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Tetrahedron Letters 46 (2005) 431–433

Tetrahedron Letters

Synthesis and photochromic properties of a dithia-dithienylethenophane

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Received 15 October 2004; revised 12 November 2004; accepted 17 November 2004

Abstract—The thermally irreversible photochromic compound dithia-dithienylethenophane was synthesized, which is the first example of a dithienylethene bridged with benzene ring and due to the fixation to the photoactive anti-conformation the quantum yield for the photocyclization reaction became higher than that of the corresponding nonbridged type dithienylethene.

Thermally irreversible and fatigue resistant photochromic compounds are potentially applicable to various types of optoelectronic devices, such as optical memory media[1] photo-optical switching[2] and display.[3,4] Hence, a great number of photochromic compounds, such as azobenzenes, fulgides, diarylethenes etc. have been developed.[5] Among the compounds, diarylethenes show unique photochromic properties such as thermal stability of both isomers and high fatigue resistance.[6]

In solution, the open ring form of a diarylethene exists as two conformational isomers, anti-parallel and parallel, and they exchange slowly at ambient temperature. The anti-parallel conformation is photochemically active and the photo-cyclization reaction can proceed only from the anti-parallel conformation upon irradiation with UV light (Fig. 1). Therefore, the quantum yields for the photocyclization reaction of diarylethenes are dependent on the ratio of anti-parallel and parallel conformations. Several attempts have been studied to increase the quantum yield of the photocyclization reaction. Introduced bulky substituents at the reactive carbons of the diarylethenes increased the photocyclization quantum yield and decreased the thermal stability of the closed ring isomer.[7] Helically locked diarylethenes could not rotate freely and the conformation was fixed in anti-parallel.[8] Supramolecular complex of diarylethene with cyclodextrins enhanced the cyclization quantum yield.[9] A thiophenophane-1-ene in which two positions of the thiophene rings were bridged at 4,4′-positions by a $-CH_2SCH_2-$ linkage increased the photoactive anti-parallel conformation could result in an increase in quantum yield.[10] The anti-parallel conformation of dithienylethene was dominated in the crystalline state also.[11]

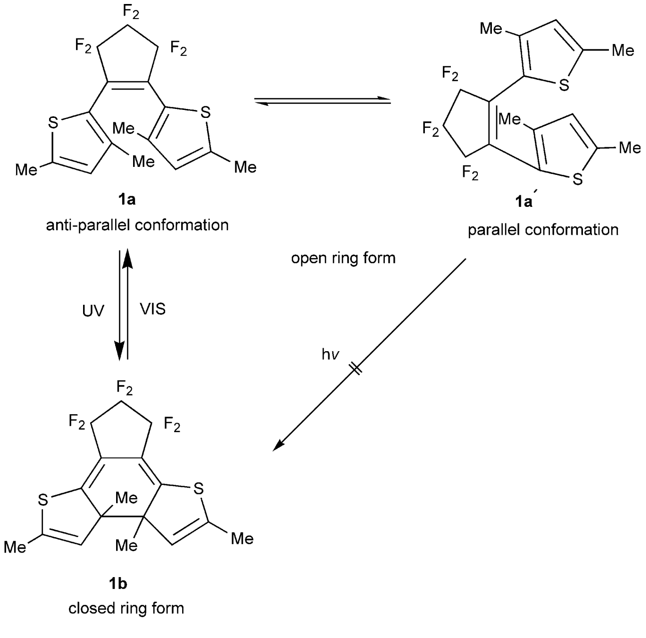

Figure 1. Photochromic reaction of 1,2-dithienylethene.

Keywords: Photochromism; Cyclophane; Quantum yield.

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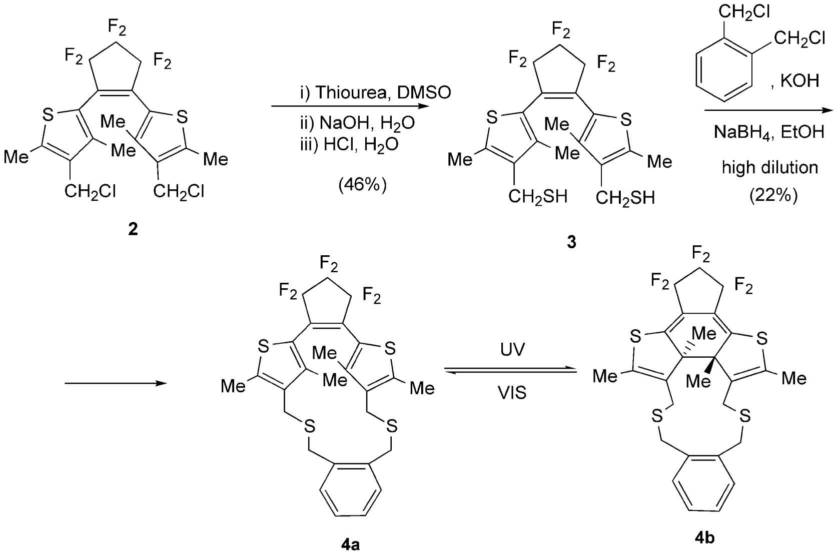
doi:10.1016/j.tetlet.2004.11.090



Scheme 1. Synthesis of dithia-dithienylethenophane.

We have designed and synthesized a novel photochromic compound dithia-dithienylethenophane, which is the first example of a dithienylethene bridged with a benzene ring. Small cyclophane such as a metacyclophan-1-ene has a large steric energy, indicating that the photoisomer would have a high energy of formation.[12] On the other hand the dithia-dithienylethenophane is expected to be thermally stable, since the energies of the formation of the both photoisomers are expected to be similar like dithienylethenes. The dithia-dithienylethenophane has little distortional energy due to its large cyclophane structure, which was calculated by AM1 in MOPAC 97.

The synthesis of dithia-dithienylethenophane is shown in Scheme 1. Compound **4a** has been synthesized via five steps from the commercially available 3-methylthiophene. Bis(chloromethyl)dithienylethene **2** was synthesized by a similar manner to that described in the literature.[10] Bis(mercaptomethyl)dithienylethene **3** was obtained by the treatment of **2** with thiourea in DMSO and following hydrolysis with aqueous NaOH solution. The coupling reaction of 1,2-bis(chloromethyl)benzene with bis(mercaptomethyl)dithienylethene **3** was carried out under high dilution conditions[13] to afford the dithia-dithienylethenophane **4a**. Purification of **4a** was performed by silica-gel column chromatography using ($CHCl_3$/hexane, 1:2) as eluent and recrystallization from hexane afforded **4a** (22%) as yellow prisms.[14]

The inner methyl groups of **4a** appeared at 1.80 ppm, in ^1H NMR spectrum, which is shifted 0.40 ppm to upfield compared with methyl protons of 2,4-dimethylthiophene. This upfield shift is due to the shielding effect of the ring current of the opposite thiophene ring. Therefore, the conformation is determined as anti-parallel. The ^1H NMR spectrum of **4a** was measured at various temperatures. At the temperature between −60 °C and 90 °C, in $C_6D_5CD_3$ no remarkable change was observed in the ^1H NMR spectrum. These results suggested that the ring flipping of dithia-dithienylethenophane **4a** is restricted and fixed in the photo-active *anti*-conformation.

Figure 2 shows the absorption spectral change of the dithia-dithienylethenophane **4** in hexane. Upon irradiation with 366 nm light, a colourless hexane solution of dithia-dithienylethenophane (4.0×10^{-5} mol dm^{-3}) afforded a yellow solution of the closed ring isomer **4b** and a new absorption appeared in the visible region. The absorption maximum was observed at 450 nm. When the yellow solution was irradiated with visible light longer than 460 nm, the spectrum returned to the initial one. The reversible photoisomerization indicates that the dithia-dithienylethenophane **4** is photochromic. At photostationary state of 366 nm light, the conversion of this dithia-dithienylethenophane was 72%.

The quantum yield for the photocyclization reaction of the dithia-dithienylethenophane **4a** was estimated comparing the initial rate for the photocyclization reaction

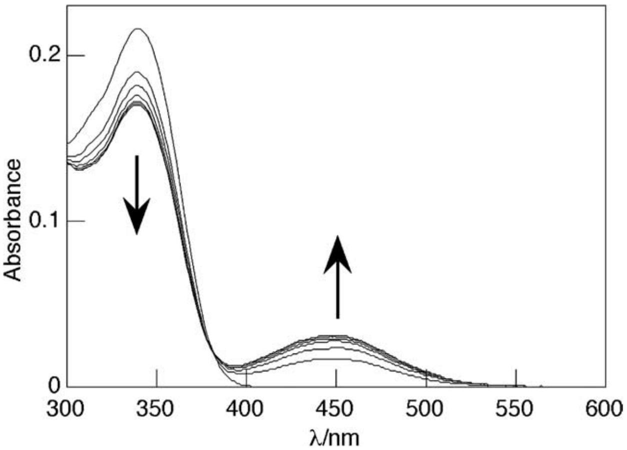


Figure 2. Absorption spectral change of dithia-dithienylethenophane (4.0×10^{-5} mol dm^{-3}) in hexane upon irradiation with 366 nm light.

with bis(2-methyl-1-benzothien-3-yl)hexafluorocyclopentene.[7] The photocyclization reaction of dithia-dithienylethenophane was measured in hexane upon irradiation with 313 nm light and the quantum yield for photocyclization reaction was 0.51. Also the ring-opening reaction of **4b** to **4a** was examined. The quantum yield for ring-opening reaction of **4b** was determined to be 0.25, which was obtained by irradiation with 465 nm light. The photocyclization quantum yield of non bridged **1a** is 0.40.[15] Hence, the photocyclization quantum yield of dithia-dithienylethenophane **4a** is 1.3 times larger than that of **1a** (Fig. 1). This enhancement of the photocyclization quantum yield is due to the fixation to the photoactive anti-parallel conformation of the dithienylethene by bridging with a benzene ring.

The thermal stability of the closed ring form **4b** was examined at 100 °C in toluene. A solution of **4b** in toluene in a sealed tube was stored in a heating oven at 100 °C for 5 h, and no change was found between the initial and the final absorption spectra. This result indicates that both photoisomers of dithia-dithienylethenophane are thermally stable and isomerization takes place only by photoirradiation at ambient temperature.

The thermally irreversible dithia-dithienylethenophane **4a** undergoes a photocyclization reaction with high efficiency. Hence, this dithia-dithienylethenophane can be one of the most preferable materials for molecular photo-memory.

Acknowledgements

This work was partly supported by JSPS, Grant in Aid for scientific research (C) 16550126. Perfluorocyclopentene was supplied by Zeon Co. Ltd to whom we feel appreciate.

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14. Compound **4a**: mp 225.0–227.0 °C; ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): $\delta = 1.80$ (s, 6H), 2.45 (s, 6H), 3.40 (d, $J = 15$ Hz, 2H), 3.50 (d, $J = 10$ Hz, 2H), 3.65 (d, $J = 10$ Hz, 2H), 4.10 (d, $J = 15$ Hz, 2H), 7.20–7.30 (m, 4H); EI (*m*/*z*): 590 (M+); IR (KBr): 1490, 1440, 1332, 1266, 1111, 1045, 982, 871, 864 cm^{-1}; Anal. Calcd for $C_{27}H_{24}S_4F_6$: C, 54.90, H, 4.10. Found: C, 54.97, H, 4.13; λ_{max}/nm (ε) open-ring form: 340 (6625), closed ring form: 450 (4448).
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