UDC 535.34 + 547.835

ABSORPTION SPECTRA AND STRUCTURE OF ACRID-9-ONE

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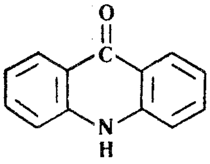
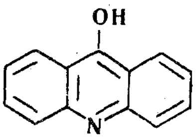
The UV spectra of acrid-9-one, 10-methyl-acrid-9-one, and 9-methoxyacridine dissolved in acids and in sodium ethoxide solution are investigated. Acrid-9-one and 10-methylacrid-9-one add a proton from the acid to their oxygens, giving the corresponding 9-hydroxyacridinium cation. In sodium ethoxide solution, acrid-9-one gives an acridolate, a derivative of the tautomeric hydroxy form.

The basic properties of acrid-9-one (I) are markedly depressed, and only heating with concentrated or 25% hydrochloric acid gave a salt, whose constitution has not been determined [1]. In ethanolic alkali, I is assumed [2] to undergo tautomeric change from the oxo form to the hydroxy one (acridol, II), followed by formation of acridolate III.


I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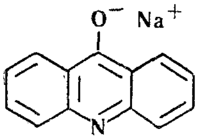
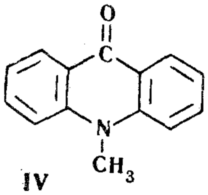

III

To determine the structure of salts of I with acids, and to check the correctness of the assumption regarding its tautomerism, the UV spectra of I in acids (ethanolic hydrogen chloride, conc. H_2SO_4, 72% $HClO_4$) and sodium ethoxide solution were first studied.

For comparison, the spectra of 10-methylacrid-9-one (IV) and 9-methoxyacridine (V), regarded, respectively, as typical oxo and hydroxy forms, were observed.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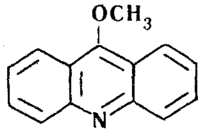
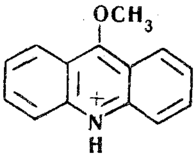
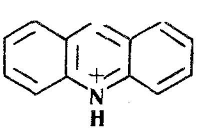
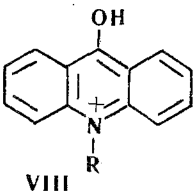

V

The resemblance of the acridine absorption curves in acids to those given by V (Fig. 1-3) indicate formation of a 9-methoxyacridinium cation VI from the latter, like the acridine cation VII [8].

The absorption curves of I, IV, V, and acridine in 72% $HClO_4$ are very similar (Fig. 3) indicating that I and IV give appropriate 9-hydroxyacridine cation VIII, analogous to the cations VI and VII.


VI


VII


VIII

R=H, CH_3

Thus, with I and IV, salt formation resembles that with amides of carboxylic acids [9], which I and IV closely resemble in properties [10].

Apparently in 5 M ethanolic hydrogen chloride of H_2SO_4, salt formation from I and IV does not go to completion, so the absorption spectra of solutions in those acids (Figs. 1, 2), but not in 72% $HClO_4$ (Fig. 3) retain absorption bands (bends) of the neutral molecules in the 295 mμ region.

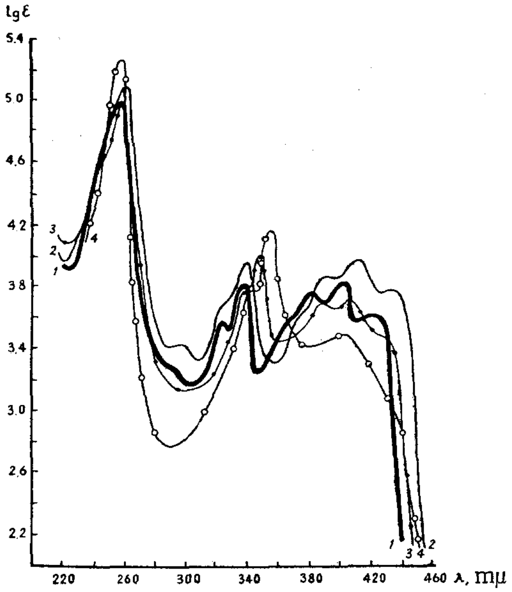


Fig. 1. Absorption spectra in 5 M ethanolic hydrogen chloride: 1) acrid-9-one 2) 10-methylacrid-9-one 3) 9-methoxyacridine 4) acridine.

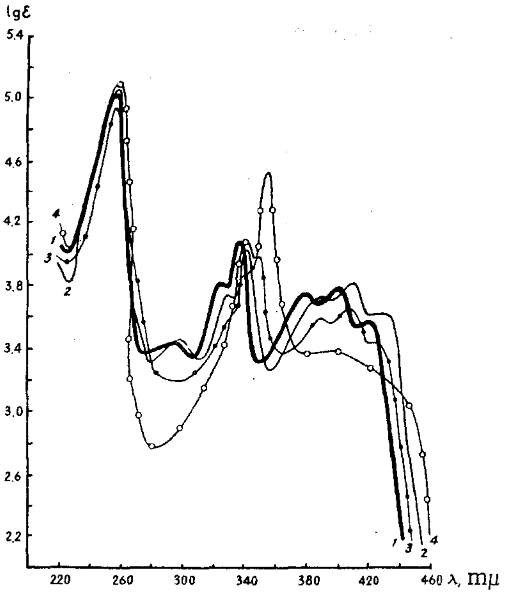


Fig. 2. Absorption spectra in conc. H_2SO_4: 1) acrid-9-one 2) 10-methylacrid-9-one 3) 9-methoxyacridine 4) acridine [8].

The absorption spectrum of I in 1 M sodium ethoxide very closely resembles the curve obtained for 9-aminoacridine in methanol [11] (Fig. 4). Apparently, in the presence of sodium ethoxide, compound I gives the corresponding phenolate ion (acridolate) III, it being known that, optically, the effect of the amino group in aromatic compounds is like the effect of the phenolate ion [12].

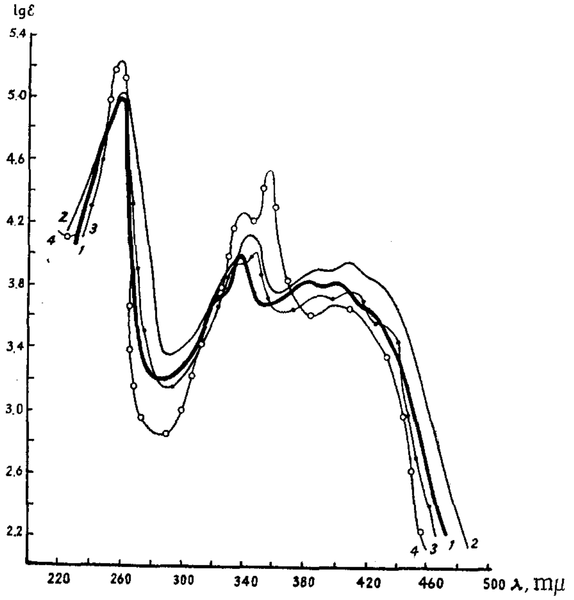


Fig. 3. Absorption spectra in 72% $HClO_4$: 1) acrid-9-one 2) 10-methylacrid-9-one 3) 9-methoxyacridine 4) acridine [8].

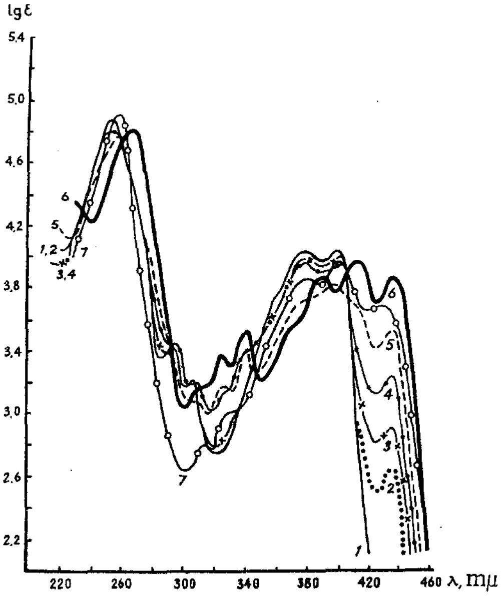


Fig. 4. Absorption spectra: 1) acrid-9-one in ethanol 2) same in NaOEt solution (molar ratio 1:1) 3) same (molar ratio 1:10) 4) same (molar ratio 1:100) 6) same in 1 M NaOEt solution 7) 9-aminoacridine in MeOH [11].

In sodium ethoxide solution conversion of I to III takes place gradually, in proportion as the ethoxide concentration rises (Fig. 4). This supports N. S. Drozdov's assumption [2] that in alcoholic alkalies I can undergo tautomeric change to II with subsequent formation of III.

Such a change is impossible for compound IV, so the absorption spectrum in sodium ethoxide solutions is the same as that in ethanol (for conciseness the plots are not given).

Experimental

The measurements for the absorption curves in the figures were made with a SF-4 spectrophotometer.

Compounds I [3] and V [4] were obtained and purified as described in the literature. 10-Me-acrid-9-one (IV) was synthesized as described in [5], and after being recrystallized twice its mp agreed with that given in the literature, 199° C [5]. Other papers have given mp 203° C [6] and 203.5° C [7]. Chromatographing the material on Al_2O_3 (solvent $CHCl_3$) gave IV mp 203.5° C, and an impurity, which was I, mp 354° C.

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