Journal of Applied Spectroscopy, Vol. 75, No. 5, 2008

GENERATION OF SINGLET OXYGEN BY INDOTRICARBOCYANINE DYES IN LOW-POLARITY MEDIA

M. P. Samtsov,[*] E. S. Voropai, K. N. Kaplevskii, and D. G. Mel'nikov

UDC 535.37

We present the results of a study of the spectral luminescence properties of three groups of indotricarbocyanine dyes, each of which is formed from compounds with the same cation and different anions. In high-polarity solvents, in the absorption and emission spectra of the dyes we see one type of center; in low-polarity solvents, due to the presence of different ionic forms of the dyes (free ions, contact ion pairs), we observe either one type or two types of centers. By analysis of the luminescence of molecular oxygen in the 1.27 μm spectral region, we determined the efficiency of photosensitization of $^1O_2$ formation by dyes in deuterated solvents. We have shown that in low-polarity solvents, the yield for singlet oxygen generation is higher for indotricarbocyanine dyes which are found in the contact ion pair state and which also contain a heavy atom (I) in the anion. We have observed that an increase in the fraction of contact ion pairs in solution as the dye concentration increases or when an additional salt is introduced leads to an increase in the quantum yield for generation of singlet oxygen. In polar deuterated acetonitrile, the counterion has no effect on the efficiency of photosensitization of oxygen by the dyes.

Key words: *indotricarbocyanine dyes, ion pairs, spectral properties, singlet oxygen.*

Introduction. Most polymethine dyes are salts whose molecules in solutions can be found in the form of an equilibrium mixture of several types of ionic forms (free ions, contact and solvent-separated ion pairs) [1]. The equilibrium between these forms is shifted toward an increase in the fraction of one form when the temperature and the nature of the solvent are varied, when the anion is substituted, and when ionic and solvating additives are added to the solution. The state of the ionic equilibrium in solutions has an effect on the processes of dissipation of the electronic excitation energy in the polymethine dye molecules. The fluorescence quantum yield and the fluorescence lifetime of the polymethine dye molecules decrease symbatically with strengthening of the anion-cation interactions [2, 3]. In the ion pairs, the probabilities of torsional vibrations in the polymethine chain are higher and the yield for photoisomerization of the molecules is higher; the degree of vibronic interactions and the probabilities of rotation about bonds are higher as more stable ion pairs are formed [4–6].

Despite the significant number of publications devoted to study of the photophysical properties of polymethine dyes in different types of solvents, due attention has not been paid to the effect of the state of ionic equilibria on the efficiency of singlet oxygen generation by polymethine dyes. At the same time, such a study is important from both a scientific and an applied viewpoint. The applied importance is due to prospects for using these dyes for photochemotherapy of cancer and as biological fluorescent labels [7–9], and also because in biological structures, their molecules are mainly found in the form of contact ion pairs [10]. In this case, the efficiency of polymethine dyes as photosensitizers mainly depends on their capability for photoinduced generation of singlet oxygen [11]. For most organic solvents, at room temperature the rate of oxygen diffusion is such that the quantum efficiency of $^1O_2$ generation for complex organic molecules practically coincides with the yield for triplet state formation [12, 13]. Accordingly, the results obtained are of interest for constructing a general picture of how photoprocesses occur in polymethine dye molecules.

---

[*] To whom correspondence should be addressed.

A. N. Sevchenko Institute of Applied Physical Problems, 7 ul. Kurchatova, Minsk 220064, Belarus; e-mail: samtsov@bsu.by. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 75, No. 5, pp. 684–693, September–October, 2008. Original article submitted April 30, 2008.

TABLE 1. Yield for Singlet Oxygen Generation (*B*) by Polymethine Dyes in Deuterated Chloroform ($CDCl_3$) and Deuterated Acetonitrile (CD_3CN)

Dye	Anion	Solvent	C_{dye}, 10^6 M	C_{salt}, 10^3 M	λ_{max}^{abs}, nm	$B\cdot10^2$
PD1	I^-	$CDCl_3$	1.2	–	756	3.60
PD1	ClO_4^-	$CDCl_3$	1.2	–	756	0.50 ± 0.10
PD2	ClO_4^-	$CDCl_3$	1.2	–	785	15.2 ± 1.4
PD2	ClO_4^-	$CDCl_3$	0.5	–	785	5.8 ± 0.8
PD2	Br^-	$CDCl_3$	1.2	–	780	10.7 ± 0.9
PD3	BF_4^-	$CDCl_3$	1.2	–	735	7.7 ± 0.7
PD3	BF_4^-	$CDCl_3$	1.2	1.0	735	7.6 ± 0.7
PD3	Br^-	$CDCl_3$	1.2	–	735	4.8 ± 0.5
PD3	Br^-	$CDCl_3$	1.2	1.0	735	4.5 ± 0.5
PD3	I^-	$CDCl_3$	1.2	–	735	6.1 ± 0.6
PD3	I^-	$CDCl_3$	0.4	–	735	3.9 ± 0.4
PD3	I^-	$CDCl_3$	1.2	1.0	735	7.2 ± 0.8
PD3	BF_4^-	CD_3CH	1.2	–	714	0.5 ± 0.10
PD3	Br^-	CD_3CH	1.2	–	714	0.5 ± 0.10
PD3	I^-	CD_3CH	1.2	–	714	0.4 ± 0.10

Materials and Methods. As the objects of investigation, we selected already known and new indotricarbocyanine dyes, which were synthesized in the spectroscopy laboratory of the A. N. Sevchenko Institute of Applied Physical Problems. For these compounds, it has been found that they can photoactivate damage to cancer cells with high efficiency [8]. The compound PD1(I) is the familiar symmetric tricarbocyanine dye HITCI [14], PD1(ClO_4) is its cationic analog with the counterion ClO_4^-; PD2(ClO_4) and PD2(Br) are cationic analogs (with the anions ClO_4^- and Br^-) of the dye with a 4-chloro-3,5-substituted heptamethine conjugation chain and *N*-modified indolenine hetero residues [15]. As the solvents, we used deuterated chloroform, deuterated acetonitrile, chloroform, dichlorobenzene (DCB), ethanol, and methylene chloride.

The dye-sensitized luminescence spectra of singlet oxygen were recorded using a spectrometer based on an MDR-23 monochromator and a G8370-01 (Hamamatsu) InGaAs photodetector. The photosensitizers were excited by the emission from a semiconductor laser with λ = 740.7 nm. The quantum yield (*B*) for generation of singlet oxygen ($^1O_2$) by the studied compounds was determined based on the directly measured quantum yield for dye-sensitized $^1O_2$ luminescence (Φ_{lum}) and the relation in [16]: $\Phi_{lum} = B\tau_0/\tau_{rad}$, where τ_0 and τ_{rad} are the lifetime and radiative lifetime of singlet oxygen. As the reference, we used the dye PD1, for which in deuterated chloroform B_{ref} = 3.6% [17]. The lifetime of singlet oxygen and the radiative lifetime 1O2 for the solvents used were taken from [18, 19].

The absorption spectra of the dyes were recorded using a PV 1251A spectrophotometer (SOLAR). The fluorescence of the dye solutions were studied using a Fluorolog spectrofluorimeter. An upgrade of the control and detection system of the spectrofluorimeter included a time-correlated photon counting circuit in the instrument [20], which made it possible to expand its functional capabilities. Replacing the continuous emission source (a xenon lamp) with a pulsed source, we used the spectrometer to study the fluorescence decay kinetics of the dyes in the time interval 0.5–100 nsec.

Experimental Results. For all the polymethine dyes, in deuterated chloroform and deuterated acetonitrile for excitation by light from a semiconductor laser (λ_{las} = 740.7 nm), luminescence of singlet oxygen ($^1O_2$) was recorded in the spectral range 1.2–1.4 μm. The position of the band with maximum at 1272 nm and its half-width were identical for all the studied compounds. By comparing the intensities of singlet oxygen luminescence and taking into account the number of absorbed photons at the excitation wavelength (λ = 740.7 nm) for the reference and the studied photosensitizer, we determined the quantum yields for generation of $^1O_2$ by a series of new polymethine dyes (Table 1).

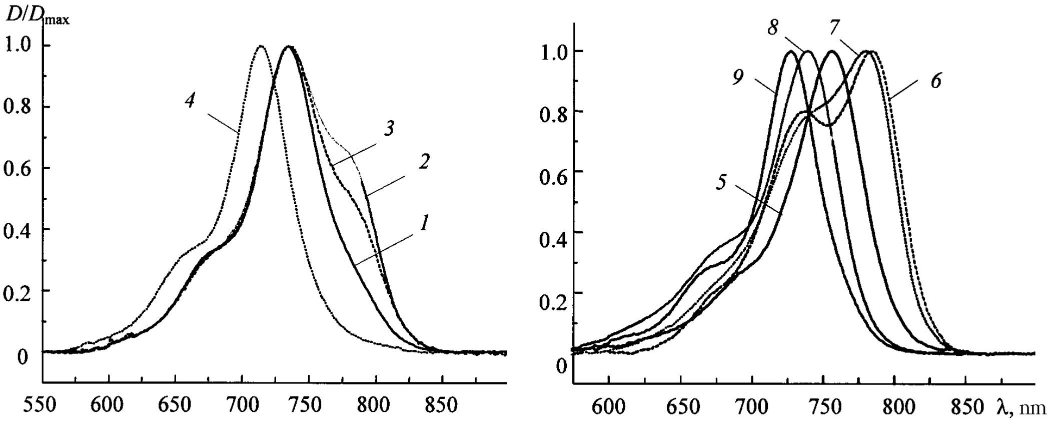

Fig. 1. Absorption spectra: 1) PD3(BF_4), 2) PD3(I), 3) PD3(Br) (in deuterated chloroform); 4) PD3(BF_4), PD3(I), and PD3(Br) (in deuterated acetonitrile); 5) PD1(ClO_4) and PD1(I), 6) PD2(ClO_4), 7) PD2(Br) (in deuterated chloroform); 8) PD1(ClO_4) and PD1(I), 9) PD2(ClO_4) and PD2(Br) (in deuterated acetonitrile).

The quantum yield for singlet oxygen generation by the dyes in deuterated chloroform fluctuates within the range 0.005–0.150 and depends on the concentration of the dye and the addition of an additional salt to the solution. In order to make sure that it was possible to compare the values of the parameter B for the studied compounds, the measurements were made for identical low dye concentrations. Significant differences were found for cationic analogs of the dyes which differed by only the counterions. Thus for PD1 with counterion ClO_4^-, the value of B is 7 times lower than for the cationic analog of PD1 with the anion I^-. For the other two groups of cationic analogs, the maximum value of B was obtained for the compounds with the anions ClO_4^- or BF_4^-. For the cationic analogs of PD2, the yield for singlet oxygen formation for PD2(ClO_4) is ≈3 times higher than for PD2(Br). Somewhat lower differences in the parameter B are observed in the series of dyes PD3(I), PD3(Br), and PD3(BF_4); the dye with the BF_4^- counterion has the maximum value of B. For the dye PD3(Br), the value of B is 1.6 times lower than for PD3(BF_4); for the dye PD3(I), it is 1.25 times lower than for PD3(BF_4). At the same time, in polar deuterated acetonitrile, for dyes with identical cations and different counterions, the quantum yields for singlet oxygen formation coincide (within the accuracy for determining this parameter). Thus for the group of dyes PD3 with anions I^-, Br^-, and BF_4^-, the yield is ≈0.5%, while for the group PD1 with counterions I^- and ClO_4^-, the yield is 0.2%. We should note that in deuterated acetonitrile, the quantum yield for singlet oxygen generation is about an order of magnitude lower than in deuterated chloroform for most of the studied dyes.

We found that for a lower concentration of the dyes PD2(ClO_4) and PD3(I) in low-polarity deuterated chloroform, the yield for singlet oxygen generation is lower. Thus B for a concentration of $0.5 \cdot 10^{-6}$ M for the dye PD2(ClO_4) is lower than for a concentration of $1.2 \cdot 10^{-6}$ M by more than a factor of 2.6 (see Table 1). The values of B differ somewhat less for the compound PD3 with the anion I^-: for a solution with dye concentration $1.2 \cdot 10^{-6}$ M, the parameter B is ≈1.5 times higher than for a concentration of $0.4 \cdot 10^{-6}$ M (Table 1). Analogous changes in the yield for singlet oxygen generation occur when an additional salt is added to a solution of the dye PD3(I), which leads to a shift of the ionic equilibrium toward a decrease in the fraction of free ions of the dye [3]. When tetrabutylammonium bromide is added to the dye solution at a concentration of 10^{-3} M, the yield increases by a factor of 1.2. Moreover, when such an additive is added to solutions of the dyes PD3(BF_4) or PD3(Br), the change in the value of B is no greater than the measurement errors (Table 1). Typically the observed changes in the yield for generation of singlet oxygen by the dyes are consistent with the differences in the spectral characteristics of the solutions. We carried out an analysis of the state of the ionic equilibria of the dyes in different solvents by studying their spectral luminescence properties. The spectral characteristics, the shape and position of the absorption and fluorescence spectra for all the studied dyes in deuterated solvents match the analogous data for conventional solvents. In this case, the photostability of the dyes in the deuterated solvents is more than an order of magnitude lower than for conventional

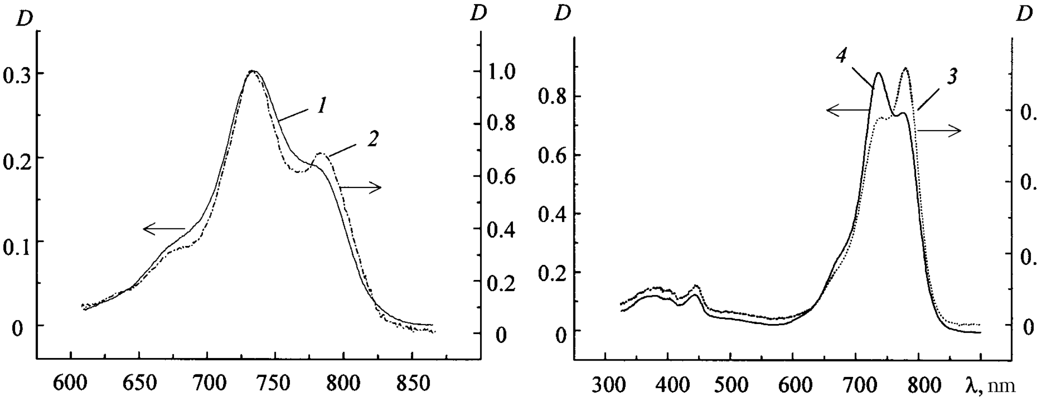

Fig. 2. Absorption spectra of PD3(I) (1, 2) and PD2(Br) (3, 4) in deuterated chloroform at a concentration of $1.2 \cdot 10^{-6}$ M (1, 3) and $4.0 \cdot 10^{-6}$ M (2, 4).

solvents [21]. Accordingly, in order to ensure the reliability of the results obtained in deuterated solvents during the experiment, we monitored the dye concentrations and also repeated the measurements. Taking into account the above, some of the spectral characteristics were studied using conventional solvents, in which the concentration and spectral properties of the dyes did not change during the experiment.

In highly polar acetonitrile or ethanol, the absorption spectra of dyes with different anions matched in shape and position when the concentration was varied from 10^{-7} to 10^{-5} M, and Beer's law was followed. The fluorescence spectra, the fluorescence quantum yield and lifetime, and also the degree of polarization for the dye solutions in acetonitrile or ethanol match for each group of cationic analogs. The fluorescence decay kinetics for the dyes in such solvents are represented by a single exponential, the fluorescence spectra do not depend on the wavelength of the exciting light, its excitation spectra do not change with the detection wavelength and their shape matches the absorption spectra of the dyes.

On going to low-polarity solvents (chloroform, methylene chloride, or dichlorobenzene), the spectral properties of dyes PD3 and PD2 change significantly. In this case, a bathochromic shift occurs for the long-wavelength absorption band of the dyes and its half-width increases. The shape of the absorption band for dyes PD3(Br) and PD3(I) in chloroform differs from the spectrum in acetonitrile by the presence of a shoulder at $\lambda = 780$ nm on the long-wavelength edge of the spectrum. For the dye PD3(BF_4) in the same region, we observe only a slight rise in the spectrum (Fig. 1). For the second group of cationic analogs PD2(Br) and PD2(ClO_4), more significant distortions of the absorption spectra occur on going to low-polarity solvents: two bands appear with maxima in the 785 nm and 735 nm regions. For both groups of dyes, dilution of the solutions in deuterated chloroform leads to a decrease in the contribution of the short-wavelength band to the overall absorption spectrum and an increase in the contribution of the long-wavelength band (Fig. 2). Introducing the additional salt trimethylbenzylammonium bromide is accompanied by a decrease in the contribution of the band with a maximum at $\lambda = 780$ nm in the absorption spectrum of dyes PD3 and PD2, while for a salt concentration $C = 10^{-3}$ M, the long-wavelength shoulder for PD3(Br) and PD3(I) at $\lambda = 780$ nm does not appear (Fig. 3). In the case of the dye PD3(BF_4), such a salt additive has practically no effect on the shape of the absorption spectrum.

The shape of the fluorescence spectra for PD2 and PD3 in low-polarity solvents (chloroform, dichlorobenzene, or methylene chloride) depends on the wavelength of the exciting light (Fig. 4). For excitation on the short-wavelength edge of the absorption band for PD3 in chloroform, the half-width of the spectrum is ≈20 nm greater than for ethanol or acetonitrile; on the long-wavelength edge of the spectrum, we observe a shoulder in the 800 nm region. On going to excitation by light with $\lambda = 760$ nm, a fluorescence band appears with maximum at 795 nm (Fig. 4). For the PD2 dyes in chloroform, for excitation on the short-wavelength edge of the absorption band, two bands appear in the fluorescence spectrum at 770 nm and 815 nm. For excitation in the region of the long-wavelength absorption band (λ = 780–785 nm), in the fluorescence spectra of PD2 a band appears with maximum at $\lambda = 815$ nm. For the dye PD3(BF_4) in chloroform, in the fluorescence spectra with excitation within the long-wavelength absorption band we do

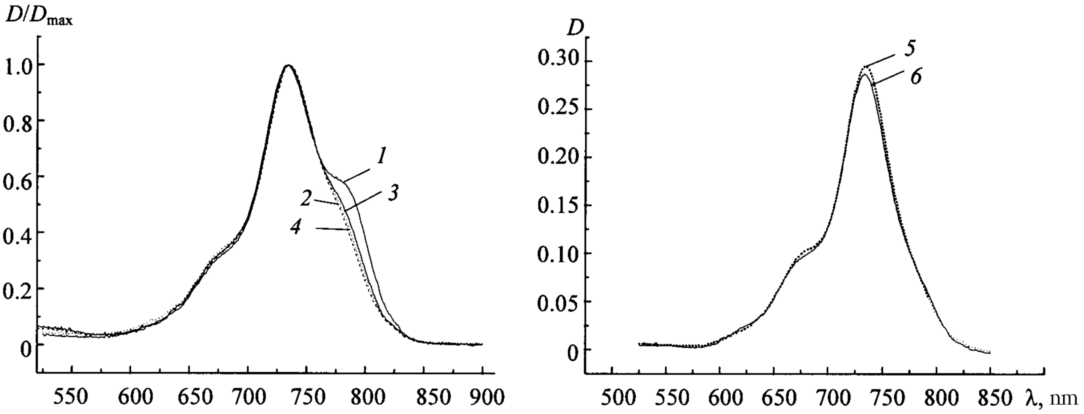

Fig. 3. Absorption spectra in deuterated chloroform for PD3(I) (1, 2), PD3(Br) (3, 4), PD3(BF_4) (5, 6) when 10^{-3} M of the salt is added (2, 4, 5).

not observe any changes in the dependence on the excitation wavelength. In this case, the fluorescence excitation spectra for the dyes PD2 and PD3 in chloroform depend to a significant extent on the detection wavelength. For detection in the region of the short-wavelength edge of the fluorescence spectrum, a band appears in the fluorescence excitation spectrum that is similar in shape and position to the absorption spectrum of the dye, while for detection on the long-wavelength edge of the fluorescence spectrum, an additional intense band appears whose position coincides with the longest-wavelength band (shoulder) in the absorption spectrum. This band has a higher relative intensity in the excitation spectrum compared with the absorption spectrum, i.e., the shapes of the indicate spectra are significantly different when detected on the long-wavelength edge of the fluorescence band. It is only for the dyes PD1(ClO_4) and PD1(I) that the absorption spectra depend weakly on the counterion; they have similar characteristics in low-polarity and high-polarity solvents. The fluorescence spectra and fluorescence excitation spectra of these dyes do not depend on respectively the excitation and detection wavelengths. The fluorescence quantum yields and lifetime are identical for PD1(ClO_4) and PD1(I) in chloroform (dichlorobenzene).

Discussion of Results. The spectral luminescence properties presented for the studied compounds in high-polarity acetonitrile and ethanol suggest that in such solvents, only one type of absorbing and fluorescent center appears for each dye. In contrast, in low-polarity solvents, for compounds PD2 and PD3 two types of such centers appear for each, which may be assigned to the different forms of ion pairs [1, 22]. The observed changes in the absorption spectra of dyes PD2 and PD3 when their concentration increases indicate the existence in solutions of these dyes of an equilibrium distribution of contact ion pairs and free ions [23]. Bands in the longer wavelength region correspond to the latter in the absorption and fluorescence spectra and in the fluorescence excitation spectra. And the less significant distortions of the absorption spectra due to dilution of the solutions or addition of salt additives, compared with the changes in the fluorescence excitation spectra of the studied dyes, suggest that the fluorescence quantum yield is higher for the longer wavelength centers. On the other hand, in deuterated chloroform, for dyes from the groups of cationic analogs PD2 and PD3, the quantum yield for singlet oxygen generation is higher for compounds having anions which promote an increase in the fraction of contact ion pairs in solution. The most marked differences are observed when comparing data for dyes PD2 with anions ClO_4^- and Br^-. In the absorption spectrum of PD2(ClO_4) in deuterated chloroform, the contribution of the band corresponding to the contact ion pairs is higher than for PD2(Br), and consequently the fraction of contact ion pairs is more significant. The yield for singlet oxygen generation for PD2(ClO_4) in this case is ≈1.5 times higher than for PD2(Br). We should note that the exciting radiation from a semiconductor laser with $\lambda = 740.7$ nm falls within the absorption band for the contact ion pairs of the indicated dyes, the maximum of which is located in the 735 nm region. An analogous correlation between the yield for $^1O_2$ formation and the increase in the fraction of contact ion pairs in the dye solutions is followed for the group of cationic analogs PD3(BF_4), PD3(B4), and PD3(I). Thus a decrease in the intensity of the long-wavelength shoulder in the absorption spectrum on going from PD3(I) to PD3(Br_4) and then to PD3(BF_4), which indicates a decrease in the fraction of free ions in solution, correlates with the increase in the value of *B* in this series of dyes (Table 1). Consequently, in the

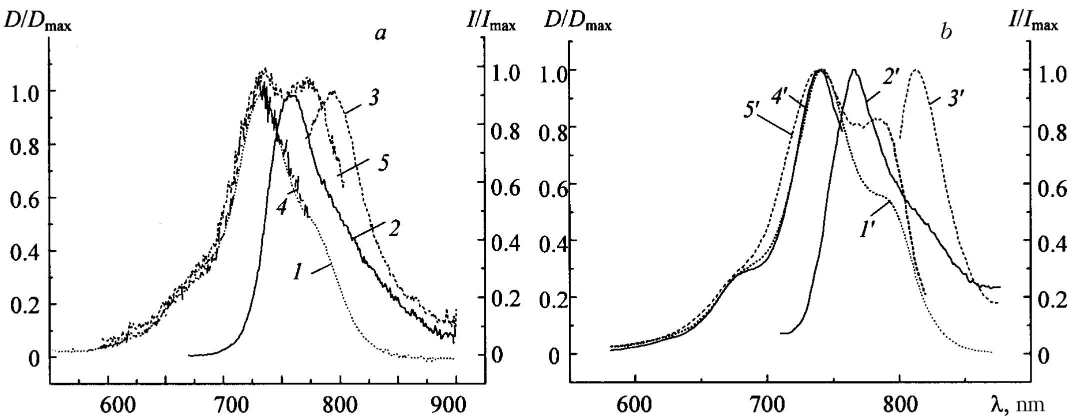

Fig. 4. Absorption spectra (1, 1′); fluorescence spectra for λ_{ex} = 730 (2), 720 (2′), 760 (3), 790 (3′) nm; fluorescence excitation spectra for λ_{det} = 785 (4), 815 (5), 764 (4′), 825 (5′) nm for the dye PD3(Br) in chloroform (a) and in dichlorobenzene (b).

groups of dyes PD2 and PD3 for states of the molecules in the form of contact ion pairs, the yield for singlet oxygen generation is higher than for free ions.

With the aim of identifying the differences in ability to form singlet oxygen for a sensitizer with the same structural formula but variation of the ratio of ionic forms of its molecules in solution, we measured *B* as the dye concentration changed and as ionic additives were added. The distortions of the absorption spectra and the changes in other spectral characteristics of the dyes PD2 and PD3 as their concentration increases or when an additional salt is introduced in both cases suggest a shift of the ionic equilibrium toward an increase in the fraction of contact ion pairs. Accordingly, for more concentrated solutions of the cationic analogs PD2 and PD3, we obtained larger values of *B* (see Table 1). From a formal standpoint, the observed increase in the quantum yield for singlet oxygen formation as the sensitizer concentration increases was quite unexpected. This is associated with the fact that the rate constant for quenching of $^1O_2$ by polymethine dyes is close to the limiting value for diffusion-controlled reactions [24]. In fact, for PD1(ClO_4) and PD1(I), the rate constants for quenching $^1O_2$ in acetonitrile, according to the data in [24], are $(4.6 \pm 0.1)\cdot 10^8$ and $(5.7 \pm 0.1)\cdot 10^8$ $M^{-1}\cdot sec^{-1}$. In our case, for the maximum dye concentration $1.2\cdot 10^{-6}$ M, the probability of quenching $^1O_2$ should be on the order of 10^3 sec^{-1}, which is comparable with quenching of $^1O_2$ by deuterated chloroform [18]. Therefore we may expect that as the dye concentration increases, the yield for singlet oxygen formation will have a constant value until quenching of $^1O_2$ by dye molecules begins to appear. Consequently, the observed increase in *B* for a higher dye concentration does not fit within such a conceptual framework; we must take into account the change in the ratio of the types of ionic forms of the dyes. In fact, the exciting radiation from a semiconductor laser with λ = 740.7 nm falls within the band corresponding to absorption of contact ion pairs, and an increase in the dye concentration promotes an increase in the contribution of this band to the absorption spectrum, i.e., the fraction of contact ion pairs increases. Thus the observed increase in *B* with an increase in the dye concentration supports the idea that the efficiency of singlet oxygen generation is higher for contact ion pairs than for free ions.

Like increasing the dye concentration, introducing an additional salt (tetrabutylammonium bromide, 10^{-3} M) leads to an increase in the quantum yield for singlet oxygen generation by a factor of ≈1.2 for PD3(I) in deuterated chloroform. Introducing this additive is accompanied by distortion of the absorption spectrum for PD3(I): the contribution of the band with maximum at λ = 780 nm decreases, which suggests an increase in the fraction of contact ion pairs. On the other hand, in the case of PD3(BF_4) or PD3(Br), such a salt additive does not lead to appreciable distortions in the spectral characteristics, and the values of the parameter *B* remain unchanged. Thus the constancy of the fraction of contact pairs for PD3(BF_4) and PD3(Br) on addition of 10^{-3} M of a salt is consistent with the absence of changes in the quantum yield for singlet oxygen generation.

In the series of studied compounds, the data on the ability to generate singlet oxygen for cationic analogs of the dye PD1 with counterions I^- and ClO_4^- stand out. For this pair of dyes, the absorption and fluorescence spectra in

TABLE 2. Spectral Characteristics of the Dye PD1 with Different Anions in Solutions

Anion	Solvent	λ_{max}^{abs}	$\Delta\lambda_{1/2}^{abs}$	λ_{max}^{FL}	$\lambda_{1/2}^{FL}$	τ	φ_{FL}	Φ	$B\cdot10^2$
ClO_4^-	Deuterated chloroform	755	60	785	49	1.8	0.36	$1.1\cdot10^{-3}$	0.5
	DCB	766	49	796	46	1.6	0.42	$1.3\cdot10^{-6}$	–
	Ethanol	742	53	773	48	1.3	0.28	$4.6\cdot10^{-7}$	–
	Deuterated acetonitrile	739	58	771	47	1.5	0.43	$3.0\cdot10^{-5}$	0.2
I^-	Deuterated chloroform	755	63	785	49	1.8	0.36	$3.1\cdot10^{-4}$	3.6
	DCB	766	49	796	46	1.6	0.42	$3.1\cdot10^{-5}$	–
	Ethanol	742	53	773	48	1.3	0.28	$4.7\cdot10^{-7}$	–
	Deuterated acetonitrile	739	58	771	47	1.5	0.43	$3.0\cdot10^{-5}$	0.2

low-polarity solvents and in acetonitrile (ethanol) are practically the same in shape and position, and the fluorescence quantum yields and lifetime coincide for them (see Table 2). The small half-width of the absorption spectrum for the dyes PD1(I) and PD1(ClO_4) in chloroform and the monoexponential character of the fluorescence decay kinetics suggest a single absorbing and emitting center. While the spectral fluorescence characteristics of the cationic analogs of this compound match, the quantum yield for singlet oxygen generation for PD1(I) in deuterated chloroform is ≈7 times higher than for PD1(ClO_4) (Table 2). Moreover, in deuterated acetonitrile, the value of B is the same for both dyes, and is less than half than the value for the dye with the anion ClO_4^- in deuterated chloroform. We should note that the quantum yield for singlet oxygen formation even in deuterated chloroform ($\sim10^{-3}$) is comparable with the absolute error in determination of the quantum yield or the fluorescence decay time for the dyes. Therefore together with such a significant relative change in deuterated chloroform for the value of *B* on going from PD1(I) to PD1(ClO_4), we do not detect any differences in the values of the quantum yield or the fluorescence decay time for these compounds (Table 2).

As shown in [25], the major mechanism for sensitization of oxygen by polymethine dyes is nonradiative transfer of energy from the dye molecules in the triplet state. Accordingly, *B* is a parameter whose value is determined by the yield for dye molecules going to the triplet state. When a heavy atom is present in the anion of the dye and when its molecules in solution are found in the form of contact ion pairs, we may expect an increase in the probability of intersystem crossing due to the external heavy atom effect [25]. In connection with the proximity of the cation and anion in the contact pairs, such an effect should also be apparent for low dye concentrations. On the other hand, for the same compound but under conditions when dissociation of the molecules to form ions occurs, the presence of heavy atoms in the anion should not affect the probability of intersystem crossing for the same concentrations. We should note that, according to the data in [25], the population of the triplet state for the dye PD1(I) in ethanol increased markedly when an additional substance (potassium iodide) was added to the solution, but only when its concentration exceeded 10^{-2} M.

The results obtained in this work, taking into account the concentration of the solutions (10^{-6} M), suggest that in low-polarity solvents, for an iodine-containing dye the efficiency of intersystem crossing is higher than for the dye PD1(ClO_4) and the yield for $^1O_2$ generation is higher. Consequently, in such solvents we see an effect from the iodine counterion, which is possible only when the anion is sufficiently close to the polymethine chain of the cation of the dye. The latter statement is substantiated by the data for symmetric polymethine dyes in [26], where it is shown that a significant increase (by more than a factor of 30) is observed in the yield for molecules going to the triplet state when the hydrogen atom is substituted by an iodine atom in the meso position of the polymethine chain. Substitution of iodine for a fluorine atom in the terminal groups of the cation of the dye leads to an increase in the population of the triplet state by only a factor of ≈3. With this in mind, the coincidence of the yield for $^1O_2$ generation for both dyes in deuterated acetonitrile for the same concentration (10^{-6} M) suggests the lack of a heavy atom effect for the anion and complete dissociation of the dye molecules to form free ions in a polar solvent. Consequently, for the dye group PD1, for which one absorbing and fluorescing center appears, the differences in the quantum yield for singlet oxygen generation in deuterochloroform are also due to the presence of the dye in solution in the form of contact ion pairs. Note that in deuterated acetonitrile, the value of *B* for both dyes of the PD1 group is less than half the value for the dye PD1(ClO_4) in deuterated chloroform. Such a ratio of the values for this parameter is consistent with the idea that the yield for singlet oxygen formation is higher for dye molecules in the form of contact ion pairs (in low-polarity solvents) than for the free ions (in high-polarity solvents).

Conclusion. From the data obtained, it follows that cation-anion interactions in polymethine dye molecules in solutions can have a significant effect on their ability to generate singlet oxygen. Higher values of the quantum yield for singlet oxygen generation correspond to dyes with anions promoting an increase of the fraction of contact ion pairs in solution. In this case, increasing the fraction of contact ion pairs by changing the concentration of the solutions or introducing an additional salt leads to an increase in the quantum yield for singlet oxygen generation. In the case when the dye is present in solution exclusively in the form of contact ion pairs, the yield for singlet oxygen formation is higher when there is a heavy atom in the anion, due to enhancement of intersystem crossing (the heavy atom effect).

Acknowledgments. We would like to thank A. V. Mudryi, chief scientist of the Radiation Laboratory of the Institute of Solid State and Semiconductor Physics (National Academy of Sciences of Belarus), for providing the equipment and assistance in recording the luminescence spectra of singlet oxygen.

REFERENCES

1. V. I. Avdeeva and M. A. Al'perovich, *Uspekhi Nauchn. Fotografii*, **22**, 84–90 (1984).
2. E. S. Voropai, M. P. Samtsov, K. N. Kaplevskii, and A. A. Lugovskii, *Vestn. Bel. Gos. Univ. Ser. 1. Fizika. Matematika. Informatika*, No. 1, 7–14 (2003).
3. E. S. Voropai, M. P. Samtsov, and K. N. Kaplevskii, *Zh. Prikl. Spektr.*, **70**, 635–641 (2003).
4. X. Yang, A. Zaitsev, B. Sauerwein, S. Murphy, and G. B. Schuster, *J. Am. Chem. Soc.*, **114**, 793–794 (1992).
5. A. S. Tatikolov, L. A. Shvedova, N. A. Derevyanko, et al., *Chem. Phys. Lett.*, **190**, 291–297 (1992).
6. A. S. Tatikolov, K. S. Dzhulibekov, L. A. Shvedova, et al., *J. Phys. Chem.*, **99**, 6525–6529 (1995).
7. E. S. Voropai, M. P. Samtsov, V. N. Chalov, and E. A. Zhavrid, *Zh. Prikl. Spektr.*, **68**, 359–362 (2001).
8. Y. P. Istomin, E. N. Alexandrova, E. S. Voropay, et al., *Exper. Oncology*, **28**, 80–82 (2006).
9. E. S. Voropai, M. P. Samtsov, K. N. Kaplevskii, et al., I*zv. Ross. Akad. Nauk. Ser. Fiz.*, **71**, 145–149 (2007).
10. E. S. Voropai, M. P. Samtsov, K. N. Kaplevskii, A. A. Lugovskii, and E. N. Aleksandrova, *Zh. Prikl. Spektr.*, **71**, 166–172 (2004).
11. E. Delaey, F. Laar, D. Vos et al., *J. Photochem. Photobiol. B*, **55**, 27–36 (2000).
12. D. R. Kearns, *Chem. Phys.*, **71**, 395–427 (1971).
13. A. U. Khan, *J. Phys. Chem.*, **80**, 2219–2227 (1976).
14. V. I. Zemskii, Yu. L. Kolesnikov, and I. K. Meshkovskii, *Physics and Technology of Pulsed Dye Lasers* [in Russian], IVA, St. Petersburg (2005), pp. 13–14.
15. E. S. Voropai, A. P. Lugovskii, M. P. Samtsov, et al., *"Indotricarbocyanine covalently bonded with glucose as a photosensitizer for photodynamic therapy of malignant tumors,"* Byelorussian Patent No. 7296 (2005).
16. A. A. Krasnovsky, Jr., *Membr. Cell Biol.*, **12**, 665–690 (1998).
17. E. S. Voropai and M. P. Samtsov, *Opt. i Spektr.*, **82**, 577–580 (1997).
18. T. A. Jenny and N. J. Turro, *Tetrahedron Lett.*, **23**, 2923–2926 (1982).
19. T. D. Poulsen, P. R. Ogilby, and K. V. Mikkelsen, *J. Phys. Chem. A*, **102**, 9829 (1998).
20. E. S. Voropai, M. P. Samtsov, K. N. Kaplevskii, et al., *Vestn. Bel. Gos. Univ. Ser. 1. Fizika. Mathematika. Informatika*, No. 3, 7–13 (2002).
21. E. S. Voropai, M. P. Samtsov, K. N. Kaplevskii, et al., *Vestn. Bel. Gos. Univ. Ser. 1. Fizika. Mathematika. Informatika*, No. 2, 3–8 (2004).
22. N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, *Theor. Exper. Chem.*, **19**, 150–157 (1983).
23. *Ions and Ion Pairs in Organic Reactions* [Russian translation from English; I. P. Beletskaya, ed.], Mir, Moscow (1975), p. 424.
24. J. R. Kanofsky and P. D. Sima, *Photochem. Photobiol.*, **71**, 361–368 (2000).
25. E. S. Voropai and M. P. Samtsov, *Opt. i Spektr.*, **62**, 64–67 (1987).
26. V. A. Kuz'min, A. P. Darmanyan, N. I. Shirokova, et al., *Izv. Akad. Nauk SSSR. Ser. Khim.*, No. 3, 581–586 (1978).