Thermally Irreversible Photochromic Systems. Reversible Photocyclization of 1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocycloalkene Derivatives

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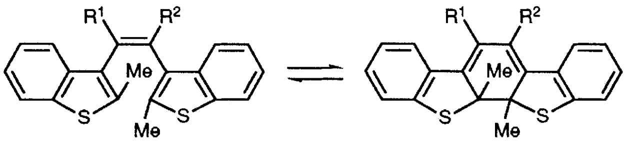
1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocylopentenes undergo thermally irreversible photochromic reactions in which colouration/decolouration cycles can be repeated more than 10^4 times without significant loss of performance.

Recently, much effort has been made to synthesize photochromic compounds for optical-data storage media.[1–5] Among these 1,2-diarylethenes containing heterocyclic rings have promising ability for this application owing to their characteristic properties of thermal stability (irreversibility) and fatigue resistance.[6–9] The compounds undergo electrocyclic reactions to produce closed-ring forms which absorb light at longer wavelengths. However, *cis–trans* isomerization can also occur and is unfavourable for practical applications since it competes with the cyclization[10] which is responsible for the change in colour. To prohibit *cis–trans* isomerization completely and so gain access to fatigue-resistant photochromic compounds, 1,2-diarylperfluorocycloalkenes containing heterocyclic rings have been synthesized.

Compounds **1a**–**4a** were prepared by elimination reactions of perfluorocycloalkenes with organolithium compounds.[11] In a typical experiment, n-butyllithium (15% hexane solution, 3.1 cm^3, 5 mmol) was added slowly into a solution of 3-bromo-2-methylbenzo[*b*]thiophene (1.24 g, 5 mmol) of diethyl ether (50 cm^3) at −78 °C under a nitrogen atmosphere for 10 min, and then perfluorocyclopentene (0.34 cm^3, 2.5 mmol) was added. The reaction mixture was warmed to room temperature and treated with dilute hydrochloric acid and the product extracted with diethyl ether. After removal of diethyl ether, the product 1,2-bis(2-methylenzo[*b*]thiophan-3-yl) perfluorocyclopentene **2a** was purified by silica gel chromatography and isolated in 75% yield.



1a; $R^1R^2 = (CF_2)_2$
2a; $R^1R^2 = (CF_2)_3$
3a; $R^1R^2 = (CF_2)_4$
4a; $R^1 = R^2 = CF_3$

1b; $R^1R^2 = (CF_2)_2$
2b; $R^1R^2 = (CF_2)_3$
3b; $R^1R^2 = (CF_2)_4$
4b; $R^1 = R^2 = CF_3$

Fig. 1 illustrates the change in spectral absorption of a hexane solution of **2a** (λ_{max} 258 nm, ϵ 1.4 × 10^4 dm^3 mol^{-1} cm^{-1}) upon irradiation with light at 313 nm. A new band appeared at 517 nm (ϵ 9.1 × 10^3 dm^3 mol^{-1} cm^{-1}) ascribable

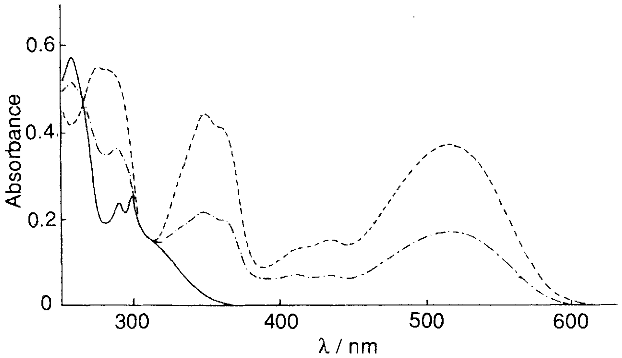


Fig. 1 Absorption spectra of **2a** (4.1 × 10^{-5} mol dm^{-3}) (——), **2b** (----) and at the photostationary state (—·—) upon irradiation with light at 313 nm in hexane

Table 1 Absorption maxima of the closed-ring forms of perfluorocycloalkene derivatives in benzene

Compound	R^1 R^2	λ_{max}/nm
1b	$(CF_2)_2$	532
2b	$(CF_2)_3$	526
3b	$(CF_2)_4$	510
4b	CF_3 CF_3	449

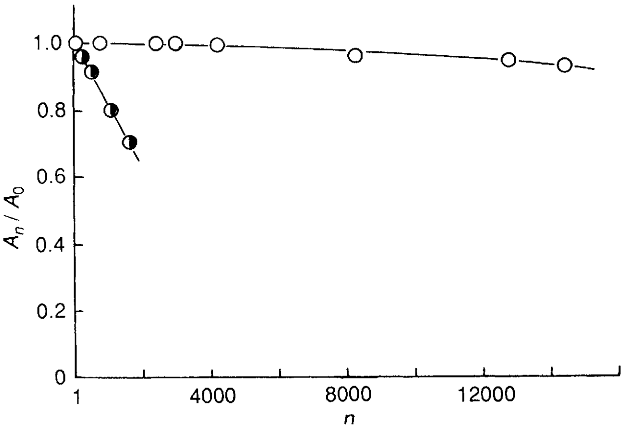


Fig. 2 Fatigue resistant properties of compounds **2** (○) and **4** (◑) in methylcyclohexane (c = 1.2 × 10^{-4} mol dm^{-3}) in the presence of air. A_0 and A_n are the absorbance of the closed-ring forms at the photostationary state under irradiation with light at 313 nm at the first and the nth cycle, respectively.

to the closed-ring form.[7] Under photostationary conditions the ratio of the closed- to the open-ring form was 45 : 55. This new band disappeared upon irradiation with light of wavelength ≥500 nm. The quantum yields of both cyclization and ring-opening reactions were found to have a value of 0.41 in hexane.

Table 1 summarizes the absorption maxima of the closed-ring forms, **1b–3b**, along with that for the perfluorobut-2-ene derivative **4b**. The maxima of the perfluorocyloalkene derivatives shift to longer wavelengths upon decreasing the ring size from a six- to a four-membered ring. The bis(perfluoromethyl) derivative **4b** has its absorption maximum at the shortest wavelength. From the absorption shift data it is inferred that the ring size controls the planarity and thus the extent of π-conjugation in the closed-ring forms. When the ring size is small, the resulting rigid structure suppresses deviation from planarity of the cyclohexadiene molecular framework so maintaining the π-conjugation. In the absence of such restriction however, as in the derivative **4b**, the dihedral angle between two benzothiophene moieties becomes large and the resulting destruction of the π-conjugation leads to a hypsochromic shift.

The photogenerated closed-ring forms were thermally stable with the absorption intensities of **2b** and **4b** remaining unchanged after more than 6 months in toluene at 80 °C. Even after 6 months storage, the compounds were still photochemically active with their colour disappearing upon irradiation with light of λ > 450 nm and reappearing again upon irradiation at 313 nm.

Fig. 2 shows the fatigue-resistant properties of compounds **2** and **4** in methylcyclohexane in the presence of air. Initially the solution containing the photochromic compound (1.2 × 10^{-4} mol dm^{-3}) was irradiated with light of wavelength $300 < \lambda < 400$ nm until the photostationary state was attained. Then, the colour due to the closed-ring form was bleached completely by irradiation at wavelengths >450 nm. Such colouration/decolouration cycles were repeated many times and the absorption intensity of the closed-ring form plotted *vs.* cycle number. Although the intensity of the perfluorobut-2-ene derivative **4** decreases to 80% of its initial value after 1200 cycles, 90% of the performance remains even after 14 000 cycles for the perfluorocyclopentene derivative **2**.

The introduction of perfluorocycloalkene moieties is thus effective in bringing about a spectral shift of the closed-ring form to longer wavelengths as well as increasing the durability of diarylethene type photochromic compounds.

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