

IR ABSORPTION SPECTRA AND ASSOCIATION OF ACRIDINIUM SALTS
WITH HYDROGEN HALIDE MOLECULES

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It was observed that the reaction of acridine with hydrogen halides under heterogeneous conditions proceeds in two steps: An acridinium salt is formed in the first step, while a complex of the salt with hydrogen halide molecules is formed in the second step. The formation of a complex leads to substantial changes in the region of the stretching vibrations of NH^+ bonds, and this makes it possible to propose the direct participation of these bonds in complexing. The band of the stretching vibrations of NH^+ bonds of the acridinium ion has a complex structure that changes markedly as a function of the sort of halogen ion and replacement of hydrogen by deuterium and in the case of complexing with the hydrogen halide. It is proposed that the structure of this band is due to Fermi resonance.

The reaction of acridine (A) with hydrogen halides (HHal) leads to the formation of ionic salts with the $\text{AH}^+\dots\text{Hal}^-$ structure, the vibrational spectra of which have been previously investigated in detail [1, 2]. We have investigated the IR absorption spectra of acridine directly during its heterogeneous reaction with gaseous HHal and observed that this reaction has two steps with distinct spectral differences.

The acridine for the spectral measurements was prepared in the form of layers on KBr plates by sublimation in vacuo. Gaseous HCl, HBr, DCl, and DBr was introduced into a vacuum cuvette with a layer up to a pressure of 500 torr, and the spectral measurements of the layers were made in the same cuvette. During the reaction HHal (or DHal) molecules penetrate the entire depth of the acridine layer (with a thickness of ~ 0.005 mm), as evidenced by the complete disappearance of its initial absorption bands. We were able to note that the intensities of the new bands that appeared in place of the decreasing bands of acridine do not increase synchronously; this constituted evidence for the nonhomogeneous composition of the product of the reaction of acridine with HHal. After a few hours, the spectral changes ceased — the final product had formed. We found that it was possible to obtain an intermediate that was virtually free of the final product by pumping out the HHal from the cuvette (in the case of HBr or DBr it was necessary to heat the layer to $40\text{--}50^\circ\text{C}$). The IR spectra of the final product and the intermediate obtained by pumping out the gas from the cuvette are presented in Figs. 1 and 2. The intermediate can be identified as the acridinium halide AH^+Hal^- , since its spectrum coincides in detail with the previously measured spectra of these salts [1, 2]. Thus, if the intermediate is the result of the addition of one HHal molecule to the acridine molecule, the final product that is formed in the case of excess HHal and undergoes decomposition to give the intermediate when this excess is removed is evidently the result of further reaction of the acridinium salt formed in the first step with HHal. A comparison of the IR spectra of the final product with the spectra of the acridinium salt makes it possible to conclude that this product is a complex of this salt with HHal molecules. In fact, in the first step during conversion of the acridine molecule to the acridinium ion the vibrational spectrum undergoes radical changes that are explained by a change in the composition and electronic structure of the molecule. In the second step of the transformations the set of absorption bands in the IR spectrum is virtually completely retained, and one observes only a small shift in them and a change in the intensities (Fig. 2) — the typical pattern for spectral changes in the case of the formation of molecular associates and complexes. The greatest changes during the formation of complexes of AH^+Hal^- with HHal and of AD^+Al^- with DHal occur in the region of the stretching vibrations of $\text{NH}^+\dots\text{Hal}^-$ and $\text{ND}^+\dots\text{Hal}^-$ bonds (Fig. 1), and this makes it possible to conclude that these bonds participate directly in complexing with HHal (DHal) molecules.

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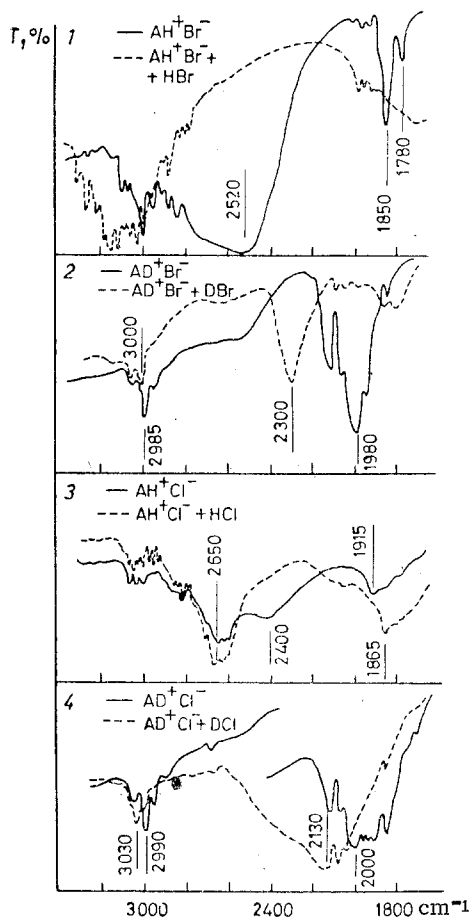


Fig. 1

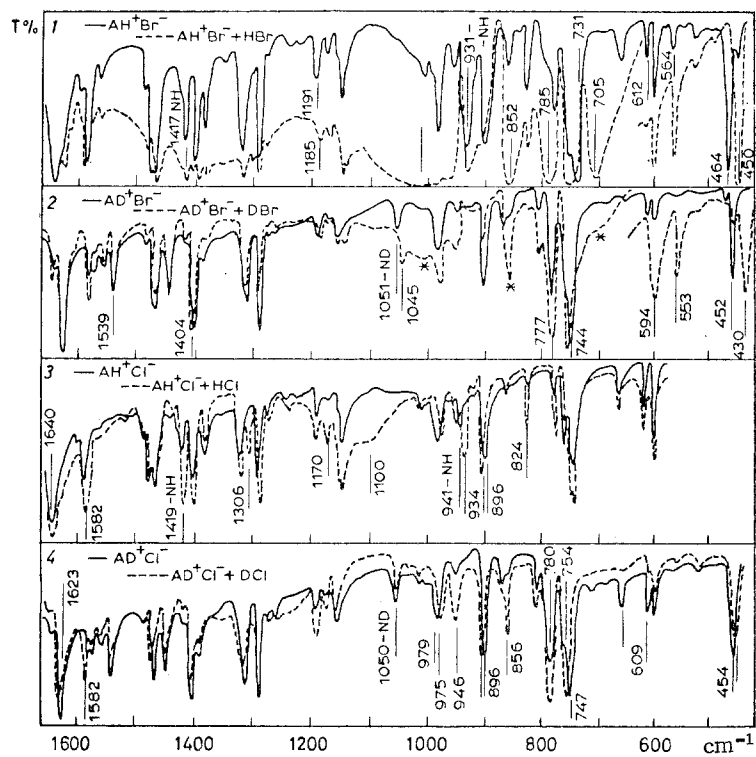


Fig. 2

Fig. 1. IR absorption spectra of acridine salts with various compositions in the region of the stretching vibrations of NH and ND bonds: 1) hydrobromide; 2) deuterobromide; 3) hydrochloride; 4) deuteriochloride. The continuous curves were obtained in vacuo, while the dash lines were obtained in the presence of HBr, DBr, HCl, and DCl, respectively, at 500 torr.

Fig. 2. IR absorption spectra at 400-1650 cm^{-1} . The designations are the same as in Fig. 1, and the asterisks pertain to the absorption bands of admixed AH^+Br^- in the spectrum of AD^+Br^- .

The absorption bands of $\text{NH}^+\dots\text{Hal}^-$ and $\text{ND}^+\dots\text{Hal}^-$ bonds in the spectra of acridinium salts and their complexes with HHal (DHal) have complex structures. A similar complex structure of the $\text{NH}^+\dots\text{Hal}^-$ band in the IR spectra of pyridinium halides is explained by Fermi resonance between the NH^+ stretching vibrations and the overtones and composite frequencies of the skeleton of the pyridinium ion [3]. This explanation is also applicable to the structure of the bands of the NH^+ bonds of acridinium salts; this is confirmed by the pronounced dependence of this structure on the position of the band in the spectrum, i.e., on precisely with which overtones and composite frequencies the stretching vibration of the NH^+ bond engages in resonance. The position itself of the band of the NH^+ bond changes substantially as a function of the sort of halogen ion (Cl^- , Br^-) with which NH^+ forms a hydrogen bond and changes in the case of isotopic substitution and in the case of the formation of complexes with HHal (Fig. 1).

The formation of complexes of acridinium salts with HBr (DBr) leads to more profound spectral changes than in the case of complexing with HCl (DCl). Broad intense bands at ~ 1400 and 1000 cm^{-1} and a number of other bands appear in the spectrum of the complex of AH^+Br^- with HBr (Fig. 2). The spectrum of the complex of AH^+Cl^- with HCl contains only a relatively weak broad band at 1100 cm^{-1} . The origin of these bands is unclear. The complex of AD^+Br^- with DBr is characterized by intense bands at 553 and 594 cm^{-1} ; the complex of AD^+Cl^- with DCl does not have analogs of these bands. The intense band at 452 cm^{-1} of the AD^+Br^- salt

in the presence of DBr is shifted to 430 cm^{-1} ; the corresponding shift of this band is considerably smaller in the case of AD^+Cl^- (Fig. 2). The electronic structure of the acridinium ion evidently experiences more profound perturbations in the case of complexing with HBr than in the case of complexing with HCl.

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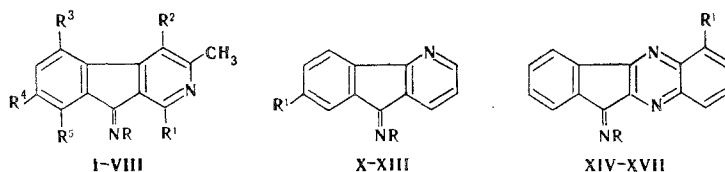
CYCLIZATION PROCESSES IN THE FRAGMENTATION OF THE MOLECULAR IONS OF N-(AZA-9-FLUORENYLIDENE)AMINES

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The dissociative ionization of 17 Schiff bases obtained from 2(4)-azafluorenones and linear benzo-1,4-diazafluorenone was investigated. The intensities of the $[\text{M} - \text{H}]^+$ and $[\text{M} - \text{CH}_3]^+$ ion peaks depend on the structures of the ketone and imine parts of the molecules and are determined by the possibility of the occurrence of cyclization processes with the participation of their structural elements. The fragmentation of the investigated azomethines is also accompanied by the elimination of an NR particle and a hydrocarbon R radical by the molecular ions. This process takes place most easily when a cyclohexyl substituent is present in the imine fragment. In contrast to previously investigated azomethines, the loss of an HCN molecule by the M^+ ion occurs without participation of the exocyclic nitrogen atom.

Research on the dissociative ionization of a new group of azomethines of the heterocyclic type, viz., N-(aza-9-fluorenylidene)amines, was begun in [1]. It was proposed that the anomalously high intensities of the peaks of some fragments in their mass spectra can be explained by cyclization processes during elimination of H and CH_3 radicals by the molecular ions. To ascertain the dependence of the direction of cyclization on the position and number of ring nitrogen atoms and on the position of the substituents in the azafluorenylidene and aryl(cyclohexyl)imine fragments of azomethines of this type we investigated the dissociative ionization of methyl-substituted and unsubstituted azomethines, viz., derivatives of 2-azafluorenes (I-VIII), N-(1,4,7-trimethyl-2-aza-9-fluorenylidene)mesidine (IX), 4-azafluorenones (X-XIII), and 5,11-diazabenzob[b]fluorenes (XIV-XVII) (Table 1).



I R = C₆H₅, R¹-R⁵ = H; II R = C₆H₅, R⁴ = CH₃, R¹-R³, R⁵ = H; III R = *o*-CH₃C₆H₄, R¹-R⁵ = H; IV R = *m*-CH₃C₆H₄, R¹-R⁵ = H; V R = *p*-CH₃C₆H₄, R¹-R⁵ = H; VI R = *p*-CH₃C₆H₄, R¹ = CH₃, R²-R⁵ = H; VII R = *p*-CH₃C₆H₄, R³, R⁵ = CH₃, R², R⁴ = H; VIII R = 2-fluorenyl, R¹-R⁵ = H; X R = 2-fluorenyl, R¹ = H; XI R = 2-naphthyl, R¹ = H; XII 2-pyridyl, R¹ = H; XIII R = C₆H₄, R¹ = CH₃; XIV R = C₆H₅, R¹ = H; XV R = *m*-CH₃C₆H₄, R¹ = H; XVI R = C₆H₄, R¹ = H; XVII R = C₄H₉, R¹ = H

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