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Fatigue resistance of photochromic 2,2-diaryl-[2H]-heteroannellated chromenes in solution

Christiane Salemi-Delvaux[a], Eliane Pottier[a], Robert Guglielmetti[a,] *, Roger Dubest[b], Jean Aubard[b]

[a]*L.C.M.O.M., ERS CNRS 158, Université de la Méditerranée, Faculté des Sciences de Marseille-Luminy, Case 901, 163 Avenue de Luminy, 13288 Marseille Cedex 9, France*

[b]*ITODYS, URA CNRS 34, Université Paris VII, 1 rue Guy de la Brosse, 75005 Paris, France*

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Abstract

The photodegradation in toluene of photochromic compounds in the [2H]-chromenes series has been studied under continuous irradiation. It is shown that the resistance to fatigue depends on the nature of the heteroatoms, the size of the ring and the annellation position. Six-membered aza-heterocycles, as in the spiro[indoline-hetero-annellated benzoxazine] series, improve the fatigue resistance to UV-light; in contrast, the five-membered heteroannellated chromenes (containing benzimidazole, benzothiazole, benzofurane, indole or pyrrole moieties) show a significant increase in the photodegradation process, but a broadening of the visible spectra for the photomerocyanines. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

The design of new organic photochromes [1,2] is always a fruitful research field because of the various potential application of these compounds, including variable optical transmission filters, data storage, non-silver photography, non linear optic materials, etc. The industrial applications [2,3] are based either on the thermal or photochemical reversibility of the coloration process, or on the variation of the physico-chemical parameters resulting from the molecular phototransformation.

Variable optical transmission materials [3] have principal applications related to their colour change in the field of ophthalmic glasses and lenses. Their commercialisation requires that several criteria are fulfilled:

- a photocoloration and a thermal bleaching rate fast enough over a large temperature range
- a suitable ‘colourability’ in the optimal concentration range
- a significant resistance to photodegradation (also named fatigue resistance)
- neutral tinted glasses (grey or brown colour) are required

A possible strategy to obtain the desired colour involves a mixture of two or more photochromic pigments, of which the corresponding photomerocyanines cover the whole visible spectra region but are endowed with nearly equivalent fading rates.

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* Corresponding author. Fax: +334-91-82-9304

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Thus, spirooxazines associated with 2H-chromenes can be considered as good candidates for that purpose. Indeed, the recent development of spirooxazines [4,5] is due to the interesting properties of their photomerocyanines, as well as for the coloration which extends from 520 to 650 nm, and for the high fatigue resistance of these species [6].

On the other hand, yellow and orange colours can be achieved from some fulgides [7] and from substituted [2H]-chromenes [8].The properties of this latter class of compounds was investigated by Becker in the late 1960s [9] and early 1970s [10]. A comparison of the photochromic behaviour between spiro[indoline-naphthopyran]**1**, spiro[indoline-naphthoxazine]**2** and 3,3-diphenylnaphthopyran **3** compounds is given in Table 1 [11].

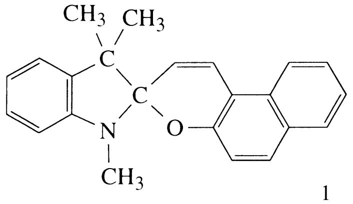
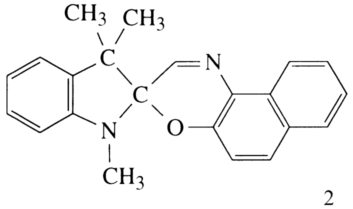
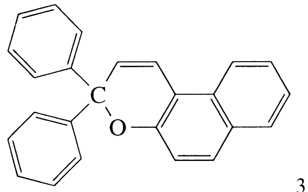
The spiro[indoline-naphthopyran] **1** has a good fatigue resistance but a bad colorability and a fast fading rate. Because compounds **2** and **3** have similar kinetics and lifetime while complementing each other in color, the basic structure of 3,3-diphenyl naphthopyran **3** was chosen by Pozzo [13] for the development of new heterocyclo annellated systems [14,15]. The influence of the position of benzoannellation on the chromene skeleton is analyzed in this present paper.

2. Results and discussion

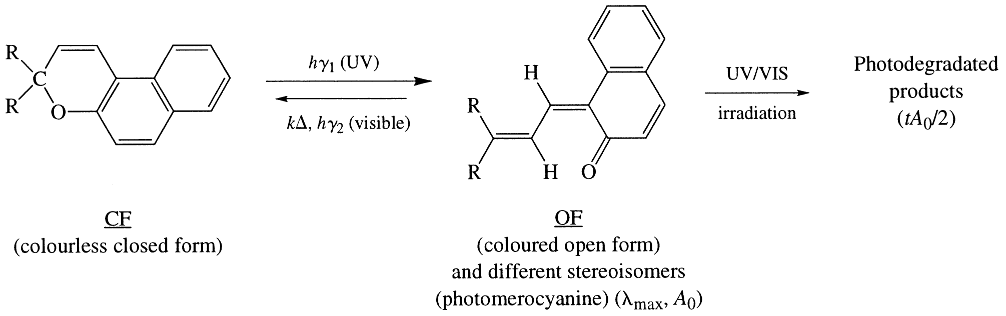
The general photochromic equilibrium for 3,3-diphenyl-[3H]-naphtho[2,1-b]pyrans could be described quite classically on Scheme 1.

These systems are predominantly thermally reversible. The photoactivity of such compounds can then be evaluated by means of measurement

Table 1
Comparative spectrokinetic parameters

Photochromic pigment	λ_{max} (O.F.)	Colorability ‘A$_o$’	$k\Delta(s^{-1})$	$tA_{o/2}$ (min)
 1	570	0.14	43	1160
 2	590	0.41	0.54	515
 3	432	0.29	0.11	460

Data were obtained with the Degraphot apparatus [12] and the kinetic and phototodegradation parameters were evaluated at a concentration of 5.10^{-6}M in anhydrous toluene at 25°C with a Schott filter WG 295. λ_{max} (O.F.) = visible absorption of the photomerocyanine (open form). $k\Delta$ = thermal bleaching rate constant. $tA_{o/2}$ = time necessary to reach, on irradiation, the half of initial absorbance.



Scheme 1. Photochromic equilibrium.

of their ‘colorability’. This parameter is related to the initial absorbance (A_o) measured at the λ_{max} of the open form immediately after irradiation by flash photolysis. The colorability is directly linked to the quantum yield of coloration [16] (ϕ col), the determination of which is particularly tedious.

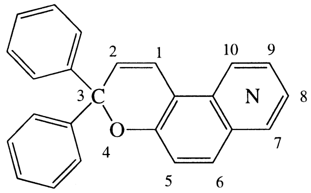
A_o = $\varepsilon_{MC} \cdot \phi_{col} \cdot k \cdot C_{CF}$,
ϵ_{MC} = molar absorptivity of photomerocyanine
C_{CF} = initial concentration of closed form
k = constant including photolysis conditions

A_o is experimentally determined on the spectrophotometric apparatus. So, we have evaluated the ‘colorability’ and the fatigue resistance of the different heteroannellated 2H-chromenes. The results of the photochemical investigations are reported in Tables 2–4 and are compared with those of 3,3-diphenyl-[3H]-naphtho[2,1-b]pyran **3**. All the cited compounds are photochromic at room temperature in toluene.

2.1. 2,2-diphenyl-[2H]-benzopyrans annellated with six membered azines nuclei.

The visible absorption maximum for the photomerocyanines of compounds **4**, **5**, **6** presents a slight bathochromic shift around 10 nm in toluene [13] and also a slight increase of the thermal bleaching rate constant [13] in comparison with the reference compound **3**. The introduction of a nitrogen atom in the 9-position (compound **5**) induces a significant increase of efficiency of coloration and resistance to fatigue. However, a

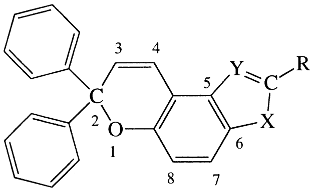
Table 2
Colorability and fatigue resistance of 2,2-diphenyl-[2H]benzopyrans annellated with an azine moiety



Compound No.	Position of N-atom	Colorability A_o	(λ_{max}, nm)	$t(A_{o/2})$ min	$f(t_{A_{o/2}})^a$
Reference **3**	–	0.29	(432)	460	1
4	7	0.27	(436)	900	1.95
5	9	0.46	(443)	600	1.30
6	7,9	0.37	(442)	1000	2.17

[a] $f(t_{A_{o/2}})$ = ratio pertaining to the resistance to fatigue with respect to the reference compound **3**. Spectrokinetic parameters measured on ‘Degraphot apparatus’. $C = 5 \times 10^{-6}$M; toluene, 25°C; Schott filter WG 295.

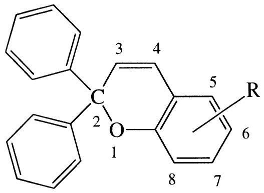
Table 3
Colorability and fatigue resistance of 2,2-diphenyl-[2H]-benzopyrans annellated with five-membered bi-hetero atomic cycles [13].



Compound No.	X	Y	R	λ_{max} OF (nm)	Colorability A_o	$t(A_{o/2})$ min	$f(t_{A_{o/2}})$
Reference **3**	–	–	–	432	0.29	460	1
7	O	N	Me	403 (513)	0.20 (0.11)	130	0.28
8	O	N	Et	420 (509)	0.18 (0.10)	65	0.14
9	N–Me	N	Me	419 (534)	0.21 (0.12	15	0.03
10	N	O	Me	409 (529)	0.12 (0.03)	125	0.27
11	S	N	Me	428 (510)	0.10 (0.07)	125	0.27

Identical experimental conditions as for Table 2.

Table 4
Colorability and fatigue resistance of 2,2-diphenyl-[2H]-benzopyrans annellated with five-membered monohetero atomic cycles [13]



Compound No.	R	λ_{max} OF (nm)	Colorability A_o	$t(A_{o/2})$ min	$f(t_{A_{o/2}})$
Reference **3**	5,6-benzo	432	0.29	460	1
12	5,6-pyrrolo	428 (520)	0.26 (0.12)	≈2	0.0043
13	5,6-indolino	436 (560)	0.30 (0.12)	90	0.19
14	5,6-benzofurano	424 (518)	0.30 (0.17)	45	0.09
15	6,7-benzofurano	427 (549)	0.46 (0.17)	≈5	0.01
16	5,6-cyclohexanefurano	420 (527)	0.40 (0.11)	35	0.075
17	5,6-cycloheptanefurano	421 (532)	0.39 (0.11)	35	0.075

Identical experimental conditions as for Table 2.

more marked improvement of fatigue resistance is achieved with the compound **4** (nitrogen atom in the 7-position). The 'quinazoline' compound **6** presents a good balance between photocoloration and photodegradation, and could be useful in applications pertinent to photochromic lenses. The main effects are very similar to those observed in the spiro[indoline-azinobenzoxazine] series [17].

2.2. 2.2-diphenyl-[2H]-benzopyrans annellated with five membered nuclei (Tables 3 and 4)

The compounds described in Tables 3 and 4 show a very important decrease of their fatigue resistance under UV-irradiation ($f\ t_{A_o}/2) \ll 1$), and more especially for the furano-derivatives which could be susceptible to be easily fragmented by photooxidation. The colorability mainly decreases for the 'benzoxazole', 'benzimidazole' and 'benzothiazole' derivatives (Table 3). Nevertheless all the five-membered systems present a broadening of the visible spectrum for the photomerocyanine, having a main band between 403 and 436 nm depending of the nature of heteroatoms, and a shoulder between 509 and 560 nm with a lower corresponding absorbance. These spectroscopic characteristics could be of interest for some applications in the field of ophthalmic lenses.

Two further comments can be made:

1. The Benzoannellation in positions 7,8 of the chromene ring produces a very strong stabilization of the corresponding photomerocyanine ($k\Delta \approx 2.10^{-3}s^{-1}$ in toluene [13]), the visible absorption is shifted to the higher wavelength (481 nm) but the fatigue resistance is considerably reduced ($t_{A_{o/2}} \sim 2$ min)
2. Concerning the basic skeleton (reference compound **3**), replacement of a phenyl group by a methyl group does not significantly modify the fatigue resistance ($t_{A_{o/2}} = 450$ min), but the presence of methyl groups does not favour the colorability, the visible absorption and the thermal bleaching constant [13].

3. Conclusion

In the [2H]-chromene series and particularly the 3,3-diphenyl-[3H]-naphtho[2,1-b]pyrans, the introduction of nitrogen atoms at the 7 and 9 positions (compounds **4**,**5**,**6**) is a good means for improving the fatigue resistance, the visible absorption spectrum being slightly modified. In contrast, [2H]-chromenes annellated by five-membered heterocycles are easily photodegradated in solution, but nevertheless these colorants show an interesting broadening of the visible spectrum of their photomerocyanines. This type of spectroscopic behaviour has also been previously noted in spiropyranic systems [15,18,19].

The phenyl nuclei on the sp^3 carbon have an important contribution on the conjugation and on the stabilization of the open form; their substitution by electron-donating or electron-withdrawing groups allows modulation of spectrokinetic parameters. The use of the specific 'Degraphot' apparatus [12] enables evaluation to be made of the photodegradation of new heteroannellated [2H]chromenes [15] and comparison of the different compounds in a same series or between two series. The results depend on the experimental conditions, but they are useful for the building of more performent new structures.

4. Experimental. Photodegradation and spectrokinetic measurements

4.1. Materials

The studied photochromic compounds, **1–16** were prepared according to literature procedures or where commercially available, viz.: **1** and **16** [10], **2**,**3** (Aldrich), **4–18**, **21** [13]. Photochromic measurements were performed at a standard concentration of 5×10^{-6}M in anhydrous toluene solutions (SDS, France) at 25°C (±0.1°C).

4.2. Equipment

Photodegradation and spectrokinetic measurements were obtained on a specially designed spectrophotometric apparatus named 'Degraphot', previously [12] described and depicted in Fig. 1. The Degraphot computer-controlled apparatus is devoted to spectrokinetic measurements, thus allowing structure–property relationships to be established between different series, or within a series of different photochromic compounds. The investigations are described in terms of fatigue resistance by the determination of the parameter $t_{A_{o/2}}$ (time in min necessary to reduce the initial colorability A_o to $A_o/2$).

The irradiation was realized in a continuous mode using a 250 W Xenon arc lamp (XBO Osram with a Schott WG 295 filter, which displays a spectrum close to the solar one. The experimental protocol used is depicted in the Fig. 1: after the initial measurements consecutive to a first flash, respectively the initial absorbance (A_o) and the thermal bleaching rate constant $k\Delta$ of the photochromic solution at the λ_{max}, the continuous degradation mode was characterised by monitoring

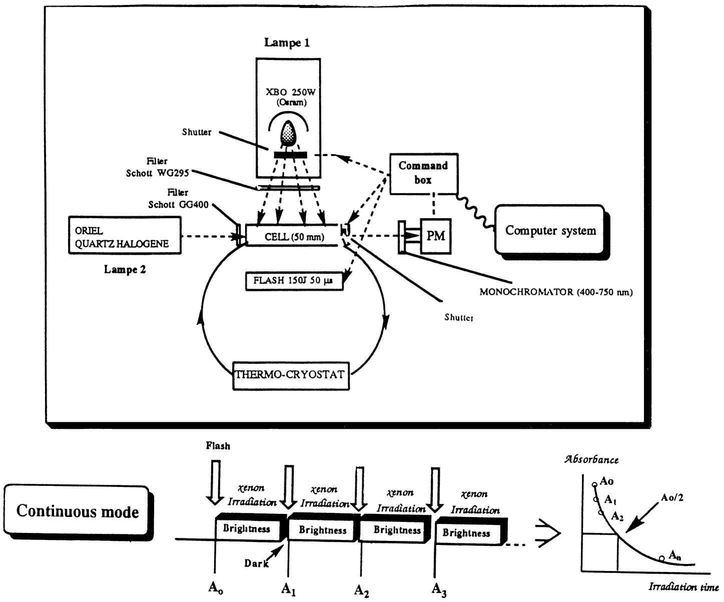


Fig. 1. The Degraphot apparatus.

the variation of absorbance with respect to the irradiation time. At the end of the experiment, the fatigue resistance time $t_{A_{0/2}}$ (time when $A_{0}/2$ is reached) was calculated by an interpolation method [12]. In the case of multiexponential signals, computation of the spectrokinetic parameters can be carried out by the well-known Marquardt non linear least squares method, or by the newly developed Padé–Laplace method.

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