Journal of Photochemistry and Photobiology A: Chemistry 200 (2008) 10–18

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Theoretical investigation on photochromic diarylethene: A short review

Shinichiro Nakamura[a,*], Satoshi Yokojima[a], Kingo Uchida[b], Tsuyoshi Tsujioka[c], Alexander Goldberg[a], Akinori Murakami[a], Keiko Shinoda[a], Masayoshi Mikami[a], Takao Kobayashi[a], Seiya Kobatake[d], Kenji Matsuda[e], Masahiro Irie[e]

[a] *Mitsubishi Chemical Group Science & Technology Research Center, Inc. and CREST-JST, 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan*
[b] *Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-2194, Japan*
[c] *Department of Arts and Sciences, Faculty of Education, Osaka Kyoiku University, Asahigaoka 4-698-1, Kashiwara, Osaka 582-8582, Japan*
[d] *Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan*
[e] *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyusyu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*

ARTICLE INFO

Article history:
Received 10 December 2007
Received in revised form 4 May 2008
Accepted 7 May 2008
Available online 15 May 2008

Keywords:
Diarylethene
Molecular orbital

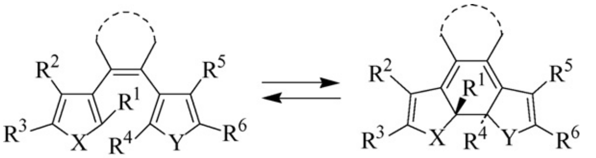
ABSTRACT

This paper presents a review of our reported theoretical studies that we performed to identify experimental spectroscopic data (NMR, Raman, IR, and ESR), find applications that utilize transport property (hole and electron), design the environmental field effect around a molecule (polymer and crystal), and to elucidate nonlinear response properties. Moreover, new results on thermal stability and reaction in crystalline state are also included. We put emphasis on how theoretical studies on photochromic systems contributed to an understanding of the experimental data on a molecular level.

1. Introduction

Organic photochromic molecules have raised considerable interest owing to their potential applications to optical memory and molecular switches [1]. Among the various photochromic molecular systems, diarylethene (DAE), whose general form is shown below, is one of the most promising organic photochromic molecules because of its high fatigue resistance. Recently, the number of experimental studies on various kinds of DAE molecules has increased. These studies are attempting to realize various potential applications [2]. In contrast, although it is necessary to understand the detailed mechanism of reactions and to establish guiding principles for designing required properties in future industrial applications, theoretical research is rather limited. Accordingly, we have performed theoretical molecular orbital and first-principles studies on organic photochromic molecules.

This paper presents a review of our reported theoretical studies with the addition of some recent results. Theoretical studies have been presented to (i) explain the origin of thermal stability [3]; (ii) design absorption wavelength [4]; (iii) discover the determining factor of quantum yield [5]; (iv) identify experimental spectroscopic data (NMR [6], Raman [7], IR [8], and ESR [4b,9]); (v) find applications that utilize the transport property (hole and electron) [10]; (vi) design the environmental field effect around the molecule (solvent [6a]; polymer [11] and crystal [12]), and (vii) elucidate nonlinear response properties [13]. We have already reviewed research pertaining to (i), (ii) [1b], and (iii) [5a]. In this report, we first show some new results on thermal stability, followed by a presentation of the remaining items from (iv) to (vi), placing emphasis on how theoretical studies contributed to an understanding of experimental data.



2. Thermal stability

We explained the remarkable thermal stability of DAE derivatives in terms of the Woodward–Hoffmann rules [14]. Fig. 1 shows the state correlation diagram (obtained by semi-empirical MNDO calculation [3a]) for thermally stable closed-ring isomers. It clarifies the thermal stability of DAE containing five-membered ring (on the left of Fig. 1), while DAE containing six-membered ring (on

---

* Corresponding author.
E-mail address: shindon@rsi.co.jp (S. Nakamura).

1010-6030/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2008.05.005

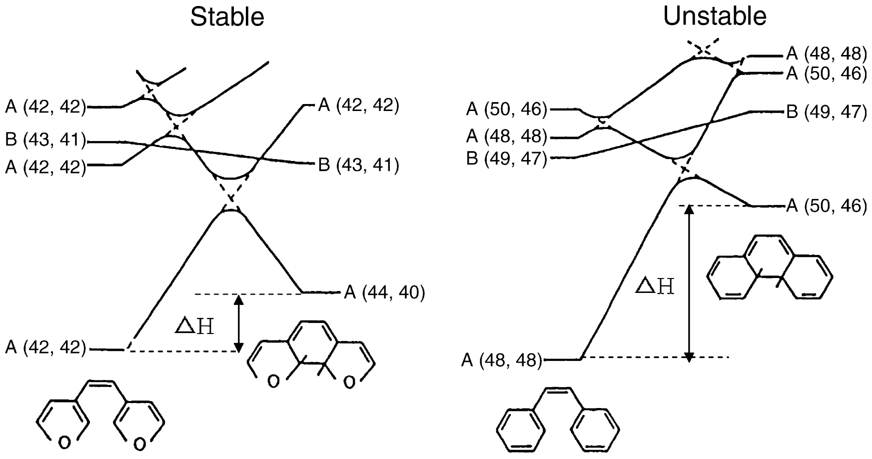


Fig. 1. State-correlation diagram of thermally stable (with five-membered ring) and unstable (with six-membered ring) closed-ring isomers. [3a].

the right of Fig. 1) is found to be less stable. The reason for this stability difference was interpreted by difference in the aromaticity of closed- and open-ring isomers [3]. This was demonstrated by theoretical computer-generated molecules (Fig. 2). These molecules are aromaticity-related components of open- and closed-ring isomers of the molecules shown in Fig. 1. Both of these molecules are consistent with the Woodward–Hoffmann rules, being in symmetry forbidden reactions. Their cyclization as well as their cycloreversion is triggered only by light, not by heat. However, the cycloreversion reaction of six-membered ring molecules by heat does occur, whereas the cycloreversion of five-membered ring molecules by heat does not. That is, the colored form of the closed-ring isomer with the six-membered ring is very unstable, owing to the considerable thermodynamic instability of the closed-ring isomer. This instability means that virtually the Woodward–Hoffmann rules are no longer valid. In fact, we showed that a simple difference in enthalpy (ΔH in Fig. 1) between ground state open- and closed-ring isomers is the criterion for determining the thermal stability of the colored forms [3].

Since we proposed this criterion to explain the thermal stability of DAE molecules, there have been no reported exceptions. To date, modifications have been made to synthesize various kinds of DAE derivatives using different substituents [2]. Indeed, they satisfy the criterion that we reported in 1988; namely, the smaller ΔH, the higher the stability. Fig. 3 shows typical examples of some recent calculations on the relative energy difference. We estimated the enthalpy difference for closed- and open-ring isomers for the various new DAE derivatives (in which there are remarkable differences in thermal stabilities) as a function of substituents. Experimental thermal stability [2] is closely correlated to the B3LYP/6-31G*-calculated ΔH for closed- and open-ring isomers in ground state. Note that the ΔH of the positively charged dication molecule (C in Fig. 3) is calculated with solvents by using the PCM method [15].

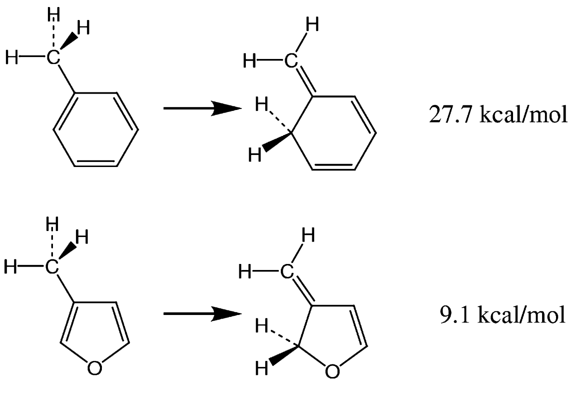


Fig. 2. Model molecules used for measuring difference in aromaticities of open- and closed-ring isomers.

3. Theoretical study to identify experimental spectroscopic data

3.1. NMR chemical shift

To determine the detailed structures of photochromic molecules, NMR chemical shift provides key information. First, we applied the ^{1}H NMR NOE technique to determine the colored form of photochromic spironaphtoxazine [16]. Then, we performed NMR chemical shift analysis on the DAE derivatives. For example, Uchida et al. determined the ratio of the anti-parallel conformer relative to the parallel conformer (see Fig. 4 for the conformers) in the equilibrium of open-ring isomers of 1,2-bis (2-methyl-3-benzothienyl)-perfluorocyclopentene [6b] and 1,2-bis (2-methyl-5-phenyl-3-thienyl)-perfluorocyclopentene [5d]. As shown in Fig. 4, a cyclization reaction is possible only via the anti-parallel conformer. Therefore, to find the factors that increase the population of anti-parallel conformer, it was necessary to monitor the equilibrium by using the chemical shift of proton NMR. Based on these NMR-shift data, a theoretical study provided a guiding principle for attaining large cyclization quantum yield which results from increased anti-parallel population both in ground state and excited state. Accordingly, molecules with large cyclization quantum yields were designed with the aid of theoretical calculations [5d].

Goldberg et al. reported NMR chemical shift calculations on 1,2-bis(3-methyl-2-thienyl)-perfluorocyclopentene (**1a** and **1b** in Fig. 4). Using the gauge including atomic orbital (GIAO) method [17], they calculated the ^{1}H NMR chemical shift for different atomic groups at the B3LYP/6-31G level. They then compared the calculated ^{1}H NMR shifts with experimental values to provide an aid to determine the ratio of conformers [6a,18]. To find the determining factor of cyclization quantum yield, it was necessary to assign experimental chemical shift values, since they reflect the ratio of the conformers.

The chemical shift of the methyl-group proton provides peaks strongly affected by the relative position of the two thiophene rings. If the methyl group faces the thiophene ring (as in the case of the anti-parallel conformer), the ring current induces a high magnetic