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Fatigue-resistant Photochromic Hemithioindigoes

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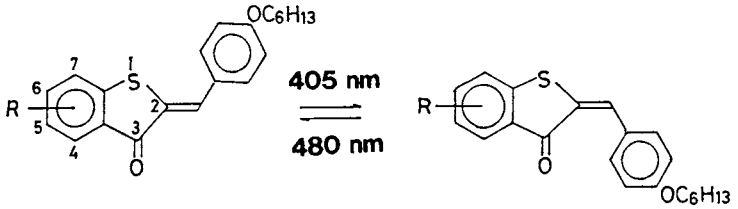
The hemithioindigo derivatives have been found to show satisfactory photoresponses even after more than 10^4 cycles of alternate irradiation with the lights which can induce a Z - E isomerization.

Despite extensive investigations on organic photochromism, only a few compounds are known as being fatigue resistant. So far, spironaphthoxazine and its analogues[1] are only commercially used as ophthalmic glasses or light shielding materials. Besides this family, the high performance of photochromism is reported for cis/trans photoisomerization and reversible electrocyclic reactions.[2,3] This letter describes excellent photofatigue resistant property of 2-arylmethylene-benzo[b]thiophene-3-(2H)-one (hemithioindigo; HT) derivatives (**1** and **2**).



Z **E**

1: R=5-$(CH_2)_5CH_3$
2: R=7-$COOC_2H_5$

The preparation of **1** and **2** is described elsewhere.[4] The absorption maxima in benzene are similar to those reported for the other analogues:[5] λ_{max} = 445 nm (Z: ε = 2.2x10^4 mol^{-1}dm^{3}cm^{-1}) and 474 nm (E: ε = 1.3x10^4 mol^{-1}dm^{3}cm^{-1}) for **1**; λ_{max} = 445 nm (Z: ε = 2.2x10^4 mol^{-1} dm^{3}cm^{-1}) and 469 nm (E: ε = 1.2x10^4 mol^{-1}dm^{3}cm^{-1}) for **2**. The benzene solutions (1.4x10^{-5} mol dm^{-3}) of **1** and **2** in 1x1 cm^2 square cuvettes were exposed under air alternately to 405 nm and 480 nm lights of a 500 W Hg lamp. The photostationary yield of the E-isomer upon exposure to the 405 nm light (through a Corning 5-58 filter) was ca. 80% for both **1** and **2**. On the other hand, the irradiation with the 480 nm light (through either a Kenko interference BP-48 filter or a Hoya Y-46 filter) gave the Z-isomer quantitatively. The irradiation was carried out for 10 s and 30 s for the 405 nm and 480 nm

respectively, in order to bring about the photostationary state.

Figure 1 shows the plots of the absorbance of the Z-isomer given immediately after exposure to the 480 nm light vs. the repetition number of alternate irradiation. Apparently, the absorbance for **2** scarcely decreases even after 10^4 irradiating cycles. Excellent fatigue resistance is also shown for **1**, though it is slightly less durable than **2**. The half-life cycle ($n_{1/2}$) at which the absorbance loss due to fatigue reaches the half of the initial absorbance is 1×10^4 and 4×10^4 for **1** and **2**, respectively. These values are comparable with those of diarylethene-type compounds,[3] but orders of magnitude are greater than those for well-known photochromic compounds such as nitrospiropyran[6] and azobenzene.[7] Furthermore, it is remarkable that the addition of 1,4-diazabicyclo[2.2.2]-octane (DABCO) improves the value of $n_{1/2}$ for these HTs. This may be due to the quenching of $^1O_2$ generated photochemically in a manner discussed in the case of thioindigo.[8]

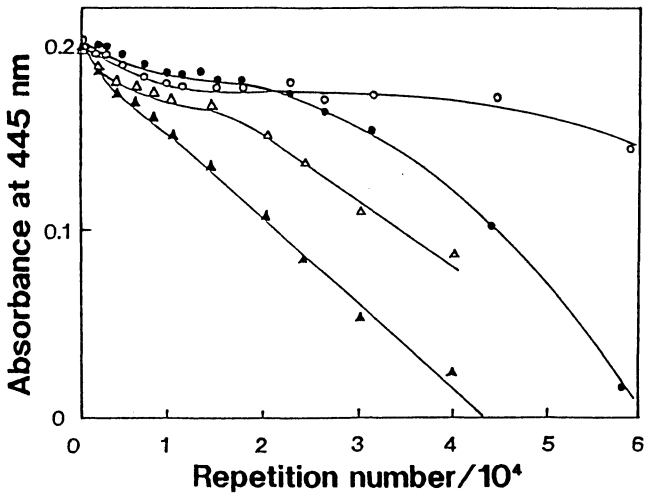


Fig. 1. Durability evaluation of **1** (△, ▲) and **2** (○, ●) by alternate irradiation with 405and 480 nm lights in the absence (closed) and presence (open) of DABCO (8×10^{-5} mol dm^{-3})

References

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