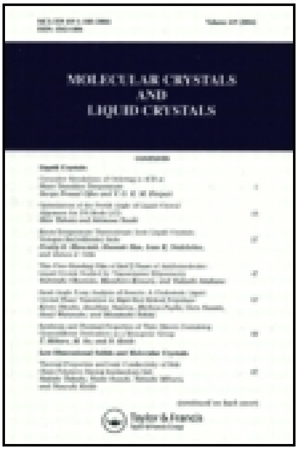

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Ab-Initio and Semiempirical mo Studies on Photochromic Molecules

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AB-INITIO AND SEMIEMPIRICAL MO STUDIES ON PHOTOCHROMIC MOLECULES

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Abstract A molecular orbital (MO) study on organic photochromic molecules was presented, where their optical properties such as absorption wavelengths and intensities were examined. The thermal stabilities of diarylethene and spironaphtoxazine were also investigated. Finaly, an unexpected dependence of quantum yield on the wavelength, in photochemical ring opening reaction of diarylethene, was studied by using a model system.

INTRODUCTION

Photochromic molecules have a huge potentiality for various applications owing to their remarkable characteristic for light-induced changes in molecular properties. Examples of the applications include optical memory storage media, light modulators, and various optical devices. For the future development, an understanding on a molecular level is of crucial importance. In this regards, these molecules provide an unique opportunity to study the mechanism of the photochemical reaction by utilizing MO method, because the important optical functions of the devices are dependent on the single molecule rather than aggregate. We present in this paper the results of the ab initio and semiempirical MO studies. The focus is on (i) the prediction of the absorption wavelength and intensities, (ii) the thermal stability, and (iii) the wavelength dependence of quantum yield in the ring opening reaction.

ABSORPTION WAVELENGTHS AND INTENSITIES

The practical light source consists mostly of the diode laser in which available wavelength region is limited. Therefore, the guiding principle toward the adjustment of the molecular absorption properties is in order. First, the structure-absorption relationship was examined by using INDO/S method for non planar[1], hydrogen bonded[2], and transition metal containing[3] organic dyes. Then we analyzed the substituent effect on the absorption wavelength of diarylethene derivatives. The calculation predicted a remarkable bathochromic shifts by electron-withdrawing substituents. Eventually the results were confirmed experimentally[4].

THERMAL STABILITY

Photochromic reactions of diarylethene derivatives are reduced to ring opening and reversal cyclization reaction. The thermal stability of the closed form 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. The stability of the closed ring form was found to depend on the difference of aromaticity in open and closed forms[5]. Not the steric hindrance but electronic property controlled the thermal stability.

Spironaphtoxazine exhibits a deep blue color by UV irradiation. For a long time, the exact structure of the open form which was responsible for the deep blue color was unknown. By means of ab initio calculation, the most stable structure was determined among various possible isomers[6]. The result was confirmed by ^{1}H NMR NOE spectroscopy.

DEPENDENCE OF QUANTUM YIELD ON THE WAVELENGTH

The diarylethene shows an unexpected dependence of quantum yield on the wavelength, in the ring opening photochemical reaction[7]. This is an apparent violation of Kasha's rule. This interesting experimental result motivated us to study theoretically the mechanism. We executed the ab initio calculation on the conrotate ring opening path: 1,3-cyclohexadiene to cis-hexatriene. The ground state geometries (S_0) were optimized by RHF energy gradient method. The first excited state geometries (S_1) were obtained by UHF energy gradient method at the 3-21G basis set, taking each C-C bond as a reaction coordinate. Other geometrical parameters were optimized within C_2 symmetry. Using these S_1 geometries, with more extended basis set of MIDI4 (with diffuse functions), the state *adhoc* iterative natural orbitals (INO) were obtained for S_1 and S_2 states, adopting five dominant references by JAMOL4 (for integrals) and MICA3 (for CI). The CSF amounted to about 5500. Then MRSDCI was performed for S_1 and S_2 states, about 5600 CSFs were selected through perturbation method, within 30m Hartree (about 117000 CSFs). The character of the first excited state S_1 for cyclohexadiene (C-C=1.54Å for optimized structure of S_0) is described mainly by HOMO-LUMO configuration having a diffused Rydberg character. This character is still retained at 1.75Å. However, at 2.00Å, before the transition state of S_0, two electron excited configuration appears to be dominant rather than HOMO-LUMO configuration. The obtained potential surface is shown in Figure 1.

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. Further calculation is in progress[8].

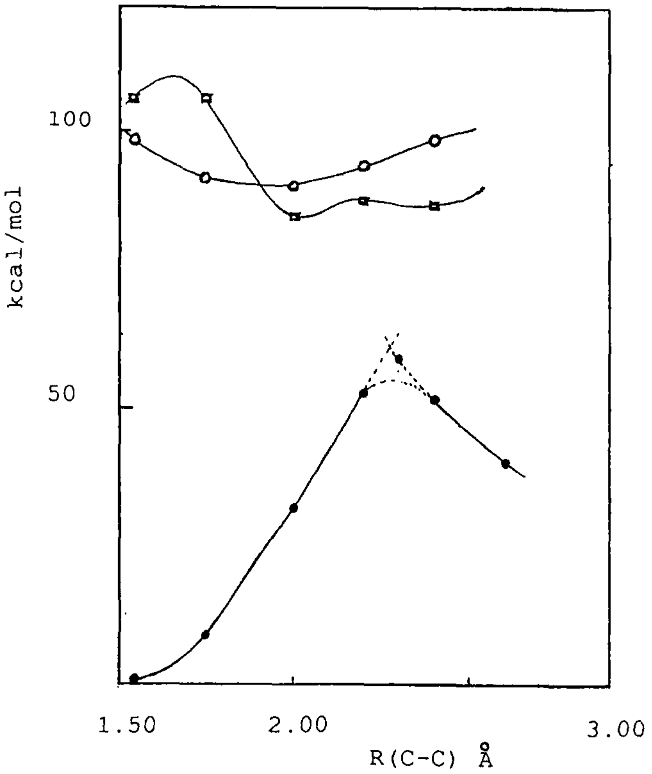

FIGURE 1 Potential Energy Surface of cyclohexadiene (left) to 1,3,5-hexatriene, obtained by MRSDCI.

REFERENCES

1. M. Adachi, Y. Murata, and S. Nakamura, J.Am.Chem.Soc., 115, 4331 (1993).
2. Y. Kubo, Y. Yoshida, M. Adachi, S. Nakamura, and S. Maeda, J.Am.Chem.Soc., 113, 2868 (1991).
3. S. Nakamura, A. Flamini, V. Fares, and M. Adachi, J.Phys.Chem., 96, 8351 (1992).
4. K. Uchida, S. Nakamura, and M. Irie, Bull. Chem. Soc. Jap., 65, 430 (1992).
5. S. Nakamura, and M. Irie, J.Org.Chem., 53, 6136 (1988).
6. S. Nakamura, K.Uchida, A. Murakami, and M. Irie, J.Org.Chem., in press.
7. M. Irie, and M. Mohri, J.Org.Chem., 53 , 803 (1988).
8. S. Nakamura, A. Murakami, and M. Irie, to be published.