ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 2, pp. 245–252. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © E.N. Gulakova, A.G. Sitin, L.G. Kuz'mina, O.A. Fedorova, 2011, published in Zhurnal Organicheskoi Khimii, 2011, Vol. 47, No. 2, pp. 253–260.

Synthesis and Structure of Styryl-Substituted Azines

E. N. Gulakova[a], A. G. Sitin[b], L. G. Kuz'mina[c], and O. A. Fedorova[a,b]

[a]*Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, Moscow, 119991 Russia*
e-mail: gulakova@ineos.ac.ru
[b]*Mendeleev Russian University of Chemical Engineering, Moscow, Russia*
[c]*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*

Received January 4, 2010

Abstract—New photochromic derivatives of 2-styrylquinoline and 2-styrylquinoxaline were obtained by the condensation of the methyl derivatives of the mentioned heterocycles with substituted benzaldehydes in the presence of basic and acidic catalysts, and also under the conditions of Wittig reaction. The structure of compounds obtained was proved by physicochemical analysis methods including XRD.

DOI: 10.1134/S107042801102014X

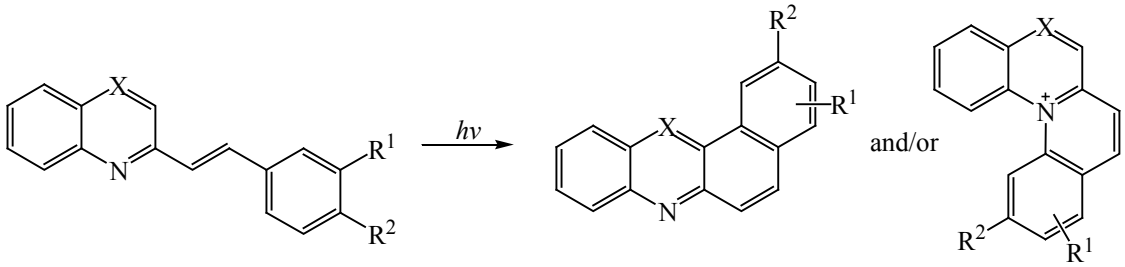
Styryl-substituted derivatives of quinoline and quinoxaline are interesting as compounds with a potential biological activity. The derivatives of quinoline and quinoxaline possess bactericidal and fungicidal properties [1, 2]. It was shown recently that quinoline derivatives are promising substrates for the photoinduced electrocyclic reaction [3]. The synthetic potential of these phototransformations is sufficiently wide and makes it possible to use them for the synthesis of new polyfused heteroaromatic compounds (Scheme 1).

π-Conjugated organic compounds based on aromatic systems attract significant attention with respect to the application as semiconductors in organic field transistors (OFETs), organic light-emitting diodes (OLEDs), and photogalvanic batteries, and also as biological active compounds, e.g., potential antitumor agents [4].

It is known [5–12] that the main procedure for the synthesis of styrylheterocycles is the aldol-type condensation of methyl derivatives of heterocyclic bases with benzaldehyde derivatives. The primary conditions of the condensation contained the use of relatively strong protic acids and bases, and the range of the possible reaction products was limited. Yet the importance of this condensation as one of the main procedures for the preparation of the polyfunctional products is so high that the development of various versions of its performance becomes nowadays a special field of research.

We tested this method for the synthesis of methoxy-substituted 2-styrylquinoline (**II**). The acidity characteristic of the alkyl groups in the α-position of the pyridine

Scheme 1.



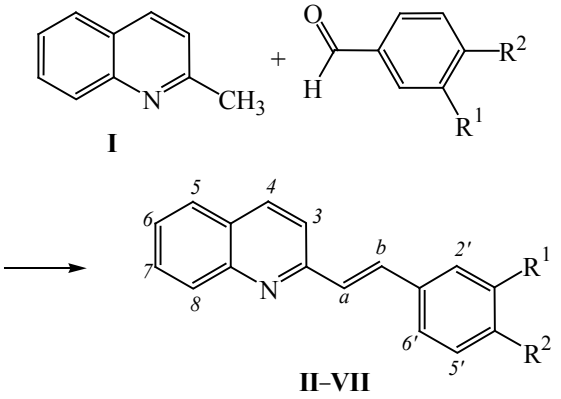
X = CH, N.

ring is also observed in the methyl group in the position *2* of quinoline. The condensation of 2-methylquinoline (**I**) with 3-methoxybenzaldehyde was performed using an additional activation both of the base and the acid; in the second case the reaction proceeded involving enamines, and in the first event the corresponding resonance-stabilized anion took part (Scheme 2).

The widely known method of preparation of olefin derivatives is Wittig reaction [13, 14] consisting in the reaction of phosphorus ylides with carbonyl compounds. The 3-methoxybenzyltriphenylphosphonium salt obtained in the first stage was further subjected to α-deprotonation under the treatment with a strong base (NaOH), and thus formed phosphonium ylide reacted with quinoline-2-carbaldehyde giving 2-styrylquinoline (**II**) in 74% yield (Scheme 3).

Although the yield of styrylquinoline (**II**) in Wittig reaction is high, the necessity of the preliminary synthesis of the phosphonium salts, and in the most cases of the substituted halobenzyl derivatives considerably reduces the synthetic value of this reaction compared to the condensation of commercially availably reagents affording the target styrylheterocycles in one stage with sufficiently high yields.

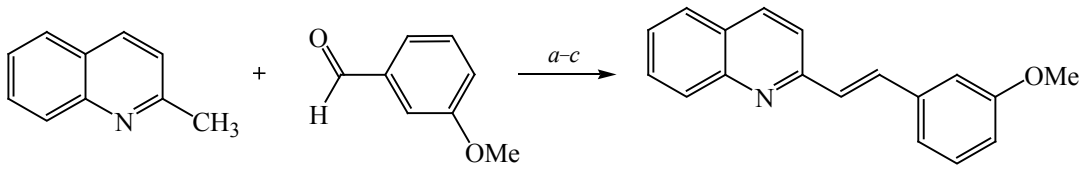
To extend the study of physicochemical properties of styryl-substituted azines it was necessary to synthesized styryl-substituted quinolines and quinoxalines both with electron-donor and electron-acceptor substituents in the benzene ring. The results of the condensation of quinaldine (**I**) with a series of substituted benzaldehydes are presented in Table 1. The introduction of electron-acceptor substituents (OH, NO_2) into the benzaldehyde activates the carbonyl group in the reactions of the nucleophilic addition and results in higher yields of substituted 2-styrylquinolines compared with 2-styrylquinoline **VII**. The electron-donor substituents (OMe, Me) on the contrary deactivate the carbonyl group of the substituted benzaldehyde in the reaction with quinaldine (**I**).



I **II–VII**

R^1 = OMe (**II, IV**), H (**III, VII**), NO_2 (**V**), OAc (**VI**);
R^2 = H (**II, V–VII**), Me (**III**), OMe (**IV**).

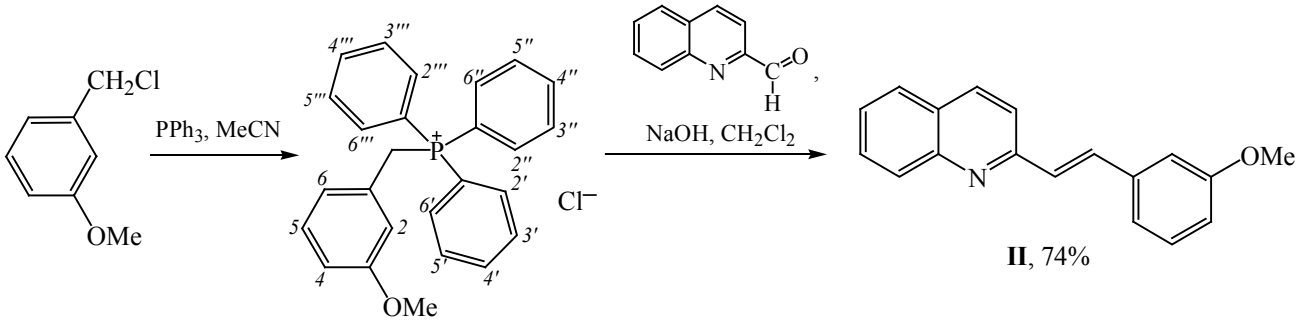
Scheme 2.



I **II**, 42 (*a*), 55 (*b*), 53% (*c*)

a: *t*-BuOK–DMF; *b*: piperidine, AcOH–toluene; *c*: Ac_2O.

Scheme 3.



II, 74%

Styrylquinolines **III–VII** were previously described in the literature. The styrylquinolines with the electron-donor substituents in the benzene ring were obtained by the condensation of reagents in the presence of $ZnCl_2$ (**IV**, yield 30% [15]) or AC_2O (**III**, yield 22% [16]). The condensation conditions that we elaborated increased the yield of the target product more than twice.

As a result of the condensation of 3-hydroxybenzaldehyde with quinaldine (**I**) oxyacetyl-substituted 2-styrylquinoline **VI** was isolated, the product of the hydroxy group acetylation.

By the reduction of nitro-substituted styrylquinoline **V** we prepared the corresponding amino derivative **VIII** (Scheme 4).

2-Methylquinoxaline (**IX**) also is capable to enter into the condensation via the intermediate deprotonation of the methyl group like 2-methylquinoline **I**. The arising intermediate anion is stabilized by the secondary negative induction effect of the second nitrogen atom, therefore the 2-styrylquinoxaline derivatives **X–XIV** form in higher yields than analogous 2-styrylquinolines **II–VII** (Table 2, Scheme 5).

All synthesized derivatives of 2-styrylquinoline and 2-styrylquinoxaline were isolated as trans-isomers as showed the coupling constants (~16 Hz) in the ^1H NMR spectra.

Below are reported the XRD results for 2-styrylquinolines **III–VIII**.

The crystal unit cells of the methoxy derivative **IV** and nitro compound **V** contain each two crystallographically independent molecules, and the unit cell of unsubstituted compound **VII** contains three independent molecules. In crystals of methyl derivative **III** a disordering was found caused by pedal motion resulting from the temperature dependent dynamic process in the solid phase [17, 18]. This dynamic process consists in the rotation of the ethylene fragment around its ordinary bonds, whereas the aromatis fragments connected thereto are subjected only to small displacements in their proper planes.

The crystal unit cell of acetoxy-substituted styrylquinoxaline **XIV** contains two crystallographically

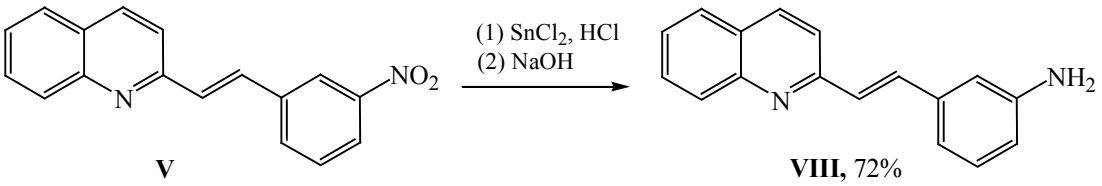
Table 1. Condensation conditions and yields of 2-styrylquinoline derivatives **II–VII**

Compound no.	Condensation conditions	Yield, %
II	PPy, ACOH–toluene, 120°C	55
III	PPy, ACOH–toluene, 120°C	60
IV	PPy, ACOH–toluene, 120°C	64
V	AC_2O, 140°C	75
VI	AC_2O, 140°C	74
VII	AC_2O, 140°C	70

Table 2. Condensation conditions and yields of 2-styrylquinoxaline derivatives **X–XIV**

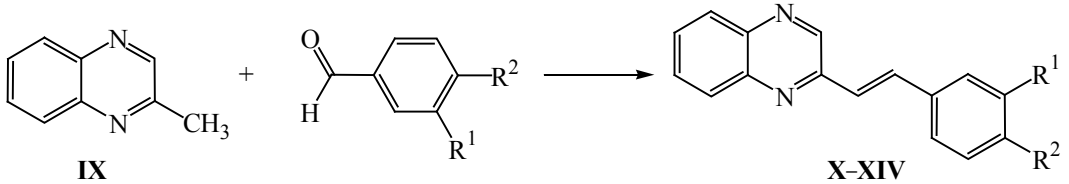
Compound no.	Condensation conditions	Yield, %
X	PPy, ACOH–toluene, 120°C	60
XI	PPy, ACOH–toluene, 120°C	77
XII	AC_2O, 140°C	67
XIII	AC_2O, 140°C	77
XIV	AC_2O, 140°C	75

Scheme 4.



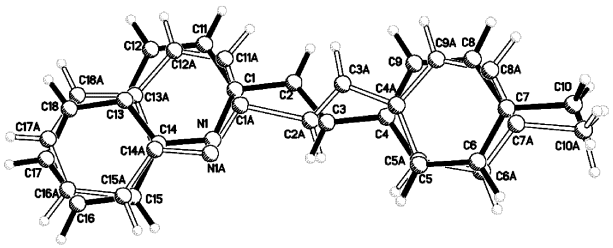
V **VIII,** 72%

Scheme 5.

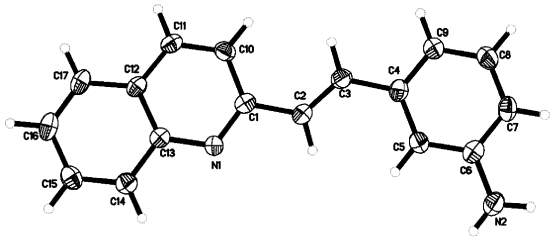


IX **X–XIV**

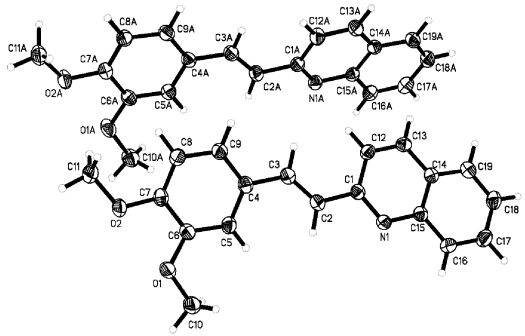
R^1 = H (**X**), OMe (**XI, XII**), NO_2 (**XIII**), OAc (**XIV**); R^2 = Me (**X**), OMe (**XI**), H (**XII–XIV**).



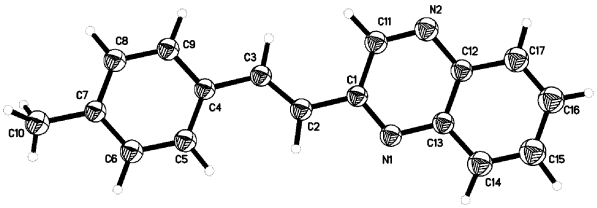
III



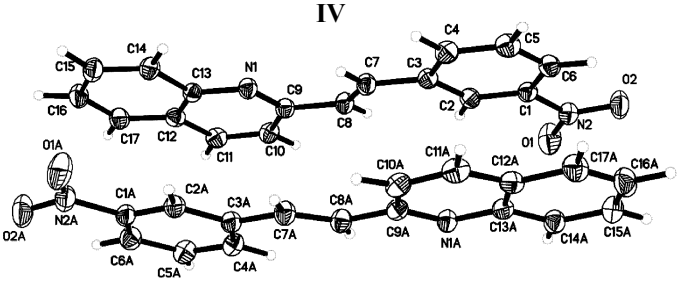
VIII



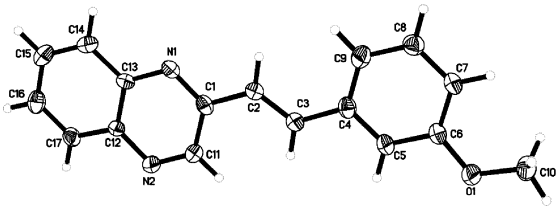
IV



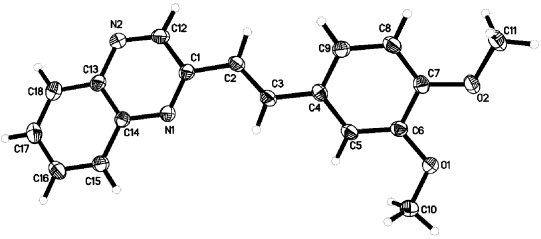
X



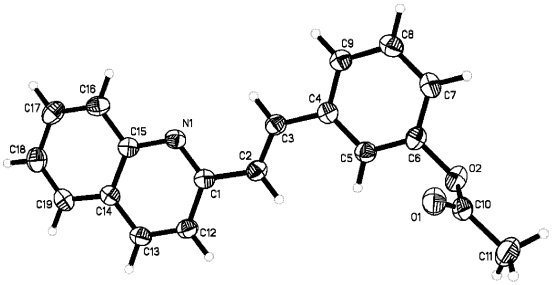
V



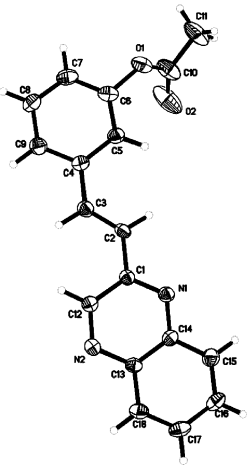
XI



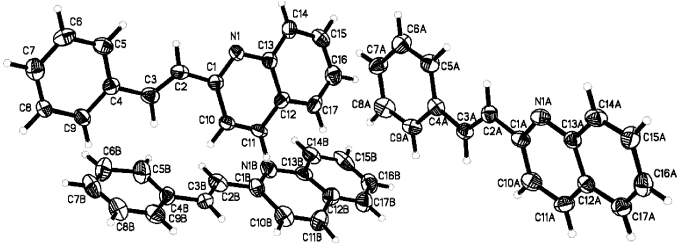
XII



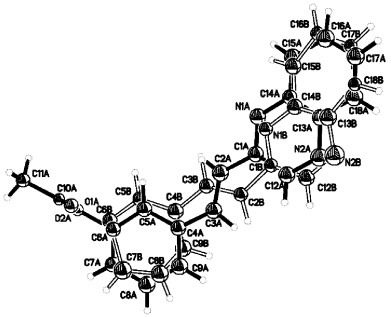
VI



XIV



VII



independent molecules, and one of them suffers the pedal disordering, whereas the other one does not.

The more comprehensive XRD investigation of compounds synthesized in this study will be published elsewhere.

Hence in this research the methods of synthesis were developed for the 2-styrylquinoline derivatives and for the previously unknown 2-styrylquinoxaline derivatives. The dependence of the yield of the target products on the substituents in benzaldehyde and the reaction conditions were investigated that made it possible to optimize the preparation conditions of the styrylheterocycle with electron-donor substituents in the styryl fragment, and to increase their yield more than twice compared to the published methods. With the use of NMR spectroscopy and XRD analysis the structure of compounds obtained in solution and in the crystalline state was established.

EXPERIMENTAL

Melting points were measured in open capillaries on a Mel-Temp II instrument. ^{1}H NMR spectra were registered on spectrometers Varian XR-250 (operating frequency 250 MHz) and Bruker DRX-300, internal reference TMS. The chemical shifts were measured with the accuracy up to 0.01 ppm, the coupling constants, to 0.1 Hz. Mass spectra were obtained on a Kratos MS-30 instrument, ionizing electrons energy 70 eV, with the direct admission of the sample into the ion source. Electron absorption spectra were recorded at 25°C on a spectrophotometer Specord-M40 coupled with a computer. The spectrophotometer control, data acquisition, and the simplest processing of the spectra was carried out using standard program SPECORD (version 2.0, Etalon). TLC monitoring was performed on DC-Alufolien Kieselgel 60 F_{254} (Merck) plates. The column chromatography was carried out on Kieselgel, 0.062–0.200mm, *d* 6 nm (Acros Organics).

Quinaldine (**I**), 2-methylquinoxaline (**IX**), benzaldehyde, 3-methoxybenzaldehyde, 4-methylbenzaldehyde, 3,4-dimethoxybenzaldehyde, 3-nitrobenzaldehyde, 3-hydroxybenzaldehyde, 1-chloromethyl-3-methoxybenzene, triphenylphosphine, quinoline-2-carbaldehyde, acetic anhydride, piperidine, potassium *tert*-butylate, $SnCl_2$ were commercial products used without additional purification.

2-(3-Methoxystyryl)quinoline (II). *a*. A solution of 0.47 ml (3.5 mmol) of quinaldine (**I**), 0.09 ml (0.7 mmol) 3-methoxybenzaldehyde, and 0.118 g (1.05 mmol) *t*-BuOK in 3.5 ml of anhydrous DMF was stirred in an argon flow at room temperature for 24 h, then to the reaction mixture 20 ml of distilled water was added. The separated precipitate was filtered off, dried, and subjected to chromatography on a column packed with SiO_2 (eluent CH_2Cl_2). Yield 0.07 g (42%), mp 44–46°C (hexane). Electron absorption spectrum, λ_{max}, nm (log ε) 281.7 (4.37), 337.2 (4.28). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.74 s (3H, OCH_3), 6.79 d (1H, C$^{4'}$H, *J* 7.9 Hz), 7.09 s (1H, C$^{2'}$H), 7.11–7.24 m (2H, C$^{6'}$H, C$^{5'}$H), 7.30 d (1H, C^{b}H, *J* 16.2 Hz), 7.38 m, 7.60 m (2H, C^{6}H, C^{7}H), 7.52 d (1H, C^{3}H, *J* 6.8 Hz), 7.54 d (1H, C^{a}H, *J* 16.1 Hz), 7.66 d (1H, C^{5}H, *J* 8.2 Hz), 7.99 m (2H, C^{4}H, C^{8}H). Mass spectrum, *m/z* (I_{rel}, %): 261.2 (42) $[M]^+$, 260.2 (100) $[M - 1]^+$, 246.2 (8), 245.2 (19), 230.4 (6), 218.3 (12), 217.3 (38), 216.3 (9), 143.3 (9), 115.2 (5). Found, %: C 82.79; H 5.91; N 5.21. $C_{18}H_{15}NO$. Calculated, %: C 82.73; H 5.79; N 5.36.

b. To a solution of 0.419 g (1 mmol) of 3-methoxybenzyltriphenylphosphonium chloride and 0.157 g (1 mmol) of quinoline-2-carbaldehyde in 3 ml of CH_2Cl_2 was added 3 ml of 50% solution of NaOH, the mixture obtained was stirred for 2 h, then 20 ml of water was added, and the reaction product was extracted into dichloromethane. The combined extracts were dried with Mg_2SO_4, and evaporated in a vacuum. The residue was subjected to column chromatography (SiO_2, gradient elution with cyclohexane–CH_2Cl_2, from 1 : 1 to 100% CH_2Cl_2). Yield 74%.

3-Methoxybenzyltriphenylphosphonium chloride. A solution of 1.86 ml (12.78 mmol) of 3-methoxybenzyl chloride and 3.55 g (13.55 mmol) of triphenylphosphine in 10 ml of acetonitrile was boiled at stirring for 12 h. On cooling the separated precipitate was filtered off and dried. Yield 374 mg (70%), mp 271–272°C (262–263°C [19]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.48 s (3H, OCH_3), 5.20 d (2H, CH_2, *J* 15.6 Hz), 6.50 s (1H, C^{2}H), 6.60 d, 6.85 d (2H, C^{4}H, C^{6}H, *J* 7.6, *J* 8.2 Hz), 7.15 t (1H, C^{5}H, *J* 8 Hz), 7.63–7.79 m (12H, C$^{2'}$H, C$^{3'}$H, C$^{5'}$H, C$^{6'}$H, C$^{2''}$H, C$^{3''}$H, C$^{5''}$H, C$^{6''}$H, C$^{2'''}$H, C$^{3'''}$H, C$^{5'''}$H, C$^{6'''}$H), 7.85–7.94 m (3H, C$^{4'}$H, C$^{4''}$H, C$^{4'''}$H).

2-Styrylazines III, IV, X, XI. General procedure. A solution of 1 mol of 2-methylheterocycle (**I** or **IX**), 1.35 mol of benzaldehyde derivative, 0.5 mol of piperidine, and 0.7 mol of acetic acid in toluene was maintained in an inert atmosphere at 115°C for 48 h, then the reaction mixture was evaporated in a vacuum. The residue was subjected to column chromatography

(SiO_2, eluent CH_2Cl_2), for compound **IV** для eluent CH_2Cl_2–ethyl acetate, 1 : 1.

2-(4-Methylstyryl)quinoline (III), mp 141–143°C (octane–toluene, 1 : 1) (140°C [16]). Electron absorption spectrum, λ_{max}, nm (log ε): 285.8 (4.5), 339 (4.5). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (3H, CH_3), 7.21 d (2H, $C^{3'}H$, $C^{5'}H$, *J* 7.90 Hz), 7.38 d (1H, C^bH, *J* 16.3 Hz), 7.49 m, 7.70 m (2H, C^6H, C^7H), 7.54 d (2H, $C^{2'}H$, $C^{6'}H$), 7.64 d (1H, C^3H, *J* 7 Hz), 7.64 d (1H, C^aH, *J* 16.1 Hz), 7.78 d (1H, C^5H, *J* 8 Hz), 8.08 d (1H, C^8H, *J* 8.4 Hz), 8.12 d (1H, C^4H, *J* 8.5 Hz).

2-(3,4-Dimethoxystyryl)quinoline (IV), mp 107–110°C (octane–toluene, 1 : 1) (112–113°C [15]). Electron absorption spectrum, λ_{max}, nm (log ε): 281 (4.6), 338 (4.5). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.71 s, 3.77 s (6H, 2 OCH_3), 6.65 d (1H, $C^{5'}H$, *J* 8.2 Hz), 6.95 d (1H, $C^{6'}H$, *J* 8.3 Hz), 7.04 s (1H, $C^{2'}H$), 7.12 d (1H, C^bH, *J* 16.3 Hz), 7.29 m, 7.53 m (2H, C^6H, C^7H), 7.39 d (1H, C^3H, *J* 8.2 Hz), 7.42 d (1H, C^aH, *J* 16.4 Hz), 7.55 d (1H, C^5H, *J* 8.7 Hz), 7.84 d (1H, C^8H, *J* 8.5 Hz), 7.93 d (1H, C^4H, *J* 8.2 Hz).

2-(4-Methylstyryl)quinoxaline (X), mp 116–118°C (octane–toluene, 1 : 1). Electron absorption spectrum, λ_{max}, nm (log ε): 294.1 (4.45), 369.6 (4.47). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.39 s (3H, CH_3), 7.30 d (2H, $C^{3'}H$, $C^{5'}H$, *J* 8.1 Hz), 7.35 d (1H, C^bH, *J* 16.3 Hz), 7.56 d (2H, $C^{2'}H$, $C^{6'}H$, *J* 8.1 Hz), 7.66–7.79 m (2H, C^6H, C^7H), 7.85 d (1H, C^aH, *J* 16.3 Hz), 8.06 d (2H, C^5H, C^8H, *J* 8.2 Hz), 9.04 s (1H, C^3H). Mass spectrum, *m/z* (I_{rel}, %): 246.1 (42) $[M]^+$, 245.2 (100) $[M-1]^+$, 244.2 (4), 243.3 (4), 232.3 (6), 231.3 (39), 230.3 (4.97), 229.3 (4), 217.4 (5). Found, %: C 82.79; H 5.62; N 11.31. $C_{17}H_{14}N_2$. Calculated, %: C 82.90; H 5.73; N 11.37.

2-(3,4-Dimethoxystyryl)quinoxaline (XI), Mp 154–156°C (methanol). Electron absorption spectrum, λ_{max}, nm (log ε): 290 (4.36), 383.6 (4.2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.93 s, 3.97 s (6H, 2 OCH_3), 6.91 d (1H, $C^{5'}H$, *J* 8.8 Hz), 7.18–7.31 m (3H, $C^{6'}H$, $C^{2'}H$, C^bH), 7.72 m (2H, C^6H, C^7H), 7.81 d (1H, C^aH, *J* 16.3 Hz), 8.05 m (2H, C^5H, C^8H), 9.06 s (1H, C^3H). Mass spectrum, *m/z* (I_{rel}, %): 292.0 (81) $[M]^+$, 291.1 (100) $[M-1]^+$, 277.2 (45), 276.2 (13), 275.3 (14), 262.2 (14), 261.2 (23), 249.2 (16), 234.2 (19), 218.2 (14). Found, %: C 74.02; H 5.60; N 9.64. $C_{18}H_{16}N_2O_2$. Calculated, %: C 73.96; H 5.52; N 9.58.

2-Styrylazines V–VII, XII–XIV. General procedure. A mixture of 1 mol of 2-methylquinoline (**I**) or 2-methylquinoxaline (**IX**), 1 mol of benzaldehyde derivative, and 1 mol of acetic acid (3 mol of Ac_2O in the synthesis of compounds **VI, XIV**) was heated under inert atmosphere at 140°C over 6 h, then it was cooled and diluted with cold water. In the synthesis of styrylazines **V, XIII** the separated precipitate was filtered off, dried, and recrystallized. In the other cases the reaction product was extracted into ethyl acetate, the extract was dried with Mg_2SO_4 and evaporated in a vacuum. The residue was subjected to column chromatography (SiO_2, eluent CH_2Cl_2), for 2-styrylquinoline **VII** eluent benzene–MeCN, 20 : 1.

2-(3-Nitrostyryl)quinoline (V), mp 157–158°C (methanol) (157–158°C [16]). Electron absorption spectrum, λ_{max}, nm (log ε): 280.6 (4.7), 323.7 (4.5). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.50 d (1H, C^bH, *J* 16.1 Hz), 7.53 m, 7.72 m (2H, C^6H, C^7H), 7.56 t ($C^{5'}H$, *J* 8.0 Hz), 7.65 d (1H, C^3H, *J* 8.5 Hz), 7.76 d (1H, C^aH, *J* 16.3 Hz), 7.81 d (1H, C^3H, *J* 8.2 Hz), 7.92 d (1H, C^8H, *J* 7.7 Hz), 8.09 d (1H, $C^{6'}H$, *J* 8.5 Hz), 8.15 m (1H, $C^{4'}H$), 8.17 d (1H, C^4H, *J* 8.5 Hz), 8.48 s (1H, $C^{4'}H$).

2-(3-Oxyacetylstyryl)quinoline (VI), mp 83–84°C (octane–toluene, 1 : 1) (83–84°C [20]). Electron absorption spectrum, λ_{max}, nm (log ε): 281.7 (4.6), 337.2 (4.5). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.94 s (3H, CH_3COO), 6.73 d (1H, $C^{4'}H$, *J* 7.9 Hz), 6.94–7.12 m (6H, $C^{2'}H$, $C^{5'}H$, $C^{6'}H$, C^bH, C^7H), 7.26 d (1H, C^aH, *J* 16.8 Hz), 7.31 d (1H, C^3H, *J* 7.7 Hz), 7.33 m (1H, C^6H), 7.58 d (1H, C^8H, *J* 8.5 Hz), 7.80 d (1H, C^4H, *J* 8.8 Hz).

2-Styrylquinoline (VII), mp 97–99°C (methanol) (100°C [16]). Electron absorption spectrum, λ_{max}, nm (log ε): 281.7 (4.2), 337 (4.1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.35–7.43 m (4H, C^bH, C^5H, $C^{5'}H$, $C^{3'}H$), 7.51 m (1H, $C^{4'}H$), 7.64–7.75 m (4H, C^3H, C^6H, C^7H, C^aH), 7.80 d (2H, $C^{2'}H$, $C^{6'}H$, *J* 8.0 Hz), 8.15 m (2H, C^4H, C^8H).

2-(3-Methoxystyryl)quinoxaline (XII), mp 120–122°C (methanol). Electron absorption spectrum, λ_{max}, nm (log ε): 289.4 (4.47), 367.8 (4.43). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.87 s (3H, OCH_3), 6.93 d (1H, $C^{4'}H$, *J* 7.9 Hz), 7.20 s (1H, $C^{2'}H$), 7.30 m (2H, $C^{5'}H$, $C^{6'}H$), 7.38 d (1H, C^bH, *J* 16.4 Hz), 7.74 m (2H, C^6H, C^7H), 7.85 d (1H, C^aH, *J* 16.4 Hz), 8.08 d (2H, C^5H, C^8H, *J* 7.90 Hz), 9.06 s (1H, C^3H). Mass spectrum, *m/z* (I_{rel}, %): 262.1 (40) $[M]^+$, 261.2 (100) $[M-1]^+$, 247.1 (11), 246.2 (10), 232.2 (5), 231.2 (19), 219.3 (17), 218.3 (27), 191.3 (5). Found, %: C 77.94; H 5.19; N 10.59. $C_{17}H_{14}N_2O$. Calculated, %: C 77.84; H 5.38; N 10.68.

2-(3-Nitrostyryl)quinoxaline (XIII), mp 196–197.5°C (acetonitrile) (199.5°C [21]). Electron absorption spectrum, λ_{max}, nm (log ε): 284.1 (4.5), 359.6 (4.36). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.51 d (1H, C^{b}H, *J* 16.3 Hz), 7.60 t (1H, C$^{5'}$H, *J* 8.0 Hz), 7.71–7.84 m (2H, C^{6}H, C^{7}H), 7.94 d (1H, C$^{6'}$H, *J* 7.8 Hz), 7.96 d (1H, C^{a}H, *J* 16.3 Hz), 8.10 d.d (2H, C^{5}H, C^{8}H, J_1 7.3, J_2 2.4 Hz), 8.20 d (1H, C$^{4'}$H, *J* 8.2 Hz), 8.52 s (1H, C$^{2'}$H), 9.05 s (1H, C^{3}H).

2-(3-Oxyacetylstyryl)quinoxaline (XIV), mp 105–107°C (methanol). Electron absorption spectrum, λ_{max}, nm (log ε): 288.8 (4.78), 364.3 (4.7). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.23 s (3H, CH_3COO), 6.98 d (1H, C$^{4'}$H, *J* 7.9 Hz), 7.12 d (1H, C^{b}H, *J* 16.3 Hz), 7.21–7.33 m (3H, C$^{2'}$H, C$^{5'}$H, C$^{6'}$H), 7.55 m (2H, C^{6}H, C^{7}H), 7.61 d (1H, C^{a}H, *J* 16.3 Hz), 7.93 m (2H, C^{5}H, C^{8}H), 8.80 s (1H, C^{3}H). Mass spectrum, *m/z* (I_{rel}, %): 290.1 (16) $[M]^+$, 289.1 (13), 249.2 (6), 248.1 (39), 247.1 (100), 232.2 (38), 220.2 (6), 219.3 (16), 218.3 (10). Found, %: C 74.66; H 5.16; N 10.57. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.47; H 4.86; N 9.65.

2-(3-Aminostyryl)quinoline (VIII). To a dispersion of 1 g (3.62 mmol) of 2-(3-nitrostyryl)quinoline (**V**) in 5 ml of concn. HCl was added a solution of 13 g of $SnCl_2 \cdot 2H_2O$ in 10 ml of concn. HCl. The mixture obtained was boiled for 3 h, then cooled, diluted with 15 ml of water, and 20% solution of NaOH was added to weak alkaline pH. The separated precipitate was filtered off, dried, and recrystallized from nonane. Yield 577 mg (72%), mp 164–165°C (nonane) (167–168°C [22]). Electron absorption spectrum, λ_{max}, nm (log ε): 281 (4.5), 338 (4.4). ^{1}H NMR spectrum (CD_3CN), δ, ppm: 6.67 d (1H, C$^{4'}$H, *J* 7.7 Hz), 6.97 s (1H, C$^{2'}$H), 7.04 d (1H, C$^{6'}$H, *J* 7.6 Hz), 7.18 t (1H, C$^{5'}$H, *J* 7.7 Hz), 7.37 d (1H, C^{b}H, *J* 16.3 Hz), 7.49 m, 7.70 m (2H, C^{6}H, C^{7}H), 7.59 d (1H, C^{a}H, *J* 16.3 Hz), 7.67 d (1H, C^{3}H, *J* 8.5 Hz), 7.78 d (1H, C^{5}H, *J* 8.2 Hz), 8.11 m (2H, C^{4}H, C^{8}H).

XRD of styrylazines III–VII, X–XII, XIV. Single crystals of compounds **III–VII, X–XII, XIV** covered with perfluorinated oil were placed in a diffractometer Bruker SMART-CCD in a flow of cooled nitrogen. The set of experimental reflections was obtained by ω-scanning of the reflections from single crystals under MoK_α radiation. The primary processing of the experimental reflections was performed using program SAINT [23].

The structures were solved by the direct method and refined by least-squares method in the anisotropic approximation for the nonhydrogen atoms. The hydrogen atoms were refined either in the isotropic approximation or in the rider model.

All calculations were carried out using SHELXTL-Plus software [24].

Compound **III**. $C_{18}H_{15}N$. *M* 245.31. Crystals rhombic, space group $P2_12_12_1$. At *T* 150 K *a* 5.9101(4), *b* 7.8477(6), *c* 28.821(2) Å, *V* 1336.76(17) Å^3, *Z* 4, μ(MoK_α) 0.071 mm^{-1}, validity by F^2 0.950, 13816 reflections collected, among them 3861 independent (R_{int} 0.0247). For reflections with C $I > 2\sigma(I)$ R_1 0.0474, wR_2 0.1251, for all reflections R_1 0.0474, wR_2 0.1251, residual electron density, min/max 0.175/0.419 e Å^{-3}.

Compound **IV**. $C_{19}H_{17}NO_2$. *M* 291.34. Crystals monoclinic, space group $P2_1/n$. At *T* 150 K *a* 10.6554(7), *b* 21.1859(14), *c* 13.5206(9) Å, *V* 1023.7(3) Å^3, *Z* 8, μ(MoK_α) 0.083 mm^{-1}, validity by F^2 1.011, 31101 reflections collected, among them 8753 independent (R_{int} 0.0462). Fot reflections with $I > 2\sigma(I)$ R_1 0.0506, wR_2 0.1171, for all reflections R_1 0.0871, wR_2 0.1294, residual electron density, min/max 0.194/0.272 e Å^{-3}.

Compound **V**. $C_{17}H_{12}N_2O_2$. *M* 276.29. Crystals triclinic, space group $P\bar{1}$. At *T* 150 K *a* 6.1153(7), *b* 10.5326(12), *c* 20.548(2) Å, *V* 1295(7) Å^3, *Z* 4, μ(MoK_α) 0.095 mm^{-1}, validity by F^2 1.096, 15291 reflections collected, among them 7516 independent (R_{int} 0.0198). For reflections with $I > 2\sigma(I)$ R_1 0.0470, wR_2 0.1364, for all reflections R_1 0.0618, wR_2 0.1456, residual electron density, min/max 0.288/0.338 e Å^{-3}.

Compound **VI**. $C_{19}H_{15}NO_2$. *M* 289.22. Crystals monoclinic, space group $P2_1/n$. At *T* 150 K *a* 6.0406(6), *b* 7.7835(7), *c* 31.213(3) Å, *V* 1463.4(2) Å^3, *Z* 4, μ(MoK_α) 0.085 mm^{-1}, validity by F^2 1.105, 14888 reflections collected, among them 4345 independent (R_{int} 0.0404). For reflections with $I > 2\sigma(I)$ R_1 0.0567, wR_2 0.1513, for all reflections R_1 0.0984, wR_2 0.1771, residual electron density, min/max 0.280/0.409 e Å^{-3}.

Compound **VII**. $C_{17}H_{13}N$. *M* 289.22.Crystals monoclinic, space group $P2_1$. At *T* 150 K *a* 6.6258(15), *b* 19.419(4), *c* 14.796(3) Å, *V* 1895.8(7) Å^3, *Z* 12, μ(MoK_α) 0.071 mm^{-1}, validity by F^2 0.946, 20967 reflections collected, among them 10020 independent (R_{int} 0.0479). For reflections with $I > 2\sigma(I)$ R_1 0.0657, wR_2 0.1783, for all reflections R_1 0.1504, wR_2 0.2184, residual electron density, min/max 0.242/0.435 e Å^{-3}.

Compound **X**. $C_{17}H_{14}N_2$. *M* 246.12. Crystals monoclinic, space group $P2_1/c$. At *T* 150 K *a* 11.888(6),

b 4.710(2), *c* 23.005(11) Å, *V* 1285.5(11) Å^3, *Z* 4, μ(MoK_α) 0.069 mm^{-1}, validity by F^2 1.033, 12731 reflections collected, among them 3880 independent (R_{int} 0.0517). For reflections with $I > 2\sigma(I)$ R_1 0.0771, wR_2 0.2016, for all reflections R_1 0.1332, wR_2 0.2418, residual electron density, min/max 0.326/0.714 e Å^{-3}.

Compound **XI**. $C_{18}H_{16}N_2O_2$. *M* 292.33. Crystals rhombic, space group *Pbca*. At *T* 150 K *a* 13.323(2), *b* 8.5813(15), *c* 25.240(4) Å, *V* 2885.6(7) Å^3, *Z* 8, μ(MoK_α) 0.089 mm^{-1}, validity by F^2 0.798, 27724 reflections collected, among them 3483 independent (R_{int} 0.1819). For reflections with $I > 2\sigma(I)$ R_1 0.0455, wR_2 0.0902, for all reflections R_1 0.1094, wR_2 0.1004, residual electron density, min/max 0.196/0.249 e·Å^{-3}.

Compound **XII**. $C_{17}H_{14}N_2O$. *M* 262.3. Crystals rhombic, space group $P2_12_12_1$. At *T* 150 K *a* 6.5510(10), *b* 11.5616(17), *c* 17.642(3) Å, *V* 1336.2(3) Å^3, *Z* 4, μ(MoK_α) 0.083 mm^{-1}, validity by F^2 1.078, 13821 reflections collected, among them 3872 independent (R_{int} 0.0240). For reflections with $I > 2\sigma(I)$ R_1 0.0557, wR_2 .1540, for all reflectionй R_1 0.0596, wR_2 0.1569, residual electron density, min/max 0.283/0.662 e Å^{-3}.

Compound **XIV**. $C_{17}H_{14}N_2O$. *M* 262.3. Crystals monoclinic, space group $P2_1/c$. At *T* 150 K *a* 28.091(5), *b* 6.2543(10), *c* 16.903(3) Å, *V* 2876.9(8) Å^3, *Z* 8, μ(MoK_α) 0.077 mm^{-1}, validity by F^2 0.895, 21910 reflections collected, among them 8236 independent (R_{int} 0.0894), *R*-factors for reflections with $I > 2\sigma(I)$ R_1 0.0885, wR_2 0.2287, for all reflectionй R_1 0.1973, wR_2 0.2737, residual electron density, min/max 0.360/1.046 e Å^{-3}.

ACKNOWLEDGMENTS

The study was carried out under the financial support of the Presidium of the Russian Academy of Sciences (Program of the fundamental research "Development of methods of preparation of chemical substances and creation of new materials") and the Russian Foundation for Basic Research (grant no. 10-03-93106-NTsNIL_a).

REFERENCES

1. Dillard, R.D., Pavey, D.E., and Benslay, D.N., *J. Med. Chem*., 1973, vol. 16, p. 251.
2. Patel, H.V., Vyas, K.V., and Fernandes, P.S., *Indian J. Chem.,* 1990, vol. 29B, p. 836.
3. Ahmed, S. A.-M., *J. Phys. Org. Chem.,* 2007, vol. 20, p. 574.
4. Starcevic, K., Kralj, M., Piantanida, I., Sauman, L., Paveli, K., and Karminski-Zamola, G., *Eur. J. Med. Chem.,* 2006, vol. 41, p. 925.
5. Horwitz, L., *J. Am. Chem. Soc*., 1955, vol. 77, p. 1687.
6. Minch, M.J. and Shah, S.S., *J. Chem. Educ*., 1977, vol. 54, p. 709.
7. Mekouar, K., Mouscadet, J.F., and Desmaele, D., *J. Med. Chem*., 1998, vol. 41, p. 2846.
8. Harms, A.E., *Org. Proc. Res. Dev.,* 2004, vol. 8, p. 666.
9. Ukhov, S.V. and Konshin, M.E., *Khim. Geterotsikl. Soedin.,* 1992, p. 92.
10. Sazaux, L., Facher, M., Picard, C., and Tisnes, P., *Can. J. Chem*., 1993, vol. 71, p. 1236.
11. Fedorova, O.A., Andryukhina, E.N., Mashura, M.M., and Gromov, S.P., *ARKIVOC.,* 2005, vol. xv, p. 12.
12. Andryukhina, E.N., Mashura, M.M., Fedorova, O.A., Kuz'mina, L.G., Khovard, Dzh.A.K., and Gromov, S.P., *Izv. Akad. Nauk, Ser. Khim.,* 2005, p. 1650.
13. Williams, J.L.R., Adel, R.E., Carlson, J.M., and Borden, D.G., *J. Org. Chem*., 1963, vol. 28, p. 387.
14. Gennari, G., Cauzzo, G., and Galiazzo, G., *J. Photochem*., 1976, vol. 5, p. 409.
15. Schläger, J. and Leeb, W., *J. Monatsh. Chem.,* 1950, vol. 81, p. 714.
16. Skidmore, S. and Tidd, E., *J. Chem. Soc*., 1959, p. 1641.
17. Harada, J. and Ogawa, K., *J. Am. Chem. Soc.,* 2004, vol. 126, p. 3539.
18. Harada, J. and Ogawa, K., *J. Chem. Soc. Rev*., 2009, vol. 38, p. 2244.
19. Grimshaw, J. and Ramsey, J.S., *J. Chem. Soc. B,* 1968, vol. 1, p. 63.
20. Zamboni, K., Belley, M., Chapnpion, E., Charette, L., Dettaven, R., Fyenette, R., Gauthier, J.Y., Jones, T.R., Leger, S., Masson, P., McFarlane, C.S., Metters, K., Pong, S.S., Piethuta, H., Rokach, J., Thérien, M., Williams, H.W.R., and Young, R.N., *J. Med. Chem. Eng.,* 1992, vol. 35, p. 383.
21. Bennett, G.M. and Willis, G.H., *J. Chem. Soc.,* 1928, p. 1960.
22. Graff, E., Fredericksen, J.M., and Burger, A., *J. Org. Chem*., 1946, vol. 11, p. 257.
23. SAINT. Version, 6.02A. Bruker AXS, Inc. Madison, Wisconsin, USA, 2001.
24. SHELXTL-Plus. Release 5.10, Bruker AXS, Inc., Madison, Wisconsin, USA, 1997.