photochemistry of ketocyanin dye – polyenic $Bis-\omega,\omega'$ -Amino

KETONES SUBSTITUTED IN THE POLYENE CHAIN

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The photochemistry of ketocyanin dyes, 15 polyenic bis- ω, ω' -amino ketones (PBAK), was studied by the methods of pulsed and laser photolysis. During the photoexcitation of the PBAK solutions, the formation of their cis-photoisomers is observed, whose relaxation kinetics into the initial trans-isomers is dependent on the intensity of the probing light. The energy of activation of the cis \rightarrow trans-isomerization process in the dark increases with decrease in the polarity of the solvent. During the photoexcitation of fluorine-substituted PBAK with a six-membered central ring, their cyclization takes place with the formation of pyran forms (PF) absorbing in the UV region; the PF then convert into the initial dye. The formation of PF partially proceeds via the intermediate formation of a cis-isomer of the dye. During the photoexcitation of deoxygenated solutions of PBAK, the formation of their triplet states is also observed; the decay kinetics of the triplet states becomes accelerated with decrease in the solvating power of the solvent. This is explained by the decrease in the $T-S_0$ splitting due to increase in the energy barrier of the cis-trans isomerization process. A scheme has been proposed for the potential surfaces of PBAK to explain this phenomenon. For some PBAK, the formation is observed of cis-photoisomers not only from the S_1 , but also from the T-state.

Polyenic bis-amino ketones (PBAK) comprise a class of ketocyanin dyes, which are of promise for the conversion and generation laser radiation [1]. Polyenic bis-amino ketones having substituents in the polyene chain (in particular $-CH_2-CH_2-$ "bridges" [1]) have good generating properties. The use of PBAK in various photochemical systems requires a detailed examination of PBAK photonics. The present work is devoted to the investigation of the primary photochemical processes occurring during the photoexcitation of solutions of PBAK with substituents in the polyene chain.

EXPERIMENTAL

The photonics of 15 PBAK solutions was studied by the method of pulsed photolysis (Table 1) (on an apparatus with parameters $\tau_{1/2}$ = 5 µsec, energy 50 J). Isopropanol ("sp. pure" grade), acetonitrile ("pure"), and toluene ("chemically pure") were used as solvents for spectroscopy (MeCN was purified by distillation). The activation parameters of the isomerization were determined for the temperature range of 20-70°C, and for the relaxation of the pyran form (PF) in the -5+60°C range. The quantum yields of PF were measured by comparison with a standard - the triplet state of eosin in isopropanol. The short life times of the triplet state of the PBAK (<10 µsec) were measured on a laser photolysis apparatus (the N₂-laser) with a converter on dyes (λ 480 nm). The deoxygenation of the solutions was carried out by purging with argon and by the freezing-thawing method. The absorption spectra of the PBAK solutions were recorded on a "Specord UV VIS" spectrophotometer.

RESULTS AND DISCUSSION

During the pulsed photoexcitation of air-saturated solutions of PBAK (concentration $\sim 10^{-5}$ M), the formation of their photoisomers is observed (with the exception of the unsubstituted dye (I), for which the yield of the photoisomer is close to zero). The differential

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Dve	<i>د.</i> 88	^λ TT	λ_{ph}	k _{ph} ,
270	nm			sec -
	470	780	нет	-
Me_2N	490	800	510	0
Me ₂ N	506	730	540	0
$Me_2N \bigvee_{F}^{O} \bigvee_{F}^{V} NMe_2 (IV)$	472	780	540	0
MerN F NMe2 (V)	477	810	550	4·10²
$Me_2N \bigvee_{F}^{0} \bigvee_{F}^{1} NMe_2 (VI)$	482	660	550	3- 10 ³
$\mathbf{Me_{2}N} \overset{O}{\underset{\mathbf{F}}{\overset{ }}} \overset{O}{\underset{\mathbf{F}}{\overset{ }}} \overset{O}{\underset{\mathbf{F}}{\overset{ }}} \overset{O}{\underset{\mathbf{F}}{\overset{ }}} \overset{(VII)}{\underset{\mathbf{F}}{\overset{(VII)}}}$	500	720	550	0
$Me_2N \downarrow I I I I I I I I I I I I I I I I I I $	484	660, 800	550	1,1.10-2
$Me_2N \downarrow I Me Me Me^{(1X)}$	491	750	560	0,31
$Me_2N \bigvee_{Me}^{O} \bigvee_{Me}^{NMe_2} (X)$	460	800	530 ·	0
Me ₇ N ¹ _{Ph} ^{Ph} _{Ph} ^(XI)	467	800	550	0
Me_2N Me Me Me NMe_2 (XII)	439	810	520	≈0
Me_2N OEt OEt NMe_2 $(XIII)$	503	650, 720	560	≈0
$Me_2N \xrightarrow{O} COEt (NIV)$	394	_	450	≈0
$Me_{*}N \bigvee_{Me} \bigvee_{Me} (XV)$	403	_	450	≈()

TABLE 1. Maxima of S-S-Absorption (λ_{SS}), T-T-Absorption (λ_{TT}) Spectra, Differential Absorption Spectra of Photoisomers (λ_{ph}), and Decay Rate Constants of Photoisomers (k_{ph} , 20°C) of PBAK in Isopropanol



Fig. 1. Differential absorption spectrum of the photoisomer of dye (VIII) in isopropanol.

absorption spectrum of dye (VIII) is shown on Fig. 1 (the intrinsic absorption spectrum is close to the absorption spectrum of the initial PBAK). The photoisomers of other PBAK have similar absorption spectra (the λ_{max} of the differential spectra are given in Table 1). Since in solution the PBAK are initially present in the trans-form [2], the photoisomers of PBAK probably have a cis-configuration with respect to one of the double bonds of the polyenic chain and are formed from the S₁-state of the initial PBAK. The photoisomers of dyes (II)-(IV), (VII), (X)-(XV) are stable, and do not convert in the dark into the initial trans-

PBAK even on heating to 70°C for several minutes. However in light, a trans-PBAK $\frac{hv}{hv}$ cis-

PBAK photostationary equilibrium is established relatively rapidly, and therefore at high intensity of the probing light (I) of the pulsed photolysis apparatus, the measured lifetime of the photoisomer turns out to be much shorter than that of the intrinsic photoisomer obtained in the dark. The relaxation rate constants of the photoisomers (k_{ph} , Table 1) were measured at $1 \rightarrow 0$. The activation parameters of the relaxation of the photoisomer of dye (VIII) were measured: in isopropanol $E_a = 51 \text{ kJ/mole}$, $\log A_0 = 7.8$; in toluene $E_a = 108.4 \text{ kJ/mole}$; $\log A_0 = 13.7$, where E_a is energy of activation, A_0 (sec⁻¹) is preexponent. The decrease in E_a in isopropanol compared with toluene is due to decrease in the order of the double bonds in the polyene chain as a result of the solvation of the carbonyl group of the dye with alcohol [3, 4], which leads to a decrease in the energy barrier of the isomerization.

During the photoexcitation of solutions of dyes (V) and (VI), besides the photoisomers, their pyran form (PF) are formed with an absorption spectrum in the UV region (Fig. 2). The PF then converts slowly (in the course of tens of seconds) into the initial dye. The presence of an isobestic point in the absorption spectra indicates a high reversibility of the system (see top of following page).

It should be noted that for (VII) having a similar structure to that of dye (VI), but a more rigid connecting bridge, the formation of PF is not observed, probably because of steric hindrances to the closure of the pyran ring. In the case of dye (IV), which has no connecting bridges in its structure, the too high mobility of the polyene chain possibly hinders the formation of the PF.



19.2 msec

Fig. 3

Fig. 2. Spectral changes observed during illumination of a solution of dye (VI) in isopropanol as the result of the formation of PF: 1) absorption spectrum of the dye before illumination; 2-6) the restoration process of the absorption spectrum with the relaxation of PF into the initial dye; 7) absorption spectrum of the dye immediately after illumination (the pyran form).

Fig. 3. Formation kinetics of PF of dye (VI) in isopropanol.



The kinetics of formation of PF (Fig. 3) consists of two components: a rapid one, coinciding with a flash front, and a slow one having a characteristic period, close to the relaxation time of the photoisomer (Table 1). The PF probably forms from two states of the dye: an excited singlet state and the photoisomer; the quantum yields of the PF are approximately the same in the two states. Thus, the photoisomer probably has a cis-configuration relative

TABLE 2. Decay Activation Parameters of PF of Dyes (V) and (VI) (k_n is the decay rate constant of PF at 20°C)

	Isopropanol			Toluene		
PBAK	$k_n \cdot 10^4$, sec ⁻¹	E _a , kJ/mole	log A (sec ⁻¹)	k _n ·10 ⁴ , sec ⁻¹	E _a , kJ/mole	log A (sec ⁻¹)
(V) (VI)	60 8	48,1 35,1	6.3 3.1	5 8	43,5 40,6	4,4 4,1

TABLE 3. Decay Rate Constants of the Triplet State of PBAK (of the slow and fast components, $k_{\rm T}\cdot10^{-4}$, $\rm sec^{-1})$ in Various Solvents

PBAK	Isopropanol	Acetonitrile	Toluene
(I)	0,076: 0,16	3.1 *	35; 47
(III)	0,075: 0.4	0.44; 1,3	15; 46
(IV)	100: 460	1000 *	1600 *
(X)	20 *	143 *	1800 *
(XII)	22 *	60; 1400	460; 1800

*Only one component is present.

to the α - β bond of the polymethine chain, which facilitates its cyclization into the PF. This additional path of decay of the photoisomer explains the high values of k_{ph} for dyes (VI) and (VII) compared with other PBAK (see Table 1). The formation and decay processes of PF can be illustrated by the following scheme

trans-PBAK (V), (VII)
$$\xrightarrow{h\nu}$$
 PF
 $h\nu$ cis-PBAK $\xrightarrow{k_{ph}}$

The photoexcitation of PF does not lead to the formation of PBAK (in a trans or cis-form).

The quantum yields of formation of PF for (V) and (VI) in isopropanol are equal to 0.19 and 0.42, respectively (the probability of formation of PF by dye (V) is approximately twice as high as in the case of (VI), since only one half of the polyene chain of dye (V) containing the substituent F can cyclize). The solvation parameters of the conversion of PF in the dark into the initial dye were measured (Table 2) and were found to be close to the values of E_a and A_0 for the cyclization reactions in the dark into PF of a series dienic monoamino ketones with substituents in the dienic chain [5].

During the photoexcitation of deoxygenated solutions of PBAK, together with the photoisomers and PF, the formation of their triplet states is observed. Table 1 shows the maxima of the T-T absorption spectra in isopropanol, while in Table 3, the decay rate constants of the triplet state (k_T) are given. For all the PBAK a dependence k_T on the nature of the solvent is observed: the k_T is minimal in isopropanol, and increases sharply with decrease in the solvating power of the solvent (Table 3). For several PBAK, the decay kinetics of the triplet state is two-component, whereby the ratio of the components varies as a function of the recording wavelength (see Table 3, Fig. 4). This is probably due to the formation and decay of the triplet state of the two isomers of the dyes: the trans- and cis-PBAK. The two kinetic components have a similar dependence of k_T on the polarity of the solvent. During a T-T energy transfer from 1,2-benzpyrene ($E_T = 18,500 \text{ cm}^{-1}$) to the PBAK (III) in isopropanol, only the short-lived component ($k_T = 3.6 \cdot 10^3 \text{ sec}^{-1}$) is observed. The T-T absorption spectrum of one of the components of dye (I) (Fig. 4) has two maxima. This splitting of the spectrum is, possibly, caused by the effect of the interaction of chromophores [6].

Figure 5 shows the potential curves of the singlet and triplet states of PBAK as a function of the rotation angle of one of the double bonds of the polymethine chain during



Fig. 4



Fig. 4. Differential spectrum of triplet-triplet absorption of dye (I) in isopropanol: 1) the spectrum of the long-lived component; the spectrum of the short-lived component.

Fig. 5. Scheme of radiationless deactivation of the triplet state of PBAK in various solvents: 1) in isopropanol; 2) acetonitrile; 3) in toluene; E_1 , E_2 , E_3) the corresponding T-S₀ energy splitting (φ is the rotation angle around the double bond of the polymethine chain).

the isomerization process. The potential curves have two minima, corresponding to trans-($q = 0^{\circ}$) and cis-configurations ($q = 180^{\circ}$). Since most of the PBAK have two triplet states, corresponding to cis- and trans-configurations (Table 3), the curve for the triplet state probably has two sharply expressed minima. The deactivation rate constant of the triplet state is determined by the T-S₀ splitting of PBAK: the distance between the lower triplet and singlet states. With decrease in the solvating power of the solvent, the energy barrier of the isomerization process increases (the E_a increases), which results in the potential curve of the S_0 state approaching the curve for the T-state (curves 1, 2, 3 on Fig. 5). This causes an increase in the deactivation rate constant of the triplet state of PBAK with the decrease in the polarity of the solvent, as the result of a decrease in the T-S₀ energy splitting. This scheme also finds confirmation in the fact that for certain PBAK (IV), (VI), (VIII), (X)-(XIII), the formation of a photoisomer is observed not only from the singlet, but also from the triplet state.

LITERATURE CITED

- L. A. Shvedova, A. S. Tatikolov, A. P. Darmanyan, et al., Dokl. Akad. Nauk SSSR, <u>276</u>, No. 1, 164 (1984).
- Zh. A. Krasnaya, T. S. Stytsenko, and E. P. Prokof'ev, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 595 (1976).
- L. A. Shvedova, A. S. Tatikolov, Zh. A. Krasnaya, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 61 (1988).
- L. A. Shvedova, A. S. Tatikolov, V. A. Kuz'min, et al., Dokl. Akad. Nauk SSSR, <u>276</u>, No. 3, 654 (1984).
- A. S. Dvornikov, Zh. A. Krasnaya, and Ya. N. Malkin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 390 (1981).
- L. A. Shvedova, Yu. E. Borishevich, A. S. Tatikolov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1421 (1983).

SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF SPIROANTHROOXAZINE

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1',3',3'-Trimethylspiro[indoline-2',3-3H-anthraceno[2,1-b][1,4]oxazine] was synthesized. The compound has photochromic properties in solutions and in polymeric matrices. It was found from the spectral data that the colored form of the spiroanthrooxazine exists in a quinoid form and is characterized by a positive solvatochromic effect.

In continuation of studies on the synthesis of compounds of the spirooxazine series and examination of their photochromic properties [1-4], the present work deals with the synthesis of 1',3',3'-trimethylspiro[indoline-2',3-3H-anthraceno[2,1-b][1,4]-oxazine] (I) and examination of its photochromic properties in solution of varied polarity and in polymeric matrices.

The scheme of the synthesis used is shown as follows:



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