



## Synthesis and Photochromic Properties of Naphthopyran Dimers

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### Abstract

We realized the synthesis of 2*H*-naphtho[1,2-*b*]pyran derivatives with substituents of halo, methyl at 6-position and/or methyl, cyclopropyl, aryl at the 2-position in addition to three different spironaphtho[1,2-*b*]pyran derivatives with terpene substituents at the 2-spiro position of the pyran ring. The prepared naphtho[1,2-*b*]pyran derivatives **1a-c**, **2a-c**, **3a-c** were subjected to dimerization in acetic acid with a few drops of concentrated sulfuric acid affording the corresponding dimers **4a-i**. The structures of the dimers were confirmed based on the spectral tools (<sup>1</sup>H-NMR and IR spectra). Upon exposure of the produced dimers to unfiltered light, a change from colorless to color state was observed. The effect of the substituent nature at the 2- or 6-positions of dimers on the photochromic properties and thermal fade characteristics was investigated.

**Keywords:** Photochromism; naphthopyrans; irradiation; Dimerization

### 1. Introduction

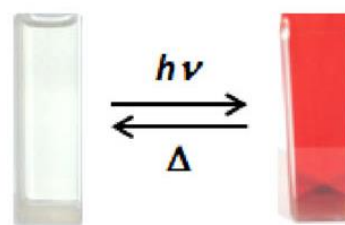
The term “photochromism” was back to the first half of the last century to express the ability of certain compounds to reversibly change their colors under the action of light [1-3].

Last decades, photochromic dyes, which exert reversible photoisomerization, have attracted significant attention due to their implications in several promising applications such as data storage, sensor protection, optical filters, displays, waveguides [4-7].

Naphthopyrans (benzochromene), a class of photochromic compounds, are considered the most

promising photochromic molecules that are used on a large scale by the ophthalmic lens industry to design photosensitive lenses having the ability to darken under sunlight and retrieve their uncolored state in the absence of direct sunlight [8]. This magical property derives from a photochemical reaction, promoted by the ultraviolet light, that induces a

pronounced structural transformation of the construct through the photoinduced heterolytic cleavage of C(sp<sup>3</sup>)-O bond of colorless naphthopyrans (closed forms) in their singlet-excited states affording the so-called *o*-quinonoid intermediates (open forms) [9]. The generation of these opened species with extended conjugation enables intensive absorption in the visible region. Figure 1 shows the development of red color upon ultraviolet irradiation of naphthopyran derivatives, while the colored intermediates could thermally revert to their precursor colorless forms.



**Figure 1.** Reversible color change of naphthopyran derivatives upon irradiation and thermal conditions

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Spironaphthopyrans (SNPs), derivatives of naphthopyrans bearing spirocyclic substituents at the 2-position of the pyran ring, are an important class of photochromics that have been reported to exert transient photochromism even in their crystalline state [10]. This unique characteristic makes them promising targets for time-resolved crystallographic studies [11]. The mechanism of the photochromic process is similar in these molecules and involves a photochemical heterolytic cleaving of the pyran ring. The major disadvantage of most spiroopyran molecules that discourage their extensive use as photochromic molecules for commercial application is the further reaction, which leads to some fatigue products of isomers.

Although the exploration of several modifications to the naphthopyran constructs in order to produce more suitable molecules for the ophthalmic industry, there are rare examples of molecules substituted at the double bond of the pyran ring. This is due to the thermal stability decrease of the photoisomers that occurs due to the steric constraints induced by these substituents, thus encouraging the increase of the fading kinetics that could suppress photochromism at room temperature [12,13].

Several approaches were reported for the synthesis of 2-substituted naphtho[1,2-*b*]pyrans and its spiro derivatives either from coumarins, *o*-hydroxyacetophenone [14], thermal rearrangement of 3-propylether [15,16], the reaction of naphthols with saturated acid chloride [17] or with substituted acrylic derivatives [18,19], and recently an efficient method using palladium/ligand catalysis to induce the cycloaddition between naphthols and Vinylethylene carbonates (VECs) was investigated [20]. The current study investigates the dimerization of several derivatives of 6- and/or 2,2-disubstituted-naphtho[1,2-*b*]pyrans as well as spironaphtho[1,2-*b*]pyrans and studying the effect of substituent nature at the 2- or 6-positions of dimers on the photochromic properties and thermal fade characteristics was investigated.

## 2. Results and discussion

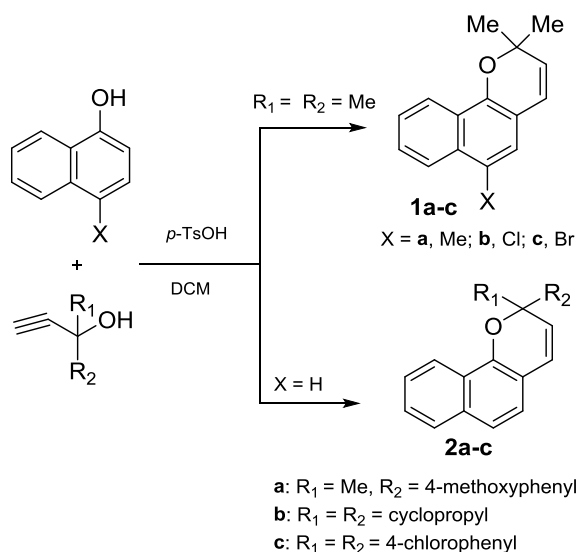
The preparation of naphthopyrans and spironaphthopyrans was reported to proceed by a one-step reaction of substituted naphthols with 1,1-

disubstituted-prop-2-yn-1-ols under the action of acid catalysis. The generated ether intermediates undergo four consecutive intramolecular transformations (Claisen rearrangement, enolization, 1,5-hydrogen shift, and electrocyclization), resulting in the in situ formation of the corresponding naphthopyran derivatives via the loss of one molecule of water [21,22]. This procedure provides a practical route to prepare a series of 2*H*-naphtho[1,2-*b*]pyran derivatives using substituted propargyl alcohol and 1-naphthol. Dimerization of pyrans and spiroopyrans could be achieved by setting aside 2*H*-naphtho[1,2-*b*]pyran derivatives in an acetic acid solution containing few drops of concentrated sulfuric acid for two days giving almost 50% mixture of two polymeric products which were separated by fractional crystallization. Nine 2*H*-naphtho[1,2-*b*]pyran derivatives were synthesized according to this protocol and then were subjected to dimerization giving the corresponding dimers. The structures of these dimeric products were elucidated by the classical spectroscopic and analytical tools.

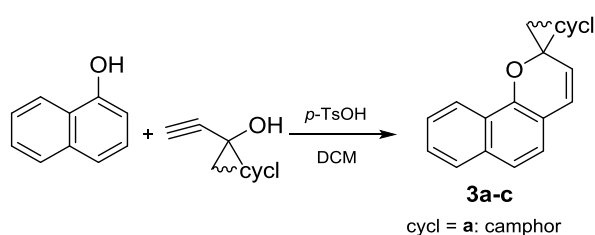
Specifically, reaction of 6-substituted-1-naphthol with 2-methylbut-3-yn-2-ol in dichloromethane (DCM) in the presence of *p*-toluenesulfonic (*p*-TsOH) acid yielded the corresponding 6-substituted 2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran derivatives **1a-c**. Similar treatment of 2,2-disubstituted derivatives of propargyl alcohol with 1-naphthol under the same conditions produced **2a-c** (Scheme 1). Additionally, three different propargyl alcohols with spiroterpenyl substituents could be used for the synthesis of 2,2-spiroterpenyl-2*H*-naphtho[1,2-*b*]pyrans **3a-c** (Scheme 2).

The naphthopyran compounds 1a-c, 2a-c, 3a-c were subjected to dimerization through setting aside of them in acetic acid solution containing few drops of concentrated sulfuric acid for two days to furnish mixture of two polymeric products 4, 5 which were separated by fractional crystallization. The dimerization products of 2,2,6-trimethyl-2*H*-naphtho[1,2-*b*]pyran 1a were identified as 3,4-dihydro-4,3'-bis(2,2,6-trimethyl-2*H*-naphtho[1,2-*b*]pyran 4a for the photochromic fraction, and 6,6,8,8,14,16-hexamethyl-5,9-dioxo-5,6a,14b,6b,7,8-,9-octahydro-benzo[*f*]naphtha[2,1-*J*]fluoranthene 5a for the other fraction. The elucidation of the structures of the produced dimers was achieved based on the spectroscopic and elemental analytical data. Taken compound 4a as an example, the IR spectrum

of this dimer showed an absorption band at  $1625\text{ cm}^{-1}$  in conjugation suggesting the presence of an olefinic bond. The UV spectrum confirmed that the olefinic bond was in conjugation with the aromatic system.



**Scheme 1.** Synthesis of 2,2-disubstituted-naphthopyran derivatives **1a-c**, **2a-c**



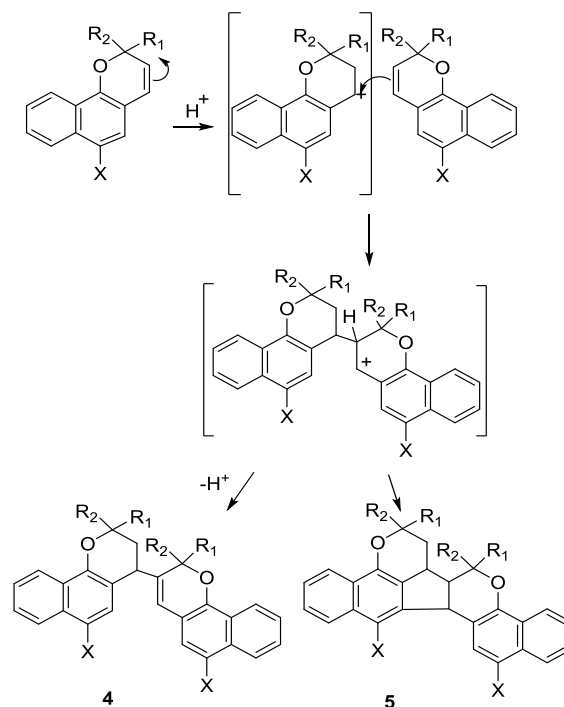
**Scheme 2.** Synthesis of spironaphthopyran derivatives **3a-c**

The  $^1\text{H-NMR}$  spectrum showed the corresponding aromatic protons at 6.4–8.5 ppm while the protons of four methyl groups appeared at 1.29, 1.54, 1.59, 1.69 ppm, and the other six protons of the rest two methyl groups appeared 2.48 ppm, while the olefinic proton of the double bond of the pyran cycle is centered at 6.14 ppm. Moreover, the elemental analysis of the product **4a** showed an empirical formula corresponds to  $\text{C}_{16}\text{H}_{16}\text{O}$ , while the mass spectrum gave the molecular ion peak ( $M^+ = 448$ ) corresponding to the formula  $\text{C}_{32}\text{H}_{26}\text{O}_2$  that establishing a dimer of the naphthopyran.

Similarly, treatment of 6-chloro or 6-bromo derivatives of 2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran **1b,1c** in acetic acid with few drops of concentrated

sulfuric acid gave dimers identified as 3,4-dihydro-4,3-bis(6-halo-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran **4b,4c** respectively. While subjecting **2a-c** to the same conditions induced the dimerization to give the corresponding dimers **4d-4f**. In the same manner, compounds **3a-c** with spiroterpenyl substituents at the 2-position yielded the corresponding dimers 3,4-dihydro-4,3-bis(2,2-spiroterpenyl-2*H*-naphtho[1,2-*b*]pyrans **4g-i**, on subjecting to the same conditions.

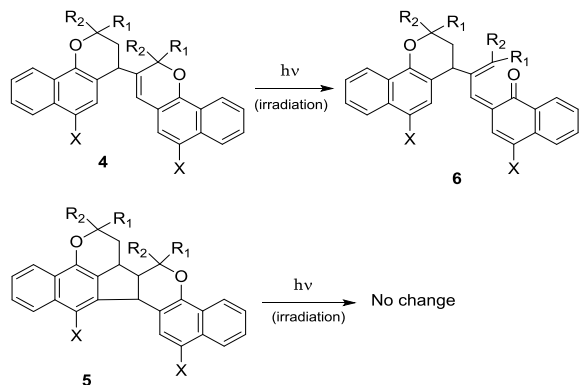
The proposed mechanism for the formation of dimers involves the initial protonation of  $\text{C}_3\text{-C}_4$  olefinic bond of 2*H*-naphtho[1,2-*b*]pyran to produce the benzylic carbonium ion [23]. This carbonium ion attacks the  $\text{C}_3\text{-C}_4$  bond in a second molecule of the naphthopyran to give another carbonium ion which yields the dimer **4** by a Friedel-Crafts type of cyclization through a proton loss, or undergoes intramolecular cyclization to produce **5**.



**Scheme 3.** Synthesis and proposed mechanism for the formation of **4,5**

Irradiation of the 3,4-dihydro-4,3-bis(2,2,6-trimethyl-2*H*-naphtho[1,2-*b*]pyran **4a** in toluene with light from a flashgun resulted in a change from colorless to red. It is expected that the dimerization of the pyran caused a more intense coloration which might be due to the faster thermal fade rate, while irradiation of 6,6,8,8,14,16-hexamethyl-5,9-dioxo-6a,14b,6b,7,7,9-octahydrobenzo[*f*]naphtha[2,1-*J*]fluoranthene **5a**

show no color change and this can be rationalized on the basis of the presence of the olefinic bond in **4** facilitates the ring-opening and lead to the generation of the extended conjugated product **6** with deep color, while the olefinic double bond is absent in case of **5**.



Scheme 3. Irradiation of **4,5**

The irradiation of compounds **4b-i** under the aforementioned conditions gave the same color change. Indeed, the introduction of the substituents at the 6-position caused a bathochromic shift of the long-wavelength absorption band of the colored form with a value of (12nm) for compounds **4b,c**, (20 nm) for **4d**, and (30 nm) for **4e** compared to **4a**.

There are some similarities in the chemical and physical properties of cyclopropyl group and double bonds of the aryl groups and this was reflected on the introduction of cyclopropyl group into the 2-position of naphthopyran that was found to induce a significant bathochromic shift of the long-wavelength absorption bands of their color forms with a value of (25 nm) for compound **4f** compared to **4a**. The red solution shows two distance fade rates, a fast and slow fade rates. The two fade rates are presumably due to subsequent cyclization of the *cis o*-quinonoid adduct (Scheme 3).

While the presence of the bulky rigid inflexible spiro groups (campher, fenchyl, adamantyl) at the 2-position is believed to weaken the C-O bond and facilitate photo-cleavage of the pyran ring and inducing a fast development of red color upon irradiation with a bathochromic shift of (18 nm) of the long-wavelength absorption band of the colored form for **4g-i** compared to **4a**. While no color change was observed upon irradiation of the counterparts **5a-i**.

## Experimental:

Chemicals were purchased from commercial sources and used as received. Melting points were determined on a Racht hot-stage microscope with thermometer. NMR spectra ( $\text{CDCl}_3$ ) were recorded on a Perkin-Elmer R32 spectrometer (90 MHz) downfield from the internal standard tetramethylsilane (TMS). IR spectra were recorded with a PerkinElmer 1720 spectrometer. Mass spectra (MS) were recorded using electron ionization (E.I.) on a Varian Mat 311A spectrometer. Compounds **1-3** were prepared following the literature protocol [13,14].

## General procedure for the synthesis of 3,4-dihydro-4,3-bis-(2H-naphtho[1,2-b]pyran) dimers (**4a-i**)

A solution of acetic acid (0.1mol) with a few drops of sulfuric acid was added gently to the substituted naphthopyrans **1-3** (0.1 mol), and the reaction mixture was left for two days. The reaction mixture solution was neutralized with an aqueous solution of sodium hydroxide (10 %) and then washed with water, dried, and the traces of solvent was removed under reduced pressure to give a gum. This formed gume was subjected to purification by column chromatography on silica gel using petroleum ether (b.p. 60-80) as eluent:

### 3,4-Dihydro-4,3'-bis(2,2,6-trimethyl-2H-naphtho[1,2-b]pyran) (**4a**)

Product **4a** was separated as colourless needles, m.p. 276 °C. IR (KBr,  $\text{cm}^{-1}$ ): 1626 (C=CH conj.).  $^1\text{H}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  8.5-6.4 (10H, aromatic); 6.14 (1H, s, =CH); 3.79 (1H, m, CH); 2.48 (6H, s, 2CH<sub>3</sub>); 2.19 (1 H, m, CH); 1.99 (1 H, m, CH); 1.69 (3H, s, CH<sub>3</sub>); 1.59 (3H, s, CH<sub>3</sub>); 1.54 (3H, s, CH<sub>3</sub>); 1.29 (3H, s, CH<sub>3</sub>). Anal. Calcd. For C<sub>32</sub>H<sub>26</sub>O<sub>2</sub> (448.24): C, 85.68; H, 7.19 %. Found: C, 85.78; H, 7.31 %.

### 3,4-Dihydro-4,3-bis(6-chloro-2,2-dimethyl-2H-naphtho[1,2-b]pyran) (**4b**)

Product **4b** was separated as colourless oil; IR (KBr,  $\text{cm}^{-1}$ ): 1627 (C=CH conj.).  $^1\text{H}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49-7.12 (m,10H, Ar-H); 6.1 (s, 1H, =CH); 3.79 (m,1H, CH); 2.22 (m,1H, CH); 1.99

(m, 1H, CH); 1.72 (s, 3H, CH<sub>3</sub>); 1.64 (s, 3H, CH<sub>3</sub>); 1.6 (s, 3H, CH<sub>3</sub>); 1.35 (s, 3H, CH<sub>3</sub>).

**3,4-Dihydro-4,3-bis-(6-bromo-2,2-dimethyl-2H-naphtho[1,2-b]pyran 4c**

Product **4c** was separated as white needles; IR (KBr, cm<sup>-1</sup>): 1627 (C=CH conj.). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 8.4-7.2 (m, 10H, Ar-H), 6.1 (s, 1H, =CH); 3.82 (s, 1H, CH), 2.22 (m, 1H, CH), 1.99 (m, 1H, CH), 1.72 (s, 3H, CH<sub>3</sub>), 1.64 (s, 3H, CH<sub>3</sub>), 1.6 (s, 3H, CH<sub>3</sub>), 1.35 (s, 3H, CH<sub>3</sub>).

**3,4-Dihydro-4,3-bis(2-methyl-2-(4-methoxyphenyl)-2H-naphtho[1,2-b]pyran 4d**

Product **4d** was separated as white needles; IR (KBr, cm<sup>-1</sup>): 1625 (C=CH conj.). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 8.43-7.22 (20H, m, Ar-H); 6.1 (1H, s, =CH); 3.82 (1H, s, CH); 3.68 (3H, s, OCH<sub>3</sub>); 3.64 (3H, s, OCH<sub>3</sub>); 2.2-2.15 (1H, m, CH) 1.97-2.0 (1H, m, CH); 1.65 (3H, s, CH<sub>3</sub>); 1.40 (3H, s, CH<sub>3</sub>).

**3,4-Dihydro-4,3-bis[2,2-di(4-chlorophenyl)-2H-naphtho [1,2-b] pyran (4e)**

Product **4e** was separated as white needles m.p. 287 °C; IR (KBr, cm<sup>-1</sup>): 1627 (C=CH conj.). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 8.41-7.20 (28H, m, Ar-H); 6.1 (1H, s, =CH); 3.82 (1H, s, CH); 2.25 (1H, m, CH); 1.96 (1H, m, CH).

**3,4-Dihydro-4,3-bis-[2,2-di-(cyclopropyl)-2H-naphtho[1,2-b]pyran (4f)**

Product **4f** was separated as white needles m.p. 252 °C; IR (KBr, cm<sup>-1</sup>): 1627 (C=CH conj.). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 8.15-7.65 (12H, m, Ar-H); 6.9 (1H, s, =CH); 4.12 (2H, m, CH<sub>2</sub>); 2.6-2.55 (m, 1H, CH), 1.25-1.18 (4H, m, CH<sub>cycl.</sub>); 0.78-0.65 (4H, m, CH<sub>2cycl.</sub>); 0.5-0.35 (12H, m, CH<sub>2cycl.</sub>).

**3,4-Dihydro-4,3-bis[2,2-(spirocampher)-2H-naphtho[1,2-b]pyran (4g)**

Product **4g** was separated as yellow oil. IR (KBr, cm<sup>-1</sup>): 1627 (C=CH conj.). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 7.65-6.70 (m, 6H, Ar-H), 6.63 (s, 1H, =CH), 6.55-6.35 (m, 6H, Ar-H); 4.35 (s, 1H, CH), 2.6-2.55 (m, 2H, CH); 2.35-2.20 (1H, m, CH), 2.10-1.99 (m, 1H, CH), 1.85-0.90 (12H, m, CH<sub>2</sub>); 1.6 (6H, s, 2CH<sub>3</sub>); 0.89 (6H, s, 2CH<sub>3</sub>); 0.72 (6H, s, 2CH<sub>3</sub>).

**3,4-Dihydro-4,3-bis[2,2-(spirofenchyl)-2H-naphtho [1,2-b] pyran (4h)**

Product **4h** was separated as colourless crystals m.p. 150 °C. IR (KBr, cm<sup>-1</sup>): 1625 (C=CH conj.). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 7.55-7.35 (m, 12H, Ar-H); 6.65 (s, 1H, =CH); 4.40 (m, 1H, CH); 2.6-2.55 (2H, m, CH); 2.19 (1H, m, CH); 2.25 (m, 1H, CH); 1.96-0.90 (m, 12H); 1.6 (6H, s, 2CH<sub>3</sub>); 0.89 (6H, s, 2CH<sub>3</sub>); 0.72 (6H, s, 2CH<sub>3</sub>).

**3,4-Dihydro-4,3'-bis[2,2-(spiroadamantyl)-2H-naphtho[1,2-b]pyran (4i)**

Product **4i** was separated as pale yellow crystals, m.p. 269 °C. IR (KBr, cm<sup>-1</sup>): 1622 (C=CH conj.). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>) δ 7.65-6.35 (m, 12H, Ar-H); 6.63 (s, 1H, =CH); 4.35 (H, m, CH); 2.20 (1H, m, CH); 1.99 (1H, m, CH); 1.80-1.56 (28H, m, adamantyl).

### 3. Conclusion

In this study, we achieved the synthesis of 6-substituted-2,2-dimethyl-2H-naphtho[1,2-b]pyran derivatives **1a-c** and other 2H-naphtho[1,2-b]pyran derivatives **2a-c**, **3a-c** with alkyl, aryl, alicyclic, or terpene substituents at the 2-position. The prepared naphtho[1,2-b]pyran derivatives were subjected to dimerization in acetic acid with a few drops of concentrated sulfuric acid affording the corresponding dimers **4a-i** whose structures were elucidated based on nuclear magnetic resonance (NMR) analysis. The prepared dimers were found to change from colorless to color adducts on exposure to unfiltered light from the flashgun. The nature of substituents at the 2- or 6-positions was found to have a considerable effect on the photochromic properties and thermal fade characteristics of the dimers.

### 4. Conflicts of interest

“There are no conflicts to declare”.

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