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RESEARCHES ON SYNTHETIC DYES
LV. Symmetrical Trimethinecyanine Dyes from N-Aryl, 5, 6-Benzolepidinium Salts*

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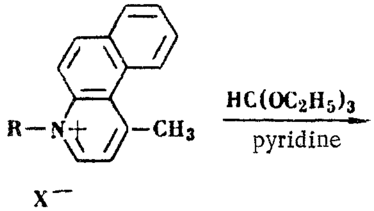
Reaction of 1-alkyl and 1-aryl-5, 6-benzolepidinium quaternary salts with orthoformic ester in pyridine gives symmetrical 9-carbocyanine dyes hitherto undescribed in the literature. The effects of substituents at the para position in the N-phenyl ring resemble the effects of the same in the heterocyclic ring, indicating that these substituents are conjugated with the latter. The molecules of the dyes synthesized are shown to exhibit steric hindrance.

The definite scientific importance of quinocyanines [1-21] made it of interest to study the reaction of 1-aryl-5, 6-benzolepidinium salts with orthoformic ester



As these onium compounds have an electrophilic radical at the hetero atom, the hydrogens of the methyl group in the para position on the quinoline ring are more mobile than in the alkyl halogenides of lepidine [22]. Furthermore, chemical reaction of the compounds investigated is somewhat depressed by the occurrence of steric hindrance between the 5, 6-benzo structure and the Me group at position 4 in the quinoline ring [23]. Here reaction is slower and yields lower than in the case of N-aryllepidinium salts lacking the 5, 6-benzo group.

Table 1 shows the dyes synthesized. Comparison of absorption maxima** shows that para substituents in the N-phenyl ring have rather a considerable effect, and that they lie in the same order as the values of the constant σ in the Hammett equation (Table 2). Obviously, this indicates some conjugation of the N-phenyl ring with the heterocyclic one, despite steric hindrance. Other carbocyanines exhibit [25, 26] a like effect for these substituents. Replacement of methyl by phenyl (dyes I and II, Table 1) results in a bathochromic shift of the absorption maximum by 17 mμ, and in a decrease in intensity. The β-naphthyl group (dyes I and IX) causes a shift in the absorption maximum by 35 mμ towards the red, and an analogous hypsochromic effect. Comparison of dyes I-IX with the isomeric carbocyanines synthesized from N-aryl-5, 6-benzoquinaldine salts [17, 25-29] shows a 76-97 mμ bathochromic absorption band shift and a decrease in intensity, due to lengthening of the conjugated chain by the vinyl group inside the ring and to steric hindrance. The steric factors are conditioned by the 5, 6-benzo groups in the quinoline rings, which create them from the basic conjugated chain. Rotation of the quinoline rings round, in the main, double bonds, which occurs in the symmetrical dyes, [30], gives rise to a bathochromic effect, while departure from coplanarity entails a lowering of absorption intensity [31].

It is of interest to note that a dye with a hydroxyl group (IV) is quite insoluble in chloroform, while an ether and an ester derived from it (VI, V) are readily soluble in that solvent. Acetylation of the OH group can be achieved rather easily, even by simply heating the hydroxylic dye with acetic anhydride. Further, all the dyes are readily soluble in ethanol, acetone, and pyridine, but insoluble in water, ether, and carbon tetrachloride.

Experimental

Bis(1-methyl-5, 6-benzoquinoline-4) trimethinecyanine perchlorate (I). 3.1 g 1-methyl-5, 6-benzolepidinium perchlorate, 7 ml orthoformic ester, 8 ml pyridine, and 3 drops of acetic anhydride were placed in a small flask fitted

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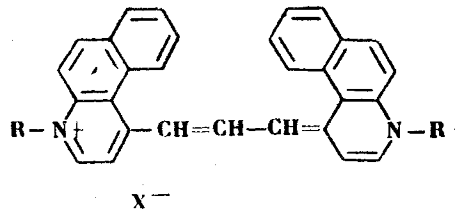
*For Part LIV see [23].

**Absorption spectra were determined in ethanol using an SF-4 spectrophotometer.

Table 1

Bis(1-aryl-5, 6-benzoquinoline-4) trimethinecyanine Perchlorates and Iodides



Compound no.	R	X	Reaction time, hr	Mp (decomp), solvent - ethanol), °C	λ_{max}, mμ	lg ε	Formula	Found, %		Calculated, %		Yield, %
								Halogen	N	Halogen	N	
I	CH_3	ClO_4	2,0	186—188 ethanol + acetone 1 : 1	710	4,75	$C_{31}H_{25}ClN_2O_4$	6.68 6.86	5.29 5.38	6.75	5.33	52
II	C_6H_5	ClO_4	1,5	129—131	727	4,49	$C_{41}H_{29}ClN_2O_4$	5.39 5.50	4.27 4.38	5.46	4.32	72
III	p-$CH_3C_6H_4$	ClO_4	1,5	191—193	730	4.72	$C_{43}H_{33}ClN_2O_4$	5.18 5.21	4.30 4.29	5.24	4.37	75
IV	p-HOC_6H_4	I	2,0	209—211	742	4,66	$C_{41}H_{29}IN_2O_2$	17.87 17.95	3.89 3.99	17.91	3.95	64
V	p-$CH_3COOC_6H_4$	I	1,5	215—217 chloroform	737	4,62	$C_{45}H_{33}IN_2O_4$	16.10 15.96	3.47 3.60	16.01	3.53	82
VI	p-$CH_3OC_6H_4$	ClO_4	1.7	165—167	739	4,69	$C_{43}H_{33}ClN_2O_6$	4.91 4.96	3.90 3.88	5.00	3.95	68
VII	p-ClC_6H_4	ClO_4	1.5	170—172	733	4,71	$C_{41}H_{27}Cl_3N_2O_4$	14.87 14.75	3.98 3.94	14.81	3.90	69
VIII	p-$O_2NC_6H_4$	I	2,0	153—155	743	4.68	$C_{41}H_{28}IN_4O_4$	17.93 17.81	7.81 7.96	17.86	7.88	66
IX	β-$C_{10}H_7$	ClO_4	1.3	194—196	745	4,48	$C_{49}H_{33}ClN_2O_4$	3.79 3.83	4.78 4.70	3.74	4.73	59

with a reflux condenser, and boiled gently for 2 hr. The reaction mixture gradually turned green, and at the end of heating, it had thickened. After heating it was allowed to stand for 24 hr at room temperature, and then poured into dilute sodium perchlorate solution. The precipitate formed was filtered off, washed with water, then with ethanol until all the pyridine was removed, and recrystallized to constant melting point from ethanol-acetone. It formed a green finely divided crystalline powder with a metallic reflex. Yield 2.7 g (52%). Mp 186-188° (decomp). An ethanol solution was green. Dyes II-IV and VI-IX were similarly synthesized, but shorter heating times were used.

Table 2

Bathochromic Shift of the Absorption Maximum of Symmetric Carbocyanines

Compound No.	p-substituent in the N-phenyl ring	Bathochromic effect	Hammett's σ [24]
X	O^-	44	−0.71
IV	OH	15	−0.52
VI	CH_3O	12	−0.27
III	CH_3	3	−0.17
V	CH_3COO	1	—
II	H	0	0
VIII	O_2	16	1.27
VII	Cl	6	0.23

Bis(1-p-acetoxyphenyl-5, 6-benzoquinoline-4) trimethinecyanine iodide (V). a) 4.1 g 1-p-hydroxyphenyl-5, 6-benzolepidinium iodide, 7 ml orthoformic ester, and 7 ml acetic anhydride were refluxed gently together for 1 hr 30 min. The reaction products were left for 24 hr, the pale green crystals formed filtered off, washed with ether, and recrystallized from chloroform. Yield 5.1 g (65%), mp 215-217° (decomp). An ethanol solution was pale green.

b) 7 g bis(1-p-hydroxyphenyl-5, 6-benzoquinoline-4) trimethinecyanine iodide (IV) and 20 ml acetic anhydride in a flask with a reflux condenser were heated for 30 min at 140° in a paraffin bath, after which the reaction products were left for 24 hr at 0°. The crystals which separated were filtered off, washed with ether, and recrystallized from chloroform. Yield 6.5 g (82%), mp 215-217° (decomp). The dye was identical with that prepared above, mixed mps undepressed.

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