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Synthesis and Photochromic Properties of [2.2]Thiophenophan-8-ene-1,2-diol

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A photochromic [2.2]thiophenophan-8-ene-1,2-diol, which is the first ethylene-bridged dithienylethene, has been synthesized by pinacol coupling and this compound indicates fairly good photochromic properties such as high quantum yield for photocyclization and high thermal stability.

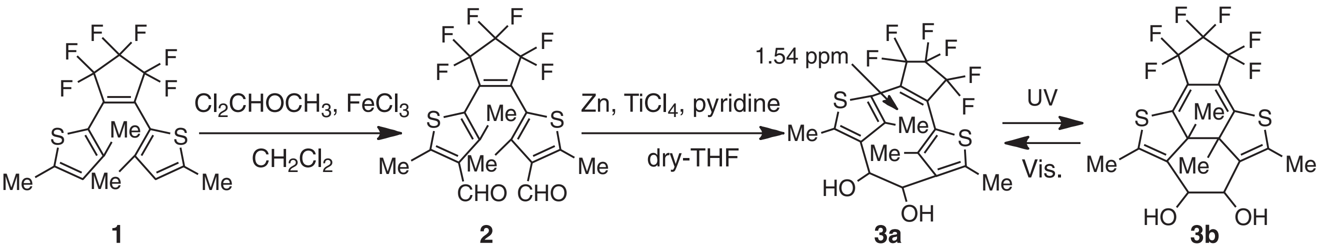
Photochromic compounds have been vigorously studied since they are expected to be useful materials for photomemory. Among them, diarylethene is the one of the most attractive molecules due to high fatigue resistance and thermal irreversibility.[1] However, the existence of the photoinactive conformer of the diarylethene reduces the quantum yield for photocyclization and, therefore, a variety of efforts to decrease the useless conformer have been investigated.[2] To solve this problem, we have developed photochromic cyclophan-1-enes, which are bridged diarylethenes.[3] For example, the quantum yield for photocyclization of a thermally reversible [2.2]metacyclophan-1-ene was reported to be 1.0, which is the first report of quantitative photochromic reaction in solution.[3a] The conformations of the small cyclophan-1-enes are fixed owing to the steric hindrance between the inner substituents and the opposite aromatic rings. Therefore, if the molecule is fixed in the photoactive conformation, the efficiency, that is the quantum yield, of the photoreaction would be increased. From this point of view, we have reported various cyclophan-1-enes and some of the thiophenophan-1-enes satisfy both high photocyclization yields and high thermal irreversibilities.[4] However, [2.2]thiophenophan-1-ene which is a dithienylethene with a ethylene bridge has not yet been reported because of synthetic difficulties. For example, small but nonphotochromic thiophenophanes have been synthesized through long routes.[5] Recently, Yamato and his co-workers reported that treatment of diformyldiphenylalkanes having a short alkane spacer under McMurry reaction conditions afforded small cyclophane-1,2-diols which are thought to be intermediates for the desired stilbene derivatives.[6] By this method, one can obtain small cyclophane-1,2-diol which are highly strained and are difficult to prepare in the usual manner. Then we planned to investigate the synthesis and photochromic properties of a [2.2]thiophenophan-8-ene-1,2-diol as a novel photochromic compound.

Dithienylethene **1** was prepared in a manner described in the literature.[7] Compound **1** was formylated with dichloromethyl methyl ether in the presence of $FeCl_3$ to give a diformyldithienylethene **2**. Treatment of **2** under McMurry reaction conditions, $TiCl_4$, Zn, and pyridine in dry THF,[6] afforded the [2.2]thiophenophan-8-ene-1,2-diol **3a** in low yield (2.4%) with large amounts of the resinous materials as shown in Scheme 1.[8] The McMurry product, a thiophenophane-diene, was not observed. The formation of **3a** accompanied with resinous materials is probably due to the high strain of the diene as described in the literature.[6] Compound **3a** was purified by silica gel column chromatography and was recrystallized from hexane. Compound **3** was the only product which indicated photochromism in the reaction mixture.

The inner methyl protons of **3a** appeared at 1.54 ppm which is 0.46 ppm upfield of those of **2** in the ^{1}H NMR spectrum. This is due to the shielding of the opposite thiophene rings. Therefore, the conformation of the obtained **3a** has *anti*-conformation which would be a photoactive conformation.

Absorption spectral changes of a CH_2Cl_2 solution of **3a** are indicated in Figure 1. Upon irradiation with UV light (330 ± 30 nm), the absorption maximum of **3a** at 345 nm decreased and a new absorption maximum appeared at 447 nm and the color of the solution changed from colorless to yellow. This new absorption is assigned to the closed isomer. The color and the spectrum returned to the initial by visible irradiation (>420 nm), indicating compound **3** is photochromic. From HPLC analysis, the photostationary state at 330 nm contained 79% closed form **3b** and 21% open form **3a**.[8]

The quantum yield of photocyclization of **3a** was obtained relatively by comparing the initial rate of a diarylethene of which quantum yield has already been reported.[9] The value was 0.75 by 313 nm irradiation in CH_2Cl_2, hence 75% of the excited state of **3a** was used for photocyclization. The quantum yield for photocyclization of **1** was reported to be 0.40,[7] and the quantum yield of **3a** is almost twice this value. This is due to the fixation of **3a** to the photoactive conformation by double bridge as



Scheme 1.

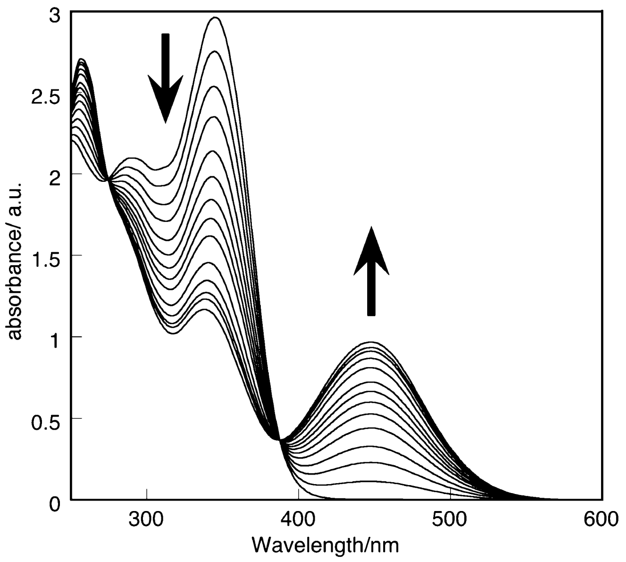


Figure 1. Absorption spectral change of a CH_2Cl_2 solution of **3a** upon irradiation with UV light ([**3**] = 4.0×10^{-4} mol dm^{-3}).

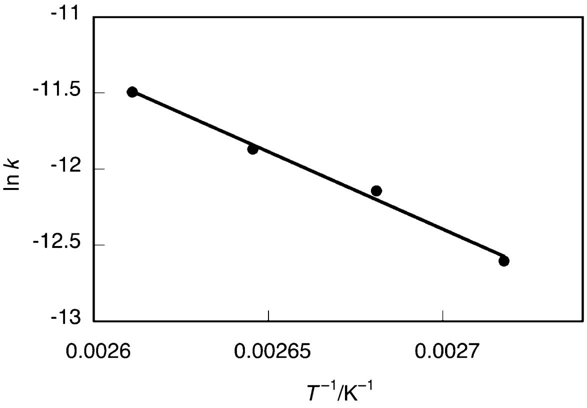


Figure 2. Arrhenius plot for thermal ring-opening reaction of **3b** in toluene.

shown in previous reports from our laboratory.[3,4] The quantum yield for photo-ring opening of **3b** was 0.40. Therefore the conversion to the closed form by UV light (79%) was not so extremely high since both reactions occurred under UV irradiation.

Dithienylethenes, of which aromatic rings are thiophenes, are known as thermally stable photochromic compounds, since thiophenes have relatively small aromatic stabilization energy.[1] Also **3b** has two thiophene rings and therefore high thermal stability could be expected. Then the thermal stability of the closed form **3b** was examined. Figure 2 shows the Arrhenius plot for thermal ring opening of **3b** in toluene. The plot was obtained by the reaction rates for decolorization reactions at various temperature in the dark.[8] The rates were measured between 366 and 386 K by the time-dependent decrease of the absorption of **3b** at 447 nm in the dark. From the plot, the activation energy (E_a) for the thermal reaction was estimated to be 84.5 kJ mol^{-1} and that for the pre-exponential factor (A) was 3.5×10^6 (s^{-1}). The lifetime of the closed form **3b** was calculated to be 7.5 years at 20 °C.

In summary, we have reported the first synthesis of [2.2]thiophenophan-1-ene and this compound shows photochromism. The quantum yield for photocyclization is quite high due to the fixation to the photoactive conformation.

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8 Compound **3a**: pale yellow powder, mp 123.0–125.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 1.54 (s, 6H, 3-Me), 1.95 (br s, 2H, OH, disappeared by addition of D_2O), 2.47 (s, 6H, 5-Me), 4.43 (d, 2H, $J = 4$ Hz, CH); Experimental details are shown in Supporting Information. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 The quantum yield for the photocyclization of **3a** was obtained relatively in comparison the initial rates obtained by absorption spectral change for photoisomerization of **3a** with those of bis(2-methyl-1-benzothien-3-yl)hexafluorocyclopentene.[2a]