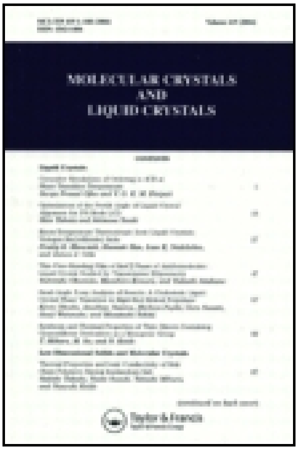

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Novel Thermally Reversible Photochromic Compounds: Dihydrobenzothiophene and Dihydronaphthalene

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*Novel thermally reversible photochromic dihydrobenzothiophenes **1** and **2**, and dihydronaphthalenes **3–6** were synthesized. The colored form **1Q** returned to the colorless **1R** within 150 min, while the decoloration of **2Q** was much slower. On the other hand, dihydronaphthalenes returned very quickly. The decoloration rate was controlled by introducing a methoxy group on the phenyl ring.*

Keywords: adamantylidene group; dihydrobenzothiophene; dihydronaphthalene; hydrogen rearrangement; photochromism; thermal reversibility

INTRODUCTION

Although a great number of thermally reversible photochromic compounds based on the cyclization-cycloreversion reaction, such as spiropyrans, spirooxazines, dihydroindolizines, and nahpthopyrans, have been reported [1–3], few are known to have the cyclohexadiene–hexatriene system. Only several fulgide derivatives [4] and diarylethenes [5] are well-known, and a plain dihydronaphthalene system [6], if it

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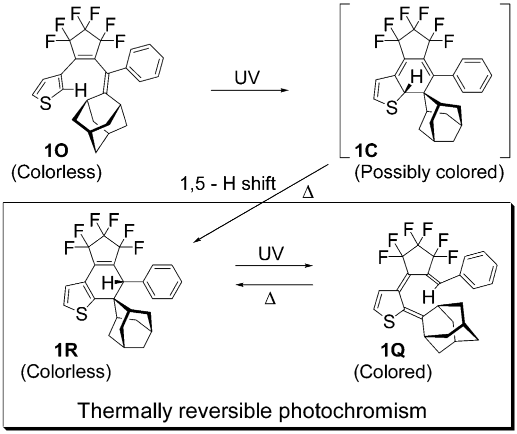


SCHEME 1 Thermally reversible photochromism of **1**.

can be regarded as photochromic, is known. In the course of our research on closely related thermally irreversible photochromic compounds [7], we found that a dihydrobenzothiophene **1R** bearing an adamantylidene group showed the thermally reversible and steady photochromism (Scheme 1) [8]. We here report the thermally reversible photochromism of several related compounds.

RESULTS AND DISCUSSION

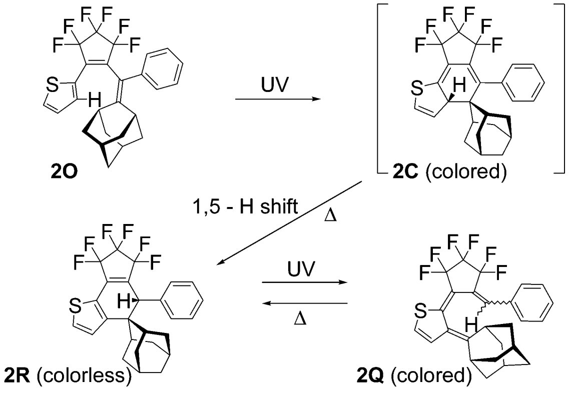
1. Synthesis of 2O

Synthesis of **2O** was done in 32% yield from 1-(1-adamantylidene-1-phenylmethyl)-2,3,3,4,4,5,5-heptafluorocyclopentene and 2-lithiothiophene, according to the similar procedures described elsewhere [8].

2. Photoreaction of 2

Photoreaction of **2O** (Scheme 2, Fig. 1) was carried out as previously reported for **1O** [8]. When a toluene solution of **2O** was irradiated with 313-nm light, an absorption band at 487 nm appeared (Scheme 3). When the irradiation was continued, it became larger while the absorption maximum moved gradually to the shorter wavelength. After 150 min (photostationary state), the maximum was 468 nm. It is attributed to the initial generation of **2C** (487 nm) and the final entire conversion to **2Q** (468 nm).

When the irradiation was stopped, the absorption band started to shrink. However, in the first 20 min, the rate of decoloration was fast



SCHEME 2 Thermally reversible photochromism of **2**.

and blue shift of the absorption maximum was observed. After that, the docoloration occurred as a first order reaction. The behavior of initial 20 min may be the result of cyclization of less stable geometric isomer of the terminal double bond of **2Q**.

One of the reasons to synthesize **2** was to accelerate the decoloration rate of **1**. However, the change of the connecting position of the thiophene ring from C-3 to C-2 brought about the wrong effect. We thus undertook the synthesis of new compounds, which should loose the large aromatic stabilization energy when generating Q-forms.

3. Synthesis and Photoreaction of 3R

Synthesis of **3O** was done in 64% yield from 1-(1-adamantylidene-1-phenylmethyl)-2,3,3,4,4,5,5-heptafluorocyclopentene and phenyllithium.

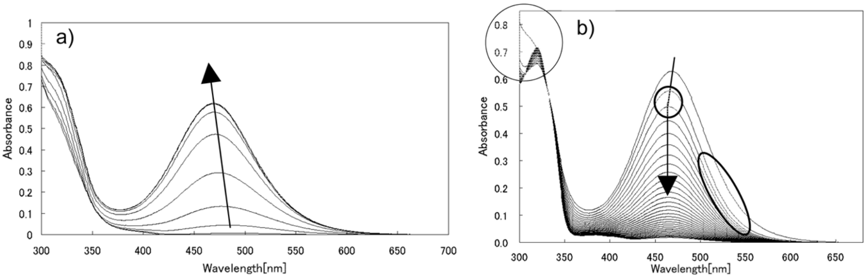


FIGURE 1 Absorption spectral change of **2** in toluene (c: 1.01×10^{-4} mol dm^{-3}). a) **2O** to **2Q** (313 nm, 0 to 150 min); b) **2Q** to **2R** (33.2°C, 0 to 320 min).

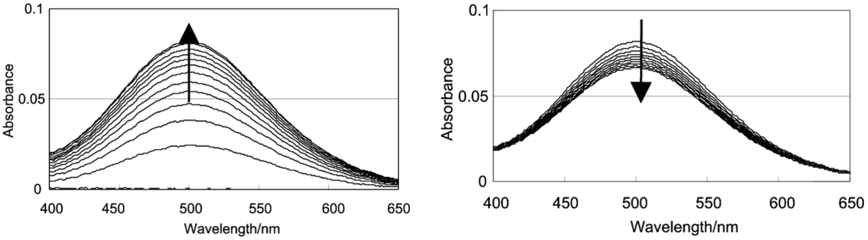


FIGURE 2 a) Photocoloration of **3R** in amorphous polyolefin film by 254 nm at 173 K. b) Thermal decoloration of **3Q** in amorphous polyolefin film at 173 K.

Irradiation of 313-nm light to the toluene solution of **3O** afforded **3R**, which was confirmed by ^{1}H NMR of the product. However, different from **1** and **2**, no color development was observed during the photoirradiation. This is because the hydrogen rearrangement reaction of **3C** and decoloration by cyclization of the colored **3Q** is so fast that the concentration of the colored species **3C** and **3Q** are quite low.

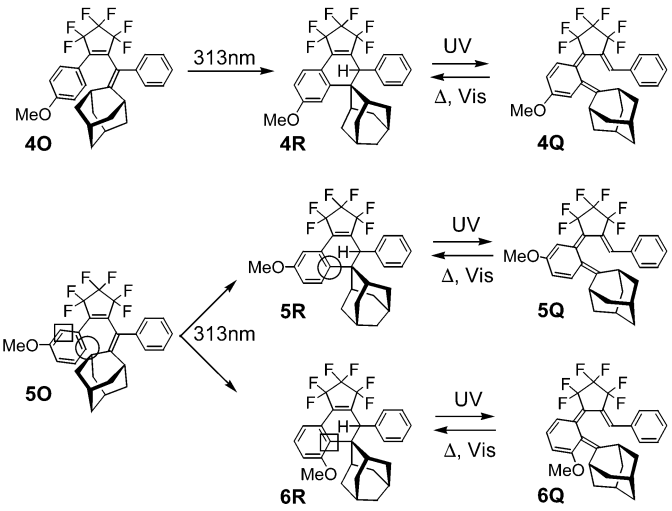
Therefore we carried out the photoreaction at low temperature. Figure 2 shows the absorption spectral change of an amorphous polyolefin film [9] containing **3R** at 173 K.

Now the decoloration is too fast at room temperature. That is because the loss of aromatic stabilization energy when **3R** is changed to **3Q** is too large. Therefore, in order to slow down the decoloration cyclization rate, the deformation of the *o*-quinodimethane structure by electronic perturbation was investigated.

4. Synthesis and Photoreaction of 4R, 5R, and 6R

Introduction of 4- and 3-methoxyphenyl groups to 1-(1-adamantylidene-1-phenylmethyl)-2,3,3,4,4,5,5-heptafluorocyclopentene afforded **4O** and **5O** in 55 and 55% yields, respectively. Irradiation of toluene solution of **4O** by 313-nm light afforded **4R**. On the other hand, similar treatment on **5O** afforded **5R** and **6R** because the electrocyclization can occur on either of the two ortho carbon atoms.

In order to evaluate the thermal reactivity of the colored forms of methoxy-substituted dihydronaphthalenes, **3Q**, **4Q**, **5Q**, and **6Q** were dissolved in 2-methylTHF and their photochemical ant thermal reactivity were examined. At low temperature, the coloration was not observed by 366-nm light irradiation. When the temperature was raised, coloration was observed because the photochemical ring opening could occur by overcoming the constraint of the cold environment. When the temperature was raised more, the coloration was no longer



SCHEME 3 Photoreactions and thermal reactions of **4**, **5**, and **6**.

observed because the decoloration by cyclization became faster than the ring opening. Therefore, the compound has its specific temperature range to show the coloration.

It is interesting that the coloration range depends on the substitution pattern. The unsbustituted **3Q** has the lowest, **4Q** next, and **5Q** and **6Q** have the highest. The participation of the lone pair on the methoxy oxygen in the conjugation may perturb the unstable *o*-quinodimethane structure to stabilize it. Therefore the decoloration is retarded. The difference of the temperature range in 100 K between **3Q** and **5Q**/**6Q** is noteworthy. The schematic presentation of the coloration temperature range is shown in Figure 3.

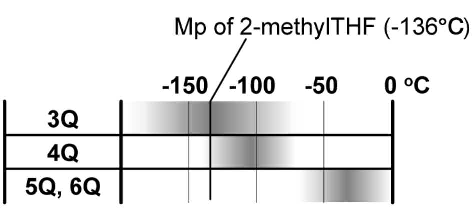


FIGURE 3 Photocoloration temperature range of dihydronaphthalenes in 2-methylTHF with 366-nm light irradiation.

CONCLUSION

New thermally reversible photochromic dihydrobenzothiophene **2R** and dihydronaphthalenes **3R**, **4R**, **5R**, and **6R** were synthesized. The rate of decoloration cyclization reaction of the latter was controlled by the substitution pattern of the methoxy group on the phenyl group.

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