

Thus, by quaternization of pyridine and its 3- and 4-derivatives with 1-bromo- and 4-iodoadamantanes in the presence of a small quantity of water it is possible to obtain the corresponding adamantylpyridinium salts (see Tables 1 and 2). Pyridine derivatives having substituents at the 2-position do not undergo a quaternization reaction with haloadamantanes.

EXPERIMENTAL

The reaction was conducted in sealed ampuls; PMR spectra were recorded on a Tesla BS-467 (60 MHz) spectrometer, with D₂O and CF₃COOH as solvents and TMS as external standard.

1-Bromoadamantane [9] and 1-iodoadamantane [10] were obtained according to known methods.

1-(1-Adamantyl)pyridinium Iodide (IIIb). General Method. 0.01 mole of compound Ib in a tenfold excess of pyridine containing 0.2% water was heated for 4 h at 180°C. The reaction mixture was poured into ether, and the precipitate was filtered off and crystallized from a benzene-ethanol mixture.

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SYNTHESIS AND SPECTRAL LUMINESCENT PROPERTIES OF CERTAIN PYRIDINE AND QUINOLINE ANALOGS OF ISOMERIC DISTYRYLNAPHTHALENES AND STYRYL- AND DISTYRYLANTHRACENES

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UDC 547.652'672'831.2.07:542.953.3:535.37

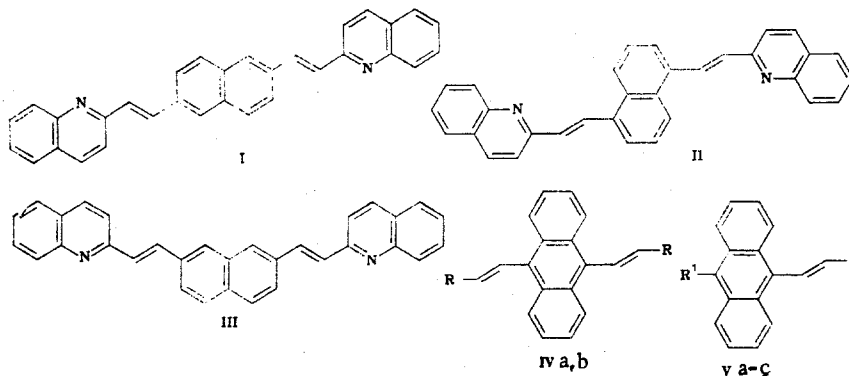
A series of pyridine and quinoline analogs of isomeric distyrylnaphthalenes and styryl- and distyrylanthraces has been synthesized. Their spectral-luminescent properties were studied. Compounds whose structures are sterically hindered in the ground state have the highest Stokes' shift.

1,4-Distyrylbenzene, 2,6-distyrylnaphthalene, and certain heterocyclic analogs of these compounds are known as organic luminophores, which effectively transform laser emission [1-3]. In continuation of the study of the hetero analogs of styrylarenes, we synthesized quinoline analogs of isomeric 2,6-, 1,5-, and 2,7-distyrylnaphthalenes (I-III), and also pyridine and quinoline analogs of 9,10-distyrylanthracene (IVa,b) and 9-styryl anthracene (Va,b), and studied their spectral luminescent properties.

All the compounds were obtained by the method described in [4], in analogy to the preparation of 1,4-di[β -(2-quinoly)vinyl]benzene (VI), by the condensation of 4-picoline or quin-

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 6, pp. 820-823, June, 1987. Original article submitted January 6, 1986.

aldine with the corresponding formyl- or diformylarenes in boiling acetic anhydride. In the reaction of quinaldine with 9,10-diformylantracene, in addition to 9,10-di- $[\beta$ -(2-quinolyl)vinyl]-anthracene (IVb), a condensation product of quinaldine with one of the formyl groups, 9-formyl-10- $[\beta$ -(2-quinolyl)vinyl]-anthracene (Vc), was also isolated.



IV, V a R = 3-pyridyl, b, c R = 2-quinolyl; a, b R¹ = H; c R¹ = CHO

The compounds synthesized have a trans-configuration; in their IR spectra there are absorption bands in the 970-990 cm^{-1} region, characteristic for trans-disubstituted alkenes [5]. In the PMR spectrum of 9,10-di- $[\beta$ -(4-pyridyl)vinyl]anthracene (IVa), two doublets of the AB spin system are observed with chemical shifts of 6.91 and 7.37 ppm, belonging to the vinyl protons. The SSCC ($J = 16.5$ Hz) indicates a trans-configuration of this compound.

The electronic absorption spectra of the toluene solutions of the synthesized compounds are shown in Table 1. 2,6-Di- $[\beta$ -(2-quinolyl)vinyl]naphthalene (I) has the same absorption spectrum as compound VI, i.e., the replacement of the central 1,4-phenylene fragment by the 2,6-naphthylene fragment does not influence the character of the spectrum. The absorption band of 1,5-di- $[\beta$ -(2-quinolyl)vinyl]naphthalene (II) is hypsochromically shifted by 15 nm relative to the 2,6-isomer I. The hypsochromic effect is evident to a still higher degree (38 nm) in the case of 2,7-di- $[\beta$ -(2-quinolyl)vinyl]naphthalene (III), having a less effective conjugation chain. We observed a similar pattern for the azole analogs of the isomeric distyrylnaphthalenes [6], which agrees with the data of the quantum-chemical calculation [7]. The hypsochromic shift of the absorption band of compound II is possibly explainable, as in the case of its azole analog [7], by the noncoplanar disposition of the central naphthalene fragment and the azastyryl substituents in the unexcited molecule.

For all the synthesized compounds, the longest wave absorption (410-430 nm) is observed in disubstituted anthracenes IVa,b and Vc. 9- $[\beta$ -(4-Pyridyl)vinyl]anthracene (Va) and 9- $[\beta$ -(2-quinolyl)vinyl]anthracene (Vb) with a shorter length of the conjugation chain absorb in a shorter wavelength region (370-395 nm). 9,10-Distyrylanthracene in the ground state has a sterically hindered structure [8, 9]; it is clear that the same holds for its heterocyclic analogs. Comparison of the absorption spectra of compound IVb with the spectra of compounds I-III shows that IVb absorbs in a longer wavelength region than the sterically unhindered compound I (see Table 1). The considerable bathochromic effect (40 nm) is possibly due to the large contribution of the anthracene fragment itself to the effective conjugation chain. Disubstituted anthracenes IVa,b are characterized by higher values of the extinction coefficient ϵ than the monosubstituted Va,b, the highest values of ϵ being reached in compounds IVb and Vb with the quinoline fragment. The values of ϵ of compounds IVa,b thus remain lower than for compounds I-III.

The maxima of the fluorescence spectra of the synthesized compounds (Table 1) are located in the 400-615 nm region (in toluene), whereby the quinoline analogs of distyrylnaphthalenes I-III have the shortest-wavelength fluorescence (400-455 nm) and the disubstituted anthracenes IVa,b and Vc have the longest wavelength fluorescence (580-615 nm). The fluorescence bands of monosubstituted anthracenes Va,b occupy an intermediate position (500-510 nm).

In the fluorescence bands of compounds I-III and VI, in contrast to their absorption bands, a vibrational structure appears which is also characteristic for several other lumino-phores [10]; in particular the azole analogs of distyrylnaphthalenes [6].

The absolute fluorescence quantum yields (Φ) of disubstituted naphthalenes are equal to 0.20-0.76, decreasing, as in the case of their azole analogs [6], in the series 2,6-, 1,5-,

TABLE 1. Analytical and Spectral Characteristics of Synthesized Compounds

Compound	Temp. °C*	Absorption in toluene		Fluorescence in toluene		Found, %			Empirical formula ^a	Calculated, %		
		λ_{\max} , nm	lg ϵ	λ_{\max} , nm	ϕ	C	H	N		C	H	N
I	263—265	385	4.83	425**, 450	0,76	88,5	5,1	6,4	C ₃₂ H ₂₂ N ₂	88,4	5,1	6,4
II	255—256	370	4,58	435**, 455	0,46	88,6	5,2	6,5	C ₃₂ H ₂₂ N ₂	88,4	5,1	6,4
III	262—263	347, 361	4,76, 4,29	403**, 423	0,20	88,2	5,2	6,4	C ₃₂ H ₂₂ N ₂	88,4	5,1	6,4
IVa	295	413	4,20	580	0,47	87,8	5,8	7,3	C ₂₈ H ₂₀ N ₂	87,5	5,2	7,3
IVb	234—235	426	4,34	590	0,65	89,3	5,1	5,6	C ₃₆ H ₂₄ N ₂	89,2	5,0	5,8
Va	146—147	371 sh., 388	3,87, 3,92	485	0,35	89,6	5,4	4,4	C ₂₁ H ₁₅ N	89,6	5,4	5,0
Vb	177—178	373 sh., 392	3,99, 4,05	505	0,35	90,7	5,3	4,0	C ₂₅ H ₁₇ N	90,6	5,2	4,2
Vc	205—207	427	4,15	615	0,14	86,9	4,9	3,7	C ₂₆ H ₁₇ NO	86,9	4,8	3,9
VI	243 [4]	382	4,81	425*, 456	0,76							

*Compounds I-III, VI were crystallized from DMFA; IVa,b, Vc from benzene, Va,b from heptane.

**The main fluorescence maximum.

and 2,7-isomers. The quantum yields of the substituted anthracenes IVa,b and Va-c are 0.14-0.65, the quinoline analog of 9,10-distyrylanthracene IVb having the highest value of ϕ

The Stokes shift in disubstituted naphthalenes I-III is 40-65 nm and the highest value is reached in the 1,5-isomer II, which is probably explainable, as in the case of its azole analog [7], by an increase in the coplanarity of the molecule in the excited state. The characteristic feature of substituted anthracenes IVa,b and Va-c is the large Stokes shift. In the monosubstituted compounds Va,b, it is equal to about 100 nm; in disubstituted IVa,b and Vc, it reaches a value almost twice that. As in 9,10-distyrylanthracene itself [8, 9], the anomalously large Stokes shift for its hetero analogs can be explained by the fact that in the excited state the molecule becomes more planar and the effective conjugation chain increases.

Compounds I, II, and VI transform laser emission, generating in the range of 430-450 nm [11].

EXPERIMENTAL

The electronic absorption spectra were measured on a Unicam SP-8000 spectrophotometer in toluene, and the fluorescence spectra - on a type SDL-1 apparatus assembled on the base of a MDR-1 monochromator. The fluorescence was excited by light from a DKSSH-1000 lamp, isolated by a MDR-3 monochromator. The spectra were corrected for the spectral sensitivity of the apparatus. The fluorescence quantum yields were determined by a relative method, using 3-aminophthalimide in ethanol as a standard ($\phi = 0.6$ [12]). The PMR spectrum of compound IVa was measured on a Bruker WP-80 spectrometer in CDCl₃, using TMS as internal standard. The IR spectra were measured on a UR-20 spectrometer in KBr tablets.

The initial isomeric diformyl naphthalenes and 9,10-diformylanthracene were obtained by methods described in [13, 14].

General Method of Condensation of Quinaldine with Diformyl naphthalenes. A mixture of 4.4 mmoles of quinaldine with 2.0 mmoles of diformyl naphthalene is boiled for 3-5 h in 5 ml of acetic anhydride, then allowed to stand overnight, the precipitate that separates is filtered, washed in 1 ml of acetic anhydride and 5 ml of ether, and recrystallized from DMFA. The yield of compound I-III is up to 70%.

Condensation of 9,10-Diformylanthracene with 4-Picoline and Quinaldine. A mixture of 2.0 mmoles of 9,10-diformylanthracene with 4.4 ml of 4-picoline or quinaldine is boiled in 5 ml of acetic anhydride for 5 h, and then allowed to stand overnight. The precipitate that separates is filtered, washed with 1 ml of acetic anhydride, 10 ml of water, 10 ml of 10% aqueous solution of sodium carbonate, and 50 ml of water; it is then dried and recrystallized from benzene. The yield of compound IVa or IVb is about 30%.

The acetic anhydride remaining in the filtrate after the separation of compound IVb is neutralized by 100 ml of 10% aqueous solution of sodium carbonate, and the resinous substance is extracted with 3 × 50 ml of benzene. The benzene extract is dried over sodium sulfate,

concentrated, and chromatographed on aluminum oxide of grade II activity (a 3 × 50 cm column) in benzene. The orange colored fraction is collected, benzene is distilled off, and the residue is recrystallized from benzene. Compound Vc is obtained in a yield of 0.11 g (12.3%).

Condensation of 9-Formylanthracene with 4-Picoline and Quinaldine. A mixture of 5.0 mmoles of 9-formylanthracene with 10.0 mmoles of 4-picoline or quinaldine is boiled in 5 ml of acetic anhydride for 11 h, and then allowed to stand overnight. Acetic anhydride is neutralized with 100 ml of 10% aqueous sodium carbonate solution, and the resinous substance is extracted with 3 × 50 ml of benzene. The benzene extract is dried over sodium sulfate, concentrated, and chromatographed on aluminum oxide of grade II activity (a 3 × 50 cm column) in benzene. The first fractions of the eluate contain unreacted 9-formylanthracene; from the subsequent fractions benzene is distilled off, and the residue is recrystallized from heptane. Compounds Va or Vb are obtained in yields of 12 and 73%, respectively.

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