

INFLUENCE OF THE MEDIUM ON THE STRUCTURE  
OF THE BIMOLECULAR COMPLEX ISOQUINOLINE-  
TRIFLUOROACETIC ACID IN THE GROUND AND  
EXCITED ELECTRONIC STATES

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Recently conducted spectroscopic investigations of the structure of complexes in systems with a strong hydrogen bond [1-4] have shown that the formation of ionic forms with a transferred proton is extremely readily induced both by local perturbations during the formation of a hydrogen bond of the molecular complex  $AH \cdots B$  with proton donors and by van der Waals interactions with the molecules of the surroundings. Therefore, in a study of the influence of the electronic structure of proton donor and acceptor molecules on the type of free energy surface of the system and changes in this surface as a result of interaction with the surroundings, it is logical to start with the properties of the bimolecular complex  $AH \cdots B$  in the gas phase or in the most inert solvents (noble gases, alkanes, perfluorocarbons). In the case of complexes of aliphatic amines with carboxylic acids or phenols in solution, an increase in the proton-donor and proton-acceptor capacity of the partners leads to the appearance of a shift of the tautomeric equilibrium molecular complex  $\rightleftharpoons$  ion pair to the right; there is a basis for believing that another, continuous type of evolution is also possible, in that there is no tautomerism, and the only complex passes through a stage of the so-called complex with quasi-symmetrical hydrogen bond  $A \cdots H \cdots B$  [5].

This communication presents the results of investigations undertaken in order to determine the nature of the change in the structure of the bimolecular complex with a strong hydrogen bond in the ground and excited electronic states with a gradual increase in the interaction with the solvent, according to the electronic absorption and emission spectra, as well as according to the IR spectra. The complex of isoquinoline (IQ) - trifluoroacetic acid (TFAA) with a hydrogen  $OH \cdots N$  was studied in solutions in saturated hydrocarbons, aromatic hydrocarbons, butyl chloride, chlorobenzene, o-dichlorobenzene, nitrobenzene, chloroform, and acetonitrile. In the UV spectrum the work was conducted on the band  ${}^1L_b$  of isoquinoline, which has a well-expressed vibrational structure (Specord UV-VIS and Hitachi H-850 instruments). The IR spectra were investigated in the region of  $1600-1800 \text{ cm}^{-1}$ , where the bands  $\nu_{CO}$  of the acid and its anion lie (UR-20 instrument).

Figure 1 shows the UV spectrum of IQ in solution with  $CCl_4$  and its changes when TFAA is added. At low acid concentrations the intensity of the spectrum of free IQ decreases, and the band shifted by 400-450  $\text{cm}^{-1}$  to low frequency appears, the intensity of which increases with the acid concentration. This band belongs to the bimolecular complex IQ-TFAA. By placing a solution of IQ in  $CCl_4$  in the reference channel of

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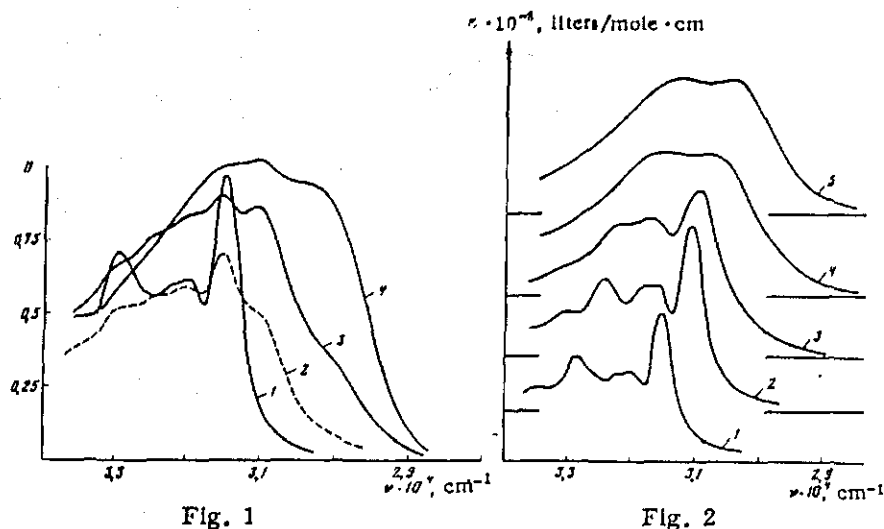


Fig. 1. Spectra of solutions in  $\text{CCl}_4$  containing  $3.2 \cdot 10^{-3}$  M isoquinoline and trifluoroacetic acid at concentrations: 1) 0; 2)  $2.2 \cdot 10^{-3}$  M; 3)  $4.4 \cdot 10^{-3}$  M; 4)  $8.8 \cdot 10^{-3}$  M. Cuvette thickness 0.1 cm.

Fig. 2. Spectra of the bimolecular complex isoquinoline-trifluoroacetic acid in various solvents: 2) in octane; 3) in  $\text{CCl}_4$ , experiment; 4) in toluene; 5) in acetonitrile; 1) isoquinoline in octane. Spectra 2, 4, and 5 were obtained by treating a family of spectra on a computer.

the spectrophotometer and selecting its concentration, it is possible to obtain the spectrum of this complex in pure form (Fig. 2, spectrum 3). The contour of the band of the complex repeats the general outlines of the band of free IQ, but the vibrational structure is appreciably blurred. The value of the low-frequency shift and the preservation of the vibrational structure are typical of IQ molecules forming a strong hydrogen bond with proton donors [6], and, consequently, the complex has the molecular structure  $\text{C}_9\text{H}_7\text{N} \dots \text{HOCCF}_3$ . At acid concentrations comparable with the concentration of IQ, a new broad band appears,  $\gamma \sim 30,000 \text{ cm}^{-1}$ , which in excess acid dominates in the spectrum (Fig. 1, spectra 3 and 4). This band belongs to complexes of more complex composition, containing two or more acid molecules. In the presence of a greater excess of acid, when the remains of the bands of free IQ and the 1:1 complex disappear, the spectrum becomes virtually identical with the spectrum of the isoquinolinium cation (for example, in acid aqueous solution); therefore, it can be concluded that in these complexes IQ is protonated, and they have an ionic structure.

In solution in acetonitrile, in the presence of excess IQ, a band of the cation appears and changes little with increasing acid concentration. In aromatic solvents, however, and in the weakly polar butyl chloride, a band occupying an intermediate position is observed in the spectrum. In the presence of excess IQ in all the solvents, the cation-like band of complexes of complex composition dominates. The isolation of the band of the equimolar complex for solutions in octane, toluene, and acetonitrile was performed by treating a packet of spectra obtained in excess IQ at various acid concentrations on a computer according to the procedure of [8]. These spectra are cited in Fig. 2, spectra 2, 4, and 5. It can be seen that with increasing interaction of the complex with the solvent, there is a broadening of the vibron components of the band and a general long-wave shift of it. These changes in the electronic spectrum of IQ in complex with TFAA are in good agreement with the changes recorded on the bands of the CO group of the acid in the vibrational spectrum with increasing activity of the solvent [6]. As we go from  $\text{CCl}_4$  to aromatic hydrocarbons and their derivatives and then to chloroform and acetonitrile, the band  $\nu_{\text{CO}}$  of the complex is smoothly shifted from  $1765 \text{ cm}^{-1}$ , the position characteristic of complexes of TFAA with a strong hydrogen bond [9], to  $1695 \text{ cm}^{-1}$ , the typical position of  $\nu_{\text{aCO}_2^-}$  of the anion of the acid, which constantly remains a single band in this region of the spectrum.

A study of the fluorescence spectra under the same conditions permit characterization of the structure of the complex in the excited electronic state. The fluorescence of IQ in the gas phase and in inert solvents is very weak, but when a hydrogen bond is formed, the quantum yield is increased by 2-3 orders of magnitude [10]. As is shown by measurements in aqueous solution [11, 12], in the singlet excited state the basicity of IQ is increased by 2-2.5 units of  $\text{pK}_a$  in comparison with the ground state, and in an inert solvent and in the phase in the case of excitation we might expect shortening of the bond and phototransfer of a proton. In [10]

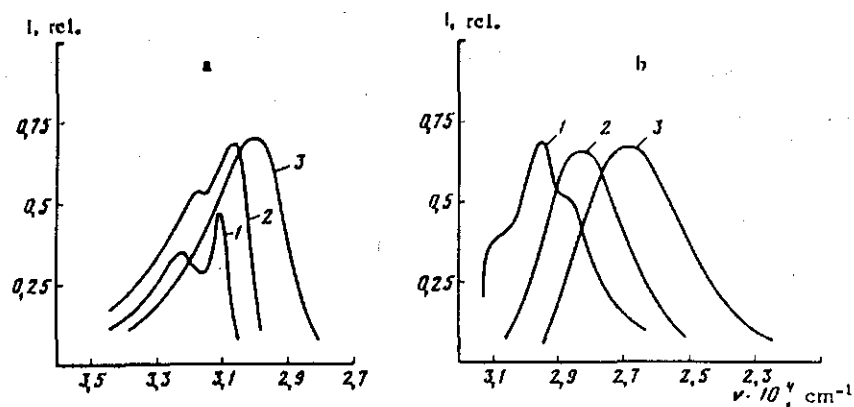


Fig. 3. Spectra of excitation (a) and fluorescence (b) of a complex with 1:1 composition. 1) In heptane; 2) in butyl chloride; 3) in acetonitrile. Concentrations of isoquinoline and trifluoroacetic acid each  $1.1 \cdot 10^{-4}$  M; for a,  $\lambda_{\text{rec}} = 340$  nm (1), 360 nm (2, 3);  $\lambda_{\text{excit}} = 310$  nm for b (1-3).

the fluorescence of complexes of IQ with fluorinated alcohols was investigated in solutions in trimethylpentane at 77°K, and it was found that when the molecular complex is excited, two bands are observed simultaneously in the emission spectrum – the band of the molecular complex with characteristic vibron structure and a broad structureless band of the cation, shifted in the long-wave direction. This is an indication of transfer of a proton along the hydrogen bond  $\text{OH} \dots \text{N}$  in the excited state, which was interpreted by Anton and Moomaw [10] as evidence of the existence of two minima on the potential surface of the complex in the singlet excited state. However, the composition of the complexes was not established, and under the conditions of [10] (an excess of the proton donor, low temperature, hydrocarbon solvent), the number of complexes containing two or more proton donors may be rather large.

In this work we obtained the fluorescence and excitation spectra of bimolecular complexes of isoquinoline with trifluoroacetic acid in heptane, butyl chloride, and acetonitrile at room temperature, as well as in the gas phase at 440°K. Figure 3 presents some of the results obtained. At equimolar concentrations ( $10^{-4}$  M) of IQ and TFAA, the spectrum of excitation of the fluorescence in the most inert of the solvents used – heptane (curve 1a) – is similar to the absorption spectrum of the bimolecular complex in octane (Fig. 2, spectrum 2). The fluorescence spectrum (curve 1b) is not mirror-symmetrical in the excitation spectrum in this case; however, the two spectra have a vibron structure (only a redistribution of it occurs), the position and shape of the fluorescence band do not depend on the wavelength of excitation, and the Stokes shift has a normal value. All this indicates that in solution in heptane in the excited state of the bimolecular complex with hydrogen bond there is no transfer of a proton and formation of an ion pair, but, in all probability, only a certain strengthening of the hydrogen bond occurs. With increasing acid content, the fluorescence band is shifted in the long-wave direction, is broadened, and its structure is blurred. The changes in the spectrum cease when the emission band lies around  $28,000 \text{ cm}^{-1}$  and has a smooth contour. The excitation band also changes similarly; moreover, at such concentrations mirror symmetry of the emission and excitation spectra is already approximately observed. It thus can be concluded that the broad cation-like fluorescence band in the indicated solvent owes its origin to complexes containing two or more acid molecules and already possessing an ionic structure in the ground state.

In the polar structure acetonitrile, the structureless fluorescence band of the complex lies at  $26,500 \text{ cm}^{-1}$ ; its position and shape do not depend on the acid concentration. The excitation spectrum is analogous to the absorption spectrum of the 1:1 complex (Fig. 3a, spectrum 3), so that in acetonitrile the structure of the complex in the ground and excited states is ionic.

In solution in butyl chloride at a low relative content of acid, a band that does not have a vibron structure, which lies approximately midway between the structural band of the molecular complex in solution in heptane and the fluorescence band of the cation, is observed in the fluorescence spectrum (Fig. 3b, spectrum 2). The excitation spectrum also occupies an intermediate position and has a highly blurred vibron structure. The complete disappearance of the vibron structure in the emission spectrum in comparison with the excitation spectrum evidently indicates a strengthening of the bond in the complex and an approach of its structure to ionic in the excited state. With increasing acid content in solution there is a blurring of the structure and a

shift of the band in the excitation spectrum in the long-wave direction. Thus, in solution in butyl chloride the bimolecular complex IQ-TFAA in the excited state has a structure intermediate between molecular and ionic. The addition of a second and subsequent acid molecules to this complex leads to transfer of a proton and the formation of a cation of isoquinoline. It becomes clear that phototransfer of a proton in complexes of IQ with  $\text{CF}_3\text{CH}_2\text{OH}$  and  $(\text{CF}_3)_2\text{CHOH}$ , far weaker proton donors than trifluoroacetic acid, in a frozen hydrocarbon solution, observed in [10], occurred in complexes containing more than one proton donor molecule, possibly under conditions of selected solvation of the complex by alcohol. Earlier a similar hypothesis was advanced in [13], where phototransfer of a proton from alcohols to quinoline at 77°K was recorded in petroleum ether under conditions of a substantial excess of alcohol.

An investigation of the absorption and fluorescence spectra of complexes of IQ with TFAA in the gas phase at 440°K showed that under these conditions in the ground state the complex has a molecular structure, and in the excited state proton transfer also does not occur; the emission spectrum corresponds to a molecular form with a strong hydrogen bond  $\text{OH} \dots \text{N}$ .

Hence, our investigations of the absorption and fluorescence spectra of the IQ-TFAA system showed that with increasing activity of the solvent there is a change in the spectrum of the bimolecular complex from that typical of a molecular complex with a strong hydrogen bond (gas, solutions in alkanes,  $\text{CCl}_4$ ) to that typical of an ion pair (solutions in chloroform and acetonitrile); in aromatic hydrocarbons and butyl chloride the position and shape of bands are intermediate. The spectra of the free molecule, the molecular complex with a hydrogen bond, the ion pair, and the solvated ion pass continuously from one into the other; there is no qualitative boundary between them. Consequently, in this series of solvents the structure of the complex changes smoothly from molecular to ionic with a gradual change in the position of the proton between the oxygen and nitrogen atoms. In not one case were two bands characteristic of two types of complexes, molecular and ionic, observed simultaneously, which would have served as an indication of the existence of tautomeric equilibrium. In the excited electronic state, the change in the structure of the complex in the series of solvents occurs more rapidly - the Stokes shift increases with increasing activity of the solvent. Evidently the increase in the basicity of IQ in the excited state affects the structure of the complex to a greater degree, the greater the interaction of the complex with its surroundings. Phototransfer of a proton in the systems studied was not detected. The addition of a second acid molecule to the bimolecular complex promotes protonation of IQ.

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