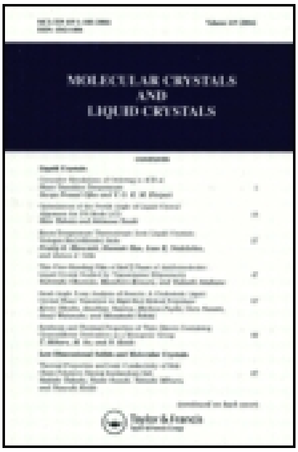

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Spiro[2H]-1-Benzopyran-2,9′-Fluorenes: Hyperchromic and Bathochromic Shifts of the Visible Absorption of Chromenes

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SPIRO[2H]-1-BENZOPYRAN-2,9'-FLUORENES: HYPERCHROMIC AND BATHOCHROMIC SHIFTS OF THE VISIBLE ABSORPTION OF CHROMENES.

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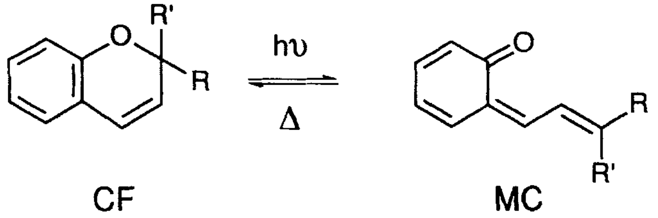
Abstract The synthesis of spiro[fluorene-naphthopyrans] and spiro[fluorene-furano[3,2-f]chromenes] allowed us to quantify the role of fluorene moiety towards photochromic properties. Compared to corresponding diphenyl-chromenes, the extended Π system delocalization causes a bathochromic shift of the visible absorption of the colored merocyanines. Whatever the right hand side in the studied series, an hyperchromic effect is observed.

INTRODUCTION

2*H*-1-benzopyrans (or 2*H*-chromenes) are an important class of oxygenated heterocyclic compounds to which research has been devoted in connection with the biological activities of natural occurring ones. [1] Furthermore, upon irradiation, they lead to photoproducts having spectra similar to those of merocyanine dyes. [2] The photochromic property is based on the reversible reaction that the colorless pyranic form CF undergoes to give colored merocyanine(s) MC when liquid solutions or polymer matrices containing CF are exposed to UV-light.



SCHEME 1 Photochromic equilibrium for 2*H*-1-benzopyrans

The research interests in the field of chromenic compounds came into sight few years ago, due to variable optical transmission materials which remain the only major commercial exploitation. Although a great number of photochromic compounds have been reported [3], the compounds which turn yellow or orange upon UV irradiation are quite rare. Spironaphthoxazine substituted by pyrazine ring [4] and dithienylethene [5] are such few examples.

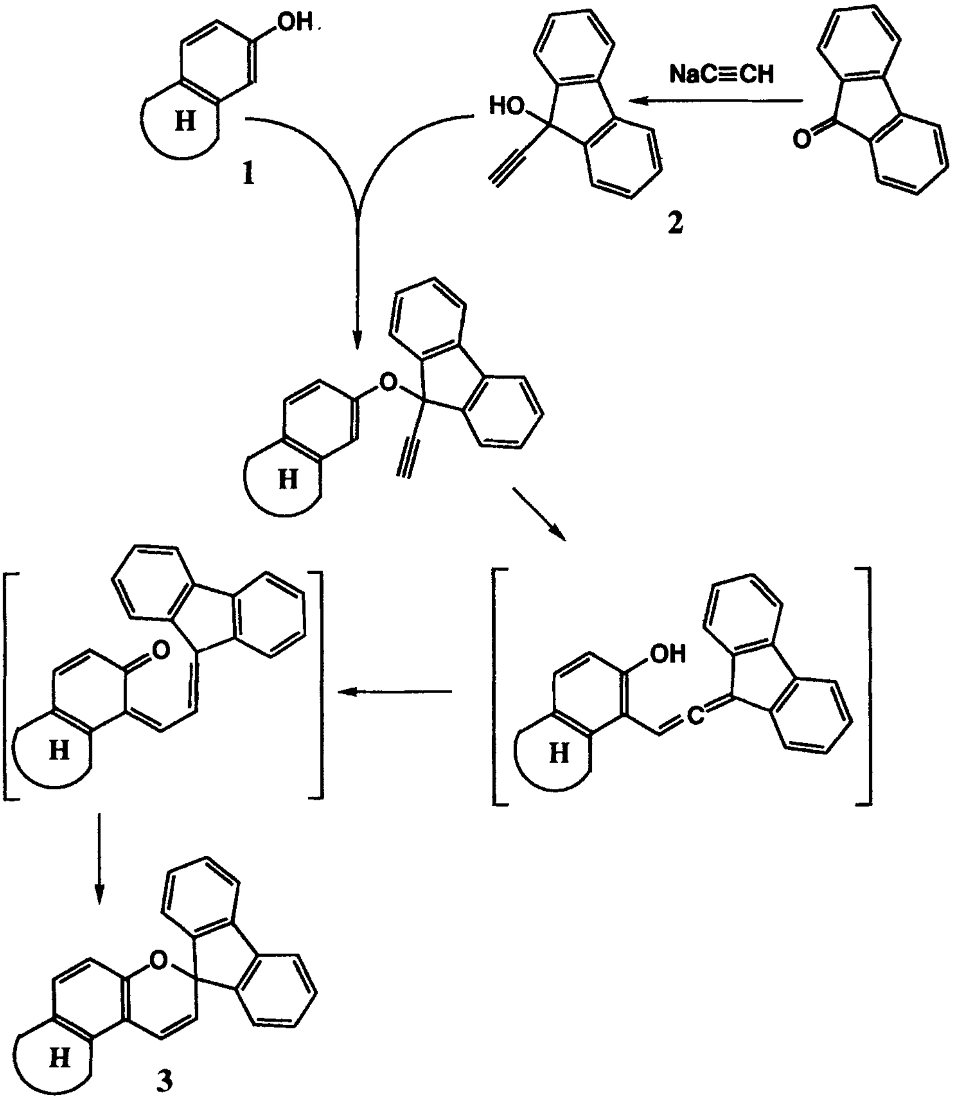
Furthermore photochromic compounds must satisfy the following performance criteria: the fatigue or the chemical instability upon repeated cycling or continuous irradiation should be minimum, a highly efficient photoresponse in the near Ultraviolet, a relatively fast thermal fading rate at ambient temperature and the quantum yield for bleaching with visible light should be minimum so the color is preserved. Despite a relatively large number of benzopyrans has been patented, this kind of requirements has initiated several structural modifications in the chromene series. [6]

During our study in the field of photoresponsive systems and more particularly of diaryl-naphthopyrans and heterofused diaryl-chromenes [7], we reasoned that extension of conjugation on resulting open form would be a good starting point for such targets.

We report here the synthesis of spiro[fluorene-benzopyrans] annelated on the right hand side with benzo (**4a** and **5**) or furano (**4b** and **4c**) nuclei along with their physico- and photochemical properties. Within the synthetized series, the role of the annelation position and the substitution pattern towards photochromic properties were studied. The direct comparison with previously described [7,8] naphthopyrans was established.

SYNTHESIS

The synthesis of 2,2-disubstitued-[2H]-chromenes may be approached either by the preparation of related ring system with subsequent variation of functionality, or by alkylation of a free phenol followed by cyclisation onto the aromatic ring.



SCHEME 2: Representation of synthetic pathway for the formation of spiro[fluorene-benzopyrans] **3a-c**

The former synthetic approach leads to very low yields in case of spiro[fluorene-benzopyrans] and suffers from tedious conditions when applied for heterofused parents. First reported by Iwai and Ide [9] , thermal cyclization of propargylaryl ethers affords chromenes. The reaction is considered to proceed *via* a Claisen-like [3,3]-sigmatropic rearrangement which is followed by a [1,5]-sigmatropic shift. An electrocylization completes the process. The desired intermediate ethers could be obtained *via* a Williamson synthesis or as in our case, the preparation of the spiro[fluorene-benzopyrans] were achieved by an one-pot method, reacting phenol, in an inert solvent, with 9-ethynyl-9H-fluoren-9-ol **2** *via* acidic catalysis. This latter compound was easily prepared from fluorenone and sodium acetylide in 68% yield. The sufficient time to complete the chromenisation is between 3 and 7 hours. The mixtures of desired compounds were initially purified by flash chromatography and were then fully characterized by electronic spectroscopy and ^{1}H, ^{13}C NMR. Corresponding yields are listed in table 1.

TABLE 1 Reaction conditions and yield for spiro[fluorene-benzopyrans].

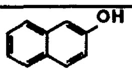
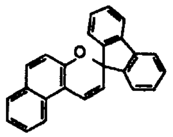
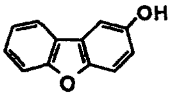
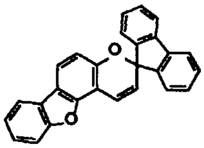
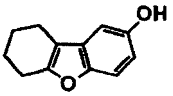
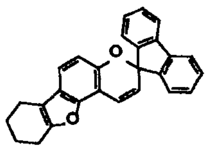
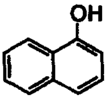
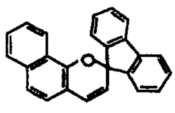
Starting Phenol	Time of reaction (h)	Yield (%)	m.p. (°C)	Spiro[fluorene-benzopyran]
 **1a**	3	57	205	 **3a**
 **1b**	3.5	42	151	 **3b**
 **1c**	3.5	35	201	 **3c**
 **4**	7	18	137	 **5**

Table 1 clearly shows that chemical yield is directly dependent on structures of starting phenols. It is estimated that efficiency for cyclisation is strictly reliable to electronic density of ortho attacked position.

PHOTOCHROMIC PROPERTIES

Upon activation by ultra-violet light, or by sunlight, 2*H*-chromenes and spiropyrans are known to undergo a reversible heterolytic scission of the carbon sp^3-oxygen bond of the pyranic ring. This is followed by extremely fast (*i.e.* 10^{-9}-10^{-12}s) bond rearrangements resulting in the formation of the chromophoric species or merocyanines MC that are responsible for the photo-generated colors.

Photochromic behavior is quantified by three main parameters, named spectrokinetic parameters and the compounds are compared according to maxima wavelengths of the colored form (photomerocyanine MC), thermal bleaching rate and the 'colorability'. The spectra of the photomerocyanines in matrice/solvent host were determined using flash photolysis (flashes of *ca.* 60J, duration of *ca.* 50µs).[10] The 'colorability' is evaluated by monitoring the absorbance A_0 at λ_{max} immediately after the flash. Taking into account that flashgun irradiates all the UV region, we acccept the assumption that MC are formed in similar conditions so it allows us to compare the efficiency of coloration of different compounds.

$$A_0 = \varepsilon_{MC} \cdot \Phi_{col.} \cdot k . C_{CF} \quad \text{(for low concentrations)}$$

ε_{MC} = molar absorptivity of merocyanines.
C_{CF} = initial concentration of closed form
k = constant including photolysis conditions
Φ_{col} = quantum yield of coloration

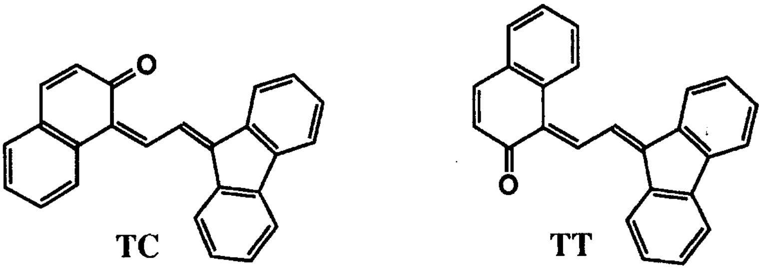
All the described spiro[fluorene-benzopyrans] exhibit photochromic behavior at room temperature in toluenic solution. We report in Table 2 the spectrokinetic parameters of the synthezised compounds along with those of related diphenyl-chromenes.

TABLE 2 Spectrokinetic properties of spiro[fluorene-benzopyrans] (and corresponding diphenyl-chromenes) in toluene solutions of 2.5 10^{-5} mol dm^{-3} at 25°C.

Compounds	λ_1 (nm)	A_1	λ_2 (nm)	A_2	k_Δ (s^{-1})
3a	**457**	**1.31**			**0.082/0.02**
	(432)	(0.84)			(0.09/0.015)
3b	**455**	**0.95**	**551**	**0.45**	**0.3/ 0.06**
	(424)	(0.77)	(518)	(0.23)	(0.21/0.04)
3c	**447**	**1.26**	**534**	**0.39**	**0.34/0.017**
	(420)	(1.08)	(527)	(0.23)	(0.04)
5	**436**	**1.14**	**495**	**1.38**	$<10^{-3}$
	(403)	(1.08)	(481)	(1.62)	(0.002)

Based on these spectral data, the increase in electronic conjugation on photogenerated forms derived from diphenyl-chromenes to spirofluorene derivatives seems to play an important role in the observed bathochromic shift. In fact, both phenyl groups of fluorene moeity are sterically allowed to participate to conjugation. This has been verified by molecular modelling on several conformations which also indicates that the polyene-like chain should be more twisted than for latter compounds. These absorption characteristics (λ_{max}) clearly make the spirofluorene potentially suitable compound for use in photochromic lenses according to achievable color.

The effect on thermal bleaching rates is less important, despite a slight stabilization of opened form is observed. According to our knowledge, four isomers can exist, namely the TC (*trans-cis*), TT, CT and CC isomers. Studies gave the TT and TC as the preferred ones, as the transoïd configuration are believed to be more stable because it minimizes the non-bonding interactions. Obviously for the cisoid isomers, the polyenic system could not be planar because of strong steric hindrance caused by the carboaromatic group. The two kinetics are interpretated as modified ratios between the different stereoisomers The most thermally stable stereoisomers are considered to be responsible for the slowest kinetic.



SCHEME 3: The two main isomers of photomerocyanine MC.of spiro[fluorene-9,3'-[3H]-naphtho[2,1-b]pyran] **4a**.

On the other hand, those compounds show significative variations of efficiency of coloration which is nicely enhanced. Furthermore, the shape of the absorption spectra is enlarged. The striking feature about the present results is the hyperchromic effect observed for compounds **4a-c**. So, a major increase in the absorption intensities of photomerocyanine in chromene series, illustrated by aforementionned examples, is simply achieved by replacing alkyl group or aromatic substituents by forcing conjugation using suitable carboaromatic moieties which have a more pronounced electron donating character. This should have drastic consequence on corresponding molar absorptivities.

CONCLUSION

Synthesis of new spiro[fluorene-benzopyrans] annelated with benzo or heterocyclic ring has been achieved using easily available phenols. Among structural modifications of promising chromenes, a such extension of conjugation is particularly interesting with respect to diaryl-benzopyran parents in view of the bathochromically shifted and broadened absorption of photoinduced forms. Furthermore, the same trend of effects due to the right hand side, namely relative position of annelation and/or heterocycle effect, are observed. This photochromic behavior make spiro[fluorene-benzopyrans] potentially useful for applications due to achievable color.

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