RESEARCHES ON SYNTHETIC DYES

LXIV. Cyanine Dyes Based on N-β-Naphthyllepidinium Salts*

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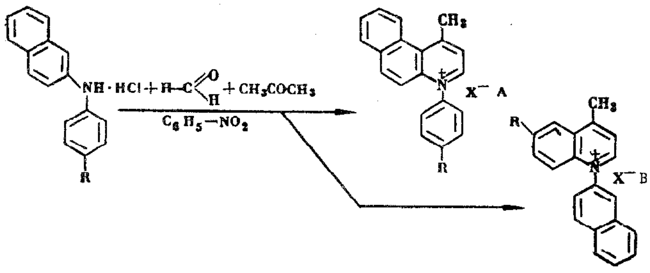
1-β-Naphthyllepidinium salts undergo the ordinary cyanine condensation to give monomethinecyanines, trimethinecyanines, and quinostyrene dyes. Starting from 1-β-naphthyllepidinium quaternary salts, 18 hitherto undescribed dyes are synthesized, and a number of color characteristics explained as a function of molecular structure.

It was previously found [2] that cyclization of para substituted phenyl-β-naphthylamines with acetone and formaldehyde in acid solution gave, along with N-aryl-5,6-benzolepidinium salts A, a small amount of isomeric N-β-naphthyllepidinium salts B:



R=H, CH₃, OH, OCOCH₃, OCH₃, Cl, NO₂; X=ClO₄, I.

It is now shown that despite steric hindrance benzolepidinium salts condense with a γ-methyl group to give trimethinecyanine, quinostyrene [3], and monomethine [4] dyes. Some peculiarities of these dyes, connected with their structures, were uncovered.

It was of interest to investigate the reactivities of isomeric N-β-naphthyllepidinium salts and the properties of the dyes synthesized from them.

The salts mentioned readily react with orthoformic ester in pyridine solution to give symmetrical trimethinecyanine dyes (VII–XII). They condense fairly readily with p-dimethylaminobenzaldehyde to give quinostyrenes (XIII–XVIII), and with 1-ethylquinolinium iodide to give unsymmetrical monomethinecyanines (I–VI). In reactivity these compounds are reminiscent of a 1-phenyllepidinium salt. Tables 1–3 give the constants of the dyes and their analytical data. Absorption spectra of ethanol solutions of the monomethine and quinostyrene dyes were measured with an SF-2M spectrophotometer, of the trimethinecyanine dyes with an SF-4 instrument.

The optical data of the monomethines I–VI synthesized are given in Table 4. They are compared with the corresponding isomeric dyes Ia–VIa, prepared from 5,6-benzolepidinium salts [4]. The table shows that the intensities of absorption for the dyes are greater than those of the isomers, and this is due to lower steric hindrance in the dyes synthesized, and is confirmed by a graphic representation of the molecule (Figs. 1, 2).* The absorption maxima of N-β-naphthyl substituted monomethinecyanines lie in the shorter wavelength region, except with compounds III and IV containing hydroxyl and acetoxy groups. Comparing the absorption maxima of the dyes XXI, XX, and I, it is evident that replacement of an alkyl group at a nitrogen heteroatom having an electron-donating action, by electron-accepting phenyl and β-naphthyl groups, causes a hypsochromic displacement of the absorption maximum (2–7 mμ). Introduction of substituents at position 6 in the N-β-naphthylquinoline ring gives rise to a bathochromic shift of the absorption maximum in all cases (dyes I and II–VII), unlike the isomeric compounds, where OH and AcO groups in the para position of the N-phenyl group give rise to a hypsochromic shift (dyes Ia, IIIa, and IVa). The substituents can be arranged in the following order in respect of bathochromic effect in dyes II–VII:

substituent	H <	Cl <	$OCOCH_3$ <	CH_3 <	OCH_3 <	OH <	O^-
bathochromic shift, mμ	0	3	4	5	13	16	53

Table 5 gives the absorption spectra of symmetrical trimethinecyanine dyes. They are compared with the corresponding isomeric carbocyanines, previously prepared [1]. The data in the table show that the absorption maximum of the dyes investigated are shifted hypsochromically 4–21 mμ compared with the isomers. Their absorption intensities are considerably greater. Comparison of dyes XXIII, XXIV, and VII shows that replacement of the N-ethyl group by phenyl or β-naphthyl causes bathochromic shifts of 14 and 19 mμ respectively. Introduction of various substituents at the 6,6' positions in the carbocyanines leads to a deepening of the color by 6–27 mμ (dyes VII–XII, XXII). The substituents can be arranged in the following order of bathochromic displacement:

substituent	H <	Cl <	$OCOCH_3$ <	CH_3 <	OCH_3 <	OH <	O^-
bathochromic shift, mμ	0	6	8	10	12	14	27

Table 6 gives the optical properties of the quinostyrenes synthesized. As previously they are compared

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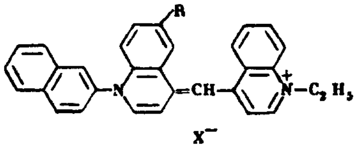
*For Part LXIII see [1].

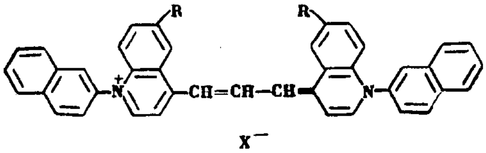
*For the atomic radii assumed in the diagram, see [7, 8].

Table 1



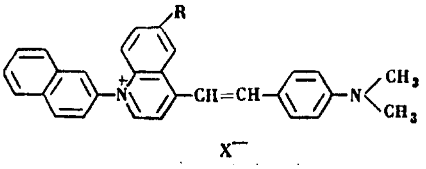
Compound No.	R	X	Mp, °C (decomp)	Formula	Found, %		Calculated, %		Yield, %
					halogen	N	halogen	N	
I	H	ClO_4	157—159	$C_{31}H_{25}ClN_2O_4$	6.69 6.78	5.30 5.23	6.75	5.34	78
II	CH_3	ClO_4	179—181	$C_{32}H_{27}ClN_2O_4$	6.64 6.62	5.27 5.23	6.58	5.20	75
III	OH	I	239—241	$C_{31}H_{25}IN_2O$	22.30 22.26	4.86 4.95	22.33	4.93	89
IV	$OCOCH_3$	I	161—163	$C_{33}H_{27}IN_2O_2$	20.71 20.76	4.66 4.52	20.79	4.59	86
V	OCH_3	ClO_4	167—169	$C_{32}H_{27}ClN_2O_5$	6.32 6.45	5.11 5.01	6.39	5.05	82
VI	Cl	ClO_4	149—151	$C_{31}H_{24}Cl_2N_2O_4$	12.70 12.65	5.09 5.06	12.68	5.01	77

Table 2



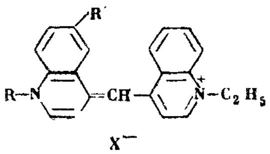
Compound No.	R	X	Mp, °C (decomp)	Formula	Found, %		Calculated, %		Yield, %
					halogen	N	halogen	N	
VII	H	ClO_4	183—185	$C_{41}H_{29}ClN_2O_4$	5.53; 5.43	4.39; 4.37	5.46	4.32	78
VIII	CH_3	ClO_4	181—183	$C_{43}H_{33}ClN_2O_4$	5.31; 5.27	4.43; 4.45	5.24	4.37	88
IX	OH	I	230—232	$C_{41}H_{29}IN_2O_2$	17.98; 17.90	3.87; 4.03	17.91	3.95	71
X	CH_3COO	I	211—213	$C_{45}H_{33}IN_2O_4$	15.93; 16.05	3.62; 3.49	16.01	3.53	87
XI	OCH_3	ClO_4	198—200	$C_{43}H_{33}ClN_2O_6$	5.08; 5.03	4.01; 4.04	5.00	3.95	76
XII	Cl	ClO_4	119—121	$C_{41}H_{27}Cl_3N_2O_4$	14.85; 14.90	3.84; 3.99	14.81	3.90	82

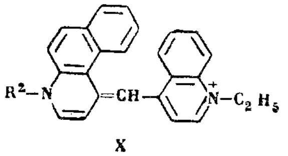
Table 3



Compound No.	R	X	Mp, °C (decomp)	Formula	Found, %		Calculated, %		Yield, %
					halogen	N	halogen	N	
XIII	H	ClO_4	214—216	$C_{29}H_{25}ClN_2O_4$	7.00; 7.11	5.47; 5.51	7.08	5.59	81
XIV	CH_3	ClO_4	189—191	$C_{30}H_{27}ClN_2O_4$	6.80; 6.91	5.52; 5.40	6.88	5.44	86
XV	OH	I	266—268	$C_{29}H_{26}IN_2O$	23.24; 23.36	5.21; 5.10	23.27	5.14	80
XVI	CH_3COO	I	259—261	$C_{31}H_{27}IN_2O_2$	21.70; 21.73	4.85; 4.80	21.64	4.78	90
XVII	OCH_3	ClO_4	139—141	$C_{30}H_{27}ClN_2O_5$	6.60; 6.63	5.23; 5.35	6.68	5.28	87
XVIII	Cl	ClO_4	189—191	$C_{29}H_{24}Cl_2N_2O_4$	13.30; 13.34	5.27; 5.31	13.24	5.23	82

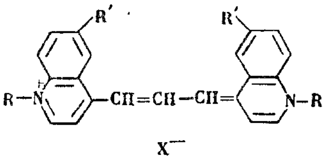
Table 4

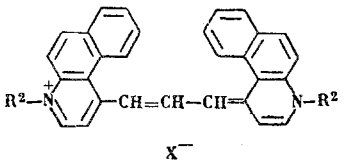




Compound No.	R	R^1	λ_{max}, mμ	lg ε	Compound No.	R^2	λ_{max}, mμ[4]	lg ε	Δλ, mμ
I	β-$C_{10}H_7$	H	587	4.66	Ia	β-$C_{10}H_7$	584	4.07	+3
II		CH_3	592	4.64	IIa	p-$CH_3C_6H_4$	604	3.96	−12
III		OH	603	4.65	IIIa	p-HOC_6H_4	594	3.85	+9
IV		CH_3COO	591	4.66	IVa	p-$CH_3COOC_6H_4$	586	3.88	+5
V		CH_3O	600	4.63	Va	p-$CH_3OC_6H_4$	606	3.97	−6
VI		Cl	590	4.59	VIa	p-ClC_6H_4	602	4.05	−12
XIX		O^-	640	4.65	XIXa	p-$^-OC_6H_4$	501	3.88	+139
XX	C_6H_5	H	592[5]	4.70	XXa	C_6H_5	596	4.06	−4
XXI	C_2H_5	H	594[6]	—	XXIa	CH_3	608	4.17	−14

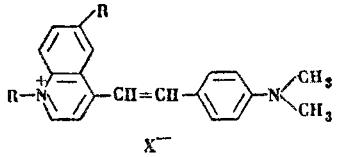
Table 5

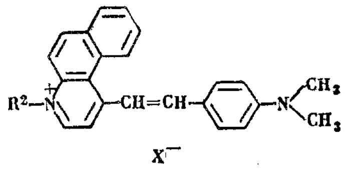




Compound No.	R	R^1	λ_{max}, mμ	lg ε	Compound No.	R^2	λ_{max}, mμ[2]	lg ε	Δλ, mμ
VII	β-$C_{10}H_7$	H	723	5.24	VIIa	β-$C_{10}H_7$	745	4.48	−22
VIII		CH_3	733	5.25	VIIIa	p-$CH_3C_6H_4$	730	4.72	+3
IX		OH	737	5.08	IXa	p-HOC_6H_4	742	4.66	−5
X		CH_3COO	731	5.21	Xa	p-$CH_3COOC_6H_4$	737	4.62	−6
XI		CH_3O	735	5.16	XIa	p-$CH_3OC_6H_4$	739	4.69	−4
XII		Cl	729	5.12	XIIa	p-ClC_6H_4	733	4.71	−4
XXII		O^-	750	5.12	XXIIa	p-$^-OC_6H_4$	771	4.70	−21
XXIII	C_6H_5	H	718[5]	5.06	XXIIIa	C_6H_5	727	4.49	−9
XXIV	C_2H_5	H	704[6]	5.03	XXIVa	CH_3	710	4.75	−6

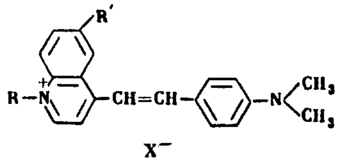
Table 6

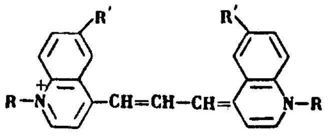




Compound No.	R	R^1	λ_{max}, mμ	lg ε	Compound No.	R^2	λ_{max}, mμ[3]	lg ε	Δλ, mμ
XIII	β-$C_{10}H_7$	H	582	4.72	XIIIa	β-$C_{10}H_7$	588	4.11	−6
XIV	β-$C_{10}H_7$	CH_3	577	4.75	XIVa	p-$CH_3C_6H_4$	570	4.09	+7
XV	β-$C_{10}H_7$	OH	570	4.68	XVa	p-HOC_6H_4	560	4.02	+10
XVI	β-$C_{10}H_7$	CH_3COO	585	4.58	XVIa	p-$CH_3COOC_6H_4$	582	4.05	+3
XVII	β-$C_{10}H_7$	CH_3O	574	4.60	XVIIa	p-$CH_3OC_6H_4$	564	3.88	+10
XVIII	β-$C_{10}H_7$	Cl	590	4.68	XVIIIa	p-ClC_6H_4	591	4.12	−1
XXV	β-$C_{10}H_7$	O^-	540	4.69	XXVa	p-$^-OC_6H_4$	552	4.02	−12
XXVI	C_6H_5	H	578[5]	4.70	XXVIa	C_6H_5	576	4.04	+2
XXVII	C_2H_5	H	542[9]	4.68	XXVIIa	CH_3	535	4.15	+7

Table 7





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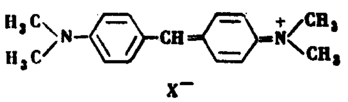


Compound No.	R	R′	λ_{max}, mμ				Deviation mμ
			B	C[10]	(B+C)/ /2	Found	
XIII	β-$C_{10}H_7$	H	723	610	666.5	582	84.5
XIV	β-$C_{10}H_7$	CH_3	733	610	671.5	577	94.5
XV	β-$C_{10}H_7$	OH	737	610	673.5	570	103.5
XVI	β-$C_{10}H_7$	CH_3COO	731	610	670.5	585	85.5
XVII	β-$C_{10}H_7$	CH_3O	735	610	672.5	574	98.5
XVIII	β-$C_{10}H_7$	Cl	729	610	669.5	590	79.5
XXV	β-$C_{10}H_7$	O^-	750	610	680	540	140
XXVI	C_6H_5	H	718[5]	610	664	578	86
XXVII	C_2H_5	H	704[6]	610	657	542	115

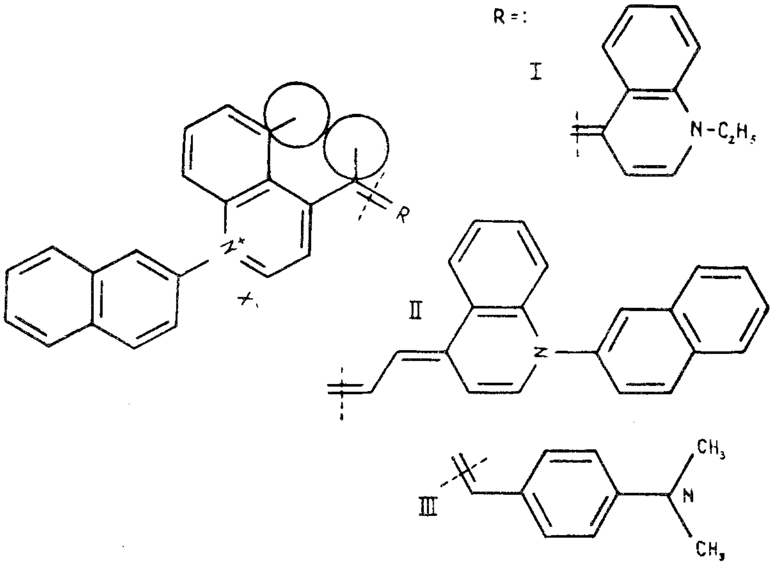


Fig. 1. Graphical representations of dye molecules: 1) (1-β-naphthylquinoline-4)-(1'-ethylquinoline-4') monomethinecyanine perchlorate; 2) bis(1-β-naphthylquinoline-4)trimethinecyanine perchlorate; 3) (1-β-naphthylquinoline-4)-p-dimethylaminostyrene perchlorate.

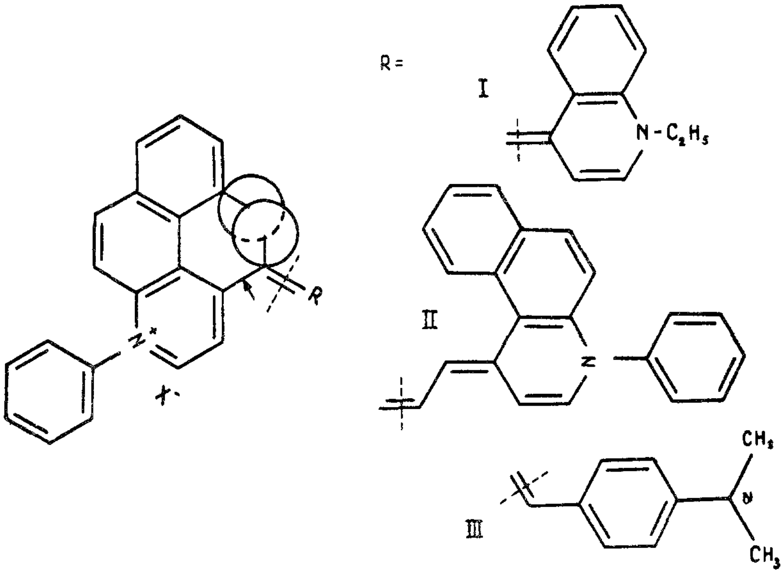


Fig. 2. Graphical representation of dye molecules: 1) (1-phenyl-5,6-benzoquinoline-4)-(1'-ethylquinoline-4')monomethinecyanine perchlorate; 2) bis(1-phenyl-5,6-benzoquinoline-4)trimethinecyanine perchlorate; 3) (1-phenyl-5,6-benzoquinoline-4)-p-dimethylaminostyrene perchlorate.

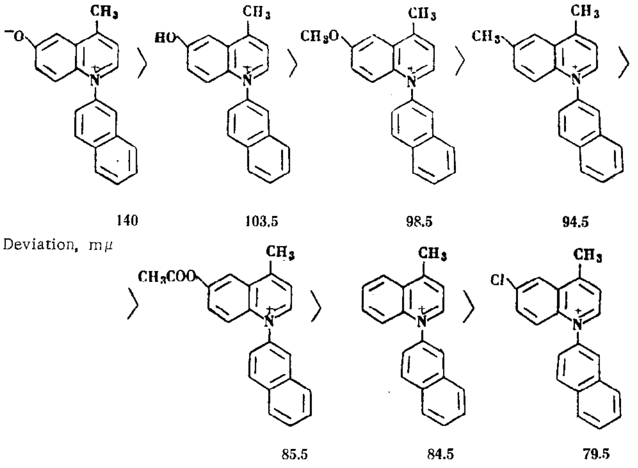
with the corresponding isomers and analogs [3]. Replacement of N-ethyl by phenyl and β-naphthyl gives rise to 36 and 40 mμ bathochromic shifts of the absorption maximum respectively (dyes XXVII, XXVI, and XIII). Introduction of electropositive substituents into position 6 of the quinoline ring of dye XIII gives rise to hypsochromic shifts of 5 to 44 mμ (dyes XIV, XV, and XXV), while introduction of electronegative ones deepens the color by 3 to 8 mμ (dyes XVI and XVIII).

The styrenes XIII–XVIII, XXV synthesized are more substantially absorbing than their isomers with a benzoquinoline ring.

It can be seen that in all cases the order of the substituents with respect to shift of absorption maximum stays the same: $H < Cl < OCOCH_3 < CH_3 < OCH_3 < OH < O^-$.

With monomethine- and trimethinecyanines there is deepening of color, while with quinostyrenes electropositive substituents brighten the color, and electronegative ones deepen it, the action of the second (Cl, AcO) being considerably less than that of the first (CH_3, CH_3O, OH, O^-).

Comparing quinostyrene dyes XIII–XVIII, XXV with the corresponding symmetrical ones (Table 7) (B and C), deviations are observed, the values of these characterizes the difference in basicity between the two rings entering into the composition of the unsymmetrical dyes [11, 12]. The data show that the basicity of the quinoline rings with N-β-naphthyl is almost equal to the basicity of the N-phenylquinoline ring (dyes XIII and XXVI) and considerably less than the basicity of the N-ethylquinoline one (dye XXVII). Quinoline rings with N-β-naphthyl group, entering into the composition of the quinostyrene molecule, can be arranged in the following order of decreasing basicity (decreasing deviation).



This order agrees with general views about basicity based on electronic considerations.

It is of interest to note that dyes with hydroxyl groups (III, IX, and XV) are completely insoluble in chloroform, while the ethers and esters (R = MeO and AcO) (dyes V and IV, XI and X, XVII and XVI) are readily soluble in it. The hydroxyl group is quite readily acetylated by heating the appropriate dye in acetic anhydride. Further all dyes are readily soluble in ethanol, acetone, and pyridine, insoluble in ether, water, hydrocarbons, and carbon tetrachloride.

EXPERIMENTAL

Dyes I–III, V–VI were prepared by heating on a water-bath 0.01 mole of the appropriate 1-β-naphthyllepidinium salt with 0.02 mole 1-ethylquinolinium iodide dissolved in 25 ml dry ethanol, in the presence of 0.024 mole 10% ethanolic KOH (or 0.02 mole dry K_2CO_3), the reaction mixture being boiled moderately for 15 min.

The reaction products were left overnight, then poured into dilute aqueous $NaClO_4$ or KI. The flocculent precipitate was filtered off, washed with water, and air-dried. It was further purified by chromatographing on Al_2O_3, the eluent and developer for the quaternary salts being EtOH-benzene (1 : 9). The dyes were washed out with 95% EtOH, the solution evaporated, and recrystallization effected from EtOH.

Dye IV was synthesized from 1.1 g compound III by heating with 10 ml Ac_2O for 30 min.

Dyes VII–IX, XI–XII were prepared by heating together for 1 hr on an oil-bath, with moderate refluxing, 0.01 mole of the appropriate 1-β-naphthyllepidinium salt, 0.05 mole orthoformic ester, and 7 ml dry pyridine. The reaction products were poured into dilute aqueous $NaClO_4$ or KI. The precipitate was filtered off, washed with water, and recrystallized from EtOH.

Dye X was prepared by boiling 7 g compound IX with 20 ml Ac_2O for 30 min.

Dyes XIII, XIV, XVI–XVIII. 0.01 mole of the appropriate 1-β-naphthyllepidinium salt, 0.015 mole p-dimethylaminobenzaldehyde, and 10 ml Ac_2O were refluxed together for 15 min in a flask in an oil-bath at 140°. The dye was precipitated with ether and recrystallized from EtOH. Dye XV was similarly prepared in pyridine.

Dyes IV, X, and XVI were purified by precipitating from $CHCl_3$ with ether.

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