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Photochromic Properties of Ferrocene Substituted Chromenes

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The spectral and kinetic characteristics for a number of ferrocenyl substituted naphthopyrans as compared with diphenyl substituted analogs are presented. The effect of the ferrocenyl substituent on photoinduced absorption and luminescent properties as well as the kinetic characteristics of photochromic transformations and photodegradation was studied.

Keywords: photochromism; naphthopyran; photodegradation; ferrocene

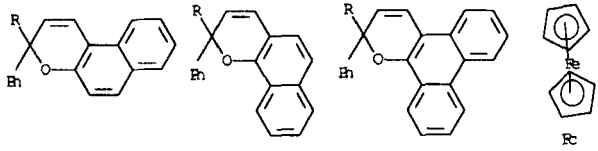
INTRODUCTION

As of now, chromenes become a very important class of photochromic compounds because of advances in the development of photochromic sun protective plastic lenses based on them [1]. There are results exhibiting dependence between structures and photochromic properties for these compounds [1].

This paper presents results of the following comparative spectral and kinetic investigations of ferrocenyl containing naphthopyrans synthesized and preliminary studied before ones by from us[2].

EXPERIMENTAL

The following naphthopyran derivatives were investigated:



NP1 : R=Ph NP3 : R=PhNP5 : R=Ph

NP2 : R=Fc NP4 : R=FcNP6 : R=Fc

The methods for the synthesis of compounds NP1-NP4 were presented earlier [2]. Compounds NP5 and NP6 were obtained by the same synthetic scheme involving reaction of ferrocenyl propargylic alcohol on phenantren-9-ol in CH_2Cl_2 [3].

Absorption spectra and kinetic curves were taken with a SHIMADZU UV-3100 spectrophotometer as well as a laboratory –

made apparatus upon excitation with continuous or pulsed irradiation from Xe-arc lamps with energy of 400 J in a pulse of 0.5 msec. Fluorescence spectra were measured with a SHIMADZU KA-5000 spectrofluorimeter. Thoroughly purified toluene, ethanol and other solvents were used in luminescence investigations. Concentration of photochromic compounds in solution was usually $C=2.10^{-4}$ M. Comparative investigation of the efficiency of naphthopyrans photodegradation was carried out using monochromatic irradiation (λ=365nm) allotted by filters from light of the mercury lamp with a power of 250 W.

RESULTS AND DISCUSSION

As it was found before [2] in all cases the change of the phenyl substituent by the ferrocenyl group leads to the appearance of photoinduced spectra with two maxima as compared with the diphenyl substituted analogs (Table 1). The appearance of two absorption maxima may be explained by manifestation of two π–electron conjugated chains including phenyl or ferrocene substituents. This speculation may be based on the absorption band of cation radical ferrocene which is surrounded at 610 nm [4].

The comparative investigations of spectral characteristics for the photoinduced forms of investigated compounds with two phenyl substituents show that asymmetric annellation (NP3) leads to the long-wave shift of the absorption maximum for the photoinduced form as

Table 1. Characteristics of photochromic transformations in toluene.

NP	D_o / λ_{max}, nm	$D_{uv\ flash} / \lambda_{max}$, nm	$D_{uv\ continuous} / \lambda_{max}$, nm	$K_{thermal}$ at 22°C	$T_{0.5}^{degrad.}$, hours
1	0	0.24 / 435	1.2 / 435	0.062	2.0
3	0	0.15 / 470	2.3 / 475	0.0007	1.7
5	0.012 / 430	0.20 / 430	1.85 / 450	0.0025	-
2	0.006 / 445 0.004 / 605	0.043 / 440 0.027 / 600	0.14 / 445 0.10 / 605	0.16	> 4.0
4	0.012 / 455 0.010 / 600	0.034 / 475 0.030 / 610	1.30 / 480 1.40 / 610	0.0013	2.4
6	0.080 / 445 0.038 / 585	0.076 / 450 0.042 / 585	1.20 / 445 0.70 / 585	0.006	2.8

compared with compounds NP1 and NP5 (Table1). For compound NP5 in toluene initial coloration is observed which is due to the shift of equilibrium between initial form and open form and the increase of the polarisability. Unlike diphenyl substituted naphthopyrans, the same effect is observed for all ferrocenyl substituted chromenes (Table1).

The change of the phenyl substituent by the ferrocenyl group decreases the photoinduced optical density in the maximum of the absorption band under flash or permanent irradiation (Table1). This effect is due partially to the decreasing of the life-time of the photoinduced forms for ferrocenyl derivatives as compared with diphenyl-naphthopyrans (Table1). Another reason is the appearance of the absorption band with two maxima. This experimental fact supports performances about two π–electron conjugation chains.

The effect of introduction of ferrocenyl substituent instead of the phenyl group is exhibited in the difference of photodegradation of photochromic properties for investigated chromenes (Table 1).

Changing the phenyl group by ferrocenyl one leads to increasing photostability of naphthopyrans. This effect is in concordance with the same effect of ferrocene on photostabilization of spiropyran solution [5]. It was explained by the metal influence on intermolecular deactivation of reactive excited states of photochromic molecules.

The strong effect of substituent chaining is exhibited in fluorescence characteristics of investigated naphthopyrans (Table 2).

Table 2. Maxima of photoinduced absorption and fluorescence spectra

NP	λ_{max}^{abs}, nm	λ_{max}^{fl}, nm
1	435	535
3	470	640
5	425	530
2	450, 610	Fast thermal bleaching
4	475, 615	485
6	445, 585	520

The diphenyl substituted naphthopyrans exhibit fluorescent properties in initial and photoinduced forms. The received data show that the changing of the maxima positions of absorption and fluorescence spectra depends on the molecular structure. We suppose that the observed difference is due to the change of the conjugation chain.

It is very interesting that the change of fluorescent characteristics depends on the substituent character. For diphenyl substituted chromenes the absorption and luminescence spectra with a single maximum are observed. The change of one from the two phenyl groups by the ferrocenyl substituent leads to appearance of the photoinduced absorption spectrum with two maxima but a single

fluorescent band. The spectrum of photoinduced fluorescence is alike one for the diphenyl containing compounds. We suggest that the absorption maxima belong to the above mentioned different π–electron conjugation chains.

CONCLUSION

The results of carried out investigation show that changing one from the two phenyl groups of naphthopyrans by ferrocenyl substitutent leads to strong differences of absorption and luminescent spectral as well as kinetic characteristics. These results may be explained by the realisation of two different π–electron conjugation molecule chains.

The 7-8 annellation is more favorable to the colorability.

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