# STUDIES OF IMIDAZO[4, 5-*f*]QUINOLINE

## II. UV Absorption and Luminescence of Imidazo[4, 5-*f*]Quinoline and Its Quaternary Salts*

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The UV absorption spectra of imidazo[4, 5-*f*]quinoline and its quaternary salts were examined. The causes of the development of luminescence in solutions of the quaternary salts of imidazo[4, 5-*f*]quinoline were elucidated.

With the object of studying in further detail the properties of imidazo[4, 5-*f*]quinoline, caused by the effect of the nitrogen atom of the quinoline ring [1], its UV absorption and luminescence spectra were examined.

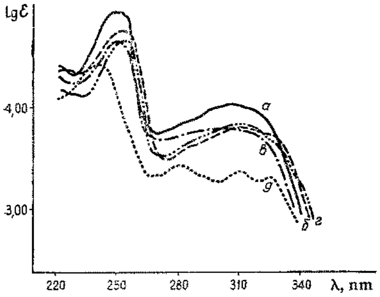

Fig. 1. Absorption spectra in methanol: (a) imidazoquinoline (**Ia**); (b) 2-methyl-3-phenylimidazoquinoline (**Ic**); (c) 3-benzylimidazoquinoline (**Id**); (d) 2, 3-dimethylimidazoquinoline (**Ib**); (e) 2-methyl-3-phenylnaphthoimidazole (**II**).

The absorption of imidazo[4, 5-*f*]quinoline (I) is characterized by the presence of two intense maxima in the middle ultraviolet: a shortwave peak ($\lambda_{max}$ =252, lg ε =4.82) and a longwave peak ($\lambda_{max}$ =315 nm, log ε =3.82) which substantially differ in width and intensity. The general contour of the curve resembles the absorption curve of naphtho[1, 2-d]imidazole (II) with the difference that the longwave absorption band of **I** and of its 3-substituted derivatives has a higher intensity (Fig. 1). The broad longwave absorption band in the imidazo[4, 5-*f*]quinoline series combines, as it were, several of the absorption maxima of naphthol[1, 2-d]imidazole, is apparently analogous to the B-band of benzimidazole [2], and probably introduces the B-band analogous to the B-band of benzimidazole.

The sharp enhancement of the intensity of the longwave band of imidazoquinoline compared with the longwave absorption of II indicates that it is to a considerable extent due to the effect of the quinoline N-atom. A similar increase in intensity of the B-bands on introducing a N-hetero atom into an aromatic hydrocarbon has been observed previously [3, 4]. Enhancement of the intensity of the longwave absorption and its bathochromic shift occurs on substituting a CH of the benzene nucleus in benzimidazole by a nitrogen atom [5]. In acid media and in the quaternary

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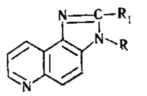
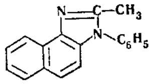
*For part I, see [6].

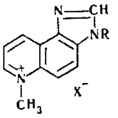


I a $R=H, R_1=H$; b $R=CH_3, R_1=CH_3$;
c $R=C_6H_5, R_1=CH_3$; d $R=C_6H_5CH_2, R_1=H$



II

salts (III) the longwave band of imidazoquinoline shows a strong bathochromic shift (~50 nm) (Fig. 2) which confirms its close connection with the quinoline N-atom, since previously [6] it has been shown that protonation in the imidazoquinoline series occurs at the quinoline ring. A similar picture of a bathochromic shift of the longwave band in acid media is observed in all six-membered nitrogen heterocycles with a single heteroatom [7–12]. Thus the longwave absorption of the imidazoquinolines is a π→π* transition band of the conjugated bond system of the whole molecule modified by the quinoline and imidazole hetero atoms.



III a $R=H, X=\bar{I}$; b $R=C_6H_5, X=C_6H_5\bar{SO_3}$; c $R=C_6H_5CH_2, X=C_6H_5\bar{SO_3}$

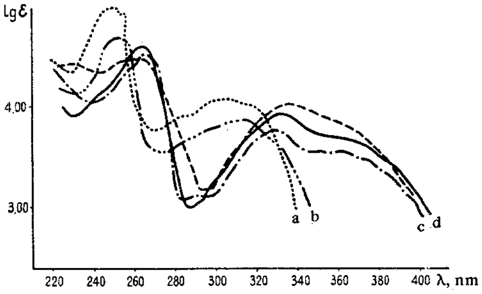


Fig. 2. Absorption spectra of the quaternary salts of imidazoquinoline and the free bases in methanol: (a) imidazoquinoline (Ia); (b) 2,3-dimethylimidazoquinoline (Ib); (c) iodide of 6-N-methylimidzaoquinoline (IIIa); (d) benzenesulfonate of 6-N-methyl-3-benzyl-imidazoquinole (IIIc); (e) benzenesulfonate of 6-N-methyl-3-phenylimidazoquinoline (IIIb).

The shortwave absorption band I ($\lambda_{max}$ = 250 nm) is probably also a π → π* band, since it differs in character from the "imidazole" band of benzimidazole situated in the same region of the spectrum [2]. Since salt formation at the quinoline nitrogen sharply reduces the basicity of the imidazole ring (the pKa of the iodide of 6-N-methylimidazoquinoline is 1.86 according to our results), a hypsochromic shift would be expected for the imidazole band of imidazoquinoline in acid media and in the quaternary salts, as occurs for the 5-nitrobenzimidazoles [12–14], whereas the absorption at 250–255 nm in acid solutions and in the quaternary salts shows a marked bathochromic shift. Intense absorption in this region is characteristic for other tricyclic aromatic hydrocarbons and their aza analogs [3].

Attention is drawn to the large bathochromic shift of the longwave band in the spectra of the quaternary salts compared with the absorption of the free base, but in the imidazo[4, 5-*f*]quinoline series this question has not been considered previously. In a paper by E. Spinner [15] a bathochromic shift in the spectra of pyridine salts is explained on the basis of an assumption of electron migration (for the N → V transition) towards the ring nitrogen atom (or group $N^+H$). We assume it is possible to apply similar ideas to explain the cause of the bathochromic shift in the spectra of imidazoquinoline quaternary salts.

It is known that the proton donor and proton acceptor properties of molecules of quite different compounds can alter under the action of light [16–23]. In luminescence studies in the acridine and quinoline series it was also noted that the luminescence yield and the luminescence and absorption spectra, depended on the pH of the medium, in which the molecule is in the ionized or unionized state [22, 24–27]. Increase of the difference in the pKa constants of the ground and excited states on increasing the dielectric constant of the solvent, which is observed for 5, 6-benzoquinoline, closely similar in structure to I, indicates that a polar environment facilitates the transition of excited molecules into polar, more proton acceptor forms, which also affects the shift of the equilibrium toward the cationic form of the substance [23].

Since an increase in the values of the bathochromic shifts in the spectra of the cations of quinoline, 5, 6-benzoquinoline, and acridine is observed together with an increase in the proton acceptor properties of these compounds in the excited state, then it may be assumed that in a number of imidazo[4, 5-*f*]quinolines there also occurs an increase in basicity in the excited state of the molecule. A reduction of the excitation energy in the cation of imidazoquinoline is explained by the fact that the positively charged nitrogen atom promotes a shift of electron charge in the same direction as does absorption of a photon.

A bathochromic shift of the absorption in the spectra of quaternary salts is a precondition for the development of luminescence in view of the approach of the absorption towards the visible region. In fact the quaternary salts of imidazoquinoline are characterized by intense luminescence (Fig. 3). The luminescence spectra of methanol solutions possess a single high intensity maximum in the 20,150-20,600 $cm^{-1}$ (458–496 nm) region. The luminescence intensity noticeably falls when substitutents are not present at position 3 of the imidazole ring.

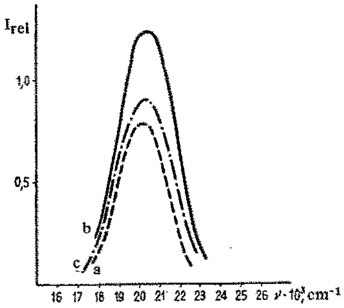


Fig. 3. Luminescence spectra of the quaternary salts of imidazoquinoline in methanol: (a) iodide of 6-N-methylimidazoquinoline (**IIIa**); (b) benzenesulfonate of 6-N-methyl-3-phenylimidazoquinoline (IIIb); (c) benzene sulfonate of 6-N-methyl-3-benzylimidazoquinoline (IIIc).

The development of luminescence in III can be explained in the following way.

The intense longwave absorption of the imidazoquinolines, due to a $\pi \rightarrow \pi^*$ transition, is not accompanied by luminescence in consequence of a transition from the excited $\pi\pi^*$ level to the $n\pi^*$, with a subsequent radiationless transition to the ground state. It is known that on $n \rightarrow \pi^*$ excitation in six-membered nitrogen heteroxycles a change occurs in the type of hybridization of the N-hetero atom. If the orbitals of the nitrogen atom are approximately $Sp^2$ hybridized, then in the excited state an increase in the S-character of the orbital of each of the nitrogen 5-bonds occurs due to a decrease in the S-character of the orbitals of the unshared pair of electrons [28]. The change in character of the nitrogen $\sigma$-bonds is observed, the S-character of the orbital of each of these $\sigma$-bonds increases, the CNC angle increases, and the proportion of S-character of the orbitals of the nitrogen unshared electrons, forming the donor–acceptor bond, is decreased.

This analogy in the processes of n → π* excitation and complex formation of six-membered heterocycles indicates that the principal cause of radiationless loss of energy is a change in the type of hybridization of the N-hetero atom in the nπ* state.

During irradiation of the quaternary salt, absorption of energy is excluded owing to a change in hybridization of the N-hetero atom, since in the quaternary state the latter has approximately the same hybridization as in the excited state. In addition an irreversible loss of energy is excluded on a change of hybridization type of the N-hetero atom, which brings about development of luminescence.

## EXPERIMENTAL

The electronic absorption spectra of methanol solutions at concentrations $1.1-1.8 \cdot 10^{-5}$ M were measured on an SF-4A spectrophotometer.

The luminescence spectra were measured at T 293° K on a ISP-51 spectrograph with a FEP attachment. The relative intensity was measured with respect to a standard luminophor "aquo-blue." The details of the method are described in reference [30].

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