(VII$_1$) 197.5 (s, C-1), 128.01 (d, C-2), 155.97 (m, C-3), 48.10 (d, C-4) 35.6 (d, C-5), 37.41 (t, C-6), 22.7 (q, C-7), 169.53 (s, C-8), 71.22 (t, C-9), 14.5 (q, C-10), 60-59 (t, C-11), 66.07 (t, C-12) 13.74 ppm (q, C-13). IR spectrum: 1770, 1680, 1640 cm^{-1}, M$^+$ 242.

2-Methyl-5-ethoxy-3-acetyl-4,5-dihydrofuran (VIa) (Table 1). Trifluoroacetic acid (0.5 ml) was added to compound Va (8.5 g: 0.05 mole) in dry CCl_4 (40 ml) and the mixture stirred at 70°C for 7 h. The course of the reaction was checked by TLC (Silufol, hexane—ether, 1:2). The reaction mixture was treated with saturated $NaHCO_3$ solution, the solution dried with sodium sulfate, and after distilling off the solvent the residue was distilled in vacuum in a stream of nitrogen. Dihydrofuran (VIa) (7.2 g: 0.042 mole) was obtained in 85% yield.

2-Methyl-5-ethoxy-3-carbethoxy-4,5-dihydrofuran (VIb). Acetic acid (4 ml) was added to the mixture (10 g: 0.05 mole) of compounds IVb-VIb in CCl_4 (40 ml). The mixture was stirred at 70°C for 2 h. After distillation dihydrofuran VIb (7.5 g: 0.038 mole) was obtained, yield was 75%.

2-Methyl-5-ethoxy-3-benzoyl-4,5-dihydrofuran (VIc) and 2-Phenyl-5-ethoxy-3-acetyl-4,5-dihydrofuran (VIc$_1$). Trifluoroacetic acid (0.5 ml) was added to a mixture (4.2 g: 0.018 mole) of compounds IVc and Vc in CCl_4 (20 ml), the reaction mixture was stirred at 70°C for 2 h, and compounds (VIc + VIc$_1$) (4 g: 0.017 mole) were obtained. Yield was 95%. ^{13}C NMR spectrum (250 MHz, C_6D_6): (VIc) 113.88 (C-2); 166.5 (C-3); 28.86 (C-4); 105.26 (C-5); 37.83 (C-6); 127.7-130.83 (C-7); 64.33 (C-8); 15.01 (C-9); 201.2 (C-10); (VIc$_1$) 116.53 (C-2); 172.5 (C-3); 29.4 (C-4); 104.8 (C-5); 38.21 (C-6); 127.7-130.83 (C-7); 64.33 (C-8); 15.23 (C-9); 196.7 (C-10). IR spectrum: 3065, 1705, 1655, 1080 cm^{-1}.

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ACID—BASE PROPERTIES AND STABILITY OF PYRYLIUM POLYMETHINE DYES IN CHLOROHYDROCARBON SOLUTIONS

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UDC 547.812.5:541.651

The reactions of pyrylocyanine dyes with aqueous alcoholic alkali and with acetic acid have been studied. It has been shown that decoloration of such dyes in chlorohydrocarbon solutions only occurred under the action of alkali and was linked with the formation of an intermediate acyclic form of the dye which was the addition product of hydroxyl ion at the α position of the pyrylium ring.

It is known from [1] that cyanine dyes are inclined to decoloration in solution both under the action of acid and of alkali. The ease of carrying out the reaction leading to decoloration may serve as a practical measure of the stability of cyanine dye molecules in solution in organic solvents. Reactions of such type have not been adequately studied for pyrylium polymethine dyes in spite of the urgency connected with the wise practical application of these dyes for example as materials for quantum electronics in [2, 3].

In the present work the special features of the development of acid—base properties of pyrylocyanine dyes in chlorohydrocarbon solutions has been considered. For this purpose the behavior of pyrylium polymethine dyes has been investigated in aqueous alcoholic alkali and acetic acid using the example of 2-[7-(4,6-diphenyl-2H-pyran-2-ylidene)-4-chloro-3,5-trimethylene-1,3,5-heptatrienyl]-4,6-diphenylpyrylium perchlorate (dye PK-15) of [4] and several of its derivatives. Methylene chloride and 1,2-dichloroethane served as solvents.

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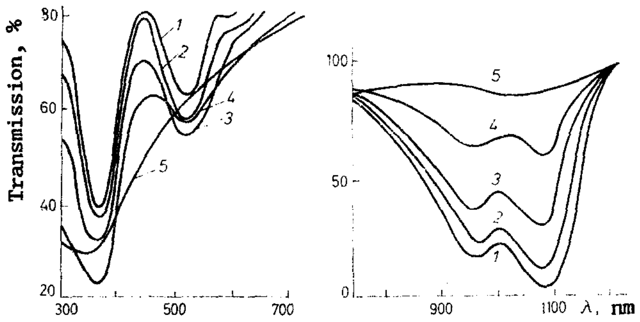


Fig. 1. Transmission spectra of PK-15 dye in methylene chloride with added 10% (by vol.) 0.5 N aqueous alcoholic alkali: 1) freshly prepared solution; 2) after 0.5 h; 3) after 1.5 h; 4) after 4 h; 5) after 20 h.

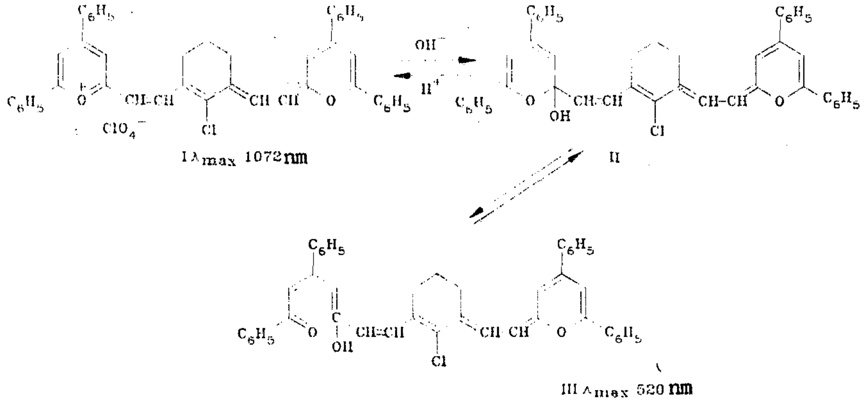
TABLE 1. Characteristics of the Synthesized Compound

Compound	Electronic spectrum, λ_{max} nm (log ε)	IR spectrum, cm^{-1}	Found, %		Empirical formula	Calculated, %	
			C	H		C	H
I (PK-15)	1072 (4,78)	1110 (ClO_4); 1525, 1610, 1640 (pyrylium cation)	72,0	4,8	$C_{44}H_{34}Cl_2O_6$	72,4	4,7
III	520 (3,61)	1190 (C—OH); 1495, 1590, 1635, 1685 (C=O) [8], 3400 (br. band, polyassociated OH)	81,34	5,30	$C_{44}H_{35}ClO_3$	81,65	5,45

An anomalous behavior was discovered for the pyrylocyanines in comparison with the salt-form cyanine dyes. It turned out that they were not decolorized by acid and were decolorized only under the action of alkali. Transmission spectra (TS) of dye PK-15 in methylene chloride with addition of 10% (by vol.) 0.5 N aqueous alcoholic alkali, recorded at various time points, are shown in Fig. 1 as an example. The changes of TS with time of a solution of PK-15 under the action of alkali showed that decoloration of the solution proceeded in several stages. In the initial step (during the first 1-2 h after adding alkali) a reduction in intensity of the main absorption band (AB) of the dye at λ_{max} 1072 nm (log ε 4.78) occurred and linked with it was a growth in intensity of absorption of the band with λ_{max} 520 nm (log ε 3.61). If the solution of dye was acidified with acetic acid at this stage then the reverse reaction began at once, proceeding with a significantly greater rate as indicated experimentally by the observed restoration of the initial optical density at wavelength 1072 nm and a corresponding (allowing for the difference in extinction) fall in intensity of the AB at λ 520 nm in less than 10 min.

After a greater duration (3-4 h) of the action of alkali on the initial solution irreversible conversions began, showing spectrally in a further fall of intensity of the main AB and in a marked growth of the AB in the 360 nm region with a simultaneous reduction in the intensity of the AB at 520 nm. After 20 h final destruction of the dye occurred which was indicated by the complete disappearance of the AB in the near IR region. The absorption in the 230 nm region was sharply increased.

The observed difference in the TS of a solution of PK-15 dye under the action of alkali and acid may be explained, from our point of view, if the specific nature of the properties of the pyrylium ring are taken into consideration, i.e., the ability readily to add nucleophilic agents at the α position observed in [5, 6]. The following conversion scheme may be proposed for the considered pyrylium polymethine dye.



Under the action of hydroxyl ion an unstable acyclic carbonyl form (III) (ACF) is formed which is readily converted on acidification into the initial form of the dye (I). Depending on the extent of the accumulation of hydroxyl ions in solution a gradual accumulation of the open form (III) occurs and subsequent destruction of it with the formation of unsaturated ketones $C_6H_5-C(O)-CH=C(C_6H_5)-CH=CHOH$ having two AB at 360 and 230 nm corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions according to [7]. Evidently the reaction proposed above also explains the stability in chlorohydrocarbon of the pyrylocyanine dyes.

For confirmation, form (III) mentioned above was isolated by us and characterized. It is interesting to note that the formation of the ACF was observed by us directly in the actual synthesis of dye PK-15 and its derivatives, but in the case of p-nitrophenyl substituted derivatives of PK-15 only the open carbonyl form of the dye with λ_{max} 520 nm was observed under the action of a strong acceptor and not even traces of the form of the dye absorbing in the near IR region were observed.

It may therefore be considered that decoloration of the pyrylium polymethine dyes in solution in chlorohydrocarbons goes through the formation of an unstable acyclic form which is the product of the addition of hydroxyl ion at the α position of a pyrylium ring of a dye molecule.

The obtained results also proved to be extremely useful for clarifying possible routes of photoconversion of pyrylocyanine molecules under the action of laser radiation. It was established experimentally by us that on irradiation of solutions of dye PK-15 in chlorohydrocarbons with a neodymium laser of nanosecond duration the spectral manifestations of the process of photodecolorization of such solutions were completely identical to the changes in their transmission spectra described above under the action of hydroxyl ions. This circumstance makes it possible to propose that the acid–base properties of molecules of pyrylium polymethine dyes also play an important role in the process of photo-decolorization of their solutions on resonance laser excitation.

EXPERIMENTAL

The electronic spectra of compounds were taken on an SF-8 spectrophotometer. IR spectra were drawn on a UR-20 spectrophotometer in KBr disks.

Preparation of Acyclic Carbonyl Form (III) of the Dye. A solution of dye PK-15 in methylene chloride was shaken with 0.5 N aqueous alcoholic alkali, washed with water, dried over $CaCl_2$, and evaporated to dryness. The dry residue was dissolved in methylene chloride and was chromatographed on a column of Al_2O_3 in the same solvent. The open carbonyl form (III) was eluted first. The spectral characteristics of this form and data of elemental analysis are given in Table 1.

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ELECTROCHEMICAL REDUCTION OF N-VINYLAZOLES

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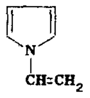
Classical polarography in aprotic solvents was used to study the reduction of N-vinyl derivatives of pyrazole, imidazole, 1,2,3- and 1,2,4-triazoles, and tetrazole. The N-vinylazoles studied were reduced in acetonitrile by a one-electron mechanism with subsequent dimerization of the radical-anions formed. The N-vinyl derivatives of pyrazole, imidazole and tetrazole were reduced analogously in DMF, while N-vinyltriazoles in DMF are reduced by a mixed mechanism with predominant two-electron transfer. Possible schemes for the electrochemical reduction of N-vinylazoles are discussed.

The study of the electrochemical initiation of the polymerization of vinyl monomers requires knowledge of the primary electrochemical steps. The reduction of the vinyl group in styrene and methyl methacrylate in DMF has been shown to occur by different mechanisms [1-3]. Styrene is reduced in a single two-electron step, initiating polymerization by dianions [1, 2], while methyl methacrylate accepts one electron under the same conditions followed by radical-anion recombination [2, 3]. N-Vinylcarbazole under analogous conditions gives one two-electron wave on the polarogram [4]. However, the nature of the solvent plays a role in the reduction of N-vinyl-1,2,4-triazole [5]. The reduction in DMF proceeds in a single two-electron step, while the depolarizer accepts only one electron in acetonitrile [5, 6]. Thus, the electrochemical reduction of even the same type of vinyl monomers may proceed by different pathways.

In order to elucidate the common features and differences in the behavior of N-vinylazoles, we studied the electrochemical reduction of N-vinyl derivatives of pyrazole, imidazole, 1,2,3- and 1,2,4-triazoles and tetrazole (II-IX) in aprotic solvents. For comparison, we investigated N-vinylpyrrole I, tetrazole X and 5-vinyltetrazole XI. In order to exclude the effect of impurities and water, the starting compounds and the solvents were subjected to careful purification.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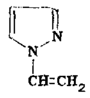
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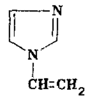
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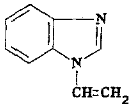
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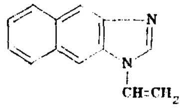
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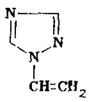
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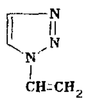
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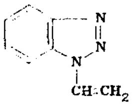
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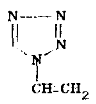
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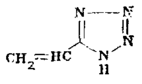
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