shows the importance of the intramolecular forces on the Franck-Condon state, further ab initio MO study is in progress.

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