56. Synthesis and Photochromic Behaviour of Naphthopyrans, Pyranoquinolines, Pyranoquinazolines and Pyranoquinoxalines

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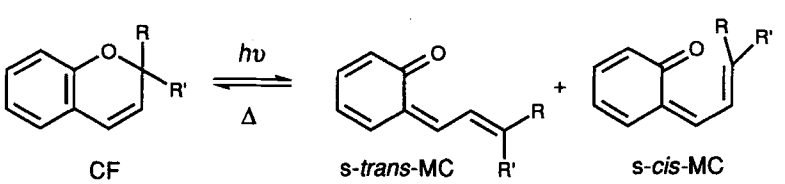
New chromenes annulated with different six-membered azaheterocycles were prepared, *i.e.*, the 3*H*-pyrano[3,2-*f*]quinolines **9**/**10** and **14**, the 8*H*-pyrano[2,3-*h*]isoquinoline **11**, the 8*H*-pyrano[3,2-*f*]quinazoline **12**, the 8*H*-pyrano[3,2-*f*]quinoxaline **13**, and the 2*H*-pyrano[2,3-*f*]isoquinoline **15**. The synthesis was achieved using conveniently substituted α,β-unsaturated aldehydes and organotitanium intermediates arising from azaheterocyclic phenols. Their photochromic behaviour (photocolouration yield, UV/VIS spectrum of photomerocyanines, rate constant of thermal bleaching) were studied besides those of corresponding naphthopyrans. The heterocycle effect and the role of substituents in the pyran moiety were investigated quantitatively through the study of the photochromic properties and the solvent effects. Diaryl-substituted azino-fused chromenes, especially isoquinoline derivatives, exhibit increased colourabilities and bathochromically shifted spectra for photomerocyanines which open up new prospects for photochromic applications.

Introduction. – The 2*H*-1-benzopyrans (2*H*-chromenes) are an important class of oxygenated heterocyclic compounds [1] to which research has been devoted in connection with the biological activities [2] [3] of naturally occurring representatives. Furthermore, upon irradiation, they have been shown to convert to products having spectra similar to those of merocyanine dyes [4]. The photochromic property is based on the reversible reaction of the colourless pyran form (closed form, CF) to the coloured merocyanine(s) (MC) when liquid solutions or polymer matrices containing CF are exposed to UV light (*Scheme 1*). This thermally reversible colour and structural change has implications in a great number of practical applications including data storage and retrieval, optical filters, displays, sensor protection and waveguides [5].

Scheme 1. *Photochromic Equilibrium for* 2H-*Chromenes*



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During the last decades, 2*H*-chromenes were not considered as interesting photochromic compounds for applications, and intensive research was preferably devoted to their well-known spiroheteroanalogs (spiropyrans) [6]. Indeed, *Becker* and coworkers established that naturally occurring or synthetic chromenes showed photochromic behaviour only at low temperature [7] [8]. In fact, the research interests in the field of chromenes came into sight few years ago, due to industrial applications related to materials undergoing variable optical transmission. Although a great number of photochromic compounds have been reported [9], the compounds which turn yellow or orange upon UV irradiation are quite rare. Spironaphthoxazines substituted by a pyrazine ring [10] and dithienylethenes [11] are such few examples. When photochromic substances were applied to full colour display, it is strongly desired to develop new yellow-producing compounds.

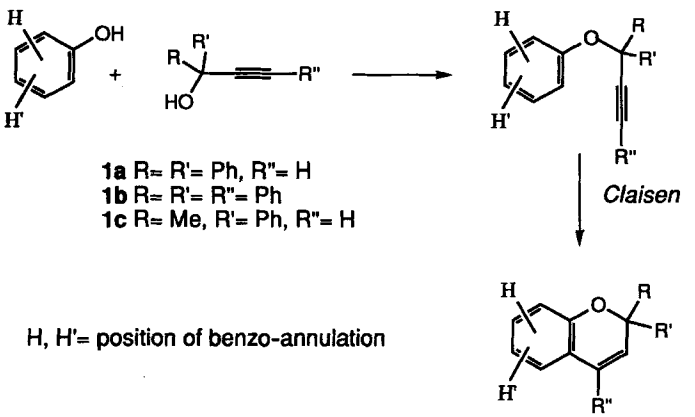
Furthermore, photochromic compounds must satisfy the following performance criteria: a minimal fatigue or chemical instability upon repeated cycling or continuous irradiation, a highly efficient photoresponse in the near-UV, a relatively fast thermal fading rate at room temperature, and a minimal quantum yield for bleaching with VIS light thus preserving the colour. Although a relatively large number of benzopyrans has been patented, these requirements have initiated the synthesis of several structurally modified chromenes. An improvement of the photochromic properties was obtained mainly by using benzo-annulated chromenes, namely the naphthopyrans. Moreover, several studies have undoubtedly shown that the alkyl groups at the sp^3-C-atoms should be replaced by a spiroadamantane moiety [12] [13], a cyclopropyl group [14] [15], or two aryl substituents to manifest photochromic behaviour at room temperature [16] [17] and to prevent rapid fatigue under photoexcitation [18].

During our study in the field of photoresponsive systems, we reasoned that 2,2-diaryl-2*H*-chromenes would be a good parent system for such species. Among structural modifications which could be carried out on chromenes, heteroannulation represents an interesting factor which could eventually promote changes of the photochromic properties. We report here the synthesis of azino-fused chromene derivatives, along with their physico- and photochemical properties. Within this series of chromenes, the influence of the fusion site and the substitution pattern on the photochromic properties was studied. The direct comparison with previously described [7] [9] or new naphthopyrans was achieved. The solvent effect on the photochromic properties was also quantified.

Synthesis. – The 2,2-disubstituted 2*H*-chromenes and related compounds could be obtained from readily available heterocyclic phenol or naphthol precursors. Such a synthetic approach, using starting materials with the heterocyclic ring already incorporated, is a multistep sequence involving the *Kabbe* synthesis [20], followed by reduction to a chromanol and dehydration; however, this approach led to very low yields in the case of 2,2-diaryl-2*H*-chromene analogues. Alternatively, thermal cyclization of propargyl aryl ethers, first reported by *Iwai* and *Ide* [21], affords chromenes directly, presumably *via* a *Claisen*-like [3,3]-sigmatropic rearrangement followed by a [1,5]-sigmatropic shift and electrocylization (*cf. Scheme 2*) [22]. The starting ethers could be obtained *via* a *Williamson* synthesis. However, in our case, the preparation of naphthopyrans according to *Scheme 2*, *i.e.*, **4**–**8** (see *Fig. 1*), was achieved by a one-pot method, starting from a suitable phenol in an inert solvent and 1,1-diphenylpropyn-1-ol (**1a**), 1,1,3-triphenyl-

propyn-1-ol (**1b**) or 2-phenylbut-3-yn-2-ol (**1c**) under acidic catalysis (see *Method A* in *Table 1*). After 2–6 h, the crude products were purified by flash chromatography and then fully characterized by UV/VIS and ^{1}H- and ^{13}C-NMR spectroscopy. This synthetic approach to chromenes (*Method A*) has been reported to be broadly applicable [19]. Nevertheless, it failed in the case of azino-fused chromenes despite varying the acidic conditions (toluene-4-sulfonic acid (TsOH), sulfuric acid, acidic alumina, *etc.*) and the stoichiometry of the reagents.

Scheme 2. *Synthesis of Chromenes* via Claisen *Rearrangement*[a])



[a]) Used for the synthesis of **4**–**8** (see *Fig. 1*) according to *Method A*.

Table 1. *Reaction Conditions and Yield for Benzo-Fused and Azino-Fused 2H-Chromenes*

Chromenes	Starting compound	*Method*[a])	Reaction time [h]	Yield [%]
3	**2b**	*B*	5	39
4	**1c**	*A*	2.5	43
5	**1a**	*A*	2	62
6	**1b**	*A*	2	89
7	**1a**	*A*	6	21
	2a	*B*	4	36
8	**1a**	*A*	3	44
9	**2a**	*B*	4	66
10	**2a**	*B*	4	59
11	**2a**	*B*	3.5	64
12	**2a**	*B*	3.5	45
13	**2a**	*B*	7	17
14	**2b**	*B*	5	47
15	**2a**	*B*	7	14

[a]) *Method A* involves a *Claisen* rearrangement (*Scheme 2*), and *Method B* is based on organotitanium reagents (*Scheme 3*).

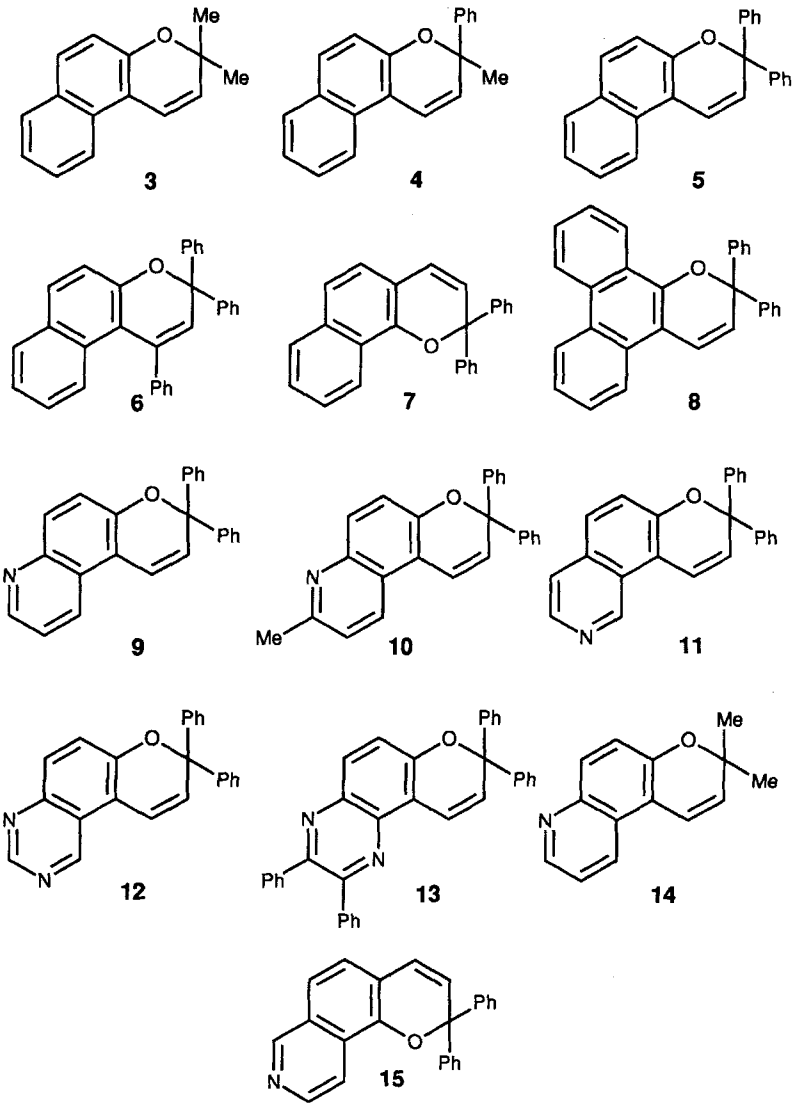
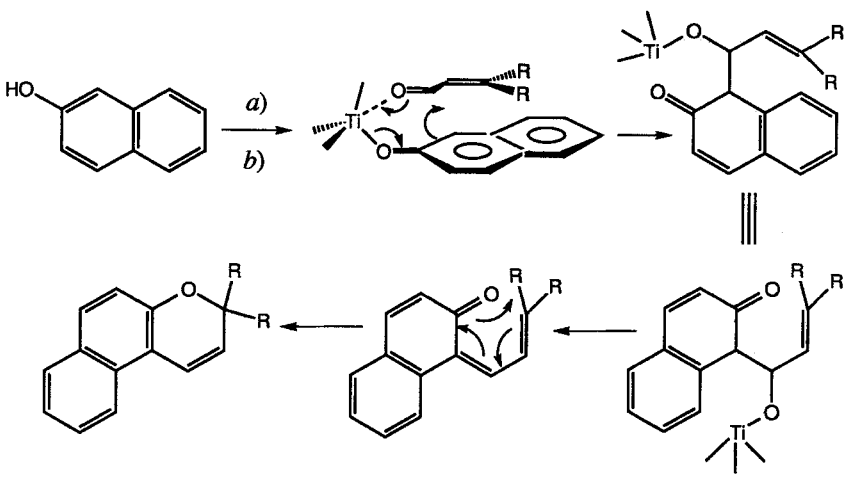


Fig. 1. *Synthesized and studied naphthopyrans and azino-fused chromenes*

Alternatively, the condensation of α,β-unsaturated carbonyl compounds with phenols has received much attention as a route to chromenes [1] [23] (*cf. Scheme 3*); it involves the titanium(IV) salt of the phenol obtained with $Ti(OEt)_4$ on azeotropic distillation of formed EtOH. ω-Vinyl-*o*-quinomethanes are generated *in situ* but are never directly observed, presumably due to their easy cyclization to benzopyrans. We used naphthols and heterocyclic phenols and added to their Ti^{IV} salts in toluene β-phenylcinnamaldehyde (**2a**) or 3-methylbut-2-enal (**2b**); the condensations were achieved after 3–5 h reflux yielding **3**, **7** and **9**–**13** (see *Method B* in *Table 1*). The new

compounds were purified by flash chromatography and recrystallization from appropriate solvents and fully characterized by ^{1}H- and ^{13}C-NMR and UV/VIS spectroscopy. As for similar compounds [24], the best yields were found using stoichiometric amounts of β-phenylcinnamaldehyde, heterocyclic phenol, and $Ti(OEt)_4$. Among the heterocyclic phenols submitted to cyclization, quinolin-8-ol did not lead to the desired compound. This could be explained by its well-known ability to complex metal salts [25], especially under basic conditions, preventing the condensation to compete. *Table 1* clearly shows that the chemical yield is directly dependent on the structure of the starting phenol. It is estimated that the cyclization efficiency is strictly related to the electronic density at the attacked *ortho* position (see *Table 1*). All phenols bearing the OH group at a β position, *i.e.*, leading to **3** and **9**–**14**, give rise to quite good yields except for 2,3-diphenylquinoxalin-6-ol (→ **13**) which could be explained by its extremely poor solubility. The organotitanium-mediated condensation (*Method B*) is also preferable for the synthesis of all kind of *gem*-dimethylbenzopyrans including naphthopyran, using 3-methylbut-2-enal (**2b**) as aldehyde. In fact, this synthetic approach prevents the formation of an appreciable amount of by-products arising from the intermediate propargylic cation involved in the *Claisen* rearrangement (*Method A*).

Scheme 3. *Synthesis of Chromenes* via *Condensation of α,β-Unsaturated Aldehydes with Phenols*[a])



a) $Ti(OEt)_4$. *b*) $R_2C{=}C{-}CHO$: R = Ph for **2a** and R = Me for **2b**.

[a]) Used for the synthesis of **3**, **7** and **9**–**15** (see *Fig. 1*) according to *Method B*.

^{1}H-NMR Spectra of 2,2-diphenyl-2*H*-chromenes display characteristic signals for the H-atoms of the pyran ring, at 6.35 and 7.35 ppm (J = 10 Hz) for compounds **9**–**13** and at 6.30 and 6.75 ppm (J = 10 Hz) for the chromene derivative **15** annulated at the 7,8 position. The ^{13}C-NMR signal of the quaternary C-atom (*ca.* 83 ppm) bearing the two Ph groups is also characteristic for such a moiety. An upfield shift due to the presence of Me groups is observed for **3** and **14** as well as **4** (*ca.* 76 and 78.8 ppm, resp.).

Photochromic Properties. – *General.* Upon activation by UV light or by sunlight, 2*H*-chromenes (closed form, CF) are known to undergo a reversible scission of the C(sp^3)–O bond of the pyran ring. This is followed by extremely fast (*i.e.*, 10^{-9} to 10^{-12} s)

bond rearrangements resulting in the formation of the chromophoric species or photomerocyanines (MCs) that are responsible for the photogenerated colours.

Photochromic behaviour is quantified by three main parameters, named spectrokinetic parameters, and the compounds are compared according to maxima wavelengths of the coloured form (*i.e.*, MC), thermal bleaching rate, and the 'colourability'. The spectra of the MCs in different solvents were determined in a 10-cm quartz cell, using flash photolysis (flashes of *ca.* 60 J, duration of *ca.* 50 μs) coupled to a *Warner-Swasey* fast-scanning spectrometer capable of recording the whole transient absorption spectrum in the VIS region in 1.25 ms [26]. The kinetics of thermal bleaching of the MCs (ring closure) k_Δ, were investigated following the fading of colour at the maximum absorption. The 'colourability' was evaluated by monitoring the absorbance A_O at λ_{max} immediately after the flash. The absorption maxima of the closed-ring form and thus the actinic wavelengths were dependent on the substitution pattern. Taking into account that the flash gun irradiates the whole UV region, we assume that the MCs are formed under similar conditions. The colourability parameter (A_o) is directly connected to the quantum yield of colouration [27] and thus allows us to compare the efficiency of colouration of different compounds under defined experimental conditions.

$A_o = \varepsilon_{MC} \cdot \Phi_{col.} \cdot k \cdot c_{CF}$ (for low concentrations)
ε_{MC} = molar absorptivity of photomerocyanines
c_{CF} = initial concentration of the closed form
k = constant including photolysis conditions
$\Phi_{col.}$ = quantum yield of photocolouration

All chromenes **3**–**15**, except **6**, exhibit photochromic behaviour at room temperature in toluene. The spectrokinetic parameters (A_o, k_Δ and λ_{max}) are reported in *Table 2* for naphthopyran derivatives and in *Table 3* for azino-fused ones. They are discussed below according to the substitution pattern, annulation position, fused heterocycle, and temperature and polarity of the medium.

Substituent Effect. Replacement of a Me group by a Ph group at the sp^3-C-atom of the closed form causes an important bathochromic shift which is additional for each replaced group (+ 23 and + 33 nm (in toluene) for **4** and **5**, resp.). The increase of conjugation on the photogenerated MCs derived from compounds **3**–**5** seems to play an important role in the bathochromic shift. These absorption characteristics (λ_{max}) clearly make the 2,2-diphenyl-substituted naphthopyrans potentially suitable for the use in photochromic lenses according to achievable colour [19].

Table 2. *Spectrokinetic Properties of Naphthopyrans in Toluene Solutions* ($2.5 \cdot 10^{-5}$ mol dm^{-3}) *at 25°*

	λ_1 [nm]	A_1	λ_2 [nm]	A_2	k_Δ [s^{-1}]
3	376	0.45			13, *0.15*
4	399	0.48			2.3, 0.2
5	432	0.84			0.09
7	403	1.08	*481*	1.62	0.002
8	425	0.98[a])			<0.001

[a]) Coloured solution, this value represents additional 'colourability' due to the flash.

Table 3. *Spectrokinetic Properties of Azino-Fused 2H-Chromene and References in Toluene Solutions* ($2.5 \cdot 10^{-5}$ mol dm^{-3}) *at 25°*

	λ_1 [nm]	A_1	λ_2 [nm]	A_2	k_Δ [s^{-1}]
5	432	0.84			0.09
9	436	0.82			0.13
10	438	0.85			0.10
11	443	1.29			0.29
12	442	1.10			0.48
13	471	0.93			0.10
3	376	0.45			13, 0.15
14	378	0.41			17, 0.19
7	403	1.08	481	1.62	0.002
15	405	0.63[a])	484	1.27[a])	0.005

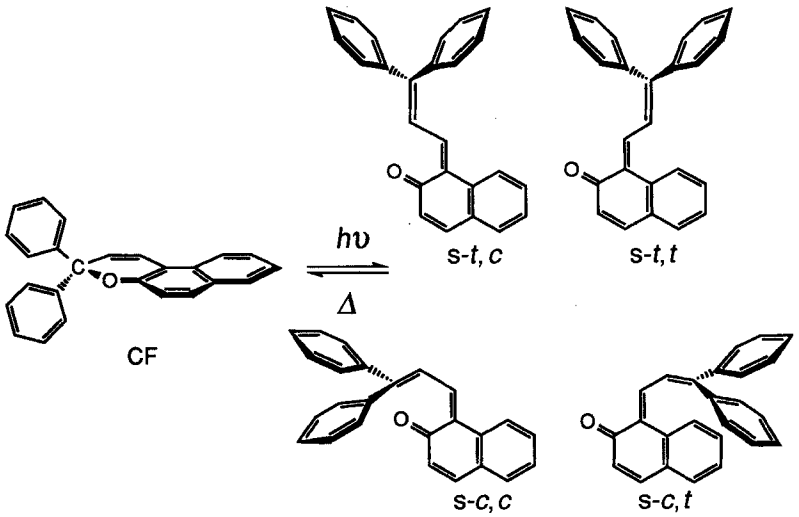
[a]) Coloured solutions, these values represent the additional 'colourability' due to the flash.

The effect of phenyl substituents on thermal bleaching rates is more important, as a significant stabilization of the opened form is observed. It seems likely that the increased stability of the MCs is due to the extension of the π system due to the Ph moieties. According to our knowledge, the two kinetics (k_Δ) are interpreted as modified ratios between the different stereoisomers which could be easily understood when Ph groups are involved. According to preliminary results [28], four isomers can exist, namely the s-*t*,*c* (s-*trans*,*cis*), s-*t*,*t* (s-*trans*,*trans*), s-*c*,*t* (s-*cis*,*trans*) and s-*c*,*c* (s-*cis*,*cis*) isomers (*Scheme 4*). Studies revealed that the s-*t*,*t* and s-*t*,*c* isomers are the preferred ones, the s-*t* conformation being more stable because it minimizes the nonbonding interactions. The thermally most stable stereoisomers are considered to be responsible for the slowest kinetics. Obviously, for the s-*cis* isomers, the polyene system cannot be planar because of strong steric hindrance caused by the Ph groups.

A major increase in the absorption intensities of the MCs in the chromene series, illustrated by examples **3**–**5**, is simply achieved by replacing alkyl groups by aromatic substituents which increase the conjugation and have a more pronounced electron-donating character. This should have a distinct impact on the corresponding molar absorptivities. Indeed, the corresponding 'colourabilities' show a two-fold increase (see *Table 2*).

Previous studies gave different results for the effect of a substituent at C(4) of the 2*H*-chromenes; so we decided to prepare the corresponding 4-Ph-substituted naphthopyran **6**. *Becker* [7] described the opposing contribution of a 4-Ph substituent on the photochromic behaviour even though *Tanaka et al.* [12] patented such compounds as photochromic pigments. Despite an increased flash-photolysis energy and an increased concentration compared to the standard conditions (see *Exper. Part*), compound **6** does not exhibit photochromic behaviour in the range of -20 to 80°. The strong steric interaction between the additional Ph group at C(4) in the closed form and the aromatic moiety in the opened form (see *Fig. 2*) causes a drastic destabilization which should lead to extremely fast ring closure. Further investigations of **6** at lower temperature (77 K), aiming to establish if ring opening occurs or not, are in progress and will be reported in due course.

Scheme 4. *Photochromic Equilibrium between the Closed Form* (CF) of *3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran* **5** *and the Four Isomers of the Corresponding Photomerocyanines* (MC; s-*trans* and s-*cis*)



Annulation Effect. The studied compounds represent two types of benzo-annulation of the chromene moiety, *i.e.*, involving the C(5)–C(6) or the C(7)–C(8) positions. The MCs obtained after photoirradiation of the 7,8-fused **7** are characterized by a VIS absorption spectrum (toluene) consisting of two maxima, a weak one at 403 nm and an intense one at 481 nm. Thus this compound covers a much larger wavelength range than the 5,6-benzo-annulated chromene **5** with a band centered at 432 nm under the same conditions. A marked difference is observed for the thermal bleaching rates. If we consider the MCs corresponding to **5** and **7** (*Figs. 3* and *4*, resp.) these results could be explained by the nonbonding interaction between the ethylenic H-atom and a naphthalenic H-atom which is more important for the β-naphthol derivative from **5** than for the α-isomer from **7**, thus leading to proportional destabilization. These results make 7,8-annulated compounds interesting for orange-developping photochromic substances, but kinetic is too

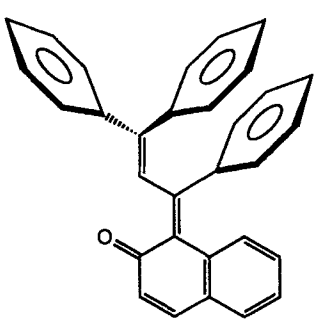


Fig. 2. *Hypothetical photomerocyanine of* **6** *represented in its s-*t,c *configuration*

slow for an application in the field of optical transmission materials. The average properties of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran **5** indicate more satisfactory behaviour for ophthalmic lenses.

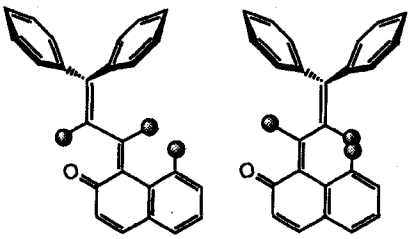


Fig. 3. *s*-trans *Photomerocyanines of* **5**

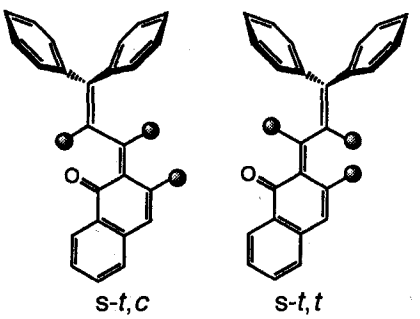


Fig. 4. *s*-trans *Photomerocyanines of* **7**

Concentrated solution of **8** ($c = 10^{-3}$ mol dm^{-3}) shows a low-intensity absorption band in the VIS region denoting that a thermal equilibrium is established between the colourless CF and the coloured opened MC in the absence of light. For all other naphthopyrans, the colour band is hardly detectable, even in a saturated solution of a polar solvent at 320 K.

Temperature and solvent polarity are responsible for increased solvatochromism. The phenanthropyran **8** is more polarizable, and the cleavage of the C–O bond takes place simply by solvatation. Although NMR spectroscopy is a suitable technique to investigate the geometry and the electronic structure of opened forms, the weak concentration of the opened form of **8** prevented us to elucidate its structure and thus to evaluate, coupled with electronic spectroscopy, the corresponding molar absorptivities. We established, however, that the MCs arising from solvatochromism are spectroscopically similar to those generated by photolysis. The two benzo-annulations of the chromene moiety of **8** lead to a great stabilization due to the important extension of the π system. A small hypsochromic shift ascribed to this kind of biannulation [29] is also observed.

Heterocycle Effect. Based on the spectral data given in *Table 3*, introduction of one N-atom at the 7-position of **5** induces slight changes in the maximum of coloured opened form of **9** (436 nm) as compared to that of **5** (432 nm). A similar effect is found for the dimethyl-substituted azino-fused compounds **14** when compared to **3**. A more marked shift of 11 nm is observed by the introduction of a N-atom at position 9 (→ **12**). This position plays a significant role in bathochromism since the quinazoline **12** does not exhibit additional changes. However, compound **13** manifests a bathochromic shift which could be explained by the extended conjugation on introduction of two other Ph groups at the heterocyclic moiety. The results show that the absorbance range of this class of photochromic compounds is bathochromically shifted with respect to comparative naphthopyrans.

For diphenylchromenes **9**–**13**, thermal bleaching is a relatively slow process (rate constant: 0.1–0.5 s^{-1}), and the kinetics are similar to those of corresponding naphthopyrans. The ring-closure reaction presents only one kinetics in the temperature range explored (from −20 to 50°). As shown for the naphthopyrans (see above), extension of conjugation is also responsible for a slight stabilization of photogenerated forms.

On the other hand, compounds **9**–**13** show significant variations of efficiency of colouration which is nicely enhanced in some cases: the striking feature is the hyperchromic effect observed for compounds **11** and **12**. It is not surprising that a compound heteroannulated at the 7,8 positions like **15** exhibits a similar photochromic behaviour than the corresponding naphtho[1,2-*b*]pyran **7** (403–481 nm). These spectrokinetic data are indicative of a more important stabilization of the open coloured form which is demonstrated by the solvatochromic equilibrium. Indeed, even at 50°, the toluene solution of **7** or **15** is still red involving the presence of coloured species. Unfortunately, their concentrations remain too weak for any measurement or characterization.

Solvent Effect. The influence of organic solvents on the absorption spectra was investigated. The UV/VIS spectral data of the open form of some chromenes in toluene and EtOH are collected in *Table 4*. These results point to a similar classification in EtOH and in toluene solutions, thus validating the remarks and conclusion made on the substitution pattern, annulation and kind of heterocyclic moiety (see above). For all tested chromenes, as the solvent polarity is increased, a bathochromic shift is observed (*i.e.*, positive solvatochromism). Such a shift depends largely on the change in the dipole characteristics between ground and excited state [30]: for a weakly polar molecule with low polarity in the ground state and increased polarity in the excited state, a bathochromic shift results. The observed bathochromic shift in the present series is hence indicative of a weakly polar ground state, *i.e.*, corresponding to an electronic distribution very close to a quinoid structure rather than to a zwitterion form or even species with in-between character.

When the photochromic behaviour is observed in a more polar medium, the thermal bleaching rates are markedly increased involving a destabilization of the photogenerated forms. One can say that, in toluene, intramolecular H-bonds are so privileged that only photomerocyanines involving such a stabilization are obtained after the flash and subsequent isomerization. The most important effect is the strong enhancement of colourability manifested by all chromenic compounds in EtOH.

By virtue of its photochromism, the metastable coloured form reverts to the colourless form upon removing the activating UV light following a first-order kinetics. The

Table 4. *Comparison of the Spectrokinetic Properties in Toluene and Ethanol Solutions* ($2.5 \cdot 10^{-5}$ mol dm^{-3}) *at 25°*. Estimated activation energy for compounds **5** and **9**.

	Toluene				Ethanol			
	λ [nm]	A_0	k_Δ [s^{-1}]	E_a [kcal/mol]	λ [nm]	A_0	k_Δ [s^{-1}]	E_a [kcal/mol]
4	399	0.48	2.3, 0.2		402	0.56	0.5	
5	432	0.84	0.9	16.9	437	0.97	0.12	16.6
8	428	0.98[a])	<0.001		436	0.89[a])	0.005	
9	436	0.82	0.13	15.7	447	0.99	0.23	14.3
11	443	1.29	0.29		454	1.37	0.41	
12	442	1.10	0.48		451	1.21	0.52	
7	481	1.62	0.002		483	1.69	0.002	
15	484	1.27[a])	0.005		487	1.19[a])	0.004	

[a]) Coloured solutions, these values represent the additional 'colourability' due to the flash.

least-squares fitting values at different temperatures (from −20 to 50° for EtOH solutions and from −20 to 75° for toluene solutions) allow us to estimate the activation energy for the transition state. The results for **5** and **9** are given in *Table 4*. These calculated values do not exhibit any relationship neither with the structure of the chromene nor with the solvent polarity. However, they are in the same range than corresponding activation energies observed for related spiro[indoline-naphthoxazines] [26].

Conclusion. – The properties of this series of 2*H*-chromenes make azino-fused compounds useful in photochromic applications such as lenses. From this study, some aspects emerge which can be generalized even if the number of molecules investigated is limited. Annulation at positions 7,8 produces a marked bathochromic shift in the spectra of photomerocyanines accompanied by an important stabilization. Both Ph groups are required at the sp^3-C-atom of the pyran ring to get interesting photochromic properties. Increasing the solvent polarity increases the rate constants and lead to bathochromic shifts. Positive solvatochromism confirms that open forms are weakly polar and should be isomers having quinoid character. Fusion of an azine ring nuclei, especially as isoquinoline, produces a hyperchromic effect.

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Experimental Part

1. *General.* Solvents used were dried over molecular sieves (4 Å). Flash chromatography (FC): *Merck 60H* silica gel (5–40 μm). Melting points: capillary tubes, *Büchi-510* apparatus; uncorrected. UV/VIS Spectra: *Beckman-Du-7500*; spectrophotometric-grade EtOH (*Carlo Erba* ACS quality); λ_{max} in nm. ε in dm^3 · mol · cm^{-1}. Photochromic measurements [30]: solns. in spectrophotometric-grade toluene (*UCB*) or abs. EtOH (*Baker*) at 25° (± 0.2°); monitored by a thermostat (*Huber* ministat); cylindric cells of 10-cm pathlength and 10-mm section; absorbance given for the standard concentration of $2.5 \cdot 10^{-5}$ mol/l. IR Spectra: *Fourier* transform, *Matson-Polaris* spectrophotometer. ^{1}H- and ^{13}C-NMR Spectra; in $CDCl_3$ *Bruker-BM-250* or *-AMX-400* instrument δ in ppm rel. to internal $SiMe_4$ *J* values in Hz. Elemental analyses were performed by the Microanalytical Services, University of Aix-Marseille III.

2. *2,2-Disubstituted-2H-1-benzopyrans. General Procedure A.* To a soln. of propargylic alcohol (30 mmol) and phenol in slight excess (33–36 mmol) in dry toluene (60 ml) under N_2, a catal. amount of TsOH was added and the mixture boiled under reflux for 2–6 h. The soln. was cooled and then washed sequentially with 10% NaOH soln. and H_2O. The aq. layer was extracted continuously with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$) and evaporated. The crude product was purified by FC (silica gel, pentane/Et_2O 95:5) and then recrystallized twice from an appropriate solvent (the 1st time with decolourization by charcoal). The 3-methyl-3-phenyl-3*H*-naphtho[2,1-*b*]pyran (**4**), 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (**5**) and 2,2-diphenyl-2*H*-naphtho-[1,2-*b*]pyran (**7**) were previously reported [31].

1,3,3-Triphenyl-3H-naphtho[2,1-b]pyran (**6**): Yield 89%. M.p. 209° (from benzene). *UV* (EtOH): 218 (36300), 246 (39500), 308 (5700), 348 (4450), 361 (4100). ^{1}H-NMR (250 MHz, $CDCl_3$): 6.18 (*s*, H–C(2)); 6.97 (*ddd*, *J* = 8.1, 6.8, 1.3, H–C(8)); 7.08 (*d*, *J* = 8.3, H–C(10)); 7.14 (*ddd*, *J* = 8.1, 6.8, 1.3, H–C(9)); 7.19 (*m*, 2H_p); 7.27 (*m*, 4H_m); 7.32 (*m*, 5H, Ph); 7.54 (*m*, 4H_o); 7.64 (*d*, *J* = 8, H–C(7)); 7.70 (*d*, *J* = 8.8, H–C(6)). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 82.1 (C(3)); 116.6 (*s*); 118.7 (C(5)); 123.1 (C(10)); 125.0 (C(8)); 126.5 (C(8)); 127.1 (C_o); 127.5 (C_p); 127.6 (C(2)); 128.0 (C(1))(Ph); 128.3 (C(6)); 128.5 (C_m); 129.4 (C(7)); 129.6 (*s*); 130.2 (*s*); 137.2 (*s*); 141.3 (*s*); 144.5 (C_{ipso}); 152.6 (C(4a)). Anal. calc. for $C_{31}H_{22}O$: C 90.70, H 5.40; found: C 90.76, H 5.31.

3,3-Diphenyl-3H-phenanthro[9,10-b]pyran (**8**): Yield 44% M.p. 184° (from heptane/benzene). UV (EtOH): 218 (19900), 242 (22500), 260 (18500), 342 (3790), 372 (2200). ^{1}H-NMR (250 MHz, $CDCl_3$): 6.33 (*d*, *J* = 9.9, H–C(2)); 7.25 (*m*, 2H_p); 7.27 (*m*, H–C(8)); 7.31 (*m*, 4H_m); 7.37 (*d*, *J* = 9.9, H–C(1)); 7.47 (*t*, *J* = 8, H–C(6)); 7.52 (*m*, 4H_o); 7.64 (*m*, H–C(10), H–C(11)); 8.03 (*d*, *J* = 8, H–C(9)); 8.53 (*t*, *J* = 7.9, H–C(7)); 8.60 (*m*, H–C(5), H–C(12)). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 82.8 (C3); 110.9 (*s*); 115.7 (*s*); 120.1 (*d*); 121.9 (*d*); 122.6 (*d*); 122.7 (*d*); 123.0 (*d*); 124.3 (*d*); 125.4 (*s*); 126.7 (*d*); 126.8 (C_o); 127.0 (*d*); 127.1 (*d*); 127.5 (C_p); 128.1 (C_m); 131.3 (*s*); 144.9 (*s*). Anal. calc. for $C_{29}H_{20}O$: C 90.60, H 5.24; found: C 90.34, H 5.38.

3. *Azino-fused 2,2-Diphenyl-2H-1-benzopyrans or 3,3-Dimethyl-3H-1-naphtho[2,1-b]pyran: General Procedure B.* Under N_2, titanium tetraethoxide (2.4 g, 10.4 mmol) in dry toluene (10 ml) was added over 10 min to the heterocyclic phenol (10.4 mmol) in dry toluene (40 ml). Then the mixture was boiled (15 min) and then slowly distilled to remove EtOH (20 ml were collected). The mixture was allowed to cool to r.t. and the α,β-unsaturated aldehyde (10.4 mmol) in dry toluene (50 ml) added dropwise. When the addition was complete, the mixture was boiled under reflux (2–5 h), allowed to cool, and poured onto 2M NH_2Cl (100 ml). The org. layer was dried ($MgSO_4$) and evaporated. The crude product was submitted to FC (silica gel, pentane/Et_2O 95:5 (*A*), 85:15 (*B*), or 60:40 (*C*)) and recrystallized twice from an appropriate solvent (the 1st time with decolourization by charcoal).

3,3-Dimethyl-3H-naphtho[2,1-b]pyran (**3**): FC(*A*), yield 39%. M.p. 43° (from EtOH). UV (EtOH): 243 (51500), 261 (5900), 289 (3300), 301 (4950), 345 (4150), 359 (4000). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.56 (*s*, Me); 5.79 (*d*, *J* = 9.9, H–C(2)); 7.10 (*d*, *J* = 9.9, H–C(1)); 7.13 (*d*, *J* = 8.75, H–C(5)); 7.39 (*td*, *J* = 8.1, 1.2, H–C(9)); 7.54 (*td*, *J* = 8.2, 1.2, H–C(8)); 7.72 (*d*, *J* = 8.8, H–C(6)); 7.81 (*d*, *J* = 8.2, H–C(7)); 8.01 (*d*, *J* = 8.3, H–C(10)). ^{13}C-NMR (100 MHz, $CDCl_3$): 27.6 (Me); 75.9 (C(3)); 113.7 (*s*); 118.2 (C(1)); 118.4 (C(6)); 121.4 (C(10)); 123.3 (C(9)); 126.4 (C(8)); 128.5 (C(7)); 129.0 (*s*); 129.2 (C(5)); 129.4 (C(2)); 129.9 (*s*); 150.9 (C(4a)). Anal. calc. for $C_{15}H_{14}O$: C 85.68, H 6.71; found: C 85.57, H 6.78.

3,3-Diphenyl-3H-pyrano[3,2-f]quinoline (**9**): FC(*C*), yield 66%. M.p. 226° (from hexane/benzene). UV (EtOH: 212 (22700), 247 (31900), 257 (27300), 286 (5620), 315 (4190), 351 (3720), 376 (sh, 1700). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.30 (*d*, *J* = 9.9, H–C(2)); 7.22 (*d*, *J* = 8.8, H–C(1)); 7.26 (*m*, 2H); 7.31 (*m*, 4H_m); 7.35 (*m*, H–C(9)); 7.42 (*d*, *J* = 9.1, H–C(5)); 7.47 (*m*, 4 H_o); 7.92 (*d*, *J* = 9.1, H–C(6)); 8.25 (*d*, *J* = 8.4, H–C(10)); 8.73 (*dd*, *J* = 4.2, 1.4, H–C(8)). ^{13}C-NMR (100 MHz, $CDCl_3$): 83.0 (C(3)); 113.6 (*s*); 118.5 (C(1)); 121.3 (C(9)); 121.8 (C(5)); 124.8 (*s*); 127.0 (C_o); 127.7 (C_p); 128.2 (C_m); 128.6 (C(2)); 129.6 (C(10)); 131.1 (C(6)); 144.5 (C_{ipso}); 148.0 (C(8)); 150.5 (C(4a)). Anal. calc. for $C_{24}H_{17}NO$: C 85.95, H 5.11, N 4.18; found: C 85.73, H 5.19, N 4.24.

3,3-Diphenyl-8-methyl-3H-pyrano[3,2-f]quinoline (**10**): FC(*C*), yield 59%. M.p. 197° (from heptane/benzene). UV (EtOH): 214 (24900), 244 (30900), 259 (26700), 288 (6620), 304 (6190), 317 (5220), 355 (3650), 364 (3220), 374 (sh, 1450). ^{1}H-NMR (250 MHz, $CDCl_3$): 2.61 (*s*, Me); 6.28 (*d*, *J* = 9.95, H–C(2)); 7.20 (*d*, *J* = 9, H–C(1)); 7.26 (*m*, 2H); 7.30 (*d*, *J* = 8.5, H–C(9)); 7.33 (*m*, 4H_m); 7.42 (*m*, H–C(5)); 7.46 (*m*, 4H_o); 7.82 (*d*, *J* = 9, H–C(6)); 8.15 (*d*, *J* = 8.5, H–C(10)). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 29.9 (Me); 82.9 (C(3)); 114.0 (*s*); 118.5 (C(1)), 122.4 (C(9)); 123.1 (C(5)); 124.9 (*s*); 127.2 (C_p); 127.8 (C_p); 128.4 (C_m); 128.8 (C(10)); 130.3 (C(6)); 144.6 (C_{ipso}); 150.6 (*s*); 162.3 (*s*). Anal. calc. for $C_{25}H_{19}NO$: C 85.95, H 5.50, N 4.0; found: C 86.12, H 5.34, N 3.89.

8,8-Diphenyl-8H-pyrano[2,3-h]isoquinoline (**11**): FC(*C*), yield 64%. M.p. 148° (from cyclohexane/benzene): UV (EtOH): 211 (27300), 246 (36550), 281 (7120), 291 (6540), 360 (6100), 373 (5860). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.36 (*d*, *J* = 10.05, H–C(9)); 7.29 (*m*, 2H_p); 7.34 (*m*, 4H_m); 7.38 (*d*, *J* = 10.05, H–C(10)); 7.42 (*d*, *J* = 8.9, H–C(6)); 7.46 (*m*, 4H_o); 7.51 (*d*, *J* = 5.7, H–C(4)); 7.63 (*d*, *J* = 8.9, H–C(5)); 8.41 (*d*, *J* = 5.65,

H–C(3)); 9.42 (*s*, H–C(1)). ^{13}C-NMR (100 MHz, $CDCl_3$): 82.6(C(8)); 114.2(*s*); 118.2(C(6)); 120.7(C(4)); 122.9(C(10)); 124.7(*s*); 127.0(C_o); 127.8(C_p); 128.1(C_m); 128.4(C(5)); 129.4(C(9)); 131.7(*s*); 141.4(C(3)); 144.3(C_{ipso}); 146.6(C(1)); 151.1(*s*). Anal. calc. for $C_{24}H_{17}NO$: C 85.95, H 5.11, N 4.18; found: C 86.07, H 5.03, N 4.06.

*8,8-Diphenyl-8*H*-pyrano[3,2-*f*]quinazoline* (**12**): FC(*B*), yield 45%. M.p. 163° (from toluene). UV (EtOH): 213(24900), 219(24250), 251(34100), 281(5290), 371(3920). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.39 (*d*, *J* = 10, H–C(9)); 7.24 (*d*, *J* = 10, H–C(10)); 7.29 (*m*, 2H$_p$); 7.32 (*m*, 4H$_m$); 7.44 (*m*, 4H$_o$); 7.59 (*d*, *J* = 8.8, H–C(6)); 7.84 (*d*, *J* = 8.8, H–C(5)); 9.19 (*s*, H–C(1)); 9.54 (*s*, H–C(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): 83.7(C(8)); 113.8(*s*); 117.2(C(10)); 121.3(*s*); 126.7(C(6)); 127.1(C_o); 128.1(C_p); 128.5(C_m); 130.0(C(2)); 130.3(C(3)); 144.1(C_{ipso}); 146.4(*s*); 151.1(*s*); 153.6(C(1)); 154.6(C(3)). Anal. calc. for $C_{23}H_{16}N_2O$: C 82.12, H 4.79, N 8,33; found: C 82.0, H 4.69, N 8.27.

*2,3,8,8-Tetraphenyl-8*H*-pyrano[3,2-*f*]quinoxaline* (**13**): FC(*B*), yield 17%. M.p. 159° (from heptane). UV (EtOH): 207(34100), 253(22700), 267(23500), 296(23550), 359(8050). ^{1}H-NMR (250 MHz, $CDCl_3$): 6.28 (*d*, *J* = 10, H–C(9)); 7.20–7.55 (*m*, 21H); 7.79 (*d*, *J* = 10, H–C(10)); 7.93 (*d*, *J* = 8.9, H–C(5)). Anal. calc. for $C_{35}H_{24}N_2O$: C 86.04, H 4.95, N 5.73; found: C 85.88, H 4.88, N 5.61.

*3,3-Dimethyl-3*H*-pyrano[3,2-*f*]quinoline* (**14**): FC(*A*), yield 47%. M.p. 81° (from heptane). UV (EtOH): 214(39500), 245(26300), 260(21900), 303(5050), 350(4150), 359(3550), 372(1525). ^{1}H-NMR (250 MHz, $CDCl_3$): 1.51 (*s*, Me); 5.75 (*d*, *J* = 10, H–C(2)); 6.98 (*d*, *J* = 10, H–C(1)); 7.30 (*d*, *J* = 9.1, H–C(5)); 7.39 (*dd*, *J* = 8.6, 4.2, H–C(9)); 7.91 (*d*, *J* = 8.5, H–C(6)); 8.28 (*d*, *J* = 8.5, H–C(10)); 8.79 (*dd*, *J* = 4.2, 1.2, H–C(8)). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 27.7(Me); 76.8(C(3)); 114.0(*s*); 117.6(C(1)); 121.4(C(9)); 122.2(C(5)); 129.9(C(10)); 124.9(*s*); 130.4(C(2)); 130.8(C(6)); 148.0(C(8)); 151.1(C(4a)). Anal. calc. for $C_{14}H_{13}NO$: C 79.59, H 6.20, N 6.63; found: C 79.47, H 6.08, N 6.68.

*2,2-Diphenyl-2*H*-pyrano[2,3-*f*]isoquinoline* (**15**): FC(*C*); yield 14%. M.p. 184° (from cyclohexane). UV (EtOH): 212(22700), 247(31900), 257(27300), 286(5620), 315(4190), 351(3720), 376(sh, 1700). ^{1}H-NMR (250 MHz, $CDCl_3$): 6.30 (*d*, *J* = 9.8, H–C(3)); 6.75 (*d*, *J* = 9.8, H–C(4)); 7.26 (*m*, 2H$_p$); 7.28 (*d*, *J* = 7.9, H–C(5)); 7.33 (*m*, 4H$_m$); 7.46 (*d*, *J* = 8, H–C(6)); 7.48 (*m*, 4H$_o$); 8.06 (*d*, *J* = 5.8, H–C(10)); 8.51 (*d*, *J* = 5.8, H–C(9)); 9.11 (*s*, H–C(7)). ^{13}C-NMR (62.5 MHz, $CDCl_3$): 83.5(C(2)); 114.7(C(10)); 116.8(C(4a)); 120.1(C(6)); 121.3(C(4)); 121.8(C(5)); 127.0(C_o); 127.7(C_p); 128.2(C_m); 128.6(C(10a)); 129.6(C(6a)); 131.1(C(3)); 142.7(C(9)); 143.7(C_{ipso}); 149.6(C(7)); 152.3(C(10b)). Anal. calc. for $C_{24}H_{17}NO$: C 85.95, H 5.11, N 4.18; found: C 85.69, H 5.22, N 4.27.

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