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Azinylarylethenes: synthesis and photophysical and photochemical properties †

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Abstract. Methods for the synthesis of styrylazines and styrylbenzazines are considered, their photophysical and photochemical properties are analyzed. The review covers both published data and own works of the authors. Important data on the prospects of application of arylhetarylethenes as components of electroluminescence materials are discussed. The bibliography includes 124 references.

I. Introduction

Compounds containing C=C bond, such as stilbene (1,2-diphenylethylene) and butadiene derivatives and styryl dyes, hold a prominent place among artificial photosensitive systems. These compounds are readily available synthetically, can act as efficient molecular photoswitches, and exhibit multiphotochromic properties, *i.e.*, they can undergo different photochemical transformations depending on the structure.[1,2]

Among such systems, a special place is occupied by dihetarylethenes as good candidates for design of optical information storage materials.[3,4] After the discovery by Prof. M Irie (Japan), in the late 1980s, of photochromic diarylethenes in which the phenyl groups are substituted by five-membered heterocyclic moieties, specifically 2,5-dimethylthiophene ones,[3] dihetarylethene photochromes have been widely studied as various modern photosensitive smart materials. Heterocyclic stilbene analogues are also a structural base of fluorescent materials with strongly pronounced photophysical and electrooptical properties.[5–7] Nitrogen-containing π-deficient heterocycles, such as pyridine, pyrimidine, quinoline and quinoxaline, have already proven to be components of electron transport layers in electroluminescent materials.[8]

Photochemistry of 1,2-diaryl- and 1,2-dihetarylethenes has been well studied and is represented by three types of photochemical reactions, namely, geometrical isomerization, dimerization and intramolecular cyclization.

Asymmetrical hetarylethenes have been less studied than symmetric derivatives. Only review articles[1,2] dedicated to crown-containing styryl derivatives with heterocyclic moieties are available in the Russian literature.

The present review summarizes literature data concerning methods of synthesis of styryl derivatives of π-deficient heterocycles, their photoisomerization and different types of photocyclization. Luminescence of azinylarylethenes is discussed. The trends in their use are considered.

II. Synthesis, *trans* – *cis* photoisomerization and luminescence

1. Styrylpyridines

a. Methods of synthesis

Styrylazines, including styrylpyridines (stilbazoles), are commonly obtained by the Wittig reaction, Heck cross-coupling or other methods. For the compounds with the styryl moiety in the α or γ position to the cyclic nitrogen atom, the most popular method is the condensation of methyl derivatives of nitrogen-containing heterocycles with aldehydes under basic or acidic conditions, as well as in the presence of Lewis acids.

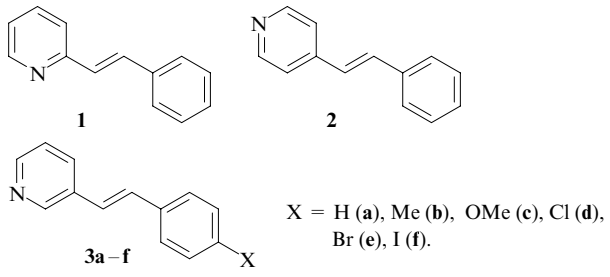
Methods of synthesis of *trans*- and *cis*-stilbazoles have been developed. In particular, *trans*-2-styrylpyridine (**1**) and *trans*-4-styrylpyridine (**2**) have been synthesized by condensation of, respectively, α- and γ-picolines with benzaldehyde in the presence of a condensing agent under rather prolonged refluxing.[9] The methyl group in β-picoline is unreactive towards aldehydes, and therefore 3-styrylpyridines

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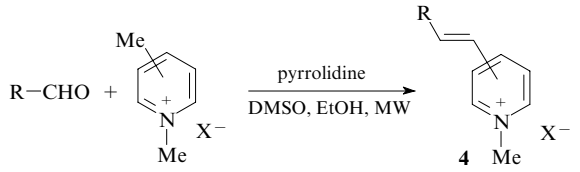
† Dedicated to Academician O M Nefedov on the occasion of his 80th birthday.

3a–f were obtained by the reaction of pyridine-3-carbaldehyde with $ArCH_2CO_2Na$ in the presence of acetic anhydride with subsequent decarboxylation.[10]

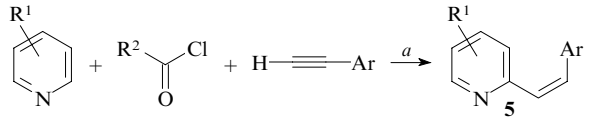


As models for fluorescent probes, isomeric 4-hydroxy-substituted 2-, 3- and 4-stilbazoles have been synthesized by addition of isomeric picoline anions to 4-methoxybenzaldehyde, followed by dehydration and deprotection.[11]

An efficient method of search for the compounds with specified wavelength and high luminescence quantum yield is a rather challenging task. A combinatorial approach to the creation of libraries of fluorescent compounds occurred to be useful for these purposes. In particular, the library of arylhetarylethenes **4**, which that are of interest as fluorescent probes has been described.[12] Styryl derivatives **4** have been synthesized by the condensation of 41 aldehydes with 14 pyridinium salts or their benzo analogues in the presence of pyrrolidine as a catalyst under microwave irradiation (MW).

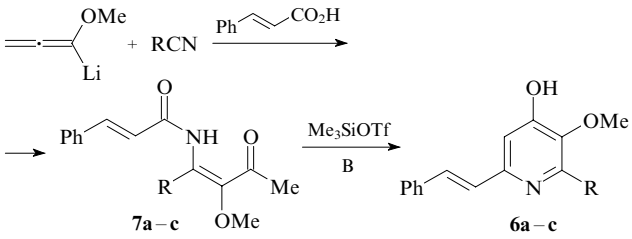


A heightened interest in useful properties of styrylpyridine derivatives has stimulated the development of new approaches to their synthesis. In particular, a method of functionalization of pyridine with alkynes yielding *Z*-ethenyl-substituted pyridines **5** has been developed.[13] The effect of the nature of the base on the yield and ratio of the isomers has been studied. If the reaction of pyridine with alkyne and acid chloride is carried out in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO), the ratio of *E* and *Z* isomers varies as a function of the nature of substituents R^1 and Ar from 0 : 100 to 1 : 1 with a total yield of 30% to 70%; if Bu^tOK is used as a base, the ratio of *E*- and *Z*-isomers is 100 : 0, but the total yield is ~5%.



R^1 = H, Br, CN, Ph, F; R^2 = Ph, OEt, OPh;
Ar = 4-XC_6H_4 (X = H, Br, F, Me, CHO), 3-Th (Th is thienyl);
(*a*) CuI, Pr^i_2NEt, DABCO, MeCN, 65 °C.

Recently, a new two-stage approach to the synthesis of alkenyl-substituted 4-hydroxypyridines **6a–c** was described. It is based on the cyclization of β-alkoxy-β-ketoenamides **7a–c** obtained by the three-component reaction of lithiated methoxyallene, nitriles and α,β-unsaturated carboxylic acids.[14] The cyclization is carried out in the presence of trimethylsilyl trifluoromethylsulfonate (Me_3SiOTf) and base (B) in sealed tubes at 90 °C for 3 days, and the yield of 4-hydroxypyridines **6a–c** is 66%–80%. The synthesized styrylpyridines **6** were characterized by luminescence spectra.



R = Bu^t (**a**), Ph (**b**), 2-Th (**c**).

b. Photophysical properties and photoisomerization

The photochemical behaviour of stilbene has been investigated in detail, and the mechanisms of *trans–cis* photoisomerization and luminescence of *trans* isomers have been established.[15–17] It has been found out that stilbene isomerizes in the singlet state. The influence of substituents on its luminescence has been studied. In particular, the introduction of an *N*-phenyl substituent into *trans*-4-aminostilbene leads to a more planar geometry of the ground state and to the red shift in the absorption and luminescence spectra.[18] The investigation of photochemical behaviour of a wide spectrum of *trans*-4-arylaminostilbenes was used to prove the concept of twisted intramolecular charge transfer (TICT) for a number of compounds and its influence on luminescence.[5]

Nitrogen-containing analogues of stilbene, namely, 2-, 3- and 4-styrylpyridines, have long attracted the attention of researches as objects for studying the photochemical behaviour since they possess definite energy states of stilbene in addition to $n\pi^*$-states.[19]

The reactions of excited states of 2-, 3- and 4-styrylpyridines, namely, direct and sensitized isomerization and luminescence, have been studied.[19] It has been shown that the excited states of stilbazoles are different from those of other substituted stilbenes. The ratio of different deactivation processes depends on the position of the styryl unit in pyridine. The luminescence spectra of compounds **1–3** are similar to the stilbene spectra but they are notable for the lower intensity of the signal. 3-Stilbazole (**3a**) has a slightly higher fluorescence quantum yield (φ_{fl} = 0.07) as compared with stilbene (φ_{fl} = 0.05), while the φ_{fl} values for 2- (**1**) and 4-stilbazoles (**2**) are one order of magnitude lower (0.003 and 0.005, respectively).

Later studies[20–23] have focused on the reactivity of styrylpyridines in the excited state and on the role of $n\pi$ state in photophysical and photochemical processes. It has been shown that under excitation the value of pK_a for protonated forms of 2-, 3- and 4-styrylpyridines increases by 5–7 units.[21] A band caused by the presence of a protonated form appears in the luminescence spectrum of compound **3a** in a water–ethanol medium at pH 8. The protonation of the pyridine moiety is accompanied by a large bathochromic shift of the luminescence maximum, from 360 to 460 nm for 3-styrylpyridines (Fig. 1).[21]

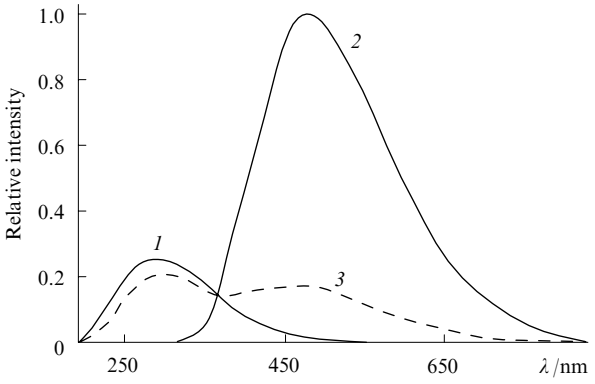


Figure 1. Luminescence spectra in a water–ethanol mixture (90 : 10 by volume) of the neutral form of *trans*-3-styrylpyridine (**3a**) at pH 13.7 (*1*), protonated form at pH 2 (*2*) and a solution at pH 8 (*3*) in which 17% of compound **3a** is protonated, in excited state [excitation wavelength (λ_{exc}) is 280 nm].[21]

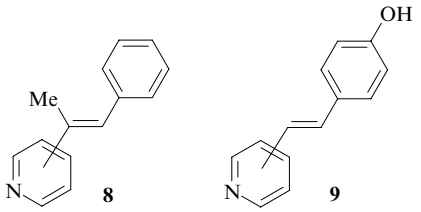
Studying the influence of the pyridine moiety, the character of substituents, the nature of solvents and the degree of protonation on photoisomerization and luminescent properties of 2-, 3- and 4-styrylpyridines and 4′-derivatives of 3-styrylpyridine in n-hexane and water–ethanol solutions in basic and acidic media has been continued.[22] The emission quantum yield remains nearly constant for compound **2** and increases for compound **1** in going from n-hexane to water, and the quantum yield of isomerization increases for both isomers in polar solvents. As a whole, compounds **1** and **2** in liquid media are characterized by very low emission intensity. The quantum yield is 0.002–0.003, but in a diethyl ether–isopentane–ethanol mixture (2 : 2 : 1 by volume, EPA) at liquid nitrogen temperature, it increases up to ~0.6.

As noted earlier,[19] radiationless processes are less typical of compounds **3**; therefore, the isomerization and luminescence efficiency is significantly higher for them. In particular, the quantum yield for derivative **3a** increases up to 0.042 at pH 8 and up to 0.21 at pH 2. Compounds **3** are also characterized by a longer emission lifetime as compared with stilbazoles **1** and **2**. The substituents in position 4′ have a different effect on luminescence: the chlorine atom leads to luminescence rise, while the iodine atom leads to luminescence decay. The quantum yields of *cis*–*trans* isomerization for all isomers are lower than the yields of the corresponding *trans*–*cis* transitions and they are always lower for 3-isomers **3**.

The luminescence spectra and quantum yields of stilbazoles **1**–**3** have been found to depend on the excitation wavelength.[23] For compounds **3,** an anomalous behaviour has been revealed consisting in that they have a minimum φ_{fl} value at $\lambda_{exc} < 290$ nm.

The results of quantum-chemical calculations of the electronic spectra of styrylpyridines **1**–**3** and their conjugate acids using the CNDO/S MO model[24] support the hypothesis that the stilbazoles under consideration possessed a low-energy $n\pi^*$ state and explain the differences in the spectra of their protonated forms.

The influence of methyl group at ethylene bridge on the luminescence and photoisomerization of styrylpyridines of general formula **8** has been studied.[25]



8 **9**

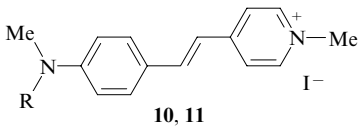
It has been shown that these sterically hindered compounds are characterized by a significant decrease in the quantum yield of luminescence. The data on the effects observed when varying temperature and solvent enabled the discussion of the intramolecular rotation of planar and nonplanar styrylpyridines in excited state, as well as its competition with other routes of deactivation. On the basis of the model suggested for the stilbenes, the mechanism of photoisomerization of these compounds has been considered.

The influence of the structural factor on the photophysical behaviour has also been studied,[26] namely, the insertion of a heterocyclic moiety into stilbenes. Systematic study of styrylpyridine properties and quantum chemical predictions have supported the previous conclusion that the effect of the $n\pi^*$ state is determined by the position of the styryl moiety. The $n\pi^*$ excitation is limited by the pyridine ring for 3-isomer, while in 2- and 4-isomers, it is involved in the process of charge transfer from the pyridine ring to the benzene one. The low-energy $n\pi^*$ state favours the appearance of new radiationless routes of deactivation of the excited state, especially for 2- and 4-stilbazoles, which is responsible for the decrease in the luminescence intensity.

All three isomers of 4-hydroxy-substituted 2-, 3-, 4-stilbazoles **9** in a neutral medium have similar luminescence spectra. The emission maximum position depends on the solvent polarity. Red shift is observed in a more polar medium, in basic and acidic media, in the latter the most significant long-wavelength shift being observed for 3-isomer.[11]

The influence of other substituents on the luminescence of 3-stilbazole has also been studied. Thus, the introduction of the *N*-phenyl or *N*-diphenyl substituent at the 4-position of the aryl moiety leads to a more planar geometry of the ground state (similar to stilbene) and to the red shift in the luminescence spectra (by 10 or 30 nm).[18]

The styrylpyridine derivative 4-[2-(4-dimethylaminophenyl)ethenyl]-1-methylpyridinium iodide (**10**) is widely used as a solvatochromic dye.[27]



10, **11**

R = Me (**10**), $(CH_2)_2SH$ (**11**).

The presence of an electron-donating group on one end of molecule **10** and an electron-withdrawing group on the other end leads to the enhancement of the luminescent properties of the compound. The replacement of the methyl group by a long-chain alkyl group makes a molecule amphiphilic and capable of the formation of Langmuir–Blodgett films (LB films). Due to the high hyperpolarizability and interesting optical properties, compounds of this

type have been intensively studied by nonlinear opticians as materials for molecular optical devices.[28,29]

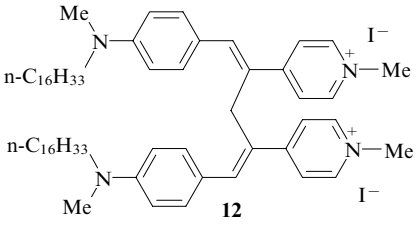
Much attention has been paid to theoretical studies of styryl dyes.[25,30] In particular, quantum chemical calculations have been used to study the possibility of intramolecular charge transfer in the TICT state under photoexcitation at the expense of the rotation of part of a molecule about definite bonds.[25] The energy barriers to rotation were calculated. It was shown that the high barrier to rotation about the central double bond is responsible for the low quantum yield of photoisomerization. Rotation about C—N and C—C single bonds leads to a low quantum yield of luminescence in solution, which strongly depends on the polarity and viscosity of the solvent.

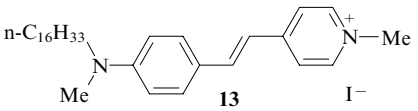
The introduction of thiol group into the styryl moiety of the dye (compound **11**) has enabled the preparation of a multilayered organic/inorganic heterostructure $ZnS \cdot 7 \cdot SiO_2$ in the form of nanobubbles.[31] The study of luminescent properties has shown that the encapsulation of dye **11** into the inorganic matrix significantly enhanced the luminescence intensity (70 times). Such materials have already been used to design solid-phase lasers, nonlinear optical devices and optical memory.

Analysis of the emission spectra of dyes **4** has revealed that the colour of luminescence varies from blue to red, *i.e.*, it covers almost the entire visible spectrum.[12]

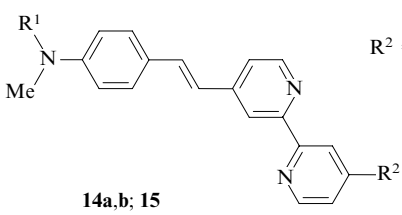
Novel amphiphilic stilbazole dyes, namely, dimer **12** and the *E* isomer of the corresponding monomer (**13**), were synthesized and studied as multifunctional organic materials.[32] Compound **12** exhibits strong second harmonic generation and photocurrent generation in monolayered LB films, the quantum yield of photocurrent generation being 0.51% for dimer **12** and 0.30% for the monomer.

The influence of a long aliphatic chain (C_{18} and C_{22}) in different positions of the skeleton of amino derivatives of styryl dyes, analogues of compound **13**, on the structure of the monolayer has been studied.[33] It has been shown that the dye in which the aliphatic substituent is situated far from the hydrophilic cationic pyridine moiety forms more stable monolayers as compared with the dye with the aliphatic substituent at the nitrogen atom of pyridine.





The solvatochromism of amphiphilic bipyridines **14** and **15** has been studied.[34] It has been shown that the emission wavelength is 426–428 nm in hexane, 440–445 nm in toluene, 475–477 nm in tetrahydrofuran, 490–495 nm in dichloromethane, 515–521 nm in acetonitrile, 518–524 nm in dimethylformamide and 530–535 nm in methanol. The quantum yields of luminescence of compounds **14a**,**b** and **15** in dichloromethane are 0.138, 0.135 and 0.096, respectively.



14a,**b**; **15**

$R^1 = (CH_2)_{10}OH$ (**a**), n-$C_{14}H_{29}$ (**b**); R^1 = n-$C_{14}H_{29}$, R^2 = Me (**15**).

Bis(styryl) dyes **16** differing in structure from compound **12** have been described.[35] The influence of the solvent on luminescence spectra, as well as the dynamics of spectra in chloroform and LB films, has been studied. It has been shown that in chloroform the luminescence intensity is significantly higher than in other polar solvents. This is presumably caused by the fact that in a low-polarity solvent the process of intramolecular charge transfer in the TICT state is blocked.

Amphiphilic stilbazolium dyes with long alkyl chains in LB films have been studied in detail as candidates for production of nanoscale devices with external control of their properties. A strong dependence of photophysical and photochemical properties of such compounds on the nature of substituents in the *para* position of the styryl moiety has been revealed. In particular, styryl pyridinium dyes with different anions (**17a**,**b**) have been synthesized.[36] Their molecular organization in monolayers at the air/water interface has been studied.

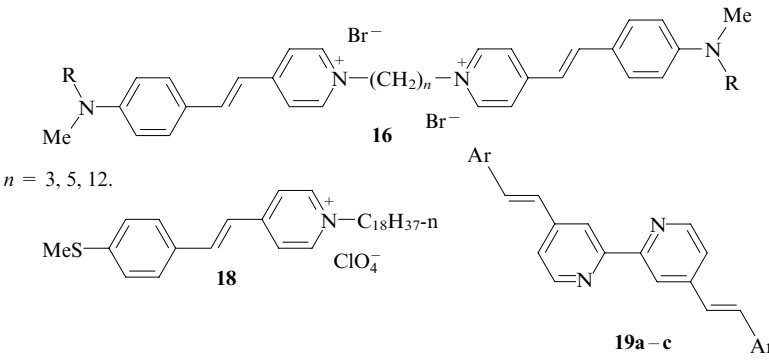
Compounds **17a**,**b** are involved in reversible photoisomerization between the strongly fluorescent *E* isomer and nonfluorescent *Z* isomer. Such a behaviour makes it possible to use them as components of optical information storage devices by means of switching between radiating and nonradiating states.

Spectroscopy and photochromic properties of transferred monolayers of amphiphilic dyes **17** on solid substrates have been studied under the different conditions of their transfer from the air/water interface in the liquid phase.[37] It has been shown that the luminescent properties of monolayers could be reversibly modulated by photoinduced *E*–*Z* isomerization. A blue shift of up to 72 nm of the emission maximum, depending on the transfer conditions of the films, was observed on irradiation with blue light. On exposure to UV irradiation, the emission maximum was shifted by 26 nm back (red shift). The presence of both photochromic and luminescent properties makes compounds **17** promising materials for the preparation of LB films, whose properties can be effectively used in photonics since these properties depend on the layer transfer conditions and irradiation.

The properties of new cationic methylthio-substituted dye **18** have been studied in comparison with the properties of dimethoxy derivatives **17**.[38] The influence of different salts in an aqueous subphase on the behaviour of the monolayer at the air/water interface has been explored.

Solutions of 4,4′-substituted 2,2′-bipyridines **19a**–**c** in dichloromethane are highly emissive in the visible region, the quantum yields being 0.59, 0.70 and 0.73, respectively (quinine sulfate in 1 M H_2SO_4 was used as a reference).[39]

Poly(aryl ether)s 20 have been synthesized, which contain at the same time both the emissive (distyrylpyridine) and electron transporting (quinoxaline) segments separated by ether groups.[40] The polymers possess a low molecular weight and are soluble in polar organic solvents. In tetrahydrofuran, the polymers show emission maxima at

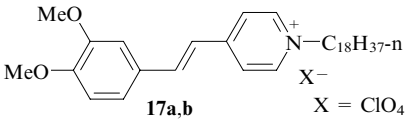


16

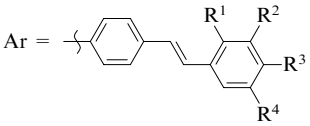
n = 3, 5, 12.

18

19a–c

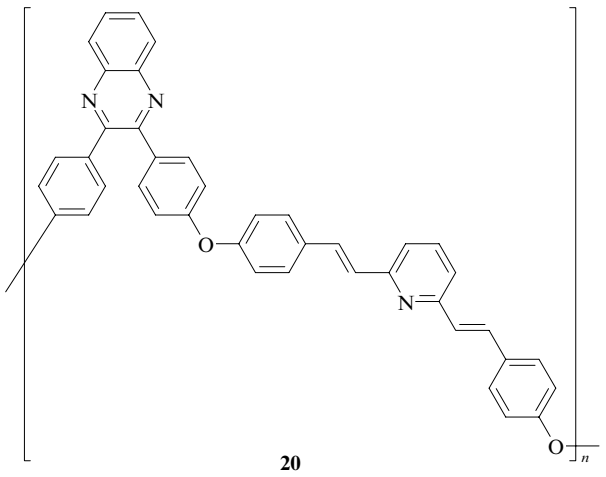


17a,b X = ClO_4 (**a**), Br (**b**).



$R^1 = R^3 = R^4 = H$, R^2 = OMe (**a**);
$R^1 = R^3$ = OMe, $R^2 = R^4 = H$ (**b**);
$R^2 = R^3 = H$, $R^1 = R^4$ = OMe (**c**).

417–454 nm, the quantum yields being 22%–41%. In the solid state, the polymers show luminescence maxima at 427–461 nm. Intrachain interactions have a significant influence on the optical properties of polymers **20** in solutions. They are also revealed in the solid state.



20

The presence of a donor centre (nitrogen atom) in styrylpyridines and a wide possibility of varying the aryl substituent allowed one to use such compounds as ligands. Metal complexes based on them have enhanced luminescent and other valuable properties. In particular, on the basis of *trans*-4-[4′-(*N*-methyl-*N*-hydroxyethyl)amino]styrylpyridine (L), the $Zn(SCN)_2L_2$, $Co(SCN)_2L_2$, $[Cd(SCN)_2L_2 \cdot 2\,L]_n$ and $[CdHg(SCN)_4L_2]_n$ complexes have been synthesized by self-assembly technique.[41] According to X-ray diffraction analysis data, the zinc and cobalt complexes are mononuclear, while the cadmium compound and the mixed cadmium mercury complex are coordination polymers. Studying the luminescence of these complexes in the solid state[41] has shown that going from the ligand to the complexes is accompanied by the red shift of the emission maximum.

Ruthenium complexes with 4,4′-diethenyl-2,2′-bipyridine moieties and residues of di- and triatomic phenols turned out to be thermally stable, slightly prone to aggregation in solutions and able to bind strongly to titanium dioxide.[42] Materials for electronic devices with improved properties have been prepared on their basis. It should be mentioned that this study reflects well the modern tendency of improving the characteristics of new materials and of using small molecules of metal complexes in electronic devices.

Terbium complexes of 4-[2-(2,6-dicarboxypyridin-4-yl)-ethenyl]pyridine-2,6-dicarboxylic acid and 4-{4-[2-(2,6-dicarboxypyridin-4-yl)ethenyl]styryl}pyridine-2,6-dicarboxylic acid are excellent green-emitters and promising materials for use in organic light emitting diodes (OLEDs) and in medical diagnostics.[43] The luminescent properties of tris-cyclometallated iridium(III) 4-styryl-2-phenylpyridine complexes have been described.[44]

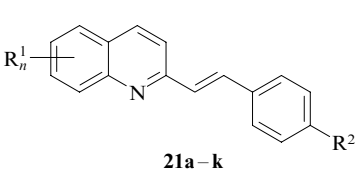
A series of new luminescent cyclometallated platinum(II) complexes have been synthesized on the basis of 4-styryl-2-phenylpyridines.[45] All the complexes undergo $E-Z$ photoisomerization in dichloromethane solution under sunlight, which is responsible for weak luminescence under these conditions. In EPA at 77 K, the emission spectra of the complexes exhibit two groups of bands due to the presence of E and Z isomers, which have significantly different triplet excited-state energies.

The hydrothermal reaction of $Cd(ClO_4)_2 \cdot 6\,H_2O$ with 4-[2-(2-pyridyl)ethenyl]benzonitrile in aqueous pyridine yields aquabis{4-[2-(2-pyridyl)ethenyl]benzoato}cadmium(II).[46] The nitrile group is hydrolyzed to carboxylic one, and the oxygen atoms of this group and the pyridine nitrogen atom of another ligand molecule are involved in the coordination of the cadmium ion. According to X-ray diffraction analysis data, the complex is a coordination polymer containing a dimer moiety of two cadmium atoms and eight ligands and displays strong blue luminescence.

2. Styrylquinolines

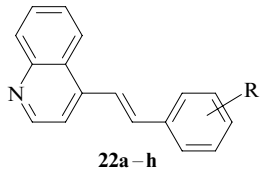
a. Methods of synthesis

Traditional methods of synthesis of styrylquinolines require continuous heating of reactants. As a result, a mixture of products is formed, the yields of target styrylquinolines **21** and **22** after time-consuming procedures of separation and purification being rather low.



21a–k

R^1_n = H: R^2 = NO_2 (**a**), NH_2 (**b**), NMe_2 (**c**), Me (**d**), OH (**f**), Cl (**g**);
R^1_n = 6-Cl, R^2 = NMe_2 (**h**); R^1_n = 6,7-F_2: R^2 = H (**i**), NO_2 (**j**), OMe (**k**).



22a–h

R = 4-NO_2 (**a**), 4-NH_2 (**b**), H (**c**), 4-F (**d**), 4-Cl (**e**), 4-Me_2N (**f**), 4-OH (**g**), 2-OH (**h**).

The conditions of synthesis of styrylquinolines containing electron-donating substituents in the styryl moiety have been optimized.[47] New derivatives of styrylquinolines have

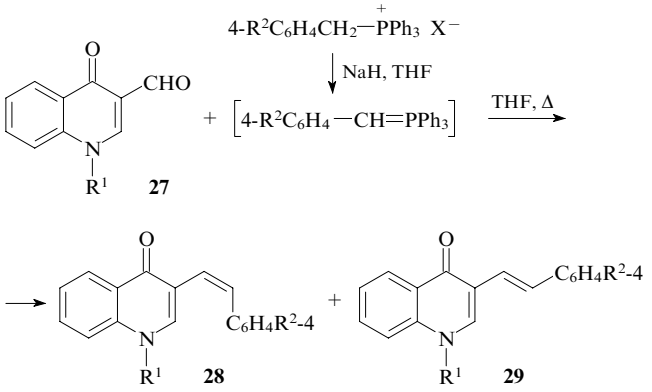
been obtained, and their structures have been studied by X-ray diffraction. In synthesis of 2-styrylquinoline derivatives, the condensation of quinaldine with aromatic aldehydes in the presence of acetic anhydride was carried out under microwave irradiation. This allowed one to significantly reduce the reaction time and decrease the amount of by-products.[48]

It was shown by other authors[49] that, although the reaction of 4-methylquinoline with aromatic aldehydes is accelerated by microwave irradiation, it was better to carry out the process in the absence of a solvent, using catalytic amounts of $ZnCl_2$. The proposed method afforded 4-styrylquinolines **22a**,**d**,**f**–**h** in yields up to 70%. The reaction time was reduced (to 5–15 min), and laborious procedures of isolation of products were avoided.

N,*N*-Dimethylaminostyrylquinolines **23** and **24** were obtained by 'anil synthesis'.[50] 2,4,6-Trimethylquinoline (**25**), formed in the reaction of *p*-toluidine with acetylacetone, and Schiff base **26** (in the ratio 1 equiv. per methyl group of compound **25**) were stirred at room temperature for 1.5 h. The compounds **23**, and **24** were isolated from the reaction mixture by column chromatography (Scheme 1).

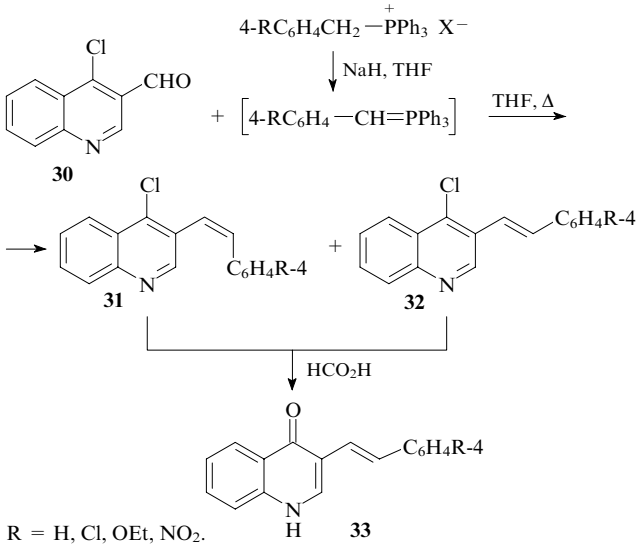
A new convenient method of synthesis of 2-styrylquinolines with various substituents in the 3-position has been proposed.[51] It is based on a combination of the reaction of 2-aminoaryl ketone with methyl ketone (the Friedlander reaction) and a Knoevenagel condensation in the presence of 1-methylimidazolium trifluoroacetate. The target products were obtained in high yields. However, unfortunately, their properties have not been discussed by the authors.

3-Styryl-4-quinolones have been synthesized by the Wittig reaction.[52] The reaction of 1-substituted 4-quinolone-3-carbaldehyde **27** with benzylidenetriphenylphosphoranes leads to a mixture of isomers **28** and **29**, in which *Z* isomer **28** prevails.



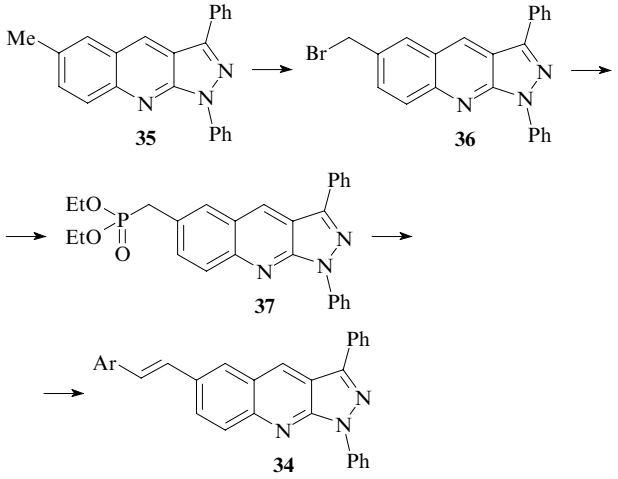
R^1 = Me, Ts; R^2 = H, Cl, OEt, NO_2.

The reaction of 4-chloroquinoline-3-carbaldehyde (**30**) with benzylidenetriphenylphosphoranes yields a mixture of styryl derivatives **31** and **32**, *Z* isomer **31** being the prevailing one. Both isomers give only (*E*)-3-styryl-4-quinolones **33** as a result of hydrolysis in 40% formic acid. Compounds **28**, **29** and **33** were obtained in order to study their biological activity, and no data on their luminescent properties have been reported.[52]



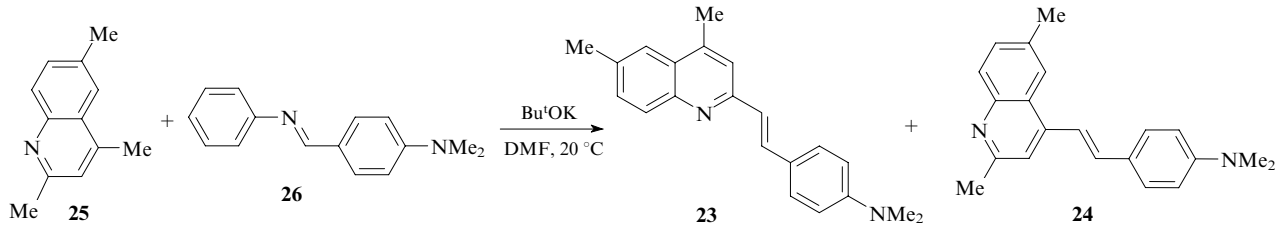
R = H, Cl, OEt, NO_2.

Among the large number of organic optoelectronic materials, 1*H*-pyrazolo[3,4-*b*]quinoline and its derivatives are of significant interest. They exhibit blue luminescence.[53] A series of 6-styryl-1*H*-pyrazolo[3,4-*b*]quinolines **34** have been synthesized, and their optical properties have been studied.[54] 6-Methyl-1,3-diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline (**35**) was first brominated by bromosuccinimide (NBS), and then bromomethyl derivative **36** was heated with triethyl phosphite in xylene at 140 °C for 24 h. Then, ester **37** was made to react with the appropriate aldehyde in anhydrous dimethoxyethane in the presence of sodium hydride.



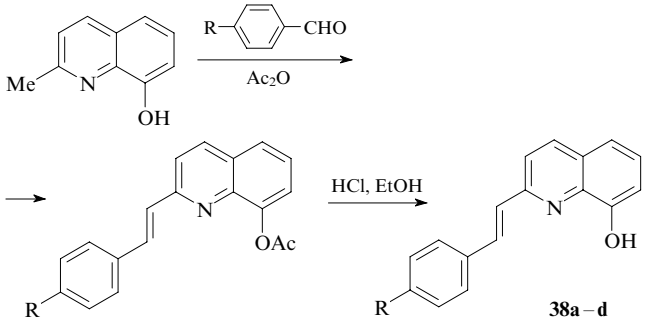
Ar = Ph, 4-MeC_6H_4, 2,4-$Cl_2C_6H_3$, 4-Py (Py is pyridyl).

Scheme 1



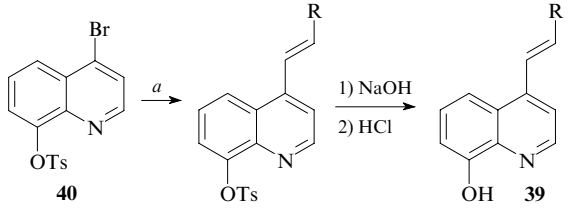
Synthesis of 2-styryl-8-hydroxyquinolines by condensation of 8-hydroxyquinaldine with aromatic aldehydes in acetic anhydride has been reported.[55] 8-Hydroxy-4-styrylquinolines have also been synthesized by the reaction of 8-hydroxylepidine with aromatic aldehydes in acetic anhydride.[56] Condensation of 8-hydroxy-2-methylquinoline with 4-diphenylaminobenzaldehyde and terephthalic aldehyde under similar conditions has been described.[57]

2-Styryl-8-hydroxyquinoline derivatives **38** were synthesized by Barberis and Mikroyannidis.[58] They have been used as chelating ligands for the preparation of complexes with zinc and aluminium.



R = Me (**a**), Cl (**b**), OMe (**c**), CN (**d**).

4-(2-Arylethenyl)-8-hydroxyquinolines **39** were synthesized in high yields by the Heck reaction, *i.e.*, by the reaction of 4-bromo-8-(*p*-toluenesulfonyloxy)quinoline (**40**) with styrene derivatives, and subsequent deprotection of the hydroxy group.[59]



a — R, $PdCl_2$, PPh_3 (2 equiv.);
R is 4-mono- or 2,4,6-trisubstituted aryl group.

b. Photophysical properties and photoisomerization

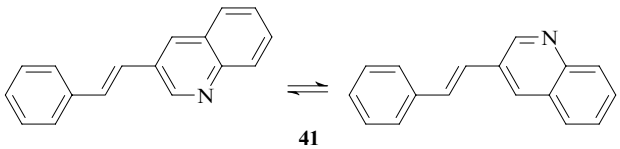
In addition to the reactions of photoisomerization and photocyclization, protonation reactions are also typical of styrylquinolines (similar to styrylpyridines). Due to that fact such compounds are convenient objects for studying the design and operation principles of molecular devices.[60] Switching between *cis* and *trans* forms of styrylquinolines can be realized by photoisomerization, and this process can be controlled by protonation of the quinoline nitrogen atom. A combination of two input signals, illumination and protonation, makes it possible to obtain different output response, thus realizing logic operations.

The reaction of *trans*–*cis* and *cis*–*trans* photoisomerization of the double bond in 2- (**21a**–**h**) and 4-styrylquinoline (**22a**–**h**) derivatives in neutral and protonated forms has been studied.[61] It has been shown that, in nitro-substituted styrylquinolines **21a** and **22a**, protonation has no effect on the quantum yields of photoisomerization. In aminostyrylquinolines **21b** and **22b**, the photoisomerization reaction is 'switched off' when the monocation is formed, due to the competitive process of intramolecular charge transfer, and is 'switched on' again when the dication is formed, the quantum yield of *trans*–*cis* photoisomerization decreasing 2–2.5 times, while the yield of *cis*–*trans* photoisomerization remaining almost the same as compared with the neutral compound.

A larger series of the derivatives of 4-styrylquinoline **22a**,**c**–**e** have been described.[62] It has been shown that all the compounds in neutral alcoholic solutions under illumination undergo reversible *trans*–*cis* photoisomerization with quantum yields close to the theoretical limit (0.5), which is typical of the diabatic mechanism of photoisomerization. In going from neutral to protonated forms, the quantum yields of photoisomerization change insignificantly.

Later on,[63] the same authors studied the process of photoisomerization of styrylquinolines **22** in more detail. The proof of adiabatic *trans*–*cis* photoisomerization (*t**–*c**) of compounds **22** in n-hexane was obtained. It was noted that such a mechanism of isomerization was realized in the presence of a naphthyl or quinoline moiety in the molecule. The diabatic mechanism of *trans*–*cis* photoisomerization of styrylquinolines **22** in ethanol was confirmed. In order to reveal the influence of the substituent in the aryl moiety on the absorption spectra in gaseous phase and solution by theoretical methods, substituted 2-styrylquinolines **21c**–**g** were studied.[64]

Previously, it was reported[65] that the excitation wavelength has an impact on the fluorescent properties of 3-styrylquinoline (**41**) and on the quantum yields of its ***trans***–*cis* photoisomerization. The experiments were carried out in different solvents and in aqueous solutions at different pH in order to obtain information on the influence of the solvent polarity and pH value on the conformational equilibrium:



41

The pK_a value of first excited singlet state for the protonated form of compound **41** was determined by fluorometric titration. The influence of the excitation wavelength on the prototropic equilibrium in the excited state was studied. It was shown that the emission spectrum of a solution of *trans*-3-styrylquinoline in cyclohexane (concentration 10^{-6} mol litre^{-1}) changed depending on the excitation wavelength. The luminescence spectra at room temperature and 77 K confirmed the presence of two types of emitting particles, which was explained by the presence of conformational isomers formed as a result of rotation about the single bond between the styryl and quinoline moieties of the molecule.

The reaction of proton transfer in the excited state and the influence of the protonation on the luminescent properties have been studied for 2(4)-dimethylaminostyrylquinolines.[66, 67] If the protonation involves only the quinoline nitrogen atom (at a low acid concentration), the long-wavelength shift is observed in both the absorption and emission spectra. In a highly acidic medium, double protonation occurs, which leads to the short-wavelength shift of absorption and emission maximums.

Many styrylquinolines prove to be dyes with pronounced photo- and electroluminescent properties. They

find application in different fields, including medicine and pharmacology. Specifically, in the spectra of *trans*-2-(4-dimethylamino)styryl-6-chloroquinoline (**21h**) synthesized by Wang and Lin,[68] the emission maximum correlates well with the polarity of the solvent (Fig. 2). In aqueous solutions, this compound in the ground state forms H-type aggregates in which the molecules are arranged head-to-head and their absorption maximum is characterized by the blue shift, but excitation leads to disaggregation. The photophysical properties of styrylquinoline **21h** in aqueous and mixed water–organic solutions recommend it as a biosensor.

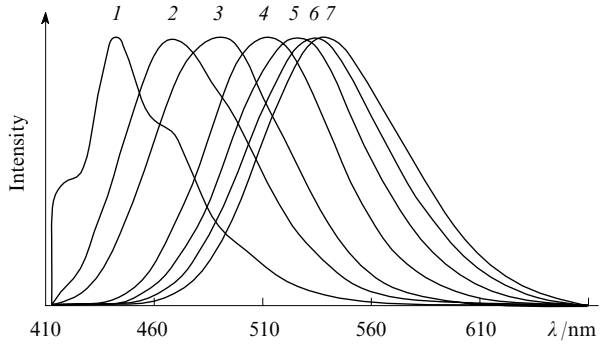
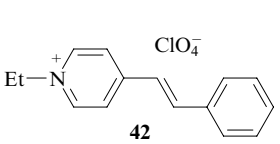


Figure 2. Emission spectra of compound **21h** (λ_{exc} = 400 nm) in cyclohexane (*1*), dibutyl ether (*2*), diethyl ether (*3*), dichloromethane (*4*), acetone (*5*), acetonitrile (*6*) and DMSO (*7*).[71]

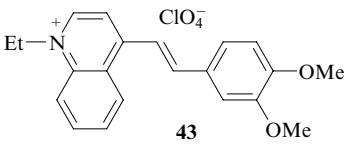
The emission spectra of styrylquinolines **21** with different substituents in the aryl moiety have been described.[69, 70] The photophysical properties of 6,7-difluoro derivatives of 2-styrylquinoline **21i–k** and their 4-carboxyl analogues have been reported.[71] 2-Styrylquinoline-4-carboxylic acid derivatives possess nonlinear optical properties, and polymer materials based thereon exhibit such properties.

On excitation by light at a wavelength of 365 nm, styrylquinolines **25** and **26** show strong yellow-green luminescence.[50]

A comparative study of phototransformations of styryl dyes of pyridine and quinoline series (exemplified by compounds **42**, **43**) in solutions and polycrystalline and polymer layers has been carried out.[72] Both compounds show significant luminescence whose intensity reduces under irradiation. A spectral kinetic study has shown that dyes **42** and **43** undergo photoinduced transformations due to the *trans–cis* isomerization and [2+2] photocycloaddition reactions. Only efficient *trans–cis* isomerization was observed in solutions, the *Z* form of compound **42** undergoing thermal relaxation to the *E* isomer unlike the (*Z*)-**43** derivative. In polycrystalline films and polycarbonate layers, the photoinduced forms of compounds **42** and **43** did not undergo thermal relaxation. A dramatic increase in the luminescence intensity of dye **43** in a polycarbonate film as compared with the solution is noteworthy.

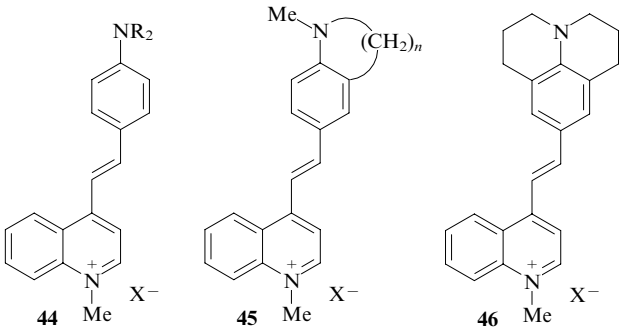


42



43

For a series of *N*,*N*-dialkylamino-substituted 1-methyl-4-styrylquinolinium salts **44–46**, the influence of the polarity of solvent on the spectral properties of compounds has been examined.[73] Such derivatives show an absorption maximum at 538–595 (in THF) and 542–597 nm (in acetonitrile). In the luminescence spectrum, the maximum is observed at 688–710 (in THF) and 693–735 nm (in MeCN). The luminescence quantum yields measured relative to Rhodamine B in ethanol are from 0.003 to 0.013.



44 **45** **46**

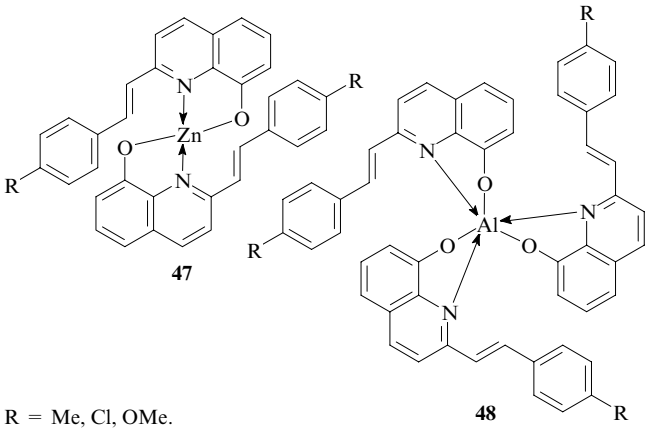
NR_2 = NMe_2, NEt_2, NPh_2, pyrrolidin-1-yl, piperidin-1-yl; n = 2, 3; X = I, ClO_4, Bu^nPh_3B.

6-Styryl-1*H*-pyrazolo[3,4-b]quinolines **34** show strong luminescence with a maximum at 475 nm.[54] The theoretical and experimental study of their absorption and emission spectra has demonstrated that the solvent nature and the character of the substituent in the aryl moiety have no effect on the optical properties of the compound.

8-Hydroxyquinoline and its derivatives (especially metal chelates based on them) have become an object of much interest to researchers since the first publications of the data on the electroluminescence of aluminium complex with 8-hydroxyquinoline (Alq_3).[74] Currently, this complex remains one of the best materials with electroluminescent properties. It possesses excellent thermal stability, high efficiency of green luminescence and rather good electron mobility.

Structural modification of 8-hydroxyquinoline and its metal complexes has been intensively studied. In particular, much effort has been focused on the synthesis of blue luminescent aluminium quinolates. Progress in this respect has been reported in the paper,[75] dealing with the effect of fluorination at different positions of quinoline on the luminescent characteristics of fluorinated 8-hydroxyquinoline aluminium complexes. The choice of such a substituent is caused by the specific properties of the fluorine atom. Due to them, for example, fluorine-containing organic semiconductors possess high electron mobility, high stability in air, low sublimation temperature and a wide band gap. It has been shown[75] that fluorination at the 5-position of quinoline leads to a red shift of luminescence maximum (λ_{max} = 547 nm, for nonfluorinated analogue 515 nm) with a tremendous decrease in both the luminescence intensity (approximately 20 times) and the quantum yield. At the same time, fluorination at the 6-position of aluminium quinolate leads to a blue shift (λ_{max} = 495 nm) with a significant increase in luminescence intensity and about a 2.6-fold increase in quantum yield. Fluorination at the 7-position has almost no effect on the luminescent properties.

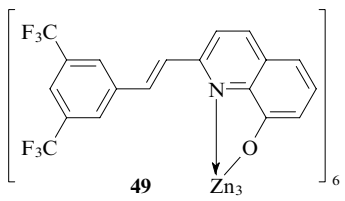
The quinoline ligand is often modified by means of extension of the conjugated chain by the substituent, for example, by the styryl one, at the 2- or 4-position. In particular, complex compounds **47** and **48** possess improved properties as compared with the corresponding complexes based on 8-hydroxyquinoline. They are soluble in common organic solvents, more thermally stable and more suitable for preparation of films. Solutions of these complexes in THF exhibit blue-green luminescence with a maximum in the range of 513–576 nm, λ_{max}^{fl} for the zinc compounds being more red-shifted.[58]



R = Me, Cl, OMe.

The hydrothermal reaction of 2-styryl-8-hydroxyquinoline derivative **38d** and $Cd(ClO_4)_2 \cdot 6H_2O$ in aqueous pyridine yielded 2-[2-(4-carboxylatophenyl)ethenyl]-8-quinolinato(pyridine)cadmium(II).[46] Under these conditions, the nitrile group is hydrolyzed into the carboxylic one. According to X-ray diffraction data, the complex is a coordination polymer containing a dimer moiety consisting of two cadmium atoms. Each of the cadmium atoms is coordinated to two oxygen atoms from the 8-hydroxyquinoline moieties, two oxygen atoms from the carboxylic group of the third ligand and two nitrogen atoms (one from the quinoline ring and the other from the pyridine ring). This complex exhibits strong red luminescence with a maximum at 600 nm.

The use of another 2-substituted 8-hydroxyquinoline ligand, namely, (*E*)-2-{2-[3,5-bis(trifluoromethyl)phenyl]-ethenyl}-8-hydroxyquinoline (L), enabled the isolation of a complex of Zn^{II} of composition Zn_3L_6 (**49**) with a unique structure[76] (Fig. 3). According to the X-ray diffraction data, this complex is trinuclear, with strong π–π-stacking between the planes of the quinoline moieties. As a whole, the molecular structure is propeller-like. Compound **49** exhibits yellow luminescence with λ_{max} at 553 nm in DMSO and 610 nm in the solid state and has high thermal stability.



Aluminium complexes based on styrylquinolines exhibit luminescence with a maximum at 566–597 nm (in chloroform) and a low quantum yield (0.006–0.013). The highest value of the quantum yield is observed for the complex with ligand **39** [R = 2,4,6-$(MeO)_3C_6H_2$] due to the minimization of the photoisomerization of the ligand.[59]

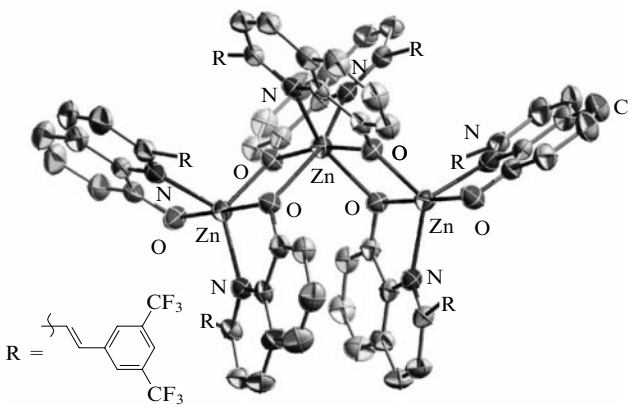
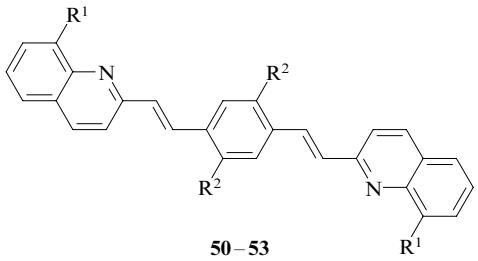
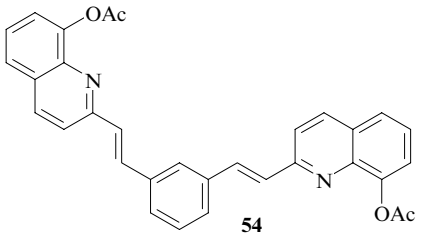


Figure 3. Structure of coordination compound **49**.[76]

A number of investigations concerning the synthesis of poly(phenylenevinylene) oligomers (PPV) containing an 8-substituted quinoline ring have been undertaken with the aim of designing OLEDs. The synthesis, characteristics and luminescent and electroluminescent properties of new bis[2-(8-R-quinolin-2-yl)ethenyl]benzenes **50**–**54** have been described.[77–79] According to X-ray diffraction data, intermolecular π–π-interactions are revealed for compounds **50**, **51** in the solid state. Colour of emission of derivatives **50**–**54** is different, from blue to yellow, depending on the character of substituents in the quinoline moieties and in the central part of the conjugated system. Electroluminescent devices have been designed using compounds **50**–**53** as emitters and electron transport layers. By the characteristics obtained, the device based on compound **53** was most promising.

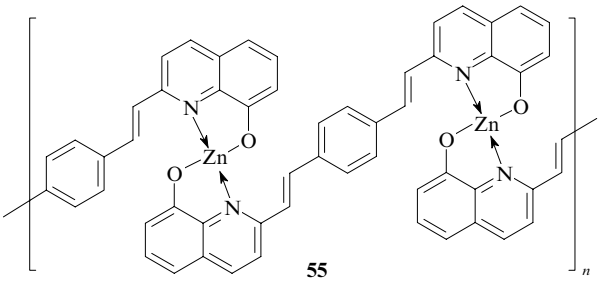


R^2 = H: R^1 = H (**50**), OMe (**51**), OAc (**52**); R^1 = OAc, R^2 = OMe (**53**).

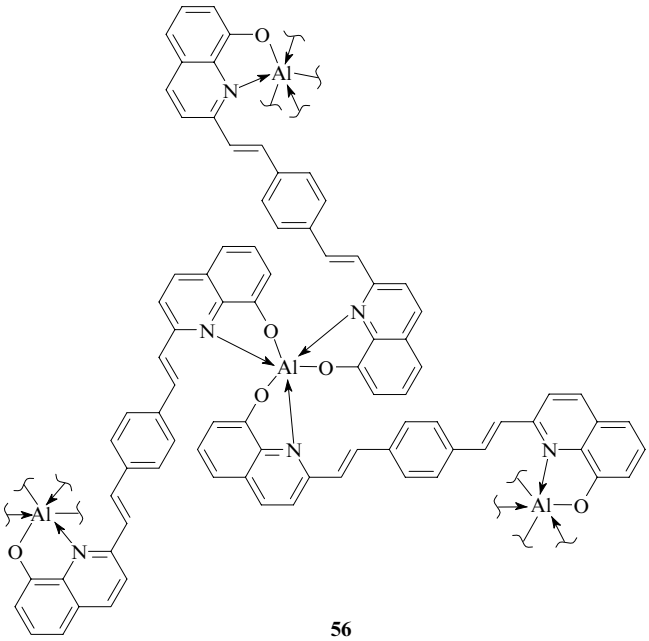


Polymeric complexes of zinc (**55**) and aluminium (**56**) with bis[2-(8-hydroxyquinolin-2-yl)ethenyl]benzene have been synthesized.[80] The electroluminescent properties of a multilayer device incorporating complexes **55** or **56** as luminescent materials have been studied. The device based

on the aluminium complex had the best characteristics: the forward bias turn-on voltage for this device was 8 V, and maximum luminescence was achieved at 15 V.

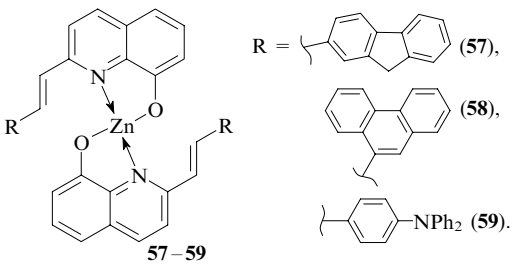


55



56

In recent years, researches have been developed to create white light LEDs. One of the approaches implies the use of emitters simultaneously containing moieties with high hole- and electron-transporting characteristics, which permits the disign of low-cost but high-performance devices. For example, such an approach has been realized in Refs 81–84. Zinc complexes based on 2-styryl-substituted 8-hydroxyquinolines **57**–**59** have been synthesized. Groups with strong hole-transporting ability, such as 9*H*-fluoren-2-yl, phenanthren-9-yl and 4-diphenylaminophenyl, have been used as substituent R. A combination of these substituents with 8-hydroxyquinoline metal chelate possessing high electron-transporting ability and strong luminescence afforded multifunctional hydroxyquinoline derivatives with high thermal stability and efficient yellow emission.



57–**59**

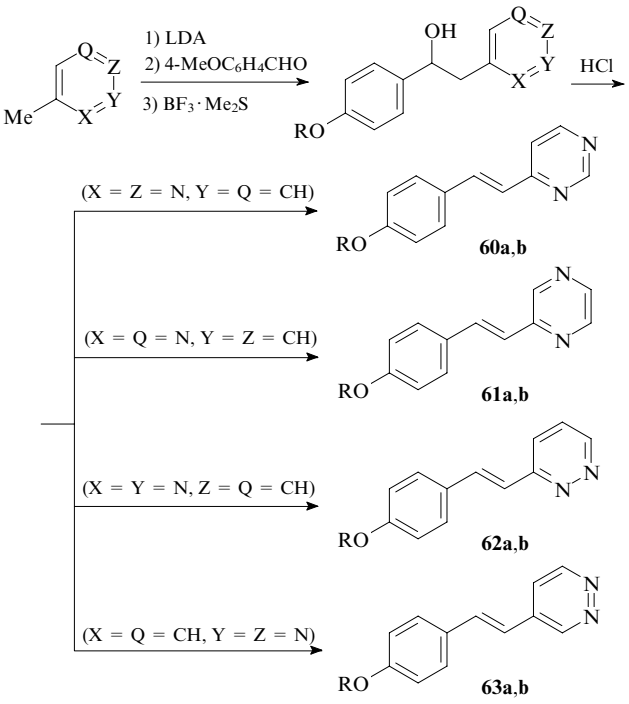
R = (**57**), (**58**), NPh_2 (**59**).

Zinc quinolates **57**–**59** have been incorporated in the structures of several single-layer OLEDs.[81–84] These devices exhibit rather high luminance, good hole conductivity and luminescence in a specified spectral region.

3. Styryldiazines

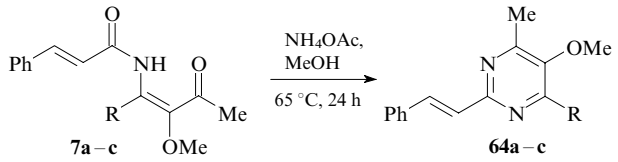
a. Methods of synthesis

An approach to the synthesis of four isomeric 4-substituted styryldiazines differing in the position of nitrogen atoms in the diazine moiety, namely, 2,4-diaza (**60a**,**b**), 2,5-diaza (**61a**,**b**), 2,3-diaza (**62a**,**b**) and 3,4-diaza isomers (**63a**,**b**), has been developed. It consists in the condensation of appropriate methyldiazines with 4-methoxybenzaldehyde.[85] Earlier, these compounds were obtained[86] in very low yields. The new technique afforded all styryldiazines in high, almost quantitative yields, in spite of the difference in the acidity of the methyl group of the starting methyldiazines. The anion generated from methyldiazine by treatment with lithium diisopropylamide in tetrahydrofuran actively reacts with 4-methoxybenzaldehyde at −50 °C. Demethylation of methoxy group by treatment of corresponding hydroxy derivatives with $BF_3 \cdot Me_2S$ is accompanied by partial dehydration, but in order to achieve the completeness of the process, it is followed by acid-catalyzed dehydration. It should be mentioned that the synthesized styryldiazines have *trans* configuration, without traces of the *cis* isomer.



R = Me (**a**), H (**b**).

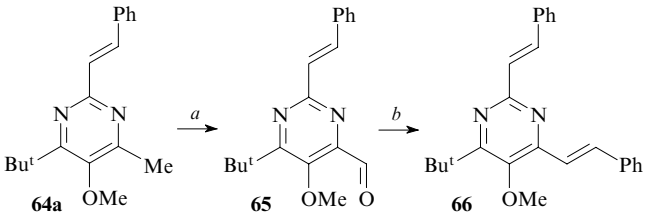
A new two-stage approach to the synthesis of alkenyl-substituted 4-hydroxypyridines based on the cyclization of β-alkoxy-β-ketoenamides **7a**–**c**[14] was mentioned in Section II.1. Compounds **7** are also convenient precursors for the synthesis of styrylpyrimidines. Their heating with ammonium salts in methanol leads to akenyl-substituted pyrimidines **64a**–**c** in a yield of 55%–85%.



7a–c 64a–c

R = Bu^t (**a**), Ph (**b**), 2-Th (**c**).

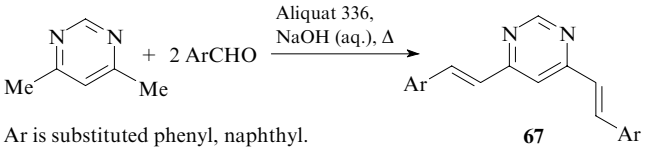
The presence of the methyl group in the 4-position of pyrimidines **64** makes it possible to carry out subsequent functionalization. In particular, the oxidation of compound **64a** by selenium dioxide leads to aldehyde **65**, which transforms into 2,6-distyryl pyrimidine derivative **66** under the conditions of the Wittig reaction.[14]



64a 65 66

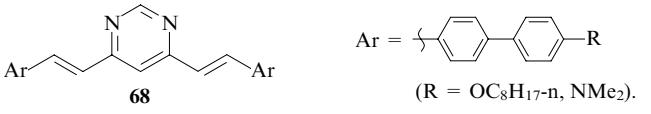
(*a*) SeO_2, dioxane, 90 °C; (*b*) Ph_3PBnBr, Bu^{n}Li, Et_2O, 0 °C.

π-Conjugated oligomers of D-π-A or D-π-A-π-D types (where D stands for an electron-donating moiety and A stands for an electron-withdrawing one), due to their luminescent properties, have attracted attention as chromophores for nonlinear optical materials. The pyrimidine ring is often introduced into the structure of such molecules. In particular, V-shaped 4,6-bis(arylethenyl)pyrimidines of symmetric, asymmetric and dendritic structure have been synthesized and characterized.[87] Aldol condensation of 4,6-dimethylpyrimidine with the corresponding aldehyde is carried out in a boiling 5 M NaOH solution using Aliquat 336 as a catalyst. This makes it possible to avoid the use of organic solvents and to achieve high yields of target products **67**.



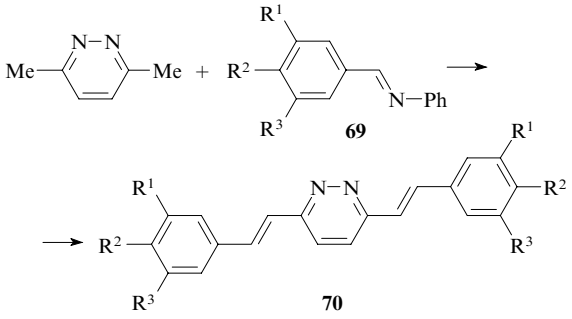
Ar is substituted phenyl, naphthyl. **67**

To extend the conjugated chain of each styryl moiety, pentacyclic V-shaped oligomers **68** were synthesized using the Suzuki cross-coupling reaction from brominated bis-derivatives **67** (Ar = 4-BrC_6H_4). According to ^{1}H NMR data, all of compounds **67** and **68** were isolated as *trans* isomers.



68 Ar = (R = OC_8H_{17}-n, NMe_2).

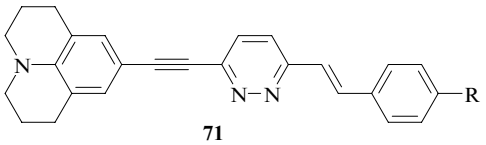
The double Siegrist reaction, *i.e.*, the reaction of 3,6-dimethylpyridazine with azomethine **69**, enabled the isolation of (*E*,*E*)-3,6-bis(styryl)pyridazines **70** containing two, four or six alkoxy groups in phenyl substituents.[88] Derivatives **70** are promising as mesogenic compounds for the preparation of liquid crystals.[88]



69 **70**

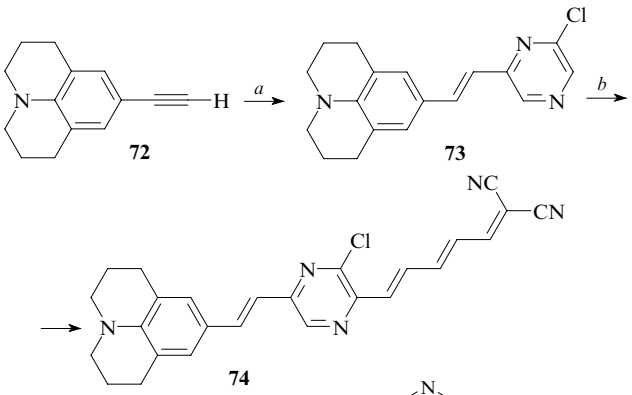
R^1, R^2, R^3 = H, OAlk.

Styrylpyridazines **71** are formed under conditions similar to those of the synthesis of compounds **67**.[89]



71

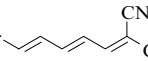
9-Ethenyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*i*,*j*]quinoline (**72**) was used for obtaining polyconjugated molecules **73** and **74** with a pyrazine core.[90]



72 **73** **74**

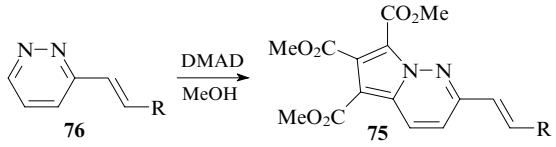
(*a*) 1) Cp_2ZrHCl, THF; 2) $ZnCl_2$, THF; 3) ;

(*b*) 1) LTMP, THF, −78 °C; 2) $ZnCl_2$, THF, −78 °C;

3) , $Pd(PPh_3)_4$; Cp is cyclopentadienyl,

LTMP is lithium 2,2,6,6-tetramethylpiperidide.

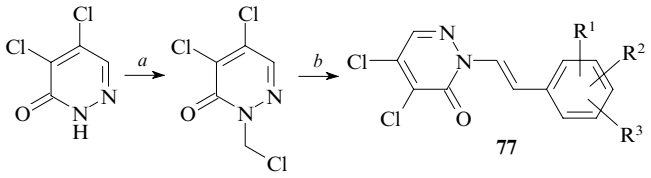
A wide range of styryl derivatives of pyrrolopyridazine **75** have been synthesized.[91] They act as blue organic luminophors. Compounds **75** are formed in the reaction of 1,3-dipolar cycloaddition between styrylpyridazines **76** and dimethyl acetylenedicarboxylate (DMAD) in methanol at low temperature.



76 **75**

R is substituted phenyl, naphthyl, diphenyl, anthranyl.

A multistage synthesis of a wide series of 2-styryl-4,5-dichloropyridazin-3(2*H*)-ones **77** from the corresponding dichloropyridazinone has been described.[92,93]

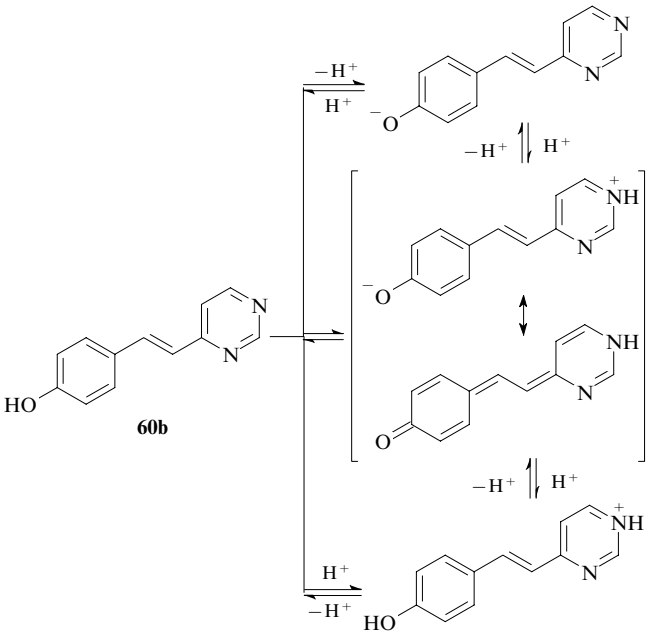


R^1, R^2, R^3 = H, Hal, Me, Ar, OMe, NO_2, CN, NMe_2; (*a*) 1) CH_2O, H_2O, 5–10 °C; 2) $SOCl_2$, DMF, CH_2Cl_2, 20 °C; (*b*) 1) KI, MeCN, Δ; 2) PPh_3, CH_2Cl_2, Δ; 3) $R^1R^2R^3C_6H_2CHO$, Bu^tOK, MeCN, Δ.

b. Photophysical properties

Styryldiazines **60**–**63** were synthesized in order to investigate the influence of the additional nitrogen atom in the 4-hydroxystyrylpyridine system on the photophysical properties. The absorption and emission spectra of these compounds have been recorded in a variety of solvents and under different pH conditions. The UV spectra of styryldiazines **60**–**63** in ethanol at neutral pH show a long-wavelength absorption band at 330–350 nm. It undergoes a bathochromic shift up to 390–420 nm in both acidic and basic media. This shift is most pronounced in cases of compounds **60b** and **63b**. All four isomers **60**–**63** show long-wavelength luminescence that is highly solvatochromic and sensitive to pH. In particular, in acetonitrile the emission maximum is observed at 400–435 nm, and in acidic or basic media it shifts up to 500–560 nm for compounds **60** and **63** and up to 590–640 nm for styryldiazines **61** and **62**.[85]

The interpretation of the fluorescent properties of 4-hydroxystyryldiazines **60b**–**63b** is complicated by proton transfer in the excited state, which can lead to the formation of not only an anion or cation but also of a bipolar (quinoid) form.[85] Since the acidity of phenol and the basicity of diazine increase in the excited state, the quinoid species is formed under conditions when proton transfer is sufficiently rapid to occur during the lifetime of the excited state. Inasmuch as the emission of bipolar (quinoid) form is observed at longer wavelengths than that of the three other forms, the presence of this form can account for the long-wavelength emission that was observed for the hydroxystyryldiazine system, much the same as for 4-hydroxystryrylpyridines.[11]



The revealed fluorescent properties of compounds **60**–**63** make them potentially useful as spectral probes for biological systems. The best results were observed for 4-methoxy- and 4-hydroxystyryl-1,2-diazines **63a**,**b**.

Styryldiazines **64** and **77** possess fluorescent properties. A rather large Stokes shift is typical of them (~110 nm).[14]

Oligomers **67** and **68** exhibit strong luminescence in a wide spectral range (407–592 nm depending on the nature of substituents) with large Stokes shift and a high quantum yield in some cases. Strong emission solvatochromism is observed for them as a red shift of maximum with increasing polarity of the solvent. The sensitivity to acids is also observed. Such properties make these compounds promising materials for colorimetric and luminescent pH-sensors.[87]

(*E*,*E*)-3,6-Bis(styryl)pyridazines are D-π-A-π-D-systems. They are characterized by strong long-wavelength absorption at 280 and 420 nm [$\varepsilon_{max} = (5-0.3) \times 10^4$]. According to calculation data (CNDO/CI), these bands correspond to nπ* transition. For these compounds $S_1(\pi\pi^*)/S_0(\pi^2)$ luminescence is not typical, while corresponding 1,4-bis(styryl)benzenes exhibit such luminescence with quantum yields of 0.8–0.9.[94]

A pyridazine moiety is also a constituent of molecular structure **71** in which it acts as an electron-withdrawing moiety. The compounds show strong luminescence with a maximum at 540–560 nm with large Stokes shift. The presence of ethenyl and ethynyl bridges promotes charge transfer along these molecules and makes them good materials for so-called two-photon dyes. Structures **71** have been introduced[89] as new intermediates for the synthesis of organic molecular materials.

The introduction into compound **73** of a polyene chain with cyano groups (compound **74**) leads to a red shift in absorption spectra (438 → 596 nm) and emission spectra (582 → 612 nm) and to a decrease in quantum yield.[90]

Compounds **77** exhibit strong luminescence in a wide spectral range. It has been found that solvatochromic shifts, position and shape of luminescence spectrum and quantum yield of derivatives **77** depend on the number, nature and position of substituents in the phenyl ring. There is a correlation between the luminescence maximum energy and the Hammett constants for the *para*-substituents.[92, 93]

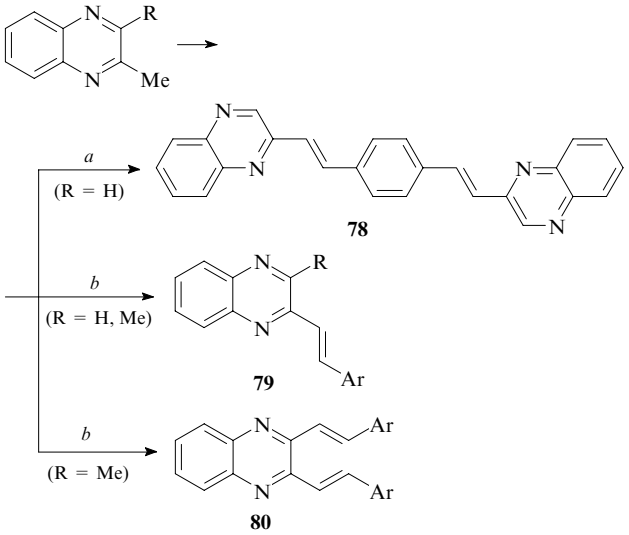
4. Styrylbenzodiazines

a. Methods of synthesis

A series of mono- (**78**, **79**) and distyryl derivatives of quinoxaline (**80**) have been synthesized.[47, 50] They are promising photo- and electroluminescent materials. 2-Methyl- or 2,3-dimethylquinoxalines were used as starting compounds (Scheme 2).

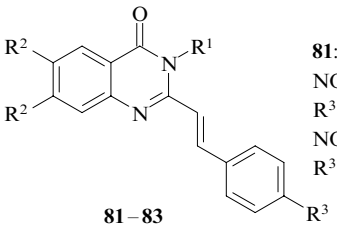
Compounds **81** were obtained by the reaction of 2-methylquinazolin-4(3*H*)-one and aromatic aldehydes under microwave irradiation, and their aromatization was realized under the action of $POCl_3$ in the presence of *N*,*N*-dimethylaniline.[95] However, the optical properties of the resulting 2-styrylquinazolines being formed under these conditions were not studied. Styrylquinazolinones **81** have also been synthesized under different conditions.[96] Dilithiated 2-methylquinoxaline reacts with aromatic aldehydes in tetrahydrofuran at −78 °C, then the corresponding

Scheme 2



Ar = C_6H_4OMe-4; (*a*) 1,4-$(HOC)_2C_6H_4$; (*b*) 4-$MeOC_6H_5CHO$.

hydroxy derivative is subjected to dehydration under the action of trifluoroacetic acid.



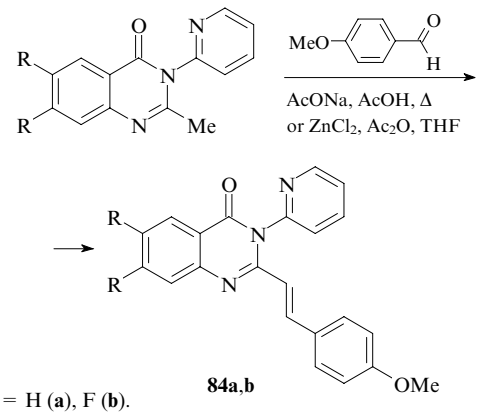
81–**83**

81: $R^1 = R^2 = H$: R^3 = H, OMe, NO_2, NMe_2; **82**: R^1 = Ph: R^2 = H, F; R^3 = H, OMe, OH, OBu^n, Et, NMe_2, NO_2, F; **83**: R^1 = 1-Naph, R^2 = H: R^3 = H, OMe, NO_2, NMe_2.

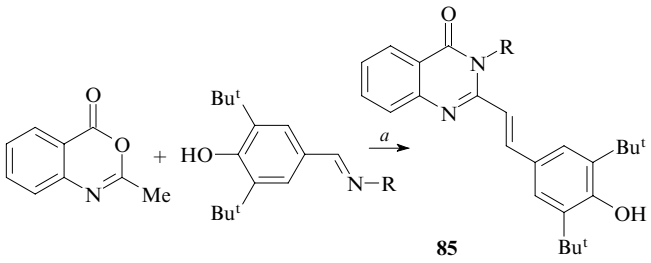
trans-2-Styryl-substituted 3-phenyl- and 3-naphtylquinazolin-4-ones, as well as the 6,7-difluoro derivatives (**82**, **83**) were synthesized by the condensation of appropriate 2-methylquinazolin-4-ones with aromatic aldehydes or by the recyclization of 2-methyl-3,1-benzoxazin-4-one by benzylidenephenylamines (*e.g.*, see Scheme 3).[97]

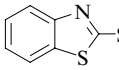
The replacement of the phenyl moiety in the 3-position of quinazolinones **82** by a 2-pyridyl one led to compounds **84a**,**b**.[97]

The synthesis of novel styrylquinazolinones **85** containing moieties of sterically hindered phenols has been described.[98] It should be noted that the authors extended the range of reagents used for transformation of the benzoxazine ring. Not only azomethines but also hydrazones and thiosemicarbazones were used. In this paper, there was no information on whether these compounds have luminescent properties.



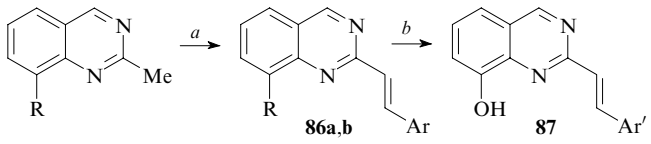
R = H (**a**), F (**b**).



(*a*) AcONa, AcOH, Δ; R = n-C_8H_{17}, 4-MeC_6H_4, 2-Py, 2-thiazolyl, PhNHC(S)NH, PhC(O)NH,  $SCH_2C(O)NH$.

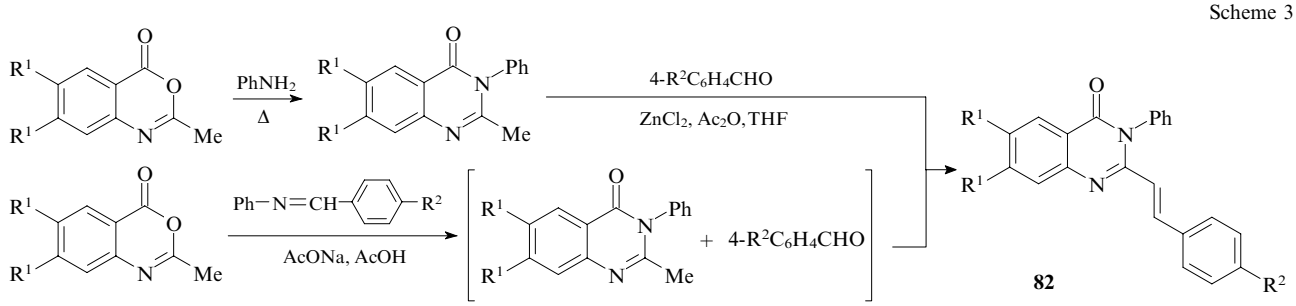
A similar reaction of 6-bromo-2-methyl-3,1-benzoxazin-4-one with Schiff bases leading to the formation of 3-aryl-6-bromo-2-stryrylquinazolin-4-ones in high yields has been described.[99]

The Perkin condensation of 2-methylquinazoline and 2-methyl-8-methoxyquinazoline with aromatic aldehydes by refluxing in acetic anhydride leads exclusively to the formation of the *E* form of quinazolines **86a**,**b**. Demethylation of compounds **86b** under the action of BBr_3 results in



(*a*) ArCHO, Ac_2O, Δ; (*b*) BBr_3 (R = OMe); R = H (**a**), OMe (**b**); Ar = $X_nC_6H_{5-n}$ (X_n = 4-OAc, 3-OAc-4-OMe, 3,4-$(OAc)_2$); Ar′ = $Y_nC_6H_{5-n}$ (Y_n = 4-OH, 3,4-$(OH)_2$).

Scheme 3

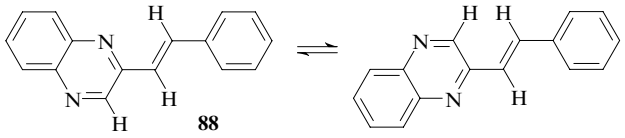


8-hydroxyquinazolines **87**.[100] Heating 8-hydroxy-2-methylquinazoline with aromatic aldehydes in acetic anhydride enables the isolation of the styryl derivatives of 8-acetoxyquinazoline.[101]

b. Photophysical properties

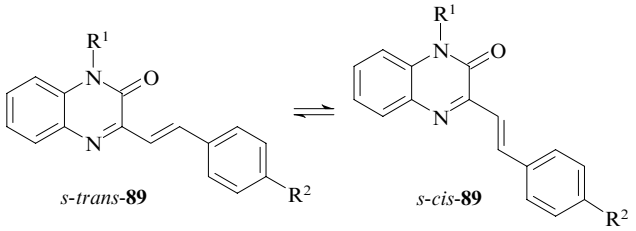
Compounds **78**–**80** show strong blue luminescence in $CHCl_3$ or DMF solutions under excitation at 365 nm,[50] but no spectral characteristics of these compounds have been reported in this paper. The photophysical properties of 6,7-difluorinated analogues of compound **79** (R = H) have been described.[71]

The photophysical behaviour of conformers was studied for *trans*-2-styrylquinoxaline **88** as an example.[102]



88

It has been shown that the luminescence and emission spectra change at different excitation wavelengths. In particular, the change in the excitation wavelength from 320 to 390 nm leads to a bathochromic shift of the emission maximum (from 428 to 442 nm), but it slightly affects the luminescence quantum yield in ethanol (0.16–0.12). The nature of solvent has a great influence on the luminescence quantum yield. The change of solvent from hexane to methanol is accompanied by a 100-fold increase in the quantum yield (from 0.002 to 0.24) at λ_{exc} = 320 nm, and only by a 50-fold increase at λ_{exc} = 390 nm. The bathochromic shift of emission maximum by 17 or 26 nm is also observed depending on λ_{exc}. The dependences of emission on the solvent polarity are different for each of the conformers, and only one of them exhibits luminescence in hexane.



s-trans-**89** *s-cis*-**89**

R^1 = H, Me; R^2 = H, Me, CF_3, CHO, NMe_2.

The photophysical properties of 3-styryl derivatives of quinoxalin-2-ones **89** have been described.[103] Rotational isomerism about the bond connecting the imine and vinyl groups in the *E* isomers has been revealed for this series of compounds. The *cis*-rotamer turns out to be the predominant isomer.

Styrylquinoxalinones **89** show luminescence in a wide spectral range (454–631 nm) depending on the character of the substituent R^2 and the nature of solvent (chloroform, acetonitrile, ethanol). The relative quantum yields for these compounds are in the range of 0.04–0.09. Only for the compounds with $R^2 = NMe_2$, a larger value was obtained, 0.18–0.20.

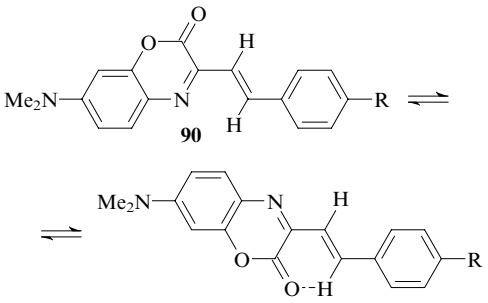
The photophysical properties of styrylquinoxalin-2-ones **89** and styrylbenzoxazin-2-ones **90**[104] have been compared.[103] In spite of the similarity of the structures, compounds **90** do not behave as stilbene derivatives. In the same solvents (chloroform, acetonitrile, ethanol), benzoxazinones display a significant long-wavelength shift of absorption and especially emission maximums as compared with quinoxalinones **89** and unusually high quantum yields (0.21–0.85) for styryl derivatives. Similar to compounds **89**, they also show rotational isomerism, one of the isomers

Table 1. Absorption and photoluminescence spectral data for quinazolinones **81**–**83**.[97]

Compound	R^1	R^2	R^3	λ_{abs}/nm	Fluorescence spectrum		Stokes shift (Δl)/nm
					λ_{fl}/nm	see [a]	
81	H	H	H	310	411	40	101
	H	H	NO_2	380	542	141	162
82	Ph	H	H	340	450	8	110
	Ph	F	H	380	445	52	65
	Ph	H	NO_2	398	540	139	142
	Ph	F	NO_2	396	521	264	125
	Ph	H	NMe_2	411	521	59	110
	Ph	F	NMe_2	427	524	62	97
	Ph	H	OMe	330	461	220	131
	Ph	F	OMe	384	514	136	130
	Ph	H	F	333	402	40	69
	Ph	F	F	350	445	109	85
	Ph	H	OH	320	458	34	138
	Ph	H	OBu^n	340, 370	470	40	100
	Ph	H	Et	300 [b]	420	45	120
	Ph	F	Et	356	460	24	104
83	1-Naph	H	H	365	465	12	100
	1-Naph	H	OMe	307	423	63	116
	1-Naph	H	NO_2	377	534	93	157
	1-Naph	H	NMe_2	425	521	100	96

[a] Intensity (rel.u.), [b] shoulder.

being stabilized by the hydrogen bond and being a predominant one.



90

R = H, CHO, CH=CHCO$_2$H, NMe$_2$, monoaza-15-crown-5.

It has been concluded [104] that the main chromophore of compounds **90** is the aminobenzoxazine ring, while the arylstyryl moiety behaves as a single substituent; that is why, on the whole, their behaviour differs from that of the stilbene derivatives.

Styrylquinazolines are less known as compared with other benzodiazines with luminescent properties. The absorption and emission spectra of 2-styrylquinazolinones **81** have been studied.[105] Quantum chemical calculations of transition energies, the geometries of ground and excited states and other characteristics have been performed. The experimental and theoretical data enabled the conclusion that compounds **81** were promising objects for the preparation of nonlinear optical materials.

2-Styrylquinazolin-4-ones **81**–**83** exhibit photoluminescence in an acetonitrile solution with a maximum in the range of 402–545 nm (Table 1).[97] The elongation of the conjugated chain by varying substituents leads to a long-wavelength shift of the emission band and to the change in the luminescence colour from blue to green. Nitro and dimethylamino groups that are different in their electronic effects have the same effect on the emission band position. At the same time, the strongest photoluminescence in the series of 3-phenyl derivatives with R^2 = H is observed for compound **82** (R^3 = OMe), whereas at R^2 = F it is observed for compound **82** (R^3 = NO_2). The presence of fluorine atoms at the 6- and 7-positions of the benzene ring affects both the emission band position and the luminescence intensity, increases the solubility of styryl derivatives in organic solvents and makes it possible to perform their further modification.

It has been shown that, with decreasing temperature from 293 to 77 K, the luminescence intensity of compounds **82** and **90** considerably increases,which is explained by the slowing down of the process of *trans*–*cis* isomerization.[97]

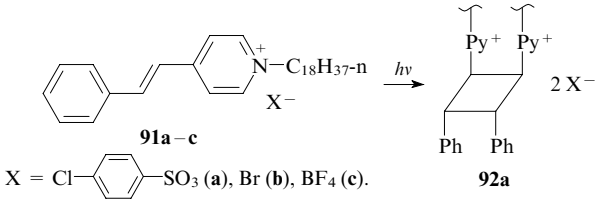
III. Cyclization reactions

1. [2 + 2] Photocycloaddition

Along with photoisomerization, other reversible photochemical (photoinitiated) processes are typical of 1,2-dihetarylethenes, in particular, the [2 + 2] photocycloaddition reaction leading to cyclobutane derivatives.[106] The efficiency of one or another photochemical process in solutions of substituted stilbenes is determined by the solvent polarity and substrate concentration. For example, the photolysis of 1-aryl-2-phenylethenes in benzene with a concentration of 10^{-4}–10^{-6} mol litre^{-1} leads only to the isomerization and cyclization into phenanthrene derivatives.[107] At the same time, in water or methanol under the same conditions, these compounds generally undergo dimerization.[108, 109] The photodimerization processes have been investigated in more detail for styrylpyridines. In one of the early papers [110] it has already been shown that the photodimerization of hydrochlorides of substituted styrylpyridines successfully occurs both in aqueous solutions and under irradiation of suspensions of these salts in heptane. However, the dimerization products have been characterized only by elemental analysis data and absorption spectra.

Later,[111] the influence of environment on the photochemistry of alkyl-4-stilbazolium salts **91** has been studied in solutions, solid state and monolayers.

As follows from the results of investigations, the nature of counterion has an effect on the behaviour of salts **91**. Under irradiation of acetonitrile solutions, only *trans*–*cis*-isomerization is observed for all compounds, whereas irradiation of salt **91a** in the solid state leads to the product to which structure **92a** has been attributed on the basis of ^{1}H NMR data. In ensembles of monolayers (in a mixture with tripalmitin), stilbazole **91** is also dimerized. It is believed that the dimer has a structure similar to compound **92a**. In case of salts **91b**,**c** dimerization does not occur.



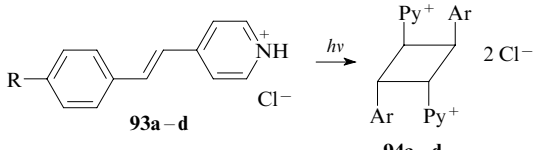
91a–**c**

X = Cl–C$_6$H$_4$–SO$_3$ (**a**), Br (**b**), BF$_4$ (**c**).

92a

The investigation of photodimerization of protonated and *N*-methylated forms of 4-styrylpyridines in reverse micelles has shown that under these conditions the predominating dimer is the head-to-head product of *syn*-conformation (structure of **92a** type).[112] The regio- and stereoselective photocycloaddition of styryl dyes has been best studied in molecular-organized microsystems in which the stereoselectivity of the process is achieved due to a certain orientation of molecules in the matrix cavity (in common or liquid crystal, in micelle, on the surface of silica gel, in host–guest complex).[1]

The controlled photocycloaddition of styrylpyridinium cations **93** intercalated in saponite clay layers has been described.[113] UV irradiation of a suspension of salts **93a**–**d** in water mainly leads to the formation of *syn* head-to-tail cyclodimers (**94a**–**d**). The selectivity of the process suggests that pyridinium cations are arranged as molecular aggregates with antiparallel orientation.



93a–**d** **94a**–**d**

R = H (**a**), Me (**b**), Cl (**c**), CN (**d**).

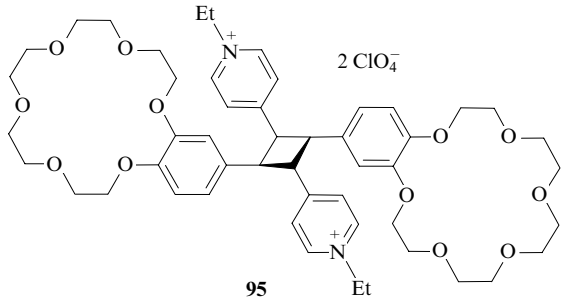
In addition to the luminescence of the monomer in the range of 380–450 nm, salts **93** exhibit strong excimer emission at 490–520 nm. It is worth noting that the excimer emission intensity is not decreased even at 0.1% adsorption.

The same authors [114] have studied photocyclodimerization of stilbazoles **93b**,**d**. It has been shown that, along with homocyclodimers, hybrid (cross) structures are formed, the cross : homo ratio being increased with an increase in the

adsorption. The quenching of excimer emission of **93b** was detected in case of joint intercalation with compound **93d**.

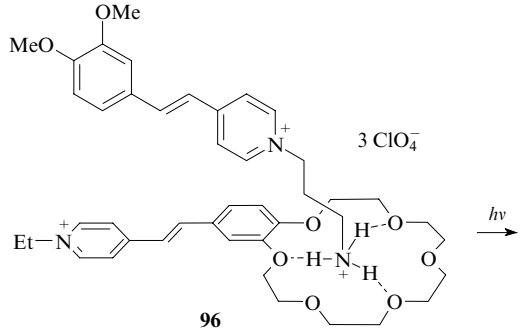
The investigation of phototransformations of pyridine and quinoline styryl dyes **42** and **43** in polycrystalline films has shown that, under these conditions, the photocycloaddition reaction does occur.[72] According to ^{1}H NMR data, the centrosymmetrical *rctt* isomer of a cyclobutane derivative is the only product.

Crown-containing styryl dyes have a pronounced capability to undergo photocycloaddition reactions. The presence of metal cations 'assembling' the molecules of dyes into dimeric complexes is a necessary condition.[1] However, the synthesized [115] 18-crown-6-containing styryl dye of pyridine series enters the photocycloaddition reaction in the absence of metal ions and on exposure to visible light. Irradiation of the dye film led only to the *rctt* isomer of tetrasubstituted cyclobutane **95** (according to the X-ray diffraction analysis data). Its isomerization into the *rcct* isomer has been revealed.

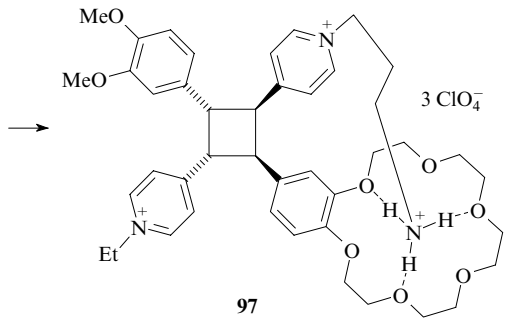


95

The formation of pseudodimeric host–guest complex **96** with hydrogen bonds in the crown-ether moiety has been described.[116] This complex undergoes stereospecific photocycloaddition into *rctt* isomer of tetrasubstituted cyclobutane **97** due to the stacking-induced pre-organization of double bonds of chromophores.



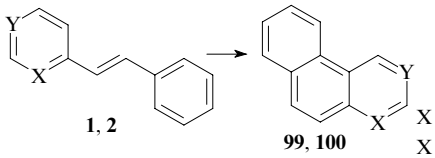
96



97

2. Intramolecular cyclizations with the formation of azaphenanthrenes

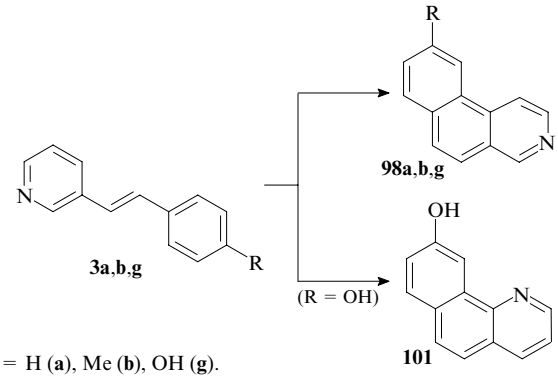
The reactions of photocyclization of stilbazoles **1**–**3** into azaphenanthrenes have been investigated. In one of the pioneering studies [117] it was shown that 3-stilbazole (**3a**) or its 4′-methyl derivative (**3b**) in cyclohexane readily underwent cyclization to form benzo[*f*]isoquinolines **98a**,**b** in high yield (~60%). 2-Stilbazole (**1**) was cyclized into benzo[*f*]quinoline **99** slower and with lower yield (~30%). The cyclization of 4-stilbazole (**2**) into benz[*h*]isoquinoline **100** was even more difficult (yield ~22%).



1, **2** → **99**, **100**

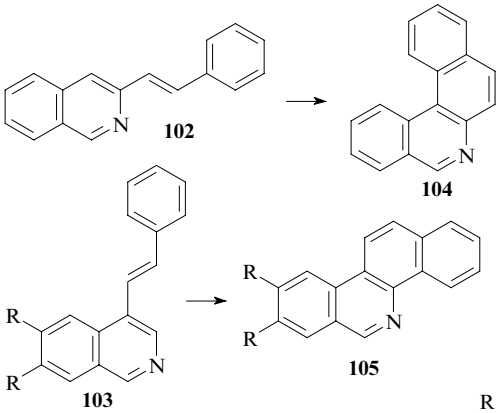
X = N, Y = CH (**1**, **99**);
X = CH, Y = N (**2**, **100**).

Later,[11] the photocyclization of hydroxystilbazoles has been described and it has been shown that, in case of hydroxy-substituted 3-stilbazole **3g** (R = OH), two isomers of hydroxyazaphenanthrenes, **98g** (R = OH) and **101**, are formed. The scheme of the process has been proposed. According to it, *cis*-stilbazole is first cyclized into dihydroazaphenanthrene, which is further oxidized into azaphenanthrene. Compounds **98**–**101** show stronger luminescence as compared with starting *trans*-stilbazoles **1**–**3**.



R = H (**a**), Me (**b**), OH (**g**).

4-Styrylquinoline **22b** in cyclohexane also undergoes photocyclization with the formation of benzo[*i*]phenanthridine.[117] The corresponding dihydro derivative has been identified on the basis of its absorption at 400–450 nm.[118] In ethanol, the photocyclization reaction did not occur. The photocyclization of 2-styrylquinoline **21l** ($R^1 = R^2 = H$) into benzophenanthridine was not realized.[119] The authors of this study also studied the photocyclization of styrylisoquinolines **102** and **103**. Irradiation of a dilute solution of 3-styrylisoquinoline **102** in cyclohexane leads to benzo[*a*]phenanthridine **104** in high yield. Under these conditions,

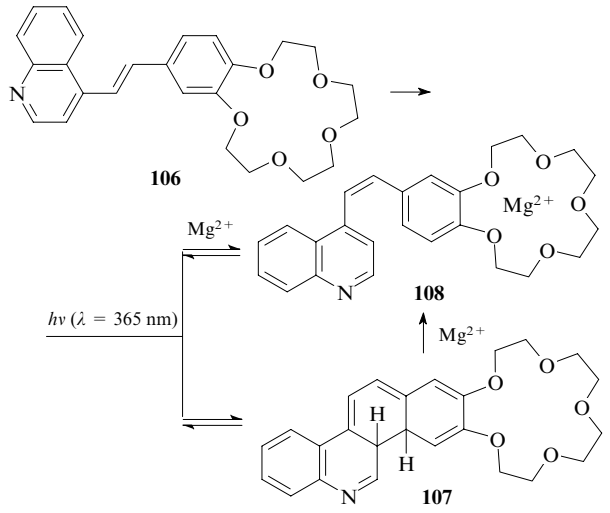


R = H, OMe.

4-styrylisoquinolines **103** also easily form benzo[*c*]phenanthridines **105**.

The photocyclization of a number of substituted 4-styrylquinolines **22** and their hydrochlorides has been studied in detail.[62] In contrast to the data in Ref 118 it has been found out that *cis* isomers of **22** in neutral alcoholic solutions are cyclized into corresponding derivatives of benzo[*i*]phenanthridine with quantum yields no higher than 0.01. The authors have suggested the scheme implying that the step of cyclization of the *cis* isomer into dihydrobenzo[i]phenanthridine is reversible and that the dihydro derivative is irreversibly oxidized by the atmospheric oxygen into the ultimate benzo[*i*]phenanthridine. For the protonated forms, the photocyclization reaction has entirely ceased. On the basis of the obtained benzo[*i*]phenanthridines, novel photochromic compounds of dihydroindolizine series have been synthesized.[120] Their photochromism is caused by the photo-induced electrocyclic reaction.

Cation-dependent photochemical transformations of crown-containing 4-styrylquinoline **106** have been described.[121] In solution under irradiation at $\lambda = 365$ nm, this compound undergoes *E*,*Z* photoisomerization (in the presence of Mg^{2+}) and photocyclization with the formation of stable product **107**.

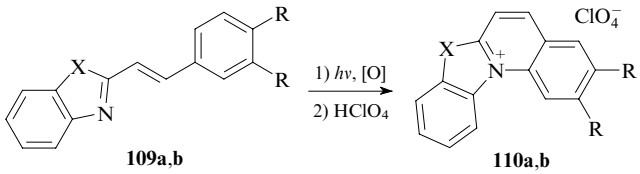


The addition of Mg^{2+} cation to a solution of compound **107** leads to the destruction of the ring and formation of *Z* isomer **108**.

3. Intramolecular cyclizations involving heteroatom

In the reactions of oxidative intramolecular cyclization discussed in Section III.2, the nitrogen atom in *ortho* position to the C=C bond in the starting hetarylethene is not involved in the photocyclization.

The electrocyclic reaction in the series of 2-styrylindoles **109a** (X = CMe_2, R = OMe or R–R is a crown-ether moiety) resulting in formation of C–N bond was revealed [122] for the first time.



109a,**b** **110a**,**b**

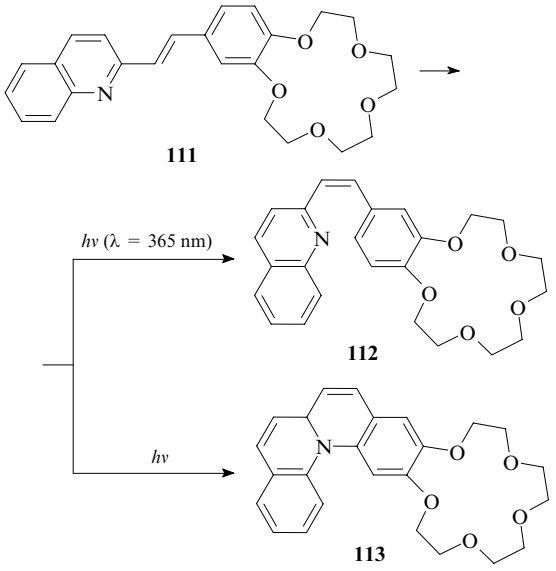
X = CMe_2 (**a**), S (**b**); R = OMe, R–R = $O(CH_2CH_2O)_5$.

In another study [123] the reaction was realized for crown-containing 2-styrylbenzothiazoles **109b** (X = S). The photolysis of styryl derivatives **109b** in acetonitrile in the presence of atmospheric oxygen leads to the formation of quaternary azonium salts **110b**. The structure of compounds **110** has been determined on the basis of ^{1}H NMR data. The signals of aromatic protons are significantly shifted downfield as compared with the starting styryl derivative, and the signals of alkene protons are absent. The authors suppose that the reaction occurs in several steps. First, *trans*–*cis* photoisomerisation occurs, and then the electrocyclic reaction of *cis* isomer leads to a 1,2-dihydroindolo(benzothiazolo)quinoline derivative, which is oxidized by the atmospheric oxygen with aromatization of the quinoline ring.

The complex formation of crown-containing derivatives **110** with alkaline-earth metal ions has been studied, and the stability constants of the complexes have been determined. For the Ba complex based on benzothiazoloquinoline **110b** [R–R = $O(CH_2CH_2O)_5$], the structure of the ligand has been confirmed by X-ray diffraction analysis.[124]

The same authors have described the intramolecular electrocyclization with the formation of C–N bond in a series of 2-styrylquinolines.[121] It was established that the direction of phototransformation of 2-styrylquinoline **111** could be controlled by changing the wavelength. In particular, irradiation at $\lambda = 365$ nm leads to the *E*,*Z* photoisomerization with the formation of compound **112**, while full-light irradiation causes the electrocyclization into product **113** (Scheme 4).

Scheme 4



Novel phototransformation of crown-containing 2-styrylheterocycles **109** may be regarded as a preparative method of synthesis of promising heteroaromatic cations that are difficult to synthesize by other methods.

* * *

The data presented in this review indicate that the main method of synthesis of styryl derivatives of azines and benzazines is the condensation of methyl-substituted heterocycles with aromatic aldehydes. In case of low reactivity of such heterocycles, other methods are applied, namely, the Wittig reaction, cross-coupling, condensation of heterocy-

clic aldehyde with $BnCO_2Na$ and other approaches. Prospects of using azinylarylethene derivatives in organic electroluminescent diodes, as fluorescent probes in biology, *etc*., encourage the development of synthetic approaches to these compounds. It is worth noting that azastilbenes are also attractive objects for studying various photochemical reactions.

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