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Structural formulas of compounds AK_1 (I), AK_2 (II), AK_3 (III), AK_4 (IV), and AK_5 (V).

Figure 1: Structural formulas of compounds AK_1 (I), AK_2 (II), AK_3 (III), AK_4 (IV), and AK_5 (V).

Abstract

Full Text

CHEMISTRY

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ABSORPTION SPECTRA OF SOLUTIONS OF DIMETHYLAMINOSTYRYL DERIVATIVES OF ACRIDINE IN NITROBENZENE

(Presented by Academician B. A. Kazanskii, January 21, 1960)

Dimethylamino derivatives of quinoline and acridine (electron-donor components of the type AK*) can form colored molecular complexes of the type $[BK \cap AK]$ with quinolinium and acridinium electrophilic components of the type BK^* ($^{1-4}$). Taking into account the ability of aromatic amines to give molecular complexes with nitrobenzene (component BK) ($^{5-7}$), it could be assumed that analogous colored complexes with nitrobenzene should also be formed by dimethylaminostyryl derivatives of acridine and quinoline. To test this assumption, the spectra were studied of solutions of molecular complexes formed upon dissolution in nitrobenzene of a series of components AK_1—AK_5 (I-V)—anhydro bases of acridine derivatives (Table 1**).

To shift the equilibrium $AK + BK \rightleftharpoons [AK \cap BK]$ toward the complex, we used nitrobenzene (BK) as the solvent in large excess. In all cases, the interaction of the above AK-components with $C_6H_5NO_2$ (BK) led to a bathochromic shift of the anhydro-base curve, which we explain by the formation of a complex in solution.

An observation that was very important from our point of view was made: in the formation of the complex of $C_6H_5NO_2$ with 9-(p-dimethylaminostyryl)-acridine,

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* AK and BK are complex chromophoric components constructed from an electron-donor chromophoric component A (for example, NMe_2) or, respectively, an electrophilic chromophoric component B (for example, $C = \overset{+}{N}, NO_2$) with a π-electron conjugated system K.

Figure 1

Figure 2: Figure 1

Figure 2

Figure 3: Figure 2

** $\lambda_{\max}$ and ε, determined approximately from the bend of the curve, are denoted by the sign $\sim$. The values of ε for solutions of complexes are only conditional quantities (^{5}), which may be used for comparing the degree of complex formation.

(AK_1, I) (2, Fig. 1) or with 9-(n-dimethylaminostyryl)-3,4-benzacridone (AK_4, IV) (11, Fig. 2), a new band appeared, whose shape and region of maximum–

Fig. 1. Absorption spectra of molecular complexes of AK_1, AK_2, and AK_3 with nitrobenzene. The numbers of the curves correspond to the numbers of the solutions in Table 1. 3—$\lambda_{\max}$ 616 m ($\varepsilon = 29810$) (2)

Fig. 2. Absorption spectra of molecular complexes of AK_4 and AK_5 with nitrobenzene. The numbers of the curves correspond to the numbers of the solutions in Table 1.

–was strikingly close to the long-wavelength band and $\lambda_{\max}$ of the corresponding dyes (3, Fig. 1 and 12, Fig. 2), formed by the addition of HCl and RX to the anhydrobase and of the corresponding complex of

Table 1

Comparison of the absorption spectra of components of the AK type with the spectra of molecular complexes of the $[AK \sim BK]$ type and the corresponding dyes B—K—A

No.	Designation and ratio of components	Solvent	C, mol/l	$\lambda_{\max}$, absorption bands of dye and complex	$\varepsilon_{\max}$, absorption bands of dye and complex	$\lambda_{\max}$, absorption bands of components	$\varepsilon_{\max}$, absorption bands of components
1	AK_1 (I)	C_2H_5OH	10^{-3}	–	–	434	12500
2	$1AK_1 : \infty BK$	$C_6H_5NO_2$	10^{-3}	621	39	443	16400
3	A—K_1—B 1 2	C_2H_5OH	10^{-3}	614	29810	356	20940

No.	Designation and ratio of components	Solvent	C, mol/l	$\lambda_{\max}$, absorption bands of dye and complex	$\varepsilon_{\max}$, absorption bands of dye and complex	$\lambda_{\max}$, absorption bands of components	$\varepsilon_{\max}$, absorption bands of components
4	AK_2 (II)	C_2H_5OH	10^{-3}	–	–	389	12080
5	$1AK_2 : \infty BK$	$C_6H_5NO_2$	10^{-3}	~ 585	~ 10	425	10200
6	$A—K_2—B$ 2	DCE³	10^{-3}	561	5850	415	12370
7	AK_3 (III)	$CHCl_3$	10^{-2}	–	–	430	4140
8	$1AK_3 : \infty BK$	$C_6H_5NO_2$	10^{-3}	~ 585	~ 400	450	7550
9	$A—K_3—B$	AK_3 4	10^{-3}	625	2715	440	8535
10	AK_4 (IV)	$CHCl_3$	10^{-2}	–	–	416	17720
11	$1AK_4 : \infty BK$	$C_6H_5NO_2$	10^{-3}	648	20	430	19300
12	$A—K_4—B$ 4	DCE³	10^{-3}	599	9910	388	17290
13	AK_5 (V)	DCE³	10^{-3}	–	–	401	25360
14	$1AK_5 : \infty BK$	$C_6H_5NO_2$	10^{-3}	~ 590	~ 7	420	17750
15	$A—K_5—B$	AK_5 (V) ⁶	10^{-3}	600	38	403	16200

[1] AK_1 (I) in 0.01 N HCl in EtOH. [2] Ethyl perchlorate AK_2. [3] 1,2-dichloroethane. [4] AK_3 (III) in 0.001 N HCl in $CHCl_3$. [5] Ethyl perchlorate AK_4. [6] AK_5 (V) in 0.01 N HCl in $CHCl_3$.

of the above-mentioned AK with the acridine component BK (²-⁴). This indicates that $C_6H_5NO_2$ appears in the complex as if in the form of an aprotonic acid. An explanation of the above-mentioned similarity of the curves and absorption regions of the complexes with $C_6H_5NO_2$, with the acridine BK-component, and with the corresponding dye could be sought in ionization during formation of the complex (⁶). Another explanation is more probable: charge transfer upon excitation by light occurs not between the components forming the complex (⁷), but within one of the components, in the present case AK, which acquires a partial charge (δ^+) (⁸) as a result of complex conjugation ("complex mesomerism"

Fig. 3

Figure 4: Fig. 3

) ([9],[10])*. Thus the systems AK_1 and AK_4 play, in the mentioned complexes, the role of the principal chromophoric component.

Fig. 3

Comparison of the spectra of solutions 1 and 3 with the spectra of solutions 4 and 6 (Table 1, Fig. 1) shows that annelation of the benzene ring in position 1,2 in 9-(*p*-dimethylaminostyryl)-1,2-benzacridine (AK_2, II) leads to a sharp hypsochromic shift of the curve compared with (AK_1, I), both for the anhydro base (4) and for the dye salt (6) (*N*-ethyl perchlorate AK_2 (II)). The cause of this could be (as a result of annelation) scattering of the conjugation effect (meso-effect) ([13]) in the ground state and upon transition to the excited state. However, the main cause should be considered the removal from coplanarity of the dimethylaminostyryl chromophoric group and the shaded parts of the molecule in Fig. 3, as may be assumed by analogy with benzo[c]phenanthrene (X-ray structural data ([14])). These circumstances were reflected to an even sharper degree in the spectrum of the solution ($AK_2 + C_6H_5NO_2$): in the visible region of the spectrum there is only a small shift of the curve toward longer wavelengths (at $\lg \varepsilon = 1$, $\Delta\lambda = +30$ mμ) and a characteristic band in the region 600–700 mμ

* The concept of "complex mesomerism" ("complex resonance") was advanced considerably earlier by Brackman ([11]) and Mulliken ([12]).

which occurred in cases 2 and 11) is absent; there is only a weakly expressed bend (5, Fig. 1).

Replacement in (I) of the CH=CH group by the CH=N group in *p*-diethylaminoanilacridine-9-aldehyde (AK_3, III), with simultaneous replacement of the NMe$_2$ group by NEt$_2$,* caused, in the anhydro base (III), a bathochromic shift of the long-wavelength branch of the curve (at $\lg \varepsilon = 1$, $\Delta\lambda = +42$ mμ).

For the solution of (III) in nitrobenzene, only a bathochromic shift of the curve with a bend at ~ 590 mμ was observed (8, Fig. 1). The shift was manifested to an even stronger degree in the dye (hydrochloride AK_3, Fig. 1, 9). Analogous phenomena were first observed by A. I. Kiprianov ([16]). A similar observation was also made later ([17]). Unfortunately, the isomer with the inverted position of the azomethine group N = CH is inaccessible, owing to the tautomeric structure of 9-aminoacridine.

In the case of 9-(*p*-dimethylaminostyryl)-3,4,5,6-dibenzacridine AK_5 (V), the presence of two condensed benzene nuclei leads to still greater dissipation of the conjugation effect. The spectra of the anhydro base and of the solution (V) in nitrobenzene are shifted strongly hypsochromically. For the molecular complex

$[AK_5 \sim C_6H_5NO_2]$, $\lambda_{\max} \sim 590$ mμ is observed, almost coinciding in bend with $\lambda_{\max}$ 600 mμ for the hydrochloride of AK_5 (Fig. 2, 14, 15).

The very small values of ε (2, 5, 8, 11, 14, Table 1), of the order of 20-40, are considerably lower than the values of ε that we observed for solutions of complexes of α- and, respectively, β-naphthylamines with nitrobenzene (ε = 1620 and 208, respectively ([18])). We explain this by the presence in the anhydro bases (I–V) of the grouping

$$> \overset{\delta+}{\mathrm{C}} = \overset{\delta-}{\mathrm{N}}-,$$

which leads to an increase in conjugation of NMe_2 (in the dimethylaminostyryl grouping) and, as a result, to a decrease in basicity and in the capacity of the AK system to interact with $C_6H_5NO_2$. In the molecules of α- and β-naphthylamines, the grouping $> C = N-$ is absent. Investigation of the question of the possibility of replacing, in "donor-acceptor" complexes, the acridine or quinoline component by nitrobenzene gave new proof that the appearance of color upon formation of the complex is not connected with alcoholysis of the onium component and the formation of halochromic adducts with the AK component (for other evidence, see ([2,3,4,7])).

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* We were forced to do this in order to increase solubility (15).