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Abstract

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Absorption Spectra of Molecular Complexes of 9-(n-Dimethylaminostyryl)acridine with 10-Ethyl-9(β-Carbomethoxyethyl)acridinium Iodide

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It is generally accepted that, for a bathochromic shift of color, there must be a continuous conjugated system K between the interacting chromophoric components—electron-accepting (B) and electron-donating (A) ones (endomolecular coupling of chromophores, "optical conjugation" ([1])). B and A together with K form a generalized π-electron system—a cochromoform ([1]) (scheme 1) ([3]).

Deep coloration may also be possessed by compounds with isolated chromophoric systems AK and BK, separated by a group that interrupts conjugation ([2], [3]), provided there are strong electron-donating AK and strong electron-accepting (BK) systems (schemes 2a or 2b). In this case the deep coloration is associated with exomolecular conjugation, i.e., direct interaction of the AK and BK systems by an external field between molecules*, arising in the solid state in a crystal, in a melt, and also in concentrated solutions at concentrations of the order of 10^{-2} and higher. Hence a third direction arose in our investigations: the study of spectra of molecular complexes of donor-acceptor type 3, i.e., constructed from strong electron-donating (AK) and strong electron-accepting (BK) chromophoric systems ([3], [4]). Molecular complexes with a BK component containing a strong electron-accepting immonium group $C = N^+$ are being systematically studied, using pyridinium and quinolinium salts ([5], [6]) and acridinium salts ([7]).

Scheme representations:

1. A—K—B

2a. B—K—Q—K—A

2b. B—K—Q—A—K

3. $|AK + BK|$ or $|AK \sim BK|^*$

* The arc $\sim$, the symbol of conjugation, denotes a partial π-bond, in this case an exo-ρ-bond ([3]).

We used as the AK component 9-(n-dimethylaminostyryl)acridine (I), containing A = $N(CH_3)_2$, and as the electron-accepting BK component the

Fig. 1

Figure 1: Fig. 1

ethyl iodide of the methyl ester of 9-acridinepropionic acid (10-ethyl-9-[β-carbomethoxyethyl]acridinium iodide) (II). Replacement of the CH_3 group in 9-methylacridine ethyl iodide (^{7}) by the $CH_2CH_2COOCH_3$ group was intended to increase solubility.

I (AK) $\lambda_{\max} = 434$ mμ^*

II (BK) $\lambda_{\max} = 406$ mμ^*

III |AK ~ BK| for a solution 3AK : 1BK
$\lambda_{\max} = 616$ mμ

IV B—K—A $\lambda_{\max} = 616$ mμ

* Me denotes CH_3, Et denotes C_2H_5.

* In special cases, exo-interaction by an external field in compounds of type 2 may also occur within a molecule as a result of bending of the chain (^{3}, ^{4}).

At a molar ratio of the components 1AK : 1VK and $c = 10^{-5}$, the color of the solution is pale yellow. The absorption curve indicates complete dissociation of the complex (Nos. 11, 14, Fig. 1, Table 1). However, already at $c = 2 \cdot 10^{-5}$ (No. 10), formation of the complex is detected in the appearance of a slight shoulder near 570 mμ ($\varepsilon_{\max} \sim 75$).

Fig. 1. Absorption spectra of molecular complexes of 9-(p-dimethylaminostyryl)acridine and 10-ethyl-9-(β-carbomethoxyethyl)acridinium iodide. The curve numbers correspond to the solution numbers in Table 1. Construction of curves Nos. 8, 10, 12, 13, 14 was begun at 380 mμ because of their overlap with other curves.

At $c = 5 \cdot 10^{-5}$ the band is already well formed (No. 9, Table 1, Fig. 1, Nos. 9, 10) (the color of the solution is yellow-green). With a further increase in concentration to 10^{-4} and 10^{-3}, the color deepens to dark blue and $\varepsilon_{\max}$ increases to 18,930 (Nos. 8, 7, Table 1, Fig. 1). This indicates a shift of the equilibrium

$$\text{AK} + \text{VK} \rightleftarrows [\text{AK} \sim \text{VK}]$$

toward the complex; relative to $\lambda_{\max}$ calculated for the sum of the components (No. 14, Table 1, Fig. 1), $\Delta\lambda = +161$ mμ. The equilibrium can be shifted toward the complex by applying an excess of one of the components, 3AK : 1VK or 1AK : 3VK* (Nos. 12, 13); $\lambda_{\max}$ up to 616 mμ ($\Delta\lambda = +12$ mμ, $\varepsilon_{\max} = 30340$ (No. 13). Of special theoretical interest is comparison of the absorption spectra of molecular complexes of acridine compounds of type 3 (III) with the spectra of the corresponding compounds with conjugated structure of type 1 (IV). For solutions of the complex [AK + VK] (III) (Table 1, Nos. 12, 13;

Fig. 1), $\lambda_{\max}$ 616 mμ coincides with $\lambda_{\max}$ of the dye with the conjugated system V – K – A (IV), containing the similarly constructed systems AK and VK (I, II) in positions superimposed on one another. The similarity is so striking that the question arises whether $\lambda_{\max}$ 616 mμ for a solution of the complex [AK + VK] is not a consequence of alcoholysis of the acridinium salt, with subsequent addition of HI to AK (I) (see No. 19, Table 1). However, the following facts speak against the hydrolysis hypothesis:

1. The direct dependence of the absorption coefficient in the region 604–616 mμ on concentration, and the disappearance of absorption in this region upon dilution

* A differential spectroscopic method was used[4,6]. With an excess of one of the components (n moles : 1), for the comparison spectrum a solution was used that contained $n-1$ moles in 1 liter of the component taken in excess.

Table 1*

Comparison of the absorption spectra of AK [I] and BK [II] with the spectra of the molecular complex $[AK \cap BK]$ (III) and the dye B–K–A (IV)

Solution No.	Structure	Ratio, mol.	c, mmol/l	$\lambda_{\max}$, mμ	$\varepsilon_{\max}$	ε, % to No. 12	$\lambda_{\max}$, mμ	$\varepsilon_{\max}$
1	10-ethyl-9-(β-carbomethoxyethyl)-acridinium iodide	(1) BK	10^{-3}				406386	3 9305 750
2	Same	(1) BK	10^{-4}				384	7 760
3	» »	(1) BK	10^{-5}				384	9 800
4	9-(n-$Me_2 \cdot N$-styryl)-acridine	(II) AK	10^{-3}				434	12 500
5	Same	(II) AK	10^{-4}				435	10 890
6	» »	(II) AK	10^{-5}				436	9 960
7	[AK + BK]	1 AK : 1 BK	10^{-3}	605	18 930	62.4	430	6 240

Solution No.	Structure	Ratio, mol.	c, mmol/l	λ_{max}, mµ	ε_{max}	ε, % to No. 12	λ_{max}, mµ	ε_{max}
8	Same	1 AK : 1 BK	10^{-4}	604	10 350	34.1	442	10 700
9	» »	1 AK : 1 BK	$5 \cdot 10^{-5}$	604	4 660	15.3	436	17 120
10	» »	1 AK : 1 BK	$2 \cdot 10^{-5}$	570	75	0.2	440387	10 58012 750
11	» »	1 AK : 1 BK	10^{-5}	none	0	0	440384	8 91012 260
12	[AK + BK] in excess AK	3AK : 1BK	10^{-3}	616	30 340	100	438	22 380
13	[AK + BK] in excess BK	1 AK : 3BK	10^{-3}	616	25 970	85.6	412	5 750
14	[AK + BK] calculated	1 AK : 1 BK	10^{-3}				434	14 390
15	Same	1 AK : 1 BK	10^{-4}				435	11 250
16	» »	1 AK : 1 BK	10^{-5}				436	10 000

Solution No.	Structure	Ratio, mol.	c, mmol/l	$\lambda_{\max}$, mμ	$\varepsilon_{\max}$	ε, % to No. 12	$\lambda_{\max}$, mμ	$\varepsilon_{\max}$
17	[AK + BK] in chloroform	1 AK : 1 BK	10^{-3}	605	27 770	91.5	384	13 200
18	10-ethyl-9-(n-Me_2N-styryl)-acridinium iodide	(IV)	10^{-3}	616		•	442	
19	9-(n-Me_2N-styryl)-acridine in 0.01 N HCl	$[AK \cdot H]^+Cl$	10^{-3}	614	29 810	98.2	358	20 940

* Nos. 1—16, 18, 19 in 96% ethanol; absorption spectra Nos. 4, 5, 14, 15, 18, 19 are given according to the data of V. A. Izmail' skii and S. V. Dmitrienko (7).

to $c = 10^{-5}$. Table 1 gives the values of $\varepsilon_{\max}$ as percentages relative to solution No. 12, taken as 100 (Nos. 7—13).

2. Complete disappearance of the color upon addition to the alcoholic solution of 2—3 drops of water (destruction of the complex).

3. In chloroform*, where alcoholysis is impossible, more complete complex formation is observed than in alcohol: the solution at $c = 10^{-3}$ has a deep blue color, and the band at 605 mμ has a considerably greater intensity than in alcohol under the same conditions (Nos. 17 and 7). That here the matter is not hydrolysis and formation of a salt with AK (I) is also shown by a certain difference from Nos. 12, 13, and 7 in the course of curve No. 17 in the 700—800 mμ region.

4. The presence of the equilibrium $[AK + BK] \rightleftarrows [AK \cap BK]$ is indicated by the intersection at one point of the spectral curves when the concentration

is decreased from $c = 5 \cdot 10^{-5}$ to 10^{-3} for solutions in alcohol (Nos. 7–10), and in chloroform (No. 17). As $\varepsilon_{\max}$ increases in the 495–650 mμ region, $\varepsilon_{\max}$ in the 400–495 mμ region decreases.

5. The formation of colored complexes from quinolinium salts was also observed with diphenylamine (^{3},^{5} ,^{9}), and with n-aminoacetanilide (^{5}).

The possibility of re-esterification must also be rejected, taking into account that: 1) solutions of the components AK and BK were prepared separately and after their mixing–

* Treated with soda, washed with water, dried over potash, and distilled.

tions were not heated before spectroscopic examination, and (2) both components are acridine compounds.

Whereas for the complex of 1-ethylquinolinium iodide with 4-(n-Me_2N-styryl)quinoline, at a component ratio of 1:1 and $C = 10^{-3}$, complex formation was absent (^{6}), formation of a complex by the acridine components (I) and (II) is already observed at $c = 2 \cdot 10^{-5}$–$5 \cdot 10^{-5}$ (Table 1, Fig. 1). The capacity for complex formation is connected with the extent and area of the π-electron system of the planar molecule and increases in the order: pyridine derivatives (^{5}) < quinoline (^{5}) < acridine (^{7}). This may be regarded as confirmation of the hypothesis that complex formation occurs as a result of layer association of planar molecules by means of a partial electronic bond, an exo-ρ-bond, acting perpendicular to the plane of the molecules along the axis of the π-electron cloud (“complex conjugation,” “complex mesomerism”) (^{2,3,5,6,10}). The striking similarity of the spectrum of the molecular complex (III) of the type [AK + BK] to the spectrum of the B–K–A system in dye (IV) we explain by the fact that the charge displacement in the complex, upon excitation of the complex system by light, takes place along the π-electron system of the AK component. Apparently this is connected with the fact that the electron-donor system, during complex formation, has acquired a partial (+) charge and that, owing to the layered structure of the complex, the vector of electronic displacement lies in the plane of the AK component (I).

In connection with the foregoing, on the basis of (^{8}) and studies of the molecular complexes of quinolinium (^{3,5,6}) and acridinium salts (^{7}) with components of the AK type, we put forward the hypothesis that the bathochromic effect upon increasing the concentration of acridinium iodide (see 1-3, Table 1), especially for solutions in chloroform, is connected with the formation of a molecular complex (VII) of the type

[[chemical scheme: V (BK) → VI (AK′); VII [BK + AK′], with acridine/acridinium structural formulas]]

$[AK' + BK]$ (BK–acridinium salt (V), and AK′–its pseudosalt, form (VI)).

10-Ethyl-9-(β-carbomethoxyethyl)-acridinium iodide (II). From ethyl alcohol, brown needles, m.p. 198–199°.

Found, %: N 3.58; 3.60
$C_{19}H_{20}O_2NJ$. Calculated, %: N 3.33

9-(*n*-Me_2N-styryl)-acridine (I). M.p. 248° (^{7}).

10-Ethyl-9-(*n*-dimethylaminostyryl)-acridinium iodide. A blue substance (from alcohol, m.p. 310° (^{7})).

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