SYNTHESIS AND SPECTRAL-GENERATIONAL CHARACTERISTICS OF PENTAMETHYLIDYNECYANINE DYES FROM 1-METHYL-3-ARYLBENZO[f]QUINOLINIUM SALTS

N. S. Kozlov, O. D. Zhikhareva,
V. A. Mostovnikov, and S. A. Batishche

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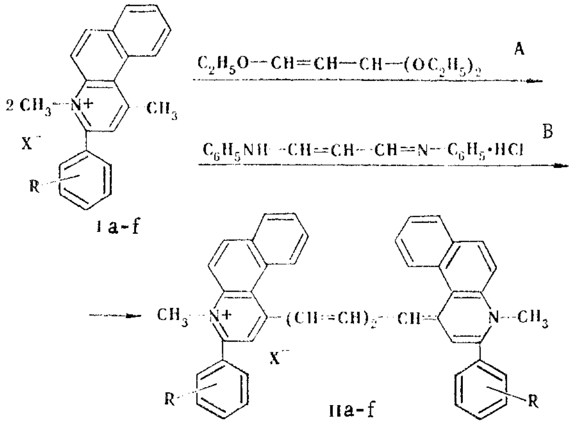
Pentamethylidynecyanine dyes were synthesized by the reaction of 1-methyl-3-(R-phenyl)benzo[f]quinolinium quarternary salts with 1,3,3-triethoxy-1-propene. Pentamethylidynecyanines substituted in the meso position of the polymethine chain were obtained by condensation of these salts with 1-anilino-2-methyl-3-dimethoxy-1-propene hydrobromide. The spectral and generational characteristics of the dyes were determined. It was shown that the presence of a phenyl group in the benzo-[f]quinoline ring of the dyes gives rise to a bathochromic shift of the absorption and generation maxima. The investigated dyes have high generation efficiencies that lie in the 20-30% range and in the 940-1010 nm spectral range.

Polymethine dyes have found application as sensitizers of photographic emulsions [1]. Quantum generators that make it possible to obtain powerful laser emission with any frequency over a broad spectral range have now been created on the basis of organic dyes [2]. Solutions of cyanine dyes are used as modulators of the quality factors of lasers [3].

The trimethylidynecyanine dyes that we previously synthesized [4] on the basis of 1-methyl-3-arylbenzo[f]quinolinium salts with an absorption spectrum at 750-780 nm are efficient laser media that generate in the 820-874 nm spectral range. In order to obtain compounds that are active in a longer-wave region of the spectrum we synthesized and studied pentamethylidynecyanine dyes.



I, II a R=H, b R=4-CH_3O, c R=3,4-(CH_2O_2), d R=3,4-$(CH_3O)_2$, e R=4-Cl, f R=4-F;
I a–d X=Tos, e, f X=I; II a–f X=I

Pentamethylidynecyanine dyes IIa-f were obtained by the reaction of 1-methyl-3-(R-phenyl)benzo[f]quinolinium methiodides or methyl-p-toluenesulfonates I with 1,3,3-triethoxy-1-propene or malonic dialdehyde dianil hydrochloride in pyridine in the presence of piperidine.

In addition to the pentamethylidynedyanines produced in the condensation by method B, we also isolated intermediates — δ-anilinobutadienyl derivatives of 3-arylbenzo[f]quinolinium salts III, the absorption maxima of which lie at 584-588 mm.

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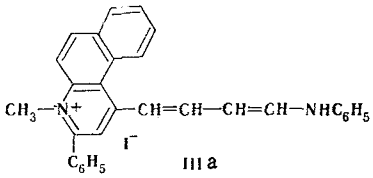
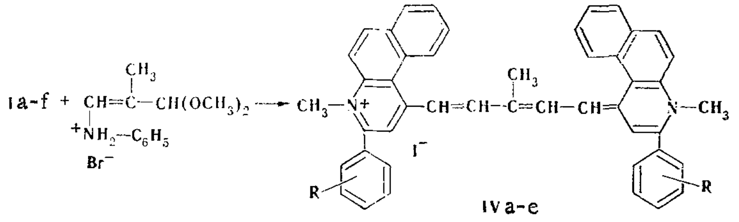
Thus 1-(δ-anilinobutadienyl)-3-penylbenzo[f]quinolinium methiodide IIIa was obtained by separation of the reaction of dyes IIIa and IIa by means of chromatography on aluminum oxide (elution with chloroform) and crystallization from ethanol.



IIIa

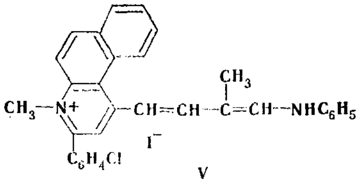
We used the same method to seperate the remaining II and III dyes. Compounds IIe, f were washed out by means of boiling ethanol from the hemicyanine impurity and were crystallized from a mixture of ethanol with nitromethane or acetone.

Pentamethylidynecyanines substituted in the meso position of the polymethine chain (IVa-e) were synthesized by condensation of the quaternary salts with 1-anilino-2-methyl-3-dimethoxy-1-propene hydrobromide obtained by the method in [5].



IV a R=H, b R=4-CH$_3$O, c R=3,4-(CH$_2$O$_2$), d R=4-Cl, e R=4-F

The pentamethylidynecyanines were isolated by washing the reaction mixtures with hot ethanol, as a result of which the hemicyanines were leached out. We isolated and characterized one hemicyanine, viz., 1-(γ-methyl-δ-anilinobutadienyl)-3-(p-chlorophenyl)benzo[f]quinolinium methiodide (V):



V

The steric effect of a condensed benzene ring of the methyl group in the 1 position of the benzo[f]quinolinium salt to a certain degree hinders the reaction of the starting compounds, as a consequence of which the reaction time is long, and the yields of the pentamethylidynecyanines decrease. The synthesized dyes are some of the most deeply colored substances of the known polymethine dyes with a chromophore of the same length (Table 1). They are stable in the crystalline state and in solutions; they are more stable in DMSO and nitromethane than in ethanol. The increase in the length of the polymethine chain as compared with the trimethylidynecyanines from 1-methyl-3-aryl-benzo[f]quinolinium salts [4] gives rise to a bathochromic shift of the absorption maxima ($\Delta\lambda \sim 100$ nm). The presence of a phenyl group in the benzo[f]quinoline ring of the dyes apparently has a favorable effect on the luminescence and generational properties of the dyes while simultaneously giving rise to a bathochromic shift of the absorption and generation maxima. Thus the bathochromic shifts of the absorption and generation maxima of the dyes obtained in this research as compared with the literature analog [6], viz., 1,1'-diethyl-4,4'-dicarbocyanine iodide (λ_{max} absorption = 810 nm, λ_{max} generation = 831 nm), depend on the nature of the solvent and average out to 60 nm. The introduction of various substituents into the phenyl ring has only a slight effect on the positions of the absorption maxima. The generational characteristics of solutions of the investigated dyes in DMSO are presented in Table 1. It is apparent from the data in Table 1 that all of the compounds have high generational efficiency, which ranges from 20-30% and allows for the possibility of overlapping of the 940-1010 nm spectral range. Compound IIe, in which a chlorine atom is present in the 4' position of the phenyl ring, has the highest generational efficiency.

TABLE 1. Pentamethylidynecyanine Dyes from 1-Methyl-3-(R-phenyl)benzo[f]-quinolinium Salts

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Absorption λ_{max}, nm (log ε)	Generation efficiency, % (in DMSO)	Generation range $\lambda_1 - \lambda_2$	Yield %
		C	H	Hal		C	H	Hal				
IIa	224—225	73,8	5,2	14,4	$C_{45}H_{35}IN_2$	73,9	4,8	17,4	870 (5,07)	22,6	940—980	5
IIb	184—185	71,3	5,0	16,2	$C_{47}H_{39}IN_2O_2$	71,4	4,9	16,0	868 (4,99)	22,0	972—1010	8
IIc	191—193	69,0	4,5	15,6	$C_{47}H_{35}IN_2O_4$	68,9	4,3	15,5	870 (5,05)	19,4	940—990	10
IId	202—203	69,3	5,2	15,1	$C_{49}H_{43}IN_2O_4$	69,2	5,0	14,9	869 (5,04)	29,0	944—978	6
IIe	241—242	67,4	4,2	24,6	$C_{45}H_{33}Cl_2IN_2$	67,6	4,1	24,8	869 (5,00)	30,0	944—980	5
IIf[a]	233—235	—	—	—	$C_{45}H_{33}F_2IN_2$	—	—	—	866 (5,04)	23,5	942—980	11
IVa	231—232	73,9	5,4	17,4	$C_{46}H_{37}IN_2$	74,1	5,0	17,0	867 (5,09)	23,3	944—980	14
IVb	226	71,6	5,2	15,8	$C_{48}H_{41}IN_2O_2$	71,6	5,1	15,7	867 (5,16)	22,0		10
IVc	227—228	69,2	4,8	15,4	$C_{48}H_{37}IN_2O_4$	69,2	4,4	15,2	867 (5,17)	21,4	972—994	10
IVd	231—232	67,6	4,5	24,9	$C_{46}H_{35}Cl_2IN_2$	67,9	4,3	25,3	877 (5,45)	21,5	960—990	10
IVe[b]	227	—	—	—	$C_{46}H_{35}F_2IN_2$		—	—	877 (5,48)	21,2	962—996	10

[a] Found: N 3.5%. Calculated: N 3.6%. [b] Found: N 3.4%. Calculated: N 3.6%.

Our experiments have shown that when ethanol is used as the solvent, the generational efficiency of all of the investigated compounds decreases in the case of excitation by the emission of a ruby laser, which impinges upon the short-wave slope of the absorption band. This effect is manifested particularly substantially for meso-substituted IV, some of which do not generate in ethanol. However, their generational capacities are fully restored in the case of excitation of generation by emission, the spectrum of which falls into the region of the maximum absorption band of the dye.

What we have stated above is illustrated by the data in Table 2, in which we present the generational characteristics of a number of meso-substituted compounds in DMSO and ethanol in the case of excitation of generation by emission with λ_{ex} = 694.3 nm or λ_{ex} = 820 nm.

The indicated effect is most likely explained by the fact that the solutions of the dyes are mixtures of several stereoisomers that have different spectral and generational characteristics [7]. Stereoisomers in series of polymethine dyes are formed because of the possibility of the existence of cis and trans forms relative to each of the double bonds. The long-wave stereoisomers have higher generational capacity. This conversion is realized most simply in low-viscosity solvents, particularly in ethanol (the viscosity of which at 25°C η = 10.8 mP). In DMSO, inasmuch as it is a more viscous solvent (η = 19.8 mP), the dye molecule turns out to be more strongly fixed sterically, which limits the possibility of conversion of one form to the other and leads to an increase in the generational efficiency. The intermolecular forces of interaction of the dye molecules with the solvent may also play a definite role in this case, since the dielectric permeability and dipole moment of DMSO are considerably higher than in the case of ethanol (for DMSO ε = 49 and μ = 3.69 D, whereas for ethanol ε = 24.3 and μ = 1.69 D).

EXPERIMENTAL

The absorption spectra of solutions of the dyes in ethanol ($c \cdot 10^{-4}$ mole/liter) were recorded with a Unicam SP-700 spectrophotometer. The generational characteristics of solutions of the dyes were studied by transverse excitation of the emission of a single-pulse ruby laser (λ_{ex} = 694.3 nm) with an emission pulse energy of up to 2 J and a pulse duration of ~25 nsec. The resonator of the dye laser was formed by a planar "opaque" mirror with a coefficient of reflection R ≈ 99.8% and an exit mirror, for which a plane-parallel support made of K-8 glass was used. The solution of the generating dye was poured into a plane-parallel cuvette with V-shaped windows and situated in the resonator at the Brewster angle. The thickness of the active layer was 1 cm. The optimal concentration that ensures the maximum generational efficiency was selected for each solution. Under the experimental conditions for all of the dyes the coefficient of absorption at λ_{ex} = 694.3 nm at the optimal concentration was ~16 cm^{-1}. Where necessary, we realized excitation of generation by the dye laser emission over the 720-900 nm range. The spectral characteristics were recorded with a DFS-13-2 spectrograph.

Bis[3-phenyl-4-methylbenzo[f]quinolin-1-yl]pentamethylidynecyanine Iodide (IIa). A mixture of 0.45 g (1 mmole) of 1-methyl-3-phenylbenzo[f]quinolinium methyl-p-toluenesulfonate, 0.14 g (0.5 mmole) of malonic dialdehyde dianil hydrochloride, 2.5 ml of dry pyridine, and

TABLE 2. Generational Characteristics of Dyes IVa–c

Compound	Generation efficiency in DMSO (λ_{ex} = 694.3 nm), %	Generation efficiency in ethanol ($\lambda_{ex.}$ = 694.3 nm), %	Generation efficiency in ethanol (λ_{ex} = 820 nm), %
IVa	23,3	1	23,0
IVb	22,0	0,1	23,0
IVc	21,4	Does not generate	23,0

1.5 mmole of piperidine was heated at 120°C for 5 h, after which it was poured into 50 ml of a 5% aqueous solution of KI. The precipitate was removed by filtration, washed with 300 ml of water and 100 ml of ether, and dried to give 0.27 g of product. The mixture of dyes was chromatographed on Al_2O_3 (from chloroform) and separated into two zones, which were removed from the Al_2O_3 with ethanol.

We isolated the hemicyanine, viz., 1-(δ-anilinobutadienyl)-3-phenylbenzo[f]quinolinium methiodide (IIIa), in the form of fine violet crystals with 197–198°C. Recrystallization from ethanol gave 0.04 g (15%) of product. Found: C 66.8; H 4.5; I 23.2%. $C_{30}H_{25}IN_2$. Calculated: C 66.6; H 4.6; I 23.5%. λ_{max} (log ε): 588 nm (4.69). After crystallization from ethanol–acetone (1:1), pentamethylidynecyanine IIa was obtained as bronze-brown needles (Table 1). Dyes IIb–d were similarly obtained. Compounds IIe, f were obtained by condensation of the corresponding methiodide with 1,3,3-triethoxy-1-propene under similar conditions and were precipitated with ether; the hemicyanines were washed with boiling ethanol, while the pentamethylidynecyanines were crystallized twice from a mixture of ethanol with acetone (1:1) or nitromethane (5:1).

meso-Methyl-Substituted Pentamethylidynecyanines (IVa–e). These compounds were obtained by the same method by condensation of the corresponding 1-methyl-3-(R-phenyl)benzo[f]quinolinium methiodides with 1-anilino-2-methyl-3-dimethoxy-1-propene hydrobromide. The dyes were precipitated with ether of a 2% aqueous solution of KI; the hemicyanines were washed with ethanol and crystallized twice.

1-(γ-Methyl-δ-anilinobutadienyl)-3-(p-chlorophenyl)benzo[f]quinolinium Methiodide (V). A 0.9-g (2 mmole) sample of 1-methyl-3-(p-chlorophenyl)benzo[f]quinolinium methiodide and 0.29 g (1 mmole) of 1-anilino-2-methyl-3-dimethoxy-1-propene were heated at 130°C in 6 ml of pyridine in the presence of two drops of piperidine for 1 h. The dye was precipitated with a 2% aqueous solution of KI, washed with water and ether, and crystallized twice from ethanol to give 0.11 g (12%) of bronze-violet needles with mp 230°C. Found: C 63.2; H 4.8; Hal 27.0%. $C_{31}H_{26}CHN_2$. Calculated: C 62.9; H 4.4; Hal 27.3%. λ_{max} (log ε): 597 nm (4.77).

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