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Fluorescence quenching of the ketocyanine dyes in polar solvents: anti-TICT behavior

A.O. Doroshenko[a,*], V.G. Pivovarenko[b]

[a] *Institute for Chemistry, Kharkov V.N. Karazin National University, 4 Svobody Sqr., Kharkov 61077, Ukraine*
[b] *Kyiv National Taras Shevchenko University, Volodymyrska 64, 01033 Kyiv, Ukraine*

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Abstract

Spectral properties and fluorescence decay in a series of differently N-substituted ketocyanine dyes belonging to the dibenzalcyclopentanone type were studied in solvents of various polarity and hydrogen bonding ability. The significant solvent-induced fluorescence quenching was explained by the increase of internal conversion rate owing to the lowering of the energy gap between S_1 and S_0 states in polar solvents. The alternative model of non-luminescent TICT states formation was shown to be less probable in the discussed series.

Keywords: Ketocyanine dyes; Donor–acceptor dialkyl–diarylamino substituted compounds; Solvent effects; Fluorescence quenching; TICT states

1. Introduction

Ketocyanine dyes are widely known for their expressed solvatochromic properties [1–3], which could be utilized, for example, in polarity sensing [4–6]. Together with the electronic absorption spectra, their fluorescence emission displays the same or even more pronounced sensitivity to the environment, which determines applicability of this class of compounds also as fluorescent probes [7–10]. Generally, ketocyanines do not belong to the most efficiently fluorescent molecules: their quantum yields do not exceed 0.5 [5–9,11,12].

As in the case of many other solvent sensitive fluorescent compounds, decrease of emission intensity in polar media is typical to the studied ketocyanine dyes [7–10]. The most pronounced loosing of fluorescence ability is detected for their solutions in highly polar proton donor surrounding, like alcohols and water [5–10,13] or even in –COOH groups containing polymers [14]. This is connected with the efficient hydrogen bonds formation between the ketocyanines carbonyl group and protic solvents molecules [15]. To the present time, there existed several attempts of investigation and clarification of such behavior of various C=O group containing dyes: ketocyanines [16,17], phthalimids [18], fluorenes [19] and naphthalenes [20], etc. The authors of [21,22] tried to explain such quenching as a result of the specific interactions with the molecules of protic solvents. Conceptions of “in-plane” and “out-of-plane” hydrogen bonding of the C=O group were elaborated for this purpose. According to [20–22], first of them is responsible for the solvatochromic behavior of the dyes, while as the second one plays the key role in the acceleration of radiationless decay in alcohol solutions.

Alternative explanation of the solvent induced fluorescence quenching in the ketocyanine series is connected with the possible formation of the low-fluorescent and highly polar TICT states [23–25]. Most of the fluorescent ketocyanine dyes contain the dialkyl-substituted amino groups in their molecules. Thus, the NR_2-groups internal twisting in the excited state and radiationless decay, determined by this excited state conformational rebuilding, must be considered among the probable reasons of the discussed emission decreasing in polar media. We have to take into account also, that the validity of the solvent–solute interactions (both specific and universal ones) in formation of TICT states was revealed by several authors [26,27].

In the present work, we decided to study the emission properties of a series of symmetric ketocyanine dyes—the derivatives of dibenzylidene cyclopentanone possessing

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[*] Corresponding author. Tel.: +380-572-457335; fax: +380-572-457130.
E-mail address: andrey.o.doroshenko@univer.kharkov.ua (A.O. Doroshenko).

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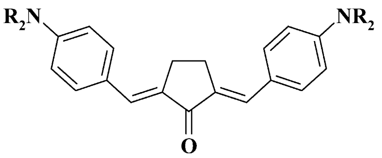
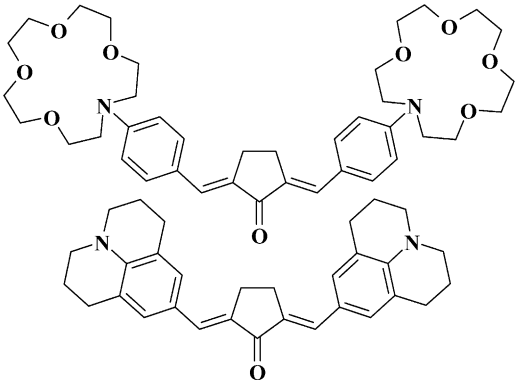
substituents of the different nature, dimensions and spatial organization at their amino-groups:



I	**R = -H**
II	**R = $-CH_3$**
III	**R = $-CH(CH_3)_2$**
VI	**R = $-C_6H_5$**



IV

V

Our efforts will be focused on the exploration of the nature of the fluorescence quenching of these compounds in polar and proton donor media.

2. Experimental

The synthesis of ketocyanines **II–IV** was described in our previous papers [7,11,28]. Compounds **V** and **VI** were obtained by the same procedure, via the condensation of the corresponding aldehyde and cyclopentanone in the alkaline ethyl alcohol–water solution [29]. However, to complete the interaction the reaction mixture was boiled for several hours. Compound **I** was obtained via condensation of 4-NO_2-benzaldehyde and cyclopentanone in acetic acid with catalytic amount of concentrated H_2SO_4, followed by the reduction of the formed nitro-dibenzalcyclopentanone by $SnCl_2$ in the concentrated aqueous HCl. Identification and purification of the synthesized compounds were conducted analogous to [28].

Commercially available solvents were purified according to the conventional procedures described elsewhere [30]. Polystyrene films were prepared by evaporation of the toluene solutions containing both dye and polystyrene on the flat glass surface.

Electronic absorption spectra were recorded on the HITACHI U3210 spectrophotometer. Fluorescence spectra and quantum yields were measured on the HITACHI F4010 spectrofluorimeter. Fluorescein solution in 0.05 M carbonate buffer served as the quantum yield reference standard ($\varphi_f = 0.85$ [31]). Fluorescence decay was studied on the pulse nanosecond single photon counting fluorometer described in [32]. Qualitative photochemical experiments were conducted with the high pressure mercury lamp DRK-120 with the UV part (below 320–340 nm) of its full spectrum cut-off by the glass filter BS-8.

Quantum chemical calculations were made by the semi-empirical method AM1 [33] incorporated into the MOPAC 6.0 program package.

3. Results and discussion

All the ketocyanine dyes have the carbonyl C=O group in their molecules. It introduces the singlet and triplet $n\pi^*$ terms into the system of the energetic levels of these compounds. This opens the possibility for their lowest singlet excited state radiationless deactivation via the efficient intersystem crossing (ISC) of $S\,(n\pi^*)$–$T\,(\pi\pi^*)$ or $S\,(\pi\pi^*)$–$T\,(n\pi^*)$ type. According to the El-Sayed rule [34], the rate of ISC between the singlet and triplet states of the different orbital nature exceeds that for the states of the identical orbital nature up to the several orders of magnitude. Owing to this circumstance, the ISC between $n\pi^*$ and $\pi\pi^*$ states successfully compete with the radiative depopulation of S_1^* energetic level. The discussed radiationless photoprocess is the main reason for the absence of fluorescence in the series of dibenzalcyclopentanone and its derivatives with substituents of low electron donor ability (alkyls, halogens, hydroxy and alkoxy groups). The lowest singlet excited state of the unsubstituted dibenzalcyclopentanone is of $n\pi^*$ type (~24,100 cm^{-1} in toluene, ~24,700 cm^{-1} in acetonitrile, Fig. 1), thus it is depopulated entirely by the ISC onto the lower-lying triplet $\pi\pi^*$ states. To make molecules of this class fluorescent, we have to shift the next excited state, $S_2^*\,(\pi\pi^*)$, down by the energy scale to make its energy lower than that of $T(n\pi^*)$ state—this is principally possible when introducing the appropriate electron donor substituents. In this case, the ISC rate between the singlet and triplet excited states of $\pi\pi^*$ type will be relatively low and such compounds might be fluorescent.

Taking into account quite low sensitivity of $n\pi^*$ levels to the changes of molecular structure, we could roughly estimate the "critical S_1^* state energy", after reaching of which the substituted dibenzalcyclopentanone molecule begin to fluoresce. Normally, the singlet–triplet splitting for the $n\pi^*$ levels of carbonyl compounds is in the range of 2500–3000 cm^{-1} [35], thus one could expect

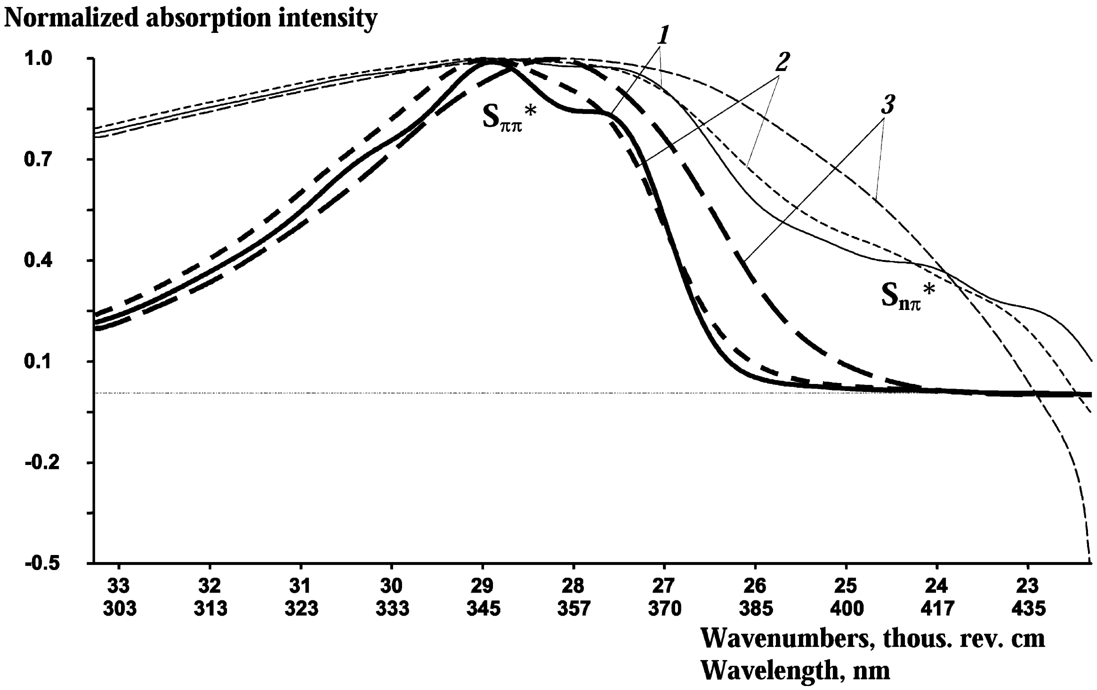


Fig. 1. Absorption spectra of the unsubstituted dibenzalcyclopentanone in their normal and semi-logarithmic presentation (thin lines, added to show both $n\pi^*$ and $\pi\pi^*$ bands in the comparable intensity scale): in toluene (1), acetonitrile (2), and ethyl alcohol (3).

the appearance of fluorescence for the ketocyanine compounds with $S_1^*(\pi\pi^*)$ state energy of 21,500–22,000 cm^{-1}. The corresponding energetic levels shifting is possible for amino- and dialkylamino-derivatives (or for any other electron donor substituents of the same donor force). Here, we have to note, that if even $S_1^*(\pi\pi^*)$ state will be lower in energy than $T(n\pi^*)$ one, there still exists a possibility for the temperature-activated ISC, thus additional low energy shifting of the S_1^*-level on approximately 600–700 cm^{-1} (thermal movement energy for the room temperature) is highly desirable. The above considerations are illustrated by the energetic Jablonsky diagrams, presented in Fig. 2.

The main spectroscopic information for the studied ketocyanine dyes is collected in the Table 1. As it follows from the data presented, the NH$_2$-group containing compound **I** is practically on the margin of the earlier mentioned "critical spectral range". Another compounds are quite close to

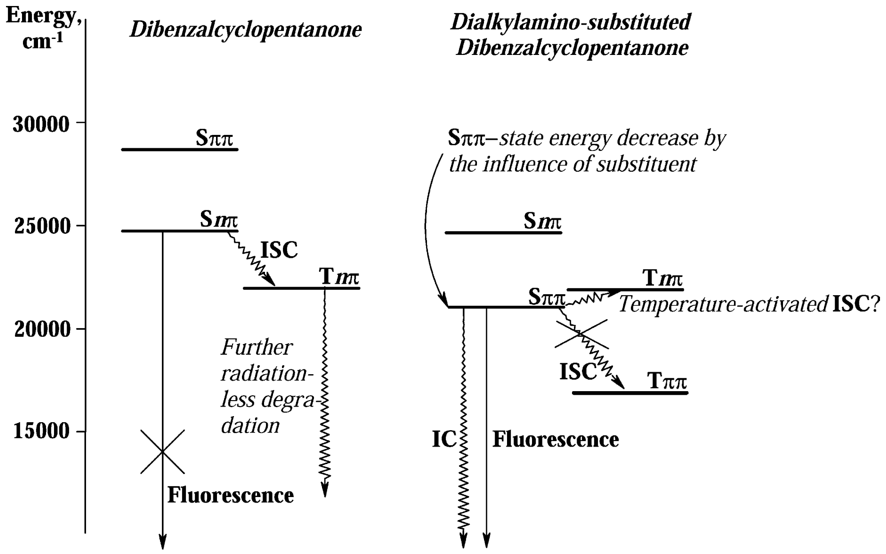
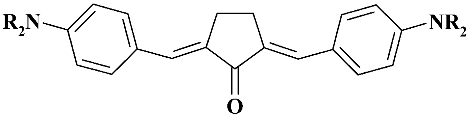


Fig. 2. Jablonsky diagrams for the unsubstituted and dialkylamino–dibenzalcyclopentanones, which demonstrate the reasons for the absence of fluorescence in the first case and for the appearance of fluorescence in the second case.

Table 1
Spectral properties of the differently N-substituted amino-dibenzalcyclopentanones



Compound	R	Solvent	E_T^N (30)	L	ν_a	λ_a	ν_f	λ_f	$\Delta\nu_{ST}$	ν_f^{CM}	φ_f	τ_f	k_f	k_d
I	–H	Toluene	0.099	0.0135	23920	418	20600	485	3320	19941	0.010	–	–	–
		Dioxane	0.164	0.0202	23880	418	19300	518	4580	18639	0.067	0.48	1.41×10^8	1.96×10^9
		Butylacetate	0.241	0.1709	23780	421	19460	514	4320	19039	0.052	0.35	1.49×10^8	2.71×10^9
		DMF	0.386	0.2744	22040	454	17980	556	4060	17647	0.135	0.45	2.97×10^8	1.91×10^9
		Acetonitrile	0.460	0.3047	23000	435	18200	549	4800	17879	0.118	0.41	2.90×10^8	2.17×10^9
		Isopropanol	0.546	0.2739	22060	453	17420	574	4640	17078	0.131	0.38	3.49×10^8	2.32×10^9
		Ethanol	0.654	0.2886	21960	455	17020	588	4940	16824	0.062	0.31	1.99×10^8	3.00×10^9
		Methanol	0.762	0.3084	22020	454	16840	594	5180	16708	0.024	0.24	1.00×10^8	4.09×10^9
II	$–CH_3$	Toluene	0.099	0.0135	22020	454	20500	488	1520	19483	0.131	0.51	2.57×10^8	1.70×10^9
		Dioxane	0.164	0.0202	22080	453	19000	526	3080	18589	0.159	0.59	2.69×10^8	1.42×10^9
		Butylacetate	0.241	0.1709	22220	450	18880	530	3340	18482	0.136	0.58	2.33×10^8	1.48×10^9
		DMF	0.386	0.2744	21300	469	17200	581	4100	16903	0.280	0.61	4.56×10^8	1.17×10^9
		Acetonitrile	0.460	0.3047	21720	460	17240	580	4480	16927	0.224	0.51	4.40×10^8	1.53×10^9
		Isopropanol	0.546	0.2739	21060	474	16900	592	4160	16613	0.246	0.55	4.46×10^8	1.37×10^9
		Ethanol	0.654	0.2886	20820	480	16320	613	4500	16175	0.092	0.29	3.20×10^8	3.18×10^9
		Methanol	0.762	0.3084	20680	484	15950	627	4730	15901	0.035	0.27	1.30×10^8	3.62×10^9
III	$–CH(CH_3)_2$	Toluene	0.099	0.0135	21560	464	20360	491	1200	19238	0.183	0.46	3.95×10^8	1.76×10^9
		Dioxane	0.164	0.0202	21580	463	18760	533	2820	18385	0.200	0.66	3.02×10^8	1.21×10^9
		Butylacetate	0.241	0.1709	21740	460	18660	536	3080	18296	0.191	0.65	2.92×10^8	1.24×10^9
		DMF	0.386	0.2744	20760	482	17220	581	3540	16879	0.380	0.83	4.61×10^8	7.52×10^8
		Acetonitrile	0.460	0.3047	21040	475	17160	583	3880	16832	0.356	0.78	4.58×10^8	8.29×10^8
		Isopropanol	0.546	0.2739	20580	486	16700	599	3880	16372	0.446	0.98	4.62×10^8	5.74×10^8
		Ethanol	0.654	0.2886	20320	492	16000	625	4320	15836	0.196	0.48	4.12×10^8	1.69×10^9
		Methanol	0.762	0.3084	20060	499	15520	644	4540	15459	0.072	0.24	3.06×10^8	3.95×10^9
IV	15-Aza-Crown-4	Toluene	0.099	0.0135	21740	460	20520	487	1220	19389	0.161	0.57	2.81×10^8	1.47×10^9
		Dioxane	0.164	0.0202	21740	460	18980	527	2760	18589	0.179	0.61	2.95×10^8	1.35×10^9
		Butylacetate	0.241	0.1709	21900	457	19040	525	2860	18658	0.156	0.62	2.53×10^8	1.37×10^9
		DMF	0.386	0.2744	21060	475	17500	571	3560	17148	0.368	0.89	4.14×10^8	7.12×10^8
		Acetonitrile	0.460	0.3047	21420	467	17440	573	3980	17116	0.367	0.84	4.35×10^8	7.50×10^8
		Isopropanol	0.546	0.2739	20840	480	16880	592	3960	16568	0.543	1.17	4.63×10^8	3.90×10^8
		Ethanol	0.654	0.2886	20660	484	16280	614	4380	16076	0.327	0.68	4.79×10^8	9.85×10^8
		Methanol	0.762	0.3084	20540	487	15880	630	4660	15733	0.138	0.32	4.26×10^8	2.66×10^9
V	$–(CH_2)_3–$, julolidinyl	Toluene	0.099	0.0135	20880	479	19500	513	1380	18475	0.273	0.58	4.74×10^8	1.26×10^9
		Dioxane	0.164	0.0202	20920	478	17880	559	3040	17597	0.323	0.84	3.85×10^8	8.07×10^8
		Butylacetate	0.241	0.1709	21080	474	17820	561	3260	17533	0.299	0.87	3.44×10^8	8.08×10^8
		DMF	0.386	0.2744	20000	500	16500	606	3500	16138	0.172	0.45	3.81×10^8	1.84×10^9
		Acetonitrile	0.460	0.3047	20280	493	16440	608	3840	16066	0.0647	0.18	3.59×10^8	5.20×10^9
		Isopropanol	0.546	0.2739	19760	506	16020	624	3740	15779	0.173	0.51	3.42×10^8	1.63×10^9
		Ethanol	0.654	0.2886	19420	515	15360	651	4060	15326	0.061	0.27	2.22×10^8	3.43×10^9
		Methanol	0.762	0.3084	19200	521	15020	666	4180	15144	0.022	0.11	1.99×10^8	8.73×10^9
VI	$–C_6H_5$	Toluene	0.099	0.0135	21600	463	19920	502	1680	18894	0.210	0.83	2.54×10^8	9.55×10^8
		Dioxane	0.164	0.0202	21800	459	18360	545	3440	17984	0.271	1.12	2.41×10^8	6.49×10^8
		Butylacetate	0.241	0.1709	21920	456	17900	559	4020	17647	0.252	1.30	1.94×10^8	5.75×10^8
		DMF	0.386	0.2744	21420	467	15880	630	5540	15828	0.190	0.81	2.33×10^8	9.95×10^8
		Acetonitrile	0.460	0.3047	21740	460	15600	641	6140	15596	0.153	0.58	2.63×10^8	1.46×10^9
		Isopropanol	0.546	0.2739	20960	477	15860	631	5100	15811	0.170	0.63	2.69×10^8	1.31×10^9
		Ethanol	0.654	0.2886	20960	477	15320	653	5640	15526	0.038	0.32	1.21×10^8	3.04×10^9
		Methanol	0.762	0.3084	20900	478	14960	668	5940	15373	0.010	–	–	–

Here: E_T^N (30) and L are the solvent polarity parameters according to Reichardt and Lippert; positions of the absorption and fluorescence maxima are presented both in wavenumber (ν_a and ν_f (cm^{-1})) and wavelength (λ_a and λ_f (nm)) scales; $\Delta\nu_{ST}$ and ν_f^{CM} are the fluorescence Stokes shift and the emission band center of mass (cm^{-1}); φ_f and τ_f (ns) are the fluorescence quantum yield and lifetime; k_f and k_d (s^{-1}) are the rates of the radiative and radiationless primary photoprocesses, estimated on the base of the quantum yield and lifetime ($k_f = \varphi_f/\tau_f$ and $k_d = (1 - \varphi_f)/\tau_f$).

Table 2
Spectral properties of the investigated ketocyanines in polystyrene

Compound	ν_a	λ_a	ν_f	λ_f	$\Delta\nu_{ST}$	$[\varphi_f]$	τ_f
I	23800	420	20460	489	3340	[0.11]	1.086
II	21680	461	20620	485	1060	[0.13]	0.521
III	21260	470	20420	490	840	[0.20]	0.681
IV	21420	467	20500	488	920	[0.15]	0.492
V	20660	484	19600	510	1060	[0.39]	0.979
VI	21280	470	18780	533	2500	[0.30]	1.219

Quantum yields were evaluated on the base of the experimental lifetimes measured for the polystyrenefilms and the corresponding k_f values taken from Table 1. Approximate E_T^N (30) value for polystyrene could be considered as close to that of styrene, 0.127.

it. This is the main reason for the relatively low fluorescence quantum yields in the investigated series.

The spectral and photophysical data for the studied ketocyanines in polystyrene films are presented in the Table 2. In this case, the quantum yields were not detected directly. They were recalculated from the experimental fluorescence lifetimes and k_f values for toluene solutions presented in the Table 1. The quantum yields in polymer surrounding could be considered as the upper limiting values for compounds **I–VI** in low polar media. The fact, that the presented φ_f did not show significant increase in comparison to the fluid solutions, testifies the low probability of the participation of various conformational changing processes in the radiationless deactivation of the investigated molecules.

As it was mentioned earlier, the expressed solvatochromism is typical to ketocyanine dyes. The solvent induced lowering of their absorption bands energy on going from toluene to methanol is near 2000 cm^{-1}, while as the same value for fluorescence bands reaches ~4000 cm^{-1}. Such a supplementary solvent induced shift of S_1^*-state energy must lead to the increase in the energy gap between it and T(nπ*). This must result in the fluorescence yield ascending. And indeed - the strong tendency to improving the ketocyanines **I–IV** fluorescence ability with solvent polarity was observed up to the quite polar DMF (Table 1, Fig. 3).

Proton donor solvents, which form hydrogen bonds with the ketocyanine C=O group, must favor higher fluorescence emission according to the above presented simple considerations based on the comparison of the energy of the excited levels of different orbital nature: if hydrogen bonding increases significantly the $n\pi^*$ states energy, this had to result in further rising of φ_f.

However, in reality we observed the nearly opposite picture—the decrease of fluorescence emission efficiency in polar media was typical to all the studied compounds. Surprisingly, the most pronounced quenching of fluorescence was detected in the most polar solvents according to the Reichardt and Lippert criteria, which are at the same time rather strong proton donors (ethanol and methanol). Such inadequacy observed in spectral behavior indicates the inclusion of some new channel of the ketocyanines excited state radiationless dissipation in the polar media. The TICT hypothesis was the first we had to check. This circumstance determined our choice of the investigated ketocyanines with the substituents of different size at nitrogen atoms of their amino groups. Attachment of the bulky groups to the latter must have two main opposite effects: (1) electron donor properties of the introduced substituents will increase the donor ability of $–NR_2$ groups, this would favor the definite bathochromic shift in the absorption and emission spectra; (2) bulky substituents will increase the steric hindrance in the molecules, violating the co-planarity of $–NR_2$ groups with the nearest benzene rings and decrease the conjugation between them, this would result in pronounced hypochromic effect.

To predict and explain the above effects on the qualitative level we conducted the series of quantum chemical calculations with the full optimization of molecular geometry by AM1 method. The averaged dihedral angles between the $–NR_2$ groups N–C bonds and the nearest to them C–C bonds of the closest benzene ring was chosen as a criterion of the initial dialkylamino group twisting. In addition, it reflects the degree of sterical hindrance and planarity violation. The approximate hybridization state of the nitrogen atoms was roughly evaluated as the deviation of their three valence angles C–N–C (mean pyramidalization angles) from the values of “classical sp^2”, 120° and “classical sp^3”, 109.1°. The obtained results are presented in Table 3.

As it was expected, the highest initial twisting was found for the most sterically hindered *N*-isopropyl derivative **III**. Probably, the aza-Crown cycle, which is characterized by the increased degree of freedom number, could be arranged in space in a definite way to diminish the steric effects in the molecule of compound **IV**. Surprisingly, the diphenylamino groups twisting in compound **VI** was lower than that in the case of isopropyl substituted compound **III**. By the degree of

Table 3
The ketocyaninic NR_2 groups state according to AM1 calculations

Compound	R	Mean twisting angle (°)	Mean pyramidalization angle	sp^2 (%)
I	H	0	115	54
II	CH_3	16	116	63
III	Isopropyl	46	118	82
IV	[15-Aza-Crown-4]	18	118	82
V	[Julolidinyl]	1	118	82
VI	C_6H_5	31	120	100

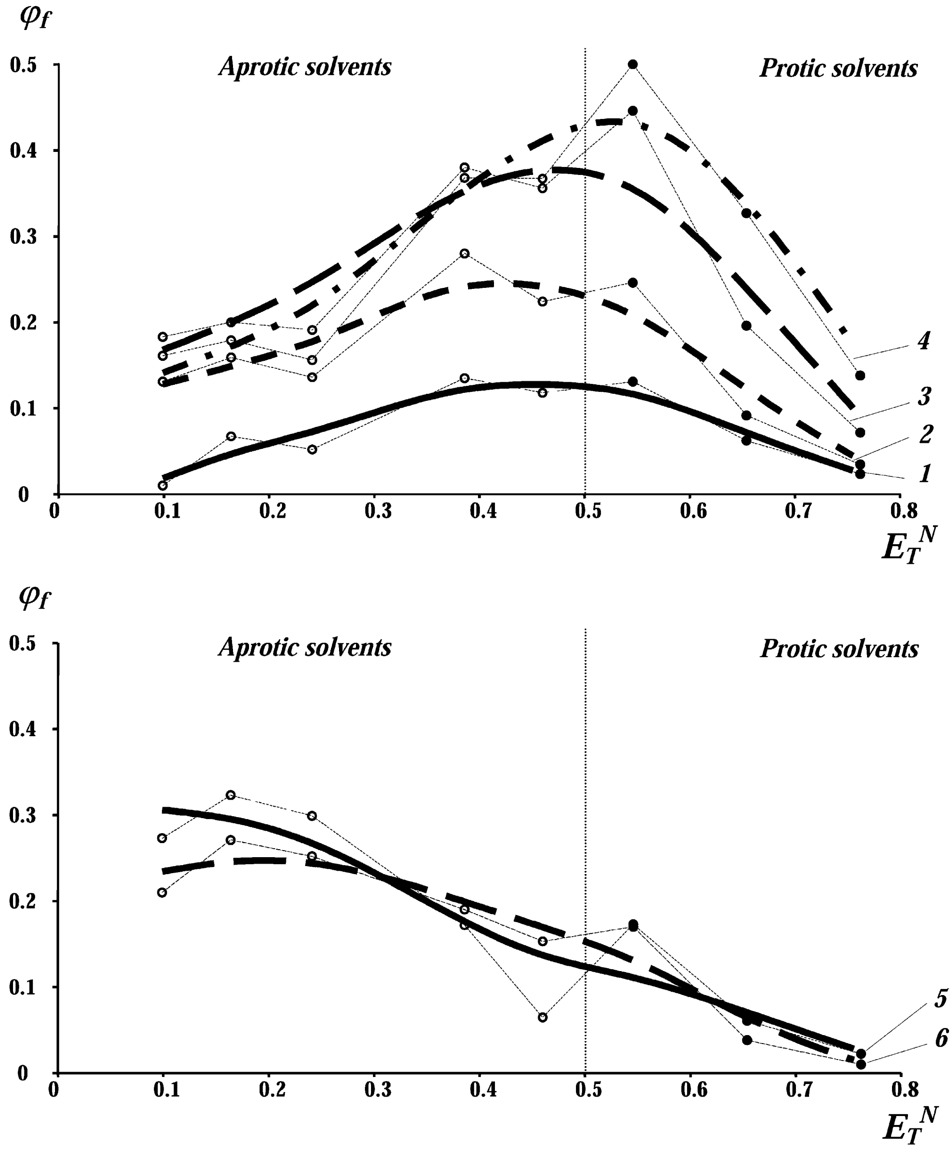


Fig. 3. Plots of the quantum yields of the studied ketocyanine dyes vs. the Reichardt solvent polarity parameter E_T^N: 1–4, compounds **I–IV**; 5–6, compounds **V** and **VI**.

pyramidalization the isopropyl (**III**), aza-Crowned (**IV**) and julolidinic compounds (**V**) were close to one another (∼80% sp^2). As it could be seen, even the “spatially fixed” julolidinic compound **V** did not display the full sp^2-hybridization state as well: with its negligible twisting angle, slight nitrogen atoms pyramidalization is typical to this molecule. In spite of this fact, we believe the compound **V** conditions of the nitrogen atoms lone pairs conjugation with the π-electron system of the rest of the molecule is the best among the studied series of ketocyanine dyes. Somewhat unforeseen was the flat configuration of diphenylamine substituted nitrogen atoms in compound **VI**, which corresponds to practically complete sp^2 hybrid state. However, conjugation between three phenyl moieties attached to the same nitrogen atom, could not be considered as ideal: owing to the repulsion of the hydrogen atoms in the *ortho*-positions of the discussed benzene rings, they rotate out of the planes of each other to the angles of ∼30°. That is why the whole $N(C_6H_5)_3$ group possesses the propeller-like configuration.

The elucidated structural features found their reflection in the spectral characteristics of the studied compounds: twisting angles satisfactory correlate with the positions of the long-wavelength absorption bands in toluene. The analogous correlation was found between the degree of sp^2-character and experimental solvatochromic shifts, for example, on going from toluene to acetonitrile. All these correlations reflect the changes in the conjugation within the studied molecules under the steric influence of the introduced substituents.

The tendencies in compounds **I–VI** fluorescence quantum yields variation with solvent polarity are depicted in Fig. 3. The initial increasing of φ_f, which corresponds completely to the above discussed influence of the solvent induced shifts

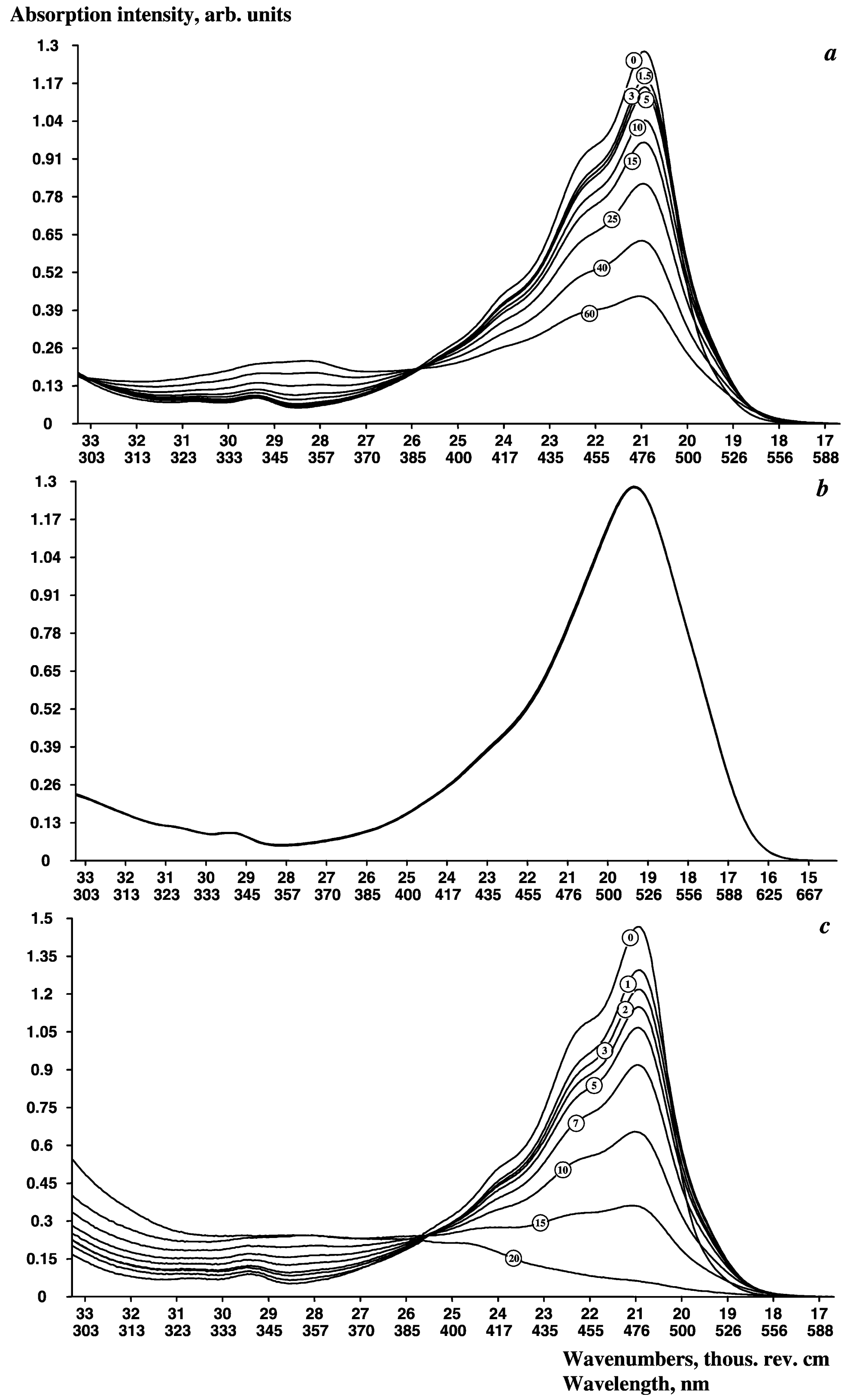


Fig. 4. Irradiation of compound **V** in toluene (***a***), methanol (***b***) by the near UV-Vis fraction of Hg spectrum and in toluene with the full spectrum of mercury high pressure lamp DRK-120 (***c***). Irradiation time (min) is indicated on the corresponding spectral curves. No changes in the spectra of methanol solution were detected during its 1.5 h irradiation, spectra were concise completely.

of energetic levels onto the photophysical parameters of the studied molecules. Nevertheless, in highly polar media, the φ_f values tend to decrease for all the compounds. Two molecules with their nitrogen atoms hybrid state close to sp^2 displayed such a falling down of their emission ability even in the moderately polar surrounding.

Sharp jump of fluorescence intensity was detected for relatively low polar proton donor solvents (particularly, isopropyl alcohol). This fact could be explained by the lowering the ISC efficiency as a result of the $T(n\pi^*)$ level energy increasing at hydrogen bond(s) formation between the ketocyanine carbonyl group and proton donor solvent molecules. However, further rise of the protonic solvent polarity (ethanol and methanol) results in significant decrease of φ_f.

All these observations might be considered in the frames of the popular during the last decades TICT model [23–25], but one circumstance does not allow us to agree with the application of this theory to the studied ketocyanines. Compound **V** with structurally fixed alkylamino groups, for which no internal rotation of $-NR_2$ moiety is possible, display the much more efficient solvent polarity induced fluorescence quenching compared to the other molecules, for which the readily TICT states formation might be expected (**II–IV**). Another compound with high sterical hindrance, **VI**, behave analogously to **V**. Their photophysical parameters are so similar, that we could even make an assumption, that the $-NR_2$ group nitrogen atom hybrid state plays the key role in the discussed quenching rather than the degree of one's initial twisting or pyramidalization. It is worthy noting, that another non-TICTing NH_2-substituted molecule, **I**, displays the same tendency in polarity quenching of its fluorescence as well. That is why we have to consider the existing of the definite general mechanism, which regulates the emission properties of the ketocyanine dyes in polar surrounding. Quite analogous behavior in polar media was reported recently to the fluorescent dye, crystal violet julolidinic analogue, which is not capable to form TICT states owing to the structural fixing of its alkylamino groups [36].

Qualitative analysis of the photochemical behavior of **V** helps us to elucidate the multiplicity nature of the excited states, involved into the discussed quenching mechanism.

The investigated ketocyanines like any other α,β-unsaturated ketones demonstrate photochemical *trans–cis* isomerization around their C=C double bond(s), which take place in the lowest triplet state. Thus, the photo-isomerization rate depends strongly from the probability of these molecules triplet levels population. Clearly, the most efficiently fluorescent compounds belonging to this group must be at the same time the most photo-stable due to the less probable population of their triplet levels, while as the lower fluorescent ones must demonstrate sufficient photochemistry. If the discussed solvent induced fluorescence quenching would result in the additional population of the triplet levels, this must enforce the observed photochemical transformations.

The results of the irradiation of compound **V** solutions in toluene and methanol are presented in Fig. 4. It is clearly seen, that no photo-transformation took place in the alcohol solution, while as spectral changes in toluene were quite typical to *trans–cis* isomerization of α,β-unsaturated ketones. Our additional experiments with the irradiation of toluene solutions by non-filtered light of the mercury lamp have shown significant acceleration of the compound **V** photo-isomerization. This fact could not be explained only by the increase of total irradiation light intensity owing to the involvement of several other Hg spectrum lines, which had been cut before by the BS-8 glass filter. We consider this effect also as sensitization of the discussed photochemistry

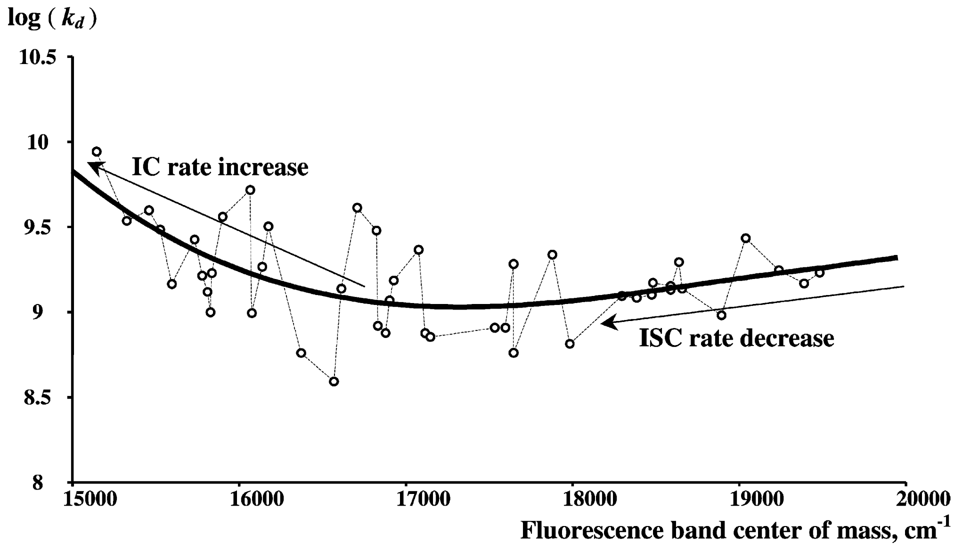


Fig. 5. Tendencies in changing of the radiationless decay rate constant values (Table 1) with the solvent induced long-wavelength shift of the fluorescence band. Data for all the studied ketocyanine dyes (**I–VI**) in all the examined solvents are presented on the same plot. Solid line is the polynomial approximation of the experimental data.

by toluene, which absorbs the far UV fraction of the mercury spectrum. After effective interconversion (high yield of triplets for toluene is widely known [37]), this energy have been used for direct population of the photoactive lowest triplet state of **V** by the mechanism of *T–T* energy transfer from the solvent. Based on these results, we concluded that the discussed fluorescence quenching of ketocyanine dyes in polar solvents is not connected with the intersystem crossing and population of the triplet levels of **I–VI**.

Analyzing all the facts at our disposal we concluded, that it is really possible to consider this fluorescence quenching as an internal conversion (IC) $S_1^{\text{relaxed}} - S_0$ induced by the polar influence of solvent. We have no doubts also in the absence of any specific photochemical mechanisms like –NR_2 group internal twisting with the formation of non-fluorescent TICT states. However, our attempt to check if the studied fluorescence quenching of the highly solvatofluorochromic ketocyanine dyes is regulated by the classical "energy gap law" [38] could not be considered as completely successive (Fig. 5), in spite of the fact that definite tendencies in the increase of the radiationless decay rate constant with the long-wavelength shift of the fluorescence band were observed.

We have to emphasize here, that increasing of the solvent polarity and hydrogen bonding ability inspires two opposite effects on the photophysics of radiationless processes in the excited ketocyanine molecule: lowering the intersystem crossing S_1 $(\pi\pi^*)$–T $(n\pi^*)$ rate and increasing the rate of internal conversion $S_1 - S_0$. The ISC rate constant depends on the nature of solvent and the chemical structure of the parent compound quite individually for any of the studied molecules, while as the IC rate must follow the general "energy gap law", common for all the investigated compounds. That is why the experimental data scattering, which is plotted in Fig. 5, in which the data for all the compounds **I–VI** in all the examined solvents are collected, might seem to be enormously increased.

4. Conclusion

The symmetric ketocyanine dyes containing different types of alkyl or aryl substituents at their nitrogen atoms display significant fluorescence quenching with the increase of solvent polarity and hydrogen bonding ability. Such behavior is not connected with the possible excited state internal twisting of their –NR_2 groups, because the compound with structurally-fixed julolidinic moiety behaves analogously to the molecules with labile dialkylamino residues. The most probable explanation of the observed fluorescence quenching in polar surrounding is the increase of the "classical" internal conversion efficiency due to the lowering of the energy gap between the ketocyanines' solvent and structurally relaxed excited singlet state and the corresponding ground state as a result of significant solvatofluorochromic effects, additionally enlarged by the hydrogen bonds formation with the protic solvents molecules.

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