



Substituent effects on the photochromic properties of 3,3-diphenylspiro[benzofluorenypyran-cyclopentaphenanthrene]s



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ABSTRACT

The introduction of electron-donating groups on the skeleton of a naphthopyran, 3,3-diphenylspiro[benzofluorenypyran-cyclopentaphenanthrene], has led to the development of a photochromic dye applicable to photochromic lenses. Introducing a methoxy group to C6 moved the absorption band of the MC form towards the longer wavelength. Further introduction of methoxy groups to the para-position of the phenyl groups on C3 induced faster decoloration of the MC form. Additional introduction of a methoxy group to C13 led to the enhancement of the absorption intensity as well as the facile, economic synthesis of the dye caused by the symmetrical property of the starting material.

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1. Introduction

Naphthopyrans have been shown to exhibit thermally reversible photochromism [1,2]. According to their substitution patterns, naphthopyrans are classified into two types: 2*H*-naphtho[1,2-*b*]pyran and 3*H*-naphtho[2,1-*b*]pyran, as shown in Scheme 1. Their photochromic reactions involve 6π-electrocyclizations between a pyran ring (NP form, usually colorless) and a 1-oxo-2,4-pentadiene skeleton (MC form, colored).

The photochromism of naphthopyrans was first reported by Becker in 1969 [3]. Their photochromism was, however, observed only at low temperatures and the fatigue resistivity was poor compared to that of spirooxazines. Therefore, spirooxazines were investigated more favorably from the viewpoint of commercial applications such as ophthalmic lenses.

Until the beginning of the 1980 s, inorganic photochromic lenses such as PhotoGray Extra[®] developed by the Corning Corp. monopolized the market. In 1982, the American Optical Co. launched

plastic photochromic lenses using spirooxazines under the name Photo Lite[®]. However, because it exhibited only a blue color upon UV irradiation, it was not widely used and neutral colors such as gray or brown were more favored. In addition, darkness of the coloring under sunlight was insufficient for use as sunglasses. Consequently, since the late 1980 s, naphthopyrans began to be more widely studied over spirooxazines, and gray and brown naphthopyrans had been developed by the mid-1990 s [4,5]. Meanwhile, several naphthopyrans were launched into the market by Tokuyama Corp. for use in photochromic auto-color-regulating ophthalmic lenses, and their properties have also been continuously improved. In fact, basic research [6–8] as well as the development of commercially applicable compounds [9] have been carried out extensively by a number of researchers and companies.

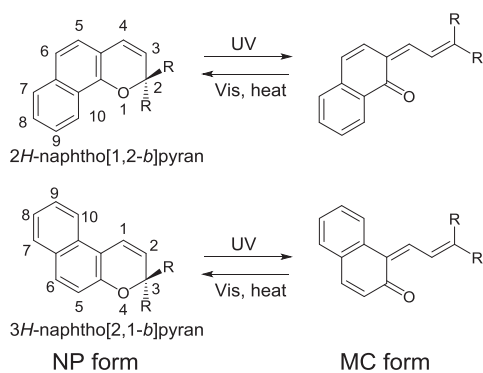
In order for a photochromic dye to be used for auto-color-regulating ophthalmic lenses, it should, by itself, satisfy the following conditions:

- 1) Completely colorless when in the closed form
- 2) Exhibits a neutral color, such as gray or brown, when in the colored open form
- 3) Coloring should be sufficiently dark when UV light is applied
- 4) The color should fade quickly when UV light is discontinued

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Scheme 1. Structure and photochromism of naphthopyrans.

5) The photochromic dyes should be highly fatigue resistant

To address these issues, we have long continued research on 2*H*-naphthopyrans with two phenyl groups on the C2 carbon atom. Recently, we have developed 3,13-dihydrobenzo [3,4] fluoreno [2,1-*b*]pyrans, which belong to the 2*H*-naphtho[1,2-*b*]pyran group for use in photochromic ophthalmic lenses [10–12]. In this article, we report on our recent research efforts to realize a dye that satisfies the above required conditions with the 3,13-dihydrobenzo [3,4] fluoreno[2,1-*b*] pyran skeleton [13].

2. Results and discussion

2.1. Acceleration of fading reaction

2.1.1. Stability of isomers and conformers for MC forms of prototype compounds estimated by DFT

The photochromic reactions including the isomerization between the conformers of the MC form of 3,13-dihydrobenzo[3,4] fluoreno[2,1-*b*]pyrans are detailed in Scheme 2 [6].

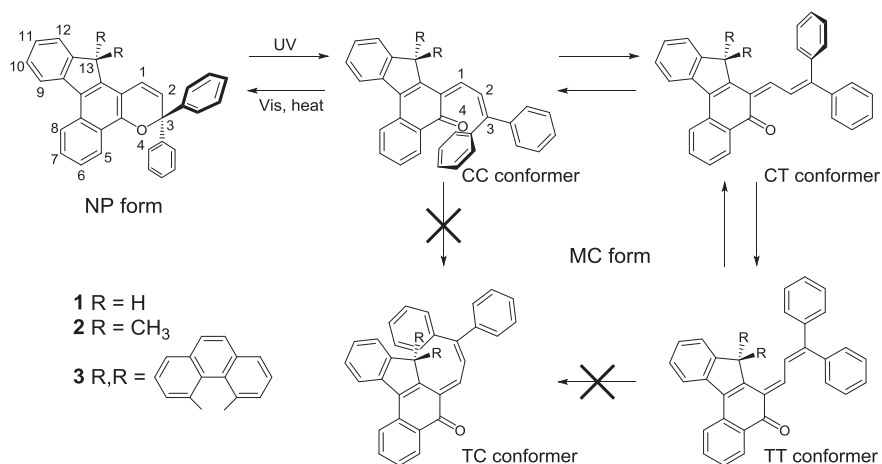
Upon UV irradiation, the colorless NP form opens its pyran ring to afford a highly congested CC (*cis* – *s-cis*) conformer which may isomerize to yield other conformers by either a fast single bond rotation and/or double bond isomerization. Namely, by the rotation of the C1–C2 single bond, the CT (*cis* – *s-trans*) conformer is formed, which then isomerizes to the TT (*trans* – *s-trans*) conformer by E-Z isomerization of the exo-cyclic double bond on the cyclohexadienone ring. The TC (*trans* – *s-cis*) conformer could

be generated either from the CC conformer by E-Z isomerization of the exo-cyclic double bond or from the TT conformer by rotation of the C1–C2 single bond. However, for compounds having a 3,13-dihydrobenzo [3,4] fluoreno[2,1-*b*]pyran skeleton, severe steric repulsion between one of the phenyl groups on C3 and the substituents on C13 causes the TC conformer to be considerably unstable. Therefore, we judged that mainly CT and TT conformers that can exist stably as the MC form of 3,13-dihydrobenzo [3,4] fluoreno [2,1-*b*]pyrans should be considered.

When the colored MC form thermally reverts back to the colorless NP form, the MC form should take the CC conformer as its immediate precursor. Since the CT conformer can isomerize to the CC conformer thermally by rotation of the C1–C2 single bond, the activation energy between the CT and CC conformers may be small. When the CT conformer is unstable, the fading rate quickens. On the other hand, the TT conformer should first convert to the CT conformer before it changes to the NP form by thermal E-Z isomerization of the exo-cyclic double bond, which usually has a higher activation energy than the single bond rotation. Thus, disappearance of the MC form takes longer when the TT conformer is stable and its proportion is large. In order to accelerate the fading rate, it would thus be effective to reduce the stability of both the CT and TT forms. In contrast, to strengthen coloration, it would be effective to increase the stability of the CT and TT forms since coloration becomes stronger when the fading reaction is slow.

DFT calculations [14] of the NP and MC forms of the prototype 3,13-dihydro-3,3-diphenylbenzo[3,4]fluoreno[2,1-*b*]pyran **1**, sterically congested 3,13-dihydro-13,13-dimethyl-3,3-diphenylbenzo [3002C4]fluoreno[2,1-*b*]pyran **2** and 3,3-diphenylspiro[benzo[3,4] fluoreno[2,1-*b*]pyran-13(3*H*),4'-[4*H*]cyclopenta[def]phenanthrene **3** showed that the CT and TT forms of **2** and **3** have considerably higher energy than **1**. This probably arises from the steric congestion between one of the phenyl groups on C3 and the substituents on C13, i.e., the geminal dimethyl group in **2** and the spiro-phenanthrene group in **3**. The calculation results are shown in Table 1, where the energy for the NP form of each compound was set at zero.

For the CC conformers, the energy values of all the compounds are much higher than their NP forms, as supposed from their sterically congested structures. The TC forms are also unstable due to their congested structures. For **3**, the TC conformer did not converge to a local minimum and showed a structure similar to its TT conformer having a local minimum energy. We, thus, needed to consider only the CT and TT conformers as the main conformers of the MC form.



Scheme 2. Photochromism of 3,13-dihydrobenzo[3,4]fluoreno[2,1-*b*]pyrans.

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