SYNTHESIS AND INVESTIGATION OF THE ELECTRONIC SPECTRA OF PERCHLORATES OF SOME SUBSTITUTED PYRIDINIUM IONS

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1,2,4,6-Substituted pyridinium perchlorates were obtained, and their electronic absorption and emission spectra were studied. When electron-donor substituents are introduced into the para position of the N-phenyl group, an intramolecular charge-transfer band ($l_a \rightarrow \pi$ transition), with which the capacity for fluorescence of these compounds in the crystalline state is associated, appears in the long-wave portion of the absorption spectrum. Replacement of the methyl groups in the heteroring by phenyl groups is accompanied by hyperchromic and bathochromic effects and by the appearance of a capacity for fluorescence in solutions at room temperature. These phenomena are explained by an increase in the polarization of the π-electron system of the molecules when phenyl groups are introduced.

Effective luminophores that have high photostability and are stable in strongly acidic media are found among pyrylium and pyridinium salts [1, 2]. At the same time, there is very little information in the literature regarding the interrelationship between the optical (including luminescence) characteristics of these compounds and the structures of their molecules; this hinders the directed synthesis of luminophores in these series.

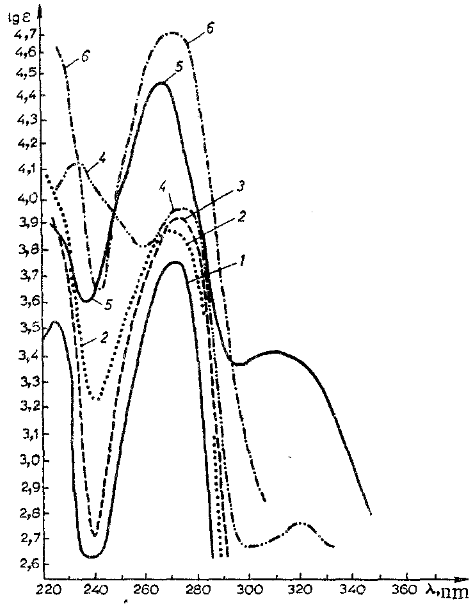

Fig. 1. Absorption spectra of pyridinium perchlorates in ethanol: 1) 1,2,4,6-tetramethylpyridinium (I); 2) 1-phenyl-2,4,6-trimethylpyridinium (II); 3) 1-(4-chlorophenyl)-2,4,6-trimethylpyridinium (VI); 4) 1-(4-acetylphenyl)-2,4,6-trimethylpyridinium (VII); 5) 1-(4-dimethylaminophenyl)-2,4,6-trimethylpyridinium (V); 6) 1-(4-methoxyphenyl)-2,4,6-trimethylpyridinium (IV).

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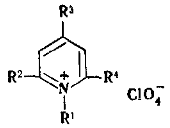
TABLE 1



Compound	R¹	R²	R³	R⁴	mp, °C	Empirical formula
I	CH_3	CH_3	CH_3	CH_3	205—206[8]	$C_9H_{14}ClNO_4$
II	C_6H_5	CH_3	CH_3	CH_3	123—124	$C_{14}H_{16}ClNO_4$
III	p-$CH_3C_6H_4$	CH_3	CH_3	CH_3	135—136	$C_{15}H_{18}ClNO_4$
IV	p-$CH_3OC_6H_4$	CH_3	CH_3	CH_3	106—107	$C_{15}H_{18}ClNO_5$
V	p-$(CH_3)_2NC_6H_4$	CH_3	CH_3	CH_3	152—153	$C_{16}H_{21}ClN_2O_4$
VI	p-ClC_6H_4	CH_3	CH_3	CH_3	134—135	$C_{14}H_{15}Cl_2NO_4$
VII	p-$CH_3COC_6H_4$	CH_3	CH_3	CH_3	130—131	$C_{16}H_{18}ClNO_5$
VIII	CH_3	CH_3	CH_3	C_6H_5	180—181	$C_{14}H_{16}ClNO_4$
IX	CH_3	CH_3	C_6H_5	C_6H_5	193—195	$C_{19}H_{18}ClNO_4$
X	CH_3	C_6H_5	C_6H_5	C_6H_5	213—215[9]	$C_{24}H_{20}ClNO_4$

Compound	Found, %		Calc., %		Absorption spectrum		Fluorescence,* λ_{max}, nm (ethanol)	Yield, %
	Cl	N	Cl	N	λ_{max}, nm	lg ε		
I	14,6	5,9	14,8	5,9	230, 270	3,53; 3,76	—	55
II	11,6	4,5	11,8	4,7	224, 270	4,06; 3,87	—	46
III	11,3	4,3	11,4	4,5	220, 270	3,90; 3,88	—	49
IV	10,5	4,2	10,7	4,3	224, 270	4,63; 4,72	415 (crystals)	57
V	10,2	8,1	10,4	8,4	224, 266, 310	3,92; 4,46; 3,42	480(crystals)	42
VI	21,4	4,1	21,6	4,2	224, 270	3,88; 3,90	—	40
VII	10,3	4,2	10,4	4,1	234, 272, 320	4,12; 3,97; 2,76	—	47
VIII	11,7	4.5	11,8	4,7	286	3,93	475	36
IX	9,7	3,7	9,9	3,9	296	4,05	470	32
X	8,2	3,2	8,4	3,3	306	4,13	450	61

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* Compounds I-III and VI and VII do not fluoresce. The absolute quantum fluorescence yields of VIII-X in ethanol are 0.13, 0.23, and 0.30, respectively.

The aim of the present study was an investigation of the electronic absorption and emission spectra and the quantum yields of the fluorescence of 1,2,4,6-substituted pyridinium perchlorates (I-X, Table 1). These pyridinium salts, the majority of which have not been described in the literature, were synthesized via the method described in [3] by reaction of the appropriate 2,4,6-trisubstituted pyrylium perchlorates with methylamine or substituted anilines. The electronic spectra of the compounds obtained were measured by standard methods.

Two bands with maxima at 224 and 270 nm (Fig. 1), which are associated with $\pi \rightarrow \pi^*$ transitions in the heteroring, the π-electron system of which is polarized under the influence of a positively charged heteroatom, are observed in the absorption spectrum of an ethanol solution of 1,2,4,6-tetramethylpyridinium perchlorate (I). Transition from I to N-phenyl-2,4,6-trimethylpyridinium perchlorate (II) is not accompanied by any appreciable changes in the absorption spectrum – only a certain broadening and an increase in the intensity of the long-wave band are observed (Fig. 1). This effect is apparently associated with the superimposition of the K band of the N-phenyl group on the long-wave absorption band of the heteroring. The fact that its maximum is bathochromically shifted to 270 nm from the usually observed region at 250 nm attests to interaction of the N-phenyl group with the pyridinium ring and with the strong electron-acceptor substituent. This assumption is confirmed by the fact that electron-acceptor substituents in the para position of the N-phenyl group do not change the absorption characteristics of the compounds under consideration. The only exception to this is N-(4-acetylphenyl)-2,4,6-trimethylpyridinium perchlorate (VII), the spectrum of which contains an additional band with a maximum at 320 nm, which is associated with an $n \rightarrow \pi^*$ transition in the carbonyl group. The assignment of the long-wave band in the absorption spectrum of VII to an $n \rightarrow \pi^*$ transition is confirmed by a comparison of its spectrum with the absorption spectrum of acetophenone, in which the indicated band is also observed. In this case, however, attention is directed to the fact that the band of the $n \rightarrow \pi^*$ transition in the spectrum of VII has a higher intensity. This fact can be explained starting from the assumption that the intensity of the band of the $n \rightarrow \pi^*$

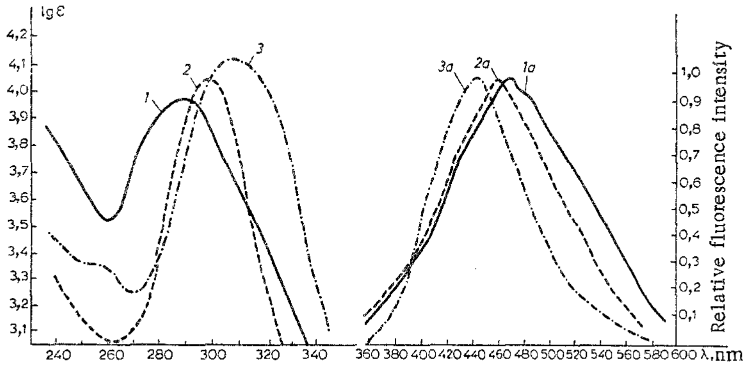

Fig. 2. Absorption (1-3) and fluorescence (1a-3a) spectra of pyridinium perchlorates in ethanol: 1 and 1a) 1-methyl-2,4-dimethyl-6-phenylpyridinium (VIII); 2 and 2a) 1-methyl-2-methyl-4,6-diphenylpyridinium (IX); 3 and 3a) 1-methyl-2,4,6-triphenylpyridinium (X).

transition, which is localized on the carbonyl group, is due to the magnitude of the effective positive charge on the carbon atom of the carbonyl group. However, the latter should have a higher value in the substituted pyridinium molecule than in the acetophenone molecule because of the strong electron-acceptor effect of the heteroring.

Electron-donor substituents in the para position of the N-phenyl group cause a small hypsochromic shift of the long-wave band and increase its intensity markedly (Fig. 1). The first of the indicated effects can be explained by weakening of the polarization of the π^*-electron system of the heteroring under the influence of an electron-donor substituent. The increase in the intensity of the long-wave band is apparently associated with an increase in the probability of the electronic transition in the substituted phenyl group, which is strongly polarized because of the interaction of substituents of different electronic natures.

However, this assumption is inadequate to explain the more appreciable increase in the intensity of the band under consideration in the spectrum of 4'-methoxy-substituted compound IV as compared with the spectrum of dimethylamino-substituted compound V. The indicated anomaly can be explained by the fact that the long-wave band in the absorption spectrum of IV contains, in addition to the absorption bands of the heteroring and the substituted N-phenyl group, a band in the long-wave region that is associated with intramolecular charge transfer ($l_a \rightarrow \pi^*$ transition). The presence in the N-phenyl group of a dimethylamino group intensifies the donor-acceptor interaction, and this leads to a bathochromic shift of the intramolecular charge-transfer band, such that for V this band is observed separately (Fig. 1). In this case, the intensity of the band of the $\pi \rightarrow \pi^*$ transition is reduced.

The presence in the molecules of IV and V of states with intramolecular charge transfer leads to the appearance in them of a capacity for fluorescence in the crystalline state. This fact confirms the conclusions in [4], in which it is shown in the case of carbonyl derivatives of benzene that one of the conditions for the appearance in them of a capacity for fluorescence is the presence in the molecule of a donor—acceptor interaction, the basis of which is the effective intramolecular transfer of charge.

On the basis of an examination of the optical characteristics of N-phenyl-substituted 2,4,6-trimethylpyridinium perchlorates (II-VII), one can conclude that the effect of the π-electron systems of the heteroring and the N-phenyl group on the electronic absorption spectra is additive. Consequently, the indicated portions of the molecule display the properties of isolated π-electron systems.

A phenyl group in the α position of the pyridinium ring (VIII) causes more appreciable changes in the spectral characteristics of the examined compounds than an N-phenyl group: considerable broadening and a bathochromic shift of the long-wave band are observed in the absorption spectrum, and the capacity for fluorescence appears. Further introduction of phenyl groups in the α and γ positions (IX, X) is accompanied by hyperchromic and bathochromic effects in the absorption spectrum (Fig. 2). In addition, the fluorescence quantum yield increases. It is interesting that the accumulation of phenyl groups in the heterocyclic ring leads to a short-wave shift in the emission band (Fig. 2). This fact can be explained by a change in the relative position of the potential energy curves, which is associated with the decrease in the difference in the equilibrium internuclear distances of the ground and excited states [10]. The reason for the indicated effect may be redistribution of the π-electron density in the molecules of the investigated compounds on passing from the ground to the excited state.

On the basis of the data presented above, it can be assumed that the π-electron system of the investigated compounds in the ground state is characterized by a tendency toward equalization of the bonds, which leads to a decrease in the effective positive charge on the heteroatom. However, the excited state is characterized by intensification of the polarization of the molecule, which is facilitated by accumulation of phenyl groups; this also explains the observed long-wave shift of the absorption band.

EXPERIMENTAL

2,4,6-Trimethyl-, 2-Methyl-4,6-diphenyl-, 2,4-Dimethyl-6-phenyl-, and 2,4,6-Triphenylpyrylium Perchlorates. These compounds were obtained by the methods described in [5-7].

1,2,4,6-Tetrasubstituted Pyridinium Perchlorates (I-X, Table 1). The appropriate primary amine (2 mole) was introduced into a saturated refluxing solution of pyrylium salt (1 mole) in ethanol, and the mixture was refluxed for 1 h. It was then cooled and diluted with an equal volume of water. The resulting crystals were removed by filtration, washed on the filter with water, and purified by two to three crystallizations from ethanol with decolorization by activated charcoal.

The UV spectra of 10^{-3}-10^{-5} M solutions in ethanol were measured with an SF-4A spectrophotometer. The fluorescence spectra and quantum yields (c 10^{-4}-10^{-5} M) were measured with a luminescence apparatus with a ZMR-3 monochromator. An FÉU-68 photomultiplier calibrated for quantum spectral sensitivity was used as the emission detector.

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