

Effect of heteroaromatic annulation with five-membered rings on the photochromism of 2H-[1]-benzopyrans

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Abstract

Photochromic properties (colorability, UV–VIS spectra of photo-merocyanines, rate constant of thermal bleaching) of chromenes annulated with different five-membered azaheterocycles or with furan cycles were investigated under flash photolysis. All the compounds, i.e., the 7H-pyrano[2,3-g]benzazoles **4–6**, the 7H-pyrano[3,2-e]benzazoles **7–10**, the 7H-pyrano[3,2-e]indoles **11–12**, the 3H-pyrano[3,2-a]carbazoles **13**, the 8H-pyrano[2,3-e]indole **14** and the 3H-furano[3,2-f]chromenes **15–18** undergo reversible photochromic reaction at room temperature. They are compared with naphthopyranic parents **1–3**. Whatever the structure of the heteroaromatic moiety, the annulation of the benzopyrans leads to the splitting into two bands of the electronic absorption spectra of the photoinduced forms with a significant bathochromic shift, a feature of interest for variable optical absorption systems. Unfortunately, diaryl-substituted azolo-fused chromenes exhibit decreased colorabilities. Furofused benzopyrans are particularly interesting with respect to naphthopyran parents owing to the bathochromically shifted and broadened absorption spectra of photoinduced forms and slightly enhanced colorabilities. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Benzopyrans; Heteroaromatic compounds; Photochromism; Spectrokinetics

1. Introduction

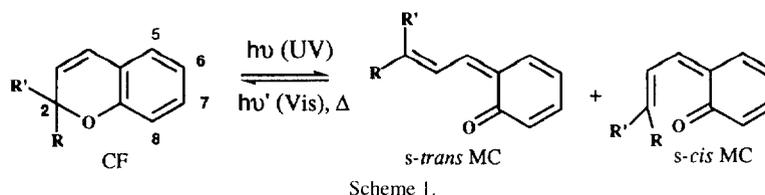
The number of investigations of the spectroscopic properties of photochromic materials has increased considerably in recent years as a result of potential commercial applications in several important areas, such as high-density optical storage, optical switchings, image processings and displays. Albeit numerous organic photochromic molecular systems or photoactive devices have been explored, and besides their intrinsic scientific interest, these systems belong to a small number of families [1–4]: diarylethenes, fulgides, spiropyrans and spiroxazines [5]. Up to now, among these photochromics, spiropyran derivatives are most widely used owing to their important color and dipole-moment changes. More recently, the 2H-[1]-benzopyrans (denoted here chromenes for convenience) and especially naphthopyrans have found applications related to materials undergoing variable optical absorption [6–9].

Exposure of chromenes either in liquid solution or in a rigid polymer matrix, to UV-A or sunlight results in a color

change due to the formation of a deeply colored 'photomero-cyanine' (MC) form that tends to revert back to its original colorless form (CF) either thermally or photochemically as depicted in Scheme 1 [10]. The photochromic reaction, i.e., a reversible ring-opening of the pyranic ring, features the dissociation of the C(sp³)–O bond producing several MC isomers.

The greatest advantage of photochromism is that it involves only a pure optical phenomenon; but, unfortunately, the materials involved in such processes do not display high stability to light. For an industrial application in the field of ophthalmic lenses, *heliochromic materials* (i.e., colored in the sun and bleached in the dark) must show highly efficient photoresponse for coloring in the near ultraviolet region, a low quantum yield for bleaching with visible light and efficient thermal fading at ambient temperatures. Furthermore, the photochromic compound must present chemical stability and indeed an interesting resistance toward light, i.e., a large number of cycles should be possible without significant degradation of the material. This last property is the key which will determine their potential applications. This is particularly

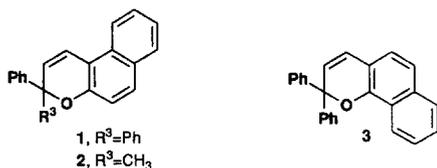
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the case for spiro[indoline-naphthoxazines] [11], which lead upon sunlight to blue or purple MCs. For full-color display applications, photochromics that are able to develop orange colors are wanted.

According to our knowledge, compounds filling all these criteria remain quite rare. For this reason, the chromenes have been considered as a good starting point owing to the absorption spectra of their open forms which display a yellow color. But, it is mainly required to introduce bulky substituents into the 2-position of pyran ring, and especially phenyl groups [6] in order to gain reasonable stability of the colored forms and to prevent rapid fatigue under photoexcitation [12].

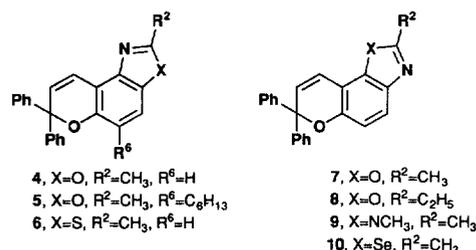
While synthetic and naturally occurring benzopyrans exhibit photochromic behavior only at *low temperature* [13], previous reports have shown that an extended conjugated π system, i.e., benzocondensation [6] or more efficiently azinoannulation [14], is a prerequisite to stabilize the open forms at *ambient temperature*. According to our observations, the photochromic ability can be tuned by varying the nature and the site of the annulation. So, we set out to introduce different five-membered rings at the 5,6-positions of 2H-benzopyran. In this paper, we investigate the role of this modification with respect to photochromic properties through the study of media and temperature effects. The direct comparison with previously described naphthopyrans 1–3 [6,15] is also established.



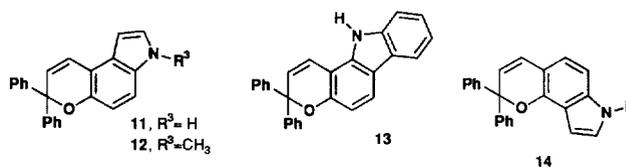
2. Materials

Different synthetic approaches to such heteroannulated chromenes, which seem to have no limitations in terms of chemical structure, have been previously reported in which corresponding heterocyclic phenols are used as key intermediates [16–18].

2.1. Azaheterocyclic compounds

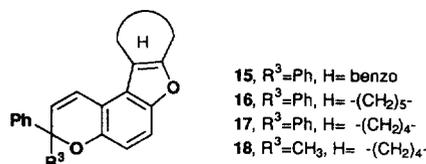


The different nitrogen-containing five-membered fused aromatic heterocycles, i.e., benzoxazole, benzimidazole, benzothiazole, benzoselenazole, indole, carbazole derivatives **4–14**, have been synthesized by an organotitanium phenoxides-mediated condensation on β -phenylcinnamaldehyde [17].



2.2. Furofused compounds

The benzofuran derivatives **15–18** have been prepared according to the widely employed thermal Claisen rearrangement of prop-2-ynyl ethers intermediately formed from adequately substituted propargylic alcohols and heterocyclic phenols [19]. But it has been shown that the obtention of the desired molecules is not always so straightforward. Albeit we were mainly interested in gem-diphenyl-substituted derivatives, we have also synthesized a methyl, phenyl-substituted derivative **18** according to this procedure.

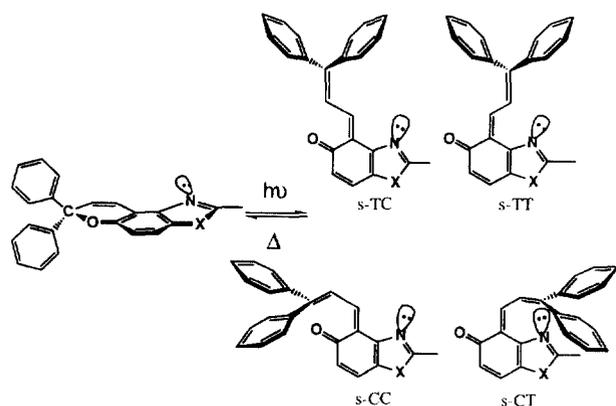


3. Photochromic properties

The heterolytic scission of the carbon sp^3 -oxygen bond upon activation by UV-A light or by sunlight, followed by extremely fast (i.e., 10^9 – 10^{12} s $^{-1}$) bond rotations produces the so-called 'photo-merocyanines' (MC) [20] which may have different electronic structures and geometries. For the diphenyl-substituted chromenes, the distribution of MC isomers consists of one stereoisomer of *cisoid* configuration *s*-CC (*s-cis, cis*) directly formed after the breaking of the C–O bond and of one *cisoid* *s*-CT (*s-cis, trans*) and two *transoid* configurations *s*-TC and *s*-TT (*s-trans, cis* and *s-trans, trans*, respectively) obtained by isomerization as exemplified for 7,7-diphenyl-7H-pyrano[3,2-*e*]benzazoles **4–7** (Scheme 2).

The *transoid* *s*-TT and *s*-TC conformations are assumed to be the preferred, the non-bonding interactions being minimized (H.P. Pommier, J.L. Pozzo, A. Samat, R. Guglielmetti, unpublished results.). Obviously for the *cisoid* isomers, the polyenic system could not be planar because of strong steric hindrance caused by the phenyl groups. The most thermally stable stereoisomers are considered to be responsible for the slowest rate of back thermal reaction.

It has been shown previously [21] that the photochromic behaviour can be properly characterized by the four major following 'spectrokinetic' parameters: the maxima wavelengths of the colored form (photo-merocyanine MC), the thermal bleaching rate, the 'colorability' and the resistance toward photodegradation. The photochromic properties for azole derivatives **4–14** and furo-fused **15–18** are collected in Table 1 along with those for naphthopyrans **1–3** considered as references. The photodeterioration of photochromics are still investigated in this series both in solution or in polymer matrix. Related results will be reported in due course [22]. The flashgun that irradiates the cell containing the photochromics, covers all the UV region and the actinic wavelength for all compounds were found near 340 nm, so assuming that the formation of MCs takes place under similar conditions, the comparison of the efficiency of photocoloration could be established.



Scheme 2. Photochromic interconversion between the closed form (CF) of 7,7-diphenyl-7H-pyrano[3,3-*e*] benzazole **4–7** and four possible isomers of the corresponding photomerocyanines (Mcs, *s*-*Trans* and *s*-*Cis*).

3.1. Experimental

The spectra of the photo-merocyanines in different solvents were determined using flash photolysis (flashes of ca. 60 J, duration of ca. 50 μ s) coupled to a Warner–Swasey fast scanning spectrophotometer capable of recording the whole transient absorption spectrum in the VIS region in 1.25 ms in a 10 cm quartz cell [23]. The kinetics of thermal bleaching of the colored forms k_{Δ} were investigated following the fading of color at the maximum absorption. The 'colorability' which is directly connected to the molar absorptivity of colored species and to the quantum yield of coloration [24] is evaluated by monitoring the absorbance A_0 at λ_{\max} immediately after the flashgun was fired.

$A_0 = \epsilon_{\text{MC}} \Phi_{\text{col}} k C_{\text{CF}}$ (for low concentrations); ϵ_{MC} = molar absorptivity of photo-merocyanines; Φ_{col} = quantum yield of photocoloration; k = constant including photolysis conditions; and C_{CF} = initial concentration of the closed form.

Photochromic measurements were performed in solutions (2.5×10^{-5} mol dm $^{-3}$) in dried spectrophotometric grade toluene (UCB) or ethanol (Carlo Erba, ACS quality) from -20°C to 75°C and from -20°C to 50°C , respectively.

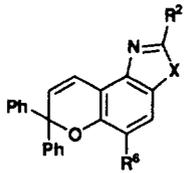
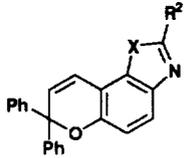
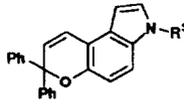
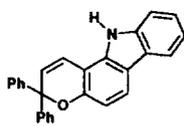
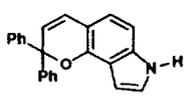
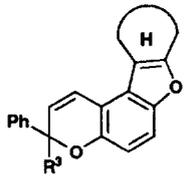
3.2. Results and discussion

We have previously reported the synthesis of compounds representing different types (denoted **I–IV** and **VI** for convenience) of heteroannulation located on the 5,6-positions of the chromenic moiety [14,17] and preliminary results concerning the photochromic behavior of some furofused derivatives [14], i.e., compounds **15–17** under different conditions. In this article, photochromic properties were investigated under flash photolysis in order to propose a structure/activity relationship with the annulation pattern. The absorption data in toluene solution for **1–19** are summarized in Table 1.

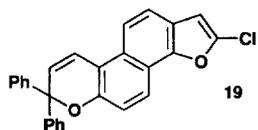
The visible absorption spectra of the photo-merocyanines obtained by U.V. irradiation of five-membered ring fused benzopyrans display two broad bands. This is markedly different from those of naphthopyran parent. We observe that, effectively, whatever the structure of the heterocycle, the annulation of the diphenyl-benzopyrans leads to the splitting into two bands of the electronic spectra with a significant bathochromic shift as shown for toluene solution in Fig. 1. One is observed near 420 nm and the other near 520 nm. Corresponding 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyran **1** is given for comparison and exhibits a single absorption band culminating at 432 nm under the same experimental conditions. Because the effects observed in the furo-fused series, for benzoannulated compound **15** or compounds having a cycloalkyl moiety **16–17** are very similar, the marked broadening of visible absorption spectra should be ascribed to the five-membered ring annulated directly on the benzopyran part, rather than an extension of the conjugated system. The photochromic parameters of furo-fused naphthopyran derivative **19** substantiate this assumption, as its spectrum is very

Table 1

Spectrokinetic properties (λ_{\max} (λ_1, λ_2)), colorability (A_{01}, A_{02}) and bleaching rate (k_{Δ}) of photo-merocyanines of naphthopyrans and heterofused benzopyrans in toluene solutions ($2.5 \cdot 10^{-5}$ mol dm $^{-3}$) at 25°C

Photochromics	Type		λ_1 (nm)	A_{01}	λ_2 (nm)	A_{02}	k_{Δ} (s $^{-1}$)
Naphthopyrans		1	399	0.48	—	—	2.3/0.2
		2	432	0.84	—	—	0.09
		3	403	1.08	481	1.62	0.002
	I	4	409	0.30	529	0.14	0.22
		5	410	0.25	527	0.13	0.19
		6	428	0.17	510	0.14	0.25
	II	7	423	0.44	513	0.24	0.25
		8	420	0.41	509	0.22	0.27
		9	419	0.49	534	0.27	0.05
		10	424	0.10	530	0.07	0.30
	III	11	428	0.70	520	0.26	< 10 $^{-4}$
		12	437	0.81	531	0.33	< 10 $^{-4}$
	IV	13	436	0.99	560	0.24	0.15
	V	14	399	0.87	523	0.19	< 10 $^{-4}$
	VI	15	424	1.02	518	0.47	0.21
		16	421	0.94	532	0.24	0.04
		17	420	1.08	527	0.23	0.04
		18	398	0.55	509	0.13	30/1
		19	427	1.37	—	—	0.32

close to that of parent compound **1**. As a consequence, all photo-merocyanines issued from the desired heteroaromatic compounds cover a much larger range of wavelengths.



For diphenylchromenes, thermal bleaching has been found to be a relatively slow process and the rate constants (0.1–

0.5 s $^{-1}$) do not vary in a great extent. The ring closure reaction was found to present only one kinetics in the temperature range explored (from -20° to 75°C) and are very similar to those of corresponding naphthopyrans except for the indole derivatives (vide infra). As mentioned during the study of naphthopyran [15], extension of conjugation is also responsible for a slight stabilization of photogenerated forms.

Surprisingly when the geometry of the azolo-annulation onto the chromene moiety was reversed, i.e., from type **I** to type **II** (Table 1), the absorption wavelengths of the colored forms were changed. Both bands are shifted to longer wave-

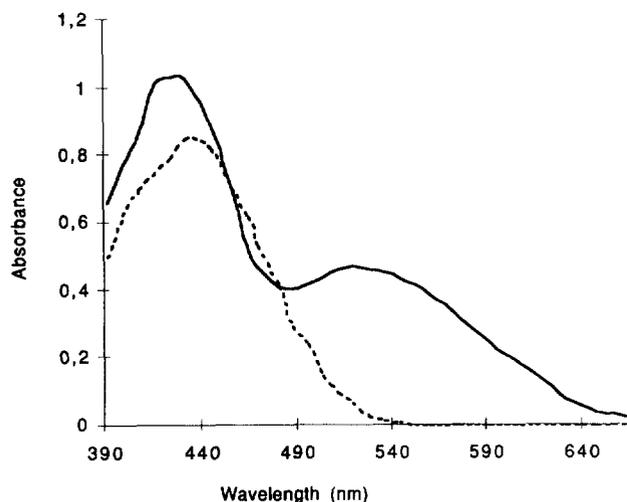


Fig. 1. Electronic absorption spectra of the colored forms of chromenes **15** (full line) and **2** (dashed line) in toluene at ambient temperature.

lengths. Another significant effect is observed on the colorabilities indicating that the nitrogen atom sp^2 connected on the 6-position of chromenic moiety plays an important role toward photochromic reaction.

The low colorabilities exhibited by both compounds **6** and **10** might be explained by the heavy atom effect (sulfur and selenium are involved), which tends to decrease the photo-response. Upon irradiation with UV light, compound **13** (type **IV**) solution changes from colorless to red. This bathochromic effect is also observed to a lesser extent for benzofuran derivatives **15–17** (type **VI**). For these compounds, a more important contribution of the second band at higher wavelengths seems to be responsible for a such behavior.

The results show that the absorption range of this class of photochromic chromenes can be tuned according to the nature of the heteroaromatic fused on the benzopyran subunit, from yellow to red. New prospects for applications are opened, since those compounds are well suited to replace the well-known spiropyrans [25]. Indeed, in the latter series the compounds having the best photochromic properties (bearing a 6-nitro group) undergo very easily photodegradation [26].

Without photoirradiation, even diluted solutions of **11** ($c = 10^{-5} \text{ mol dm}^{-3}$) showed a low intensity absorption band in the visible region denoting that the opened form was present prior to irradiation. For all other benzopyranic compounds, the colored band was hardly detectable even in a saturated solution of a polar solvent at 320 K. Temperature and solvent polarity are responsible for increased colorability [27]. The 7,7-diphenyl-[7H]-pyrano[3,2-e]indole **14** is more polarizable and the cleavage of the C–O bond takes place simply by solvation. This fact could also explain the great gain of stability observed for the photomerocyanine ($k_d < 10^{-4} \text{ s}^{-1}$). Despite NMR spectroscopy is a suitable technique to investigate the geometry and the electronic structure of opened form, the weak concentration of this form prevented us to elucidate its structure and so to evaluate, coupled with electronic spectroscopy, the corresponding

molar absorptivities. We verified that the MCs arising from solvolysis are spectroscopically similar to those generated by photolysis. The spectrokinetic parameters for the corresponding methylated compound **12** showed that this important stabilization could not be ascribed to the potential hydrogen-bonding available for the indole derivative **11**.

3.2.1. Substituent and annulation effects

As previously reported for naphthopyrans [6,15], the replacement of a phenyl group by a methyl group on C- sp^3 causes an important *hypsochromic* shift which is noticeable for each band (-23 and -18 nm, respectively). Indeed the *second phenyl* group on C- sp^3 enhances the electronic conjugation, provides further stabilization and induces an increase of molar absorptivities and colorabilities (two fold enlargement; see **17** and **18**, Table 1) of the open forms. For the monoaryl-substituted compound **18**, the two rates observed for ring closure might be explained by the presence of two slowly interconverting sets of isomers.

We have also previously prepared compound representing an other type of annulation, i.e., involving the C(7)–C(8) positions. The photo-merocyanines of 8,8-diphenyl-[8H]-pyrano[2,3-e]indole **14** (type **V**) obtained after photoirradiation are also characterized by a visible absorption spectrum displaying two maxima. A global bathochromic shift was observed when compared to the parameters concerning the corresponding naphthopyran **3** for which a weak peak is observed at 403 nm and a large band is centered at 481 nm in toluene solution. If one considers their corresponding photo-merocyanines, the non-bonding interaction between an ethylenic proton and a chromenic proton is less efficient than for corresponding 5,6-annulated derivatives so this kind of annulation was reported to lead to a drastic stabilization of the open forms [6], but in the case of indole derivatives no additional stabilization of open forms could be quantitatively measured. Although this compound seems interesting as an orange color-developing substance its bleaching rate ($k_d = 10^{-4} \text{ s}^{-1}$) is detrimental for industrial development since one expects a further rate drop when the compound is incorporated in a solid matrix.

3.2.2. Solvent effect

The UV–VIS spectral data of the open form of the chromenes in *ethanol* are collected in Table 2 and some data in *toluene* issued from Table 1 are mentioned for comparison. The classification between chromenes according to photochromic parameters appears very similar to those observed in toluene solutions. A *positive* solvatochromism is observed for all heliochromic chromenes. Indeed as the solvent polarity is increased, a bathochromic shift is observed which depends largely on the change in dipolar characteristics between ground and excited states [28]. This observation is indicative of a weakly polar ground state, in keeping with a quinoidic structure. This is in agreement with previous work in the benzopyran series [5,20].

Table 2

Compared spectrokinetic and thermodynamic characteristics both in toluene and ethanol (reported in bold) solutions for some heterofused benzopyrans ($2.5 \cdot 10^{-5} \text{ mol dm}^{-3}$) at 25°C

Photochromics	λ_1 (nm)	A_{01}	k_3 (s^{-1})	E_a (kcal mol^{-1})
4	409	0.30	0.22	17.9
	417	0.54	0.56	16.8
7	423	0.44	0.25	15.9
	427	0.61	0.46	14.5
12	428	0.70	$< 10^{-4}$	—
	437	0.81	$< 10^{-4}$	—
15	424	1.02	0.21	14.6
	427	1.11	0.28	14.1
17	420	1.08	0.04	15.2
	425	1.12	0.04	14.9

In a more polar medium, thermal bleaching rates are markedly accelerated involving a destabilization of the photoinduced forms. Taken into account the MC isomers distribution and that toluene promotes intramolecular H-bond [28], the photomerocyanines obtained after the flashgun and subsequent isomerization should be more stabilized in apolar medium. The striking feature has been found to be the strong enhancement of colorability manifested by all chromenic compounds when going from toluene to ethanol.

Upon switching off the UV light, the metastable MCs most often revert to the pyranic form following a first order kinetics. The least-square fittings values (Arrhenius plot) at different temperatures (from -20°C to 75°C for toluene and from -20°C to 50°C for ethanol, respectively) allow us to estimate the activation energy for the bleaching reaction E_a (Table 2) [25]. Because of the complexity of the process involved in the reformation of chromenes, these data should be considered as apparent activation energies; they do not seem to exhibit any relationship either with the structure of the chromenic compound, or with the medium polarity. One can notice that corresponding activation energies derived for related spiropyran [29] and naphthoxazines [30] have been found to be in the same range.

4. Experimental procedure for the preparation of 3-methyl-3-phenyl-8,9-tetramethylene-[3H]-furan[3,2-f]chromene (18)

Commercially available 3-phenylbutyn-3-ol (60 mmol) and 5-hydroxy-2,3-tetramethylenebenzofuran in slight excess (66 mmol), which was prepared as described earlier [31], were dissolved in dry toluene (100 ml). Under an atmosphere of nitrogen, a catalytic amount of APTS was added and then the solution was boiled for 4 h. The mixture was then cooled, washed with 10% sodium hydroxide. The organic layer was then dried over magnesium sulfate, filtered and finally concentrated. The crude product was purified by flash chromatography on silica gel using pentane as eluent to provide **18** as a crystalline colorless solid in 55% yield, (m.p.,

173°C (from hexane)). $^1\text{H NMR}$ (250 MHz) δ : 1.79 (3H, s, CH_3), 1.86 (4H, m, H-2'', 3''), 2.67 (2H, m, H-1''), 2.77 (2H, m, H-4''), 6.09 (1H, d, $J=9.9\text{Hz}$, H-2), 6.72 (1H, d, $J=8.6\text{Hz}$, H-5), 6.84 (1H, d, $J=9.9\text{Hz}$, H-1), 7.04 (1H, d, $J=8.6\text{Hz}$, H-6), 7.21 (1H, m, H4'), 7.27 (2H, m, H-3'), 7.39 (2H, m, H-2'). $^{13}\text{C NMR}$ (62.5 MHz, decoupled) δ : 22.6 (C-2'', 3''), 23.0 (C-1''), 23.7 (C-4''), 29.8 (CH_3), 79.9 (C-3), 109.7 (C-6), 111.7 (C-5), 113.6 (C-9), 115.8 (C-1a), 120.1 (C-1), 125.6 (C-9a), 126.9 (C-2'), 127.3 (C-4'), 128.2 (C-3'), 128.7 (C-2), 145.2 (C-1'), 147.2 (C-6a), 148.6 (C-4a), 156.2 (C-8a). UV λ_{max} (EtOH) nm (log ϵ): 210(4.41), 251(4.13), 306(4.19), 334(3.49), 345(3.17) nm. Analysis: calculated for $\text{C}_{22}\text{H}_{20}\text{O}_2$ C, 83.52; H, 6.37; found: C, 83.40; H, 6.41.

5. Conclusion

Despite the limited number of compounds investigated, some interesting features emerge from the study of *heteroannulation of 2H[1]-benzopyrans with 5-membered rings*: variation of the nature of the heterocyclic subunit allows a *fine tuning* of the *spectrokinetic parameters*; particularly remarkable is the presence of two markedly red-shifted broad bands in the electronic absorption spectra of the photomerocyanine forms, thus displaying a yellow to red scale of colors. The properties make *azolofused* and especially *furofused* derivatives useful for photochromic applications.

Acknowledgements

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