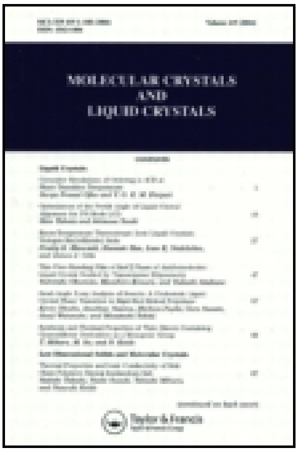

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# High Photodegradability of Spirocfluorene-[2H]-Chromenes]

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# HIGH PHOTODEGRADABILITY OF SPIRO[FLUORENE-[2H]-CHROMENES]

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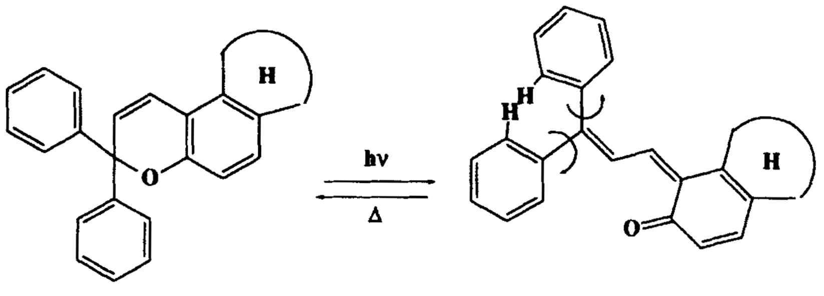
Abstract : The photodegradation of photochromic compounds in spiro[fluorene-[2H]-chromene] series in toluene has been studied by continuous irradiation. We have shown that the resistance to the photodegradation is a function of the introduced heterocycle. As in spiro[indoline-naphthoxazine] series, the chromenes heteroannelled by a benzofurane or a pentamethylene pattern present a dramatic decrease of their resistance to the photodegradation. Then, comparatively to the diaryl-[2H]-chromenes, the increasing flatness of the open forms issued from the spiro[fluorene-[2H]-chromenes] leads to a lower stability in connection with a bathochromic shift and the apparition of an additional band in the visible spectrum.

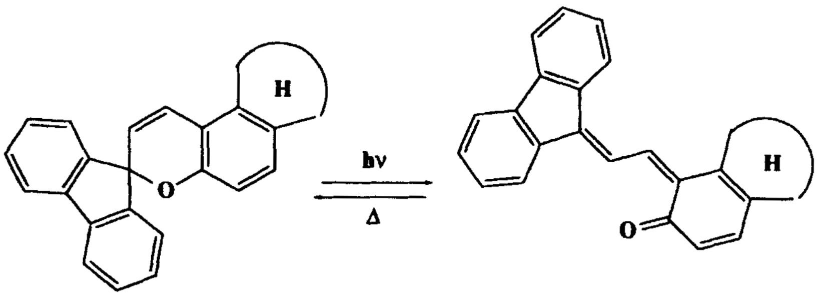
## 1 - Introduction

Although organic photochromic compounds have been known for decades, their tendency to fatigue, that is their tendency to lose their ability to reversibly switch from the colorless form to the colored form and back again, has limited their utility[1-7] (scheme 1).



**Type I : [2H]-chromene series**

**Ib**



**Type II : Spiro[fluorene-[2H]-chromene] series**
**H = heterocycle**

**IIIb**

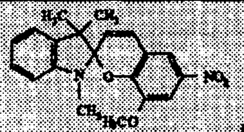
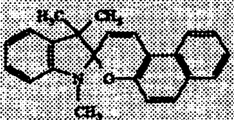
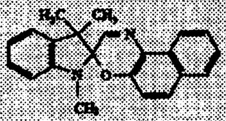
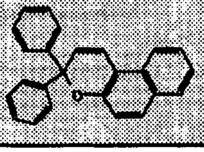
Scheme 1 : Photochromic interconversion

Spiropyrans[8] are generally considered more fatigue prone than the indolinospirooxazines. Spiropyrans bearing a nitro group degrade very rapidly due to the involvement of triplet states in the coloration process[9, 10]. Non nitro containing compounds such as spiroindolinonaphthopyrans have better stability but poor colorability[1].

With pyrans not containing a spiro heterocyclic group, such as diarylnaphthopyrans, we have better colorability and lower fading rate constant but interesting resistance to fatigue closed to indolinospironaphthoxazines (table 1).

So, it was attempted to increase the optical density after a flash by introducing a conformational hindrance upon the open form.

Table 1 : Inter-series comparison of the photochromic properties and of the fatigue resistance

| Photochrome | $\lambda_{max}$ (nm) | $A_0$ | $k_{\Delta A0}$ ($s^{-1}$) | $k_{\Delta A0/2}$ ($s^{-1}$) | $t_{A0/2}$ (min) |
|---|---|---|---|---|---|
|  IV | 615 | 0,66 | 0,03 | 0,03 | 7 |
|  III | 570 | 0,14 | 43 | 104 | 1160 |
|  I | 590 | 0,41 | 0,54 | 2,03 | 515 |
|  II | 432 | 0,31 | 0,11 | 0,105 | 460 |

$k_{\Delta A0/2}$ : thermal bleaching kinetic constant at the time $t_{A0/2}$

$k_{\Delta A0}$ : thermal bleaching kinetic constant at the time t = 0 (after the first flash)

C = $5\times10^{-6}$ M, toluene. 25°C, filter Schott France WG295.

## 2 - Experimental details

### 2. 1 - *Materials*

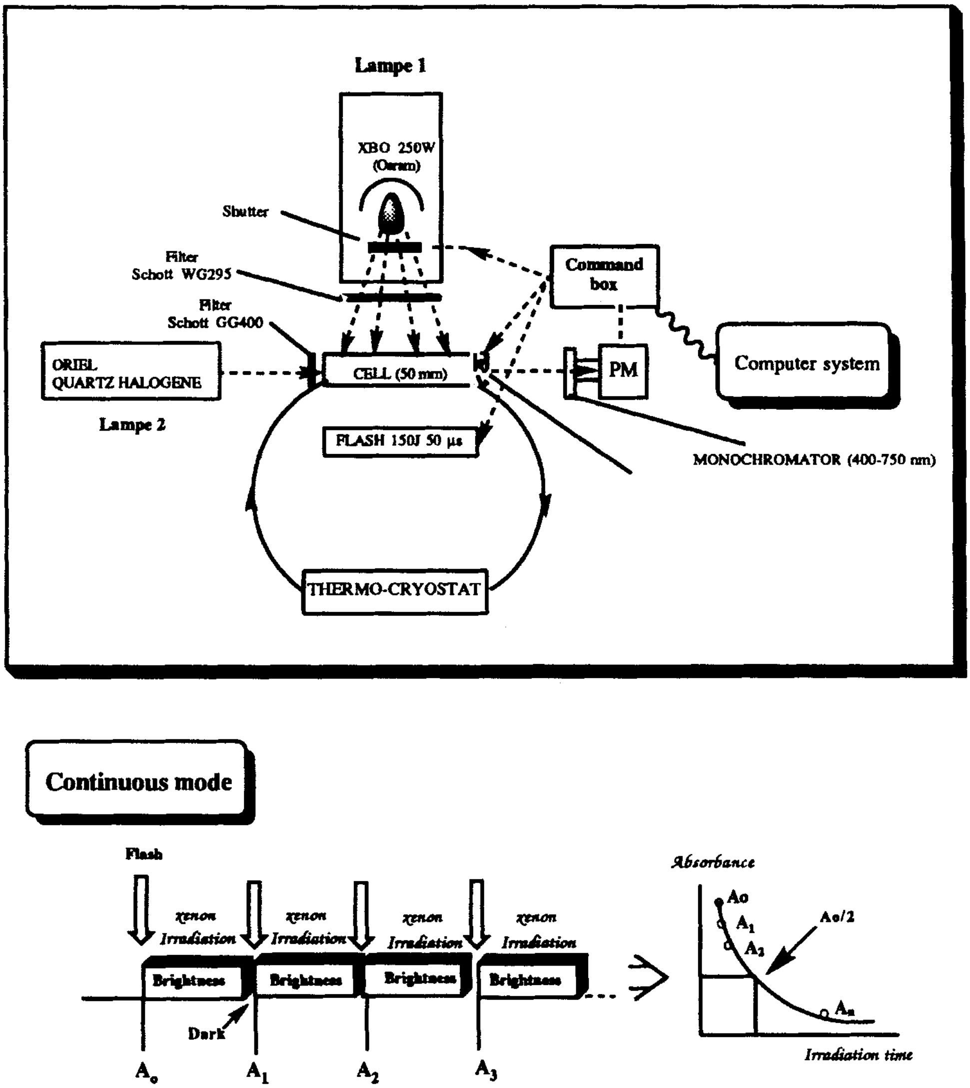
Compounds **I** to **VIII** used in this work were prepared as described in the literature **[11,12]** and purity was controlled by HPLC-DAD chromatography. Toluene (SDS France, anhydrous for analysis) was used as solvent.

### 2. 2 - *Apparatus*

Photochromic properties were measured at room temperature (25°C ± 0.1) on an apparatus using a 250W xenon lamp arc (lamp 1) to photodegradate and a 150W flash xenon lamp 2 to measure the colorability ($A_0$). Light from lamp 1 was passed through a filter WG295

(Schott France) cutting off at 280nm in order to remove UVB and a filter WG114 is positioned in front of the flash lamp 2 to eliminate infrared radiation. The change in optical density was determined as a function of the irradiation time.

This system called " Degraphot " is described[13] in scheme 2.



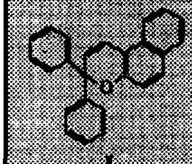
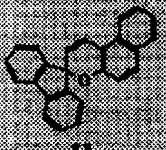
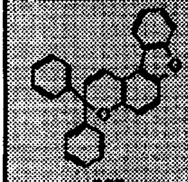
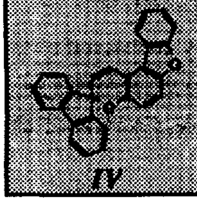
Scheme 2 : Set up of the Degraphot apparatus

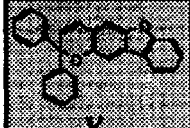
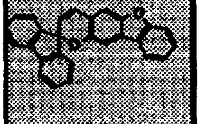
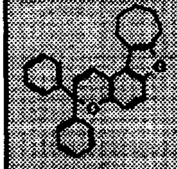
## 3 - Results and Discussion

Comparatively to diarylnaphthopyrans (type I), spiro[fluorene-[2H]-chromenes] (type II) present a very good colorability, a slowly fade rate but no achieve a good resistance to fatigue (-100% < $\Delta t_{A0/2}$ <-71%) (table 2).

The large difference in photochromic properties between types I and II compounds is explained by examining the most stable open colored forms **IIb**. In these open forms, there is a steric hindrance whereas no such flatness exists in **I** (scheme 1). The net result is that **IIb** returns to its colorless closed form (fades) much more slowly and is more colorable than **I**, so more exposed to the attack by singlet oxygen species.

Table **2** : Spectrokinetic and fatigue resistance properties of [2H]-chromenes and spiro[fluorene-[2H]-chromenes].

| Photochromic Compound | $\lambda_{max}$ (nm) | $A_0$ | $k_{\Delta A0}$ ($s^{-1}$) | $k_{\Delta A0/2}$ ($s^{-1}$) | $t_{A0/2}$ (min) | $\Delta t_{A0/2}$ (%) |
|---|---|---|---|---|---|---|
|  *I* | 432 | 0.29 | 0.11 | 0.105 | 460 | 0 |
|  *II* | 453 | 0.49 | 0.04 | 0.04 | 135 | -71 |
|  *III* | 424-(518) | 0.30 - (0.17) | **0.21*** | 0.22 | 45 | -90 |
|  *IV* | 442-473-<br>(551) | 0.30 - 0.30-<br>(0.17) | 0.3/**0.06** | 0.3/**0.07** | < 5 | -100 |

| Photochromic Compound | $\lambda_{max}$ (nm) | $A_0$ | $k_{\Delta A0}$ ($s^{-1}$) | $k_{\Delta A0/2}$ ($s^{-1}$) | $t_{A0/2}$ (min) | $\Delta t_{A0/2}$ (%) |
|---|---|---|---|---|---|---|
|  V | 427-(549) | 0.46 - (0.17) | **0.58***/0.03 | **0.4***/0.07 | < 5 | -100 |
|  VI | 462-491-(569) | 0.51 - 0.52-(0.27) | **0.52***/0.01 | **0.5***/0.01 | < 5 | -100 |
|  VII | 421-(532) | 0.39 - (0.11) | 0.04 | 0.04 | 35 | -92 |
|  VIII | 449-(535) | 0,49 - (0,16) | 0,3/**0,02*** | 0,28/**0,02*** | 15 | -96 |

$k_{\Delta A0/2}$ : thermal bleaching kinetic constant at the time $t_{A0/2}$

$k_{\Delta A0}$ : thermal bleaching kinetic constant at the time t = 0 (after the first flash)

C = $5 \times 10^{-6}$ M, toluene. 25°C, filter Schott France WG295.

$\Delta t_{A0/2}$ (%) = $[(t_{A0/2\,(photochrome)} - t_{A0/2\,(I)}) / t_{A0/2(II)}] \times 100$ : variation rate of the fatigue resistance of the photochromic compound against the reference molecule (**I**)

* $k_\Delta$value:for maximal amplitude

## 4 - Conclusion

Spiro[fluorene-[2H]-chromenes] represent a class of photochromic compounds less fatigue resistant than diaryl-[2H]-chromenes. This property seems to be directly connected to the stabilization of their open forms which undergoes photoinduced degradation processes such as free radical recombination or attack of singlet oxygen on the ene systems of the photomerocyanines.

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