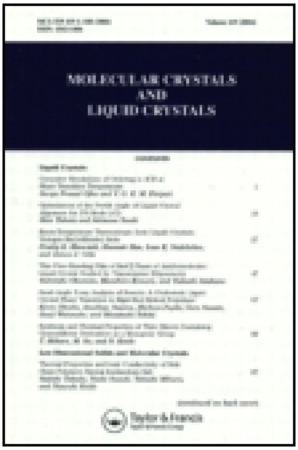

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Synthesis and Photochromic Properties of Thiophene Linked [2*H*]-Chromenes

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Successive coupling reactions (catalysed by Cu(I)/Pd(II) systems) between 8-bromo-3,3-diphenyl-[3H]naphtho[2,1-b]pyran, 2-methylbut-3-yn-2-ol and appropriate thiophene- or bithiophene halides afforded mono- or bichromophoric chromenes bearing a thienylethynyl or a bithienylethynyl group. Spectrokinetic study using flash photolysis conditions showed interesting photochromic properties regarding, especially, the " colorability " of the new compounds.

Keywords: Chromenes; Photochromism; Spectrokinetics; Coupling reactions; Thiophene

INTRODUCTION

Organic materials for which structure and macroscopic properties can be controlled by external stimuli are presently a major focus of research due to their promising applications for optical and optoelectronic devices. Then, a photochromic system working through an external UV irradiation can be the basis for molecular switch.

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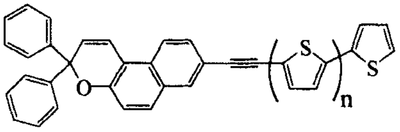
Regarding this context, the synthesis of [2*H*]-chromenes linked to thiophene oligomer by acetylenic junction has been developed.

Indeed, on one hand chromenes show interesting photochromic behaviour [1] (good fatigue resistance, wide range of absorption in the visible region) and on the other hand, oligothiophenes are well known for their conducting properties. The acetylenic junction ensures the π conjugation between both entities while keeping the rigidity of the system.

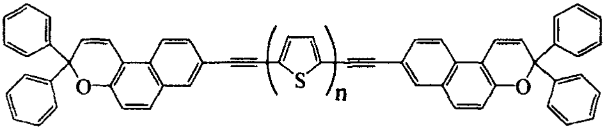
Above the drastic colour change due to the formation of merocyanine dye, the photoinduced transformation between coloured and colourless form, involves changes of geometry and polarity of the photochromic moiety which can lead to a topologic change of the oligomer, modifying in turn the intrinsic conducting properties of material.

We now report the synthesis of two such photochromic systems **I** and **II**.

On the other hand, in order to investigate the effect of the number of thiophene units on the photochromic properties spectrokinetic measurements have been performed using flash photolysis conditions.



I$_a$, n=0 and **I**$_b$, n=1)

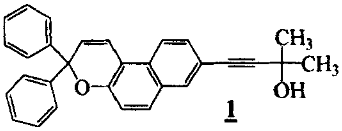


II$_a$, n=1 and **II**$_b$, n=**2**

DISCUSSION

- *Synthesis*

The widely accepted procedure for the introduction of an acetylenic substituent onto an aromatic nucleus is the Stephens-Castro coupling reaction between an aryl and a protected cuprous acetylide in pyridine at reflux [2]. An elegant alternative to this method was described for the first time by Sonogashira-Hagihara [3]. These authors reported a coupling reaction of terminal alkynes with aryl halides in the presence of Cu(I)/Pd(II) co-catalyst system in an amine as solvent. Following on this result, different modifications of experimental conditions were developed in the literature.



$\underline{1}$

The synthesis of the compound $\underline{1}$, precursor of the target molecules proceeds as follows : a Sonogashira coupling of 8-bromo-3,3-diphenyl-[3*H*]-naphtho[2,1-b]pyrane with excess of commercially available 2-methylbut-3-yn-2-ol, gives $\underline{1}$ in quantitative yield. The reaction is performed in diethylamine at room temperature for 14h, in the presence of catalytic amounts of bis[triphenylphosphine]palladium(II) dichloride and copper (I) iodide.

Preparation of $\underline{I}_{a,b}$ was accomplished by Sonogashira coupling carried out under phase-transfer conditions [4]. Condensation of $\underline{1}$ with the appropriate thiophene halide (2-iodothiophene or 5-bromo-2,2'-bithiophene), using benzyltriethylammonium chloride as phase-transfer agent, aqueous 5.5 N sodium hydroxide as base, benzene as solvent and a mixture of tetrakis[triphenylphosphine]palladium and copper (I) as catalysts, affords $\underline{I}_{a,b}$ in 88 % and 60 % yield respectively.

According to the same procedure, the bichromophoric systems $\underline{\mathbf{II}}_{a,b}$ were synthesised from the condensation of $\underline{\mathbf{1}}$ with 2,2-diodothiophene and 5,5'-diodo-2,2'-bithiophene. $\underline{\mathbf{II}}_{a,b}$ were obtained in 73 % and 80 % respectively.

- *Spectrokinetic Measurements :*

The photochromic properties are described by three main parameters : the thermal fading rate (k_Δ), the maximum wavelength of absorption of the coloured form (λ_{max}), and its " colorability" defined as the initial absorbance (A_0) obtained at λ_{max} just after the photoactivation. The spectra of photomerocyanines in toluene at 298 K and the rate constants of thermal ring closure were determined using a flash-photolysis apparatus coupled to a fast scanning spectrophotometer [5]. Concentration of photochromic solutions : 2.5 10^{-5} M in toluene. The results are reported in the Table 1 and compared to those of the parent compound of this series (2,2-diphenyl-[3*H*]-naphtho[2,1-b]pyrane, $\underline{\mathbf{III}}$).

Table 1 : Spectrokinetic parameters of new chromenes (25°C, 2.5 10^{-5} M in toluene)

Compound	**λ_{max} (nm)**	**A_0**	**k_Δ (s^{-1})**
$\underline{\mathbf{I}}_a$	471	3.10	$k_1 = 0.20$
			$k_2 = 0.07$
$\underline{\mathbf{I}}_b$	484	5.30	$k_1 = 0.23$
			$k_2 = 0.01$
$\underline{\mathbf{II}}_a$	476	7.10	$k_1 = 0.21$
			$k_2 = 0.05$
$\underline{\mathbf{II}}_b$	480	1.40	$k = 0.19$
$\underline{\mathbf{III}}$	432	0.84	$k = 0.09$

Concerning the absorption of the coloured form the addition of a thienylethynyl group on the position 8 of the chromene leads to a bathochromic shift of about 40 nm due to the extension of the π system (comparison $\underline{\mathbf{I}}_a$, $\underline{\mathbf{II}}_a$/$\underline{\mathbf{III}}$). When a bithienylethynyl group is bounded to the photochromic unit, the bathochromic shift is slightly higher (about 50 nm). Two kinetics are generally observed during the thermal fading (except for $\underline{\mathbf{II}}_b$), corresponding certainly to the disappearance of two different isomers of the open form [6]. The faster rate being of major amplitude (80 - 90%), the decoloration of the new compounds is ten times more rapid than that observed in the case of the parent compound $\underline{\mathbf{III}}$.

Finally, the most interesting improvement concerns the colorability. The high increase of A_0 when one thienylethynyl (A_0=3.10) or a bithienylethynyl (A_0=5.30) is linked to a chromene unit can be explained by the chromophoric effect of these groups (high molar absorptivity). Results concerning the bi-photochromic system $\underline{\mathbf{II}}_a$ and $\underline{\mathbf{II}}_b$ are more surprising . In the case of $\underline{\mathbf{II}}_a$ the very high colorability (A_0=7.1) could be due to the opening of both chromene rings (comparison $\underline{\mathbf{II}}_a$/$\underline{\mathbf{I}}_a$). The dramatic fall of the colorability in the case of $\underline{\mathbf{II}}_b$ is more difficult to understand, even if only one photochromic unit is active (comparison $\underline{\mathbf{II}}_b$/$\underline{\mathbf{I}}_b$). A possible explanation is the decrease in this case of the quantum yield of photocoloration (complementary photochemical experiments are necessary to confirm this assumption).

CONCLUSION

The coupling method using Sonogashira-Hagihara reaction is quite appropriate for obtaining acetylenic linkages between functionalized oligothiophenes and [2*H*]-chromenes in mild conditions. It opens new areas for the development of such structures and also of bichromophoric systems.

The preliminary spectrokinetic results obtained show interesting photochromic behaviour mainly in the field of colorability. The thermal bleaching rates are

quite in the same order compared to the reference compound (3,3-diphenyl-[*3H*]-naphtho[2,1-b]pyran. Electronic emission spectroscopy measurements and theoretical approaches are in progress in order to explain the role of acetylene and thiophene linkages regarding excited states.

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