

# Photophysical and photochemical processes in cinnamoyl pyrones: influence on spectral properties and photostability

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*Received May 23, 2011*

The presented work is devoted to investigations of the relationship between spectral properties, photo stability and excited-state kinetic characteristics of cinnamoyl pyrone (CP) derivatives and photochemical/photophysical processes taking place in their excited molecules. The obtained results permit to obtain a general scheme of photophysical and photochemical processes in excited CP molecules. It is found that spectral properties of CP depend on relative positions of underlying  $n\pi^*$  and  $\pi\pi^*$  excited states. If  $E_{\pi\pi^*} < E_{n\pi^*}$ , the corresponding compound has the fluorescence and is stable under irradiation. In the opposite case, when CP derivatives have  $E_{\pi\pi^*} > E_{n\pi^*}$ , they have no fluorescence or photostability, but can phosphoresce under low temperatures. These results can be used for synthesis of new photostable emitting dyes for fluorescent polymer compositions.

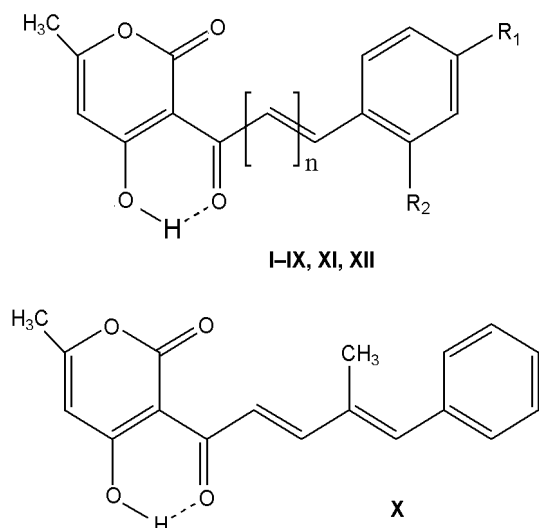
Работа посвящена исследованию взаимосвязи между спектральными свойствами, фотостабильностью, фотокинетическими характеристиками производных циннамоил-пиронов (ЦП) и фотофизическими/фотохимическими процессами, протекающими в возбужденных молекулах ЦП. Полученные результаты позволили сформировать общую схему фотофизических и фотохимических процессов, имеющих место в возбужденных ЦП. Обнаружено, что спектральные свойства ЦП зависят от относительного расположения нижележащих возбужденных состояний  $n\pi^*$  и  $\pi\pi^*$  типа. Если  $E_{\pi\pi^*} < E_{n\pi^*}$ , соответствующее соединение флуоресцирует и обладает фотостойкостью. В противоположном случае, если  $E_{\pi\pi^*} > E_{n\pi^*}$ , соединение не имеет флуоресценции, не обладает фотостабильностью, но фосфоресцирует при пониженных температурах. Данные результаты могут быть использованы для синтеза новых фотостабильных флуоресцентных красителей для полимерных композиций.

## 1. Introduction

Cinnamoyl pyrones (CP) are known as medicaments and as intermediate products in medicament synthesis [1–3]. Investigations of CP spectral properties has shown that the application field of mentioned compounds is significantly broader. They can play a role of fluorescent indicators in the wide range of the acidity: from  $H_0 = -6$  to  $pH = 13$ . Moreover, CP can be used as fluo-

rescent dyes and markers for polymer media, which permits to create new emitting functional materials based on polymer compositions.

The investigations of CP showed that these compounds must be divided into two groups having different spectral properties. CP with neutral or weak electron-donating substituents in side phenyl cycle have no fluorescence in liquid solutions nor in poly-



Compound	R <sub>1</sub>	R <sub>2</sub>	n
I	H	H	1
II	H	OCH <sub>3</sub>	1
III	OCH <sub>3</sub>	H	1
IV	H	OCHF <sub>2</sub>	1
V	OCHF <sub>2</sub>	H	1
VI	N(CH <sub>3</sub> ) <sub>2</sub>	H	1
VII	N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	H	1
VIII	morpholinyl	H	1
IX	H	H	2
X	H	H	2
XI	H	H	3
XII	N(CH <sub>3</sub> ) <sub>2</sub>	H	2

Scheme 1. Structures of cinnamoyl pyrones investigated.

mer matrices irrespectively of medium polarity. CP with strong electron-donating substituents intensively emit in non-polar solvents [4], however, the polarity increase results in a drastical decrease of quantum yields. In polymeric matrices, CP fluorescence is intense not depending on medium polarity, that is very important, if CP are used as polymer markers.

To understand causes of CP fluorescence quenching and to explain dependence between CP spectral properties and medium parameters, we tried to investigate and to simulate photophysical and photochemical processes taking place in the molecules.

## 2. Experimental

Twelve CP derivatives and vinylogs with different length of polymethine chain synthesized according to [4, 5] have been investigated. Structures of studied compounds are depicted on Scheme 1. Solvents used for spectral investigations were previously dried and purified according to [6]. The presence of absorbing or emitting impurities in the solvents, as well as in polymeric matrices at 70 and 298 K is examined using photometric and fluorimetric methods. Absorption and emission spectra were registered using Hitachi U3210 spectrophotometer and Hitachi F4010 fluorimeter, correspondingly. Lifetimes of CP molecules in solutions and polymer matrices were measured using pulse picosecond photon-counting photometer PicoQuant with  $\lambda_{exc} = 335$  nm. Phosphorescence spectra and life-

times were measured in polymer matrices at temperature 70 K on fluorescence spectrophotometer Cary Eclipse Varian operated in phosphorimeter mode.

Geometry optimization and calculations of electronic transitions were carried out by semi-empirical method RM1 [7] implemented to MOPAC 2009 program package [8]. Spin-orbit interaction coefficients were calculated using CNDO/S/SOI program [9]. Intersystem crossing constants  $k_{ISC}$  were obtained by the equation

$$k_{ISC} = 3.95 \cdot 10^{11} \sum_i \beta_{1i}^2 e^{-\frac{E_{T_i} - E_{S_1}}{5}} \cdot 10^3,$$

where  $\beta_{1i}$  — matrix coefficients of operator of spin-orbit interaction between the lowest singlet excited state  $S_1$  and underlying triplet states (energies ( $E_{T_i}$ ) of which are similar or lower than energy of  $S_1$  ( $E_{S_1}$ )) [10].

The estimation of experimental and theoretical kinetic characteristics ( $k_f$ ,  $k_d$ ), as well as theoretical lifetime ( $\tau$ ) and fluorescence quantum yield ( $\phi$ ) were carried out according to formulae:

$$\tau = \frac{1}{k_f + k_d} \text{ and } \phi = \frac{k_f}{k_f + k_d},$$

$\tau$  and  $\phi$  were calculated under the assumption that intersystem crossing is a main channel of radiationless deactivation of  $S_1$  state, i.e.  $k_d \approx k_{ISC}$ .

Table 1. Mulliken charges ( $\bar{e}$ ) on oxygen atoms of hydroxy group and carbonyl fragments in the ground ( $S_0$ ) and excited ( $S_1$ ) states

CP	Hydroxy group		Endocyclic carbonyl fragment		Exocyclic carbonyl fragment	
	$S_0$	$S_1$	$S_0$	$S_1$	$S_0$	$S_1$
I	-0.296	-0.336	-0.414	-0.455	-0.455	-0.485
II	-0.297	-0.336	-0.420	-0.494	-0.455	-0.513
III	-0.298	-0.331	-0.414	-0.494	-0.455	-0.512
IV	-0.297	-0.337	-0.413	-0.493	-0.454	-0.502
V	-0.297	-0.331	-0.414	-0.498	-0.455	-0.504
VI	-0.298	-0.334	-0.415	-0.424	-0.458	-0.548
VII	-0.299	-0.338	-0.414	-0.422	-0.458	-0.550
VIII	-0.298	-0.330	-0.413	-0.427	-0.456	-0.540
IX	-0.299	-0.368	-0.420	-0.446	-0.458	-0.494
X	-0.297	-0.356	-0.415	-0.420	-0.455	-0.492
XI	-0.299	-0.351	-0.422	-0.423	-0.459	-0.517
XII	-0.261	-0.385	-0.422	-0.445	-0.453	-0.573

### 3. Results and discussion

*Photochemical processes in CP molecules.* The diversity of CP spectral properties may be explained by several causes due to physical and chemical processes in the excited state. The most probable photochemical processes are following:

- excited-state intramolecular proton transfer (ESIPT) from hydroxy group in  $\alpha$ -pyrone fragment onto exocyclic carbonyl group. The hydroxy and carbonyl groups form a strong intramolecular hydrogen bond, closing a six-membered cycle. Proton transfer in such conditions takes places in many organic compounds [11–13].

- ESIPT from  $\alpha$ -pyrone hydroxy group onto endocyclic carbonyl group and  $\gamma$ -pyrone tautomer formation. Such a tautomerism takes place with participation of solvent molecules and is typical for 4-hydroxycoumarines and 2-hydroxyisoflavones [14, 15].

- *trans/cis*-isomerization and dimerization of polymethine chains typical for chalcones [16], polymethine dyes and other compounds [17, 18].

ESIPT probability can be estimated using both experimental and theoretical methods. In the last case, the information may be obtained by the comparison of charges on CP oxygen atoms in the ground and excited states. Proton photo transfer is possible if the excitation of a molecule results in substantial decrease of negative charge on oxygen atom of hydroxy group corresponding to increase of its acidity, and in simultaneous increase of negative charge on oxygen atoms of carbonyl groups corresponding to growth of their basicity. Since first stage of

proton transfer is the dissociation of the hydroxy group (a proton donor), the increase of its acidity is a necessary condition of ESIPT.

Table 1 presents values of Mulliken charges on CP oxygen atoms in the ground and excited states. The influence of medium polarity (water) on the charge redistribution in CP molecules was taken into account using COSMO method [19]. Table 1 shows that the  $S_0 \rightarrow S_1$  transition leads to the increase of negative charge both on hydroxy and carbonyl fragments. Thus, the excitation results in increase of carbonyl group basicity and in substantial decrease of hydroxy group acidity. The last phenomenon evidences a very weak probability of both types of ESIPT mentioned above.

Experimental estimation of ESIPT probability has been carried out by comparison of CP dissociation and protonation constants in the ground and excited state.  $pK_a$  values were determined by acid-base titration in a wide range of pH/ $H_0$ . The  $pK_a$  estimation in the excited state was made using Forster method [20].

The titration in basic media permitted to observe an anion formation due to the hydroxy group dissociation. The titration in the acidic range of pH/ $H_0$  showed, that the most of CP gives only one — monocationic form. Consequently, only one of carbonyl groups undergoes the protonation process. CP derivatives with nitrogen-containing substituents have an additional nucleophilic center — nitrogen atom, that is why, they demonstrate two-step protonation, first stage of which is ammonium ion formation.

Table 2. PC dissociation constants in the ground ( $pK_a$ ) and excited ( $pK_a^*$ ) states \*

CP	$pK_{a,1}$	$pK_{a,1}^*$	$pK_{a,2}$	$pK_{a,2}^*$	$pK_{a,3}$	$pK_{a,3}^*$
I	7.59±0.12	7.76			-4.72±0.21	1.23
II	7.79±0.05	8.46			-4.60±0.16	4.37
III	7.84±0.06	8.01			-4.36±0.11	3.40
IV	7.80±0.09	7.62			-4.64±0.09	3.29
V	7.52±0.12	8.22			-4.45±0.07	3.48
VI	8.11±0.02	13.70	2.06±0.02	-3.36	-6.03±0.28	1.38
VII	8.16±0.04	13.85	2.09±0.09	-3.65	-6.24±0.07	2.55
VIII	8.40±0.04	~14.0	2.08±0.05	-4.90	-6.43±0.09	-0.12
IX	7.74±0.04	6.80			-4.18±0.06	2.45
X	7.69±0.05	8.68			-4.26±0.09	2.54
XI	7.80±0.06	8.69			-4.01±0.09	5.19
XII	8.34±0.08	11.27	2.18±0.07	-2.68	-6.88±0.13	2.15

\*  $pK_{a,1}$  and  $pK_{a,1}^*$  are protolytic constants of hydroxy group,  $pK_{a,2}$  and  $pK_{a,2}^*$  are protolytic constants of nitrogen atom in VI, VII, VIII and XII,  $pK_{a,3}$  and  $pK_{a,3}^*$  are protolytic constants of carbonyl group.

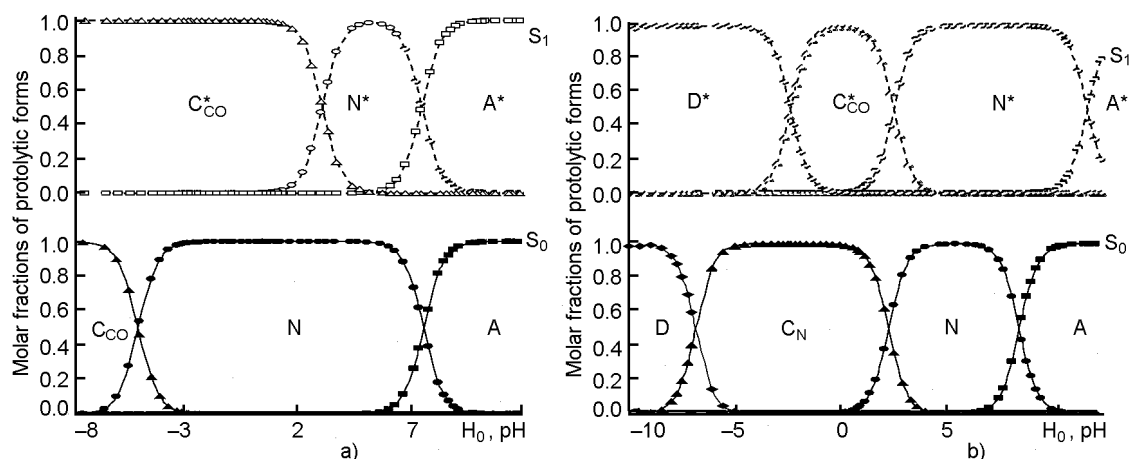


Fig. 1. Molar fractions CP protolytic forms in the ground ( $S_0$ ) and excited ( $S_1$ ) states. a — V, b — XII. A — anions, N — neutral forms,  $C_N$  — ammonium monocations,  $C_{CO}$  — monocations with protonated carbonyl group, D — dications. Protolytic forms in the excited states are marked by (\*).

The  $pK_a$  values listed in Table 2 evidence the increase of carbonyl basicity and the decrease of the hydroxyl group acidity in the excited state, that fully corresponds to results obtained by quantum-chemical methods. The pH/ $H_0$  ranges, where is possible the existence of cationic, neutral and anionic CP forms, are depicted in Fig. 1. The ESIPT tautomer formation may take place in pH/ $H_0$  ranges, where simultaneous presence of a cation and an anion is possible. Since there are no the overlapping of "anion and cation areas" in the ground nor excited states (Fig. 1), the proton-transfer formation of photo tautomers seems to be hardly possible.

Investigations of *trans/cis* photo isomerization of *trans*-chalcones [16] showed that the irradiation of their solutions by a light beam results to *cis*-isomer formation. As polymethine chain in *cis*-isomer is not plain, the formation of this last leads to partial brake of the conjugation, and, consequently, to hypsochromic shifts of absorption and fluorescence bands. Moreover, polymethine chains may undergo photo dimerization resulting in the formation of cyclobutane derivatives [18]. Breaking  $\pi$ -conjugation in the polymethine chain under the photo dimerization leads to the disappearance of long-wavelength absorption bands and of emission band.

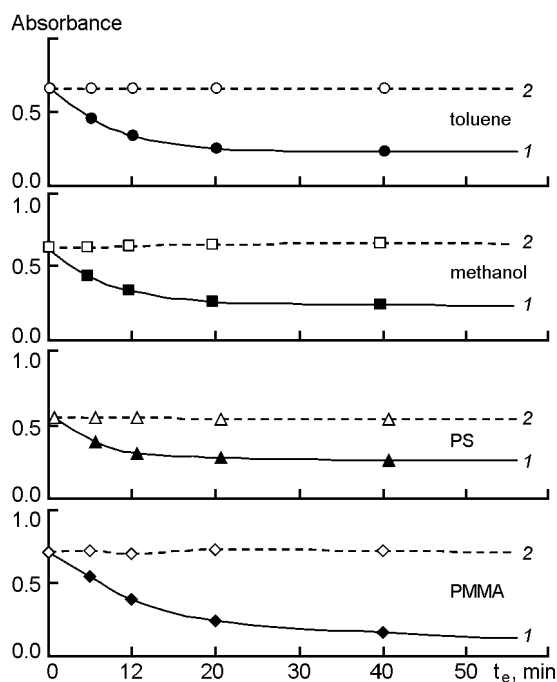


Fig. 2. Dependence of absorbance in a maximum of long-wavelength absorption band of non-fluorescent I (1) and fluorescent VI (2) CP on exposition time in toluene, methanol, polystyrene (PS) and polymethylmetacrylate (PMMA).

The investigations of CP *trans/cis* photo isomerism and dimerization were carried out by means of sample irradiation by the monochromatic light with  $\lambda = 360$  nm and the intensity —  $1.7 \cdot 10^{-8}$  Es/min. The photochemical processes were studied in hexane (non-polar) and methanolic (polar) solutions, as well as in polystyrene (non polar) and polymethylmetacrylate (polar) matrices. *Trans/cis* isomerization does not result in substantial changes of CP molecular volume, therefore this process can take place both in liquid solvents and polymeric matrices. Photo dimerization needs the diffusion of CP molecules and results in the doubling their molecular volume, which are not possible in polymeric matrices. That is why, the differences in CP behavior in liquid and polymeric media permit to distinguish chemical processes taking place in the excited state.

The investigations showed that non-fluorescent CP have a weak photo stability (Fig. 2). The irradiation of I–V and XI–IX results in hypsochromic shift of long-wavelength bands in their absorption spectra (Fig. 3). This shift is detected both in liquid and polymeric media that evidence the absence of noticeable photo dimerization process.

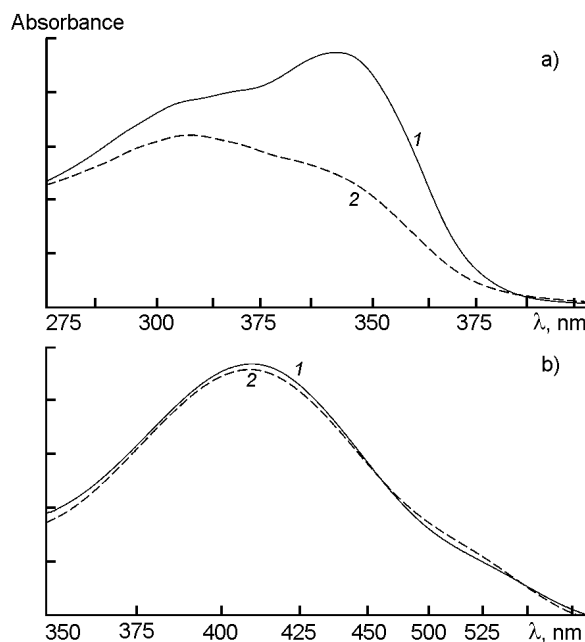


Fig. 3. Changing absorption spectra of I (a) and VI (b) in PS matrices under light exposition ( $\lambda = 360$  nm, light intensity —  $1.7 \cdot 10^{-8}$  Es/h) during 5 hours: 1 — before exposition, 2 — after exposition.

The formation of *cis*-isomer in polar liquid and polymeric media is faster, than in the non-polar ones.

Fluorescent CP demonstrate a high photostability: their absorption and fluorescence spectra do not change under the irradiation.

It is known that *trans/cis*-isomerization occurs through intermediate long-living triplet state [16]. The fact that isomerism takes place only in the case of non-fluorescent CP proves that I–V, XI–IX have an intense inter-system crossing in the excited state.

*Photophysical processes in CP molecules.* It is well known that, upon excitation, a molecule, undergoing fast processes of internal conversion, structural and solvate relaxations, achieves a relatively long-living relaxed excited state. This last can undergo radiative and radiationless internal conversions into the ground state, intersystem crossing and chemical reactions [21]. Rate constants of corresponding processes are marked below as  $k_f$ ,  $k_d$ ,  $k_{ISC}$  and  $k_{chem}$ .

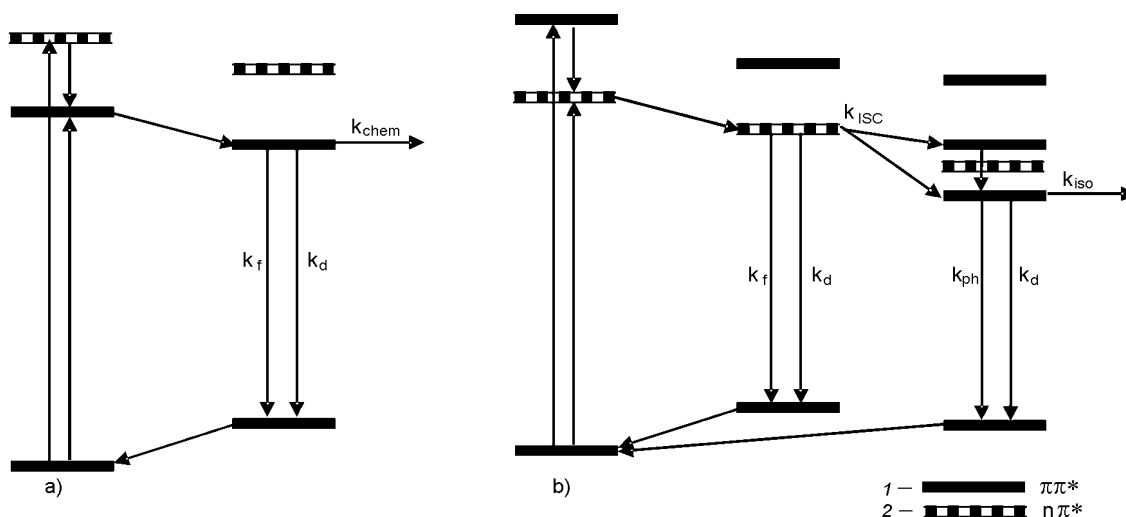
To analyze processes taking place in molecules of fluorescent CP — VI–VIII and XII, extinction coefficients in long-wavelength absorption band maxima ( $\epsilon_{max}$ ), fluorescence quantum yields and lifetimes ( $\phi$  and  $\tau$ ) in solvents and polymer matrices of different po-

Table 3. Photophysical characteristics of fluorescent CP in solutions and polymer matrices \*, \*\*

CP	Medium	$\nu_{abs}$ , $\text{cm}^{-1}$	$\lg \epsilon_{max}$	$\phi$ , %	$\tau$ , ns	$k_f$ , $\text{s}^{-1}$	$k_d$ , $\text{s}^{-1}$
VI	DCM	476	4.54	54.6	0.77	$7.09 \cdot 10^8$	$5.90 \cdot 10^8$
	AN	464	3.10	1.7	2.64	$6.44 \cdot 10^6$	$3.72 \cdot 10^8$
	PS				2.08		$2.75 \cdot 10^8$
	PMMA				3.59		$2.72 \cdot 10^8$
VIII	DCM	437	3.90	42.9	1.42	$3.02 \cdot 10^8$	$4.02 \cdot 10^8$
	AN	433	3.54	6.8	3.01	$2.02 \cdot 10^7$	$3.12 \cdot 10^8$
	PS				1.94		$2.13 \cdot 10^8$
	PMMA				3.01		$3.12 \cdot 10^8$
XII	DCM	492	4.01	89.0	1.98	$4.49 \cdot 10^8$	$5.56 \cdot 10^7$
	AN	439	3.70	4.60	3.70	$1.24 \cdot 10^7$	$1.46 \cdot 10^8$
	PS				1.86		$8.86 \cdot 10^7$
	PMMA				2.80		$3.45 \cdot 10^8$

\* The media are: DCM — dichloromethane, AN — acetonitrile, PS — polystyrene matrix, PMMA — polymethyl metacrylate matrix,  $\nu_{abs}$  — positions of long-wavelength absorption band maxima,  $\epsilon_{max}$  — molar extinction coefficient at  $\nu_{abs}$ ,  $\phi$  — quantum yield of fluorescence,  $\tau$  — fluorescence lifetime,  $k_f$  — fluorescence rate constant,  $k_d$  — radiationless rate constant.

\*\*  $\nu_{abs}$ ,  $\epsilon$  and  $\phi$  — are taken from [4].



Scheme 2. Photophysical processes in fluorescent (a) and non-fluorescent (b) CP. 1 —  $\pi\pi^*$ -states, 2 —  $n\pi^*$ -states.

larity were measured (Table 3). Obtained kinetic parameters showed that mentioned CP have sufficiently low rates of the radiationless deactivation. In the case of VI and VIII,  $k_d$  values are on the order of  $4\text{--}6 \cdot 10^8 \text{ s}^{-1}$  in non-polar solvents, and 1.5 times lower in polar media. Lower  $k_d$  values have been also observed in polymeric matrices. CP vinylog — XII demonstrates another behavior: the lowest  $k_d$  value ( $k_d \sim 5.6 \cdot 10^7 \text{ s}^{-1}$ ) is typical for non-polar environment, and it increases in more polar and condensed media.

Low  $k_d$  values evidence the absence of any substantial contribution of intersystem crossing, thus, it is possible to suppose that  $k_{ISC} < k_d$ . Taking into account a low probability of the proton transfer, of the *trans/cis*-isomerism and of the photo dimerization (i.e.  $k_{chem} \sim 0$ ), photophysical processes in fluorescent CP molecules could be represented by a simple scheme (Scheme 2a).

Data listed in the Table 3 show that fluorescence quenching on going from non-polar media to polar ones is substantially due to solvatochromic effects: to the decrease of

Table 4. Theoretical estimations of intersystem crossing rates, intrinsic fluorescence rates and emission parameters of CP\*

	$k_r$ , $\text{c}^{-1}$	$k_{ISC}$ , $\text{c}^{-1}$	interacting states	$\varphi^{**}$ , %
I	$3.57 \cdot 10^5$	$1.21 \cdot 10^{10}$	$S_1 \rightarrow T_3, T_2, T_1$	0.0
II	$1.25 \cdot 10^5$	$3.78 \cdot 10^{11}$	$S_1 \rightarrow T_4, T_3$	0.0
III	$6.29 \cdot 10^4$	$2.33 \cdot 10^{11}$	$S_1 \rightarrow T_3$	0.0
IV	$4.97 \cdot 10^6$	$1.32 \cdot 10^{11}$	$S_1 \rightarrow T_4, T_3$	0.0
V	$1.88 \cdot 10^5$	$2.84 \cdot 10^{11}$	$S_1 \rightarrow T_3$	0.0
VI	$6.15 \cdot 10^8$	$4.86 \cdot 10^9$	$S_1 \rightarrow T_5, T_4, T_3$	11.2
VII	$6.17 \cdot 10^8$	$6.02 \cdot 10^9$	$S_1 \rightarrow T_5, T_4, T_3$	9.3
VIII	$6.05 \cdot 10^8$	$6.06 \cdot 10^9$	$S_1 \rightarrow T_5, T_4, T_3$	9.1
IX	$1.54 \cdot 10^6$	$7.03 \cdot 10^{11}$	$S_1 \rightarrow T_4, T_3$	0.0
X	$2.02 \cdot 10^6$	$2.91 \cdot 10^{11}$	$S_1 \rightarrow T_4, T_3$	0.0
XI	$1.54 \cdot 10^9$	$2.15 \cdot 10^{11}$	$S_1 \rightarrow T_4, T_3$	0.5
XII	$8.98 \cdot 10^8$	$7.34 \cdot 10^8$	$S_1 \rightarrow T_3$	55.0

\*  $k_r$  is intrinsic fluorescence rate constant,  $k_{ISC}$  is intersystem crossing rate constant,  $\varphi$  is theoretical quantum yield.

\*\* Theoretical quantum yield were calculated by equation  $\varphi = k_r / (k_r + k_{ISC})$  on the assumption of  $k_r$  is equal to  $k_f$ , and  $k_d$  is equal to  $k_{ISC}$  (i.e. the main way of radiationless deactivation is the intersystem crossing).

extinction coefficients of long-wavelength absorption bands with the increase of environment polarity. This is proved by low values of intrinsic radiation rate constants ( $k_r$ ), obtained from  $\varepsilon_{max}$  values and comparable with  $k_f$  values.

As it was mentioned above, the photo isomerism of non-fluorescent CP **I–V** and **IX–IX** denotes an activation of the intersystem crossing. The cause of the activation of this new channel of radiationless deactivation become evident after analysis of CP spectral behavior in different media.

The investigations of spectral properties of CP [4] show that emission ability depends on the position of the long-wavelength absorption band ( $\lambda_{abs}$ ). Compounds, which  $\lambda_{abs}$  is in the range of 340–360 nm, have no fluorescence. On the other hand, fluorescent CP absorb at  $\lambda_{abs}$  400 nm. The emission of **IX** disappears, when the increase of solvent polarity leads to hypsochromic shift of the absorption band from 390 nm to 370 nm. Such a spectral behavior permits to conclude about the presence of a forbidden electronic transition, whose absorption band is at ~ 380 nm. This electronic transition, most probably located on exocyclic carbonyl group, is responsible for the activation of the intersystem crossing.

Results of theoretical estimations of kinetic parameters of the spin-orbit interaction in CP molecules obtained using

CNDO/S/SOI method are listed in the Table 4. The comparison of theoretical values  $k_r$  and  $k_{ISC}$  shows that the kinetic parameters calculated by CNDO/S/SOI exceeds by a factor of ten the results obtained from  $\tau$  and  $\varphi$  measurements. However, the comparison of theoretical  $k_r$  and  $k_{ISC}$  for different CP permits to conclude about fluorescence quenching mechanism. The data presented in Table 4 show that  $k_r$  values of non-fluorescent CP are 3–4 orders of magnitude lower, than  $k_r$  values of fluorescent compounds. Such low values are typical for  $n\pi^*$  transitions, that is in agreement with experimental observations.  $k_{ISC}$  values for **II–V** and **IX–IX** are two orders of magnitude higher than in the case of **VI–VIII** and **XII**. Thus, the rate of intersystem crossing in molecules of non-fluorescent CP is approximately 100 times higher than that in molecules of fluorescent CP.

Theoretical quantum yields of fluorescent **VI–VIII** and **XII** are lower than experimental values (Tables 3 and 4), however calculated  $\varphi$  values for non-fluorescent **I–V**, **IX–IX** are in the range of  $10^{-3}$ – $10^{-4}$  % (i.e. these compounds have no fluorescence), that is also in agreement with experimental results.

The comparison of theoretical and experimental kinetic parameters permits to propose a mechanism of excited state deactivation depicted on Scheme 2b. According

Table 5. Luminescence parameters of cynammoyl pyrones \*

Compound	Polymer matrix	$T$ , K	$\lambda_{max,l}$ , nm	$\Delta\nu_{St,l}$ , $cm^{-1}$	$\tau_{ph}$ , mks
I	PMMA	298	–	–	–
		77	448	5610	2.52
	PS	298	–	–	–
		77	457	6130	2.27
VI	PMMA	298	564	3820	–
		77	571	4040	–
	PS	298	591	4090	–
		77	593	4150	–
IX	PMMA	298	–	–	–
		77	486	6450	2.90
	PS	298	–	–	–
		77	491	5540	2.71
XI	PMMA	298	–	–	–
		77	527	5180	3.35
	PS	298	–	–	–
		77	527	6930	3.20
XII	PMMA	298	602	4140	–
		77	601	4110	–
	PS	298	589	3350	–
		77	597	3580	–

\* PMMA — polymethylmetacrylate matrix, PS — polystyrene matrix,  $T$  is matrix temperature,  $\lambda_{max,l}$  — fluorescence and phosphorescence band maximum positions,  $\Delta\nu_{St,l}$  — Stokes shifts of fluorescence and phosphorescence,  $\tau_{ph}$  — phosphorescence lifetime.

to the scheme, the lowest excited state  $S_1$  deactivates by intersystem crossing into one or several triplet states  $S_1 \rightarrow T_i$  (see Table 4). After internal conversion processes, a molecule achieves long-living lowest triplet state —  $T_1$ , which, then, undergoes as radiationless deactivation ( $k_d$ ), as *trans/cis*-isomerization process ( $k_{iso}$ ). At low temperatures, when  $k_d$  value decreases and becomes comparable with the rate of radiative deactivation ( $k_{ph}$ ), the appearance of the phosphorescence may be expected.

The proposed deactivation mechanism (Scheme 2b) was corroborated by luminescence measurements of some fluorescent and non-fluorescent CP in polystyrene and polymethyl metacrylate matrices at 70 K (Table 5). It was found that VI and XII have more intense emission than at the room temperature, however other spectral characteristics as positions of emission band maxima ( $\lambda_{fl}$ ) or fluorescence Stokes shifts ( $\Delta\nu_{St}$ ) do not depend on temperature level. In the case of non-fluorescent CP, the decrease of the temperature results in the appearance of phosphorescence having Stokes shifts in the range of 5100–6930  $cm^{-1}$  and lifetimes ( $\tau_{ph}$ ) — 2.3–3.3 mks.

The data presented in Table 5 show that the elongation of polymethine chain results in the increase of the phosphorescence lifetime (0.5 mks per one double bond). Moreover,  $\tau_{ph}$  value in non-polar media is lower than in polar ones.

#### 4. Conclusion

The presented work permits to obtain a general scheme of photophysical and photochemical interactions in excited CP molecules. Spectral (in the first place, fluorescent) properties of CP depend on relative positions of underlying  $n\pi^*$  and  $\pi\pi^*$  excited states. If a substituent in CP molecule leads to a situation, when  $E_{\pi\pi^*} < E_{n\pi^*}$ , the corresponding compound has the fluorescence and is stable under irradiation. In the case, when CP derivative has  $E_{\pi\pi^*} > E_{n\pi^*}$ , it has no fluorescence nor photostability, but can phosphoresce under low temperatures.

These results can be used for synthesis of new photostable emitting dyes for fluorescent polymer compositions.

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## Фотофізичні та фотохімічні процеси у молекулах цинамоїлпіронів: вплив на спектральні властивості і фотостабільність

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Робота присвячена дослідженню взаємозв'язку між спектральними властивостями, фотостабільністю, фотокінетичними характеристиками похідних цинамоїлпіронів (ЦП) та фотофізичними/фотохімічними процесами, що відбуваються у збуджених молекулах ЦП. Отримані результати дозволяють сформулювати єдину схему фотофізичних і фотохімічних процесів, що мають місце у збуджених ЦП. Знайдено, що спектральні властивості ЦП залежать від відносного розташування найнижчих збуджених станів  $n\pi^*$  і  $\pi\pi^*$  типу. Якщо  $E_{\pi\pi^*} < E_{n\pi^*}$ , відповідна сполука випромінює і є фотостабільною. У протилежному випадку, якщо  $E_{\pi\pi^*} > E_{n\pi^*}$ , сполука не має флуоресценції чи фотостабільності, але випромінює фосфоресценцію при низьких температурах. Дані результати можуть бути використані для синтезу нових фотостабільних флуоресцентних барвників для полімерних композицій.