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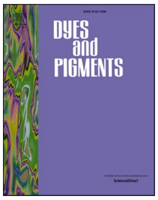

# Spectral manifestation of protonation of photochromic naphthopyrans

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ABSTRACT

The formation of proton complexes of the photoinduced colored open form of naphthopyrans in solutions was first discovered and investigated by spectral-kinetic method. The complexes exhibit a new absorption band in the visible region, which is bathochromically shifted relative to the absorption band of the photoinduced colored open form. With an increase in the concentration of perchloric or hydrochloric acid, this long-wavelength absorption band appears immediately after the addition of acids to solutions of photochromic compounds. The protonation efficiency depends on the strength of the acids.

## 1. Introduction

The protonation processes of spiropyrans have been most widely studied to date [1–5]. Studying the protonation of nitro-substituted indoline spiropyrans has shown that adding acids to solutions of photochromic compounds results in proton complexes with molecules of the merocyanine form of spiropyrans. The complexes absorb in a shorter-wavelength spectral region (400–430 nm) than the merocyanine form of these compounds (500–650 nm).

Unlike the protonation of spiropyrans, the protonation of photochromic naphthopyrans (chromenes) has not been adequately studied. These compounds are of particular scientific and practical interest because of their use for the manufacture of photochromic ophthalmic lenses [6–9] and the prospects for their application as chemosensors for metal ions [10–12], neuromorphic engineering [13], photoswitches, photocontrolled molecular electronic devices, etc. [7].

Photochromic transformations of chromenes are based on reversible photodissociation of the —C—O— bond in the pyran ring of the initial colorless cyclic compound A and the subsequent *cis-trans* isomerization forming the colored open form B. The back reaction is spontaneous and is accelerated by heating or by the action of visible light (Scheme 1).

The key studies concerned with the formation of proton complexes of the photoinduced colored open form B of chromenes addressed the effect of intramolecular hydrogen bonds on the thermal stability of form B of functionalized chromenes [14–20]. It was found that, in contrast to aryl-substituted naphthopyrans, nitrogen-containing chromenes, when react with acids, become colored and give rise to a new long-wavelength absorption band without UV irradiation [21]. N-Protonated pyranoquinolines lose the photochromic properties [22].

This paper describes a spectral-kinetic study of the protonation of naphthopyrans containing no functional substituents.

## 2. Experimental

3,3-Diphenyl-3H-naphtho[2,1-*b*]pyran (I), 3,3-di(4-methoxyphenyl)-3H-naphtho[2,1-*b*]pyran (II), and 3,3-di(4-methoxyphenyl)-3H-anthro[2,1-*b*]pyran (III) were used in the study as photochromic compounds (Scheme 2).

Naphthopyrans I and II were obtained using 2-naphthol and 1,1-diphenyl-2-propyn-1-ol or 1,1-(4,4′-dimethoxyphenyl)-2-propyn-1-ol, respectively, by heating 2-naphthol with a propynol in toluene at 50–60 °C in the presence of toluene sulfonic acid as a catalyst. Naphthopyran III was synthesized according to a similar procedure, but using 2-anthrol as a substrate. Propargyl alcohols were obtained from benzophenone and 4,4′-dimethoxybenzophenone by procedures commonly used for reactions of this type. Thus, 1,1-(4,4′-dimethoxyphenyl)-2-propyn-1-ol was isolated from the reaction of 4,4′-dimethoxybenzophenone with the ethylenediamine complex of lithium acetylide in anhydrous dimethyl sulfoxide. 1,1-Diphenyl-2-propyn-1-ol was a commercial chemical.

For preparing solutions, acetonitrile (Aldrich) was used as a solvent.

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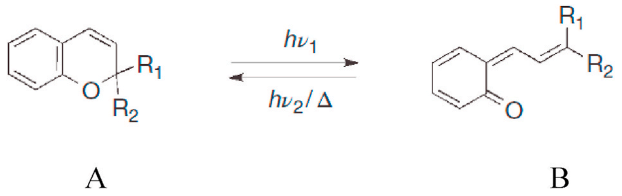


**Scheme 1.** Photochromic transformations of chromenes.

The initial concentration of photochromic compounds in the solution was C = 4 × $10^{-4}$ M. Protonation processes were studied using citric, hydrochloric (HCl), and perchloric ($HClO_4$) acids, with naphthopyran to acid molar ratios being 1:10 and 1:100. When studying the effect of acids, solutions of photochromic compounds and acids were mixed in a ratio of 1:1 (by volume). In these mixed solutions, the concentration of photochromic compounds was constant (C = 2 × $10^{-4}$ M), while the concentration of acids varied from C = 2 × $10^{-2}$ M to C = 2 × $10^{-4}$ M.

The spectral-kinetic measurements were performed on the Cary 60 UV–Vis spectrophotometer (Varian) in a quartz cell with an optical path length of 0.2 cm.

The UV irradiation of the solutions was carried out with the light of a LC-4 L8253 xenon lamp (Hamamatsu) through a UFS-1 glass light filter that transmits UV light.

## 3. Results and discussion

The spectral-kinetic characteristics of the photochromic transformations of naphthopyrans in acetonitrile are presented in Table 1.

Table 1 shows that the introduction of methoxy groups into the phenyl moieties of naphthopyran I virtually does not affect the positions of the absorption bands of the initial closed form A, but leads to a bathochromic shift of the photoinduced absorption maximum of form B for compound II by 50 nm. In this case, the rate of dark bleaching of photoinduced form B increases, which leads to a decrease in the photoinduced change in optical density at the absorption maximum of this form located in the visible region.

In the case of compound III, annulation of the benzene ring causes a bathochromic shift of not only the absorption band of the photoinduced open form B, but also the absorption bands of the closed isomer A. In contrast to compounds I and II, this compound is colored in the initial state, since it absorbs in the 400–450 nm range. It discolors most slowly in the dark and, therefore, it is characterized by the most pronounced change in the optical density under UV light.

Fig. 1 and Table 2 show that, in contrast to the absorption spectra of the initial colorless closed form A (Fig. 1, curve 1) and photoinduced colored open form B (Fig. 1, curve 3) of naphthopyran I, in this case, the addition of hydrochloric acid to the solution gives rise to a new long-wavelength absorption band with a maximum at 600 nm (Fig. 1, curve 4). This band is absent in the absorption spectrum of a photochromic solution containing an acid before irradiation (Fig. 1, curve 2). The intensity of the photoinduced absorption band with a maximum at 420 nm decreases upon addition of the acid compared to that for acid-free solution (Fig. 1, curve 3). This can be attributed to the formation of the protonated colored open form, which absorbs in the long-wavelength spectral range.

**Table 1**
Spectral-kinetic characteristics of photochromic transformations of naphthopyrans I-III in acetonitrile.

| Compound | $\lambda_A$ $^{max}$, nm | $\varepsilon_A$, $cm^{-1}.M^{-1}$ | $\lambda_B$ $^{max}$, nm | $\Delta D_B^{phot}$ | $k_{db}$, $s^{-1}$ |
|---|---|---|---|---|---|
| I | 302 | 7600 | 425 | 0.49 | 0.158 |
| | 315 | 9000 | | | |
| | 345 | 6000 | | | |
| | 358 | 5800 | | | |
| II | 303 | 5900 | 475 | 0.01 | 0.869 |
| | 316 | 6825 | | | |
| | 347 | 4575 | | | |
| | 357 | 4400 | | | |
| III | 324 | 4350 | 485 | 0.66 | 0.092 |
| | 344 | 3950 | | | |
| | 362 | 4075 | | | |
| | 385 sh | 3475 | | | |
| | 402 | 5400 | | | |
| | 424 | 4600 | | | |

Note: $\lambda_A^{max}$, $\lambda_B^{max}$ are the wavelengths of the absorption maxima for initial and photoinduced forms, respectively; $\varepsilon$ is the molar extinction coefficient at the absorption maximum of form A; $\Delta D_B^{phot}$ is the photoinduced change of absorbance at the absorption maximum of the photoinduced form at the photoequilibrium; $k_{db}$ is the rate constant of dark relaxation of absorbance at the photoinduced long-wavelength absorption maximum.

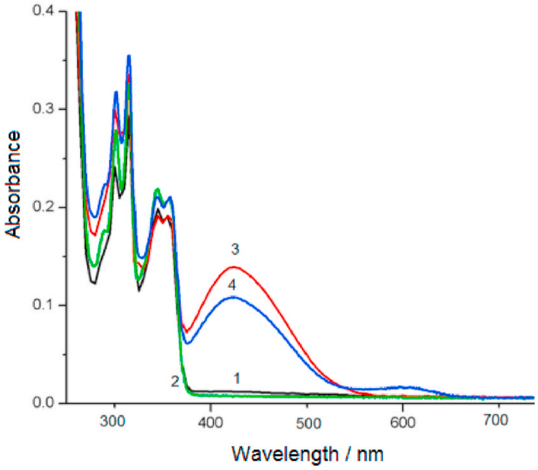
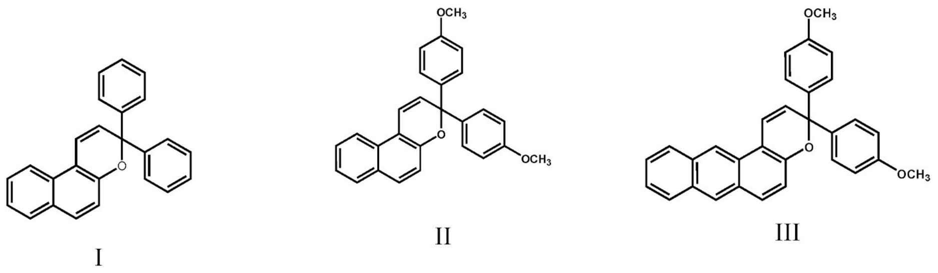


**Fig. 1.** Absorption spectra of naphthopyran I in acetonitrile in the absence (1, 3) and in the presence (2, 4) of hydrochloric acid HCl (1:1) before (1, 2) and after (3, 4) UV irradiation.

Similar spectral changes are also observed in the presence of perchloric acid (Table 2). With increasing acid concentration in solution, the magnitude of the photoinduced absorbance at the absorption maximum of the photoinduced protonated form increases simultaneously with an increase in the rate of its dark relaxation to the initial



**Scheme 2.** Structures of chromenes.

**Table 2**
Spectral-kinetic characteristics of naphthopyran I and its protonated complexes in acetonitrile.

| Acid (chromene: acid molar ratio) | $\lambda_B^{max}$, nm | $\Delta D_B^{phot}$ | $k_{db}$, $s^{-1}$ |
|---|---|---|---|
| – | 425 | 0.49 | 0.158 |
| HCl (1:100) | 420 | 0.41 | – |
| | 600 | 0.02 | |
| $HClO_4$ (1:10) | 420 | 0.28 | 0.173 |
| | 595 | 0.18 | 0.177 |
| $HClO_4$ (1:100) | 595 | 0.44 | 0.257 |

closed form (Table 1).

Similar photoinduced spectral changes were also observed in solutions of naphthopyran II, which differs from compound I by the presence of methoxy groups in the *p*-positions of the benzene rings (Fig. 2, Table 3). The absorption bands of the colored open form B are bathochromically shifted by 50 nm, and the absorption band of the photoinduced protonated colored open form B undergoes a bathochromic shift of 25 nm relative to the corresponding bands of naphthopyran I. The introduction of the methoxy groups into the molecule increases the intensity of the long-wavelength absorption band of the protonated form.

It can be seen from Fig. 2 that at a 1:10 concentration ratio of photochromic chromene II and hydrochloric acid, the long-wavelength absorption band appears immediately after the addition of the acid, i.e., before UV irradiation of solutions. Its intensity increases with increasing acid concentration in the solution (Fig. 3, curves 5 and 7). This is the dark protonated form.

Dark and photoinduced spectral changes of the same type are also observed for naphthopyran II in acetonitrile in the presence of perchloric acid $HClO_4$ (Fig. 3, Table 2).

In contrast to naphthopyran I, the rate constant of dark relaxation of the photoinduced protonated form of naphthopyran II decreases with increasing acid strength in comparison with the relaxation rate constant of the photoinduced colored open form B in the absence of an acid in solution. The constant is not significantly dependent on the acid concentration, but decreases sharply with increasing acid strength.

Compound II in acetonitrile, in the presence of HCl and $HClO_4$, shows reversibility of changes in the intensity of the long-wavelength bands of the photoinduced protonated complex during alternate UV irradiation and dark relaxation (Fig. 4). However, visible light irradiation of the photoinduced colored solution does not change the intensity of these absorption bands.

The absorption band observed in the visible spectral region and appearing immediately when an acid solution is added to a solution of a photochromic compound (a dark protonated complex) gradually but slowly disappears during storage of the solution in the dark (Fig. 5). As in the case of photoinduced coloration, visible light does not affect the spontaneous bleaching of the dark protonated complex in the solution.

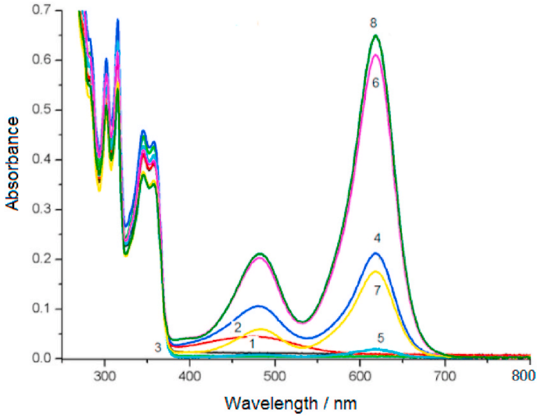


**Fig. 2.** Absorption spectra of naphthopyran II in acetonitrile in the absence (1, 2) and in the presence of hydrochloric acid for molar ratios of 1 : 1 (3, 4), 1 : 10 (5, 6); and 1 : 100 (7, 8) before (1, 3, 5, 7) and after (2, 4, 6, 8) UV irradiation.

**Table 3**
Spectral-kinetic characteristics of naphthopyran II and its protonated complexes in acetonitrile.

| Acid (chromene:acid molar ratio) | $\lambda_B^{max}$, nm | $\Delta D_B^{phot}$ | $k_{db}$, $s^{-1}$ |
|---|---|---|---|
| – | 475 | 0.01 | 0.869 |
| HCl (1:10) | 475 | 0.14 | 0.522 |
| | 620 | 0.30 | |
| HCl (1:100) | 478 | 0.17 | 0.520 |
| | 620 | 0.50 | |
| HClO4 (1:10) | 480 | 0,62 | 0.076 |
| | 620 | 1.70 | |
| $HClO_4$ (1:100) | 480 | 0.70 | 0.075 |
| | 620 | 1.80 | |

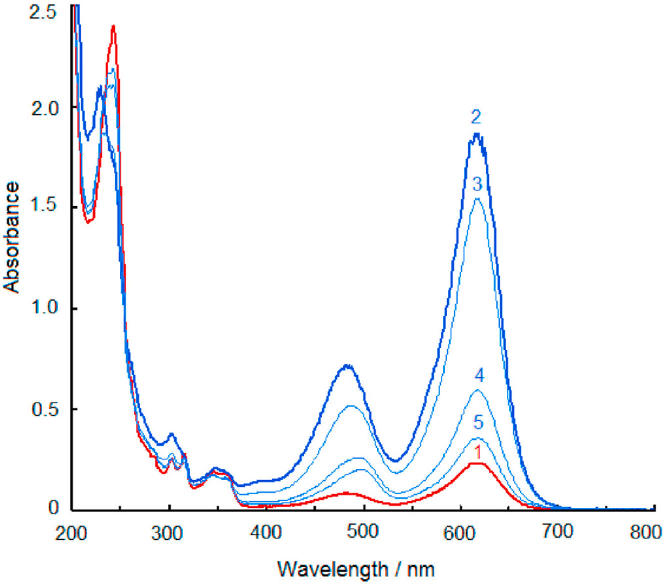


**Fig. 3.** Absorption spectra of naphthopyran II in acetonitrile in the presence of $HClO_4$ in 1:100 M ratio before (1) and after UV irradiation (2) and during dark relaxation (3–5).

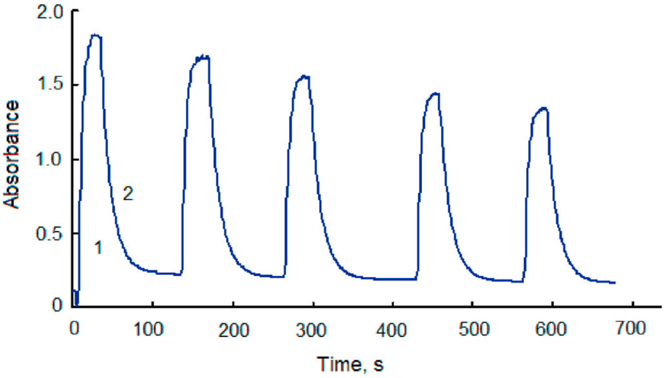


**Fig. 4.** Kinetics of UV coloration (1) and dark bleaching (2) for naphthopyran II in acetonitrile in the presence of $HClO_4$ (1:100) measured at a wavelength of 620 nm.

The results obtained for naphthopyran III are similar to those observed for compounds I and II (Fig. 6, Table 4). The difference is only in the shift of the absorption maxima observed in the visible region. The short-wavelength photoinduced absorption band is shifted bathochromically by 10 nm and the long-wavelength band is shifted by 75

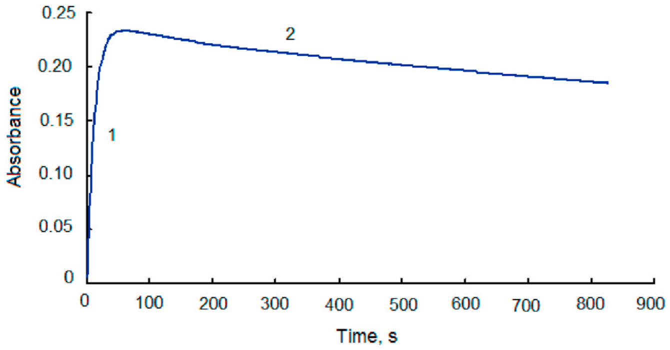


**Fig. 5.** Kinetics of dark coloration and subsequent bleaching of naphthopyran II in acetonitrile after addition of $HClO_4$ (1 : 100) to the photochromic compound solution measured at a wavelength of 620 nm.

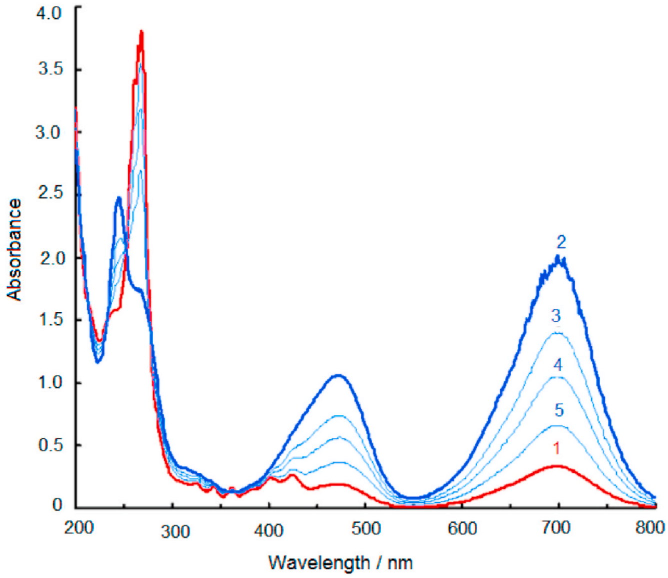


**Fig. 6.** Absorption spectra of naphthopyran III in acetonitrile in the presence of $HClO_4$ (1:100) before (1) and after UV irradiation (2) and during dark relaxation (3–5).

**Table 4**
Spectral-kinetic characteristics of naphthopyran III and its protonated complexes in acetonitrile.

| Acid (chromene: acid molar ratio) | $\lambda_B^{max}$, nm | $\Delta D_B^{phot}$ | $k_{db}$, $s^{-1}$ |
|---|---|---|---|
| – | 485 | 0.66 | 0.092 |
| Citric acid (1:10) | 487 | 0.55 | – |
| Citric acid (1:100) | 488 | 0.52 | – |
| HCl (1:10) | 480 | 0.63 | 0.068 |
|  | 695 | 0.19 |  |
| HCl (1:100) | 470 | 0.74 | 0.066 |
|  | 695 | 0.95 |  |
| $HClO_4$ (1:10) | 470 | 1.00 | 0.016 |
|  | 695 | 1.62 |  |
| $HClO_4$ (1:100) | 470 | 1.10 | 0.014 |
|  | 695 | 1.93 |  |

nm on going from naphthopyran II to compound III in the presence of perchloric acid $HClO_4$ (1: 100).

When weak citric acid is introduced into the solution of naphthopyran III in acetonitrile, the long-wavelength absorption band is not observed either before or after UV irradiation (Fig. 7, Table 4). Consequently, the efficiency of naphtopyran protonation depends on the acid strength [20].

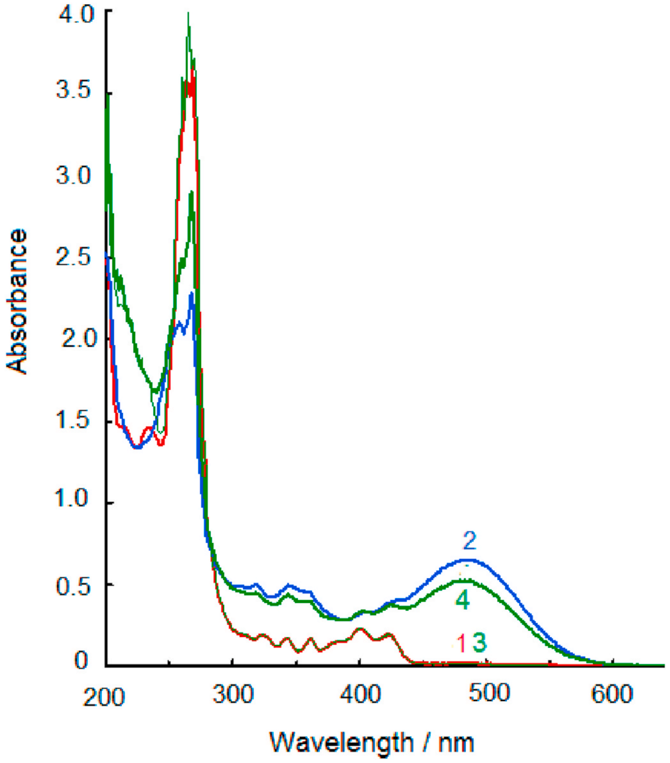


**Fig. 7.** Absorption spectra of naphthopyran III in acetonitrile without (1,2) and with citric acid (3,4) at 1:100 M ratio before (1,3) and after UV irradiation (2,4).

Thus, unlike the proton complexes of spiropyrans, which are characterized by a hypsochromic shift of the absorption band of the merocyanine form to the UV spectral range, photoinduced protonation of naphthopyrans is manifested, on the contrary, in the appearance of an absorption band in the long-wavelength spectral region with a maximum more than 120 nm away from the maximum of the photoinduced absorption band of chromene observed in the absence of acid in solution. The intensity of this band increases with increasing acid concentration. Photoinduced colored proton complexes experience reversible dark relaxation, but are insensitive to visible light. No absorption band of the protonated complexes appears when weak citric acid (pKa = 3.1) is added to the solution. The band is observed in the presence of strong hydrochloric (pKa = −9) or perchloric (pKa = −10) acid.

As the acid concentration in the solution increases, a similar absorption band, along with the absorption band of the colored open form B of chromenes, appears in the absorption spectra of chromene solutions before irradiation. This is a result of equilibrium shift from the initial closed form A towards the formation of protonated complexes, which do not bleach under visible light, but slowly disappear in the dark.

Experimental data indicate that proton complexes are formed in acetonitrile solutions of chromenes in the presence of strong acids. These complexes arise as a result of interaction between negatively charged phenoxide oxygen of the open form and a proton. The photoinduced proton complexes are thermally unstable, insensitive to visible light, and are transformed into their original closed form A in the dark. The colored proton complexes formed in the dark in the presence of high concentrations of strong acids and possessing spectral properties of the photoinduced complexes do not exhibit photochromic properties and are extremely slowly spontaneously bleached. Perhaps, their appearance is attributable to the formation of associates of proton complexes with a closed and/or photoinduced open form.

## 4. Conclusion

A spectral-kinetic study of the protonation of photochromic compounds of the naphtopyran class in acetonitrile was carried out. It was shown for the first time that the protonation of these compounds upon the addition of acids to solutions gives rise to a photoinduced long-wavelength absorption band, which is bathochromically shifted by 120 nm relative to the absorption band of the photoinduced colored open form. Its appearance depends on the strength of the acid. The arising proton complexes exhibit positive photochromism. When strong acids are introduced into the solutions of naphthopyrans in high concentrations, non-photochromic colored products are formed.

## CRediT authorship contribution statement

**Alexander M. Gorelik:** Methodology, Investigation, Synthetic Investigation. **Olga V. Venidiktova:** Methodology, Investigation, Spectral – Kinetic Investigation, Data curation. **Olga I. Kobeleva:** Methodology, Investigation, Spectral – Kinetic Investigation, Data curation. **Tatyana M. Valova:** Investigation. **Valery A. Barachevsky:** Project administration, Conceptualization, Investigation, Writing - original draft, Writing - review & editing, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108833.

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