Thermally Reversible Photochromic Systems. Photochromism of a Dipyrrolylperfluorocyclopentene

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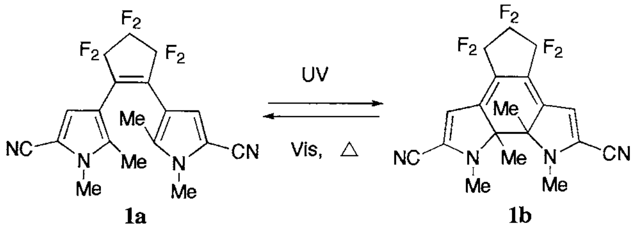
(Received May 19, 1999; CL-990406)

A diarylethene having 2-cyanopyrrole rings turned blue upon UV irradiation in ethyl acetate. The colored form was unstable and returned to the colorless open-ring form with a half-life time of 37 s at room temperature. The activation energy of the thermal fading was obtained to be 32.5 kJ / mol, which is less than half of that of spironaphthoxazine.

Thermally reversible photochromic molecules are required for light attenuation control, such as eyeglass wears. Fundamental requirements for such application are rapid fading of the photo-generated colored form and a low activation energy of the thermal fading.

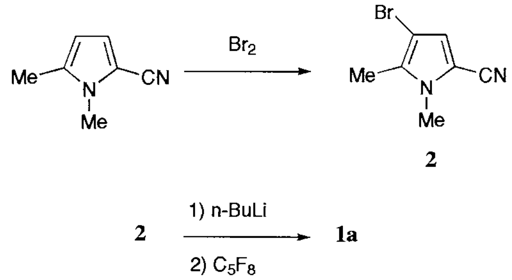
Although spiropyranes and spironaphthoxiazines are possible candidates for the application,[1] the formers are easily decomposed under UV irradiation, and the latters lack the thermal stability applicable to injection molding and their thermal fading activation energies are too large. Therefore development of new thermally reversible and robust photochromic compound with the low activation energy is strongly desired.

Diarylethenes having thiophene and/or benzothiophene rings as the aryl groups are known to exibit excellent thermal stability of both isomers and fatigue resistant characteristic property.[2-6] When the aryl groups are pyrolle, indole or phenyl groups, the diarylethenes undergo thermally reversible photochromic reactions.[6-8] In this paper, we report a new diarylperfluorocyclopentene derivative having pyrrole rings as the aryl groups and studied the photochromic behavior.



Scheme 1. Photochromic reaction of diarylethene **1.**

1,2-Bis(2-cyano-1,5-dimethyl-4-pyrrolyl)hexafluorocyclopentene (**1a**), having pyrrolecarbonitrile as the aryl groups, was synthesized as follows. 1,5-Dimethyl-2-pyrrolecarbonitrile (2.40 g, 20.0 mmol) was brominated with 1.00 ml (20.0 mmol) of bromine in 35 ml of $CHCl_3$ at – 10 ℃ to form 3.32 g (16.7 mmol, 83%) of 4-bromo-1,5-dimethyl-2-pyrrolecarbonitrile (**2**). To the mixture of 5.00 g (25.0 mmol) of **2** and 60 ml of THF, 15.0 ml of n-butyl lithium hexane solution (15% hexane solution, 23.0 mmol) was added at -100 ℃ followed by addition of 0.80 ml (11.3 mmol) of octafluorocyclopentene to give 0.56 g (1.36 mmol) of **1a** (11%).[9]



Scheme 2. Synthetic route of compound **1a.**

The ethyl acetate solution of **1a** (λ max: 311 nm, ε: 1.19×10^4 $M^{-1}cm^{-1}$) was colorless. Upon irradiation with 313 nm light in the presence of air the solution containing **1a** (3.0×10^{-3} M) turned blue, and a new band appeared at 630 nm as shown in Figure 1. The absorption maximum of **1b** was extremely red-shifted in comparison with dithienylperfluorocyclopentene derivatives. Such large red-shift of the absorption band of the closed-ring form was also observed for diarylethenes with indole rings and indole fulgides.[10,11] This is due to the electron-donating character of N of pyrrole rings of **1b**.

The blue color readily disappeared even at room temperature. The decay of the blue color at 630 nm obeyed the first-order kinetics. The half-life time of **1b** at 294 K was 37 s in ethyl acetate. The fading rate of **1b** is comparable with those of spirobenzopyrane derivatives.[12]

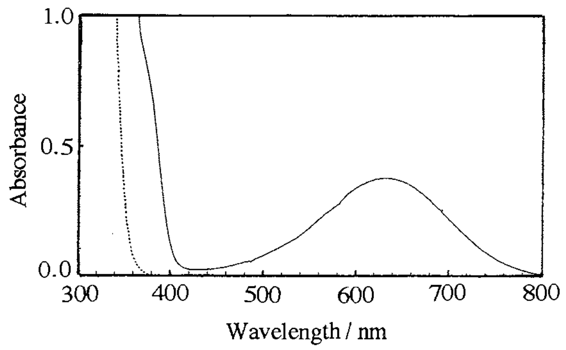


Figure 1. Absorption spectral change of **1a** (------) upon irradiation with 313 nm light. The line (——) is due to the closed-ring form.

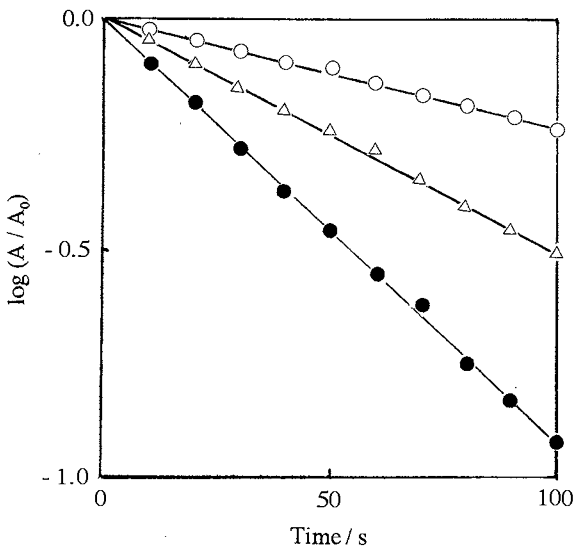


Figure 2. The thermal fading of **1b** in ethyl acetate at 274 K (—○—), 284 K (—△—), and 294 K (—●—).

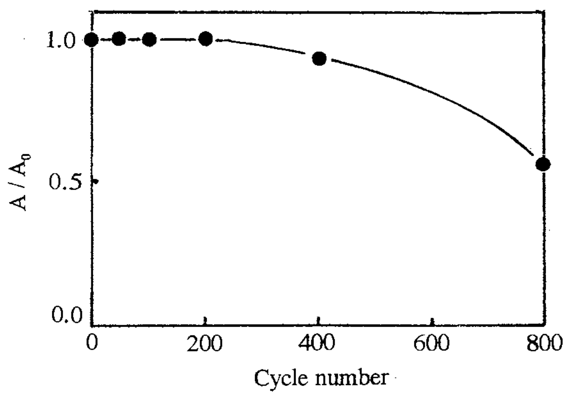


Figure 3. Fatigue resistant characteristic of **1a** (—●—) in an ethyl acetate solution in Ar gas atmosphere. Initial absorbance of the sample was fixed to 1.0.

It has been reported that the half life times of the fading for the closed-ring forms of 1,2-bis(2,6-dimethylphenyl)perfluorocyclopentene[7] and 2,3-bis(5-cyano-2-methyl-3-pyrrolyl)-2-butene[8] at room temperature are 15 and 32 min, respectively. The combination of a perfluorocyclopentene ring as the ethene moiety and 5-cyano-2-methyl-3-pyrrolyl rings as the aryl groups largely increased the fading rate of the colored form.

Another requirement for the light attenuation control is the low activation energy for the fading reactions, because constant fading rate regardless of the environmental temperatures is desired for the application. In order to estimate the activation energy of the thermal fading, the decay process of the closed-form was also measured at same wavelength at 284 K, and 274 K in ethyl acetate solution as shown in Figure 2. The half-life times were 68 s, and 121 s, respectively. The activation energy was 32.5 kJ/mol. The activation energy is much smaller than the values reported for the thermal fading of spirobenzopyrane derivatives (60 – 126 kJ / mol),[13] spironaphthoxazine (80 kJ / mol),[14] and 1,2-di-(2-naphtyl)cyclopentene (121 kJ / mol at 25 ℃).[15]

Fatigue resistant property, i. e., how many times photocyclization and ring-opening reaction cycles can be repeated without loss of performance, was examined in Ar atmosphere at room temperature. The ethyl acetate solution of **1** was irradiated alternatively with 313 nm light for 5 s and visible light ($\lambda > 500$ nm) for 5 s. The irradiation time was long enough for coloration to reach the photostationary state and for the color to be completely bleached. The absorbance of the open-ring form remained almost constant even after 400 coloration / decoloration cycles as shown in Figure 3.

This work was supported by a Grant-in-Aid for Scientific Research (C) No. 09640692 from the Ministry of Education, Science, Sports ,and Culture and by CREST of Japan Science and Technology Cooperation (JST).

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9 **1a:** pale yellow prisms; mp 274-275 ℃; IR (KBr) ν 2214 cm^{-1} (CN). ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.80 (s, 6H), 3.63 (s, 6H), 6.87 (s, 2H). ; MS (m / z) 412 (M^+). Found: C, 55.19; H, 3.23; N, 13.44%. Calcd for $C_{19}H_{14}N_4F_6$: C, 55.34; H, 3.42; N, 13.59%.
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