Synthesis, Structure, and Photochromic Properties of Dithia-(dithienylethena)phane Derivatives

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Keywords: Cyclophanes / Diarylethene / Photomemory / Photochromism / Quantum yields

Dithia-(dithienylethena)phane derivatives, composed of dithienylethene moieties and benzene bridges, were synthesized by a coupling reaction of the corresponding bis(chloromethyl)benzene with bis(mercaptomethyl)dithienylethene under high-dilution conditions. The products exhibit photochromic properties upon irradiation with ultraviolet and visible light. The photocyclization and cycloreversion quantum yields were determined, and a relationship between the photocyclization quantum yield and distance between the reactive carbon atoms of the phane derivatives established. The *ortho* isomer has a high efficiency in photocyclization due to its fixation in the photo-active *anti* conformation and short distance between the two reactive carbon atoms. The thermal stability of these photochromic compounds has been studied and the *ortho* isomer found to show thermal irreversibility.

Introduction

The reversible phototransformation of a chemical species between two photoisomers having distinguishably different absorption spectra is referred to as photochromism.[1] Thermally irreversible photochromic compounds have become important targets for various types of optoelectronic devices, such as optical memory media,[2] photo-optical switching,[3] displays,[4] and nonlinear optics.[5] Several types of photochromic compounds, such as azobenzenes, spiropyrans, furylfulgides, diarylethenes etc. have been developed.[6] Among these compounds, diarylethenes display excellent photochromic properties, such as the thermal stability of both isomers and high fatigue resistance.[7]

In solution, the open-ring form of diarylethene exists as two conformational isomers, antiparallel and parallel, which exchange slowly at ambient temperature. The parallel conformation is photochemically inactive and the photocyclization reaction can proceed only from the antiparallel conformation upon irradiation (Figure 1). Therefore, the quantum yield for the photocyclization reaction is dependent on the ratio of the parallel and antiparallel conformations. Several attempts have been made to increase the quantum yield of the photocyclization reaction. Bulky substituents at the reactive carbons of the diarylethene have been found to increase the photocyclization quantum yield and decrease the thermal stability of the closed-ring isomer,[8] and helically locked diarylethenes have been synthesized that cannot rotate freely, meaning that the antiparallel conformation is therefore fixed.[9] Formation of a supramolecular complex of diarylethene with cyclodextrins has been found to enhance the cyclization quantum yield,[10] and fixation of thiophenophane-1-ene in the photoactive antiparallel conformation by introduction of a bridged chain increases the photocyclization quantum yield.[11] The antiparallel conformation of dithienylethene is dominant in the single crystalline state.[12]

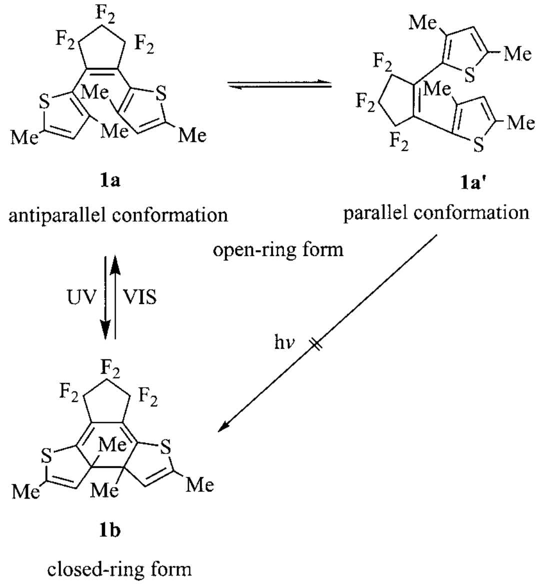

Figure 1. Photochromic reaction of a dithienylethene.

In this study, we have designed and synthesized novel photochromic compounds based on dithia-(dithienylethena)phanes. These compounds are composed of a dithienylethene, a bridge chain, and a benzene ring. This is the

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DOI: 10.1002/ejoc.200400807

first example of a dithienylethene bridged by a benzene ring.

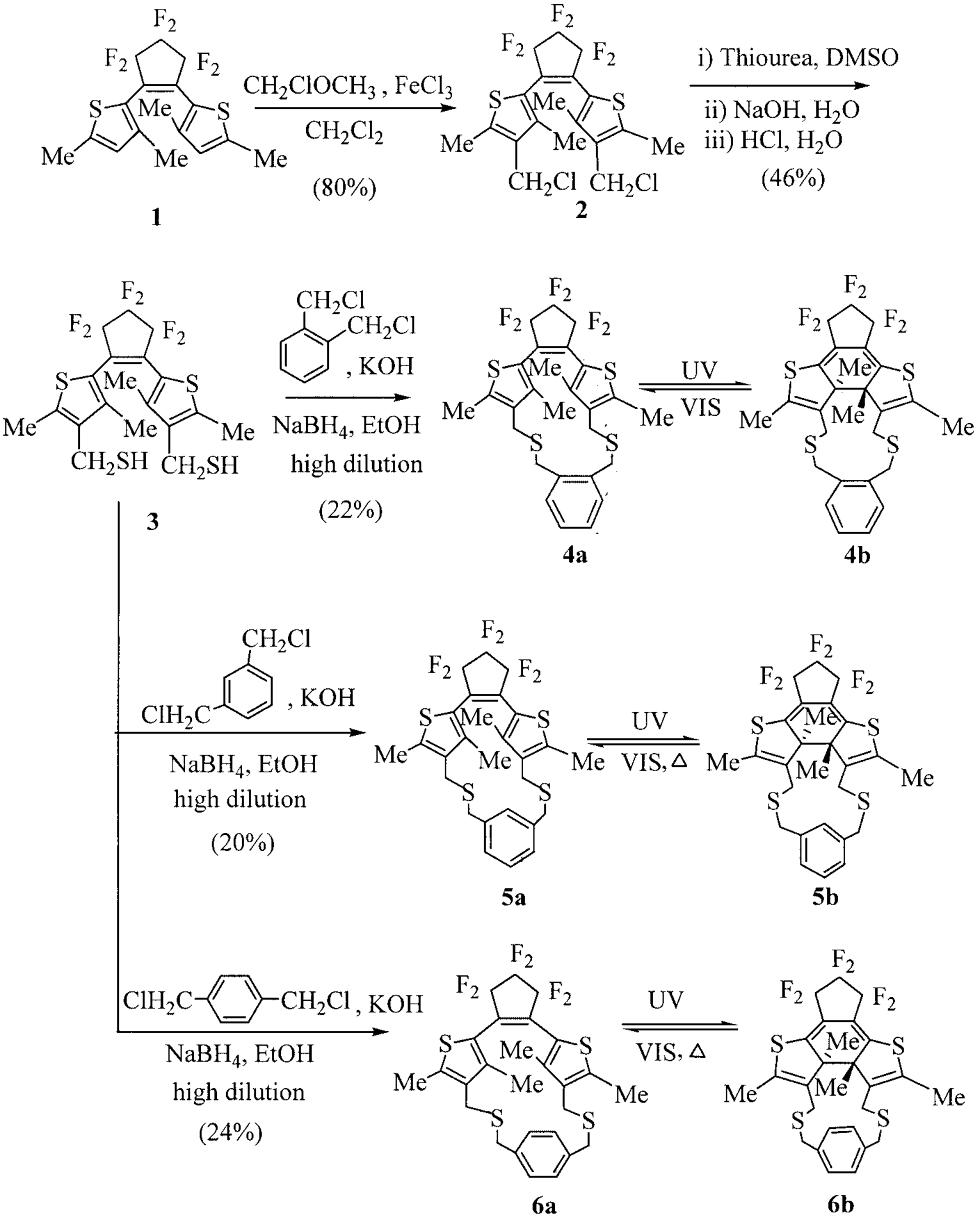
Results and Discussion

Synthesis and Structure of Dithia-(dithienylethena)phanes

The synthesis of dithia-(dithienylethena)phane derivatives is shown in Scheme 1. Compounds **4**–**6** were prepared in five steps from commercially available 3-methylthiophene. Bis(chloromethyl)dithienylethene (**2**) was synthesized by the treatment of 1,2-bis(3,5-dimethyl-2-thienyl)perflurocyclopentene (**1**)[11] with chloromethyl methyl ether in the presence of $FeCl_3$ as Lewis acid. Bis(mercaptomethyl)dithienylethene (**3**) was obtained by the treatment of **2** with thiourea in DMSO followed by hydrolysis with aqueous NaOH solution. The coupling reactions of bis(chloromethyl)benzene with bis(mercaptomethyl)dithienylethene (**3**) were carried out under high-dilution conditions[13] to afford the dithia-(dithienylethena)phanes **4**–**6**. Purification of **4**–**6** was carried out by silica-gel column chromatography with ($CHCl_3$/hexane, 1:2) as eluent.

The structures of **4**–**6** were determined by ^1H NMR, ^{13}C NMR, and IR spectroscopy, mass spectrometry, and elemental analysis, as described in the Experimental Section.

The ^1H NMR spectrum of **6a** shows a pair of singlets at δ = 3.65 and 3.75 ppm for the two CH_2SCH_2 methylene groups. The ^1H NMR spectrum of *para* isomer **6a** does not change between –60 °C and 90 °C. The spectrum of *ortho* isomer **4a** shows two sets of doublets for the two CH_2SCH_2 methylene groups at δ = 3.40 (J = 15 Hz) and 3.50 ppm (J = 10 Hz) and 3.65 (J = 10 Hz) and 4.10 ppm (J = 15 Hz)



Scheme 1. Synthesis of dithia-(dithienylethena)phane derivatives.

at 25 °C in CD_3CN. Even at lower (–60 °C in $C_6D_5CD_3$) or higher temperature (90 °C in $C_6D_5CD_3$) no remarkable change was observed in the ^1H NMR spectrum. These results suggest that the free rotation of the bridge protons of the dithia-(dithienylethena)phane **4a** is restricted and that one of the conformations is dominant. The ^1H NMR spectrum of *meta* isomer **5a** also shows two singlets at $\delta = 3.57$ and 3.59 ppm integrating for eight methylene protons. These results suggest that the free rotation of the bridge protons of the dithia-(dithienylethena)phane **5a** may occur under these conditions. However, since the inner methyl protons of **5a** appear at $\delta = 1.80$ ppm, which is a similar chemical shift to the *ortho* isomer, the *anti* conformation must be dominant. Also, one can estimate that the *anti* conformation is dominant, but that ring flipping may occur, in the *para* isomer **6a**.

Photochromism

Figure 2 illustrates the absorption spectral change of dithia-(dithienylethena)phane **4a** in hexane. Upon irradiation with 366-nm light, a colorless hexane solution of the *ortho* isomer ($\lambda_{max} = 336$ nm) of dithia-(dithienylethena)phane **4a** (4.0×10^{-5} M) afforded a yellow solution with a new absorption at 450 nm. This new band is ascribed to the closed-ring form **4b**. When the yellow solution was irradiated with visible light at wavelengths longer than 460 nm, the spectrum returned to the initial one. This reversible photoisomerization indicates that the dithia-(dithienylethena)phane **4a** is photochromic.

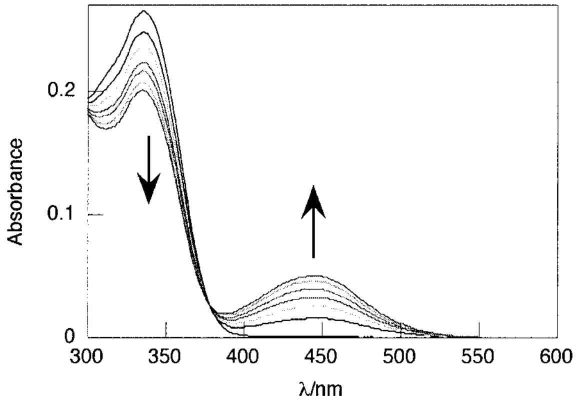


Figure 2. Absorption spectral change of *ortho* isomer **4** (4.0×10^{-5} M) in hexane upon irradiation with 366-nm light.

Figure 3 shows the absorption spectral change of compound **5a**. Upon irradiation with 366-nm light **5a** undergoes a similar photochromic reaction. The colorless solution of **5a** ($\lambda_{max} = 342$ nm) becomes yellow, with an absorption maximum at 450 nm. This color change is due to the formation of the closed-ring isomer **5b**. Upon irradiation with visible light the yellow solution becomes colorless and the open-ring isomer formed.

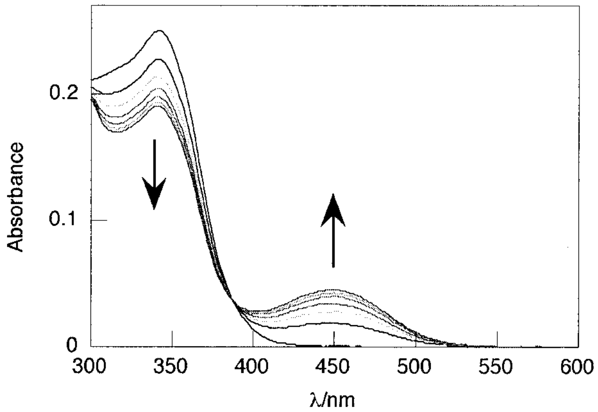


Figure 3. Absorption spectral change of *meta* isomer **5** (4.0×10^{-5} M) in hexane upon irradiation with 366-nm light.

Irradiation of a colorless hexane solution of compound **6a** ($\lambda_{max} = 313$ nm) with 366-nm light also afforded a pale-yellow solution of the closed-ring isomer, with one of the absorption maxima appearing at 464 nm (Figure 4). When this pale-yellow solution is irradiated with visible light the spectrum returns to the initial one. This reversible photoisomerization indicates that the *para* isomer of the dithia-(dithienylethena)phane **6a** is also photochromic.

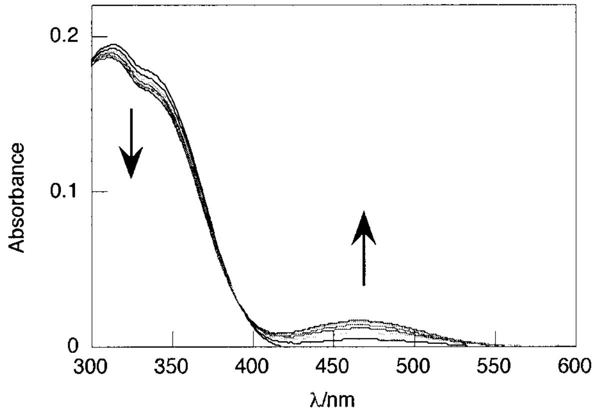


Figure 4. Absorption spectral change of *para* isomer **6** (4.0×10^{-5} M) in hexane upon irradiation with 366-nm light.

Thermal Stability of the Colored Forms of Dithia-(dithienylethena)phanes

The thermal stability of the open- and closed-ring forms of the phanes was examined at 100 °C in toluene. A solution of a mixture of **4a** and **4b** in toluene in a sealed tube was stored in an oven for 5 h; no change was found between the initial and the final absorption spectra. These results indicate that both photoisomers of this phane are thermally stable and isomerization takes place only upon photoirradiation at ambient temperature.

The thermal stability of the closed ring form **5b** was also examined at 100 °C in toluene. The absorbance of the closed-ring isomer **5b** decreased slowly when kept at 100 °C for 5 h, and 20% of the initial closed form **5b** was thermally isomerized to give the open form of *meta* isomer **5a**. The rate at 100 °C is $1.13\times10^{-5}\,s^{-1}$ and the half-life of **5b** at 373 K was calculated as 15 h.

The rates of the thermal decoloration reaction of **6b** were estimated at 70–105 °C in toluene. Even at 70 °C, the absorbance of the closed-ring isomer decreased slowly. It was found that the decay curve follows first-order kinetics. An Arrhenius plot of the decoloration reaction of **6b** is shown in Figure 5. The activation energy for the thermal ring-opening reaction was estimated to be $10.3\,kcal\,mol^{-1}$, with a pre-exponential factor of $2.17\times10^{2}\,s^{-1}$. The half-life of **6b** at 373 K was calculated to be 1.8 h. Therefore, the closed form of *meta* isomer **5b** is more thermally stable than that of the *para* isomer **6b**.

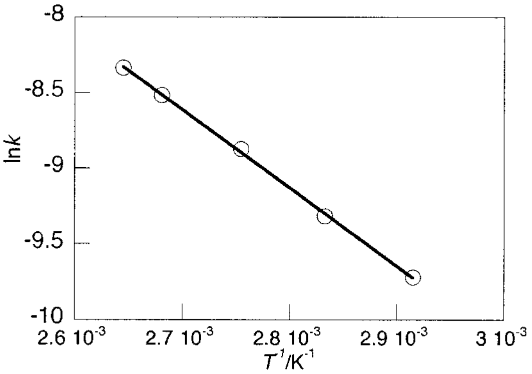


Figure 5. Arrhenius plot of the thermal decoloration reaction of **6b**.

The heat of formation of the closed-ring form **6b** is $3\,kcal\,mol^{-1}$ higher than that of the open-ring form **6a**, as calculated with the AM1 procedure in MOPAC 97.[14] Thus, the activation energy of thermal decoloration is assumed to be relatively small due to the large difference between the energies of formation[15] of the open-ring form **6a** and the closed-ring form **6b**. The instability of the closed form **6b** is due to the distortion by its long bridge.[14]

Quantum Yields of the Photochromic Reactions

The photocyclization and the cycloreversion quantum yields of **4**–**6** were measured in hexane at 25 °C. The quantum-yield measurements were carried out as follows. The *ortho* isomer **4a** was dissolved in hexane and the solution was irradiated with ultraviolet light (λ = 313 nm). A 500 W super high pressure Hg lamp was used as the light source and the irradiating light (λ = 313 nm) was generated by passing the source light through a band-pass filter and a monochromator. The photocyclization quantum yields were determined by comparing the initial rate for the photocyclization reaction of bis(2-methyl-1-benzothien-3-yl)hexafluorocyclopentene in hexane solution.[8] The quantum yield of **4a** to **4b** was determined to be 0.51. Following the same method, we examined the photocyclization quantum yields of the *meta* and *para* (**5** and **6**) isomer of phane, and the estimated quantum yields of the *meta* and *para* isomer were found to be 0.42 and 0.11, respectively.

The quantum yield for the photocycloreversion reaction of **4b** to **4a** was also determined. A hexane solution of **4b**, which was obtained by irradiation with UV light, was irradiated with 465-nm light to determine the quantum yield of the photocycloreversion reaction. The quantum yield of photocycloreversion of **4b** was determined to be 0.25. By applying the same method we also estimated the cycloreversion quantum yields of the *meta* and *para* isomers **5b** and **6b** to be 0.22 and 0.26, respectively. The photocycloreversion

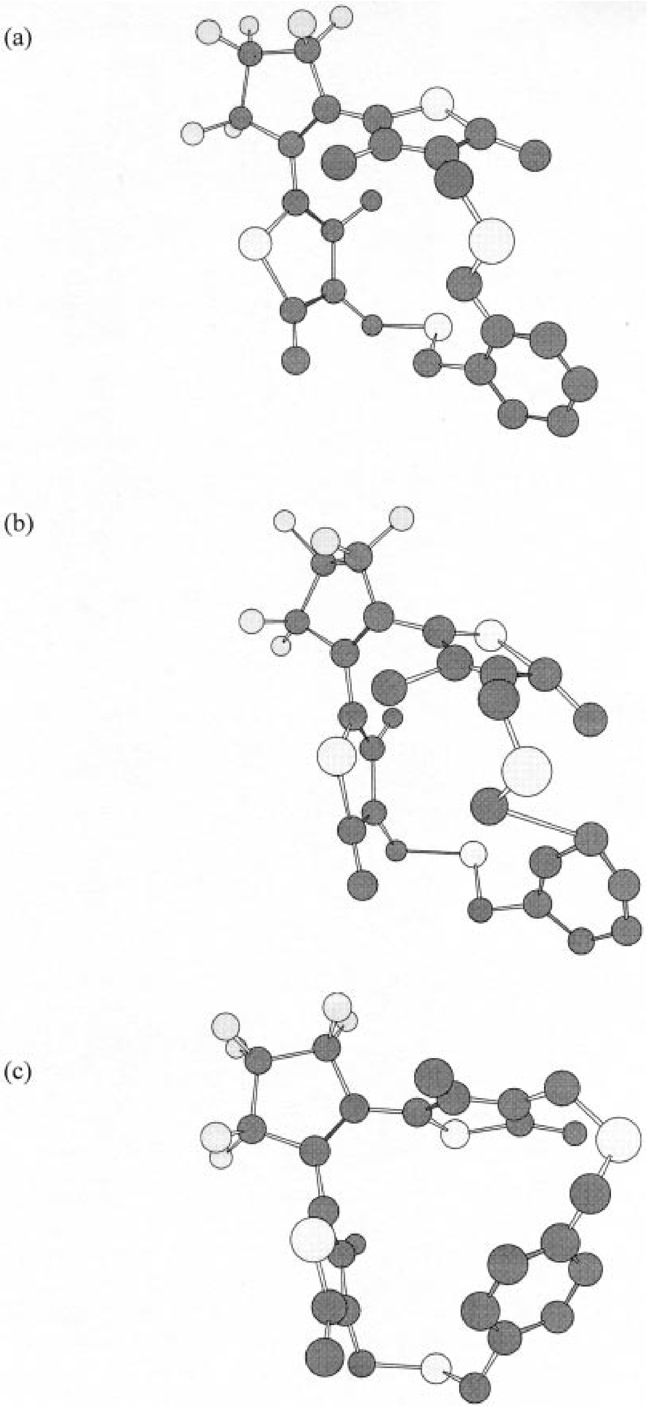


Figure 6. Energy-minimized structures of (a) *ortho*, (b) *meta*, and (c) *para* isomers.

quantum yields of the *ortho*, *meta*, and *para* isomers of phane are very similar. The photocyclization and cycloreversion quantum yields of nonbridged **1a** are 0.40 and 0.58, respectively,[16] which mean that the photocyclization quantum yield of the *ortho* isomer is 1.3-times larger than that of **1a**. This enhancement of the photocyclization quantum yield of **4a** is due to the fixation in the photoactive antiparallel conformation of dithienylethene by the benzene bridge. At the photostationary state with 366-nm light the conversions of **4**, **5**, and **6** are 72%, 65%, and 32%, respectively.

Figure 6 shows the calculated minimized energy structures of the *ortho*, *meta*, and *para* isomers of phane. The distances between the reactive carbon atoms of these isomers were estimated by an analysis based on an AM1-MOPAC calculation. The photocyclization quantum yields depend on the distance between the reactive carbon atoms. It has been reported that the photocyclization reaction in the crystal is suppressed when the distance between the reactive carbon atoms is longer than 4.2 Å.[17] The distance between the reactive carbon atoms of the *ortho* isomer (3.96 Å), which is less than 4 Å, and its antiparallel conformation are fixed in solution, therefore the *ortho* isomer undergoes the photocyclization reaction with high quantum yield (0.51). The distances obtained from the calculations are those in the most stable conformation, and the photocyclization takes place even if the distance is longer than 4.2 Å, although the efficiency for the reaction should decrease in this case. Indeed, the photocyclization quantum yields decrease dramatically when the distance between the two reactive carbon atoms becomes longer, as in the *meta* and *para* isomers (Table 1). The photocyclization quantum yields of the *meta* (0.42) and *para* (0.11) isomers are relatively small due to the long distances between the reactive carbon atoms (4.26 Å and 4.68 Å, respectively).

Table 1. Cyclization, cycloreversion quantum yields, and distance between the two reactive carbon atoms of dithia-(dithienylethena)-phane derivatives and the nonbridged compound.

Compounds	$\Phi_{\text{cyclization}}$	$\Phi_{\text{cycloreversion}}$	Distance between the two reactive C atoms (C3–C12)
4	0.51	0.25	3.96 Å
5	0.42	0.22	4.26 Å
6	0.11	0.26	4.68 Å
1	0.40	0.58	–

Conclusions

We have synthesized dithia-(dithienylethena)phane derivatives that exhibit photochromism. The distance between the reactive carbon atoms and the photocyclization quantum yields of the *ortho*, *meta*, and *para* isomers are 3.96 Å, 4.26 Å, and 4.68 Å and 0.51, 0.42, and 0.11, respectively. The fact that the photocyclization quantum yield increases when the distance between the two reactive carbon atoms decreases in solution is a novel finding. Both photoisomers of the *ortho* isomer **4** are thermally stable and undergo a photocyclization reaction with high efficiency. The cycloreversion quantum yields of the *ortho*, *meta*, and *para* isomers are 0.25, 0.22, and 0.26, respectively. The closed form of the *meta* (**5b**) and the *para* (**6b**) isomers are not thermally stable and the activation energy for the thermal decoloration reaction of the *para* isomer was estimated to be 10.3 kcal mol^{-1}. Therefore, the thermally stable and highly efficient photochromic compound **4** is a better candidate for use as a material for molecular photomemory.

Experimental Section

General Remarks: Absorption spectra were measured with an absorption spectrophotometer (Hitachi, U-3310). ^{1}H NMR spectra were recorded on an FT NMR (JEOL-AL300) spectrometer at 300 MHz. All chemical shifts are given in ppm relative to TMS and coupling constants in Hz. ^{13}C NMR spectra were recorded at 75 MHz. IR spectra were recorded with an FT-IR, 2000, Perkin–Elmer spectrometer, and mass spectra with a JEOL JMS-GCMATE II (EI, 70 eV). Photoirradiation was carried out with a 500-W super high pressure mercury lamp and monochromic light was obtained by passing it through a monochromator (JOBIN YVON). The quantum yields were determined in a manner similar to that described in the literature.[8] The samples were not degassed.

1,2-Bis(chloromethyl)dithienylethene (2): A mixture of 1,2-dithienylethene (**1**; 1.40 g, 3.54 mmol) and chloromethyl methyl ether (1.42 g, 17.6 mmol) in 7 mL of dry CH_2Cl_2 was stirred in an ice-bath. Anhydrous $FeCl_3$ (1.72 g, 10.6 mmol) was added to this mixture and stirred for 3 h. The reaction mixture was then poured into ice water. The organic phase was washed with brine, dried with $MgSO_4$, and the solvent was evaporated in vacuo. Recrystallization of the residue from hexane afforded **2** (1.38 g, 80%) as orange prisms (hexane). M.p. 140.0–143.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.68 (s, 6 H), 2.50 (s, 6 H), 4.40 (s, 4 H) ppm. EI: m/z = 492 [M$^+$].

1,2-Bis(mercaptomethyl)dithienylethene (3): A solution of **2** (1.97 g, 5.00 mmol) and thiourea (760 mg, 10.0 mmol) in 10 mL of DMSO was stirred for 14 h under N_2 at room temperature. The reaction mixture was then poured into 25 mL of 5% aqueous NaOH solution and stirred for 1 h. The solution was acidified with 10% HCl and the precipitate was extracted with $CHCl_3$. The organic layer was washed with brine and dried with $MgSO_4$. The solvent was evaporated in vacuo and recrystallization of the residue from hexane afforded **3** (1150 mg, 46%) as orange prisms (hexane). M.p. 129.0–131.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.90 (t, J = 7 Hz, 2 H), 1.70 (s, 6 H), 2.45 (s, 6 H), 3.50 (d, J = 7 Hz, 4 H) ppm. EI: m/z = 487 [M$^+$].

General Procedure for the Synthesis of Dithia-(dithienylethena)-phanes: A mixture of 1,2-bis(chloromethyl)benzene (43.5 mg, 0.25 mmol) and **3** (122 mg, 0.25 mmol) in 2.5 mL of ethanol/benzene (1:1) was added dropwise, over 24 h, to a refluxing solution of KOH (55.0 mg, 1.00 mmol) and $NaBH_4$ (4.75 mg, 0.13 mmol) in 75 mL of ethanol. The solvent was then distilled off and the residue was poured into ice-cold water. The mixture was extracted with CH_2Cl_2 and the extract was washed with brine. The solution was dried with $MgSO_4$ and the solvent was evaporated in vacuo. The residue was subjected to column chromatography (silica gel, hexane/chloroform, 2:1). The solvents were then removed from the eluent by evaporation and the residue was recrystallized from hexane to afford 32 mg of **4** (22%) as pale-yellow prisms.

3,3,4,4,5,5-Hexafluoro-9,24,26,27-tetramethyl-8,12,21,25-tetrathia-pentacyclo-[21.2.1.^{17,10}0^{2,6}0^{14,19}]heptacosa-1(26),2(6),7(27),9,14(19),15,17,23(24)-octaene (4): M.p. 225.0–227.0 °C. ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): $\delta = 1.80$ (s, 6 H), 2.45 (s, 6 H), 3.40 (d, $J = 15$ Hz, 2 H), 3.50 (d, $J = 10$ Hz, 2 H), 3.65 (d, $J = 10$ Hz, 2 H), 4.10 (d, $J = 15$ Hz, 2 H), 7.20–7.30 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.5$, 27.1, 28.3, 32.5, 37.2, 43.3, 118.1, 127.4, 128.2, 132.7, 135.2, 137.1, 138.2, 142.4 ppm. EI: $m/z = 589$ [M$^+$]. IR (KBr): $\tilde{\nu} = 1490$, 1440, 1332, 1266, 1111, 1045, 982, 871, 864 cm^{-1}. $C_{27}H_{24}F_6S_4$ (590.73): calcd. C 54.90, H 4.10; found C 54.97, H 4.13.

10,10,11,11,12,12-Hexafluoro-6,16,26,27-tetramethyl-3,7,15,19-tetrathiapentacyclo-[19.3.1.1^{5,8}1^{14,17}0^{9,13}]heptacosa-1(25),5(6),8(26),9(13),14(27),16,21,(22),23-octaene (5): A similar procedure to that described above was used but with 1,3-bis(chloromethyl)benzene instead of 1,2-bis(chloromethyl)benzene. Pale-yellow prisms. Yield: 29 mg (20%), m.p. 146.0–149.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.80$ (s, 6 H), 2.45 (s, 6 H), 3.57 (s, 4 H), 3.59 (s, 4 H), 6.90–7.20 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.4$, 28.8, 29.4, 31.2, 37.1, 43.2, 119.5, 127.2, 128.7, 132.2, 135.4, 138.1, 140.3, 142.2 ppm. EI: $m/z = 589$ [M$^+$]. IR (KBr): $\tilde{\nu} = 1373$, 1336, 1270, 1185, 1111, 1052, 982, 882, 709 cm^{-1}. $C_{27}H_{24}F_6S_4$ (590.73): calcd. C 54.90, H 4.10; found C 55.12, H 4.22.

10,10,11,11,12,12-Hexafluoro-6,16,26,27-tetramethyl-3,7,15,19-tetrathiapentacyclo[19.2.2.1^{5,8}1^{14,17}0^{9,13}]heptacosa-1(23),5(6),8(26),9(13),14(27),16,21,(22),24-octaene (6): A similar procedure to that described above was used but with 1,4-bis(chloromethyl)benzene instead of 1,2-bis(chloromethyl)benzene. Yellow prisms. Yield: 35 mg (24%). M.p. 128.0–130.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.80$ (s, 6 H), 2.45 (s, 6 H), 3.65 (s, 4 H), 3.75 (s, 4 H), 6.90 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.5$, 27.3, 29.2, 33.4, 37.6, 44.1, 118.3, 128.2, 129.3, 132.1, 135.3, 137.3, 139.3, 141.4 ppm. EI: $m/z = 589$ [M$^+$]. IR (KBr): $\tilde{\nu} = 1594$, 1472, 1270, 1188, 1041, 971, 875, 849, 768 cm^{-1}. $C_{27}H_{24}F_6S_4$ (590.73): calcd. C 54.90, H 4.10; found C 55.09, H 4.19.

Acknowledgments

This work was partly supported by JSPS with a Grant-in-Aid for scientific research (C) 16550126.

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Received: November 11, 2004