## INVESTIGATION OF THE REACTION OF N-ACETYLINDOXYL WITH SUBSTITUTED ANILINES. SYNTHESIS OF DERIVATIVES OF INDOLO[3,2-*b*]QUINOLINES

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1-Acetyl-2,3-dihydrospiro[indolo-3,2'-(1',2',3',4'-tetrahydroquinazolin-4'-one) was obtained from the reaction with anthranilamide, and 3-(2'-acetylaminophenyl)quinoxalin-2-one from the reaction with o-phenylenediamine, along with the normal products of the condensation of N-acetylindoxyl with substituted anilines. Derivatives of indolo[3,2-b]quinoline were synthesized from the obtained condensation products.

Keywords: aniline, acetylindoxyl, indoloquinoline, quinazoline, quinoxaline.

A series of 3-arylaminoindoles, from which derivatives of [3,2-b] quinolines were synthesized, was obtained by the reaction of N-acetylindoxyl (1) with a number of aromatic amines. In a study of some properties of the quinolines it was established that functionalization of these compounds is possible by alkylation at the indole NH group and by quaternization of the quinoline nitrogen atom with subsequent treatment with base to convert the quaternary salt into a derivative of indolo[3,2-b] quinolin-11-one with the oxo functional group in position 11 [1].

The present work is concerned with further study of reactions of compound 1 with substituted anilines. Condensation of N-acetylindoxyl (1) with *m*-nitroaniline (2a) under conditions previously used for *p*-nitroaniline [2] – refluxing in acetic acid – gave 3-(*m*-nitrophenyl)aminoindole (3a) in 52% yield. Other reactions conditions – refluxing the components in toluene in the presence of *p*-toluenesulfonic acid with removal of water – were optimal for this reaction with the yield of the desired product (3a) reaching 95%. Reaction of the aminoindole (3a) with Vilsmeier's reagent gave a mixture of 10-acetyl-1-nitroindolo[3,2-*b*]-quinoline (4) and 3-aryl-2-formylaminoindole (5), but the two products were isolated in much smaller yield than the previously prepared 2-nitro derivatives of this system [2]. Under the same conditions *o*-nitroaniline did not react with acetylindoxyl 1; only the starting materials were isolated. As a result we paid particular attention to the reaction of 1 with *o*-substituted anilines.

It appeared that derivatives of aniline with an electron-donating or relatively weak electron-accepting (in comparison with the nitro group) substituent in the *o*-position reacted readily under the same conditions with compound **1** to give the corresponding 3-aminoindoles. For example, N-acetyl-3-(*o*-substituted phenylamino)indoles (**3b-d**) were readily obtained from *o*-aminophenol, anthranilic acid, and ethyl anthranilate

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(2b-d). When compound 1 was refluxed in acetic acid with anthranilic acid (2c) or its ethyl ester (2d) complex mixtures of products were obtained which included, according to the <sup>1</sup>H NMR and mass spectra, indolo[3,2-*b*]-quinolin-11-one (6) along with the indoles 3c,d. The tetracycle 6 was isolated in 10% yield from the mixture obtained by condensation of compounds 1 and 2c. According to the <sup>1</sup>H NMR spectrum the mixture contained compounds 3c and 6 in a 1:1 ratio. Attempts to cyclize the ester 3d under various conditions gave a positive result only on refluxing in ethylene glycol when the tetracycle 6 was isolated in 21% yield.

On reaction of N-acetylindoxyl (1) with anthranilamide (2e) a mixture of two compounds was obtained in a ratio of 3:7 according to the <sup>1</sup>H NMR spectra. According to the spectra the minor product was 3-arylaminoindole 3e. Compound 7 was isolated by recrystallization from the mixture. According to the mass spectrum it had a molecular mass, m/z 293 (M<sup>+</sup>). The <sup>1</sup>H NMR spectrum of this compound shows a quartet at 4.22 ppm, corresponding to the methylene protons 2-CH<sub>2</sub> of the N-acetylindole fragment. That the protons of this group are not equivalent arises from the presence in the molecule of an asymmetric center at C<sub>(3)</sub>. The <sup>13</sup>C NMR spectrum of compound 7 reveals a signal of the *sp*<sup>3</sup>-hybridized quaternary carbon C<sub>(3)</sub> at 74.8 ppm. It was concluded from these results that 7 is a spiro compound.



**2**, **3 a** R = *m*-NO<sub>2</sub>, **b** R = *o*-OH, **c** R = *o*-COOH, **d** R = *o*-COOEt, **e** R = *o*-CONH<sub>2</sub>, **f** R = *o*-NH<sub>2</sub>

Prolonged heating of a mixture of compounds **3e** and **7** in anhydrous conditions (toluene, *p*-toluenesulfonic acid) gave no change in their ratio (according to the <sup>1</sup>H NMR spectrum), however in the presence of water led to a decrease in the content of the spiro compound **7** and a corresponding increase in amide **3e** ( when the mixture was heated under reflux for 3 h in toluene in the presence of *p*-toluenesulfonic acid and water, the ratio of **3e** to **7** changed from 26:74 to 60:40). It may be proposed that when N-acetylindoxyl (**1**) reacted with the carbamide **2e** the carbonylamine formed in the first step may be stabilized in two ways with the elimination of water, to form the substituted aminoindole **3e** or the spiro compound **7**. Product **3e** is completely stable and undergoes no further transformations, whereas compound **7** may undergo ring opening under the influence of H<sub>2</sub>O (H<sup>+</sup>), that leads eventually to an increase in the content of 1-acetyl-3-(*o*-carbamoylphenyl)aminoindole (**3e**) in the mixture.



When N-acetylindoxyl (1) was heated with *o*-phenylenediamine (2f) in isoamyl alcohol the product obtained did not correspond to the expected condensation product 3f according to its elemental analysis and mass spectrum. The mass spectrum reveals a molecular ion peak at m/z 279 (M<sup>+</sup>) which indicates the presence of an additional oxygen atom. In the literature [3, 4] the reaction of N-acetylisatin (8) with a series of *o*-diamines has been described and it has been proposed that the products have the spiro structure 9.

On repeating this reaction we obtained a product identical in physical constants with the compound synthesized from N-acetylindoxyl and *o*-phenylenediamine and corresponding in mp and mass spectrum with the compound described previously [3]. However its IR spectrum did not contain an absorption band at 1690 cm<sup>-1</sup>, characteristic of an amide fragment, but absorption bands were observed at 1650 and 1635 cm<sup>-1</sup>. Moreover, there was no signal of a quaternary  $sp^3$  carbon atom in the <sup>13</sup>C NMR spectrum (not described in [3, 4]), which rules out the spiro structure **9**. In the <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>), along with the signals of the aromatic protons, signals were observed at 1.90 and for NH groups at 9.77 (s) and 12.50 ppm (br). <sup>13</sup>C NMR spectrum ,  $\delta$ , ppm: 24.1 (CO<u>C</u>H<sub>3</sub>), 123.3, 123.5, 128.9, and 129.9 (CH-Ph), 115.5, 123.5, 130.5, 131.1 (CH-arom), 128.0, 132.2, 132.6, 137.1, 157.2 (quaternary C-arom), 154.8 (s, CO), and 168.3 (q, <u>C</u>OCH<sub>3</sub>). The absence of signals for NH<sub>2</sub> protons in the <sup>1</sup>H NMR spectrum rules out the structure **10a**, but the possibility of N→N transacetylation to give a compound with the structure **10b** is not completely excluded.



Opening of the pyrrole ring was observed when N-acetylisatin (8) reacted with amines to give substituted phenylglyoxamides 11 which were readily converted to the imino derivatives 12 [5].



In our case the reaction may occur as follows:



Unambiguous choice between structures 10b and 13 on the basis of spectroscopic data is rather complex, so the corresponding model compounds were synthesized – 3-phenyliminoindolin-2-one (14) [6, 7] and 3-phenylquinoxalin-2-one (15) [8].



To judge from the <sup>1</sup>H and <sup>13</sup>C NMR spectra, compound **14** exists in DMSO-d<sub>6</sub> solution as a mixture of two geometric isomers (87 and 13%) relative to the C=N bond: the chemical shift of the 4-H proton of the predominant isomer is equal to 6.30 and of the minor isomer to 7.59 ppm. The <sup>13</sup>C NMR spectrum of compound 14 contains, along with signals of the carbon atoms of a monosubstituted benzene ring, signals which are typical for isatin derivatives, in particular the signal of the quaternary carbon atom  $C_{(3a)}$  at 116.0 ppm. The <sup>13</sup>C NMR spectrum of the model compound 15 differs considerably from that of 14: the signals of  $sp^2$ -hybridized quaternary carbon atoms were observed at 132.3 (m), 132.4 (m), 135.9 (t), 154.3 (t), and 154.9 (s) ppm which are very close to those of the compound isolated from the reaction which therefore may be ascribed the structure 13. The UV spectra of compound 13 and the model 15 contain absorption maxima at 311.8, 366.1 and 310.0, 362.0 nm respectively, whereas for compound 14  $\lambda_{max}$  = 296.6 and 408.6 nm, i.e., there is no doubt about the similarity of the electronic structures of 13 and 15. Additional evidence that 3-(o-acetylamino)phenylquinoxalin-2-one (13) is formed in the reaction of N-acetylisatin (8) with o-phenylenediamine (2f) is provided by experiments of the nuclear Overhauser effect in the <sup>1</sup>H NMR spectrum and isotopic substitution in the <sup>13</sup>C NMR spectrum. Irradiation of the COCH<sub>3</sub> signal (1.91 ppm) leads to an increase in intensity of the signal at 9.77 ppm (NH, sharp signal), and on the other hand irradiation of this NH signal increases the intensities of the COCH<sub>3</sub> signal and the broad doublet at 7.82 ppm (in the o-position relative to the NHCOCH<sub>3</sub> group). The effect of isotopic substitution is observed in the <sup>13</sup>C NMR spectrum for the signals of the acetyl fragment:  $\Delta \delta^{13}C = -0.08$  (168.3, C=O), -0.03 (24.1 CH<sub>3</sub>); for the quaternary carbon atom  $C_{(2')}$ :  $\Delta\delta^{13}C = -0.11$  (137.1, t); for the protonated carbon  $C_{(3')}$  at 123.3  $\Delta\delta^{13}C = -0.09$ ; and for the quaternary carbon  $C_{(1')}\Delta\delta^{13}C = -0.09$  (128.0 m). This confirms the presence of the NHCOCH<sub>3</sub> substituent in the benzene ring. Finally, the mass spectrum agrees well with the structure proposed. The basic fragmentation is shown in Scheme 1.

When N-acetylindoxyl (1) and *o*-phenylenediamine (2f) were heated in isoamyl alcohol compound 13 was formed which was identical in physical properties and spectroscopic characteristics with the product obtained from N-acetylisatin (8) and amine 2f in either ethanol or isoamyl alcohol. The spectra were more complex when the reaction of N-acetylindoxyl (1) with *o*-phenylenediamine (2f) was carried out in toluene with the removal of water in the presence of *p*-toluenesulfonic acid. To judge from the <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>) a mixture of two substances was formed one of which was readily identified as the quinoxalinone 13 by comparison with the spectrum of a known sample. The second compound was characterized by the presence in the <sup>1</sup>H NMR spectrum of an acetyl group at 2.09, 8 aromatic protons (7.20-7.82 ppm), a CH–COH



fragment with the corresponding signals at 5.26 (–CH) and 6.52 ppm (OH,  ${}^{4}J_{CH,OH} = 1.6$  Hz), and downfield NH signals at 9.75 and 10.70 ppm. In the  ${}^{13}$ C NMR spectrum the signals of the carbon atoms of the acetyl group (24.2 and 168.7 ppm), 8 aromatic protonated and 4 quaternary  $sp^{2}$ -hybridized carbon atoms and the CH–C–OH fragment were clearly identified. Carbon with a neighboring heteroatom absorbed at 55.2 (CH,  ${}^{1}J_{CH} = 143$ ), and the quaternary  $sp^{3}$ -hybridized carbon atom, with no less than two heteroatom substituents resonated at 79.5 ppm. After this mixture was heated in DMSO-d<sub>6</sub> on a water bath for 5 h the content of the second component decreased, and after 10 h the spectrum corresponded to the spectrum of individual compound 13. To judge by the data obtained for the second compound it is proposed that it is 6-acetyl-5a-hydroxy-5,5a,10b,11-tetrahydroindolo[2,3-*b*]quinoxaline (16). The following scheme is proposed for the formation of compounds 16 and 13:



The driving force for the proposed scheme is the presence in intermediate 3f of a strong electron donating substituent (NH<sub>2</sub>) in the benzene ring which facilitates oxidation at position 2 of the indole ring. Further transformations of the intermediate oxoindole leads to the tetracycle 16 and then to the quinoxaline 13.

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Com-	Empirical formula	Found, % Calculated, %			mp, °C	Yield, %
pound		С	Н	Ν		(inctitod)
3a	$C_{16}H_{13}N_3O_3$	<u>65.28</u> 65.08	$\frac{4.43}{4.41}$	$\frac{14.41}{14.24}$	198-199 (propanol-2)	52 (A) 95 (B)
3b	$C_{16}H_{14}N_2O_2$	<u>72.18</u> 72.09	$\frac{5.40}{5.26}$	$\frac{10.39}{10.53}$	185-186 (propanol -2)	99
3c	$C_{17}H_{14}N_2O_3$	<u>69.23</u> 69.39	$\frac{4.90}{4.76}$	<u>9.51</u> 9.52	211-213 (propanol-2)	74
3d	$C_{19}H_{18}N_2O_3$	$\frac{70.79}{70.81}$	<u>5.79</u> 5.59	$\frac{8.67}{8.70}$	108-110 (propanol-2)	90
4	$C_{17}H_{11}N_3O_3$	<u>67.15</u> 66.89	$\frac{3.85}{3.61}$	$\frac{13.87}{13.77}$	250-251 (propanol-2–DMF, 1:1)	10
5	$C_{17}H_{13}N_3O_4$	<u>63.21</u> 63.16	$\frac{4.06}{4.02}$	$\frac{13.00}{13.00}$	196-197 (MeOH–DMF, 7:4)	7
6	$C_{15}H_{10}N_2O$	<u>76.92</u> 76.92	$\frac{4.29}{4.27}$	<u>11.89</u> 11.97	>355	21 (A) 7 (B)
7	$C_{17}H_{15}N_3O_2$	$\frac{69.29}{69.62}$	$\frac{5.45}{5.12}$	$\frac{14.36}{14.33}$	289-292 (propanol-2–DMF, 2:1)	31

TABLE 1. Characteristics of the Compounds Synthesized

## **EXPERIMENTAL**

IR spectra of nujol mulls were recorded on a Perkin-Elmer 457 spectrometer. Mass spectra were obtained with a Finnigan-MAT SSQ-710 mass spectrometer with direct inlet of the sample into the ion source, energy of the ionizing electrons 70 eV, ionization chamber temperature 150°C. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian UNITY plus 400 spectrometer (400 and 100.6 MHz respectively) with TMS as internal standard. The course of reactions and purity of the products were monitored by TLC on Silufol UV-254 plates with chloroform–methanol, 1:10 as eluant and visualization with UV light. Characteristics of the compounds synthesized are given in Table 1.

**1-Acetyl-3-(3'-nitrophenyl)aminoindole (3a). A.** A solution of N-acetylindoxyl (1 g, 5.7 mmol) and *m*-nitroaniline (0.8 g, 5.8 mmol) in acetic acid (5 ml) was refluxed for 2 h. The reaction mixture was cooled to 20°C, the precipitate was filtered off and washed with ethyl acetate to give 3a (0.88 g).

**B**. *p*-Toluenesulfonic acid (0.3 g, 1.6 mmol) was added to solution of N-acetylindoxyl (5 g, 28.6 mmol) and *m*-nitroaniline (4 g, 29 mmol) in toluene (50 ml). The mixture was refluxed with a Dean and Stark trap for 30 min and then cooled to 20°C. The precipitate was filtered off, washed with toluene and ether to give compound **3a** (5.3 g). *p*-Toluenesulfonic acid (0.05 g) was added to the filtrate which was again refluxed with a Dean and Stark trap for 15 min until a precipitate appeared. An additional 2.7 g of **3a** was obtained. IR spectrum, v, cm<sup>-1</sup>: 3340, 1670, 1610, 1590. M<sup>+</sup> 295. A mixture of compound B with a sample prepared by method A gave no depression of the melting point.

**1-Acetyl-3-(2'-hydroxyphenyl)aminoindole (3b).** *o*-Aminophenol (0.64 g, 5.9 mmmol) and *p*-toluenesulfonic acid (0.05 g) were added to a suspension of N-acetylindoxyl (1 g, 5.7 mmol) in toluene (20 ml). The mixture was refluxed with a Dean and Stark trap for 2 h, adding toluene when necessary. The precipitate which formed during reflux was filtered off after cooling the reaction mixture to 20°C to give compound **3b** (1.5 g).  $M^+$  266.

**1-Acetyl-3-(2'-hydroxycarbonylphenyl)aminoindole (3c)** was obtained from N-acetylindoxyl (1 g, 5.7 mmol) and anthranilic acid (0.8 g, 5.8 mmol) as for the synthesis of compound **3b**, reflux time 3 h. The precipitate was washed with a small amount of ether to give compound **3c** (1 g). IR spectrum, v, cm<sup>-1</sup>: 3310, 1710, 1670, 1600, 1520. M<sup>+-</sup> 294.

**1-Acetyl-3-(2'-ethoxycarbonylphenyl)aminoindole (3d)** was obtained from N-acetylindoxyl (2 g, 11.4 mmol) and ethyl anthranilate (2 g, 12 mmol) as for the synthesis of compound **3b**, reflux time 5 h. Methanol was added to the reaction mixture and the precipitate filtered off to give compound **3d** (3.3 g).  $M^+$  322.

**10-Acetyl-1-nitroindolo**[3,2-*b*]**quinoline (4).** A solution of compound **3a** (5 g, 17 mmol) in DMF (25 ml) was added at 20°C to Vilsmeier complex prepared in the normal way from POCl<sub>3</sub> (5 ml) and DMF (10 ml). The reaction mixture was stirred for 3 days at 18°C. The precipitate was filtered off and washed with water to give crude 4 (1.65 g). It was recrystallized from 1:1 DMF-propanol-2 to give pure compound **4** (0.5 g). IR spectrum, v, cm<sup>-1</sup>: 1695, 1615, 1525. M<sup>++</sup> 305.

1-Acetyl-2-formyl-3-(3'-nitrophenyl)aminoindole (5) was obtained from compound 3a (0.5 g, 1.7 mmol) and the Vilsmeier complex as for the synthesis of compound 4. The reaction mixture was kept at 18°C for 2.5 h and then poured into ice water. The precipitate which formed over 1.5 h was filtered off and washed with water to give compound 5 (0.22 g). It was recrystallized from 7:4 MeOH–DMF to give 0.04 g of pure compound 5.  $M^+$  323.

**5,10-Dihydroindolo**[**3,2-***b*]**quinolin-11-one (6). A.** A solution of compound **3d** (0.2 g, 0.6 mmol) in ethylene glycol (3 ml) was refluxed for 10 h. The reaction mixture was cooled to 20°C, the precipitate was filtered off and washed with acetone to give compound **6** (0.03 g).  $M^+$  234. <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>),  $\delta$ , ppm: 7.20 (1H, t, 2-H); 7.30 (1H, t, 7-H); 7.47 (1H, t, 8-H); 7.54 (1H, d, 9-H); 7.69 (1H, t, 3-H); 7.75 (1H, d, 4-H); 8.20 (1H, d, 1-H); 8.37 (1H, d, 6-H); 11.71 (1H, s, 5-NH); 12.54 (1H, br. s, 10-NH).

**B**. A solution of N-acetylindoxyl (1 g, 5.7 mmol) and anthranilic acid (0.8 g, 5.8 mmol) in acetic acid (5 ml) was refluxed for 5 h. The precipitate was filtered off and washed with methanol to give a mixture of compounds **3c** and **6** (0.25 g, 1:1 according to the <sup>1</sup>H NMR spectrum;  $M_1^+$  294,  $M_2^+$  234). The mixture was treated with aqueous alkali, the insoluble residue was filtered off and washed with water to give compound **6** (0.09 g). A mixture of compound B with a sample prepared by method A gave no depression of the melting point.

**1-Acetyl-2,3-dihydrospiro[indolo-3,2'-(1',2',3',4'-tetrahydroquinazolin-4'-one)]** (7) was obtained from N-acetylindoxyl (1 g, 5.7 mmol) and anthranilamide (0.82 g, 6 mmol) as for the synthesis of compound **3b**, reflux time 3 h. The precipitate was ground in methanol (5 ml), filtered off, washed with methanol to give compounds **3e** and **7** (1.1 g, 32:68 according to the <sup>1</sup>H NMR spectrum). The material was recrystallized from 2:1 propanol-2–DMF to give compound **7** (0.51 g). M<sup>+</sup> 293. <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>), δ, ppm: 2.17 (3H, s, CH<sub>3</sub>); 4.22 (2H, q, 2-H); 6.69 (1H, d, 8'-H); 6.76 (1H, t, 6'-H); 7.04 (1H, t, 5-H); 7.30 (1H, d, 6-H); 7.31 (1H, d, 4-H); 7.35 (1H, t, 7'-H); 7.46 (1H, s, NH); 7.68 (1H, d, 7-H); 8.12 (1H, d, 5'-H); 8.63 (1H, s, CONH). <sup>13</sup>C NMR spectrum (DMSO-d<sub>6</sub>), δ, ppm: 24.4 (CH<sub>3</sub>), 62.9 (CH<sub>2</sub>), 74.8 (C<sub>(3)</sub>), 114.9, 116.9, 118.2, 123.4, 124.2, 127.7, 130.6, 134.3 (arom. CH), 114.3 (C<sub>(3a)</sub>), 134.7 (C<sub>(4a')</sub>), 141.4 and 146.5 (C<sub>(8a')</sub>, C<sub>(7a)</sub>), 163.1 (CONH).

**3-(2'-Acetylaminophenyl)quinoxalin-2-one (13). A.** A solution of N-acetylindoxyl (1.4 g, 8 mmol) and *o*-phenylenediamine (0.8 g, 8.1 mmol) in isoamyl alcohol was refluxed for 10 h. The mixture was cooled to 20°C, the precipitate was filtered off to give compound **13** (0.55 g, 22%); mp 292-294°C (DMF). IR spectrum, v, cm<sup>-1</sup>: 3215, 3100, 1650, 1635, 1600, 1585. M<sup>+-</sup> 279.

**B.** A suspension of N-acetylisatin (0.3 g, 1.6 mmol) and *o*-phenylenediamine (0.17 g, 1.6 mmol) in isoamyl alcohol (7 ml) was refluxed for 5 min, then was cooled, the precipitate was filtered off and washed with isoamyl alcohol and ether to give compound **13** (0.29 g, 66%).

C. Compound 13 (0.23 g, 52%) was obtained from N-acetylisatin (0.3 g, 1.6 mmol) and o-phenylenediamine (0.17 g, 1.6 mmol) in ethanol (10 ml) analogously to method B. A mixture of samples prepared by methods A and B gave no melting point depression.

Mixture of 3-(2'-acetylaminophenyl)quinoxalin-2-one (13) and 6-acetyl-5a-hydroxy-5,10b,11-Hindolo[3,2-b]quinoxaline (16) was obtained from N-acetylindoxyl (0.5 g, 2.9 mmol) and *o*-phenylenediamine (0.32 g, 3.0 mmol) under the conditions for the synthesis of compound 3b, reflux time was 4 h. The precipitate which appeared after 48 h at 20°C was filtered off and washed with toluene and methanol to give a mixture of compounds 13 and 16 (0.15 g).

**3-Phenyliminoindolin-2-one (14)** [6, 7]. <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>),  $\delta$ , ppm, major isomer: 6.30 (1H, d, 4-H); 6.71 (1H, t, 5-H); 6.97 (2H, d, 2',6'-H); 7.33 (1H, m, 4'-H); 7.33 (1H, m, 6-H); 7.46 (2H, t, 3',5'-H); 7.90 (1H, d, 7-H); 11.00 (1H, br.s, NH). Minor isomer: 6.86 (1H, d, 7-H); 6.99 (2H, d, 2',6'-H); 7.06 (1H, t, 5-H); 7.30 (1H, t, 4'-H) 7.45 (2H, t, 3',5'-H); 7.45 (1H, t, 6-H); 7.59 (1H, d, 4-H); 10.90 (1H, br.s, NH). <sup>13</sup>C NMR spectrum (DMSO-d<sub>6</sub>),  $\delta$ , ppm: principle isomer: 111.8 (C<sub>(7)</sub>), 116.0 (C<sub>(3a</sub>)), 117.5 (C<sub>(2',6')</sub>), 122.0 (C<sub>(4)</sub>), 125.2, 125.7 (C<sub>(4')</sub>) or (C<sub>(5)</sub>), 129.9 (C<sub>(3',5')</sub>), 134.8 (C<sub>(6)</sub>), 147.3 (C<sub>(1')</sub>), 150.9 (C<sub>(7a)</sub>), 155.3 (C<sub>(3)</sub>), 163.8 (C<sub>(2)</sub>).

**3-Phenylquinoxalin-2-one (15)** [8]. <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>),  $\delta$ , ppm: 7.30-7.36 (2H, m); 7.46-7.57 (4H, m); 7.84 (1H, m); 8.30 (2H, m, 2',6'-H); 12.60 (1H, br. s, NH). <sup>13</sup>C NMR spectrum (DMSO-d<sub>6</sub>),  $\delta$ , ppm: 115.4, 123.7, 130.5, 130.6 (C<sub>(5-8)</sub>), 128.2 (2C), 129.0 (1C), 129.2 (2C) (Ph), 132.3, 132.4 (C<sub>(4a)</sub>, C<sub>(8a)</sub>), 135.9 (C<sub>(1')</sub>), 154.3 (C<sub>(3)</sub>), 154.9 (C<sub>(2)</sub>).

This work was carried out with a financial subvention from the Russian for Fundamental Research (grant 97-03-33066).

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