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Photoswitch based on remarkably simple naphthopyrans

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Abstract—Photochromic switches built around 5-carbonyl-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran unit have been synthesized. Their open forms are constituted of a 1:1 ratio of TC and TT-isomers according to ^{19}F and ^{1}H NMR investigations. Electrocyclization of TT isomers back to the closed form is efficiently achieved upon visible irradiation whereas it has been found to be a particularly unfavoured thermal process. These simple 2H-chromenes could act as molecular photoswitch at ambient temperature.

Photochromism is usually defined as the reversible photoinduced transformation between two molecular states whose absorption spectra are significantly different.[1] Besides this colour change, the light-induced transformation causes reversibly important structural and physico-chemical changes, organic photochromes could also offer the unique possibility to modify the self-assembly process of the individual molecules and also the resulting supramolecular network by means of light.[2] The current interest in miniaturizing the components of electronics down to the molecular level is a major driving force in the research of molecular systems with switchable properties.[3] In the course of development of novel applications, synthesis of readily available compounds, whose photochromic properties can be used to create photoreversible systems is highly desired. Among the numerous organic photochromes already reported, few of them possess two thermally stable states.[4] Obviously diarylethenes constitute the most promising molecules among the rare bistable photochromes and have been extensively developed since the pioneering work of Irie.[5] The 2H-chromenes and more precisely the 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans have been studied during the past decades due to their easy access and pronounced resistance to fatigue, which have promoted their use in ophthalmic applications.[6] Photochromism in 2H-chromenes involves photocleavage upon UV irradiation of the C–O bond, leading to the formation of open and coloured isomers being assigned as the Transoid-Cis (TC) and the Transoid-Trans (TT) photomerocyanines,[7] which reversibly revert back by electrocyclization to the colourless closed form.

TC has been found to be the predominant structure formed exhibiting a fast thermal decay at ambient temperature, which is suitable for variable optical transmission materials, TT open forms representing usually 0–15%.[8]

Here we report the synthesis and the photochromic properties of a new series based on the 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans incorporating a carbonylated substituent on position 5. Such naphthopyrans bearing a methoxycarbonyl group **1a**,**b** are easily prepared in two steps starting from 3-hydroxy-2-naphthoic acid, which is first converted to its methyl ester and then reacts with conveniently substituted 1,1-diphenylprop-2-yn-1-ol in the presence of *p*-toluenesulfonic acid as catalyst to afford the photochromic compound.[9] UV irradiation of toluene solution of **1b** (5×10^{-4} M) reveals a broad absorption in the visible-region centred at 449 nm. When irradiation ceases partial fading is observed following a monoexponential decay ($k_{\Delta}(1) = 0.66\ \mathrm{s}^{-1}$) until an equilibrium is reached. The remaining thermostable absorbance has been found to correspond to $A_{\max}/2$. When this solution is kept in the dark a significant decrease can only be detected after 48 h indicating that the conversion of the remaining

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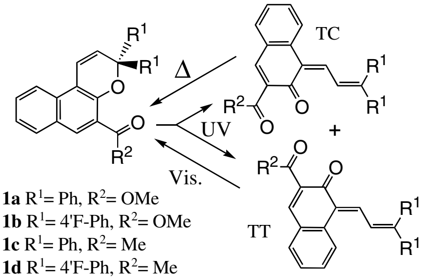

Figure 1. Photochromic equilibrium for 3,3-diphenyl-3*H*-naphthopyrans **1a**–**d**.

isomer towards the closed form is particularly an unfavoured thermal process. ($k_\Delta(2) \ll 10^{-6}\,\mathrm{s}^{-1}$). In contrast complete bleaching is simply achieved by irradiation with visible light ($\lambda = 450$ nm) (Fig. 1). As depicted in Figure 2, this has been repeatedly cycled without any noticeable photodegradation. This remarkable feature prompts us to prepare some additional examples of naphthopyrans bearing carbonylated groups. This has been achieved by transforming the previously prepared esters into methylketones.[9] These derivatives **1c**–**d** exhibit similar photochromic response. This attractive behaviour has also been investigated using NMR spectroscopy. At low temperature, a solution (10^{-2} M in toluene) has been irradiated with UV light ($259 < \lambda < 388$ nm). ^{19}F and ^{1}H NMR spectra recorded before and after irradiation indicate the conversion of **1b** into three new structures. Indeed, two pairs of ^{19}F resonances between −109 and −111 ppm are detected and are straightforwardly assigned to the fluorine atoms borne by phenyl groups in both transoid isomers of photomerocyanines, TC and TT (Fig. 3).[8] The other new signal at −113.6 ppm is attributed to an allenyl–naphthol **A**, which is produced from TC-isomer.[10] The time-evolution of irradiated solution has been followed at 243 K by recording NMR spectra at regular time intervals. Only isomer TC decreased rapidly ($k_\Delta = 3.310^{-4}\,\mathrm{s}^{-1}$), while TT and **A** present no significant time-evolution (Fig. 3c–f). Consequently, we observe in spite of rather different experimental conditions of temperature and concentrations, similar results when compared with previous spectrokinetic measurements. The same 1:1 ratio of isomers TC and TT is obtained and only TC is thermoreversible.

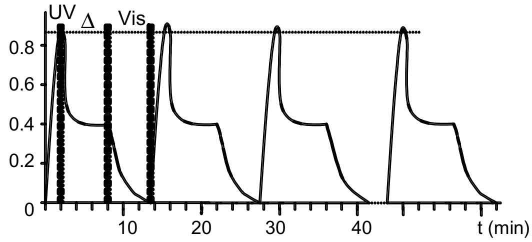

Figure 2. Absorbance evolution at 460 nm ($\lambda_{\max}$) for **1b** according UV or Vis irradiation or thermal decay.

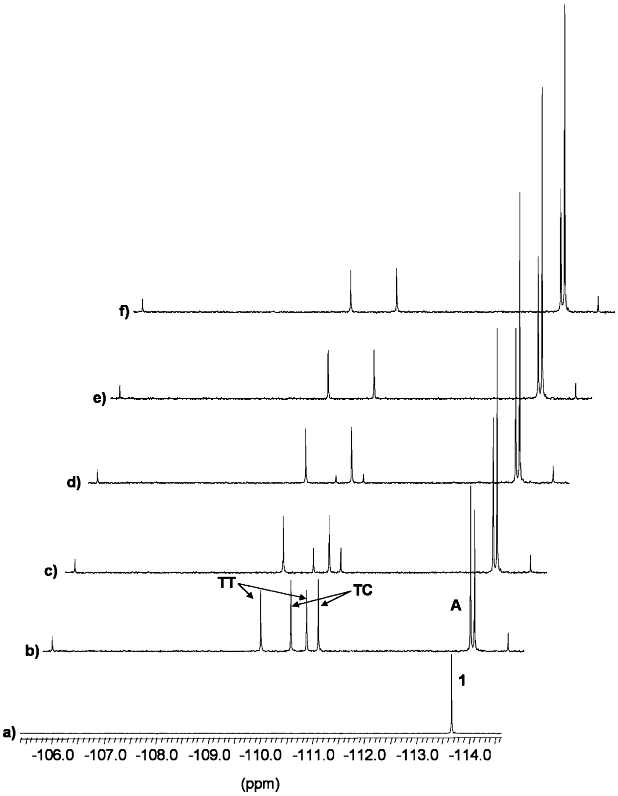

Figure 3. ^{19}F NMR spectra of **1b** in toluene at 243 K. (a) Before irradiation, (b) after 10 min of UV irradiation (time $t = 0$ of thermal fading), (c) $t = 1$ h 30 min, (d) $t = 2$ h 30 min, (e) $t = 6$ h and (f) $t = 12$ h 30 min after end of irradiation.

The 3,3-diphenyl-3H-naphtho[2,1-*b*]pyrans substituted by a carbonyl group in the 5-position are easily prepared. Fifty percent of the open forms are constituted by the TT isomer for all the investigated derivatives. These latter species have been shown to convert back to the closed forms extremely slowly through a thermal process and very efficiently using visible irradiation. All these properties, which were determined at ambient temperature, enable the use of these chromenes as P-type photochromes, that is, photoswitches.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.tetlet.2005.02.091.

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