Tetrahedron Letters 49 (2008) 4972–4976

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Photochromic properties of tetrakis(2-methylthien-3-yl)ethene and its tetrakis(methylthio) derivative

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ARTICLE INFO

Article history:
Received 12 April 2008
Revised 13 May 2008
Accepted 16 May 2008
Available online 22 May 2008

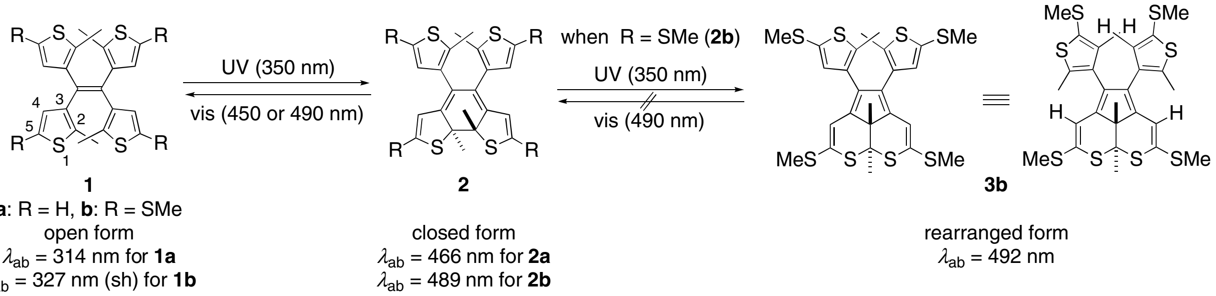
Keywords:
Tetrathienylethene
Photochromism
Electrochromism
Reaction mechanism

ABSTRACT

The photoreaction of tetrakis(2-methylthien-3-yl)ethene (**1a**) and its tetrakis(methylthio) derivative **1b** was investigated in the context of a potentially new chromic system responsive to both photoexcitation and electron transfer. UV irradiation of **1** at low conversion leads to production of its cyclic isomer **2** while **2** returns to **1** upon vis irradiation, representative of facile photochromic behavior. In contrast, UV irradiation at high conversion transforms **1b** to rearranged product **3b** via the intermediacy of **2b**.

1. Introduction

Recently, we reported[1] the synthesis, X-ray crystallographic analysis, and semiempirical calculations of tetrakis(2-methylthien-3-yl)ethene (**1a**, Scheme 1) and its tetrakis(methylthio) derivative **1b**, substances that were designed to be both photo-[2,3] and electrochromic.[5,6] In **1a**, the two pairs of vicinal thienyl groups are oriented in a *parallel* arrangement. Likewise, in **1b**, two pairs of vicinal thienyl groups are arranged in a *parallel* orientation. As a result, **1a**–**b** are not expected to form the cyclized forms **2a**–**b** in the crystalline state on photoexcitation. Indeed, the crystalline state photochemistry of **1a**–**b** did not produce **2a**–**b**.[1] However, the results of PM3 calculations suggest that 46% and 31% of **1a** and **1b** at +25 °C, respectively, exist in metastable conformations in which both or either pair of vicinal thienyl groups are oriented in an *antiparallel* arrangement.[1] These conformations in solution should undergo photocyclization to form **2**. In the studies described below, we explored the photochemistry of **1** and **2** in CH_2Cl_2 solution. The results of this effort show that **1** and **2** display photochromic behavior in that their reversible interconversion can be promoted by low conversion irradiation with UV and vis light. In contrast, at high conversion (i.e., by a prolonged irradiation with UV light) **1b** is converted to the rearrangement product **3b**, formed via the intermediacy of **2b**.



Scheme 1. Photochromic behavior of **1** and **2** in CH_2Cl_2.

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doi:10.1016/j.tetlet.2008.05.080

2. Photochromic properties of 1a–b

Absorption spectroscopic analysis shows that irradiation of a CH_2Cl_2 solution of **1a** (5×10^{-5} M) with UV light ($\lambda = 350$ nm)[7] for 1 min resulted in the appearance of an absorption band at $\lambda_{ab} = 466$ nm (Fig. 1a). This band disappeared almost completely when the resulting solution was irradiated with vis light ($\lambda = 450$ nm)[7] for 5 min (Fig. 1a). Similarly, UV irradiation of a CH_2Cl_2 solution of **1b** for 0.5 min resulted in the formation of an absorption band at $\lambda_{ab} = 489$ nm (Fig. 2a) and again this band disappeared almost completely when the resulting solution was irradiated with vis light ($\lambda = 490$ nm)[7] for 5 min (Fig. 2a). The observations suggest that the photochromic behavior displayed by the systems is a consequence of the formation of the cyclic photoproducts **2**.[8]

Interestingly, the photochromic properties strongly depended on the degree of the conversion of the initial UV-promoted photoreactions. Thus, a CH_2Cl_2 solution of **1a** upon irradiation with UV light for 30 min underwent a color change from colorless to pale yellow associated with growth of absorption bands at $\lambda_{ab} = 303$ and 461 nm (Fig. 1b). Unlike the 1-min irradiation process described above, the 461-nm band did not disappear, the 303-nm band decreased, and a new band at ca. 380 nm band appeared when the resulting solution was irradiated with vis light ($\lambda = 450$ nm)[7] for 30 min (Fig. 1b). The results suggest that **2a**, formed from **1a** by photocyclization, readily undergoes a secondary photoreaction under UV irradiation conditions.

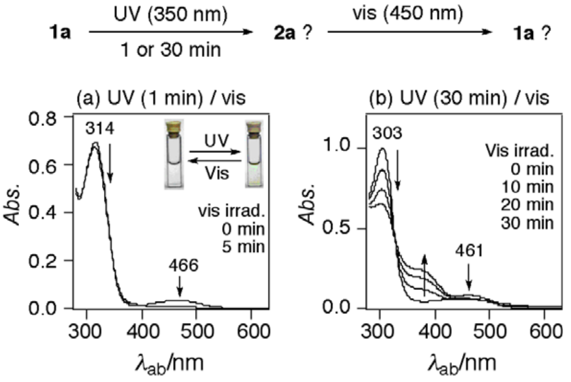


Figure 1. UV–vis absorption spectral changes of a CH_2Cl_2 solution of **1a** (5.0×10^{-5} M) on vis (450 nm) irradiation (a: 0–5 min, b: 0–30 min) after UV (350 nm) irradiation (a: 1 min, b: 30 min).

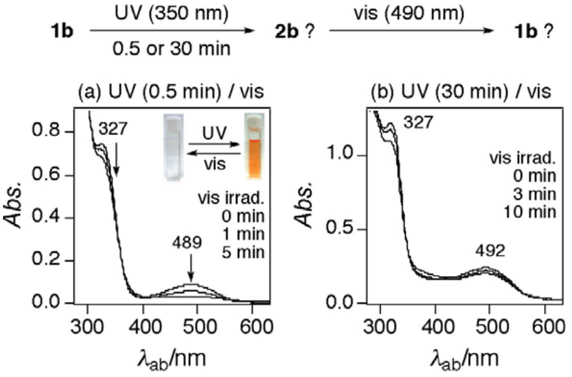


Figure 2. UV–vis absorption spectral changes of a CH_2Cl_2 solution of **1b** (5.0×10^{-5} M) on vis (490 nm) irradiation (a: 0–5 min, b: 0–10 min) after UV (350 nm) irradiation (a: 0.5 min, b: 30 min).

Several efforts to isolate **2a** and the possible product(s) from **2a** and to assign them structures were unsuccessful.[9]

More informative results came from an analysis of the photoreaction of **1b**, promoted by irradiation in a CH_2Cl_2 solution with UV light for 30 min. In this case, the colorless solution turned to red-orange in conjunction with growth of absorption bands at $\lambda_{ab} = 327$ and 492 nm (Fig. 2b). Unlike the case of the 0.5-min irradiation, the 492-nm band did not disappear when the resulting solution was irradiated with vis light ($\lambda = 490$ nm) for 10 min (Fig. 2b). The results suggest that **2b** reacts readily to produce by-product(s) on UV irradiation. Indeed, UV irradiation of a CH_2Cl_2 solution of **1b** (5 mM) for 1 h led to the formation of the rearranged product **3b** (Scheme 1), isolated as viscous red oil in 26% yield (conversion 71%).[10] Several attempts to generate a single crystal of **3b** for X-ray crystallographic analysis were unfruitful. However, the structure of **3b** could be determined by using ^1H and ^{13}C NMR,[11] UV–vis spectroscopy, and mass spectroscopy, together with cyclic voltammetry.[12]

3. Structural analysis of the rearranged product 3b

As shown in Figure 3, the ^1H NMR spectrum of **3b** comprised broad bands even at +60 °C. This is especially true of the resonance for the two Me groups (Me^a) at $\delta = 2.10$ ppm and one for two aromatic protons (H^a) at $\delta = 6.41$ ppm.[11,13] Peaks for several Me groups at $\delta = 2.36$–2.50 ppm and two olefinic-protons (H^b) at $\delta = 6.18$ ppm were also broadened slightly at +60 °C. These findings suggest that severe steric hindrance exists between Me^a and H^b, and H^a and another H^a, as depicted in Figure 3 (top). When the temperature was lowered to −35 °C, Me^a, H^b, and H^a yield a set of four singlet peaks, at 1.95–2.16, 6.09–6.12, and 6.27–6.49 ppm, respectively. These phenomena can be explained by suggesting that three conformers [*parallel-A*, *antiparallel*, and *parallel-B*, Figure 3 (top)] exist for **3b**. Accordingly, four peaks of H^a observed at 6.27–6.49 ppm at −35 °C are due to a pair of 2 equiv protons in **3b** (two singlet peaks of *parallel-A* and *-B* at 6.48 and 6.49 ppm) and two nonequivalent protons of **3b** (two singlet peaks of *antiparallel*, 6.27 and 6.29 ppm). Similarly, the four peaks associated with H^b and Me^a are accounted for by these three conformers.[14] Note that **3b** (*parallel-A*) and **3b** (*parallel-B*) are symmetric, while **3b** (*antiparallel*) is not symmetric. An analysis of ^1H NMR spectra at −35 °C suggests that **3b** (*antiparallel*) exists to the extent of 50% while **3b** (*parallel-A*) and **3b** (*parallel-B*) comprise 16% and 34% of the conformer mixture.

These results indicate that **3b** (*parallel-A*) and **3b** (*parallel-B*) are higher in energy than **3b** (*antiparallel*) by 0.18 and 0.54 (or 0.54 and 0.18) kcal/mol, respectively.

The three conformers of **3b** were predicted by using PM3 and density functional theory (DFT) calculation-based conformational analysis. [15] Interestingly, the order of stability of the conformers depends on the calculation method used. This result is probably due to the small energy differences that exist between them (Table 1). The existence probabilities (%) calculated with DFT match the results elucidated from ^1H NMR spectra at −35 °C, but those with PM3 did not, unfortunately. Namely, the DFT (B3LYP/3-21G*) calculation indicates that the rearranged product **3b** can exist in three conformationally isomeric forms, including (i) *parallel-A*, (ii) *antiparallel* (+0.3 kcal/mol relative to *parallel-A*), (iii) *parallel-B* (+0.4 kcal/mol), and in a ratio of 40:43:17 at −35 °C (Fig. 4).

Formation of rearranged products in diarylethene photochromic processes was reported by Irie and co-workers for **4** and **9** (Scheme 2).[18] The dimethyl derivative **4** affords two products **5** and **6** upon extended irradiation, in which the structure of the former corresponds to that of **3b**.[18a] Note that the possibility of a substance related to **6** cannot form in our system. The phenyl

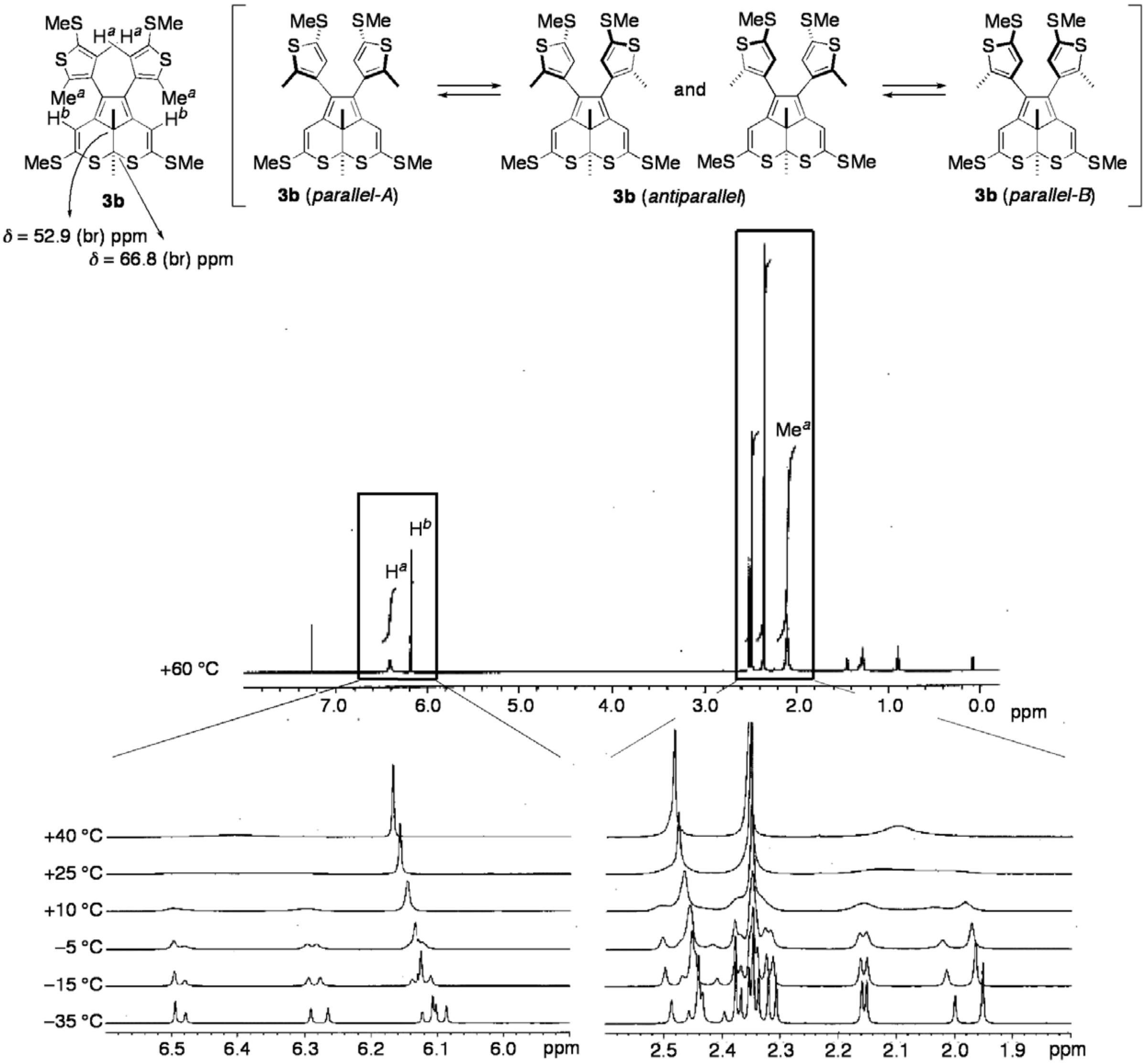


Figure 3. Three possible conformers of **3b** (top) and ^{1}H NMR spectra (600 MHz, $CDCl_3$) of **3b** observed at various temperatures (bottom).

Table 1
Calculated relative energies (ΔE) of the three conformers of **3b**[a]

Method	ΔE (**3b**)/(kcal/mol)		
	Parallel-A	*Antiparallel*	*Parallel-B*
PM3	+1.3 (6)	+1.8 (24)	0[b] (90)
B3LYP/3-21G*	0[b] (40)	+0.3 (43)	+0.4 (17)
B3LYP/6-31G*	0[b] (51)	+0.4 (40)	+0.8 (9)
B3LYP/6-31G**	0[b] (53)	+0.5 (38)	+0.8 (9)

[a] The numbers in parentheses are the calculated existence probabilities (%) at −35 °C.

[b] The base of calculation of ΔE (**3b**) for other conformers.

derivative **9** gave a rearranged product **10**. The chemical shifts of the two aliphatic carbons in the ^{13}C NMR spectrum of **10** were reported to be 59.6 and 65.8 ppm in $CDCl_3$ (Scheme 2).[18b] Similar chemical shifts of **3b** were found at 52.9 (br) and 66.8 (br) ppm in $CDCl_3$ at +35 °C (Fig. 3). This comparison adds further support for the assignment of the structure of **3b**. In addition, **3b** displayed a reversible one-electron oxidation wave in cyclic voltammetry ($E^{ox}_{1/2} = +0.45$ V vs Ag/Ag^+ in CH_3CN containing 0.1 M $Et_4N^+ClO_4^-$).[12] The observed stability upon single electron-transfer oxidation is consistent with the assigned structure of **3b**.

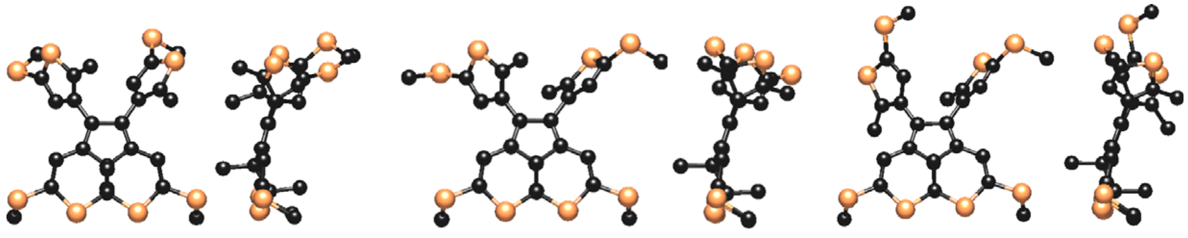
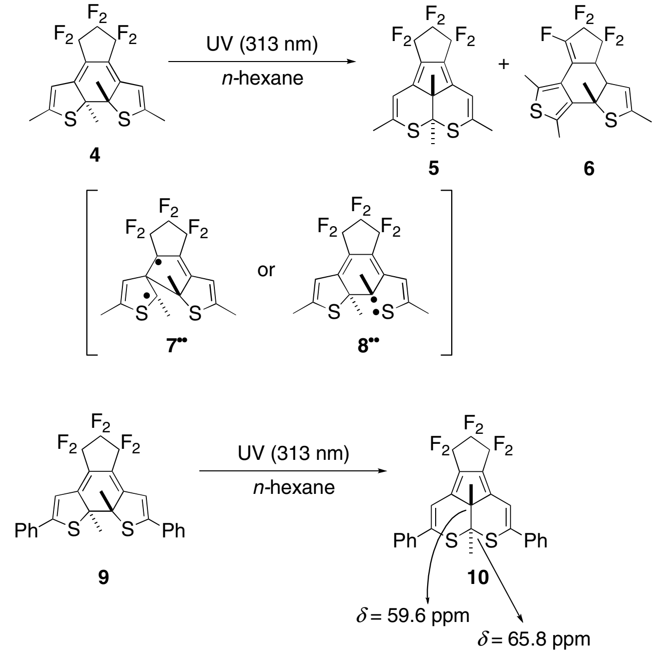

(i) **3b** (*parallel-A*) (ii) **3b** (*antiparallel*) (iii) **3b** (*parallel-B*)

Figure 4. Three possible conformers of **3b** calculated by using the B3LYP/3-21G* method. Left: front view, right: side view.



Scheme 2. Photorearrangement of **4** and **9** reported by Irie and co-workers. See Ref. 18.

Regarding the mechanism for photochemical formation of **5** from **4**, Irie and co-workers suggested a stepwise pathway via the intermediacy of biradicals **7** or **8**.[18b] Although the mechanism for the formation of **3b** is not clear at this stage, a similar stepwise mechanism may be operative.

4. Conclusion

The photochromic behavior of new tetrathienylethenes **1**, designed to respond to not only photoexcitation but also electron transfer, has been explored. The results of the investigation show that **1** and **2** are photochromic at low conversions, showing color changes from colorless to pale yellow (**2a**) or red-orange (**2b**). Upon prolonged irradiation, **1b** yields the rearranged isomer **3b**, which has unique ^{1}H NMR spectroscopic characteristics caused by a slow interconversion of three possible conformers. Detailed studies of the electrochromic properties of **1**, **2**, and **3b** are now in progress, the results of which will be published elsewhere.

Acknowledgments

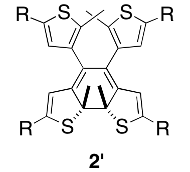
H.I. and K.M. gratefully acknowledge financial support from a Grant-in-Aid for Scientific Research on Priority Areas (Area No. 471, Project No. 20044027) and others (Nos. 19350025) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan. H. I. also thanks the Shorai Foundation, the Mazda Foundation, and the Iketani Science and Technology Foundation for providing financial support for the work. We also appreciate Mr. J. Kurita and Mr. K. Kushida (Varian Technologies Japan Ltd) for their technical assistances in measuring NMR spectra.

Supplementary data

^{1}H and ^{13}C NMR spectra, UV–vis absorption spectra, and the PM3 and DFT calculation results for **3b**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.05.080.

References and notes

1. Ikeda, H.; Sakai, A.; Namai, H.; Kawabe, A.; Mizuno, K. *Tetrahedron Lett.* **2007**, *48*, 8338–8342.
2. (a) Matsuda, K.; Irie, M. *J. Photochem. Photobiol., C* **2004**, *5*, 169–182; (b) Matsuda, K.; Irie, M. *Chem. Lett.* **2006**, *35*, 1204–1209; (c) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.
3. Recently, Maurel and Belen'kii reported the synthesis and photochromic properties of tri- and tetrathienylethenes. See Ref. 4.
4. (a) Bougdid, L.; Perrier, A.; Heynderickx, A.; Maurel, F.; Shilova, E.A.; Muostrou, C. 'Synthesis and Photochromic Properties of Tri-thienyl Substituted Ethylene: Combined Experimental and Theoretical Study'; International Symposium on Photochromism 2007, 2007, Vancouver: British Columbia, Canada.; (b) Belen'kii, L. I.; Gromova, G. P.; Kolotaev, A. V.; Nabatov, B. V.; Krayushkin, M. M. *Russ. Chem. Bull. Int. Ed.* **2005**, *54*, 1208–1213.
5. (a) Gorodetsky, B.; Branda, N. R. *Adv. Funct. Mater.* **2007**, *17*, 786–796; (b) Matsuda, K.; Yokojima, S.; Moriyama, Y.; Nakamura, S.; Irie, M. *Chem. Lett.* **2006**, *35*, 900–901; (c) Moriyama, Y.; Matsuda, K.; Tanifuji, N.; Irie, S.; Irie, M. *Org. Lett.* **2005**, *7*, 3315–3318; (d) Gorodetsky, B.; Samachetty, H. D.; Donkers, R. L.; Workentin, M. S.; Branda, N. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2812–2815; (e) Peters, A.; Branda, N. R. *J. Am. Chem. Soc.* **2003**, *125*, 3404–3405; (f) Peters, A.; Branda, N. R. *Chem. Commun.* **2003**, 954–955.
6. (a) Suzuki, T.; Ohta, E.; Kawai, H.; Fujiwara, K.; Fukushima, T. *Synlett* **2007**, 851–869; (b) Suzuki, T.; Shiohara, H.; Monobe, M.; Sakimura, T.; Tanaka, S.; Yamashita, Y.; Miyashi, T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 455–458.
7. A CH_2Cl_2 solution of **1** (5×10^{-5} M) was irradiated with a 150 W Xe lamp [$\lambda = 350$ nm for UV, 450 or 490 nm for vis, band pass 20 nm] through a spectrometer equipped to a JASCO FP-6300 spectrofluorometer.
8. The relative stereochemistry of the methyl groups in **2** that would arise from the conrotately cyclization of the metastable *antiparallel* conformers of **1** is *trans*. This result is strongly suggested by PM3 calculations. Alternatively, the *cis* conformer **2′** is suggested to have high internal energy (ca. 40 kcal/mol) as compared with **2**, which is unlikely from the point of view of the conservation of orbital symmetry theory (Woodward-Hoffmann rules).



2′
a: R = H, **b**: R = SMe

9. It may be assumed that one of the possible photoproducts of **2a** is **3a**. However, this is not likely because Figures 1b and 2b demonstrate different behavior of **2a** and **2b** on vis irradiation.
10. *Physical data of* **3b**: Viscous red oil; ^{1}H NMR ($CDCl_3$, +60 °C, 600 MHz) δ_{ppm} 2.10 (br s, 6H), 2.36 (br s, 12H), 2.50 (br s, 6H), 6.18 (br s, 2H), 6.41 (br s, 2H); ^{13}C NMR ($CDCl_3$, +35 °C, 75 MHz) δ_{ppm} 14.6 (br), 18.0 (br), 22.9 (br), 24.8 (br), 29.2–30.0 (br), 52.9 (br), 66.8 (br), 118.1 (br), 131.3 (br), 132.7 (br), 133.1 (br), 134.0 (br), 135.0 (br), 139.2 (br), 142.0 (br); IR (neat) 778, 966, 1311, 1365, 1431, 1655, 1685, 1719, 2918 cm^{-1}; HRMS (ESI) calcd for [$C_{26}H_{28}S_8$+Na]$^+$, 618.9849, found, 618.9847; UV (CH_2Cl_2) 289, 320, 493 nm.
11. ^{1}H NMR spectra were recorded on a Varian NMR System (600 MHz) in $CDCl_3$ at −35 to +60 °C. Assignments of the peaks for Me^a, H^a, and H^b observed in ^{1}H NMR were based on the results of application of the Heteronuclear Single Quantum Correlation (HSQC) and Heteronuclear Multiple-Bond Correlation (HMBC) methods. ^{13}C NMR spectra were recorded on Varian XL-300 (75 MHz) in $CDCl_3$ at +35 °C or a Varian 500-MR (125 MHz) in $CDCl_3$ at −35 °C. For the detail, see the Supplementary data.
12. The $E^{ox}_{1/2}$ of **3b** was measured on the ALS model 600C electrochemical analyzer by cyclic voltammetry (Pt electrode, scan rate 100 mV/s) in CH_3CN containing $Et_4N^+ClO_4^-$ (0.1 M) as a supporting electrolyte.
13. Similarly broadened ^{1}H NMR bands were reported by Uchida and Irie for a diarylethene derivative with the steric hindrance. See: Uchida, K.; Nakayama, Y.; Irie, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1311–1315.
14. The four peaks for Me^a observed at 1.95–2.16 ppm at −35 °C are due to a pair of 2 equiv Me protons of **3b** (two singlet peaks of *parallel-A* and *-B* at 1.95 and 2.00 ppm), and two nonequivalent Me protons of **3b** (two singlet peaks of *antiparallel*, 2.15 and 2.16 ppm).
15. PM3 and DFT calculations were performed by using the programs GAUSSIAN 98.[16] The Cartesian coordinates for **3b** are given in the Supplementary data. Molecular geometries in Figure 4 were drawn using the WINMOPAC 3.9 software.[17]
16. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.;

Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN 98, Revision A.11.4; Gaussian: Pittsburgh PA, 1998.

17. WINMOPAC 3.9, Fujitsu Ltd, Tokyo, Japan, 2004.
18. (a) Irie, M.; Lifka, T.; Uchida, K.; Kobatake, S.; Shindo, Y. *Chem. Commun.* **1999**, 747–750; (b) Higashiguchi, K.; Matsuda, K.; Kobatake, S.; Yamada, T.; Kawai, T.; Irie, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2389–2394.