Chemistry of Heterocyclic Compounds, Vol. 48, No. 10, January, 2013 (Russian Original Vol. 48, No. 10, October, 2012)

SYNTHESIS AND SPECTRAL PROPERTIES OF AZAHETERO-AROMATIC DERIVATIVES OF 2-STYRYLANTHRACENE

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Novel azaheteroaromatic derivatives of 2-styrylanthracene: 2-styrylbenzo[g]quinoline and 3-styryl-acridine were obtained from 3-nitro-2-naphthaldehyde and 2-bromo-4-methylbenzoic acid. Spectral properties of the new compounds were studied.

Keywords: 3-styrylacridine, 2-styrylanthracene, 2-styrylbenzo[*g*]quinoline, crotonic condensation, Friedlander reaction.

Heterocyclic stilbene analogs are widely used as photosensitizers, organic luminophores, fluorescent dyes, and as optical brightening agents [1]. They invariably cause much interest for many investigators as evidenced by the large volume of work related to studying their spectral and photochemical properties. Among their photochemical properties, the greatest interest is focused on those relating to *trans-cis* photoisomerization reactions [2-4], photocycloaddition to form a cyclobutane [5-7], and electrocyclic reactions [8-10]. At this time, azaheteroaromatic derivatives of 2-styrylanthracene remain unstudied, even though for 2-styrylanthracene itself the so-called one-way *cis-trans* photoisomerization is widely known, when the reverse *trans-cis* photoisomerization reaction does not occur [11]. In this work, we report the synthesis of two isomeric azaheteroaromatic 2-styrylanthracenes, *viz*. 2-styrylbenzo[*g*]quinoline (**1**) and 3-styrylacridine (**2**).

Benzo[*g*]quinoline derivatives are difficult to obtain, since the majority of traditional methods for constructing a quinoline system involve use of β-naphthylamine and lead to an angularly structured benzo[*f*]quinolines [12]. An alternative method for building a linear benzoquinoline system is the Friedlander reaction between 3-amino-2-naphthaldehyde and various ketones [13]. The Friedlander reaction can also be used for the preparation of 2-styrylquinoline if methyl styryl ketone (benzalacetone) is used in the condensation with 2-aminobenzaldehyde [14]. In a contemporary modification of the Friedlander reaction the 2-aminobenzaldehyde is generated *in situ* by reduction of 2-nitrobenzaldehyde using iron powder in acid medium, and is then introduced into the reaction with the benzalacetone [15].

3-Nitro-2-naphthaldehyde (**3**) [16] was used as a starting material in the synthesis of compound **1** and was reduced with iron powder in alcoholic medium containing about 10^{-2} mol/l HCl. The 3-amino-2-naphthaldehyde (**4**) so obtained was introduced without isolation into the condensation with benzalacetone in alkaline medium.

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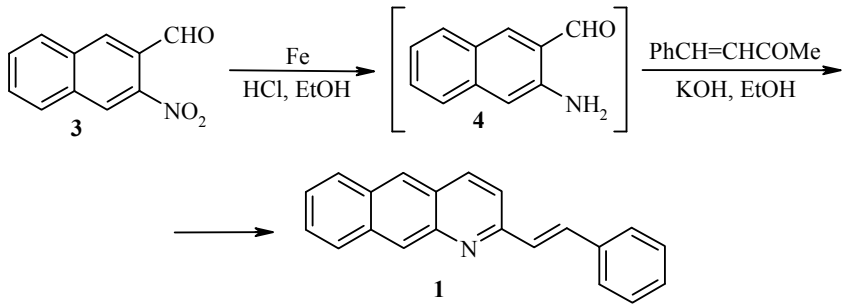
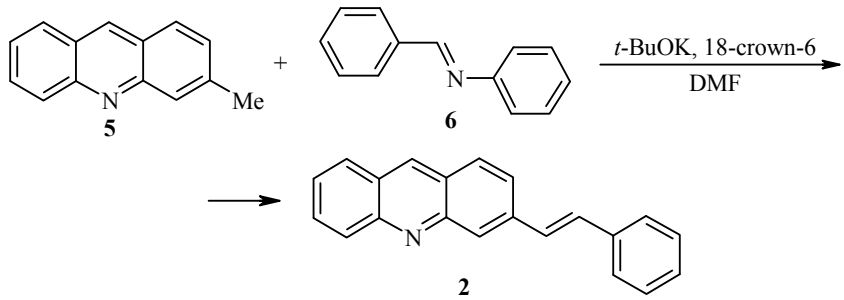
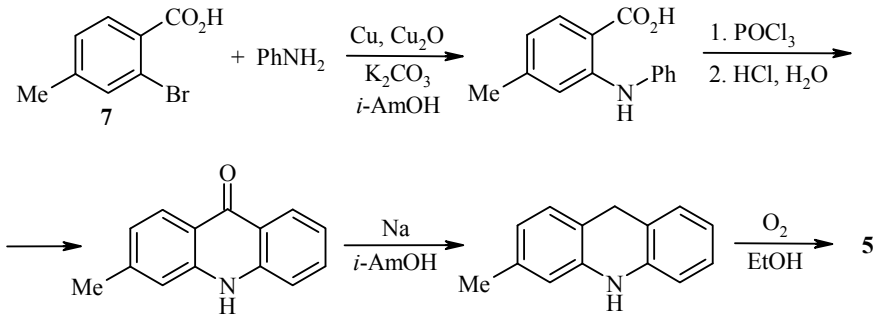
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1587-1591, October, 2012. Original article submitted July 9, 2011.



3-Styrylacridine (**2**) was prepared by a crotonic condensation of 3-methylacridine (**5**) with benzalaniline (**6**) in the presence of potassium *tert*-butoxide and 18-crown-6.



Compound **5** was prepared from the 2-bromo-4-methylbenzoic acid (**7**) by a standard scheme for construction of the acridine system [17, 18].



The ^{1}H NMR spectrum of compound **1** shows signals for the ethylenic H_α proton at 7.52 ppm and H_β proton at 7.76 ppm, with J = 16.4 Hz indicating a *trans*-configured double bond. The large chemical shift of the β-ethylenic proton (relative to the heterocyclic ring) when compared to H_α has been seen before in analogous compounds and is apparently due to formation of an N···H_β type intramolecular hydrogen bond between this proton and the nitrogen atom [19-21]. In compound **2** formation of such a hydrogen bond is not possible, and its ethylenic protons appear in the ^{1}H NMR spectrum as a multiplet with the phenyl group protons in the region 7.37-7.45 pm.

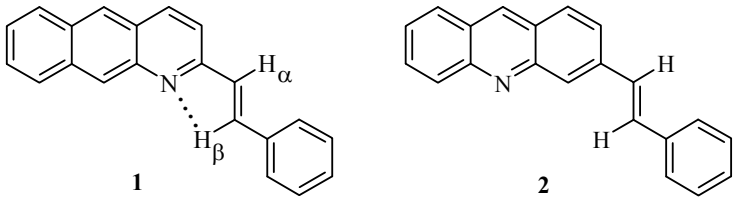


TABLE 1. Spectroscopic Parameters for Compounds **1** and **2** in the Neutral and Protonated Forms

Compound	λ_{max}, nm	ε_{max}, $M^{-1}\cdot cm^{-1}$	Compound	λ_{max}, nm	ε_{max}, $M^{-1}\cdot cm^{-1}$
1	309	48600	**2**	308	45100
	322	53700		322	44800
	376	13500		384	13700
1·HCl	338	42900	**2**·HCl	307	29500
	411	34400		410	20900
				437	18100

The IR spectra of both compounds show the presence of an out-of-plane C–H bond deformation vibration band at 965-967 cm^{-1}, and this also confirms the *trans* configuration of the double bond in compounds **1** and **2**.

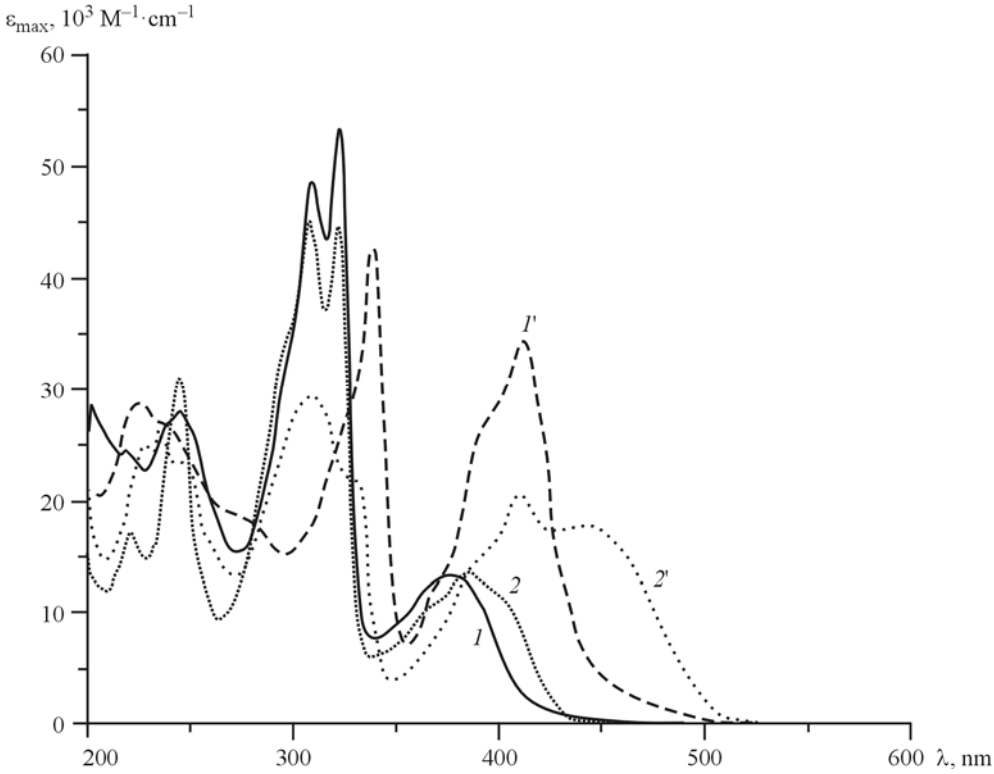


Fig. 1. Absorption spectra of compounds **1** and **2** in neutral (*1*, *2*) and in the protonated forms **1**·HCl and **2**·HCl (*1*', *2*') in ethanol.

When comparing the absorption spectra of compounds **1** and **2** it is evident that the neutral forms show two almost coincident long wavelength bands (Table 1 and Fig.1, spectra *1* and *2*). Protonation of compound **1** causes a bathochromic shift of the long wavelength absorption band by 35 nm and a marked increase in its intensity (Fig. 1, spectrum *1*'). On the other hand, for compound **2** a small increase is observed in the long wavelength band intensity, and a marked bathochromic shift of 53 nm (Fig. 1, spectrum *2*'). This large bathochromic shift for the compound **2** hydrochloride when compared to compound **1** hydrochloride is

evidently due to the fact that there is a longer chain of conjugation between the styryl group and the protonated nitrogen atom in compound **2**.

Hence, using different methods of constructing heteroaromatic rings we have synthesized the *trans* isomers of two 2-styrylanthracene aza analogs: 2-styrylbenzo[*g*]quinoline and 3-styrylacridine. Comparison of the properties of the synthesized compounds has shown that introduction of an aza function into aromatic systems has little effect on the absorption spectra for the neutral form. However, the protonated form spectra depend markedly on the position of the nitrogen atom in the anthracene system (in the central or side benzene ring).

EXPERIMENTAL

IR spectra were recorded on a Spectrum BX-2 Fourier spectrometer using KBr. Electronic absorption spectra were recorded on a Specord M-400 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance III spectrometer (500 MHz) using $CDCl_3$ with TMS as internal standard. Elemental analysis was performed on an Elementar vario MICRO cube analyzer. Melting points were determined on a Koffler hot stage apparatus with a heating rate of 4°C/min.

2-[(*E*)-2-Phenylethenyl]benzo[*g*]quinoline (1). A mixture of 3-nitro-2-naphthaldehyde (250 mg, 1.24 mmol), powdered iron (312 mg, 5.58 mmol), 0.1 M HCl (1 ml), and EtOH (6 ml) was heated at 90-95ºC for 2 h. A solution of benzalacetone (181 mg, 1.24 mmol) in EtOH (1.5 ml) and KOH (90 mg, 1.60 mmol) were carefully added and heated at the same temperature for a further 2 h. The reaction mixture was cooled, diluted with water (30 ml), and extracted with dichloromethane (3×25 ml). Solvent was evaporated *in vacuo*, and the residue was treated with conc. HCl (1 ml) and washed with EtOAc. The hydrochloride obtained was neutralized by heating with an aqueous-acetone solution of alkali, and the precipitated free base **1** was filtered off and recrystallized from 80% EtOH. Yield 103 mg (30%). Yellow crystals; mp 163-165ºC. IR spectrum, ν, cm^{-1}: 3054, 3028, 1635 (ν, C=C), 1604, 967 (δ, –CH=CH–), 887, 807, 744, 694. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.39 (1H, t, *J* = 7.4, H Ph); 7.47 (2H, t, *J* = 7.5, H Ph); 7.52 (1H, d, *J* = 16.4, Ph–CH=C<u>H</u>–); 7.54-7.59 (2H, m, H Ph); 7.70-7.73 (2H, m, H-7,8); 7.74 (1H, d, *J* = 8.8, H-3); 7.76 (1H, d, *J* = 16.4, Ph-C<u>H</u>=CH-); 8.06 (1H, d, *J* = 9.0, H-6(9)); 8.12 (1H, d, *J* = 9.0, H-9(6)); 8.34 (1H, d, *J* = 8.9, H-4); 8.40 (1H, s, H-5); 8.69 (1H, s, H-10). Found, %: C 89.33; H 5.48; N 4.76. $C_{21}H_{15}N$. Calculated, %: C 89.65; H 5.37; N 4.98.

3-[(*E*)-2-Phenylethenyl]acridine (2). A mixture of 3-methylacridine (**5**) (0.80 g, 4.1 mmol), benzalaniline (**6**) (1.50 g, 8.3 mmol), *t*-BuOK (0.82 g, 7.3 mmol), 18-crown-6 (0.50 g, 1.9 mmol), and DMF (10 ml) was heated at about 100ºC for 4 h under an argon atmosphere. The reaction mixture was cooled, treated with water, and the precipitate formed was filtered off. The filtrate was extracted with benzene (2×30 ml). Benzene was distilled off, and the solid residue formed was chromatographed together with the previously isolated precipitate on silica gel with acetone–petroleum ether (1:5) as eluent. Yield 0.66 g (57%). Light-yellow crystals; mp 159-161ºC. IR spectrum, ν, cm^{-1}: 3054, 3025, 1626 (ν, C=C), 1613, 1506, 965 (δ, –CH=CH–), 908, 791, 746, 693. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.33 (1H, d, *J* = 7.4, H Ph); 7.37-7.45 (4H, m, Ph–C<u>H</u>=C<u>H</u>–Ph, H Ph); 7.55 (1H, t, *J* = 7.4, H-7); 7.62 (2H, d, *J* = 7.3, H Ph); 7.81 (1H, t, *J* = 7.4, H-6); 7.85 (1H, d, *J* = 8.8, H-2); 7.99-8.03 (2H, m, H-1,8); 8.24-8.30 (2H, m, H-5,9); 8.75 (1H, s, H-4). Found, %: C 89.43; H 5.25; N 5.05. $C_{21}H_{15}N$. Calculated, %: C 89.65; H 5.37; N 4.98.

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