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RESEARCHES ON SYNTHETIC DYES

LXI. Unsymmetrical Monomethinecyanines From 1-Aryl-5, 6-benzolepidinium Salts*

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1-Alkyl- and 1-aryl-5, 6-benzolepidinium salts undergo cyanine condensation with 1-ethylquinolinium iodide in ethanol in the presence of basic condensation catalysts to give unsymmetrical monomethinecyanine dyes. The steric hindrance present in the molecules of these dyes is responsible for a low absorption intensity of ethanol solutions of these dyes.

The main products of reaction of aryl-β-naphthylamines with acetone and formaldehyde in acid solution [1] are 1-aryl-5, 6-benzolepidinium salts. It has been shown that, under the usual conditions, these compounds undergo cyanine condensations to give carbocyanines and quinostyryls [2]. The present paper describes the reaction of 1-aryl-5, 6-benzolepidinium salts with 1-ethylquinolinium iodide, to give unsymmetrical monomethinecyanines:

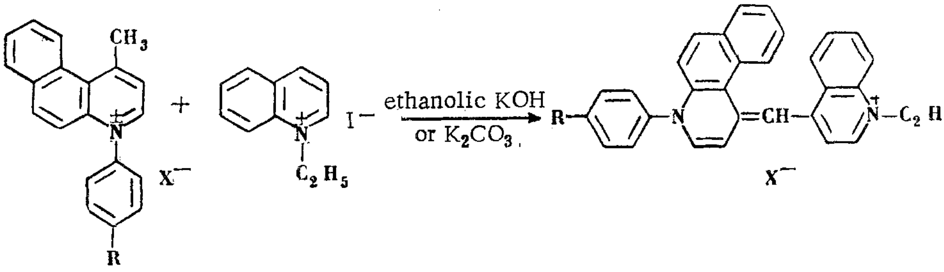

Table 1 gives the constants of the compounds synthesized and the analytical data obtained for them. They were all fine crystalline powders, readily soluble in alcohols, pyridine, and acetic anhydride, insoluble in hydrocarbons, carbon tetrachloride, water, and ether.

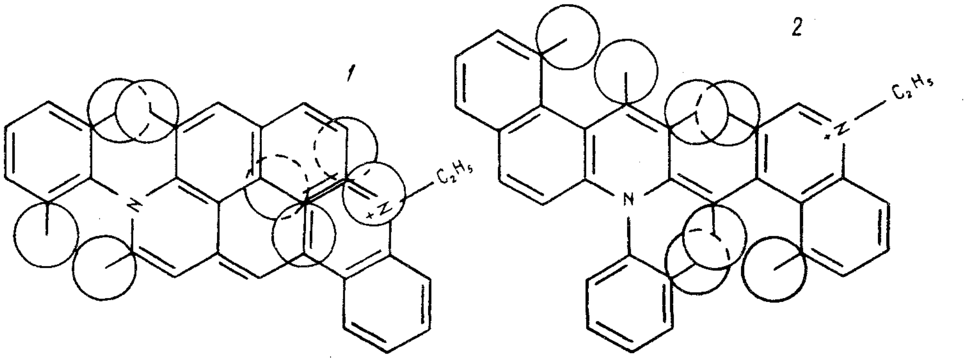

Fig. 1. Pictorial representation of dye molecules: 1) cis-(1-phenyl-5, 6-benzoquinoline-4)-1(1'-ethylquinoline-4')monomethinecyanine perchlorate; 2) cis-(1-phenyl-5, 6-benzoquinoline-2)-(1'-ethylquinoline-4') monomethinecyanine perchlorate.

Dye IV, containing a hydroxyl group, is, unlike the other dyes, insoluble in chloroform. When it is heated in acetic anhydride, the hydroxyl group is acetylated to give dye V. However, the ester group is rather easily hydrolyzed, e.g., even when an attempt is made to recrystallize the compound from ethanol.

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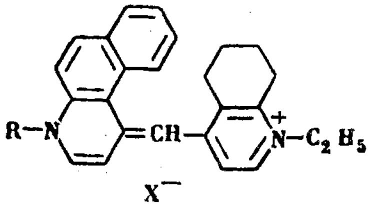
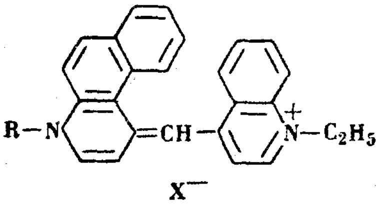
*For Part LX see [2].

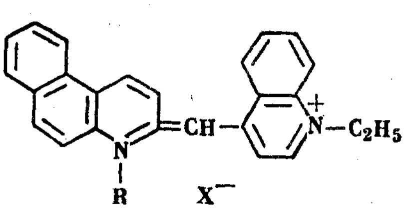
Table 1



Compound number	R	X	Mp °C decomp	Formula	Found, %		Calculated, %		Yield, %
					Halogen	N	Halogen	N	
I	CH_3	ClO_4	147—149	$C_{26}H_{23}ClN_2O_4$	7.60 7.72	6.18 5,97	7,66	6.05	45
II	C_6H_5	ClO_4	186—188	$C_{31}H_{25}ClN_2O_4$	6.71 6,66	5,39 5.28	6.75	5.34	58
III	p-$CH_3C_6H_4$	ClO_4	133—135	$C_{32}H_{27}ClN_2O_4$	6.53 6.56	5,11 5.16	6.58	5.20	54
IV	p-HOC_6H_4	I	201—203	$C_{31}H_{25}IN_2O$	22,28 22.36	5.00 4.98	22.33	4,93	65
V	p-$CH_3COOC_6H_4$	I	207—209	$C_{33}H_{27}IN_2O_2$	20.81 20,85	4,54 4,62	20.79	4.59	89
VI	p-$CH_3OC_6H_4$	ClO_4	144—146	$C_{32}H_{27}ClN_2O_5$	6.43 6,47	4.98 4,96	6,39	5,05	59
VII	p-ClC_6H_4	ClO_4	198—200	$C_{31}H_{24}Cl_2N_2O_4$	12,73 12.76	4,97 4.95	12.68	5.01	62
VIII	p-$O_2NC_6H_4$	I	159—161	$C_{31}H_{24}IN_3O_2$	21.20 21.29	6,98 7.09	21,24	7,03	60
IX	β-$C_{10}H_7$	ClO_4	169—171	$C_{35}H_{27}ClN_2O_4$	6.01 6.09	4.92 4,84	6,17	4.87	70

Table 2





Compound number	R	λ_{max}, mμ	lg ε	Compound number	λ_{max}, mμ	lg ε	Bathochromic shift, mμ
I	CH_3	608	4,17	XI*	571[3]	—	37
II	C_6H_5	596	4.06	XII	578[4]	5.02	18
III	p-$CH_3C_6H_4$	604	3.96	XIII	578[4]	5.00	26
IV	p-HOC_6H_4	594	3,85	XIV	580	4,82	14
V	p-$CH_3COOC_6H_4$	586	3,88	XV	578	4,88	8
VI	p-$CH_3OC_6H_4$	606	3,97	XVI	575[5]	—	31
VII	p-ClC_6H_4	602	4.05				
VIII	p-$O_2NC_6H_4$	505	3,95				
IX	β-$C_{10}H_7$	584	4.07				
X	p-$^{-}OC_6H_4$	501	3,88				

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* $R = C_2H_5$

The absorption spectra of ethanol solutions of the dyes synthesized were measured with a SF-2M automatic recording spectrophotometer. Table 2 gives the results of the spectrographic measurements.

Comparison of the absorption spectra of the synthetic dyes I–X with those of the corresponding isomeric compounds XI–XVI reveals large lowering of the first absorption intensities (by about 10-fold), due to considerable steric hindrance to planar configuration of the dye rings (Figs. 1, 2).* At the same time, a considerable bathochromic shift of absorption maxima is observed, due to seteric hindrance and lengthening of the conjugated chain to the vinyl group.

Comparison of absorption maxima for dyes I and II shows that replacement of the electron-donating N-methyl group of the benzoquinoline ring by an electron-donating phenyl group, is accompanied by a hyposochromic effect (12 mμ). Replacement of the methyl group (dye I) by β-naphthyl (dye IX) gives rise to a more considerable hypsochromic effect (24 mμ).

Introduction of various substituents at the para position in the N-phenyl ring gives on the one hand a bathochromic effect, and on the other a hypsochromic one. Thus introduction of Me, MeO, and Cl gives rise to a bathochromic shift of the absorption maximum (8, 10, and 6 mμ), while OCOMe, NO_2 and O^- give rise to an opposite effect (10, 91, and 94 mμ). The hydroxyl group is practically without effect on the absorption maxima of the dyes (dye IV). It is interesting to note that introduction of these very same groups into the isomeric isocyanine dyes (dyes XII–XVI) is practically without effect on the absorption maxima.

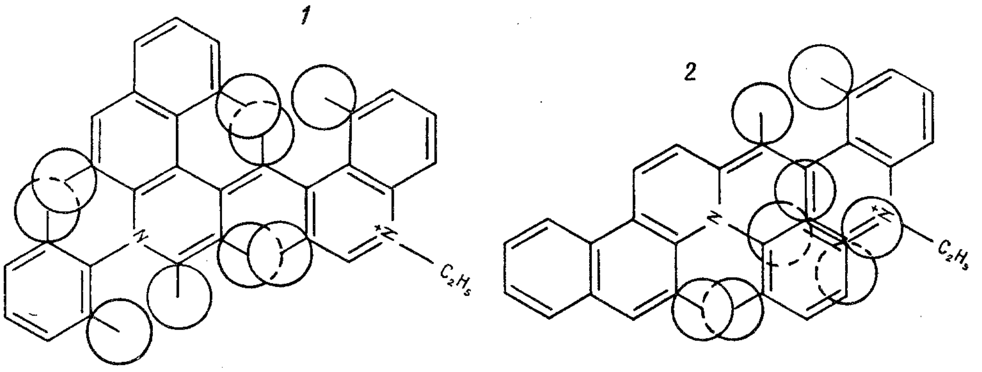

Fig. 2. Pictorial representation of dye molecules: 1) trans-(1-phenyl-5, 6-benzoquinoline-4)-(1'-ethylquinoline-4')-monomethinecyanine perchlorate; 2) trans-(1-phenyl-5, 6-benzoquinoline-2)-(1'-ethylquinoline-4') monomethinecyanine perchlorate.

Experimental

The dyes were synthesized by the method of [8]. 0.01 mole of the appropriate 1-alkyl- or 1-aryl-5, 6-benzolepidinium salt, 0.02 mole 1-ethylquinolinium iodide, 20 ml dry EtOH, and 0.014 mole ethanolic KOH (or 0.015 mole finely powdered K_2CO_3) were gently refluxed together on a water-bath for 30 min, when the mixture gradually turned bluish-violet. It was then left for 24 hr at room temperature, after which it was poured into 150 ml dilute aqueous $NaClO_4$ of KI solution. The flocculent precipitate formed was filtered off, washed with water, and air dried. The dyes were further purified by chromatographing on Al_2O_3, using EtOH-benzene (1 : 9) for developing and eluting the quaternary salts. The dyes were washed out with 95% EtOH. The EtOH solutions were evaporated in air until crystals began to appear, then left to crystallize. The dyes separated out were recrystallized to constant mp (except the acetylated dye V).

Dye V was prepared by heating 1.1 g (2 mmole) IV with 5 ml Ac_2O in a paraffin bath at 140° C for 30 min. The homogeneous reaction products were left for 24 hr at room temperature, then treated with ether. The fine crystalline dye powder which separated was filtered off, and washed with ether to remove Ac_2O completely. It was purified by precipitation with ether from $CHCl_3$ solution.

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*Regarding the atomic radii assumed in the figures, see [6, 7].

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