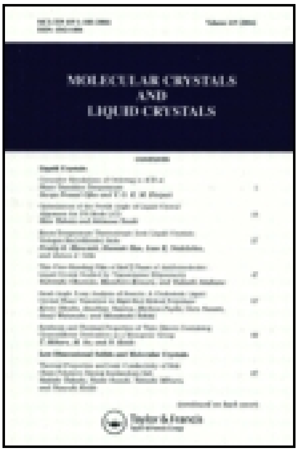

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Heterocyclo-Annulated Spirooxazines and 2H-Caromenes: Two Complementary Series of Photochromic Compounds

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HETEROCYCLO-ANNULATED SPIROOXAZINES AND 2H-CHROMENES : TWO COMPLEMENTARY SERIES OF PHOTOCHROMIC COMPOUNDS

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Abstract Our purpose was to prepare heterocyclo-annulated spirooxazines and 2H-chromenes in order to extend the scale of the main photochromic properties (spectro-kinetical and photodegradation parameters) and to characterize the influence of the nature and positions of heteroatoms.

- Nitrogenated six-ringed systems have very slight influence on k_Δ, λ_{max} and colorability of the photomerocyanines but an interesting power of enhancing the resistance to the fatigue. On the other hand the polyheteroatomic five-ringed systems present a broadening of the visible absorption spectrum but the photodegradation behaviour is not so satisfying.
- The replacement of the indoline moiety by hindered azaheterocyclic systems has also an interesting effect on the visible absorption and (or) the thermal bleaching kinetics.
- The accumulation of benzene nuclei and nitrogen atoms especially in the case of a 7-8 annulation on the spirobenzoxazine skeleton shifts the photochromic equilibrium toward a permanent merocyanine, the transoïd structure of which has been studied by X-Ray diffraction, ^1H NMR and dipole moment. All these data are in agreement with a quinoïd or polyenic electron distribution.

As a conclusion, the heterocyclic annulation is a good means for modulating the photochromic properties and can be coupled also to the effect of substitutents.

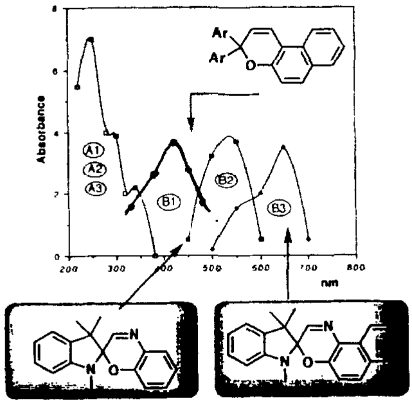
INTRODUCTION

The organic photochromic molecules or systems have been continuously developed since 1950 and particularly the spiropyrans compounds. Their spectacular and remarkable properties have suggested many potential applications in different fields such as photochromic glasses and lenses, cosmetics, consumer gadgets, optoelectronic devices, holography, reprography, optical switches, liquid crystals, optical memories and disks...

By now, the variable optical transmission materials [1](glasses and ophthalmic lenses) have really started the commercialization step in USA, Europe and Japan. Since 1982 many works have been realized involving spirooxazines compounds [2] (parent of spiropyrans) and also 2H-chromenes[3]. Moreover many patents have been deposited by industrial laboratories.

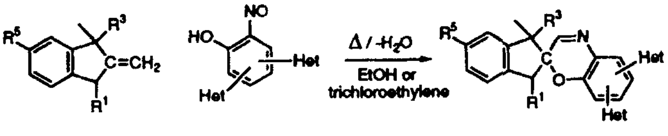
Our purpose was to synthesize heterocyclo-annulated structures involving the spirooxazine and 2H-chromene skeletons in order to extend the scale of the photochromic properties and to characterize the effect of the nature and positions of heteroatoms on the spectrokinetical and photodegradation parameters. The complementarity between the two kinds of pigments is related to the visible absorption spectrum of the colored forms of the 2H-chromenes and the spirooxazines respectively in the regions 400-500 nm and 550-650 nm (Scheme 1)

Scheme 1 General visible absorption spectrum of the photomerocyanines issued from 2,2-diaryl [2H]chromenes, spirobenzoxazines and spironaphthoxazines



SYNTHESIS OF HETEROCYCLO-ANNULATED SPIRO-BENZOXAZINES

The different general synthesis pathways involved in the building of the naphthoxazine moiety could be used for the heterocyclo-annulated benzoxazine one, the goal being to obtain an ortho-hydroxy nitroso heterocyclic derivative.



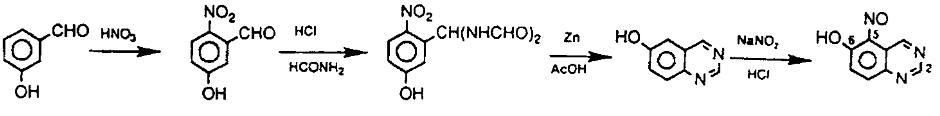
Different strategies could be used for the structural modifications on the skeleton of the photochromic pigments :

1- Classical electronic effect of substituents on spiro[indoline-naphthoxazine].

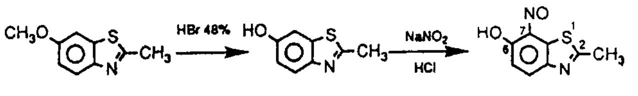
2- Heterocycloannulation in [5-6] positions of spiro[indoline-benzoxazine]

Some examples could be given for six-ringed and five-ringed systems[4] :

- quinazoline synthon (via Riedel synthesis)



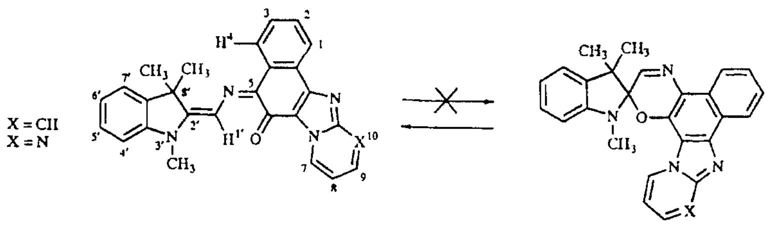
- benzothiazole synthon



3- Heterocyclo-annulation in [7-8] positions of spiro[indoline-benzoxazine] and extension of the π-system.

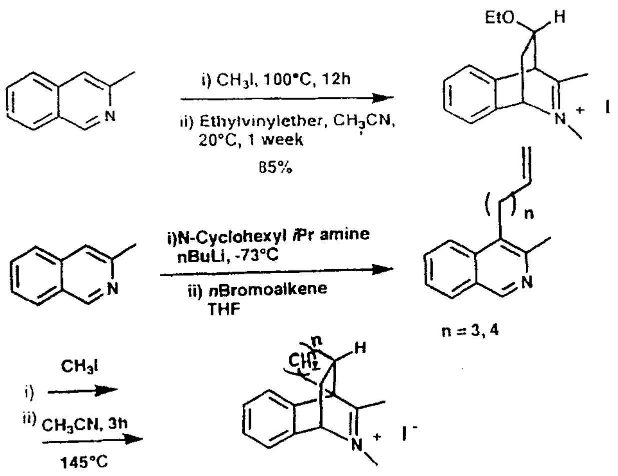
Indeed coloured compounds such as 5-[(1,3,3-trimethyl indolin-2-ylidene) methylimino]-5,6-dihydronaphtho[1',2':4,5]imidazo[1,2-a] pyridine -6-one and 5-[(1,3,3-trimethyl indolin-2-ylidene) methylimino]-5,6 dihydronaphtho[1',2':4,5] imidazo [1,2-a]pyrimidin-6-one have been isolated[5] and studied by different spectroscopic technics, dipole moment and X-Ray diffraction.

All the results are in agreement with a transoïd TTC structure having a quinoïd or polyenic electron distribution. It is the first example of a permanent open form (ε=48 000-49 000) in spiro-[indoline-naphthoxazine] series.



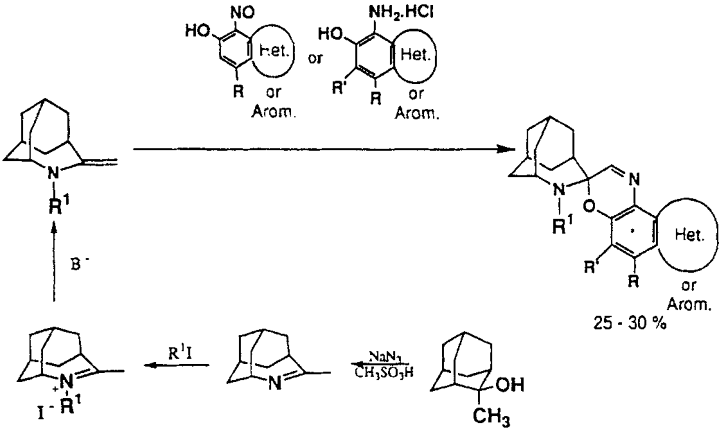
4-. steric effect of bulky "left" azaheterocycles replacing the indoline nucleus, the "right" moiety being a naphthoxazine.

For this aim, a Bradsher reaction involving an intermolecular cycloaddition [4^++2] of the ethyl vinylether or the cyclopentadiene on a methyl isoquinolinium methyl iodide salt in acetonitrile or also an intramolecular cyclo addition of the same type (Scheme 2) were used[6].



Scheme 2 .General pathway of synthesis for azabicyclo or azatricyclo salts intermediates.

More recently[7], the homoazadamantane nucleus was used as "left" heterocyclic moiety replacing the indoline one (Scheme 3).

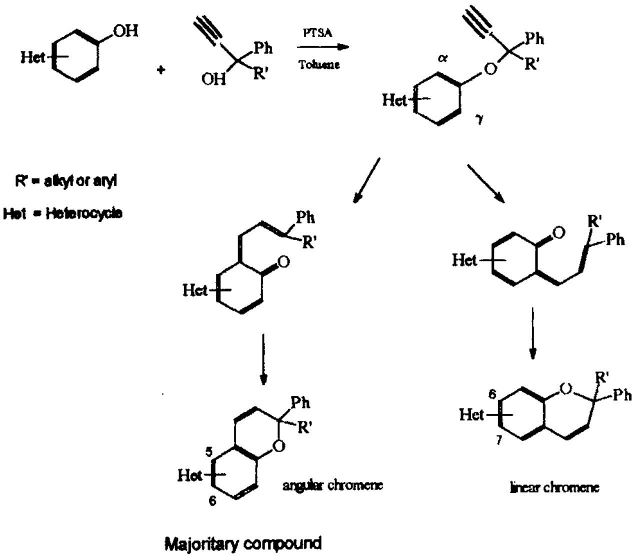


Scheme 3 . Synthesis steps in the homoazadamantane series

SYNTHESIS OF HETEROCYCLO-ANNULATED 2,2-DIPHENYL BENZOPYRANS.

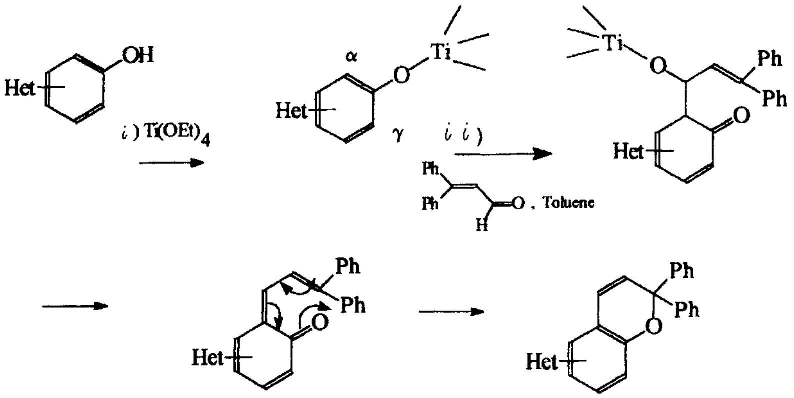
Two general methods (A and B) have been used for the synthesis, they are briefly described in Schemes 4 and 5 for introduction of five-ringed and six-ringed heterocyclic nuclei involving oxygen, sulphur and nitrogen atoms, particularly with an annulation in [5-6] positions. [8,9]

The choice of substitution by aryl groups on Sp^3 carbon atom of the chromene skeleton is quite important or indispensable for showing good photochromic properties.[8,9]



Scheme 4 . Mechanistic pathway for the method A [8].

This pathway is well adapted for oxygenated and sulphurated heterocyclo-phenols but not convenient for the nitrogenated ones.



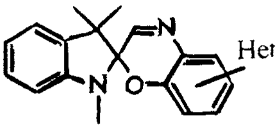
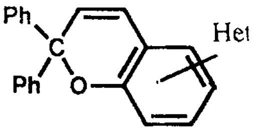
Scheme 5 . Mechanistic pathway for the method B[10]

This pathway involving the reactivity of the titanium (IV) salt of the heterocyclic phenol on b-phenyl cinnamaldehyde (or α, β unsaturated carbonyl compound) is particularly interesting for the nitrogenated systems. With this synthesis pathway no trace of linear chromene (annulation [6-7]) was detected. This regio selectivity could be explained by the less carbanionic character at C-δ relative to C-α, arising from resonance stabilization.

PHOTOCHROMIC BEHAVIOR OF HETEROCYCLO-ANNULATED SPIRO [AZAHETEROCYCLO -BENZOXAZINES] AND 2,2-DIPHENYL-BENZOPYRANS.

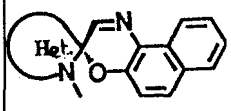
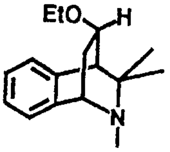
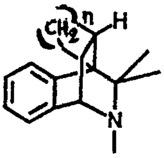
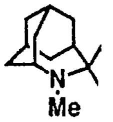
The main results concerning the annulation in [5-6] positions could be presented in the Table 1, (by comparison to the reference compounds spiro[indoline-naphthoxazine] and 3,3 diphenyl-3H-naphtho[2,1-b] pyrans).

Table 1 Evolution of photochromic parameters in toluene at 25°C

CF = colored form UF = uncolored form - k_Δ = (thermal bleaching constant)	 Ref.4	 Ref. 11,12
	* Six-ringed azaheterocyclic systems	
- k_Δ CF → UF	slight decrease	slight increase
- λ_{max} (CF)	slight bathochromic shift	slight bathochromic shift (enhanced by aryl substituents)
- colorability	slight decrease	slight increase
- resistance to the fatigue	enhancement	important enhancement
	* Five ringed polyheteroatomic systems	
- k_Δ CF → UF	slight decrease	slight increase generally
- λ_{max}(CF)	—	(apparition of a new absorption band at high wavelength (500-600 nm)
- colorability	important decrease	decrease generally
- resistance to the fatigue	important decrease	decrease

The main results issued from the structural modifications of the "left" part in spirooxazines could be summarized in the Table 2 (by comparison to the reference compound the spiro[indoline-naphthoxazine]).

Table 2 Evolution of photochromic parameters in toluene at 25°C

	Het = Azabicyclo-alcane..Ref. 6a 	Het = Azatricyclo-alcane, Ref. 6a 	Het = Homoazaada-mantane, Ref. 7 
k_Δ (CF -->UF)	slight decrease	important increase	important decrease
λ_{max} (CF)	hypsochromic shift	very slight hypsochromic shift	slight hypsochromic shift
Colorability	identical	–	identical
Resistance to the fatigue	important decrease	–	not evaluated

- The linkage between the 2 phenyl groups of 3,3-diphenyl-3H-naphtho[2,1-b] pyran give a spirocarbocyclic system called spiro[fluorene-chromene][11]. The main interest of a such system is a stabilization of the colored form (decrease of k_Δ), a slight bathochromic shift of the λ_{max} of the colored and uncolored forms, an increase of the "colorability" in agreement with a better planarity of the system.

Unfortunately we observe an important decrease for the resistance to the fatigue considerably accentuated for the oxygenated five-ringed systems.

Moreover, for spiroxazines and chromenes compounds, the solvatochromy is positive corresponding to a quinoïd or polyenic electron distribution and the photocoloration process is involved mainly through the excited singlet state.

All these results checked in solution are generally available in polymer matrices but it is difficult to generalize in some complex media.

The fragmentation of such molecules upon hard irradiation and the structural characterization of the photoproducts put in evidence different concomittant mechanisms involving heterolytic and homolytic opening processes of the photochromic pigments.

Three types of mechanism could be advanced [13,14]: i) Radicalar processes with triplet molecular oxygen. ii) Cycloaddition on double bonds of the quinoïd photomerocyanine of singlet oxygen generated by the photomerocyanine itself as photosensitizer.

iii) Nucleophilic addition of radical anion superoxide on the photomerocyanine.

CONCLUSION

The heterocyclic annulation of spiro oxazines and 2H-chromenes is a good means for modulating the photochromic properties.

It can be coupled also to the effect of different substituents on the skeleton of these pigments.

The known relationships between structure and properties allow to design new systems with wanted properties.

ACKNOWLEDGMENTS

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