THERMALLY IRREVERSIBLE PHOTOCHROMIC MATERIALS FOR ERASABLE OPTICAL DATA STORAGE MEDIA

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Organic compounds which possess the photochromic property have attracted a significant amount of attention from the viewpoint of using them as optical memory media. Despite favorable conditions provided by the recent development of laser technology, the compounds have found little applications in optical information storage. Among various reasons for this, the most important one is the lack of thermal stability. The present study proposed a guiding principle for molecular design of the thermally irreversible diarylethene type photochromic compounds on the basis of molecular orbital calculation of state correlation diagrams. According to the theoretical prediction, a new type of thermally irreversible photochromic compounds, diarylethene derivatives having heterocyclic rings, were developed. The compounds had no thermochromic property and the colored state was stable for more than three months at 80°C.

INTRODUCTION

Optical data storage systems, that use write-once organic recording media, are now beginning to become available. Organic media have the following advantages as compared to inorganic ones:
1) They are less subject to degradation by air and moisture.
2) They are generally less toxic.
3) They can be prepared by spin coating, leading to lower fabrication costs.

Because of these advantages, there is an increasing interest in using organic materials not only for write-once recording media but also for rewritable media. By far the most extensively studied rewritable media are inorganic compounds, which use the magneto-optic effect or phase change as the basis of optical recording. Although several organic rewritable media, which include pit-forming media, bump-forming media, and organic phase changing media, were reported, the bump-forming dye-polymer is the only media directed toward commercial use. Organic media have not yet been fully explored.
All of these media are based on a heat-mode optical recording method. In order to utilize the versatile function of light fully, photon-mode recording should be ultimately superior to the heat-mode system. Photon-mode recording will be advantageous in the sense of resolution, speed of writing, and multiplex recording. One of the candidates for the photon-mode and organic erasable recording media is a photochromic material.

Photochromism is defined as a reversible change in a chemical species between two forms having different absorption spectra,

\[ \text{A} \xrightarrow{\text{hv}} \text{B} \]

The instant image forming property without processing has led to the consideration of their use in rewritable direct read after write systems. Despite favorable conditions provided by the recent development of laser technology, organic photochromic compounds have found little application in optical information storage. The requirements for a reversible optical recording medium are as follows:

1) Archival storage capability (thermal stability).
2) Sensitivity at diode laser wavelength.
3) Low fatigue (can be cycled many times without significant loss of performance).
4) Non-destructive read out capability.

The limitation of the application is due to the lack of suitable compounds which fulfill the above requirements. Among the requirements, the most important property is the thermal stability of both A and B forms of the above scheme. Although 3-furyl-fulgide was reported to have the thermal stability, the open ring E form, A, was rather unstable and showed thermochromism above 130°C.

In this paper, we propose a new guiding principle for molecular design of thermally irreversible diarylethene type photochromic compounds based on MNDO calculation of state correlation diagrams. Based on this principle, we have synthesized several thermally irreversible photochromic compounds, which have no thermochromic property and the colored forms are stable for more than 3 months at 80°C.

RESULTS AND DISCUSSION

Theoretical Study

We chose a 1,3,5-hexatriene to cyclohexadiene type reaction as the model photochromic system. In order to come up with a guiding principle for molecular design of thermally irreversible compounds, we carried out a theoretical study of the system.

According to the Woodward-Hoffmann rule based on the pi orbital symmetries for 1,3,5-hexatriene, a conrotatory cyclization reaction to cyclohexadiene is brought out by light, and a disrotatory cyclization by heat.

The cycloreversion reaction is also allowed both photochemically in the conrotatory mode and thermally in the disrotatory mode. From the simple symmetry consideration of the hexatriene framework, we might not expect the thermal irreversibility of the reaction.