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RESEARCHES ON SYNTHETIC DYES

LX. Styryls from 1-Aryl-5, 6-benzolepidinium Salts

G. T. Pilyugin, Ya. O. Gorichok, and S. I. Gorichok

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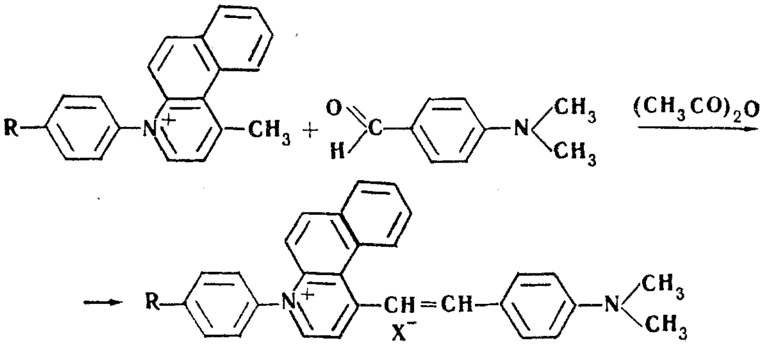
1-Aryl-5, 6-benzolepidinium salts condense with p-dimethylaminobenzaldehyde to give the corresponding quinostyryl dyes. The effects of various substituents at the para position of the N-phenyl group at the quinoline ring on the absorption spectra of the dyes synthesized are investigated. Steric hindrance in the molecules of the dyes is postulated.

It was previously shown that cyclization of p-substituted phenyl-β-naphthylamines under Bayer's reaction conditions [1, 2], proceeds in two directions to give isomeric lepidinium salts [3]. It was of interest to investigate reactivity and other properties of these salts. The present paper describes condensation of 1-aryl-5, 6-benzolepidinium salts with p-dimethylaminobenzaldehyde to give quinostyryl dyes.

It is known that quinostyryls are of interest as subjects for research on the relationship between color and molecular structure, as photoemulsion sensitizers and desensitizers, plant growth regulators, and physiologically active compounds [4].

The equation for the condensation of 1-aryl-5, 6-benzolepidinium salts with p-dimethylaminobenzaldehyde is:



Despite these salts containing an electron-accepting aryl group at the nitrogen heteroatom, and despite the enhanced activity of the 4-methyl group, they condense more slowly with p-dimethylaminobenzaldehyde, evidently because of steric hindrance due to the benzene group at positions 5 and 6 of the quinoline ring [3].

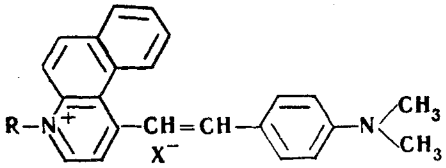
Table 1 gives properties of and analytical data for the dyes synthesized. All dyes are fine, crystalline powders, soluble in the usual solvents for that class of compound, except for IV, which is insoluble in chloroform. When an ethanol solution of dye is allowed to stand, the ester group is exchanged for a phenyl one, giving dye IV. The dye is quite stable in chloroform solution and in the crystalline state. The spectra of the dyes were measured with a SF-2M automatic recording spectrophotometer (Table 2).

The absorption spectra maxima of the dyes I-X synthesized were compared with those of the corresponding isomeric quinostyryls XI-XVIII. In all cases, there is a rather significant bathochromic effect (11-40 mμ), evidently due to combined effect of lengthening of the chromophoric polymethylene chain and the presence of steric hindrance. Comparison of absorption intensities of dyes II and XII, IV and XIV, V and XV indicates the presence of such hindrance. Pictorial representation of a dye molecule (figure) also confirms this [13, 14].

The data of Table 2 show that replacement of an electron-donating methyl group (I) at the nitrogen heteroatom by an electron-accepting phenyl (II) and β-naphthyl (IX) groups results in bathochromic displacements of the absorption maximum by 41 and 53 mμ, respectively.

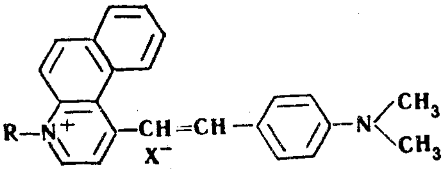
Comparison of the dyes with substituents at the para position of the N-phenyl group (dyes III-IX), with the corresponding unsubstituted ones (dye II), shows that electron-donating substituents CH_3, OH, OCH_3, O^- give rise to a hypsochromic shift of the absorption maximum to a rather significant extent (7-16 mμ). Electron-accepting

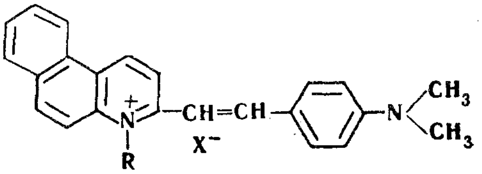
Table 1



Compound number	R	X	Mp °C (decomp, ex EtOH)	Formula	Found, %		Calculated, %		Yield, %
					Halogen	N	Halogen	N	
I	CH_3	ClO_4	139—141	$C_{24}H_{23}ClN_2O_4$	8.14 8.01	6.41 6.48	8.08	6.38	68
II	C_6H_5	ClO_4	113—115	$C_{29}H_{25}ClN_2O_4$	6.99 7.14	5.64 5.67	7.08	5.59	68
III	p-$CH_3C_6H_4$	ClO_4	179—181	$C_{30}H_{27}ClN_2O_4$	6.95 6.83	5.38 5.49	6.38	5.44	74
IV	p-HOC_6H_4	I	241—243	$C_{29}H_{26}IN_2O$	23.33 23.21	5.08 5.18	23.27	5.14	70
V	p-$CH_3COOC_6H_4$	I	218—220 ($CHCl_3$)	$C_{31}H_{27}IN_2O_2$	21.59 21.55	4,71 4.83	21.64	4.78	88
VI	p-$CH_3OC_6H_4$	ClO_4	183—185	$C_{30}H_{27}ClN_2O_5$	6.74 6.64	5.33 5.36	6.68	5.28	75
VII	p-ClC_6H_4	ClO_4	174—176	$C_{29}H_{24}Cl_2N_2O_4$	13.18 13.27	5.29 5.18	13.24	5.23	72
VIII	p-$O_2NC_6H_4$	I	172—174	$C_{29}H_{24}IN_3O_2$	22.05 22.09	7.27 7.38	22.13	7.33	61
IX	β-$C_{10}H_7$	ClO_4	158—160	$C_{33}H_{27}ClN_2O_4$	6.50 6.37	4.99 5.13	6.43	5.08	79

Table 2





Compound number	R	λ_{max}, mμ	lg ε	Compound number	λ_{max}, mμ	lg ε	Bathochromic shift, mμ
I	CH_3	535	4.15	XI	524^6 *	—	11
II	C_6H_5	576	4.06	XII	552^7	5.07	24
III	p-$CH_3C_6H_4$	570	4.09	XIII	543^8	—	27
IV	p-HOC_6H_4	560	4.02	XIV	544^9	4.72	16
V	p-$CH_3COOC_6H_4$	582	4.05	XV	558^9	4.83	24
VI	p-$CH_3OC_6H_4$	564	3.88	XVI	545^{10}	—	19
VII	p-ClC_6H_4	591	4.12	XVII	560^{11}	—	31
VIII	p-$O_2NC_6H_4$	598	4.06	—	—	—	—
IX	β-$C_{10}H_7$	588	4.11	XVIII	548^{12}	—	40
X	p-$^{-}OC_6H_4$	552	4.02	—	—	—	—

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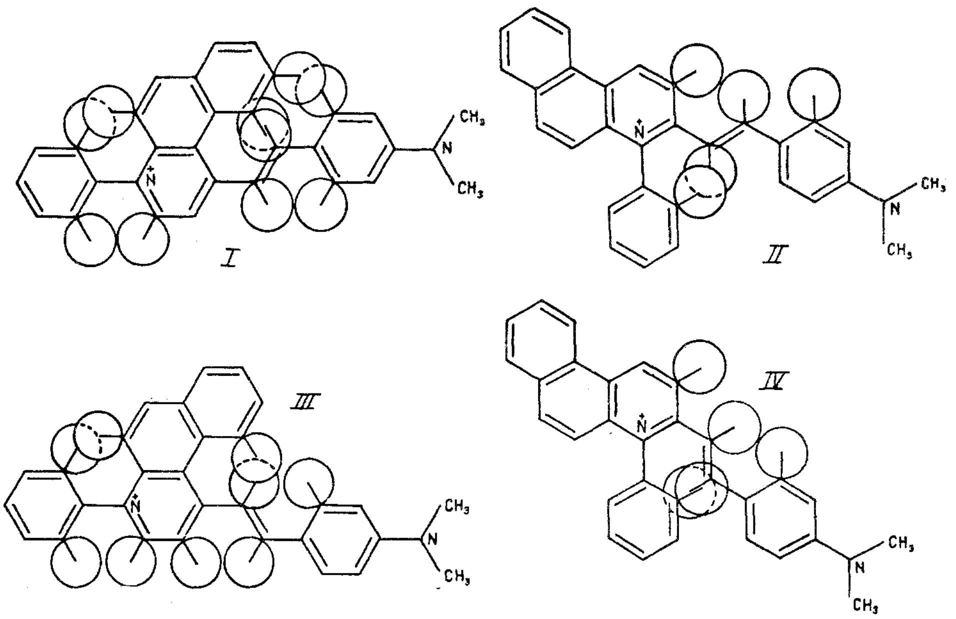
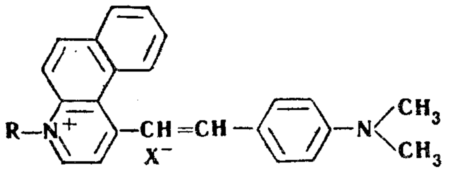
* $R = C_2H_5$

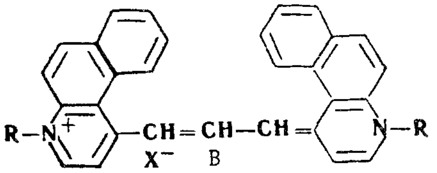


Pictorial representation of dye molecules: I) cis- (1-phenyl-5, 6-benzoquinoline-4)-p-dimethylaminostyryl perchlorate; II) cis-(1-phenyl)-5, 6-benzoquinoline-2)-p-dimethylaminostyryl perchlorate; III) trans-(1-phenyl-5, 6-benzoquinoline-4)-p-dimethylaminostyryl perchlorate; IV) trans-(1-phenyl-5, 6-benzoquinoline-2)-2-dimethylaminostyryl perchlorate.

Table 3



A



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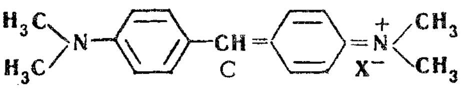

C

Compound number	R	λ_{max}, mμ				Deviation, mμ	$K_{base} \cdot 10^{10}$ R−NH₂
		B [15]	C [16]	(B + C) [2]	A		
X	p-−OC_6H_4	771	610	690.5	552	138.5	—
I	CH_3	710	610	660	535	125	4380000[17]
IV	p-HOC_6H_4	742	610	676	560	116	66.0[18]
VI	p-$CH_3OC_6H_4$	739	610	674.5	564	110.5	14.7[17]
III	p-$CH_3C_6H_4$	730	610	670	570	100	11.3[17]
II	C_6H_5	727	610	668.5	576	92.5	4.6[17]
V	p-$CH_3COOC_6H_4$	737	610	673.5	582	91.5	—
IX	β-$C_{10}H_7$	745	610	677.5	588	89.5	2[19]
VII	p-ClC_6H_4	733	610	671.5	591	80.5	1.5[17]
VIII	p-$O_2NC_6H_4$	743	610	676.5	598	78.5	0.01[17]

substituents (CH_3COO, Cl, NO_2) give rise to a bathochromic effect (6–22 mμ), most significant with the NO_2 group.

Comparison of the spectroscopic data obtained for the synthesized styryl dyes (A) with those calculated additively from the two symmetrical ones (B and C) (Table 3), gives the deviations of the absorption maxima, the value depending on the difference in the basicities of the rings of which a dye molecule is composed [20, 21]. It is known that the dimethylaminophenyl ring is less basic than the benzoquinolinium one. Comparison of dye deviation values with basicity constants of the corresponding primary amines shows that there is some connection between these two lots of quantities. As the deviation decreases, so does the basicity of the corresponding amine.

Experimental

1-Methyl-5, 6-benzoquinoline-4-p-dimethylaminostyryl perchlorate (I). Into a conical flask fitted with a reflux condenser were placed 3 g (0.01 mole) 1-methyl-5, 6-benzolepidinium perchlorate, 2.2 g (0.015 mole) p-dimethylaminobenzaldehyde, and 15 ml Ac_2O, and the mixture heated, with moderate refluxing, in a paraffin bath for 40 min. The violet reaction products were then left for 48 hr at room temperature, the crystals filtered off, washed with a small amount of EtOH, and then with ether until the washings ceased to be colored. Yield 3 g. Fine crystalline powder, with a metallic reflex. Violet solution in EtOH.

Dyes II, III, V-IX were synthesized similarly, using a 25 min heating period.

(1-p-Hydroxyphenyl-5, 6-benzoquinoline-4) p-dimethylaminostyryl perchlorate (IV). a) A preparation was obtained by heating 4.1 g (0.01 mole) p-hydroxyphenyl-5, 6-benzolepidinium iodide, 2.2 g (0.015 mole) p-dimethylaminobenzaldehyde, and 10 ml pyridine together, with moderate refluxing, in a paraffin bath for 25 min. The reaction mixture gradually turned violet, and solidified at the end of the reaction. After standing for 24 hr at room temperature, it was repeatedly extracted with ether until the extract was no longer colored, when the dye was obtained as a fine dark powder, yield 3.8 g. Violet solution in EtOH.

b) The dye was also obtained from 4.5 g (0.01 mole) 1-p-acetoxyphenyl-5, 6-benzolepidinium iodide and 2.2 g (0.015 mole) p-dimethylaminobenzaldehyde in 15 ml pyridine. Yield 4.3 g (79%), mp 241–243° (decomp). Undepressed mixed mp with the dye prepared as above. Absorption maximum in EtOH at 560 mμ (lg ε 4.00). Found: I 23.38, 23.30; N 5.03, 5.20%. Calculated for $C_{29}H_{26}IN_2O$: I 23.27; N 5.14%.

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