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.

LITERATURE CITED


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

E. M. Vernigor, M. V. Koz'menko,
S. A. Lebedev, E. A. Luk'yanev,
L. P. Savvina, and V. K. Shalaev

A series of pyridine and quinoline analogs of isomeric distyrylnaphthalenes and styryl- and distyrylanthracenes 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-quinolyl)vinyl]benzene (VI), by the condensation of 4-picoline or quin-
aldine with the corresponding formyl- or diformylarenes in boiling acetic anhydride. In the reaction of quinaldine with 9,10-diformylanthracene, in addition to 9,10-di-[β-(2-quinolyl)-vinyl]-anthracene (IVb), a condensation product of quinaldine with one of the formyl groups, 9-formyl-10-[β-(2-quinolyl)vinyl]-anthracene (Vc), was also isolated.

![Chemical structures](image)

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[β-(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 SSQC (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 I. 2,6-Di-[β-(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-[β-(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-[β-(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-[β-(4-Pyridyl)vinyl]anthracene (Va) and 9-[β-(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 I). 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 IVa 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 I) 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 lumophores [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-, 678