STUDIES IN THE FIELD OF SYNTHETIC DYES

LXXVIII. Synthesis of Quinohemicyanines

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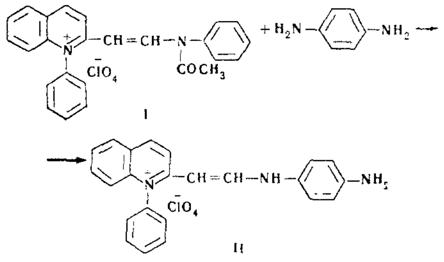
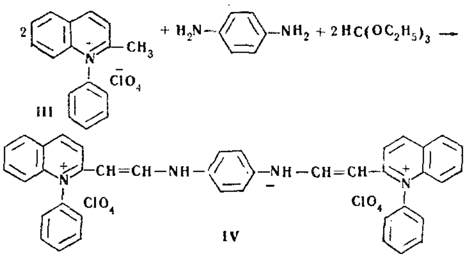
By condensation of the perchlorates of N-phenyl-2-(β-acetanilidovinyl)quinaldine (I) and N-phenylquinaldine (III) with aromatic amines (o-, m-, p-phenylene diamine, benzidine, o-tolidine, dianisidine, 4,4'-azoaniline, aminoazobenzene, and aniline) symmetrical and asymmetrical quinohemicyanines not previously described in the literature were synthesized and their absorption spectra in the visible region were determined.

In studies of the relationship between the colors of organic molecules and their structure it was of interest to synthesize hemicyanines of the quinoline series which had not been previously described in the literature and which contained aromatic radicals on the heterocyclic nitrogen atom. Hemicyanines benzoxazole, benzothiazole, selenazole, which have been used as sensitizers and desenstizers of silver halide emulsions, and also as dyes for acetate silk [1,2] have been partly described in the literature. Hemicyanines, aminovinyl derivatives of quaternary heterocyclic salts, are intermediate products during the synthesis of certain cyanine dyes which, because of their asymmetrical structure, are useful in correlating structure with color in organic compounds [3,4]. In order to obtain new members of this class of compound and to study their optical properties and biological activity, the perchlorate of N-phenyl-2-(β-acetanilidovinyl)-quinaldine (I) [3] and the perchlorate of N-phenylquinaldine (III) were condensed with the aromatic diamines, aniline, 4,4'-isoaniline, and aminoazobenzene.

The hemicyanines of the same kind as the perchlorate of N-phenyl-2(β-p-aminoanilinovinyl) quinaldine (II) were synthesized according to the following scheme:



The hemicyanines of the type bis-β,β'-(N-phenyl-2-vinylquinaldine perchlorate)-p-phenylene diamine (IV) were obtained by condensing the perchlorate of N-phenylquinaldine with diamines in the presence of orthoformic ether according to the scheme and also by counter synthesis from compound(I) using the same diamines.



Type (IV) hemicyanines were identified by their absorption maxima and melting points in the displacement test. Spectral characteristics of the synthesized hemicyanines are presented in Table 1.

It is apparent from the data in Table 1 that when the group p-$NHC_6H_4NH_2$ (II, 484 nm) is introduced into the conjugated chain, there is a strong displacement of the absorption maximum into the shortwave region, as seen by comparing II with 1-phenylquinoline-2-(p-aminostyryl) perchlorate (536 nm) [5]. This is caused by the appearance of a new pair of mobile unshared electrons of the NH group nearer to the electron acceptor which sharply decreases the displacement constant (not dependent on the action of light) of the electrons in the portion between the old and new electron donor substitutes. This action is equivalent to a shortening of the conjugated chain and leads to an increase in color.

Introduction of benzidine into the conjugated chain is scarcely reflected in the absorption maxima of the hemicyanines V and VI in comparison with the dyes II and IV. This phenomenon is possibly on account of the partial damage to the planar structure of the hemicyanines as a result of the possible rotation around the single bond uniting the two benzene rings, which limits the interaction of the neighboring π-electrons [6]. When the CH_3 group was introduced into benzidine in the ortho-position to the imino group in the dyes VIII and VII, there was an increase in color over compounds V and VI, which illustrates that the phenomenon is also associated with possible difficulties in coplanarity of the hemicyanines. Substitutes which possess a mesomer effect have a stronger action. Thus, the group OCH_3 in the position ortho to the imino group in the benzidine part of the molecule (IX and X) causes a marked deeping in color (compared to V and VI). Introduction of the azo group into the conjugated ring (XI, XII) has almost no effect on the position of the absorption maximum. However, when the primary amino group is substituted for the tertiary group there is a strong deepening in color (cf. XII and XIII).

Table 1

Spectral Characteristics of Hemicyanines of the Quinoline Series

Compound	Name	λ_{max}, nm	$\varepsilon_{max} \times 10^4$	$\Delta\lambda_{max}$, nm
II	N-Phenyl-2-(β-p-aminoanilinovinyl)quinaldine perchlorate	484	2.57	a) −14; b) −91; c) −48
IV	Bis-β,β'-(N-phenyl-2-vinylquinaldineperchlorate)-p-phenylene diamine	502	2.95	d) −47
V	N-Phenyl-2-(β-aminobenzidinovinyl)quinaldine perchlorate	486	2.48	a) −12; b) −89; c) −46
VI	Bis-β,β'-(N-phenyl-2-vinylquinaldine perchlorate)benzidine	504	2.97	d) −45
VII	N-Phenyl-2-(β-p-aminotolidinovinyl)quinaldine perchlorate	479	2.57	a) −19; b) −96; c) −53
VIII	Bis-β,β'-(N-phenyl-2-vinylquinaldine perchlorate)-o-tolidine	486	2.51	d) −60.5
IX	N-Phenyl-2-(β-p-aminodianisidine)quinaldine perchlorate	498	1.20	a) 0; b) −77; c) −33
X	Bis-β,β'-(N-phenyl-2-vinylquinaldine perchlorate)dianisidine	510	1.30	d) −46
XI	N-Phenyl-2-(β-azobenzolanilinovinyl)quinaldine perchlorate	484	3.00	a) −14; b) −91; c) −48
XII	N-Phenyl-2-(β-p-aminoazoanilinovinyl)quinaldine perchlorate	488	1.90	a) −10; b) −87; c) −44
XIII	N-Phenyl-2-(β-p-diethylaminoazoanilinovinyl)quinaldine perchlorate	534	3.30	b) −41
XIV	N-Phenyl-2-(β-m-aminoanilinovinyl)quinaldine perchlorate	486	2.30	—
XV	Bis-β,β'-(N-phenyl-2-vinylquinaldine perchlorate)-m-phenylene diamine	420	0.10	—
XVI	N-Phenyl-2-(β-o-aminoanilinovinyl)quinaldine perchlorate	471	1.94	—
XVII	Bis-β,β'-(N-phenyl-2-vinylquinaldine perchlorate)-o-phenylene diamine	—	—	
XVIII	N-Phenyl-2-(β-anilinovinyl)quinaldine perchlorate	450	2.70	a) −48.5

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*Neutral solutions in ethanol; spectra were determined in an SF-2M apparatus.

**$\Delta\lambda_{max}$ was calculated in relation to the absorption maxima: a) bis(N-phenyl-2-quinoline)trimethine cyanine perchlorate [7]; b) bis(N-phenyl-2-quinoline)trimethine cyanine perchlorate [7] and N-phenylquinoline-2(p-aminostyryl)perchlorate [5]; c) bis(N-phenyl-2-quinoline)trimethine cyanine perchlorate [7] (XVI); d) bis(N-phenyl-2-quinoline)trimethine cyanine perchlorate [7] and the corresponding dyes (II, V, VII, IX, XI). Minus sign = hypsochromic displacement.

Table 2

Hemicyanines of the Quinoline Series

Compound	Method of synthesis	Original amine, g	Temperature of experiment, °C	Mp, °C	Empirical formula	N, %		Yield, %
						Found	Calculated	
V	—	Benzidine, 0.54	80.0	157.0	$C_{29}H_{24}ClN_3O_4$	8.13; 8.25	8.17	72.7
VI	A	Benzidine, 0.09	80.0	285 (decomp.)	$C_{46}H_{36}Cl_2N_4O_8$	6.59; 6.56	6.64	62.3
	B	Benzidine, 0.21	90.0	285.6 (decomp.)	$C_{46}H_{36}Cl_2N_4O_8$	6.58; 6.70	6.64	57.0
VII	—	o-Tolidine, 0.62	85.0	178.0	$C_{31}H_{28}ClN_3O_4$	7.67; 7.80	7.77	80.8
VIII	A	o-Tolidine, 0.10	85.0	260.0	$C_{48}H_{40}Cl_2N_4O_8$	6.39; 6.36	6.43	44.2
	B	o-Tolidine, 0.27	100.0	259.9	$C_{48}H_{40}Cl_2N_4O_8$	6.45; 6.49	6.43	58.7
IX	—	Dianisidine, 0.68	140—150	267.0 (decomp.)	$C_{31}H_{28}ClN_3O_6$	7.27; 7.36	7.33	89.2
X	B	Dianisidine, 0.30	160—165	294.0 (decomp.)	$C_{48}H_{40}Cl_2N_4O_{10}$	6.10; 6.15	6.20	49.7
XI	—	Aminoazobenzene, 0.60	60.0	140.0	$C_{29}H_{23}ClN_4O_4$	10.54; 10.59	10.63	92.3
XII	—	4,4'-Azoaniline, 0.64	65.0	161.0	$C_{29}H_{24}ClN_5O_4$	12.85; 12.97	12.91	89.7
XIII	—*	p-Nitrosodiethylaniline, 0.16	55.0	210.0	$C_{33}H_{32}ClN_5O_4$	11.81; 11.77	11.72	43.5
XIV	—	m-Phenylene diamine, 0.30	60.0	215.0	$C_{23}H_{20}ClN_3O_4$	9.52; 9.47	9.60	29.0
XV	A	m-Phenylene diamine, 0.055	80.0	227.0	$C_{40}H_{32}Cl_2N_4O_8$	7.39; 7.34	7.30	35.0
	B**	m-Phenylene diamine, 0.14	95.0	227.0	$C_{40}H_{32}Cl_2N_4O_8$	7.26; 7.38	7.30	30.0
XVI	—	o-Phenylene diamine, 0.30	60—70	188.0	$C_{23}H_{20}ClN_3O_4$	9.69; 9.57	9.60	50.0
XVII	B**	o-Phenylene diamine, 0.14	75.0	195.0	$C_{40}H_{32}Cl_2N_4O_8$	7.24; 7.32	7.30	62.5
XVIII	—**	Aniline, 0.25	80.0	162.0	$C_{23}H_{19}ClN_2O_4$	6.57; 6.71	6.62	50.3

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*From 0.42 g of hemicyanine II.

**0.2 g of orthoformic ether was taken.

The quinohemicyanines are readily soluble in acetone, pyridine, dioxane, ethanol, and acetic acid (except dyes XV and XVII) and are almost insoluble in benzene and toluene. All quinohemicyanines develop solvatochroism. The dyes can be isolated in the form of crystals and powders and are dark red in color.

EXPERIMENTAL

N-Phenyl-2-(β-p-aminoanilinovinyl)quinaldine perchlorate (II). A 0.55 g quantity (0.0012 mole) of N-phenyl-2-(β-acetanilidovinyl) quinaldine perchlorate (I) and 0.30 g (0.003 mole) of p-phenylene diamine were dissolved in 20 ml alcohol and heated in a water bath with reflux condensation for 20 minutes. When the solution cooled, dark claret shining crystals were formed, mp 230° C (decomp. from ethanol). Yield, 77.1%. Found, %: N 9.71, 9.80. Calculated for $C_{23}H_{20}ClN_3O_4$, %: N 9.60.

Bis-β,β'-(N-Phenyl-2-vinylquinaldine perchlorate)-p-phenylene diamine (IV). A. In a water bath 0.46 g (0.001 mole) of compound I and 0.55 g (0.0055 mole) of p-phenylene diamine in 25 ml of ethanol were heated for 40 minutes. On cooling of the solution dark red crystals were formed, mp 297°–298° C (from pyridine). Yield, 77.7%. Found, %: N 7.27, 7.20. Calculated for $C_{40}H_{32}Cl_2N_4O_8$, %: N 7.30.

B. A 0.87 g quantity (0.002 mole) of N-phenylquinaldine perchlorate (III), 0.14 g (0.0014 mole) p-phenylene diamine, and 1 ml orthoformic ether were heated in a reflux condenser at 160°–170° C for 1 minute and then at 80°–90° C for 30 minutes. The reaction mass was dissolved by heating in alcohol and was then filtered. After two-fold crystallization from alcohol, the separated crystals melted at 298°–298.5° C. Yield, 57.1%. Found, %: N 7.33, 7.40. Calculated for $C_{40}H_{32}Cl_2N_4O_8$, %: N 7.30.

The remaining hemicyanines (Table 2) were synthesized similarly from 0.46 g of compound I (method A) or from 0.86 g of compound III and 0.15 g of orthoformic ether (method B).

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