New fluorescent dye of dibenzalcyclopentanone series possessing increased solvatochromism and "energy gap law" regulated fluorescence quenching in polar solvents

Andrey O. Doroshenko [a,*], Mikhail D. Bilokin [b], Vasyl G. Pivovarenko [b]

[a] *Department of Physical Organic Chemistry, Institute for Chemistry, Kharkov V.N. Karazin National University, 4 Svobody Square, Kharkov 61077, Ukraine*
[b] *Chemical Faculty, Kyiv National Taras Shevchenko University, Volodymyrska 64, 01033 Kiev, Ukraine*

Abstract

New ketocyanine dye of dibenzalcyclopentanone series, characterized by the increased solvatochromism, was synthesized. Its spectral behavior was examined 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, instead of the alternative scheme with the possible formation of non-fluorescent TICT states.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Dibenzalcyclopentanone; Solvatochromism; Fluorescence quenching; Energy gap law

1. Introduction

Solvatochromism of various ketocyanine dyes was a subject of numerous publications during the last decades [1–17]. The pronounced solvent effects both in the absorption and in the emission spectra of these compounds make them promising probes for monitoring solvent polarity [8,9], for the hydrogen bond complexes formation [10], metal ions sensing [11–15] or investigation of the cell membranes structure [16], etc.

To shift the absorption of ketocyanine dyes onto the range of YAG–Nd laser second harmonic emission we have synthesized a new representative of this class with the increased length of its π-conjugated system, the chemical structure of which is shown below:

I
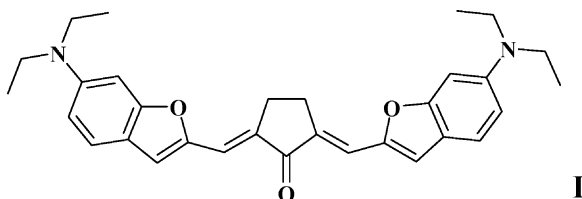
We expected of this compound much more pronounced solvent-induced spectral effects in comparison with other ketocyanines studied earlier [1–16].

In our last paper on this subject, we examined the solvatofluorochromic behavior and fluorescence quenching connected with the solvent polarity of several related ketocyanins of the dibenzalcyclopentanone series with different substituents at their aminogroups nitrogen atoms (R = H, several normal and branched alkyl groups including "structurally-fixed" julolidinyl moieties, aryl groups) [17].
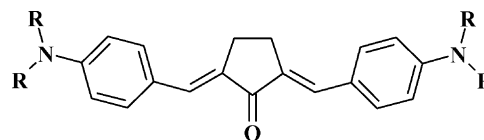
Owing to the fact, that dialkylamino, diphenylamino and, the most important, julolidinic derivatives displayed practically the same polarity-induced significant emission decrease, we came to conclusion that changing their quantum yield in polar surrounding could not be described by the traditional TICT approach [18–21]. Moreover, the clear trend in linear changing of their radiationless decay rate constants with the positions of their lowest excited singlet states was observed [17]. Thus, the photophysics of the dyes of this group in polar surrounding must be regulated by the classical "energy gap law" [22–24] between S_1^* and S_0 levels

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

rather than TICT-like conformational rebuilding. However, this statement demanded additional provements, and we have found them during our study of the newly-synthesized representative of the ketocyanine series—the main object of the present article.

2. Experimental

The compound **I**, 2,5-bis{(E)-[6-(diethylamino)-1-benzo-furan-2-yl]methylidene}cyclopentanone, was synthesized by the condensation of 0.02 mol 6-diethylaminobenzo[b]-furan-2-carbaldehyde with 0.01 mol of cyclopentanone in the presence of excess KOH (total concentration ∼30 mol/l) in aqueous ethanol. The appropriate aldehyde was kindly presented by Klymchenko [25]. The obtained precipitate of **I** (black crystals, 0.007 mol, 70%) was further recrystallized from ethanol, identified by ^{1}H-NMR and its purity was tested by TLC. The main physico-chemical data of compound **I** were the following: chemical formula $C_{31}H_{34}N_2O_3$; mp 182 °C (uncorrected); molecule composition found (%): C 77.0, H 7.0, N 5.8; calculated (%): C 77.15, H 7.10, N 5.80. Mass spectrum (Waters TMD spectrometer) shows molecular ion M^+ at 482. ^{1}H-NMR spectrum was recorded on Mercury-400 apparatus (Varian) in $CDCl_3$ with TMS as internal standard. The decreased in half quantity of signals in the NMR spectrum points on C_{2v} symmetry of the compound **I** and the similar (E,E)-configuration of the both olefinic fragments in the molecule, ^{1}H-NMR: 7.40d, $J = 8$ Hz (2H); 7.39s (2H); 6.91s (2H); 6.71d, $J = 2$ Hz (2H); 6.70m, $J_1 = 8$ Hz, $J_2 = 2$ Hz, (2H); 3.43q, $J = 6$ Hz (8H); 3.22s (4H); 1.23t, $J = 6$ Hz (12H); here 's' stands for singlet, 'd' for doublet, 't' for triplet, 'q' for quartet and 'm' for multiplet. IR spectrum was measured in KBr tablets on Specord 75IR apparatus: 1125 cm^{-1} (ν_{C-O}), 1605 cm^{-1} (broad band, $\nu_{C=O}$ and $\nu_{C=C}$), 2980 cm^{-1} (ν_{C-H}).

Electronic absorption spectra were recorded on the HITACHI U3210 spectrophotometer. Fluorescence spectra and quantum yields were measured on the HITACHI F4010 spectrofluorimeter with fluorescein solution in the carbonate buffer as the quantum yield reference standard ($\varphi_f = 0.85$ [26]). Fluorescence decay was studied on the pulse nanosecond single photon counting fluorometer described in [27]. Quantum chemical calculations were made by the semi-empirical AM1 method [28] incorporated into the MOPAC 6.0 program package. Solvent parameters were taken from [8,29].

3. Results and discussion

Absorption and emission spectra of **I** in solvents of different polarity are presented in Fig. 1, corresponding solvatochromic plots in Fig. 2, and numerical data are collected in Table 1. The $E_T^N(30)$ polarity scale was chosen here only for informational purposes because it is a single-parameter

one and no other multi-parameter solvatochromic scales could be easily presented on the two-dimensional plot. The $E_T^N(30)$ based approach was used by the authors [3,4] and it was found, that the data points for protic (except water solutions) and aprotic solvents fall onto the same line on the contrary to more common case, when data for these two types of solvents form clearly distinct near parallel lines. Ketocyanins, which solvatochromism was studied by us earlier [10–12,17], behaved analogously. We have to emphasize here, that no quantitative results were obtained in this paper from the correlations between the spectral data of **I** and $E_T^N(30)$: functions of universal interactions based on dielectric constants and refraction indices were used for this purpose (see further). Data points for octane and toluene (in much less extent) deviate from the common solvatochromic plots. Similar behavior was reported recently for several fluorescent dyes of coumarin series [30,31]. Among the possible reasons of such deviation we consider also the dramatic changing in the shape of absorption and emission bands of **I** on going from the non-polar solvents to more polar ones.

It is clearly seen that going from octane to ethanol shifts the absorption maxima from ∼510 to 560 nm, while as the emission demonstrates much more pronounced shifting—from 526 to 755 nm. Such behavior shows that the S_1^* state is more polar (and probably more planar) then the ground state of **I**. This is typical for most of the keto-cyanine dyes [1–17], however solvent effects demonstrated in the present case are the largest among all the studied compounds of this class.

Estimation of the excited state dipole moment of **I** was made according to the approach proposed in [32,33], which allow to avoid the evaluation of the Onzager cavity radius—rather uncertain parameter for the long linear molecules, moreover for the molecules, which might exist in solution as a mixture of conformers with different spatial dimensions. Solvatochromic plots of the electronic spectra positions (ν_a, ν_f) versus the universal interaction functions (F_1, F_2) must be constructed on the first step:

$$\nu_a - \nu_f = S_1 F_1(\varepsilon, n) + \text{const}_1 \tag{1}$$

$$\frac{1}{2}(\nu_a + \nu_f) = S_2 F_2(\varepsilon, n) + \text{const}_2 \tag{2}$$

Here, $F_1(\varepsilon, n)$ and $F_2(\varepsilon, n)$ are the functions of universal interactions by Bilot and Kawsky [34]:

$$F_1(\varepsilon, n) = \frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) \tag{3}$$

$$F_2(\varepsilon, n) = \frac{1}{2}F_2(\varepsilon, n) + \frac{3}{2}\frac{n^4-1}{(n^2+2)^2} \tag{4}$$

S_1 and S_2 are the main detectable parameters, which depend on the ground (μ_G) and the excited state (μ_e) dipole moments of the solvatochromic molecule and also include its
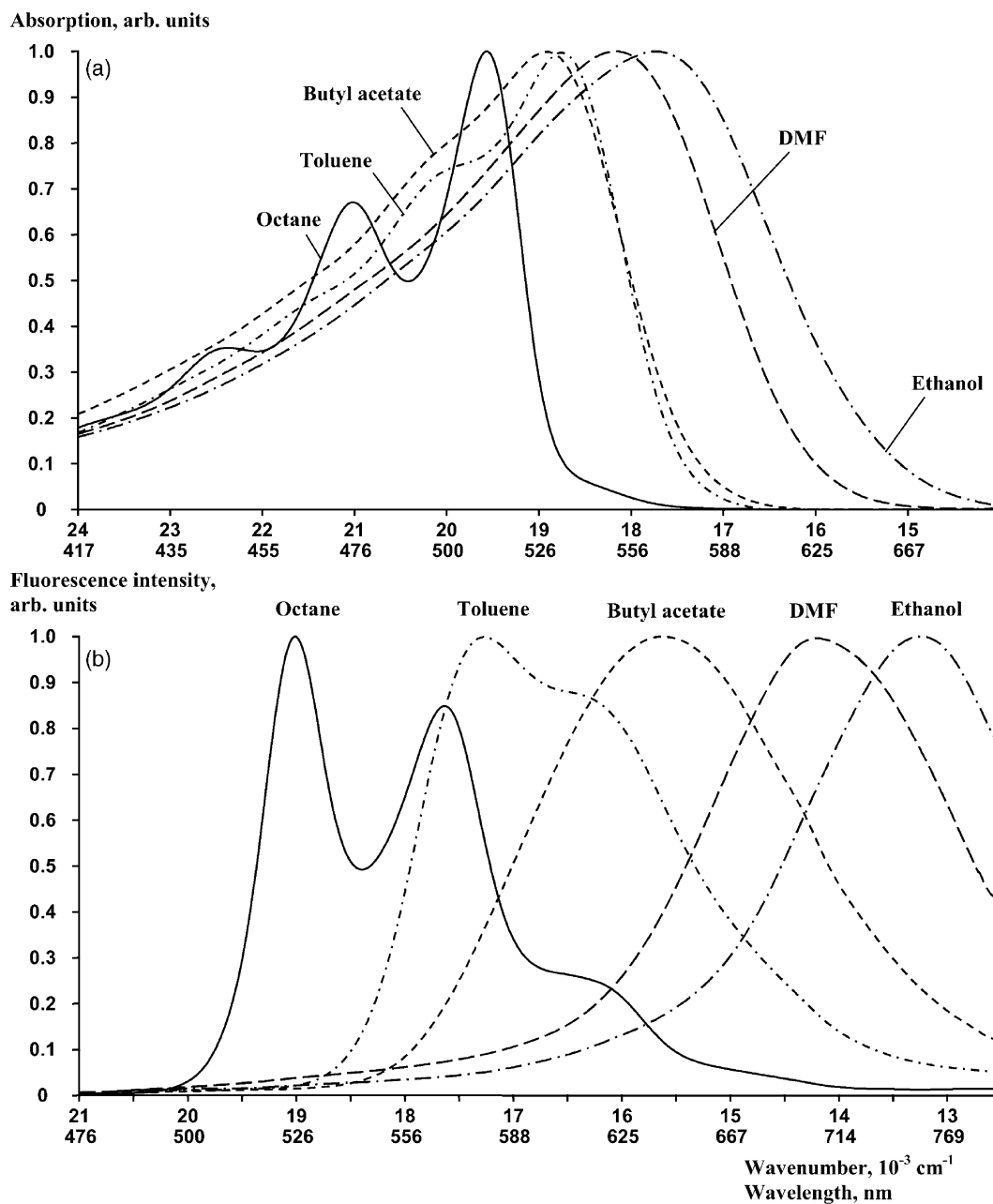
Absorption, arb. units

Fig. 1. Normalized absorption (a) and emission (b) spectra of compound **I** in solvents of different polarity.

Onzager cavity radius value (a):

$$S_1 = 2\frac{(\mu_e - \mu_G)^2}{hca^3} \qquad (5)$$

$$S_2 = -2\frac{\mu_e^2 - \mu_G^2}{hca^3} \qquad (6)$$

Combining (5) and (6) one can get the final equation, which connects the ground and excited states dipole moments values and the solvent sensitivity parameters obtained from the solvatochromic plots:

$$\mu_e = \mu_G \frac{S_2 - S_1}{S_2 + S_1} \qquad (7)$$

Thus, the only one parameter, which must be estimated prior to the application of Eq. (7), is the ground state dipole moment μ_G. In our case, we decided to calculate it theoretically using the semi-empirical method AM1, which demonstrated rather high precision in predicting dipole moments of organic compounds, compared to that of modern "first principles" methods, having much lower calculation cost at the same time [35].

Another circumstance, which we have to take into account, is the possible conformational inhomogeneity of **I**. The existence of various rotamers in solutions of ketocyanine dyes was known from the middle 70th, and validity of this fact to understanding the spectral behavior of this
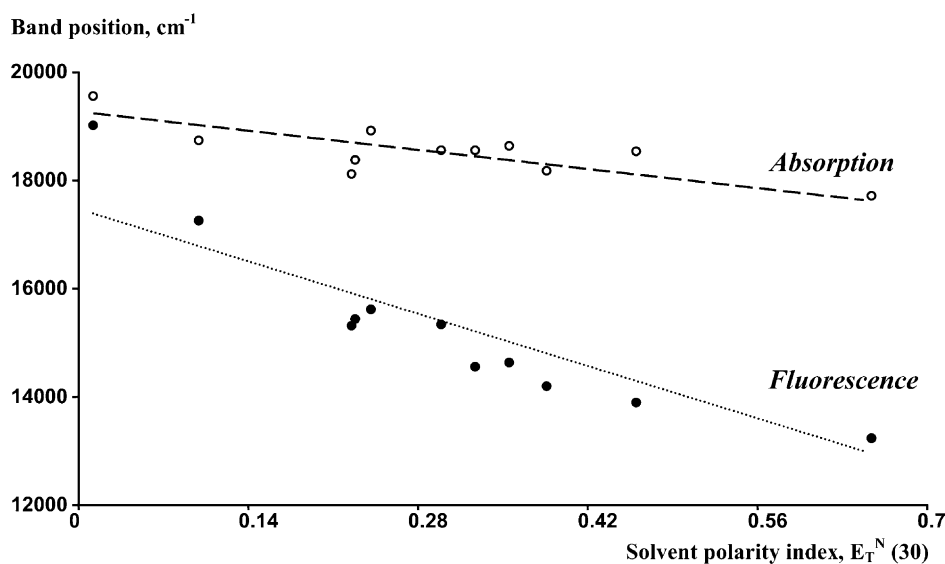
Fig. 2. Solvent-induced shifts in the absorption and emission spectra of **I** (formal maxima) vs. the Reichardt solvent polarity parameter, $E_T^N(30)$.

class of compounds was once more emphasized recently [36,37]. Unfortunately, no direct experimental evidences of the existence of several rotamers could be obtained for **I**: NMR is too slow physical method for detection of their rapid mutual transformations; the pronounced overlap between rather low-frequency C=O vibrations band and falling into the same spectral region bands of C=C and aromatic/heterocyclic rings vibrations did not allow us to use IR data (the corresponding absorption band near $1600\,cm^{-1}$ in KBr or CCl_4 is substantially asymmetric and broad with total half-width $\sim50\,cm^{-1}$). However, the absence of any sterical hindrance for the rotation around the single bonds of **I** and proximity in calculated energies of its conformers (see further) leave no doubts in the existence of rotamers in solutions of the studied compound.

Thus, we calculated three possible conformers of **I** with full optimization of their molecular structure by AM1

method, and then estimated their relative concentration (molar fraction, m_i) in equilibrium mixture at room temperature basing on their calculated heat of formation values (ΔH_i, kcal/mol):

$$m_i = \frac{\exp(-\Delta H_i/RT)}{\sum_i \exp(-\Delta H_i/RT)} \tag{8}$$

After this, the resulting dipole moment could be obtained with the account of the equilibrium composition of the mixture of rotamers and the individual dipole moments of any of them:

$$\mu^2 = \sum_i m_i \mu_i^2 \tag{9}$$

The results of our calculations were collected in Table 2. The calculated ΔH_i values of the three rotamers of **I** were quite close one to another, so their molar fractions in the

Table 1
Spectral parameters of compound **I** in various solvents

Solvent	$E_T^N(30)$	ε	n	ν_a	λ_a	ν_f	λ_f	$\Delta\nu_{ST}$	ν_S	φ_f	τ_f
Octane	0.012	1.95	1.3974	19560	511	19020	526	540	19240	0.489	1.19
Toluene	0.099	2.38	1.4961	18740	534	17260	579	1480	17940	0.464	1.18
o-Dichlorobenzene	0.225	9.93	1.5515	18120	552	15320	653	2800	16660	0.219	1.35
Ethyl benzoate	0.228	6.13	1.5050	18380	544	15440	648	2940	17000	0.282	1.24
Butylacetate	0.241	5.01	1.3940	18920	529	15620	640	3300	17770	0.308	1.18
Triacetin	0.299	7.01	1.4305	18560	539	15340	652	3220	17040	0.230	0.99
Methyl ethyl ketone	0.327	18.85	1.3790	18560	539	14560	687	4000	16720	0.117	0.35
Acetone	0.355	20.70	1.3588	18640	536	14640	683	4000	16780	0.117	0.50
DMF	0.386	36.70	1.4303	18180	550	14200	704	3980	16420	0.056	0.44
Acetonitrile	0.460	36.20	1.3441	18540	539	13900	719	4640	16160	0.035	0.20
Ethanol	0.654	24.30	1.3611	17720	564	13240	755	4480	15100	0.019	0.13

ν_a and λ_a are the positions of the long-wavelength absorption band maxima (cm^{-1} and nm); ν_f and λ_f the same for the fluorescence spectra; $\Delta\nu_{ST}$ (cm^{-1}), φ_f and τ_f (ns) the fluorescence Stokes shift, quantum yield and lifetime values; ν_S the normalized absorption and emission spectra crossing points (cm^{-1}), which estimate the energy of 0–0 electronic transition; $E_T^N(30)$, ε and n the polarity by Reichardt, dielectric constant and refraction index of the solvents used. Owing to the low emission intensity, fluorescence lifetime of **I** in ethanol was measured with much higher experimental error.

S_0 state equilibrium mixture would be of the same order as well. The final averaged ground state dipole moment value of compound **I**, estimated with the account of its conformational composition, was found to be 4.88 D. We consider the above result as "satisfactory enough theoretical estimation" of the real μ_G, even if the related composition of the conformational mixture would vary in different solvents, because the polarity of three possible rotamers of **I** do not differ significantly one from another and from the averaged value as well. The mathematical treatment of the numerical spectral data according to Eqs. (1) and (2) (data for octane and ethanol were not included) resulted in the following values: $S_1 = 2896 \, cm^{-1}$ (correlation coefficient $r = 0.951$) and $S_2 = -4914 \, cm^{-1}$ ($r = 0.918$). In both cases the linearity of the solvatochromic plots was quite satisfactory and the regression equations were statistically valid on the 95% confidential level. Thus, the averaged

excited state dipole moment of **I**, estimated from the obtained μ_G, S_1 and S_2 values by Eq. (7), is ∼18.9 D, this is approximately 4 times higher than the ground state value. Indeed, the total increase of polarity of the investigated ketocyanine dye is rather significant and comparable to that of the classical "intramolecular charge transfer dye", 4-dimethylamino-4′-nitro-stylbene [38]. Probably, such pronounced change in polarity at electronic excitation of **I** is due to participation of both electron donor groups in the excited state electron density redistribution in this molecule. Like the ground state value, the μ_e is the averaged characteristic of the three conformers of the investigated molecule.

The compound **I**, being highly fluorescent in non-polar surrounding, displays significant lowering of its fluorescence quantum yield in polar solvents (Table 1 and Fig. 3a).

Recently, we have dealt with the analogous situation on the example of a series of several other ketocyanine
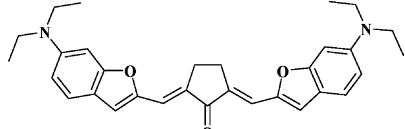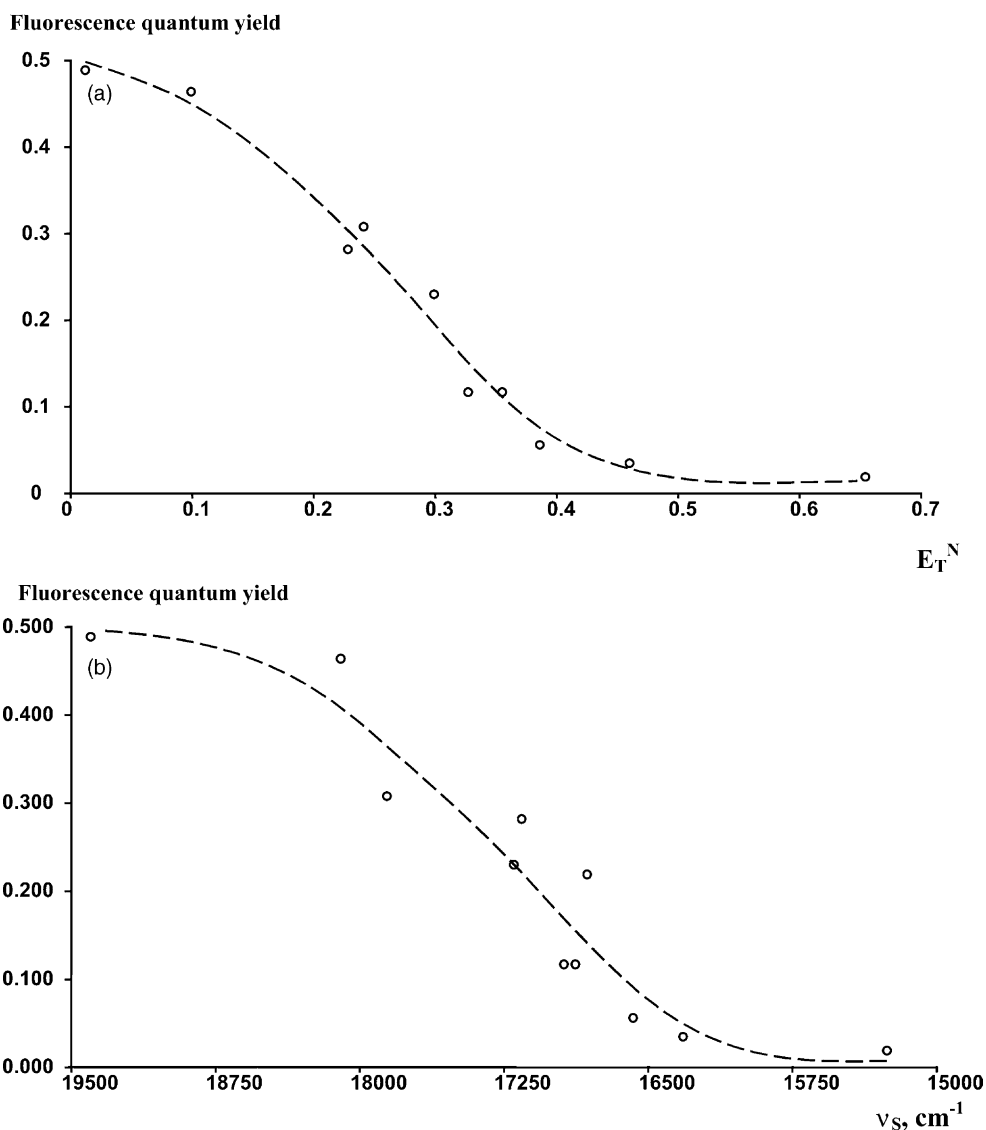

Fig. 3. Plot of fluorescence quantum yield of **I** vs. the solvent polarity parameter E_T^N (a) and position of the 0–0 electronic transitions in its electronic spectra in different solvents (b).

Table 2
Calculated parameters of the three possible rotamers of compound **I** and composition of the conformational mixture at equilibrium, m_i (molar fraction)

Rotamers	ΔH_i (kcal/mol)	m_i (%)	μ_i (D)
	56.4	46	4.70
	56.6	34	4.81
	56.9	20	5.38

dyes of dibenzalcyclopentanone type [17]. Then we came to conclusion, that decreasing their fluorescence ability in polar solvents is not connected with the formation of poorly fluorescent TICT states [18–21], but rather with the acceleration of "classical" internal conversion (IC) S_1^*–S_0 owing to the decrease of the energy gap [22] between the above-mentioned electronic states in highly polar media.

Thus, we tried to disseminate the above assumption also onto the case of compound **I**, for which we expected to find the definite correlation between the emission efficiency and S_1^* state energy as well. This would be the additional provement in favor of the conclusions made by us in [17].

The S_1^* state energy of **I** could be estimated as the position of the crossing point ν_S between the normalized absorption and emission spectra (also this is the estimation of the energy of entirely electronic 0–0 transition). The

corresponding plot of φ_f versus ν_S is shown in Fig. 3b. Owing to the expressed solvatofluorochromism of **I**, both curves in Fig. 3 are looking very similar one to another. These facts are in line with our assumption concerning the connection between the emission efficiency and electronic spectra shifting by the influence of solvent observed for this compound and the related ketocyanine dyes studied in [17].

To support the above statements, we consider the plot of the radiationless deactivation efficiency of **I** (estimated from the fluorescence quantum yield and lifetimes values, $k_d = (1 - \varphi_f)/\tau_f$) against the energy of its fully solvent- and structurally relaxed S_1^* state (approximated by the fluorescence spectrum maxima), which is presented in Fig. 4.

Analyzing the data of Fig. 4, we could conclude, that the main radiationless decay channel of **I** in low polar solvents is the intersystem crossing (ISC), like in the case of any other keto compounds [39]. At solvents, which induce
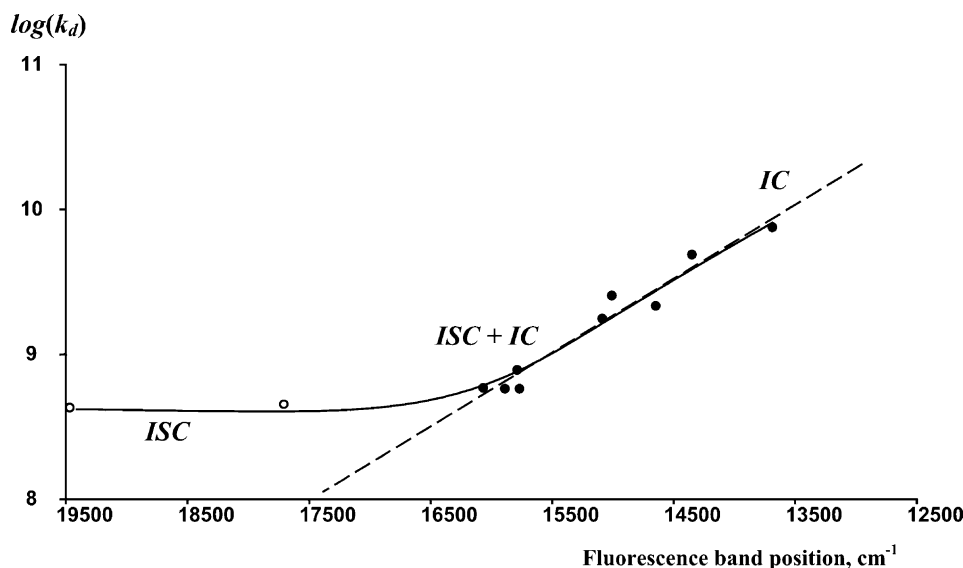

Fig. 4. Semi-logarithmic representation of the compound **I** radiationless decay rate constant vs. the energy of its solvent and structurally relaxed S_1^* state, estimated as the maxima of its fluorescence spectra in solvents of various polarity.

lowering of the S_1^* state energy, the ISC rate must only decrease [17], which have to favor improving the emission efficiency. However, the opposite behavior of **I** as well as the other ketocyanine dyes of dibenzalcyclopentanone series [17] was observed indeed.

Starting from the S_1^* state energy of ∼16000 cm^{-1}, a clear linear increasing of the radiationless decay rate logarithm is observed. This fact together with the data presented in [17] indicates the regulation of k_d rate by the simple energy gap law [22–24] and finally confirms our insights [17] about the heading role of the "classical" internal conversion in the formation of fluorescence behavior of compound **I**, instead of the alternative "TICT model", traditionally applied to description of polarity-induced radiationless decay of dialkylamino-substituted organic molecules during the last decades.

Owing to the pronounced sensitivity to solvent polarity: dramatic changes in fluorescence band position and intensity, high hydrophoby (log $P \sim 8.8 \pm 1.0$ estimated according to [40,41]), we could consider this compound and also its further water soluble derivatives, which we plan to synthesize soon, as the promising fluorescent probe(s) for investigating the cell membranes structure and dynamics.

4. Conclusion

The ketocyanine dye of dibenzalcyclopentanone series displaying high solvent sensitivity both in its absorption and especially fluorescence spectra was synthesized by the condensation of 6-diethylaminobenzo[b]furan-2-carbaldehyde with cyclopentanone. The fluorescence emission efficiency of this compound is shown to be regulated predominantly by the internal conversion rate, enforced in polar surrounding due to the lowering of the energy gap between the excited singlet and the ground states under the influence of the polar solvents. This result is the additional provement for the non-TICT photophysics of the dibenzalcyclopentanone series of ketocyanine dyes, anticipated by us in [17].

References

[1] N.B. Arzheukova, V.V. Danilov, V.S. Libov, Absorption and fluorescence spectroscopic study of the solvatochromism of ketocyanines in liquid crystals, Russ. J. Phys. Chem. (Engl. Transl.) 56 (1982) 1212–1215.

[2] V.V. Danilov, G.G. Dyadyusha, A.A. Rykov, The solvatochromism of ketocyanines and the formation of hydrogen bonds by the carbonyl group, Russ. J. Phys. Chem. (Engl. Transl.) 58 (1984) 556–560.

[3] M.A. Kessler, O.S. Wolfbeis, New highly fluorescent ketocyanine polarity probes, Spectrochim. Acta A 47 (1991) 187–192.

[4] M.V. Barnabas, A. Liu, A.D. Trifunac, V.V. Krongauz, C.T. Chang, Solvent effects on the photochemistry of a ketocyanine dye and its functional analogue, Michler's ketone, J. Phys. Chem. 96 (1992) 212–217.

[5] D. Banerjee, A.K. Laha, S. Bagchi, Solvent dependent absorption and fluorescence of a ketocyanine dye in neat and binary mixed solvents, Ind. J. Chem. Sect. A 34 (1995) 94–101.

[6] D. Banerjee, P.K. Das, S. Mondal, S. Ghosh, S. Bagchi, Interaction of ketocyanine dyes with cationic, anionic and neutral micelles, J. Photochem. Photobiol. A: Chem. 98 (1996) 183–186.

[7] P.K. Das, R. Pramanik, D. Banerjee, S. Bagchi, Studies of solvation of ketocyanine dyes in homogeneous and heterogeneous media by UV-Vis spectroscopic method, Spectrochim. Acta A 56 (2000) 2763–2773.

[8] C. Reichardt, Solvatochromic dyes as solvent polarity indicators, Chem. Rev. 94 (1994) 2319–2358.

[9] K. Rurack, J.L. Bricks, G. Reck, R. Radeglia, U. Resch-Genger, Chalcone-analogue dyes emitting in the near-infrared (NIR): influence of donor–acceptor substitution and cation complexation on their spectroscopic properties and X-ray structure, J. Phys. Chem. A 104 (2000) 3087–3109.

[10] V.G. Pivovarenko, A.V. Klueva, A.O. Doroshenko, A.P. Demchenko, Bands separation in fluorescence spectra of ketocyanine dyes: evidence for their complex formation with monohydric alcohols, Chem. Phys. Lett. 325 (2000) 389–398.

[11] A.O. Doroshenko, A.V. Grigorovich, E.A. Posokhov, V.G. Pivovarenko, A.P. Demchenko, Bis-azacrown derivative of di-benzili dene-cyclopentanone as alkali earth ion chelating probe: spectroscopic properties, Mol. Eng. 8 (1999) 199–215.

[12] A.O. Doroshenko, A.V. Grigorovich, E.A. Posokhov, V.G. Pivovarenko, A.P. Demchenko, A.D. Sheiko, Complex formation between azacrown derivatives of dibenzalcyclopentanone and alkali-earth metal ions, Russ. Chem. Bull. Int. Ed. 50 (2001) 404–412.

[13] K. Rurack, M.L. Dekhtyar, J.L. Bricks, U. Resch-Genger, W. Rettig, Quantum yield switching of fluorescence by selectively bridging single and double bonds in chalcones: involvement of two different types of conical intersections, J. Phys. Chem. A 103 (1999) 9626–9635.

[14] N. Marcotte, S. Fery-Forgues, D. Lavabre, S. Marguet, V.G. Pivovarenko, Spectroscopic study of a symmetrical bis-crown fluoro-ionophore of the diphenylpentadienone series, J. Phys. Chem. A 103 (1999) 3163–3170.

[15] N. Marcotte, P. Plaza, D. Lavabre, S. Fery-Forgues, M.M. Martin, Calcium photorelease from a symmetrical donor–acceptor-donor bis-crown fluoroionophore evidenced by ultrafast absorption spectroscopy, J. Phys. Chem. A 107 (2003) 2394–2402.

[16] A.O. Doroshenko, L.B. Sychevskaya, A.V. Grygorovych, V.G. Pivovarenko, Fluorescence probing of cell membranes with azacrown substituted ketocyanine dyes, J. Fluorine 12 (2002) 451–460.

[17] A.O. Doroshenko, V.G. Pivovarenko, Fluorescence quenching of the ketocyanine dyes in polar solvents: anti-TICT behavior, J. Photochem. Photobiol. A: Chem. 156 (2003) 55–64.

[18] Z.R. Grabowski, K. Rotkiewicz, A. Semiarczuk, D.J. Cowley, W. Baumann, Twisted intramolecular charge transfer states (TICT). A new class of excited states with a full charge separation, Nouv. J. Chim. 3 (1979) 443–453.

[19] W. Rettig, Charge separation in excited states of decoupled systems—TICT compounds and implications regarding the development of new laser dyes and the primary processes of vision and photosynthesis, Angew. Chem. Int. Ed. 25 (1986) 971–988.

[20] Z.R. Grabowski, Excited states with full separation of charges, Acta Phys. Pol. A 71 (1987) 743–754.

[21] K. Bhattacharyya, M. Chowdhury, Environmental and magnetic field effects on exciplex and twisted charge transfer emission, Chem. Rev. 93 (1993) 507–535.

[22] R. Englman, J. Jortner, The energy gap law for radiationless transitions in large molecules, Mol. Phys. 18 (1970) 145–164.

[23] W. Siebrand, Franck–Condon factors for radiationless transitions, J. Chem. Phys. 55 (1974) 5843.

[24] G.W. Robinson, R.P. Frosch, Electronic excitation transfer and relaxation, J. Chem. Phys. 38 (1963) 1187–1203.

[25] A.S. Klymchenko, T. Ozturk, V.G. Pivovarenko, A.P. Demchenko, A 3-hydroxychromone with dramatically improved fluorescence properties, Tetrahedron Lett. 42 (2001) 7967–7970.

[26] J.N. Demas, G.A. Crosby, The measurement of photoluminescence quantum yields. A review, J. Phys. Chem. 75 (1971) 991–1025.

[27] A.O. Doroshenko, A.V. Kirichenko, V.G. Mitina, O.A. Ponomaryov, Spectral properties and dynamics of the excited state structural relaxation of the *ortho* analogues of POPOP—effective abnormally large Stokes shift luminophores, J. Photochem. Photobiol. A: Chem. 94 (1996) 15–26.

[28] M.J.S. Dewar, E.G. Zoebich, E.F. Healy, AM1: a new general purpose quantum mechanical molecular model, J. Am. Chem. Soc. 107 (1985) 3902–3908.

[29] J.-L.M. Abboud, R. Notario, Critical compilation of scales of solvent parameters. Part I. Pure, non-hydrogen bond donor solvents, Pure Appl. Chem. 71 (1999) 645–718.

[30] S. Nad, H. Pal, Photophysical properties of Coumarin-500 (C500): unusual behavior in nonpolar solvents, J. Phys. Chem. A 107 (2003) 501–507.

[31] S. Nad, M. Kumbhakar, H. Pal, Photophysical properties of Coumarin-152 and Coumarin-481 dyes: unusual behavior in nonpolar and in higher polarity solvents, J. Phys. Chem. A 107 (2003) 4808–4816.

[32] S. Kumar, V.C. Rao, R.C. Rastogi, Excited-state dipole moments of some hydroxycoumarin dyes using an efficient solvatochromic method based on the solvent polarity parameter E_T^N, Spectrochim. Acta A 57 (2001) 41–47.

[33] S. Kumar, S.K. Jain, R.C. Rastogi, An experimental and theoretical study of excited-state dipole moments of some flavones using an efficient solvatochromic method based on the solvent polarity parameter E_T^N, Spectrochim. Acta A 57 (2001) 291–298.

[34] L. Bilot, A. Kawski, Zur Theorie des einflusses von Losungsmitteln auf die Elektronenspektren der Molekule, Z. Naturforsch. 17a (1962) 621–627.

[35] O.V. Prezhdo, Assessment of theoretical approaches to the evaluation of dipole moments of chromophores for nonlinear optics, Adv. Mater. 14 (2002) 597–600.

[36] N. Marcotte, S. Fery-Forgues, Spectrophotometric evidence for the existence of rotamers in solutions of some ketocyanine dyes, J. Photochem. Photobiol. A: Chem. 130 (2000) 133–138.

[37] N. Marcotte, S. Fery-Forgues, Influence of a second donor and of rotational isomers on the solvatochromic properties of ketocyanine fluorophores, J. Chem. Soc., Perkin Trans. 2 (2000) 1711–1716.

[38] E. Lippert, Dipolmoment und Elektrononstrukur von angergtn Molekulen, Z. Naturforsch. 10 (1955) 541–545.

[39] J.A. Barltrop, J.D. Coyle, Excited States in Organic Chemistry, Wiley, New York, 1975.

[40] R.F. Rekker, H.M. de Kort, The hydrophobic fragmental constant. An extension to a 1000 data point set, Eur. J. Med. Chem. 14 (1979) 479–488.

[41] J.M. Mayer, H. van der Waterbeemd, B. Testa, A comparison between the hydrophobic fragmental methods of Rekker and Leo, Eur. J. Med. Chem. 17 (1982) 17–25.