CYANINE DYES BASED ON 2-PHENYL-3,4-DIMETHYL-5,6-BENZOQUINOLINE

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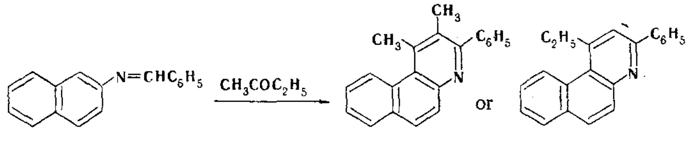
It is shown that the only product in the condensation of benzylidene-2-naphthylamine with methyl ethyl ketone is 2-phenyl-3,4-dimethyl-5,6-benzoquinoline, on the basis of the quaternary salt of which cyanine dyes were synthesized.

In our current research we have investigated the condensation of benzylidene-2-naphthylamine (I) with methyl ethyl ketone. According to the previously expressed [1] concepts regarding the reaction mechanism, one might have expected the formation of two products – 2-phenyl-4-ethyl-5,6-benzoquinoline and 2-phenyl-3,4-dimethyl-5,6-benzoquinoline – theoretically as a result of the condensation and subsequent cyclization. However, the only reaction product proved to be 2-phenyl-3,4-dimethyl-5,6-benzoquinoline (II). Consequently, the condensation of methyl ethyl ketone at the azomethine bond occurs with the participation of the methylene group. The presence in the PMR spectra of benzoquinoline II of signals of two nonequivalent methyl groups at 2.41 and 2.92 ppm confirms the proposed structure.



I

II

Cyanine dyes, the characteristics of which are presented in Table 1, were synthesized from 2-phenyl-3,4-dimethyl-5,6-benzoquinoline methiodide (III).

The absorption maxima of the dyes obtained are shifted to the long-wave region of the spectrum as compared with analogous dyes – derivatives of other heterocyclic bases; this is apparently associated with the introduction of phenyl and methyl groups into the dye molecules.

EXPERIMENTAL

The absorption spectra of alcohol solutions of the dyes were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of CCl_4 solutions were recorded with an HA-100 spectrometer with tetramethylsilane as the internal standard.

2-Phenyl-3,4-dimethyl-5,6-benzoquinoline (II). A 5.4 ml (0.06 mole) sample of methyl ethyl ketones, 0.6 ml of concentrated HCl, and 0.6 ml of nitrobenzene were added to 4.6 g (0.02 mole) of I in 35 ml of alcohol, and the mixture was refluxed on a water bath for 2 h. It was then cooled and neutralized with NH_4OH. The resulting oil was washed repeatedly with water, dissolved in alcohol, and precipitated with ether to give 10% (twice from alcohol) of colorless needles with mp 142-144°. Found, %: C 89.2; H 6.0; N 5.0. $C_{21}H_{17}N$. Calculated, %: C 89.0; H 6.0; N 4.9. UV spectrum, λ_{max} (log ε): 258 (4.63), 340 (3.66), 356 (3.71) nm.

2-Phenyl-3,4-dimethyl-5,6-benzoquinoline Methiodide (III). This compound was prepared by heating 1.25 g of benzoquinoline II with 3 ml of methyl iodide and 3 ml of acetic anhydride in a sealed ampule at

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TABLE 1. Characteristics of the Cyanine Dyes

Compound	mp, deg °C	Empirical formula	N, %		λ_{max}, nm	lg ε	Yield, %
			found	calc.			
IV	181—183	$C_{45}H_{37}N_2I$	3,86	3,82	780	4,75	11
V	274—275	$C_{35}H_{31}N_2I$	4,91	4,62	608	5,40	10
VI	166—167	$C_{33}H_{29}N_2I$	4,78	4,82	620	4,94	34
VII	243—245	$C_{31}H_{27}N_2IS$*	—	—	539	4,49	34
VIII	234—235	$C_{28}H_{24}N_2OS_2$ †	—	—	630	4,86	43
IX	165—167	$C_{31}H_{29}N_2I$	4,65	5,03	542	4,14	50
X	143—145	$C_{30}H_{24}NO_2I$	2,52	2,51	380	4,06	50

*Found, %: S 5.60. Calculated, %: S 5.46.

† Found, %: S 13.79. Calculated, %: S 13.69.

100° for 6 h. The yield of yellow prisms with mp 190-192° (from alcohol) was 90%. Found, %: N 3.0. $C_{22}H_{20}NI$. Calculated, %: N 3.3.

The dyes were obtained by standard methods for the preparation of this type of compound (for example, see [2]).

Bis(1,3-dimethyl-2-phenyl-5,6-benzo-4-quinolyl)trimethylidynecyanine Iodide (IV). A mixture of 0.42 g (0.001 mole) of methiodide III, 1 ml of ethyl orthoformate, 3 ml of pyridine, and three drops of acetic anhydride was heated at 140° for 3 h. The dye was precipitated with ether, chromatographed in chloroform on Al_2O_3, and crystallized from alcohol to give green needles (Table 1).

(1,3-Dimethyl-2-phenyl-5,6-benzo-4-quinolyl)-(1-ethyl-2-quinolyl)trimethylidynecyanine Iodide (V). A mixture of 0.21 g (0.5 mmole) of III, 0.21 g (0.5 mmole) of 2-(β-acetanilinovinyl)quinoline, 0.23 g of sodium acetate, and 3 ml of acetic anhydride was heated at 130° for 1.5 h. The precipitate was removed by filtration, washed with water, and crystallized from alcohol to give 0.02 g of shiny green needles.

1,3-Dimethyl-2-phenyl-4-[(1-ethyldihydro-4-quinolylidene)methyl]-5,6-benzoquinolinium Iodide (VI). A mixture of 0.21 g of III, 0.28 g (0.001 mole) of quinoline ethiodide, 0.14 g (0.001 mole) of anhydrous K_2CO_3, and 4 ml of absolute alcohol was heated from 1.5 h on a water bath. The dye was precipitated with aqueous KI solution, washed with water, chromatographed in chloroform on Al_2O_3, and crystallized from alcohol to give 0.1 g of violet crystals.

1,3-Dimethyl-2-phenyl-4-[(3-ethylbenzo-2-thiazolinylidene)methyl]-5,6-benzoquinolinium Iodide. This compound was similarly obtained from 0.21 g of III and 0.17 g of 2-methylmercaptobenzothiazole ethiodide in the presence of sodium acetate. The precipitate that formed on cooling was removed by filtration, washed with water, and crystallized from alcohol to give 0.1 g of violet-bronze needles.

3-Ethyl-5-[1,3-dimethyl-2-phenyl-5,6-benzodihydroquinolylidene-4-ethylidene]thiazolidene-2-thion-4-one (VIII). A mixture of 0.21 g of III, 0.15 g (0.5 mmole) of 3-ethyl-5-N-phenylacetamidomethylenerhodanine, and 0.2 g of sodium acetate in 4 ml of alcohol was refluxed for 2 h. The precipitate was removed by filtration, washed with water, and crystallized from alcohol to give 0.1 g of shiny green needles.

4-(p-Dimethylaminostyryl)-2-phenyl-3-methyl-5,6-benzoquinoline Methiodide (IX). This compound was obtained from 0.21 g of III and 0.1 g of p-dimethylaminobenzaldehyde by heating for 1.5 h in 3 ml of alcohol in the presence of three drops of piperidine. The dye was precipitated by ether, washed with water, and crystallized from alcohol (with the addition of ether) to give 0.14 g of fine violet crystals.

4-(3,4-Methylenedioxystyryl)-2-phenyl-3-methyl-5,6-benzoquinoline Methiodide (X). This compound was similarly obtained as yellow needles from 0.21 g of III and 0.12 g of piperonal.

LITERATURE CITED

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