

Effects of chromophore interaction in photophysics and photochemistry of cyanine dyes

A. S. Tatikolov,¹ Zh. A. Krasnaya,² L. A. Shvedova,¹ and V. A. Kuzmin¹

¹Institute of Biochemical Physics, Russian Academy of Sciences, Kosygin Str. 4, 117334 Moscow, Russia

²Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Pr. 47, 117913 Moscow, Russia

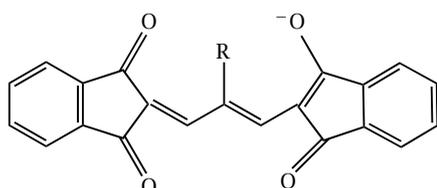
ABSTRACT. Spectral and fluorescent properties of ketocyanine dyes (polyenic bis- ω, ω' -aminoketones) and cation-anionic polymethine dyes of various structures were studied. The symmetric ketocyanines were shown to have a long-wavelength absorption band bathochromically shifted in comparison with that of the asymmetric ketocyanines with the same total length of the polyenic chain. The nonlinear ketocyanines exhibit the additional short-wavelength band in their absorption spectra, which can be more intense than the long-wavelength band. The absorption spectra of ion pairs of cation-anionic dyes with overlapping cation and anion bands contain a new intense short-wavelength band inactive in fluorescence excitation. These spectral peculiarities are explained on the basis of chromophore interaction model. It has also been shown that the T_1 levels of ketocyanine chromophores do not essentially interact with each other in a ketocyanine molecule in nonpolar solvents; in polar solvents this interaction becomes appreciable due to lowering the potential barrier for conjugation.

1. INTRODUCTION

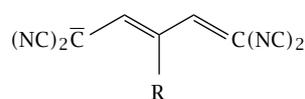
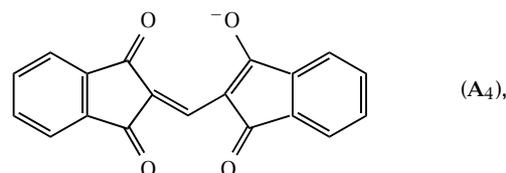
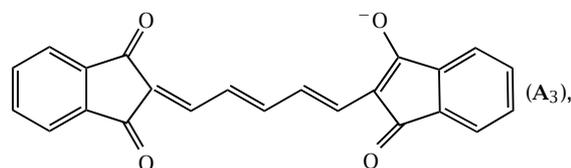
Dyes with single chromophores have wide applications in various fields of science and technology. Along with such simple dyes, a number of bichromophoric dyes were synthesized (*e.g.*, biscyanine dyes [1]), which possess interesting photochemical properties different from those of simple dyes. In the three recent decades, two new classes of bichromophoric cyanine dyes were obtained, ketocyanines [2, 3, 4] and cation-anionic dyes [5]. Ketocyanine dyes (polyenic bis- ω, ω' -aminoketones) consist of two ω -aminopolyenic units bound to the central carbonyl group; cation-anionic dyes contain in their structure cationic and anionic polymethine dyes. This work is devoted to investigation of the spectral and photochemical properties of these dyes and their features owing to interaction of chromophores in the dye molecules.

2. EXPERIMENTAL

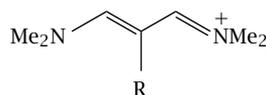
Ketocyanine dyes studied in this work were synthesized as described earlier [3, 4, 6]. The structures of the ketocyanines are presented in Table 1. The cation-anionic dyes obtained as described earlier [5] and contained the following dye anions:



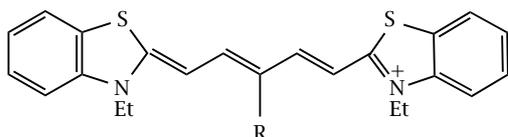
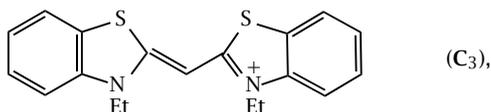
where R = H (A₁), Me (A₂),



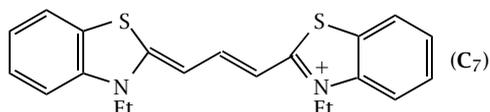
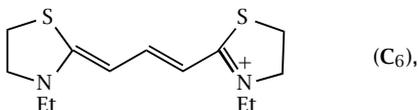
where R = H (A₅), Me (A₆); and the dye cations:



where R = H (C₁), Me (C₂),



where R = H (C₄), Me (C₅),



Acetonitrile, chloroform, toluene, dioxane, ethanol, n-propanol, and isopropanol were used as solvents. Chloroform was passed through an Al₂O₃ column to purify from traces of acids. Ethyl acetate was stored over molecular sieves; toluene was refluxed over metal sodium and stored over molecular sieves. The absorption spectra were recorded on a Specord UV-VIS spectrophotometer using cells with 1 cm path length. The fluorescence spectra were recorded using an Aminco-Bowman spectrofluorimeter equipped with an R136 photomultiplier (the spectra were not corrected for spectral sensitivity of the spectrofluorimeter). Concentrations of the dyes were in the range of 10⁻⁶–10⁻⁵ M.

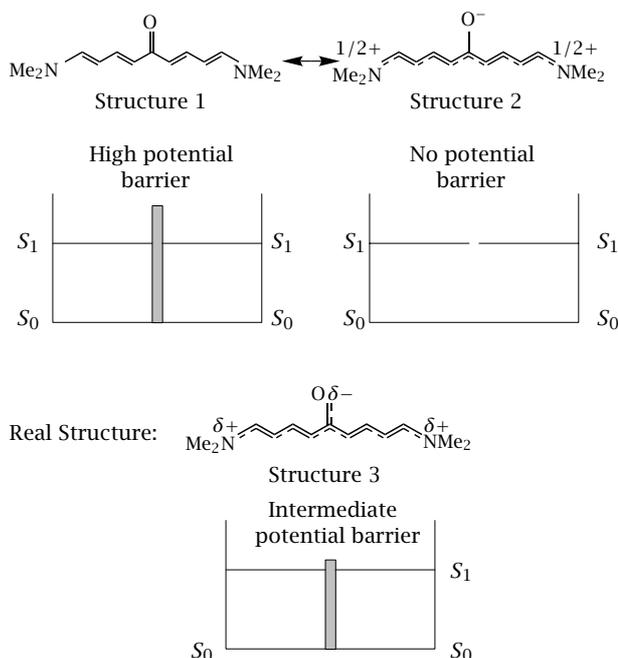
The triplet levels of ketocyanines were determined by measuring the rate constants for triplet-triplet energy transfer from anthracene ($E_T = 14700 \text{ cm}^{-1}$ [7]) and tetracene ($E_T = 10250 \text{ cm}^{-1}$ [7]) to ketocyanines and from ketocyanines to perylene ($E_T = 12600 \text{ cm}^{-1}$ [7]), tetracene and azulene ($E_T = 13600 \text{ cm}^{-1}$ [8]) using a conventional flash photolysis equipment (flash fwhm $\sim 7 \mu\text{s}$ with the energy 50 J [9]).

All measurements were performed at $20 \pm 2^\circ \text{C}$.

3. RESULTS AND DISCUSSION

Ketocyanine dyes. Table 1 presents the absorption and fluorescence maxima for the dyes studied. It can be seen that the symmetric dyes (with two aminopolyenic

fragments of the equal length) have the absorption bands shifted bathochromically compared to the asymmetric dyes with the same total length of the polyenic chain ($n + m$) (Table 1, *cf.* dyes 2 and 3; 5 and 7; 11 and 12; even dye 6 with asymmetric structure and longer total polyenic chain than that of dye 7 has the absorption spectrum located in the short-wavelength region with respect to the symmetric dye 7). This can be explained on the basis of interaction of two aminopolyenic chromophores in the dye molecule. The π -electronic structure of a ketocyanine dye can be represented as intermediate between two limiting resonance structures (structures 1 and 2; see Scheme 1). Structure 1 is characterized by alternating polyenic bonds and absence of charge separation; structure 2 has completely equalized polyenic bonds (complete π -electron conjugation along the whole polyenic chain) and separate charges (zwitterionic structure). The latter structure of a polyenic chain is characteristic for a cationic polymethine having the most bathochromic absorption band, so the shift of the real structure of a ketocyanine (structure 3) toward structure 2 (*e.g.*, due to solvation in polar and, in particular, protic solvents) will lead to a bathochromic shift of the ketocyanine absorption band. This can explain strong positive solvatochromism and thermochromism of ketocyanines observed experimentally [10].



Scheme 1. π -Electronic structure of ketocyanine dyes.

The spectral properties of polymethine dyes are known to be described well by the “free electron” model [11]. In this approach, a dye chromophore is represented by a potential box, whose width corresponds to the chromophore length. Thus, ketocyanine can be represented by two potential boxes corresponding to two aminopolyenic units (two chromophores) separated by

Table 1. Maxima of absorption ($\lambda_{\text{abs}}^{\text{max}}$) and fluorescence ($\lambda_{\text{fl}}^{\text{max}}$) spectra and extinction coefficients (ϵ) of ketocyanines (for dyes 1-19 in ethanol; $\lambda_{\text{fl}}^{\text{max}}$ in n-propanol).

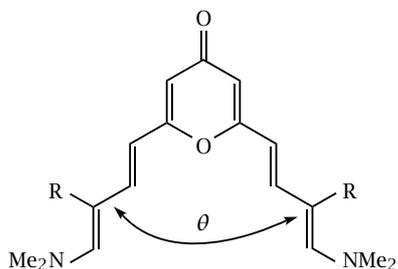
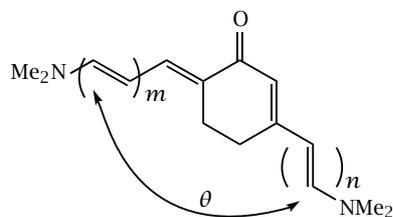
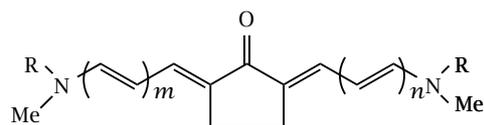
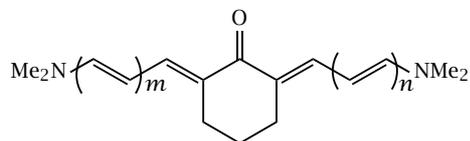
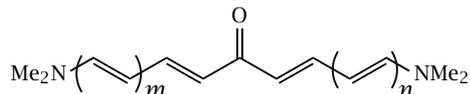
Dye	m	n	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\epsilon \times 10^{-4}$ ($\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{fl}}^{\text{max}}$ (nm)
1	0	1	430	7.27	—
2	0	2	450	5.45	—
3	1	1	470	6.4	540
4	1	2	507	8.55	625
5	1	3	522	10.4	—
6	1	4	530	—	—
7	2	2	550	8.66	673

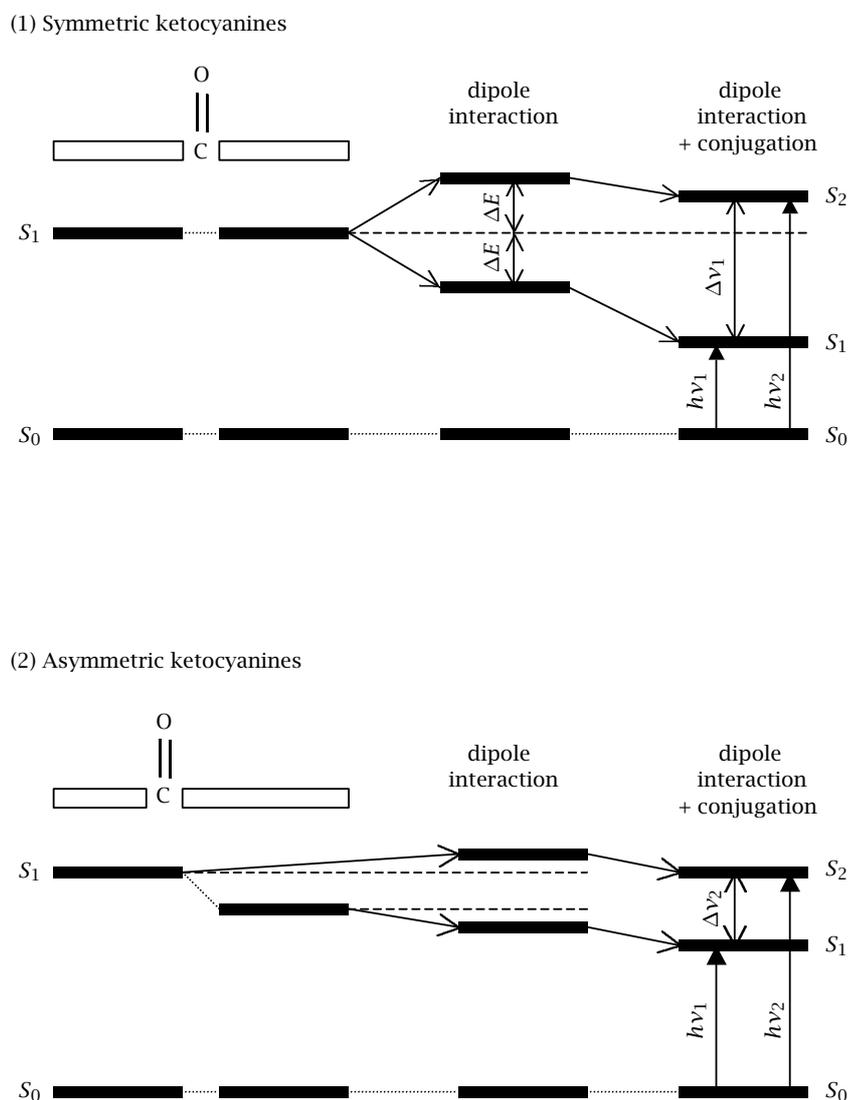
Dye	m	n	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\epsilon \times 10^{-4}$ ($\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{fl}}^{\text{max}}$ (nm)
8	0	1	440	5.64	—
9	1	1	450	5.45	550
10	1	2	512	6.6	625
11	1	3	532	—	—
12	2	2	550	7.9	668
13	2	3	575	—	—

Dye	R	m	n	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\epsilon \times 10^{-4}$ ($\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{fl}}^{\text{max}}$ (nm)
14	Me	1	1	508	8.16	570
15	Ph	1	1	503	—	580
16	Me	2	2	585	5.91	700
17	Me	3	3	625	—	—

Dye	m	n	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\epsilon \times 10^{-4}$ ($\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{fl}}^{\text{max}}$ (nm)
18	1	1	469	6.68	565
19	1	2	505	7.85	—

Dye	R	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\epsilon \times 10^{-4}$ ($\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{fl}}^{\text{max}}$ (nm)
20	H	360,	6.69,	566
		472	3.10	
21	Me	366,	6.65,	564
		472	3.54	
22	Ph	364,	9.23,	570
		475	5.12	





Scheme 2. Interaction of the chromophores (their excited singlet states) in symmetric and asymmetric ketocyanines.

a potential barrier (see Scheme 1). This barrier is due to the presence of two single bonds at the carbonyl group of the dye; it is highest for structure 1 and vanishes for structure 2 with complete (barrierless) π -electron conjugation. So the real structure of a ketocyanine has a moderate potential barrier.

Interaction of the excited singlet levels of the chromophores in a ketocyanine can occur by two ways: dipole-dipole interaction and conjugation through the potential barrier. The first one corresponds to exciton coupling in Davydov's model [12], the second corresponds to electron tunneling through the barrier. The dipole-dipole interaction results in symmetric splitting of the chromophore singlet levels [11]; the conjugation leads to further splitting and lowering of these levels [13] (see Scheme 2). Therewith, the maximum energy of the interaction (and the maximum splitting of the singlet electronic levels) occurs for the dyes with the sim-

ilar chromophores (for symmetric ketocyanines). For the linear ketocyanines **1–17**, the radiative transition $S_0 \leftrightarrow S_2$ is symmetry forbidden and the transition $S_0 \leftrightarrow S_1$ is allowed, so the chromophore interaction in linear ketocyanines manifests itself as bathochromic shift of the long-wavelength absorption band ($S_0 \rightarrow S_1$) of the dyes. Thus, the bathochromic shift of the absorption band of symmetric ketocyanines compared to that of asymmetric ones can be explained by stronger chromophore interaction in symmetric ketocyanines.

The $S_0 \leftrightarrow S_2$ transition, forbidden in linear ketocyanines, is allowed in nonlinear ones, so the energy gap $\Delta\nu$ between the absorption bands $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ can serve as a measure of the chromophore interaction in the nonlinear ketocyanines. Indeed, for the nonlinear symmetric ketocyanine **18** the value of $\Delta\nu$ is greater than that for the nonlinear asymmetric dye **19** (see Figure 1; $\Delta\nu_1 = 4400 \text{ cm}^{-1}$, $\Delta\nu_2 = 3500 \text{ cm}^{-1}$).

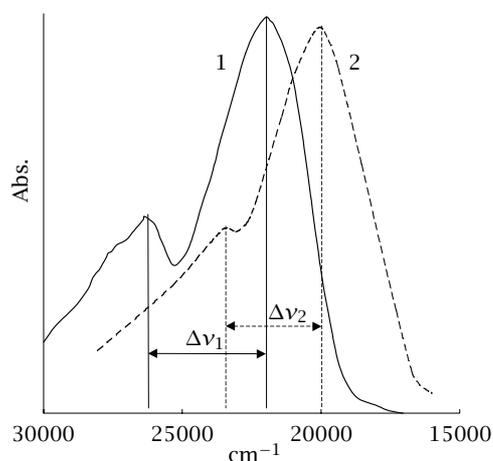


Figure 1. Absorption spectra of dyes **18** (1) and **19** (2) in *n*-propanol.

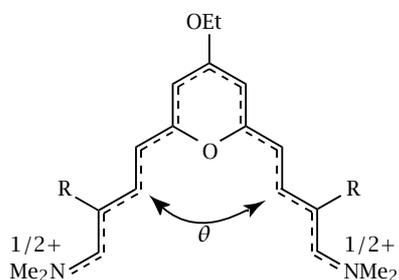
Generally, the intensities of the long-wavelength and the short-wavelength bands in the dipole-dipole approximation are related by the following expression [12, 14]:

$$\cos \theta = \frac{r-1}{r+1}, \quad (1)$$

where θ is the angle between the chromophores; $r = (\lambda_1 \varepsilon_1) / (\lambda_2 \varepsilon_2)$; λ_1, ε_1 and λ_2, ε_2 are the wavelength and extinction coefficients in the maxima of the short-wavelength and long-wavelength band, respectively. The estimation of the θ value from expression (1) for dyes **18** and **19** gives $\theta \sim 120^\circ$, which corresponds to the simple geometrical evaluation.

The absorption spectra of ketocyanines **20–22** are unusual: they consist of the long-wavelength band with relatively low intensity and the intense short-wavelength band (see Figure 2 and Table 1). This can be explained on the basis of the model of chromophore interaction. According to this model, ketocyanines with acute angles between the chromophores should have the short-wavelength absorption band more intense than the long-wavelength band. Indeed, the estimation of the angle θ from expression (1) gives $\theta = 75^\circ, 81^\circ$ and 83° for dyes **20**, **21**, and **22**, respectively.

It is of interest to note that even for the polymethine salts



where $R = H$ (**23**), Me (**24**), and Ph (**25**), the absorption spectra are unusual: they have the intense short-wavelength peaks (388 nm for **23**) and relatively weak long-wavelength bands (616 nm for **23**) (Figure 3),

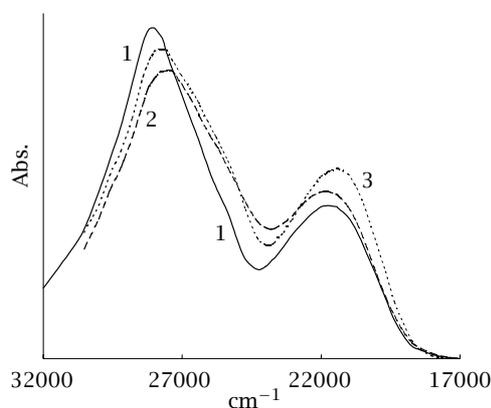


Figure 2. Absorption spectra of dyes **20** (1), **21** (2), and **22** (3) in isopropanol.

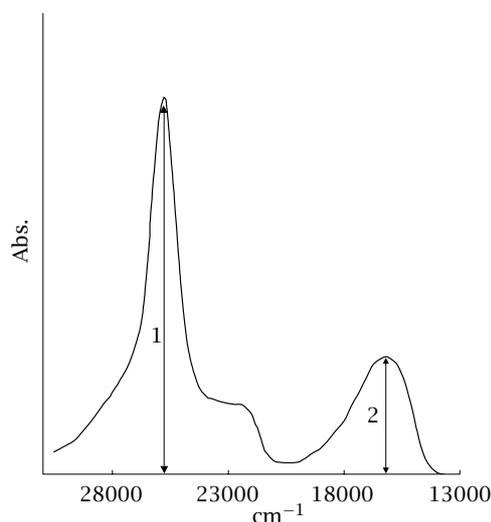
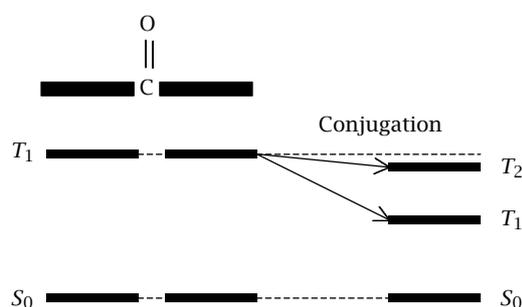


Figure 3. Absorption spectra of the polymethine salt **23** in isopropanol.

whereas other similar polymethine salts (even the polymethine salts-derivatives of the nonlinear ketocyanines **18** and **19**) have only one absorption band that is located in the long-wavelength region. So we have to conclude that there is no complete conjugation in the whole polymethine chain characteristic for conventional cationic polymethines, and the central pyran unit in the structure of salts **23–25** creates some potential barrier for the conjugation. In this case we can use the model of chromophore interaction for evaluation of the angle θ between the chromophores; it was found from expression (1) that for dye **23** $\theta = 71^\circ$.

Apart from the singlet levels, the triplet levels of ketocyanine chromophores can interact with each other only by conjugation, with no dipole-dipole coupling, because the dipole transition moment for the $S_0 \leftrightarrow T_1$ transitions is close to zero. This interaction could cause splitting and lowering of the triplet levels similar to that for the singlet levels (see Scheme 3), and we might expect lower T_1 levels for symmetric ketocyanines compared to corresponding asymmetric ones.



Scheme 3. Interaction of the chromophore triplet states in ketocyanines.

Table 2. Triplet energy levels (E_T) for ketocyanine dyes in toluene and n-propanol [15].

Dye	m	n	E_T in toluene (cm^{-1})	E_T in n-propanol (cm^{-1})
2	0	2	13580	13510
4	1	2	13330	13020
7	2	2	13190	12440
6	1	4	~10250	—
26	2	3	~11500	—
27	3	3	~11500	—

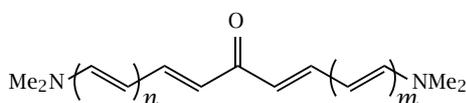


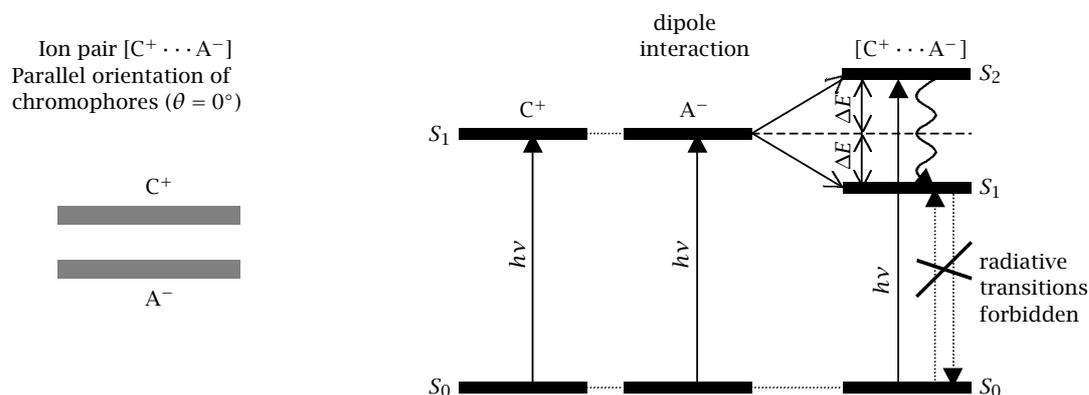
Table 2 presents the triplet energy levels for some ketocyanines [15]. It can be seen that ketocyanine symmetry is not a decisive factor in determining these levels, and the dyes with the same longer chromophore (the same n) have essentially the same E_T in toluene independent of their symmetry (*cf.* dyes 2, 4, and 7; 26 and 27 in Table 2). Hence the triplet level of the whole ketocyanine molecule in toluene is determined only by the length of the longer chromophore (longer polyenic fragment of the molecule), and there is no essential influence of the shorter chromophore in the molecule. So we can conclude that the T_1 triplet levels of ketocyanine chromophores do not essentially interact with each other in ketocyanine molecule (in toluene), which is probably due to their low triplet energy insufficient to overcome the potential barrier for chromophore interaction (conjugation). In the polar and protic solvent, n-propanol, this barrier is lowered due to solvation, and interaction of the triplet levels becomes appreciable, which is reflected in the slightly lower E_T value for the symmetric dye 7 compared to those for the asymmetric dyes 2 and 4 (Table 2).

Cation-anionic dyes. The photophysical and photochemical properties of cation-anionic polymethine dyes, in which both a cation and an anion are dyes, have some interesting features making them perspective for technical application, *e.g.* in the systems of solar energy conversion, laser technology, information stor-

age *etc.* In polar solvents cation-anionic dyes behave as equimolar mixtures of corresponding simple cationic and anionic dyes, whereas in weakly polar and nonpolar solvents, where the dyes form ion pairs, their properties can change drastically as a result of the interaction between the cation and anion chromophores [16]. We might expect that in ion pairs the cation and the anion will have parallel orientation (the angle θ between the cation and anion chromophores would be equal to zero). The maximum interaction effect should be expected for the S_1 electronic levels of the chromophores having the same energy, *i.e.*, for a cation and an anion with coinciding or close absorption bands. Indeed, in going from polar solvents, ethanol and acetonitrile, to weakly polar chloroform and dioxane and nonpolar toluene, no essential changes are observed in absorption spectra of the dyes with completely different position of cation and anion absorption bands (dyes 28–32, 34, 36 in Table 3; only slight bathochromic shift of the bands is observed), whereas a new short-wavelength band appears in the absorption spectra of the dyes with overlapping cation and anion absorption bands accompanied by simultaneous diminishing of the initial, long-wavelength band (dyes 33, 35, 37; see Table 3 and Figure 4). This new band is inactive in fluorescence excitation and appears as a result of interaction of the S_1 levels of the cation and anion chromophores in the cation-anionic ion pair (Scheme 4). In this case, the

Table 3. Maxima of absorption spectra ($\lambda_{\text{abs}}^{\text{max}}$) and extinction coefficients (ϵ) of cation-anionic polymethine dyes in ethanol, acetonitrile, chloroform, and toluene. (* new short-wavelength absorption bands due to chromophore interaction.)

Dye	Anion	Cation	$\lambda_{\text{abs}}^{\text{max}}$ (nm) ($\epsilon \times 10^{-4}$, $\text{M}^{-1}\text{cm}^{-1}$)			
			in EtOH	in MeCN	in CHCl_3	in toluene
28	A ₁	C ₁	555 (anion),	550,	568 (17.1),	574,
			312 (cation)	310	312 (4.66)	310
29	A ₁	C ₃	555 (anion),	550,	571,	575,
			420 (cation)	421	425	427
30	A ₁	C ₄	555 (anion),	550,	560 (16.1),	555,
			655 (cation)	650	680 (17.1)	668
31	A ₁	C ₆	555 (anion),	550,	561,	564,
			445 (cation)	442	446	448
32	A ₂	C ₂	560 (anion),	557,	578 (11.7),	573,
			324 (cation)	322	325 (3.90)	326
33	A ₃	C ₅	655 (anion and cation)	664	600*, 666	598, 664
34	A ₄	C ₁	470 (anion),	465,	471,	471
			312 (cation)	310	312	
35	A ₅	C ₆	444 (anion and cation)	442	420*, 446	420*, 452
36	A ₅	C ₇	440 (anion),	436,	450 (5.9),	446,
			560 (cation)	555	565 (16.3)	574
37	A ₆	C ₆	443 (anion and cation)	442	420*, 448	420*, 458



Scheme 4. Interaction of the chromophores in cation-anionic dyes.

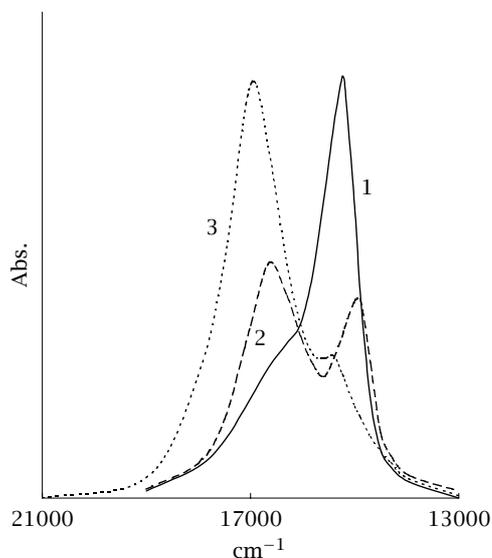


Figure 4. Absorption spectra of dye 33 in acetonitrile (1), chloroform (2), and dioxane (3).

long-wavelength transition $S_0 \rightarrow S_1$ is forbidden, whereas the short-wavelength transition $S_0 \rightarrow S_2$ is allowed (see expression (1) for $\theta = 0$), so we should observe only the short-wavelength band $S_0 \rightarrow S_2$ in the absorption spectrum of the ion pair. After absorbing light, this cation-anionic pair undergoes transition to the S_2 state followed by fast nonradiative deactivation to the S_1 state. Because the radiative $S_1 \rightarrow S_0$ transition is forbidden, the ion pair is nonfluorescent.

ACKNOWLEDGEMENTS

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