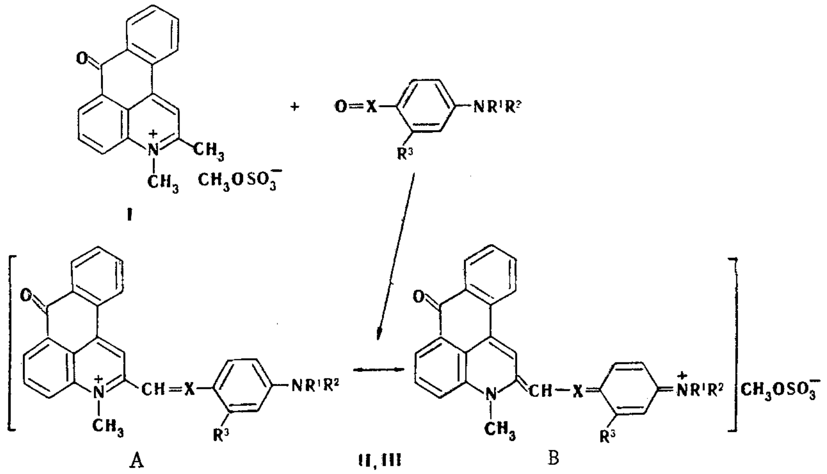
HEMICYANINE AND AZAHEMICYANINE CATIONIC DYES CONTAINING AN ANTHRAPYRIDINIUM RING

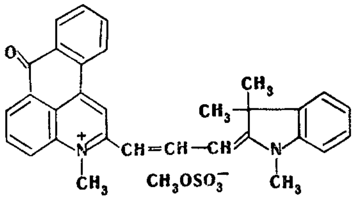
M. V. Gorelik and A. K. Arinich

UDC 547.837.6

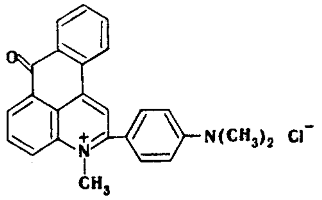
Green dyes were obtained by the reaction of 2,3-dimethylanthrapyridinium methylsulfate with N,N-disubstituted p-aminobenzaldehydes and p-nitrosoanilines. The features of the electronic spectra of the dyes are discussed.

Anthrapyridinium cationic dyes obtained by quaternization of 6-arylaminoanthrapyridines [1] or their 1,2-benzo derivatives (ceramidonines), as well as by the reaction of N-methylanthrapyridones with arylamines in the presence of $POCl_3$ [4], are well known. We have synthesized hemicyanine and azahemicyanine cationic dyes from a 2,3-dimethylanthrapyridinium (2,3-dimethyl-7-oxo-7H-dibenzo[f,ij]isoquinolinium) salt (I) obtained by condensation of 1-aminoanthraquinone with acetone in an alkaline medium [5] with subsequent methylation [6]. The reaction of salt I with N,N-disubstituted aminobenzaldehydes and p-nitrosoanilines leads to dyes II and III, the characteristics of which are presented in Table 1.





IV



V

II X=CH; III X=N

The visible region of the electronic spectra of dyes II and III contains two bands, viz., a long-wave band with $\lambda_{max} \geqslant 600$ nm, and a short-wave band with a maximum at ~400 nm (Fig. 1). Owing to the superimposition of the colors due to each of these bands, the dyes give green solutions and impart a green coloration to polyacrylic fibers.

The long-wave band, which is an intramolecular charge-transfer band [7], corresponds to transition to the excited state with redistribution of the electron density from the amine residue to the heterocyclic ring, which is reflected by an increase in the contribution of

---

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 236-239, February, 1981. Original article submitted April 19, 1980.

TABLE 1. Characteristics of Hemicyanine (II) and Azahemicyanine (III) Dyes

Compound	X	R¹	R²	R³	mp[a], °C (from ethanol)	Electronic spectra, λ_{max}, nm ($\log \varepsilon$)	Found, %		Empirical formula	Calc., %		Yield, %
							N	S		N	S	
IIa	CH	CH_3	CH_3	H	—[b]	378 (4,03), 400 (4,30), 613 (4,50)	5,6	6,2	$C_{28}H_{26}N_2O_5S$	5,6	6,4	95
IIb	CH	C_2H_5	C_2H_5	H	250	379 (4,36), 400 (4,42), 629 (4,62)	5,4	5,8	$C_{30}H_{30}N_2O_5S$	5,3	6,0	62
IIc	CH	C_2H_5	CH_2CH_2CN	H	158	377 (4,30) sh, 394 (4,26), 596 (4,28)	7,6	5,7	$C_{31}H_{29}N_3O_5S$	7,6	5,8	94
IId	CH	C_2H_5	$CH_2C_6H_5$	H	235	379 (4,42), 396 (4,43), 613 (4,54)	4,7	5,1	$C_{35}H_{32}N_2O_5S$	4,7	5,4	59
IIe	CH	CH_3	CH_2CH_2Cl	H	—[b]	378 (4,39) sh, 394 (4,36), 599 (4,41)	5,1	5,5	$C_{29}H_{27}ClN_2O_5S$	5,1	5,8	75
IIf	CH	CH_3	p-$C_6H_4OC_2H_5$	H	291	382 (4,46) sh, 396 (4,48), 613 (4,58)	4,8	5,6	$C_{35}H_{32}N_2O_6S$	4,6	5,3	82
IIg	CH	C_2H_5	CH_2CH_2Cl	CH_3	235	379 (4,30) sh, 396 (4,31), 616 (4,42)	4,7	5,5	$C_{31}H_{31}ClN_2O_5S$	4,8	5,5	65
IIh	CH	C_2H_5	$CH_2C_6H_5$	CH_3	264	380 (4,40) sh, 398 (4,44), 629 (4,59)	4,8	5,3	$C_{36}H_{34}N_2O_5S$	4,6	5,3	57
IIi	CH	$CH_2C_6H_5$	$C_2H_4COOCH_3$	CH_3	235	380 (4,25) sh, 398 (4,29), 616 (4,45)	4,0	4,5	$C_{38}H_{36}N_2O_7S$	4,2	4,8	75
IIIa	N	CH_3	CH_3	H	198	401 (4,18), 650 (4,46)	8,5	6,6	$C_{27}H_{25}N_3O_5S$	8,3	6,4	42
IIIb	N	C_2H_5	C_2H_5	H	—[b]	389 (4,26), 666 (4,41)	7,7	5,7	$C_{29}H_{29}N_3O_5S$	7,9	6,0	49
IIIc	N	C_2H_5	CH_2CH_2CN	H	167	392 (4,29), 625 (4,43)	9,8	5,5	$C_{30}H_{28}N_4O_5S$	10,0	5,8	57
IIId	N	C_2H_5	CH_2CH_2CN	CH_3	190	386 (4,26), 647 (4,38)	9,8	5,5	$C_{31}H_{30}N_4O_5S$	9,8	5,6	68

[a] With decomposition. [b] Does not melt up to 350°C.

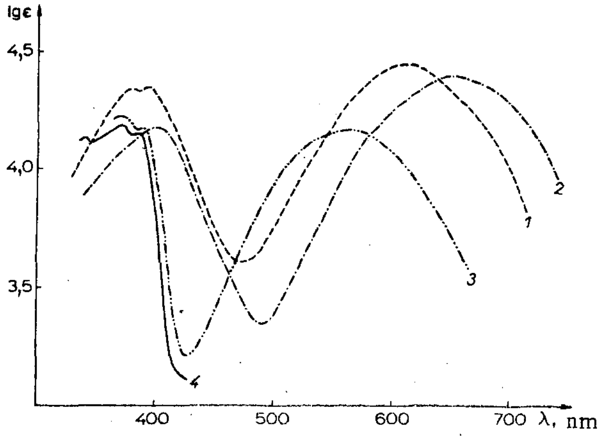


Fig. 1. Electronic spectra in ethanol: 1) 2-(4-dimethylaminostyryl)-3-methylanthrapyridinium methylsulfate (IIa); 2) 2-(4-dimethylaminoazastyryl)-3-methylanthrapyridinium methylsulfate (IIIa); 3) 2-(4-dimethylaminophenyl)-3-methylanthrapyridinium chloride (V); 4) 2,3-dimethylanthrapyridinium methylsulfate (I).

boundary structures B. In conformity with this, an increase in the electron-donor character of the amine residue is accompanied by a bathochromic shift, while a decrease is accompanied by a hypsochromic shift (Table 1). Thus replacement of the dimethylamino group by a diethylamino group (compare IIa and IIb and IIIa and IIIb) or the introduction of a methyl group in the 3 position (compare IId and IIh and IIIc and IIId) gives rise to a 16-22 nm shift to the long-wave region, whereas the introduction of an electron-acceptor substituent (Cl, CN, $COOCH_3$, C_6H_5) in the alkyl group gives rise to a shift in the opposite direction; for example, a shift of 33-41 nm is observed when a β-cyano group is introduced in the ethyl group (compare IIb and IIc and IIIb and IIIc). Replacement of an N-alkyl group by an N-aryl group leads to a hypsochromic shift even when an electron-donor substituent is present in the aryl residue (compare IIa and IIf).

The maximum of the long-wave band in the spectra of azahemicyanines III is shifted bathochromically 30-40 nm with respect to the maximum of the corresponding hemicyanines II in agreement with the rule in [8]. Trimethylidynecyanine IV, which was prepared by the reaction of salt I with 1,3,3-trimethyl-2-formylmethyleneindoline, has a maximum at 652 nm, i.e., in the longer-wave region than in the spectrum of hemicyanine II.

As compared with dyes that contain a quinolinium ring, the dyes with an anthrapyridinium ring display a significant bathochromic shift: 83 nm for 2-(p-dimethylaminostyryl)anthrapyridinium salt IIa [9, 10], 90 nm for azastyryl IIIa [9], and 105 nm for p-dimethylaminophenyl derivative V [11]. This effect is caused by annelation of the electron-acceptor o-phenylenecarbonyl grouping in the 4 and 5 positions of the quinolinium ring. The deepening of the color as the electron-acceptor character of the heterocyclic fragment increases is in agreement with what we stated above regarding the nature of the long-wave band. For a comparison of the magnitude of the effect let us point out that the introduction of a strong electron-acceptor substituent such as the trifluoromethylsulfonyl group in the 6 position of the quinolinium ring of the 4-(p-dimethylaminostyryl)quinolinium salt gives rise to a bathochromic shift of 78 nm [12].

In contrast to the long-wave band, the short-wave band is sensitive to substitution in the amine residue or replacement of a methylidyne group by a nitrogen atom (Table 1). It evidently corresponds to a π,π^* electron transition localized in the heterocyclic anthrapyridinium ring. In fact, a band of this sort is present in the spectrum of 2,3-dimethylanthrapyridinium salt I, and its position and structure remain unchanged on passing to p-dimethylaminophenyl derivative V (Fig. 1). However, broadening of the band vis-a-vis a small bathochromic shift occurs when a p-dimethylaminostyryl or -azastyryl grouping is introduced in dyes II and III, as a consequence of which the descending branch of the curve encompasses the visible region. It is precisely for this reason that dyes II and III are green rather than blue, as would be the case if the band of the anthrapyridinium fragment as a whole were found in the UV region.

Thus the presence of an anthrapyridinium ring in dyes II and III leads to a decrease in the energy of the first electron transition due to the chromophore system of the hemicyanine (azahemicyanine) dye and the development of a second chromophore, the role of which is played by the electron system of the heterocyclic ring. This analysis makes it possible to propose that the use of polycondensed heterocyclic compounds may prove to be of promise for the synthesis of polymethine dyes with complex colors.

EXPERIMENTAL

The electronic spectra of solutions of the compounds in ethanol were measured with a Specord spectrophotometer. The melting points were determined with a microheating stage in sealed capillaries.

2,3-Dimethyl-7-oxo-7H-dibenzo[f,ij]isoquinolinium Salts (I). A solution of 4.6 g (37 mmole) of dimethyl sulfate in 5 ml of dichloroethane was added in the course of 30 min to a solution of 1.0 g (4 mmole) of 2-methyl-7H-dibenzo[f,ij]isoquinolin-7-one [5] in 20 ml of dichloroethane, and the mixture was refluxed for 1 h. It was then cooled, and the yellow precipitate was removed by filtration and washed with dichloroethane to give 1.34 g (90%) of methylsulfate I with mp 236-238°C (from ethanol). Found: C 61.3; H 4.6; N 3.8; S 8.6%. $C_{19}H_{17}NO_5S$. Calculated: C 61.4; H 4.6; N 3.8; S 8.6%. Perchlorate I was obtained by the addition of potassium perchlorate to an aqueous solution of the methylsulfate and decomposed above 340°C (from water). Found: C 60.1; H 3.9; N 3.9%. $C_{18}H_{14}ClNO_5$. Calculated: C 60.1; H 3.9; N 3.9%.

2-(4-Dialkylaminophenyl)ethenyl-3-methyl-7-oxo-7H-dibenzo[f,ij]isoquinolinium Methylsulfates (II). A mixture of 2.5 mmole of methylsulfate I, 5 mmole of the corresponding 4-dialkylaminobenzaldehyde, 20 ml of acetic anhydride, and a drop of piperidine was refluxed for 30 min, after which it was cooled, and the precipitate was removed by filtration and washed with dioxane (Table 1). Similarly, dye IIf was obtained by condensation with 4-formyl-4'-ethoxy-N-methyldiphenylamine (Table 1). Trimethylidynecyanine IV was obtained under the same conditions by condensation of methylsulfate I with 1,3,3-trimethyl-2-formylmethyleneindoline. The product was obtained in 57% yield and had mp 264-265°C (from water). UV spectrum, λ_{max} (log ε) in ethanol: 377 (4.07), 443 (4.33), and 652 nm (4.65). Found: C 68.7; H 5.6; N 4.9%. $C_{32}H_{30}N_2O_5S$. Calculated: C 69.3; H 5.5; N 5.0%.

2-(4-Dialkylaminophenyl)iminomethyl-3-methyl-7-oxo-7H-dibenzo[f,ij]isoquinolinium Methylsulfates (III). A mixture of 2 mmole of methylsulfate I, 2.6 mmole of the corresponding 4-nitroso-N,N-dialkylaniline, 20 ml of ethanol, and a drop of piperidine was refluxed for 1 h, after which it was cooled, and the precipitated methylsulfate III was removed by filtration and washed with ethanol (Table 1).

2-(4-Dimethylaminophenyl)-3-methyl-7-oxo-7H-dibenzo[f,ij]isoquinolinium Chloride (V). This compound was synthesized by the method in [4].

LITERATURE CITED

1. Farbenfabrik Bayer, West German Patent No. 1040500; Chem. Abstr., 55, 3077 (1961).
2. Farbenfabrik Bayer, British Patent No. 794807; Chem. Abstr., 53, 4754 (1959).
3. N. I. Grineva, V. V. Puchkova, and V. N. Ufimtsev, Inventor's Certificate No. 176021; Byul. Izobr., No. 21, 34 (1965).
4. Farbenfabrik Bayer, German Patent No. 269894; Frdl., 11, 269 (1915).
5. Farbenfabrik Bayer, German Patent No. 185548; Frdl., 9, 730 (1911).
6. I. G. Farbenindustrie, German Patent No. 630219; Frdl., 23, 984 (1940).
7. J. Fabian, J. Prakt. Chem., 322, 1 (1980).
8. M. Dewar and R. Dougherty, Molecular Orbital Theory of Organic Chemistry, McGraw (1969).
9. B. Das, B. K. Patnaik, and M. K. Rout, J. Indian Chem. Soc., 37, 603 (1960).
10. É. R. Zakhs, E. V. Bashut-skaya, and L. S. Éfros, Khim. Geterotsikl. Soedin., No. 6, 818 (1976).
11. D. L. Garmaise and G. Y. Paris, Chem. Ind. (London), 1645 (1967).
12. Z. Ya. Krainer, P. F. Gudz', and L. M. Yagupol'skii, Khim. Geterotsikl. Soedin., No. 2, 235 (1973).