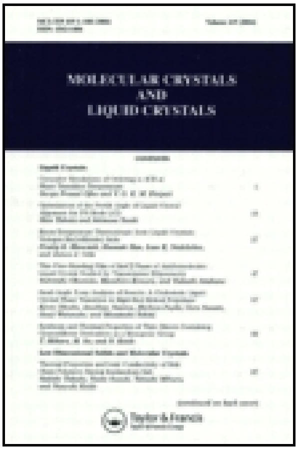

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THE MOLECULAR DESIGN AND APPLICATIONS OF SPIROOXAZINES

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Abstract The molecular structure by X-ray crystal analysis and *ab-initio* MO calculation, mechanism of photochemical process and two applications are discussed.

INTRODUCTION

Recently we have paid attention to spirooxazines as photochromic compounds, which show a reversible switching property between a non-colored state and a colored state as shown in FIGURE 1. On account of high fatigue resistance and high rate of photoresponse, they are attractive materials for industrial applications in various fields.

Our final goal is the design for the improved lifetime and photochromic activity of the compounds. We reported the polymer matrix effects on the response and spectra.[1]

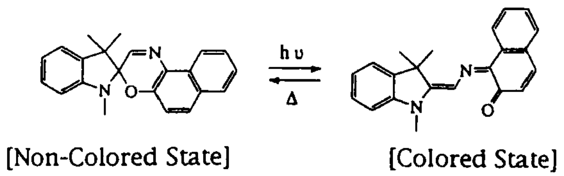


FIGURE 1 Spirooxazine as photochromic compounds.

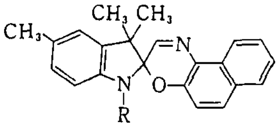
In this paper, our purpose is to report molecular structures through X-ray crystal analysis and by using *ab-initio* MO method, and mechanism of the photochemical process on the basis of the heavy-atom effect. Furthermore, we will present technological applications of photochromic polymer systems, e.g. microencapsulated photochromic ink and photochromic lamiglass for applied automobile windshields.

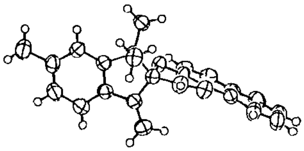
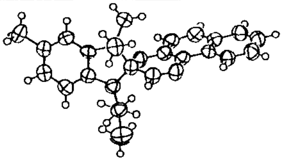
MOLECULAR STRUCTURES

X-RAY CRYSTAL ANALYSIS

In order to clarify the molecular structure of the closed form, we have carried out the determination of the crystal structures of spirooxazines (1) and (2) with the different substituent group.[2] As shown in TABLE I, it was proved that two types of crystal structures exist, namely, type-I and type-III. Concerning global difference, the oxazine ring in the type-III is bent towards the *gem*-methyl ring, while that in the type-I is bent in the opposite direction.[3]

TABLE I Crystal structure of closed form by X-ray analysis.



	- R		Molecular Structure
(1)	- CH_3	Type-I	
(2)	-$C_2H_4OCH_3$	Type-III	

Usually, the configuration of type-III is expected to be more unstable thermodynamically than that of type-I, because of the steric repulsion against the *gem*-methyl group. X-ray data indicates that, in the type-III structure, a weak intramolecular interaction is present between hydrogen of oxazine ring and oxygen of R group. This appears to contribute to the stabilization of the type-III configuration.

AB-INITO MOLECULAR ORBITAL CALCULATION

The open-form structure has not yet been determined; except only in a few cases, because of the instability. MO calculation method can provide optimized structure and determine thermodynamic relative stabilities. Actually, in this case, such MO calculation method become an effective tool. Therefore, we have optimized the structures of the closed and the four open-forms by using the *ab-initio* molecular orbital method (HF 6-31G**/3-21G).

At first, we have optimized the closed form and compared it with the established X-ray data. The results are very good in agreement with the X-ray data. Consequently, we can confirm the reliability of our calculation method.[4]

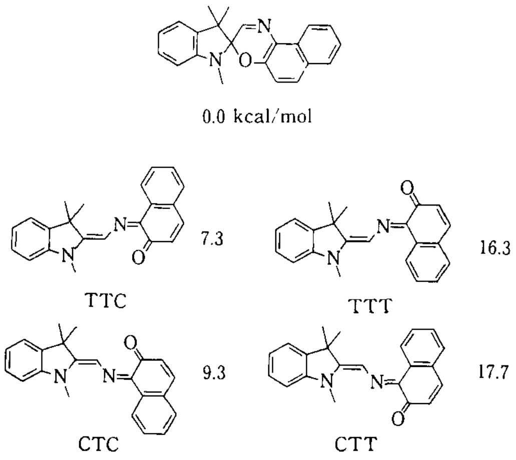


FIGURE 2 Relative stabilities of isomers by HF 6-31G**/ 3-21G.

Secondly, relative stabilities of open form isomers are obtained (see FIGURE 2). The calculation indicates that, 1) all isomers converged to the planar form, 2) the most stable isomer is TTC (trans-trans-cis), and 2nd most stable is CTC (cis-trans-cis), 3) the electrostatic interaction between central H and O of the carbonyl group contributes to the stability, and 4) hydrogen-hydrogen repulsion is the reason for the destabilization.

TABLE II Optimized structure of the four isomers.
(in Å and deg.)

	TTC	CTC	TTT	CTT
Cspiro - C(CH3)2	1.534	1.540	1.536	1.539
Cspiro = C	1.350	1.351	1.356	1.358
Cspiro - N	1.371	1.366	1.365	1.358
C(H) - N	1.376	1.374	1.359	1.357
C = N	1.281	1.283	1.271	1.274
C(N) - C(O)	1.491	1.490	1.507	1.506
C = O	1.227	1.227	1.221	1.221
Cspiro -C- N	119.6	122.6	117.3	120.4
C(H)- N - C	128.6	128.1	139.9	139.2

For these open form isomers, the important bond angle and distance are shown in Table II. All C=N bonds show double bond character, whereas, the other bonds in the azomethine bridge appear to have intermediate character. In the TTT (trans-trans-trans) and CTT (cis-trans-trans) isomers, the H-H repulsion and resulting large bond angle of C(H)-N-C are clearly shown to be responsible for the destabilization.

From the standpoint of application, it is an important question whether the electronic structure is ketone-like or zwitterionic-like. The calculation results indicate that the C=O bond distance is in the region of the normal carbonyl length, consequently, the electronic ground state is ketone-like.[5]

MECHANISM OF THE PHOTOCHROMIC REACTIONS

A recent study by laser flash photolysis showed that a triplet state is not involved in the coloration mechanism of spirooxazines when immersed in solution. Similar conclusion has been reported noting that the photocoloration occurs only in the excited singlet state, on account of the independence of oxygen.[6]

To obtain further information about the mechanism, we have investigated the heavy-atom solvent effect. FIGURE 3 shows the change in absorption by the addition of n-propyl bromide in cyclohexane. The degree of the open form decreased with increasing concentration of alkylhalide heavy-atom solvent. This means that the intersystem crossing was promoted by the heavy atom and that the photochromic reaction was disturbed. This is responsible for the photocoloration.

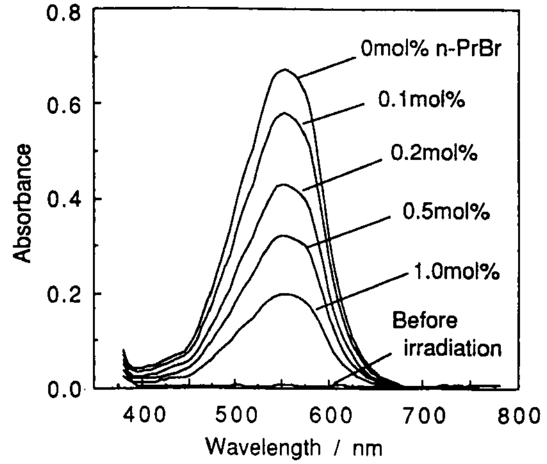


FIGURE 3 Effect of n-C_3H_7Br concentration in cyclohexane on the absorption of merocyanine.

Moreover, we have obtained results that the Stern-Volmer plot of the relative quantum efficiency yields a linear relationship. The linearity confirms that the process via the excited triplet state rarely occurs.

Next, we compared the solvent effects by the nature of halogen, e.g., Cl, Br and I. The result shows that the amount of merocyanine was strongly suppressed by increasing atomic weight of the halogen. Among the solvents we examined, the iodine-containing derivatives showed the largest solvent effect. It is well known that the heavier the spin-orbital coupling ratio is, the larger the intersystem crossing becomes.[7]

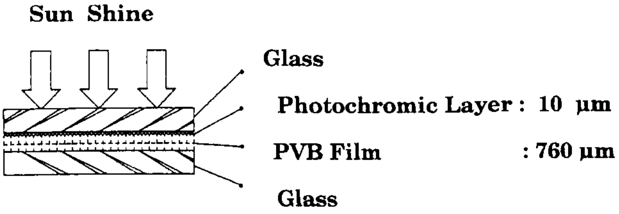


FIGURE 4 Composition of photochromic lamiglass.

INDUSTRIAL APPLICATIONS

The first practical example is microencapsuled photochromic materials. The average particles size of capsules containing photochromic spirooxazine and antioxidant is 20 μm. These capsules mixed with an aqueous polymer binder to provide a water-base ink composition.[8]

By using this ink composition, we made printed photochromic samples. This printed part showed coloration within 10 seconds when exposed to sunlight, and exhibited a good light resistance. Furthermore, it bleached within 15 seconds in the dark, and this process was observed repeatedly. This water-base ink is commercially available by Mitsubishi Kasei Corporation.

The next example is photochromic lamiglass, which consists of the photochromic layer, the intermediate polyvinyl butyral film and glass plates. The photochromic intermediate film was sandwiched between two clear glass plates (see FIGURE 4). The absorption spectra in the dark is shown in FIGURE 5. The clear glass filters the shorter wavelengths. So, this lamiglass is activated by solar light of approximately 350 nm.

This feature proves to be very useful when applied to automobile windshields. It controlled the transmittance in proportion to solar light intensity. This material provided a comfortable driving atmosphere, particularly, because of high glare protection. Under low light intensity, the lamiglass exhibited a high transmission of 80%. On the other hand, when exposed to sunlight, the transmittance gradually decreased and it showed a blue color. The maximum wavelength is 630 nm.

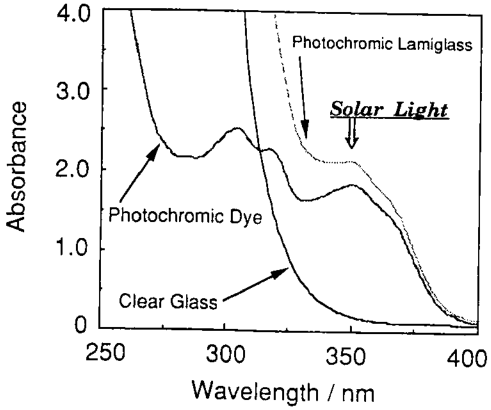


FIGURE 5 Absorption spectra in the dark.

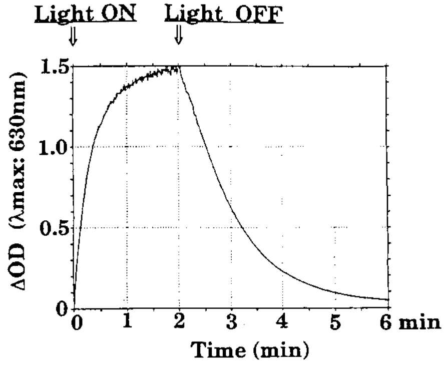


FIGURE 6 Photo-induced absorbance change.

This lamiglass shows high optical density in the saturation state. The coloring time reaches 50 % of its saturated value is 20 seconds. The decoloration speed is slower (see FIGURE 6). Furthermore, it has excellent resistance to visible & UV sunlight. The photochromic activity changed little after exposure for over 3,000 hours with the Xenon Fademeter.

CONCLUSION

We have clarified that the non-colored closed form has two types of configurations through X-ray crystal analysis. Furthermore, the result of *ab-intio* MO calculation leads to the conclusion that the most stable colored open form of spirooxazine is the TTC and CTC structure, and the electronic ground state is as ketone-like.

With respect to photocoloration, we have investigated the heavy-atom effect. These solvents accelerated the intersystem crossing and suppressed the ring opening reaction. These results show that the process via the excited triplet state rarely occurs.

In addition, we have exhibited technological applications, e.g., microencapsulated photochromic ink for applied T-shirt printing matter and photochromic lamiglass for applied automobile windshields.

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