STUDIES IN THE FIELD OF SYNTHETIC DYES

LXIX. Unsymmetrical Carbocyanines from N-Arylquinolinium Salts*

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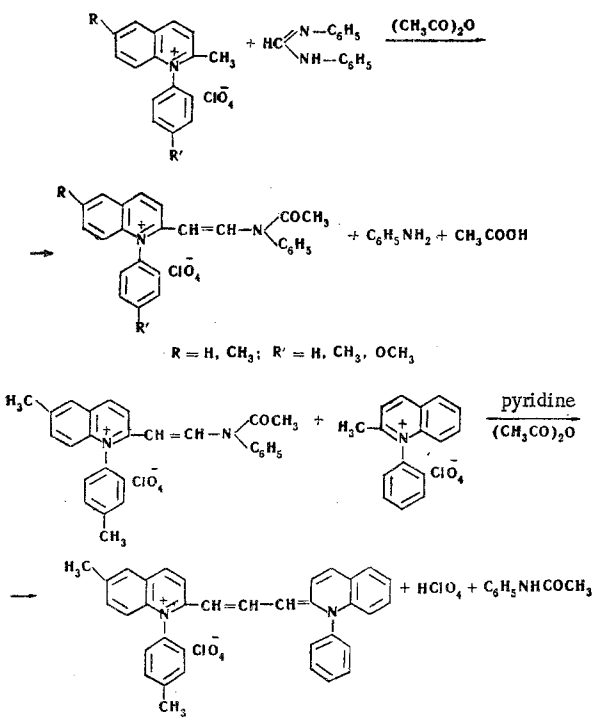
β-Acetanilidovinyl derivatives of the quinoline series have been synthesized, and their condensation with quaternary salts of heterocyclic bases has given 12 unsymmetrical carbocyanines.

Unsymmetrical carbocyanines containing a quinoline ring with an aryl radical on the nitrogen atom have been studied little. In order to investigate the properties of unsymmetrical dyes, we have synthesized β-acetanilidovinyl derivatives of the quinoline series [1–3] (see table).

When diphenylformamidine was condensed with N-p-tolyl-6-methylquinaldinium perchlorate, N-p-methoxyphenylquinaldinium perchlorate, and N-phenyllepidinium perchlorate in acetic anhydride, the β-acetanilidovinyl derivatives were obtained with yields of 52–78%,



Unsymmetrical carbocyanines are of interest in the study of questions of the asymmetry of molecules. It is known [3, 4, 8–10] that molecules of unsymmetrical dyes formed by heterocycles differ markedly in basicity and have absorption maxima displaced hypsochromically from the additive value for the corresponding symmetrical dyes as a consequence of a disturbance of the symmetry of the equivalence of the molecules. As a result of the disturbance of symmetry it must be assumed that there is a decrease in the delocalization of the π-electrons and also in the equivalence of the bonds in the chain of conjugation. When unsymmetrical molecules are formed from heterocycles of similar basicities, the reverse effect is found.

It follows from the table that heterocycles at the ends of a trimethine chain, in our case carbocyanines, do not differ greatly in basicity and therefore in a number of dyes we observe a small hypsochromic and bathochromic effect which does not go beyond the limits of error of the optical measurements. Thus, the greatest shift in the absorption maximum into the long-wave region by 3.5 mμ is found for carbocyanine IV with a substituent in the para position of the phenyl nucleus (p-OCH_3), while dyes II and IX show no deviation from additivity at all.

Consequently, only a very slight hypsochromic or bathochromic shift from the additive value occurs with a disturbance in the symmetry of the molecule of carbocyanines containing quinoline rings with aryl radicals on the nitrogen atoms, the basicities of which are affected only by the nature of the substituents in the quinoline and phenyl nuclei.

EXPERIMENTAL

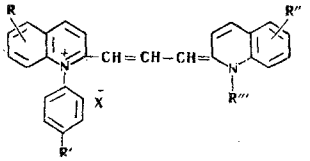
N-Phenyl-2-β-acetanilidovinyl)quinolinium perchlorate was obtained as described previously [4]. Yield 80.0%.

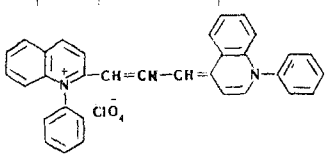
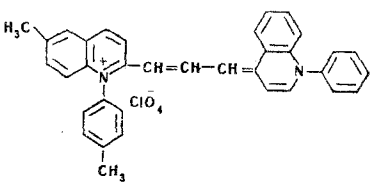
N-p-Tolyl-2-(β-acetanilidovinyl)-6-methylquinolinium perchlorate. A mixture 0.5 g of N-p-tolyl-6-methylquinaldinium perchlorate, 0.4 g of diphenylformamidine, and 2 ml of acetic anhydride was heated at a gentle boil for 30–40 min. At the end of the reaction, the mixture had acquired a bright green coloration, and crystals of N-p-tolyl-2-(β-acetanilidovinyl)-6-methyl-quinolinium perchlorate had deposited. (The yield of the product is affected by the purity of the starting materials). After the reaction mass had cooled, the crystals were filtered off, and were washed on the filter with ethanol and then with ether. Yield 0.54 g (77.7%). Mp 233°–234° C. Found, %: N 5.57, 5.60. Calculated for $C_{27}H_{25}ClN_2O_5$, %: N 5.68.

The following compounds were obtained similarly: N-(p-methoxyphenyl)-2-(β-acetanilidovinyl)quinolinium perchlorate (yield 52%: mp 194° C. Found, %: N 5.71, 5.76. Calculated for $C_{26}C_{23}ClN_2O_5$, %: N 5.60), and N-phenyl-2-(β-acetanilidovinyl)lepidinium perchlorate (yield 75%; mp 192° C. Found, %: N 6.12, 6.07. Calculated for $C_{25}H_{21}ClN_2O_5$, %: N 6.00).

(1-Phenyl-2-quinolyl)(6'-methyl-1'-p-tolyl-2'-quinolyl)trimethinecyanine perchlorate. A mixture of 0.5 g (0.001 mole) of N-phenyl-2-(β-acetanilidovinyl)-quinolinium perchlorate, 0.56 g (0.0016 mole) of 6-methyl-1-p-tolylquinaldinium perchlorate, and 4 ml of pyridine was heated under reflux for 10 min, and then 1 ml of acetic anhydride was added and the mixture was heated for an additional 15 min. After the cooling of the reaction mixture, the dye was precipitated with ether. Two recrystallizations from ethanol gave the dye in the form of small green crystals with mp 275°–276° C.

*For communication LXVIII, see [12].



Dye						λ_{max}, nm		Mp, °C	Empirical formula	N, %		Yield, %
No.	R	R′	R″	R‴	X	found	calculated[a]			found	calculated	
I	H	H	6-CH_3	*p*-$CH_3C_6H_4$	ClO_4	617.5	615.5	275—276 (decomp.)	$C_{35}H_{29}ClN_2O_4$[b]	—	—	50.0
II	H	H	H	α-$C_{10}H_7$	I	616	616	255—256 (decomp.)	$C_{37}H_{27}IN_2$[c]	—	—	62.5
III	H	H	5.6- benzo	β-$C_{10}H_7$	ClO_4	631	634	253—254	$C_{41}H_{29}ClN_2O_4$[d]	—	—	44.6
IV	H	H	H	*p*-$CH_3OC_6H_4$	ClO_4	619	615.5	197—198	$C_{34}H_{27}ClN_2O_5$	4.79; 4.71	4.84	48.0
V	H	H	5 6-benzo	C_6H_5	ClO_4	630	628	277—278 (decomp.)	$C_{35}H_{29}ClN_2O_5$	4.37; 4.30	4.45	51.0
VI	H	H	6-OH	*p*-HOC_6H_4	ClO_4	627	626	226 –227	$C_{33}H_{26}ClN_2O_6$	4.95; 5.00	4.80	89.0
VII	6-CH_3	CH_3	H	*p*-$CH_3OC_6H_4$	ClO_4	617	617	270—271	$C_{36}H_{31}ClN_2O_5$	4.70; 4.57	4.62	82.0
VIII	6-CH_3	CH_3	5.6-benzo	*p*-$CH_3OC_6H_4$	ClO_4	630	629.5	265—266	$C_{40}H_{33}ClN_2O_5$	4.20; 4.31	4.26	78.0
IX	6-CH_3	CH_3	5.6-benzo	C_6H_5	ClO_4	631	631	195—197	$C_{39}H_{31}ClN_2O_4$	4.40; 4.51	4.45	61.0
X	5.6-benzo	H	H	*p*-$CH_3OC_6H_4$	ClO_4	633	631	263—264	$C_{38}H_{29}ClN_2O_5$	4.39; 4.30	4.45	58.0
XI						668	666	244—245	$C_{33}H_{25}ClN_2O_4$	4.97; 5.03	5.10	70.0
XII						669.5	667.5	260 (decomp.)	$C_{35}H_{29}ClN_2O_4$	4.82; 5.09	4.90	82.0

[a]Arithmetic mean of λ max of the symmetrical dyes. [b]Found, %: Cl 6.09, 6.24. Calculated, %: Cl 6.14. [c]Found, %: I 20.17, 20.08. Calculated, %: I 20.27. [d]Found, %: Cl 5.53, 5.50. Calculated, %: Cl 5.46.

Yield 0.31 g (50%). λ_{max} 618 nm. Found, %: Cl 6.09, 6.24. Calculated for $C_{35}H_{29}ClN_2O_4$, %: NCl 6.14.

The other carbocyanines were synthesized similarly.

The purity of the carbocyanines was checked by thin-layer chromatography.

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