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Structure and spectal properties of cinnamoyl pyrones and their vinylogs

Research Article

Dmytro A. Tykhanov¹, Irina I. Serikova², Fedor G. Yaremenko², Alexander D. Roshal^{1*}

¹ Institute of Chemistry at Kharkov National University, Department of Physical Organic Chemistry, Kharkov 61077, Ukraine

² Danilevskii Institute of Endocrine Pathology Problems, Ukrainian Academy of Medical Sciences, Kharkov 61002, Ukraine

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- **Abstract:** The 'H-NMR and quantum chemical analysis of the stability of tautomers of cinnamoyl pyrone derivatives and vinylogs has been studied. The relationship between the structure of the most stable tautomer and its spectral properties has been investigated. It has been determined that the tautomer of highest stability (88-100 molar %) has an α-pyrone structure and exhibits a trans-conformation in the cinnamoyl fragment. An intense fluorescence of dyes has been observed in non-polar solvents with cinnamoyl fragments having electron-donating substituents or several double bonds in the polymethine chain. A gradient in solvent polarity resulted in fluorescence quenching which permits the use of the dyes as intensometric fluorometric probes for medium polarity examination.
- Keywords: Cinnamoyl pyrones Fluorescent dyes Quantum chemical calculations Absorption and fluorescence spectral properties Fluorescent probes

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1. Introduction

Dehydroacetic acid (3-acetyl-4-hydroxy-6-metyl-2Hpyran-2-one, DHA) is a natural product of polyketide biosynthesis. It is well known that DHA, its salts and other 3-acylpyrones have a high biological activity [1]. For example, sodium dehydroacetate in rats induces severe hemorrhaging in multiple organs and prolongation of blood coagulation factors [2].

Some derivatives of DHA contain fragments of α , β -unsaturated ketones: 5-crotonyl-4-methoxy-6-methyl-2H-pyran-2-one (citreopyrone) [3] and 3-(β -hydroxycinnamoyl)-4-hydroxy-6-methyl-2H-pyran-2-one (pogopyrone A) [4] are widespread natural compounds.

3-Cinnamoyl derivatives of 4-hydroxy-2-pyranone are anticoagulants and have blood platelet aggregation inhibiting activity [5]. They were also used as I type collagen gene transcription suppressing agents [6]. Difluoroborate complexes of 3-cinnamoyl 4-hydroxy-2pyranone are known as a novel class of HIV-1 integrase inhibitors [7]. Moreover, cinnamoyl pyrones can be used for a synthesis of many heterocyclic compounds [8], particularly for the production of thiazepines, which are apoptosis inducers [9].

The relationship between the molecular structure of DHA derivatives and their biological activity is a very important problem, because even unsubstituted DHA can form seven tautomers [10]; each having different chemical and biological properties. Moreover, some derivatives of DHA have an intense fluorescence that permit their use as fluorescent dyes and biological probes.

The present work is devoted to the analysis of the structure and spectral properties of cinnamoyl derivatives, which are structural analogs of chalcones.

^{*} E-mail: alexandre.d.rochal@univer.kharkov.ua





Scheme 1. The structure of cinnamoyl pyrone derivatives.

2. Experimental Procedure

2.1. General procedure for preparation of I-XI

3-Cinnamoyl-4-hydroxy-6-methyl-2H-pyran-2-ones and their vinylogs depicted in scheme 1 have been prepared under reaction conditions described ealier [11].

Dehydroacetic acid (0.01 M) and aldehyde (0.01 M) were refluxed for 1-8 hours in dry chloroform (12-15 mL) containing piperidine (few drops). Then, half of the solvent volume containing chloroform-water azeotrope was evaporated. Solid products were obtained by slow evaporation of the remaining

chloroform and recrystallizing in an ethanol or ethanolchlorofom mixture.

The identity of the compounds was examined by elemental analysis and ¹H NMR spectra. Elemental analyses were carried using Element Analyzer EA-3000. Melting points were determined on a Koeffler heating block. The data obtained for **I-XI** are listed in Table 1.

The purity of obtained dyes has been detected by the thin-layer chromatography on silicagel plates (Silusorb) and by both-scan fluorescence spectroscopy.

2.2. Spectral measurements

¹H NMR spectra were registered on the spectrometer Varian-200 in DMSO-*d*6 solutions. TMS was used as internal reference. The spectral data for compounds **I-XI** are given in Table 2.

The investigations of absorption and fluorescence spectra have been carried out using a Hitachi U3210 spectrophotometer and a Hitachi F4010 spectrofluorimeter. The fluorescence spectra were measured at excitation wavelengths corresponding to long-wavelength absorption-band maxima of investigated compounds. Solvents for spectral measurements were dried and purified according to methods previously described [15]. The treatment of the spectra of **I-XI** and the calculations of their spectral characteristics have been made with Spectra DataLab packet [16].

Compound	R,	R ₂	n	M.p. (°C)	Yield (%)	Elemental analysis (%)
l	Н	Н	1	131-132 (130-132) [11]	49	*
II	н	OMe	1	168-169	76	Found: C, 67.10; H, 4.90. Calcd. for $C_{16}H_{14}O_5$ (286.29): C, 67.12; H, 4.92
Ш	OMe	Н	1	205-206 (208-209) [12]	83	*
IV	н	$OCHF_{\scriptscriptstyle 2}$	1	175-178	31	Found: C, 59.61; H, 3.67; F, 11.72. Calcd. for $C_{16}H_{12}F_2O_5$ (322.27): C, 59.63; H, 3.75; F, 11.79
v	OCHF ₂	Н	1	162-163	65	Found: C, 59.62; H, 3.69; F, 11.73. Calcd. for C ₁₆ H ₁₂ F ₂ O ₅ (322.27): C, 59.63; H, 3.75; F, 11.79
VI	NMe ₂	Н	1	223 (218-219) [12]	64	*
VII	NC ₄ H ₈ O	Н	1	241-242	44	Found: C, 66.81; H, 5.57; N, 4.08. Calcd. for C ₁₉ H ₁₉ NO ₅ (341.37): C, 66.85; H, 5.60; N, 4.10
VIII	Н	Н	2	186-187 (185) [11] (180) [13]	55	*
IX	н	Н	2	146-147	54	Found: C, 72.91; H, 5.40. Calcd. for C ₁₈ H ₁₆ O ₄ (296.33): C, 72.95; H, 5.44
x	н	Н	3	225-227	55	Found: C, 73.98; H, 5.20. Calcd. for C ₁₉ H ₁₆ O ₄ (308.34): C, 74.01; H, 5.23
XI	NMe ₂	Н	2	257-259 (204-205) [14]	56	Found: C, 70.05; H, 5.82; N, 4.29. Calcd. for C ₁₉ H ₁₉ NO ₄ (325.37): C, 70.14; H, 5.88; N, 4.31

Table 1. Characterization data of compounds I-XI.

* - the results of the elemental analysis of the dyes I, II, VI, VIII correspond to those in cited references





2.3. Quantum chemical calculations

The geometry optimization for molecules **I-XI** with calculation of their thermodynamic characteristics has been carried out using the RM1 method [17] (which is a re-parametrized version of the AM1 method [18]) implemented in MOPAC 2002 program [19]. The influence of medium polarity has been estimated by the COSMO method [20].

3. Discussion

3.1. ¹H-NMR-spectra of cinnamoyl pyrones

As it follows from Scheme 2, cinnamoyl pyrones can form five tautomers. These are α - and γ -cinnamoyl pyrones (structures **a** and **c**, correspondingly), tautomers **b** and **d**, which result from keto-enol rearrangement of **a** and **c**, as well as pyranedion **e**, formed due to the migration of a proton to the atom C2 of pyrone cycle. To determine the structure of more stable tautomers, ¹H NMR spectra of compounds *I-XI* were measured.

The positions of peaks in ¹H NMR spectra of *I-XI* are listed in Table 2. Examination of the data shows that only one cinnamoyl pyrone tautomer is present in solutions.

The coupling constants of H_{α} and H_{β} , proton doublets, in spectra of *I*, *II*, *IV*, *V VII* are 15.5-15.9 Hz which is typical for trans-configurations of the cinnamoyl fragment, *i.e.*, the trans-relationship of phenyl ring and carbonyl fragment relatively to the double bond.

At the same time, the NMR spectra do not permit a definitive conclusion about the structure of the pyrone fragment. The peaks of 6-Me (2.23-2.29 ppm), 5-H (6.20-6.33 ppm), 4-OH (12.9-18.2 ppm) protons could be typical for the majority of proposed tautomer forms. Only **e** tautomer could be rejected, because singlet signals of 3-H protons have not been found.

0	C 14-	.	н н Ar				4.011	
Compound	6-IVIE	5-H	Ηα	Η _β	о'	m'	4-0H	ĸ
I	2.28 d /0.6/	6.33 d /0.6/	7.92 d /15.6/	8.19 d /15.6/	7.73 m (2H)	7.49 m (3H)	17.6	-
					7.67 d /8.1	/ (6´-H)		
11	2.29 s	6.12 s	8.23 s	(2H)	7.41 <i>t</i> /8.0	/ (4´-H)	12.9	3.95 s (3H OMe)
					6.95-7.05	m (2H)		
<i>III</i>	2.26 d /0.7/	6.26 d /0.7/	7.89 d /15.8/	8.06 d /15.9/	7.696 d /8.8/	7.045 d /8.8/	17.7	3.82 s (3H OMe)
					7.85 d /8.0	/ (6´-H)		
IV	2.29 s	6.29 s	8.05 d /15.6/	8.23 d /15.6/	7.55 <i>t</i> /8.0 7.38 <i>t</i> /8.0	/ (4´-H) / (5´-H)	13.6	7.34 <i>t</i> /73.2/ (CHF ₂)
					7.32 d /8.0	/ (3´-H)		
V	2.28 s	6.32 s	7.90 d /15.8/	8.12 d /15.9/	7.80 d /8.6/	7.27 d /8.6/	17.6	7.36 <i>t</i> /74.0/ (CHF ₂)
VI	2.25 s	6.22 s	7.95 s	(2H)	7.59 d /8.8/	6.79 d /8.8/	17.7	3.04 s (6H NMe ₂)
VI**	2.25 s	5.90 s	7.99 d /15.0/	8.12 d /15.0/	7.61 d /8.2/	6.68 d /8.2/	-	3.07 s (6H NMe ₂)
VII	2.26 s	6.22 s	7.90 d /15.8/	8.02 d /15.8/	7.60 d /8.1/	7.02 d /8.1/	18.2	3.74 s (4H (CH ₂) ₂ O) 3.30 s (4H (CH ₂) ₂ N)
VIII	2.27 s	6.29 s		7.2-7.7	m (9H)		17.9	-
IX	2.27 s	6.30 s		7.2–7.7	m (8H)		17.8	2.10 s (3H γ-Me)
X	2.26 s	6.22 s		6.7-7.7 1	n (11H)		17.8	-
XI	2.23 s	6.20 s		6.7-7.9	m (8H)		>17	2.23 s (6H NMe ₂)

Table 2. ¹H NMR characteristics of the synthesized compounds (DMSO-d_a)*.

* the data are presented according to a following form $-\delta a$ /y/ (zH b), where " δ " is a chemical shift (in ppm), "a" is a shape of pick (**s** – singlet, **d** – doublet, **t** – triplet, **m** – multiplet), "/y/" is a coupling constant (Hz) for doublets and triplets, "z" is a number of protons, "b" is a position of proton or substituent type. ** in CDCl_n

	$\Delta G_{\rm f}^{298}$, kcal/mol ⁻¹	$K_{_{eq}}$	m, molar %	μ, D	$\Delta G_{\rm f}^{\rm 298}$, kcal/mol ⁻¹	$K_{_{eq}}$	m, molar %	μ, D
	DCM				AN			
la	-147.06	0.09	91.6	2.82	-149.10	0.02	98.1	3.03
lb	-145.64		8.4	0.86	-146.75		1.9	0.90
lc	-140.46			2.39	-141.56			2.59
ld	-143.63			1.28	-144.98			1.27
le	-139.87			3.16	-142.14			3.95
Vla	-170.86	0.06	93.9	1.45	-171.79	0.12	89.7	1.58
VIb	-169.24		6.1	3.47	-170.51		10.3	3.48
Vlc	-163.20			2.88	-163.73			2.88
Vld	-166.92			3.84	-167.86			3.85
Vle	-163.52			5.30	-163.30			5.98

Table 3. Theoretical parameters calculated for tautomers of cinnamoyl pyrones I and VI in dichloromethane (DCM) and acetonitrile (AN)*.

* - ΔG_f²⁹⁸ is a Gibbs formation energy (kcal/mol⁻¹), µ is a dipole moment (D), K_{eq} is an equilibrium constant between the most stable tautomers, and m is a molar fraction of tautomer (%). Tautomer marking: Ja is a tautomer "a" of cinnamoyl pyrone J.

Table 4. Theoretical parameters calculated for the most stable tautomers of cinnamoyl pyrones *II-V* and *VII* in dichloromethane (DCM) and acetonitrile (AN)*

	lla	llb	Illa	IIIb	IVa	IVb	Va	Vb	VIIa	VIIb
					D	СМ				
$\Delta G_{\rm f}^{298}$	-200.92	-188.36	-205.12	-190.41	-310.55	-298.39	-316.15	-301.64	-195.80	-194.82
kcal/mol-1										
K _{eq}	0.	.00	0.	00	0.	00	0.	00	0.	19
m . molar %	100.00	0.00	100.00	0.00	100.00	0.00	100.00	0.00	83.90	16.10
μ . D	1.78	2.68	2.69	2.62	4.55	1.08	7.24	4.26	2.58	1.41
					А	N				
$\Delta G_{\rm f}^{298}$	-204.81	-190.03	-206.07	-191.45	-317.69	-302.28	-319.31	-303.74	-198.79	-197.56
kcal/mol-1										
$\mathbf{K}_{_{\mathrm{eq}}}$	0.	.00	0.	00	0.	00	0.	00	0.	13
m . molar %	100.00	0.00	100.00	0.00	100.00	0.00	100.00	0.00	88.80	11.20
μ. D	2.06	2.69	2.94	2.75	4.81	1.16	7.43	4.45	2.87	1.40
* – se	e ΔG ²⁹⁸ , μ,	K m in Table	9.3.							

3.2. Theoretical investigations of equilibria between cinnamoyl pyrone tautomers

To determine which tautomers of cinnamoyl pyrones are dominant, the quantum chemical estimation of *I-XI* thermodynamic characteristics has been carried out. We have taken into account not only electrical and sterical effects of substituents in cinnamoyl fragment, but also the influence of solvent polarity.

The relative stability of the tautomers was estimated using theoretical values of Gibbs energies of formation $(\Delta G_{\rm f}^{298})$ calculated by the semi-empirical method (RM1) for two media of low (dichloromethane) and high (acetonitrile) polarity.

The data listed in Table 3 show that the tautomers **a** and **b** have minimal $\Delta G_{\rm f}^{298}$ values, and consequently, they have maximal stability in comparison with other tautomers. The presence of these last tautomers seems to be improbable because their $\Delta G_{\rm f}^{298}$ values are 3 kcal/mol⁻¹ higher than the ones of **a**.

The estimation of relative amount of tautomers **a** and **b** in their mixture (Tables 3 and 4) shows that the tautomer **a** is always predominant. In fact, in the case of II - V, the equilibrium constant values are close to zero, and the tautomer **a** may be the only stable form existing in all the media.

According to calculated values of ${}_{\Delta G_{\rm f}^{298}} {}_{\rm and} {}_{\rm k_{eq}},$ some quantity of the tautomer ${\it b}$ may be observed in

	VIIIa	VIIIb	IXa	IXb	Xa	Xb	Xla	Xlb
				D	M			
$\Delta G_{\rm f}^{\rm 298}$ kcal/mol ⁻¹	-150.44	-148.84	-160.73	-159.51	-142.56	-140.41	-143.68	-142.45
$\mathbf{K}_{_{\mathrm{eq}}}$	0.	05	0.	01	0.	01	0.	13
m . molar %	95.3	4.7	99.3	0.7	99.2	0.8	88.9	11.1
μ . D	3.06	0.94	3.92	0.15	2.85	1.27	2.29	2.25
				A	N			
ΔG_{f}^{298}	-151.07	-149.29	-160.66	-157.75	-142.82	-139.98	-146.26	-144.84
KCal/IIIOI	0	07	0	02	0	03	0	na
•• _{eq} m. molar %	93.7	6.3	97.7	2.3	97.40	2.60	91.6	8.4
μ . D	3.52	2.43	4.30	0.13	3.11	1.32	1.33	3.21

Table 5. Theoretical parameters calculated for the most stable tautomers of vinylogs of cinnamoyl pyrones VIII-X in dichloromethane and acetonitrile*

* – see ΔG_{f}^{298} , μ , K_{eq} , m in Table 3.

the case of unsubstituted compound *I* and of cinnamoyl pyrones having substituents of high electron donating ability such as *VI* and *VII*.

The relations between the medium polarity and equilibrium constants also depends on the nature of substituents. The increase in the polarity results in the decrease of K_{eq} in the case of *I* (from 0.09 (dichloromethane) to 0.02 (acetonitrile)) and *VII* (from 0.19 (dichloromethane) to 0.13 (acetonitrile)) and to the increase of K_{eq} in the case of *VI* (from 0.06 (dichloromethane) to 0.12 (acetonitrile)).

The explanation of different behavior of $a \leftrightarrows b$ equilibria in solvents of different polarity can be based on the comparison of tautomer dipole moments. According the data listed in Tables 3 and 4, the tautomers a of cinnamoyl pyrones as well as I and VII have higher dipole moments than the tautomer b. On the contrary, the dipole moment of the tautomer b of VI is higher than that of a. As the increase of medium polarity results in the stabilization of the most polar form, it is obvious that the concentrations of tautomers Ia, VIIa and VIb in acetonitrile are higher than in dichlorometane.

The ΔG_{f}^{298} and K_{eq} values for tautomers **a** and **b** of cinnamoyl pyrone vinylogs **VIII** – **XI** are listed in Table 5. These data show that the lengthening of the polymethine chain or the distortion of its flatness by the addition of a methyl group (compound *IX*) do not influence substantially the equilibrium between **a** and **b** tautomers. In all cases, the form **a** is predominant in media of different polarity and is in the range of 94-99 molar %.

The above mentioned theoretical data correspond well to the results of ¹H NMR spectroscopy which indicate that only one cinnamoyl pyrone tautomer exists in solution. The concentration of any other tautomer is too low to be registered using NMR method.

It is worth noting that our conclusions correlate with data obtained earlier for DHA *XII*, which may be used as a model molecule for cinnamoyl pyrone investigations. ¹³C and ¹H NMR investigations as well as quantum chemical calculations (carried out using the AM1 method) were made for *XII* [10] and demonstrated that this molecule always exists in a α -pyrone form and corresponds to the tautomer *a* of cinnamoyl pyrone.

Summarizing the results of quantum chemical calculations, ¹H-NMR investigations and the data obtained earlier for model molecule **XII**, we have proposed that all studied cinnamoyl pyrones have the α -pyrone structure, as it is depicted on Scheme 1.

3.3. Spectral properties of cinnamoyl pyrone derivatives

As all the investigated cinnamoyl pyrones are represented by the *a* tautomers, we have supposed that electronic spectra obtained for these compounds are also due to the same tautomer. It is noteworthy that the preliminary analysis of excitation and synchronous-scan fluorescence spectra of the compounds having any fluorescence which were investigated, showed that this fluorescence is represented by only one emitting form.

The data listed in Table 6 show that unsubstituted cinnamoyl pyrone *I* absorbs in the range of 355-360 nm and has no fluorescence. The addition of difluoromethyl

Compound	Solvent	λ _{abs}	lg ε	λ ₁₁	Δv _{st}	φ
1	DCM	357	3.67	-	-	-
,	AN	358	3.57	-	-	-
	DCM	380	4.11	503	6440	0.4
11	AN	375	3.22	512	7140	0.6
	DCM	383	3.97	497	5990	0.2
	AN	382	3.12	505	6380	0.2
	DCM	357	3.90	-	-	-
IV	AN	356	3.18	3.90 3.18	-	-
V	DCM	361	4.04	491	7040	0.1
V	AN	359	3.88	505	8060	0.07
14	DCM	476	4.54	575	3610	54.6
VI	AN	464	3.10	591	4630	1.7
	DCM	437	3.90	575	5490	42.9
VII	AN	433	3.54	584	5970	6.8

Table	6.	Influence of substituents on spectral properties of cinnamovI pyrones*	
	•••		

* – λ_{abs} is a position of long-wavelength absorption band maximum (nm), *Ig* ε is a logarithm of the molar exctinction coefficient for long-wavelength absorption band maximum, λ_{fi} is a position of emission band maximum (nm), Δv_{st} is a Stokes shift of fluorescence (cm⁻¹), ϕ is a fluorescence quantum yield (%).

substituents having low electron-acceptor ability on the side phenyl ring (*IV* and *V*) does not lead to changes of spectral properties. However, in the case of *V*, a very weak emission at 490-510 nm with quantum yield $\leq 0.1\%$ has been observed.

The presence of electron-donating methoxy groups (*II* and *III*) results in a bathochrome shift of the long-wavelength absorption band (relatively the same band of *I*) up to 375-385 nm. *II* and *III* have a weak emission similar to *V*; however, their quantum yields of fluorescence are slightly higher than that of *V* and reach 0.2-0.6%

Of interest are anomalously high Stokes shifts (Δv_{st}) of *II*, *III* and *V* having values in range of 6000-8000cm⁻¹. Such values can indicate either a substantial structural relaxation of these molecules in the excited state or the presence of photochemical processes such as photo-tautomerization in α -pyrone moiety or cis/transisomerisation of a cinnamoyl fragment.

The presence of substituents with high electrondonating ability (*VI* and *VII*) results in the substantial shift of long-wavelength absorption bands into the red region, up to 470-480 nm and 430-440 nm, respectively.

In contrast to compounds I - V, long-wavelength electronic transitions in absorption spectra of diethylamine VI or morpholine VII derivatives are formed with participation of higher occupied molecular orbitals localized on nitrogen atom of substituents. As it was earlier found for other organic substances [21-23], these transitions are of different nature, and they are accompanied by inter-fragmental charge transfer. The long-wavelength bands corresponding to these transitions have different shapes (see Figs. 1A and 1B) with the corresponding compounds having high intensity fluorescence and "ordinary" Stokes shifts at the range of $3500-6000 \text{ cm}^{-1}$.

To estimate the influence of the solvent polarity on spectral properties of cinnamoyl pyrones, the absorption and fluorescence spectra of investigated substances using dichloromethane and acetonitrile were performed.

Absorption characteristics of cinnamoyl pyrones listed in Table 6 show that I - VII have no substantial solvatochromisme. On going to more a polar medium, long-wavelength bands of *II*, *VI*, *VII* undergo either a negligible hypsochromic shift or are not sensitive to solvent polarity. It is obvious that, in all the cases, the increase of solvent polarity results in the decrease of extinction coefficients of long-wavelength bands.

The comparison of cinnamoyl pyrone emission spectra in dichloromethane and acetonitrile has shown the presence of a positive solvatofluorochrome effect. In the case of *II*, *III*, *V* and *VII*, the bathochromic shift taking place under increasing solvent polarity is small and in the range of 8 - 15 nm (270 - 570 cm⁻¹). However, under such conditions, the derivative having a dimethylamino group (*VI*) exhibits a substantial bathochromic shift – from 550 nm to 590 nm (1210 cm⁻¹)

The change in solvent drastically influences the emission intensity. In all cases, the increase in solvent polarity leads to fluorescence quenching, but the most dramatic effect was observed in the intensively fluorescing compounds *VI* and *VII*. The quantum yields of these compounds are respectively ~32 and ~6 times lower in acetonitrile than in dichloromethane.



Figure 1. Normalized absorption (A) and fluorescence (B) spectra of *I* – *VII* in dichloromethane. (The excitation of the fluorescence has been carried out at wavelengths corresponding to long-wavelength absorption-band maxima of investigated compounds).

The analysis of spectral properties of cinnamoyl pyrone vinylogs (Table 7, Figs. 2A and 2B) demonstrates that the lengthening of the polymethine chain by one vinyl fragment leads to a bathochromic shift of long-wavelength band equal to approximately 30 nm. The distortion of the flatness of the chain (to compare *VIII* and *IX*) results in the 10 nm hypsochromic shift.

The compounds with planar (*VIII*, *X*, *XI*) and not planar (*IX*) polymethine chains demonstrate a different spectral behavior when solvent polarity is changing. In the case of *VIII*, *X* and *XI*, the increase in the polarity leads to a hypsochromic shift of the long-wavelength absorption band indicating a decrease in the dipole moment of these compounds upon excitation. The compound *IX* demonstrates an opposite spectral effect in with its long-wavelength absorption band undergoes the bathochromic shift. The extinction coefficients of these bands are always lower in a medium of higher polarity.





Analysis of the data listed in Table 7 allows some interesting conclusions to be drawn.

First, the positions of emission band maxima for substances with the same length of the polymethine chain are similar regardless of its planarity. Consequently, the chains of **VIII** and **IX** have similar conformations in the excited state. Taking into account a greater Stokes shift of **IX**, we propose that the excited-state structural relaxation results in flattening of the chain, but not in the opposite process.

Second, the substances with longer polymethine chain are more sensitive to the influence of electrondonating substituents. The addition of dimethylamino group in the cinnamoyl pyrone system leads to a bathochromic shift of the emission band at 2800 cm⁻¹ (in comparison to the spectra *V* and *VI* in dichloromethane). In the case of vinylogs with n=2, the displacement of the emission band is 4930 cm⁻¹ (the comparison of *VIII* and *IX* spectra). This spectral effect is well known

Compound	Solvent	λ_{abs}	lg ε	λ _{fi}	Δv _{st}	φ
VIII	DCM	386	3.81	515	6490	4.10
	AN	370	3.58	-	-	-
IX	DCM	377	3.65	512	6990	1.00
	AN	413	3.55	-	-	-
x	DCM	414	3.88	579	6880	7.10
	AN	386	3.57	593	9040	0.52
хі	DCM	492	4.01	662	5220	89.0
	AN	482	3.70	690	6250	4.60

Table 7. The influence of length and planarity of the polymethine chain on spectral properties of cinnamoyl pyrones*.

* – see $\lambda_{abs'}$ Ig ϵ , $\lambda_{ff} \Delta v_{st'} \phi$ in Table 6.

and explained by higher polarizability of π -electronic systems in molecules with longer polymethine chains. However, in the case of cinnamoyl pyrone derivatives, this effect may be of a great practical importance while taking into account a very high quantum yield of *IX* and the flattening (increase of rigidity) of the polymethine chain in the excited state. The lengthening of the chain would permit formation of dyes fluorescing in near infrared region.

All the conclusions drawn above are based upon the fluorescence spectra obtained in dichloromethane solutions. As observed from the data in Table 7, the emission of **VIII** and **IX** in polar acetonitrile is completely absent. However, the lengthening of the polymethine chain up to n=3 (compound **X**) results in the appearance of fluorescence. This spectral effect would not be possible if the emission quenching was due to cis/trans isomerization in the excited state. The longer chain is less rigid, and its lengthening must promote the isomerization process. Meanwhile, the longer polymethine chain is more polarizable in the excited state, and it could act as an electron-donating fragment for the pyrone moiety.

The quantum yield of compound XI in acetonitrile is 4.6%. It is higher than that of X, but 19.3 times weaker than its emission in dichloromethane solution. It is

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obvious that the emission of XI in acetonitrile is due to the presence of an electron-donating substituent whose electronic density transmits itself through polymethine chain into the pyrone moiety.

Thus, it is possible to suppose that the fluorescence quenching in cinnamoyl pyrones is probably due to some processes taking place in the pyrone fragment in the excited state and does not originate from cis\trans isomerisation of cinnamoyl fragment.

Finally, it is worth noting that the solvatofluorochromy and dramatic fluorescence quenching in polar media permit the use of the substances *VI*,*VII*, *X* and *XI* as sensors in the examination of medium polarity in biological and medical investigations.

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