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Influence of ion pair formation on the photochemistry of asymmetric cationic indobenzimidazolo cyanines

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Abstract

The influence of counterions in ion pairs of asymmetric cationic indobenzimidazolo cyanines formed in low polarity solvents on the main photochemical processes of the cyanine cations (fluorescence emission, photoisomerization and thermal ground state back isomerization, $S_1 \rightarrow T$ and $T \rightarrow S_0$ intersystem crossings) was experimentally studied. The previously found structural similarity of the ion pairs of symmetric benzimidazolo cyanines and those of asymmetric indobenzimidazolo cyanines is reflected in the similarity of the effects of ion pairing on the dynamics of isomerization of these dyes in the ground and lowest excited singlet states. Indirect evidence based on fluorescence steady-state and time-resolved measurements indicates a weak catalytic counterion effect on the S_1-state isomerization dynamics of the investigated benzimidazolo and indobenzimidazolo cyanines. The I^- counterion in ion pairs strongly affects the S_1 state of the asymmetric cyanines by inducing $S_1 \rightarrow T$ and $T_1 \rightarrow S_0$ intersystem crossings (heavy atom effect).

Keywords: Asymmetric cyanines; Ion pairs; Fluorescence; Photoisomerization; Thermal back isomerization

1. Introduction

The photochemistry of ionic polymethine cyanine dyes is usually studied in polar media, where the dye salts are completely dissociated. On the other hand, the data obtained over the past decade show that ionic cyanines may change their spectroscopic and photochemical properties in a little-polar and nonpolar environment mainly as a result of the electrostatic influence of the counterion in ion pairs [1–3], but, also, because of steric interactions between the two partners in the ion pair [4,5]. In addition, the back isomerization of some cationic symmetric cyanines was found to be strongly affected by ion pair formation, an effect attributed to a distortion of the electronic symmetry in the dye cations caused by their interaction with nucleophilic counterions [2,3]. Hence, symmetric cyanines may lose their symmetry and become asymmetric in ion pairs. In the recent experimental and theoretical work [4], we studied the photo- and the back isomerizations of three asymmetric indobenzimidazolo cyanines, and some of the corresponding symmetric dyes (indo- and benzimidazolo cyanines) in polar solvents. These asymmetric cyanines feature moderate asymmetry and might serve as models for the behaviour of the corresponding symmetric dyes in ion pairs. It has been shown that the activation barriers for back isomerization of cyanine photoisomers are always higher for asymmetric cyanines than for corresponding symmetric ones [6]. On the other hand, the symmetric indo- and benzimidazolo cyanines behave differently in ion pairs: under the influence of counterions the isomerization barriers increase for the former and decrease for the latter dyes [2,3]. Therefore, considering free asymmetric indobenzimidazolo cyanine cations is not adequate to the modelling of the behaviour of symmetric cyanines in ion pairs, and counterions have to be also taken into account.

In this work, we have studied experimentally the influence of some counterions in ion pairs of asymmetric cationic indobenzimidazolo cyanines on the main photochemical processes of the cyanine cations: fluorescence emission, photoisomerization and thermal ground state (S_0) back isomerization, $S_1 \rightarrow T$ and $T \rightarrow S_0$ intersystem crossings (S_1 and T indicate the lowest excited singlet states and the triplet-state manifolds, respectively). We used 1,3-diphenyl-3,3′-dimethyl-indo-2-benzimidazolo carbo-, dicarbo-, and tricarbocyanines (compounds IB1, IB2, and IB3 in Scheme 1) with different counterions X^- (for IB1 $X^- = ClO_4^-$ and I^-; for IB2 and IB3 $X^- = ClO_4^-$, I^-, and Cl^-). Acetonitrile, butyronitrile, toluene, and nitrile–toluene mixtures of variable composition were used as solvents. The introductory

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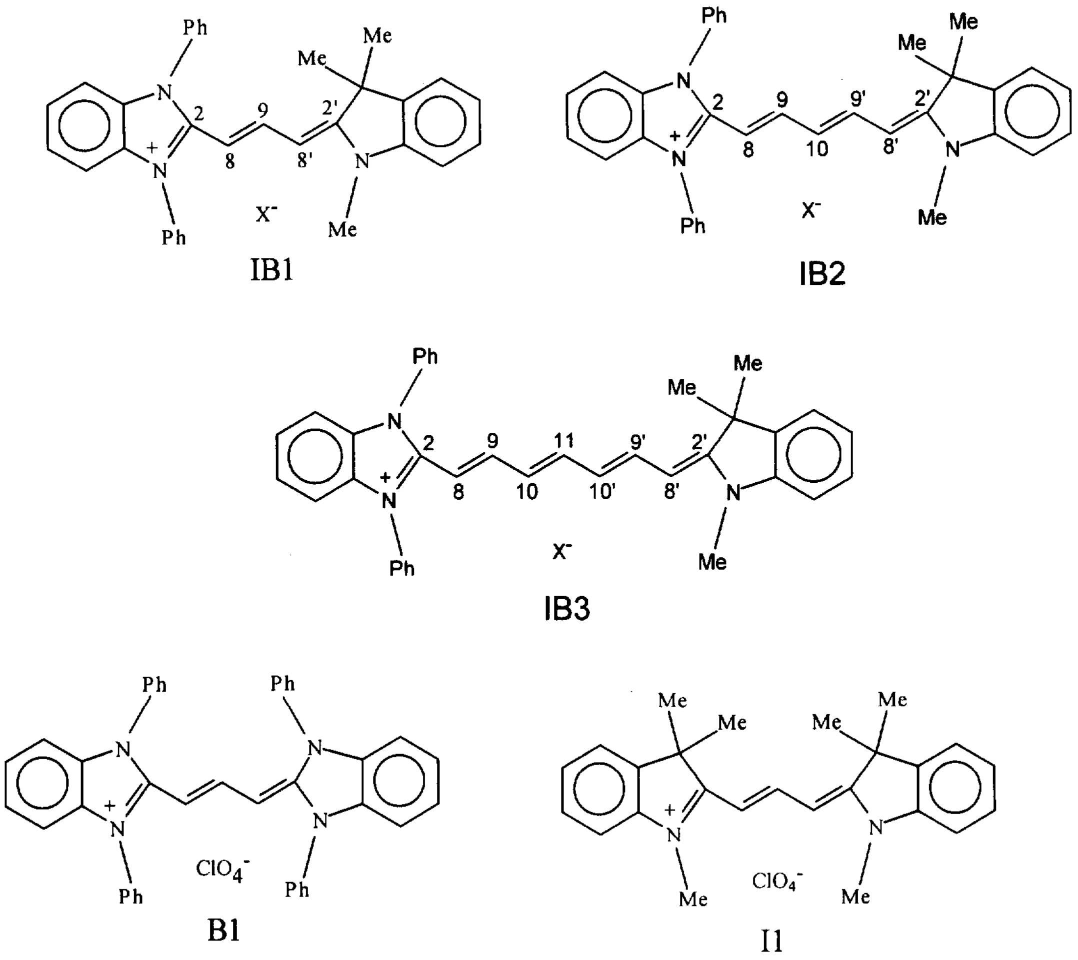

Scheme 1.

structural study on IB1 and IB2 and the symmetric indo (I1) and benzimidazolo (B1) carbocyanines [7] has shown that, while the dye salts are completely dissociated in the two nitriles, ion pairs mainly of the contact type are obtained in toluene. While structural differences are found between the ion pairs of I1 and B1, the asymmetric dyes show homogeneous structural features, with the counterion likely located near the benzimidazole groups, which carry most of the positive charge. As we shall see, this structural homogeneity between the contact ion pairs with different counterions of the indobenzimidazolo cyanines, also extending to the ion pairs of symmetric B1, is completely reflected in the observed effects of ion pairing on the mentioned photophysical and photochemical processes of these dyes.

2. Experimental

1,3-Diphenyl-3,3′-dimethyl-indo-2-benzimidazolo carbo-, dicarbo-, and tricarbocyanines (IB1, IB2, and IB3) with different counterions were synthesized as described in Ref. [8]. The solvents employed were all of spectrophotometric grade (usually Merck UVASOL) and were checked to give no significant absorption or emission in the experimental conditions. Toluene was dried by refluxing over metal sodium or by treatment with activated 0.4 nm molecular sieve. All absorption spectra and the slower kinetics of ground-state back isomerization of the cyanine photoisomers at variable temperature were measured with a Lambda 15 Perkin-Elmer UV–Vis spectrophotometer. Fluorescence spectra and quantum yield measurements were obtained on a Jobin-Yvon JY3CS spectrofluorimeter. All spectra were corrected for the instrumental spectral response curve. The fluorescence quantum yields (Φ_{fl}) of IB1 and IB2 in different solvent mixtures were determined at room temperature (20–21°C) using, respectively, eosin in 0.01 NaOH ($\Phi_{fl} = 0.20$ [9]) and cresyl violet in methanol ($\Phi_{fl} = 0.66$ [10]) as the standard reference systems. Uncertainties were ca. 10%. Transient triplet–triplet absorption spectra were measured on a previously described laser flash photolysis instrument [11] having 10–20-ns time resolution and on a lamp flash photolysis setup with flash energy 50 J and FWHM 7 μs [12]. The fluorescence lifetimes were measured with an IBH single photon counting apparatus having time resolution of about 0.5 ns after deconvolution of the measured fluorescence time profiles from the instrument time response function.

3. Results and discussion

3.1. Counterion effects on the excited-state properties

The fluorescence emission spectra of the perchlorates of IB1, IB2, and B1 exhibit very weak bathochromic shifts in butyronitrile (BuN)–toluene mixtures having nitrile content from 100% to 20% v/v (the spectral maxima are plotted in Fig. 1). The increase in the fluorescence maximum wavelength becomes steeper with a further decrease in a BuN concentration in the mixture, the effect being less pronounced with the symmetric dye. The behaviours of the two carbocyanines qualitatively parallel the dependence on the solvent mixture composition exhibited by their absorption maxima [7]. On the other hand, the bathochromic shift of the fluorescence maximum of IB2 is at variance with the very pronounced hypsochromic shift exhibited by its absorption maximum, as well as that of IB3, in binary mixtures going from 80 to 100% toluene [7].

The monotonic character of the three curves in Fig. 1 does not enable us to conclude whether the formation of contact ion pairs adds to the bathochromic shift due to solvatochromism, i.e., associated with the increase in the toluene content in the solvation shell of the dye cations, or it acts in the opposite direction but is weaker than the solvatochromic effect. However, while the effect of ion pairing on the absorption spectra is much more pronounced for IB2 and IB3 than for IB1, a fact likely associated with higher polarizabilities of the former and reduced steric hindrance in the longer dyes [7], the shift of the fluorescence maximum of IB1 is even slightly larger than that of IB2. Also, the curve of the latter in Fig. 1 shows a tendency to levelling off at very low nitrile content. These observations support the view of a very weak effect of tight ion pairing on the fluorescence spectrum, leading to partial compensation of negative solvatochromism, in keeping with the interpretation of the clearer fluorescence data of a model open-chain cyanine [5].

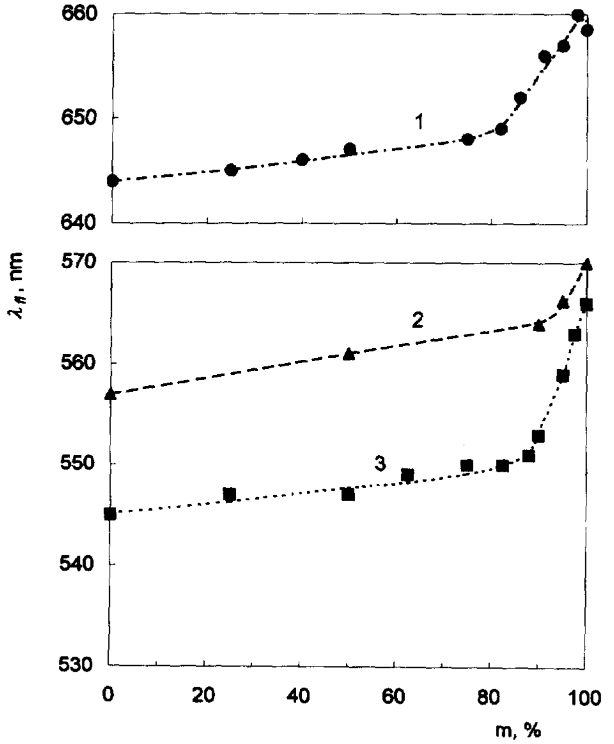

Fig. 1. Fluorescence emission maxima (λ_{fl}) of IB2 (*1*), B1 (*2*), and IB1 (*3*) perchlorates in butyronitrile–toluene solvent mixtures (*m* is the toluene content in the mixtures).

Table 1

Fluorescence quantum yields (Φ_{fl}) of asymmetric indobenzimidazolo cyanines in different solvents (experimental uncertainties are ± 10–20%)

Cyanine	Φ_{fl} (20°C)		
	In CH_3CN	In C_3H_7CN	In toluene
IB1[a]	0.04	0.055	0.003 ($X^- = ClO_4^-$) 0.001 ($X^- = I^-$)
IB2[b]	0.07	0.10	0.05 ($X^- = ClO_4^-$) 0.005 ($X^- = I^-$)

[a] $\lambda_{ex} = 480$ nm.
[b] $\lambda_{ex} = 500$ nm.

The fluorescence quantum yields (Φ_{fl}) of IB1 and IB2 slightly increase on moving from acetonitrile to BuN (Table 1), an effect attributable to the increased solvent viscosity [13]. BuN and toluene, on the other hand, have very similar viscosities, so that changes in Φ_{fl} observed on moving from one to the other, across the composition range of their binary mixtures, must be attributed to other causes. The quantum yields in the two nitriles are independent of the counterion, thus confirming the complete dissociation of the dye salts in these solvents. Instead, changes in Φ_{fl} are found in toluene upon changing the counterion from perchlorate to iodide, the latter giving lower (IB1) or much lower (IB2) values.

The fluorescence quantum yields of IB1 and IB2 perchlorates show a slight increase with decreasing polar solvent content in BuN–toluene mixtures ranging from pure nitrile to 70–80% toluene (Fig. 2). A more pronounced increase is exhibited, in the same solvent composition range, by the quantum yield of B1, as shown in Fig. 3. Because cyanine fluorescence emission competes with its photoisomerization, this increase in Φ_{fl} may be explained by the influence of the solvent polarity on the S_1-state potential energy surface for the cyanine isomerization: with decreasing polarity or, in this case, with decreasing amount of a polar solvent in the cation solvation shell, the isomerization potential barrier increases [5,11], which leads to a drop in the isomerization rate and hence to enhancement of fluorescence emission.

In all cases, a further decrease in the nitrile content in the binary mixture causes a strong decrease in Φ_{fl}, likely associated with the formation of contact ion pairs. Such a fluorescence quenching goes together, for perchlorates in toluene, with an increase in the photoisomerization efficiency. This was observed qualitatively, but it could not be stated quantitatively because of a rather complex superposition of transient absorptions observed at early delay times in toluene. Anyway, we can at least qualitatively conclude that tight ion

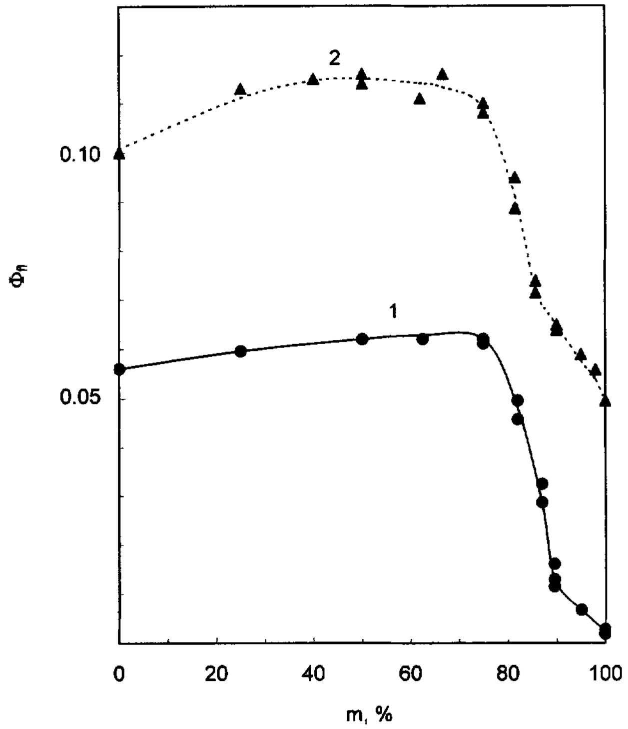

Fig. 2. Fluorescence quantum yields (Φ_{fl}, 20°C) of IB1 (*1*) and IB2 (*2*) perchlorates in butyronitrile–toluene solvent mixtures (*m* is the toluene content in the mixtures).

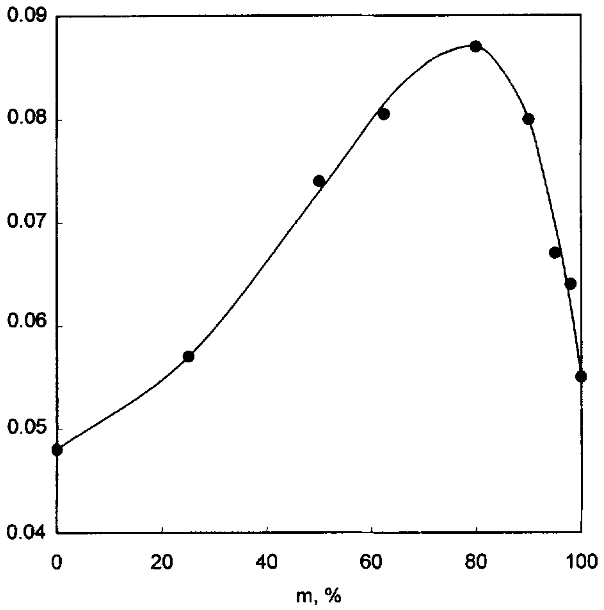

Fig. 3. Fluorescence quantum yields (Φ_{fl}, 20°C) of symmetric cyanine B1 perchlorate in butyronitrile–toluene solvent mixtures (*m* is the toluene content in the mixtures).

pairing has a weak catalytic effect on the photoisomerization reaction.

The weakness of this effect is confirmed by the behaviour of the fluorescence lifetimes (τ) of B1 perchlorate measured in BuN, toluene, and the 20–80 nitrile–toluene mixture between 180 and 260 K. These lifetimes show, in parallel with the Φ_{fl} values, an increase on moving from BuN (e.g., τ(240 K) = 1.0 ns) to the 20–80 mixture (τ(240 K) = 1.40 ns), followed by a decrease on going to toluene, where all the lifetimes are almost identical to those found in BuN (τ(240 K) = 0.99 ns). Due to the high sensitivity to the choice of the low-temperature limit lifetime of the activation energies (E_a) and preexponential factors (A_0) obtained from an Arrhenius-law analysis of the data, these parameters are found to be affected by rather large uncertainties and to be the same, within such uncertainties, in the three solvents: $E_a = 24 \pm 4$ kJ mol^{-1} and $\log(A_0(\mathrm{s}^{-1})) = 13.9 \pm 0.6$. Attempts at measuring the lifetimes of IB1 perchlorate and iodide at temperatures lower than 240 K in toluene and in mixtures with low amounts of nitrile have yielded complex decays, possibly due to shifts in the ion-pair equilibria and structural changes brought about by the temperature lowering.

Upon laser photoexcitation of the asymmetric cyanines with an I^- anion in toluene, together with the signals of the photoisomers, a strong transient absorption is observed, whose spectrum lies mainly in the long-wavelength region with a weaker short-wavelength contribution (the spectrum for IB3 iodide is shown in Fig. 4, curve *1*). The lifetime of this species was limited by the instrumental time resolution (10–20 ns) for IB1 and IB2, and it was about 50 ns for IB3. Because this species is not formed upon photoexcitation of the cyanines with Cl^- and $\mathrm{ClO_4}^-$ counterions, we may reasonably suppose it to be the cyanine lowest triplet state ($\mathrm{T_1}$) formed in ion pairs with an I^- anion as a result of $\mathrm{S_1} \rightarrow \mathrm{T}$ intersystem crossing (where T represents the triplet-state manifold) induced by the anion (heavy atom effect of I^-). Its short lifetime is a consequence of fast $\mathrm{T_1} \rightarrow \mathrm{S_0}$ intersystem crossing also induced by I^-. For its identification we performed triplet–triplet energy transfer from anthracene to IB3 with I^- and $\mathrm{ClO_4}^-$ anions in toluene using the lamp flash photolysis setup. The absorption spectrum of the IB3 triplet

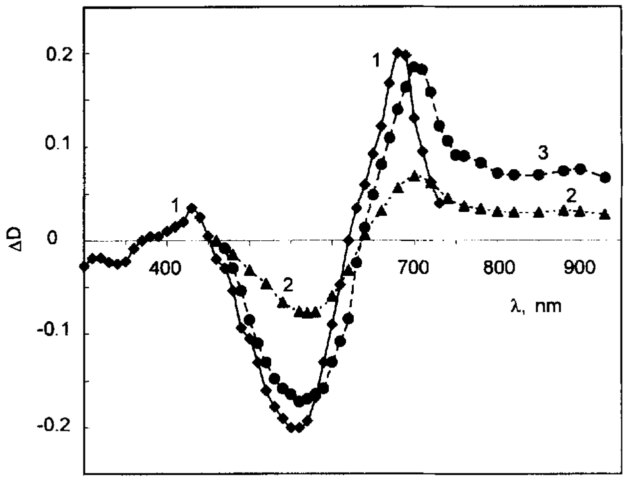

Fig. 4. Difference absorption spectra of the triplet state of cyanine IB3 in toluene: the spectrum of the cyanine with a I^- counterion upon direct laser excitation (*1*, delay time 20 ns) and the spectra obtained upon triplet energy transfer from anthracene to the cyanine with a I^- (*2*) and $\mathrm{ClO_4}^-$ (*3*) counterion (delay time 20 μs).

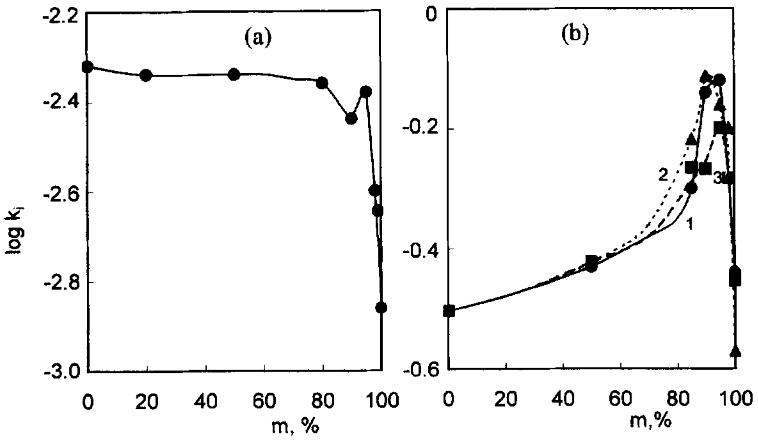

Fig. 5. Dependences of log k_i (20°C) on the composition of the acetonitrile–toluene solvent mixture (m is the toluene content in the mixture) for back isomerization of the photoisomer of IB1 with a I^- counterion (a) and one of the two photoisomers of IB3, which has an absorption maximum at 460 nm [6] (b), with ClO_4^- (*1*), I^- (*2*), and Cl^- (*3*) counterions.

state obtained by this means (Fig. 4, curves *2* and *3*) is similar to that detected upon direct photoexcitation (Fig. 4, curve *1*), but the lifetime is much longer (~300 μs for IB3 with any anion). We may suppose that IB3·I^- is present in toluene as both contact and solvent-separated ion pairs; upon direct photoexcitation of the relatively concentrated cyanine solutions used in the laser experiments (about 10^{-4} mol l^{-1}) the ionic dissociation equilibrium is shifted toward the contact ion pairs, where the cyanine triplet state is characterized by the low lifetime due to strong interaction with I^- anion. In the lamp flash photolysis experiments we used the dilute cyanine solutions ((1–5) × 10^{-6} mol l^{-1}), in which the concentrations of contact and solvent-separated ion pairs are comparable. In these experiments, the cyanine triplet state was not detected in the contact ion pairs due to insufficient time resolution of the flash photolysis instrument, whereas in the solvent-separated ion pairs the interaction of the triplet cyanine with the I^- anion is too weak to substantially affect its intrinsic lifetime (~300 μs). Indeed, in the experiments on triplet–triplet energy transfer to IB3 in toluene using lamp flash photolysis setup the measured lifetimes of the IB3 triplet state with ClO_4^- and I^- anions were the same (~300 μs), but the apparent triplet yield for IB3·ClO_4^- was roughly twice as high as for IB3·I^-.

3.2. Counterion effects on the ground-state back-isomerization kinetics

Fig. 5 presents semilogarithmic plots for the back isomerization rate constants k_i of the main photoisomers of cyanines IB1–IB3 as functions of composition of acetonitrile–toluene solvent mixtures. At varying m, maximum changes in k_i are observed in the mixtures with $m = 85$–100%; i.e., they are determined by formation of cyanine ion pairs with counterions. The most drastic changes (decrease) in k_i are observed in the solvent mixtures with $m = 95$–100%, where more tight and contact ion pairs are formed. To elucidate the mechanism of the counterion effects, Arrhenius parameters (activation energy E_a and preexponential factor A_0) for the back isomerization of the main photoisomers of cyanines IB1–IB3 were measured in those solvent mixtures (Fig. 6). The dependences of E_a and A_0 on m show that, as for the symmetric cyanines [2,3], E_a and A_0 have small variations at $m = 0$–80%. Those variations likely result from a change in the solvation of the free cyanine cation and the previously recognized solvation effects on the isomerization barrier and preexponential factor [5,11]. At $m > 80$%, great changes in

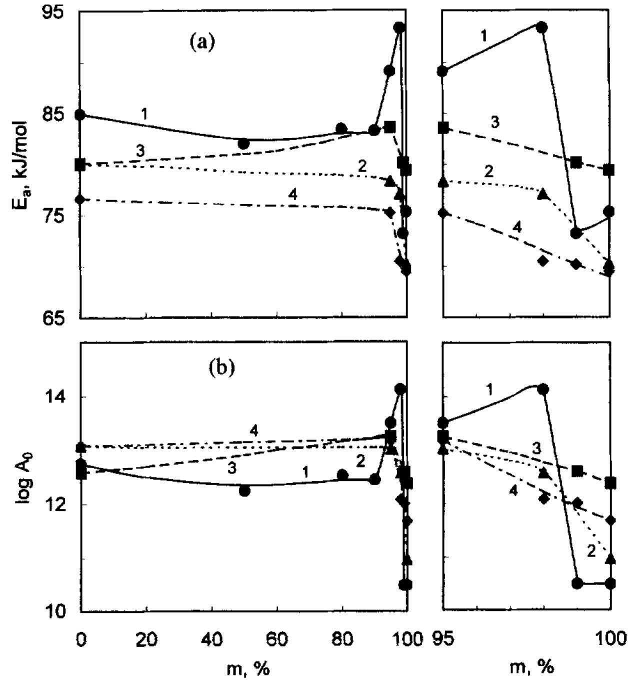

Fig. 6. Dependences of E_a (a) and log(A_0) (b) on the composition of the acetonitrile–toluene solvent mixture (m is the toluene content in the mixture) for back isomerization of the photoisomer of cyanine IB1 with a I^- counterion (*1*), the photoisomer of IB2 with a ClO_4^- counterion (*2*), and two photoisomers of IB3 (*3* and *4*, corresponding to the photoisomers with absorption maxima at 350 and 460 nm, respectively [6]) with a ClO_4^- counterion. On the right-hand are shown the dependences extended in the region of ion pair formation.

E_a and A_0 are observed, which are determined by the effect of a counterion on a cyanine cation in ion pairs. Note that the changes in E_a and $\log(A_0)$ are almost parallel in the whole range of variation of m, so that some compensation of their effects on k_i will result. With growing m from 95 to 100%, a monotonous decrease in E_a and $\log(A_0)$ is observed for the photoisomer of IB2 and for both photoisomers of IB3, with $\log(A_0)$ decreasing somewhat more steeply than E_a, which leads to a resulting decrease in k_i. For IB1, the behaviour of E_a and A_0 is unique: at $m<90\%$ E_a and A_0 are essentially constant; then, with growing m from 90 to 98% they increase and from 98 to 99% fall down extremely steeply; at $m=99$–100% they suffer very small variations.

The cause of the influence of a counterion on E_a for the back isomerization of asymmetric cyanines is apparently the same as was proposed earlier for the back isomerization of symmetric cyanines [2,3,5]; it mainly consists in the electrostatic influence of an anion on the potential-energy surface of the isomerization path. This influence may be accomplished in two ways. The first one is the electrostatic influence of an anion on the isomerization potential energy surface at the perpendicular geometry of the cyanine cation, which roughly corresponds to the transition state. Localization of a counterion near the cyanine polyenic fragment (i.e., the one with an even number of polymethine atoms), which bears the positive charge in the S_0-state perpendicular geometry, leads to stabilization of this state and lowering of the isomerization barrier, whereas its localization near the uncharged polymethinic fragment (the one with an odd number of polymethine atoms) leads to an increase in the isomerization barrier [11,14]. This mechanism may be called the dynamic counterion effect. The second possible way in which the counterion may affect E_a is by changing the π bond orders within the polymethine chain through electrostatic (or nucleophilic) interaction with the cyanine cation. Because of the concentration of the positive charge density on the terminal heterocycles of the cyanine cations ([2,3]), a counterion in an ion pair will preferentially interact with some atom in the heteroresidues. In case of a symmetric cyanine, this may result in asymmetry in the electron density distribution and alternation of the π bond orders along its polymethine chain, which will lead to changes in the energy barriers for isomerization around those bonds (the static counterion effect). The introductory ^{1}H NMR study [7] has shown, however, that π bond orders of a cyanine polymethine chain do not change upon ion pair formation in I1 and B1 and suffer insignificant changes in IB1 and IB2, so this effect on the isomerization potential energy surface has to be considered of minor importance, at least for the cyanines mentioned above.

The effect on the isomerization dynamics of steric cation–anion interaction should also be considered [5]. This, however, should be of little importance in the cases under study, as suggested by the absence of significant geometric distortion of the dyes in the ion pairs indicated by ^{1}H NMR measurements [7].

The asymmetric indobenzimidazolo cyanines in Scheme 1 have been shown to feature alternating polymethine bond orders, with the C_8–C_9, C_{10}–C_{11}, $C_{10'}$–$C_{9'}$, and $C_{8'}$–$C_{2'}$ bonds more double than the adjacent bonds [6,7]. Parallel wise, alternating potential energy barriers for the S_0-state back isomerization were calculated [6]. According to the static counterion effect, the interaction of an anion with the benzimidazole heteroresidue in the ion pairs of these cyanines is expected to enhance the asymmetry and increase the alternation of bond orders along the polymethine chain. Therefore, if in toluene these cyanines photoisomerize around one of the more double bonds, as was found to be the case in acetonitrile [6], then an increase in E_a will be expected. On the other hand, the opposite is expected if the photoisomerization takes place around one of the bonds with lower bond order in the ground state.

Analogous consequences on E_a are expected from the electrostatic dynamic counterion mechanism if the anion is supposed to be held fixed in the region of the benzimidazole group, for electrostatic reasons or by steric constraints, during isomerization. The arguments concerning the localization of the positive charge in one of the molecular subunits at the perpendicular geometry can, in fact, be extended to these moderately asymmetric dyes [6], and a catalytic or a retarding counterion effect will be operative, depending around which bond the isomerization takes place, i.e., whether the benzimidazole nucleus is a part, respectively, of the polyenic or the polymethinic fragments. On the other hand, if the counterion is supposed to move along the polymethine chain during isomerization (such a motion was found to be facilitated by very low electrostatic barriers in the *all–trans* geometry of streptopolymethinecyanine chlorides [14]), then any shift and localization of the positive charge will go together with a corresponding counterion shift, leading to optimum electrostatic stabilization of the transition state and decrease of the observed E_a value.

The validity of either of the two views (with fixed or movable counterion) probably depends on the value and localization of the charge on the polyenic and polymethinic fragments during back isomerization. Strong positive charge localization in the polyenic fragment at the transition state of the back isomerization will favour the model with a movable counterion, which will lead to a decrease in E_a. Lower charge localization on this fragment will promote the model with a fixed counterion and will increase E_a in ion pairs. As can be seen in Fig. 6, the photoisomers of IB2 and IB3 suffer a decrease in E_a in ion pairs. So, in the assumption that, like in acetonitrile, these molecules photoisomerize around one of the more double bonds, then a movable counterion must be invoked to account for these results. For the photoisomer of IB1, in the relatively polar region of ion pair formation corresponding to $m=90$–98%, an increase in E_a is observed, which suggests a fixed counterion. But with decreasing amount of a polar solvent (at $m=98$–99%), an abrupt drop of E_a occurs corresponding to a probable shift from the fixed to the movable counterion view. We may explain this behaviour of E_a by a shift of the counterion in the transition state from polymethinic (benzimidazole) fragment to the strongly charged polyenic fragment due to increased electrostatic interactions in the low-polarity media. The benzimidazole heteroresidue, bearing a high positive charge in the initial configuration of the cyanine cation, may lose its charge in the transition state, which will promote such a shift of the counterion. This change from the fixed to the movable counterion case may be the consequence of a decrease in the dielectric constant of the solvent mixture, which results in an increase in electrostatic interaction between the counterion and the polyenic fragment. Beyond this polarity region, in essentially nonpolar media (at $m=99$–100%), the movable counterion model is apparently valid for explaining an experimental decrease in E_a.

In addition to E_a, ion pairing also affects the preexponential factor (A_0) of the Arrhenius plot for back isomerization. For all cyanines studied, an increase in A_0 is observed in the initial region of ion pair formation (with growing m from 80 to 95–100%, cf. Fig. 6). This effect may be explained by a change in the entropy of the twisted solvated transition state of cyanine isomerization. As mentioned above, this transition state has higher charge localization than the initial cation; therefore, it will be more strongly solvated by nitrile molecules. In moderately polar media and in mixtures with lower nitrile content a partial desolvation of the transition state occurs. This increases the entropy of the transition state and hence the preexponential factor A_0. The decrease in A_0 for most of the photoisomers at $m > 95$–98% (Fig. 6) may be the result of ion pair reorganization with a change in their structure from loose to tight with a corresponding decrease in the entropy of the isomerization transition state.

4. Conclusions

The previously recognized structural similarity of the ion pairs of symmetric benzimidazolo cyanines and those of some asymmetric indobenzimidazolo cyanines is completely reflected in the similarity of the effects of ion pairing on the dynamics of isomerization of these dyes in the ground and lowest excited singlet states: in all cases, a preferential location of the counterions in the region of the benzimidazole heteroresidue [7] in the ground-state *all-trans* geometry goes together with a substantial catalytic effect of ion pairing on the S_0-state back isomerization, consistent with a mechanistic description of this process in which the anion is allowed to shift along the polimethine chain, thus leading to optimum electrostatic stabilization of the perpendicular transition state. On the other hand, the observed opposite, retarding effect of the formation of contact ion pairs on this reaction of symmetric indocyanines [2,3] correlates with significantly different structural features exhibited by the ion pairs of the indocarbocyanine, suggesting a strong interaction of the perchlorate counterion with a polymethine carbon atom (C_8) in the S_0-state *all-trans* geometry [7] and, accordingly, its lower mobility during the isomerization reaction.

Indirect evidence based on fluorescence steady-state and time-resolved measurements indicates a weaker, but still catalytic counterion effect on the S_1-state isomerization dynamics of the investigated benzimidazolo and indobenzimidazolo cyanines. On the other hand, the I^- counterion in ion pairs strongly affects the first excited singlet state of the asymmetric cyanines by inducing $S_1 \rightarrow T$ and $T_1 \rightarrow S_0$ intersystem crossings (heavy atom effect), whereas for symmetric cyanines $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ (but not $S_1 \rightarrow T$) conversions are induced by the I^- anion [3]. This difference may be connected with higher energy of I^- interaction with cations of asymmetric cyanines due to stronger charge localization in cations of asymmetric cyanines as compared to cations of corresponding symmetric ones.

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