

HETEROCYCLIC ANALOGS OF 5,12-NAPHTHACENEQUINONE.

5*. SYNTHESIS OF 2,3-DIAMINO-1,4-DIMETHOXYANTHRAQUINONE

AND ITS HETEROCYCLIC DERIVATIVES

A. E. Shchekotikhin¹, Yu. N. Lusikov¹, V. N. Buyanov²,
and M. N. Preobrazhenskaya¹

A new method for the synthesis of 2,3-diamino-1,4-dimethoxyanthraquinone from quinizarin has been developed. Heterocyclic analogs of 5,12-naphthacenequinone have been synthesized based on this o-diamine – 4,11-dimethoxyanthra[2,3-d]imidazole-5,10-dione, 4,11-dimethoxyanthra[2,3-d][1,2,3]triazole-5,10-dione, and 5,12-dimethoxynaphtho[2,3-g]quinoxaline-6,11-dione.

Keywords: 2-amino-3-nitroquinizarin, anthra[2,1-d][1,3]oxazole-6,11-dione, anthra[2,3-d][1,2,3]triazole-5,10-dione, 2,3-diamino-1,4-dimethoxyanthraquinone, methoxy derivatives, naphtho[2,3-g]quinoxaline-6,11-dione, acylation, hydrolysis, condensation.

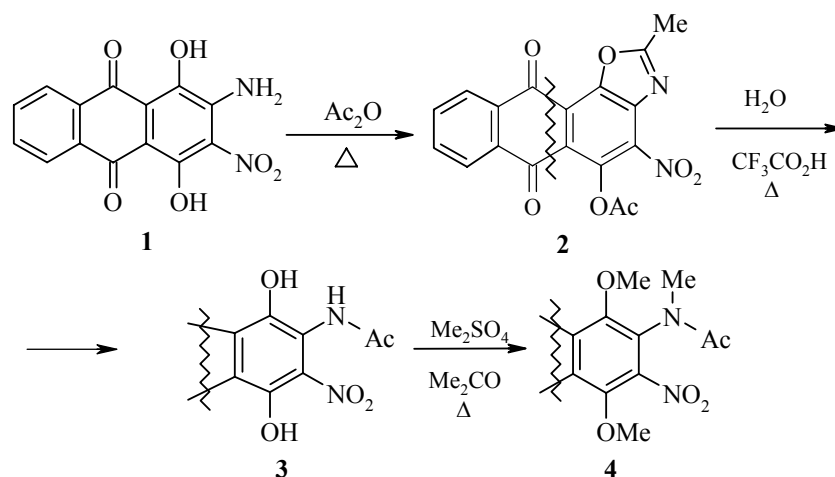
We have previously prepared 2,3-diaminoquinizarin, a key compound for the synthesis of imidazo-, triazolo-, and pyrazino derivatives of quinizarin [2]. However O-methyl derivatives of these heterocyclic analogs of 5,12-naphthacenequinone were not obtained. The synthesis of such derivatives may be of practical interest, because in similar compounds the methoxy groups are in *ortho* positions to carbonyl groups and are activated for nucleophilic attack, and may be used for preparation of amino derivatives of heterocyclic analogs of 5,12-naphthacenequinone [3]. Consequently the aim of the present work was the synthesis of heterocyclic derivatives of 2,3-diamino-1,4-dimethoxyanthraquinone.

Direct O-methylation of previously obtained heterocyclic derivatives of quinizarin [2] is hindered by the low solubility of these compounds in the majority of organic solvents and the possibility of N-methylation of the heterocyclic unit. We chose 2-amino-3-nitroquinizarin (**1**), prepared by amination of 2-nitroquinizarin [2], as starting material. Clearly it is necessary to protect the amino group in order to carry out the O-methylation of compound **1**, we therefore studied the possibility of the synthesis of its N-acetyl derivative. We were unsuccessful in finding conditions for the selective N-acetylation of anthraquinone, since a mixture of compounds was obtained on acetylation. For example, on boiling anthraquinone **1** with acetic anhydride, the basic reaction product is derivative of angular anthra[2,1-d][1,3]oxazole-6,11-dione **2**.

* On the 70th Birthday of Professor E. Lukevics.

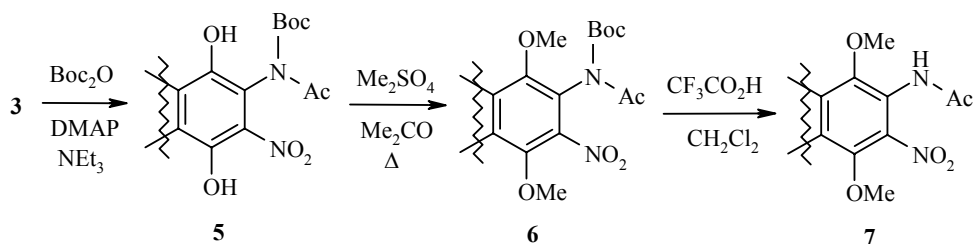
* For part 4, see [1].

¹G. F. Gauze Institute of New Antibiotics, Moscow 119021, Russia; e-mail: chekotikhin@mtu-net.ru, mnp@space.ru. ² D. I. Mendeleev University of Chemical Technology of Russia, Moscow 125190. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No.1, 96-102, January 2007. Original article received June 6, 2006.

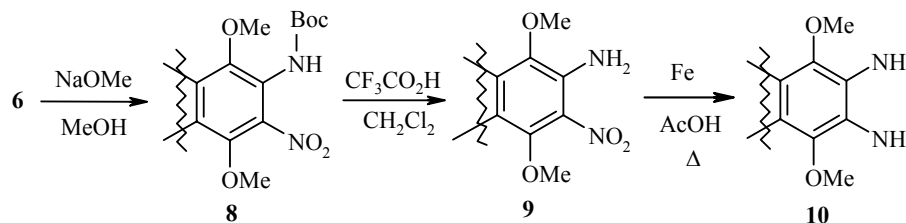


It appears that the derivative of oxazole **2** is hydrolytically unstable and in the mild conditions of hydrolysis used for the selective scission of α -acetoxyanthraquinones [4], heating with trifluoroacetic acid, opening of the oxazole ring occurs with formation of the N-acetamide **3** in high yield. Evidently the reason for this easy hydrolysis of the aromatic heterocycle is the weakening of the protonated oxygen atom in the oxazole unit as a result of closing of the hydrogen bond.

N-Methylation occurs on treatment of acetamide **3** with dimethyl sulfate in the presence of potassium carbonate in acetone to give as the basic product the trimethyl derivative **4**. It is clearly necessary to use an additional protective group for the NH groups. For this we chose the *tert*-butoxycarbonyl (Boc) group [5]. Acylation of compound **3** by the known method [6] with Boc-anhydride in the presence of 4-(N,N-dimethylamino)pyridine (DMAP) and triethylamine occurred selectively to give the N-Boc-N-acetyl derivative **5**. Methylation of this compound with dimethyl sulfate in the presence of potassium carbonate occurred without any resinification to give the O,O-dimethyl derivative **6** as the basic product.

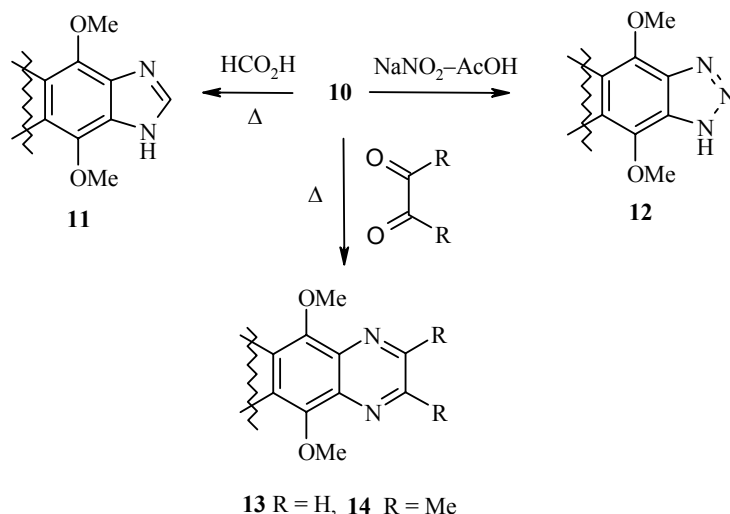


Removing the N-protecting groups in compound **6** must be carried out selectively. Treatment of the anthraquinone **6** with trifluoroacetic acid gave the acetamide **7** in high yield. In N-Boc-acetamides the acetyl group is activated for attack by nucleophilic reagents [7], so the reaction of sodium methoxide with the N-Boc-acetamide **6** permits the removal of the acetyl group under mild conditions to give the carbamate **8**.



Removal of the Boc group from the latter with trifluoroacetic acid gave 2-amino-1,4-dimethoxy-3-nitroanthraquinone (**9**). Reduction of the methoxynitroanthraquinone to the corresponding amine can be carried out with iron in acetic acid [8]. The key compound 2,4-diamino-1,4-dimethoxyanthraquinone (**10**) was obtained from the nitroanthraquinone **9** by this method in high yield.

As with diaminoquinizarin [2], the O,O-dimethyl derivative **10** undergoes condensation reactions to give a series of heterocyclic derivatives. For example, heating the diamine **10** with formic acid gave 4,11-dimethoxyanthra[2,3-*d*]imidazole-5,10-dione (**11**). The linear triazoloanthraquinone **12** was obtained by nitrosation of the diamine **10** in acetic acid. Condensation of diamine **10** with glyoxal or diacetyl in THF gave the derivatives of naphtho[2,3-*g*]quinoxaline-6,11-dione **13** and **14** respectively.



Some changes in the electronic absorption spectra of the compounds synthesized should be noted. Condensation of 2-amino-3-nitroquinizarin **1** into derivative of anthra[2,1-*d*]oxazole-6,11-dione **2** caused a considerable hypsochromic shift of the long-wavelength absorption band (λ_{max} 345 nm). Comparison of the absorption spectrum of compound **1** with its N-acetyl derivatives **3** and **5** showed the appearance of an additional long-wavelength absorption band (λ_{max} 570 nm). Methylation of the hydroxy groups in these compounds led to a considerable hypsochromic shift of the long-wavelength absorptions in the spectra of compounds **4** and **6-8**, so that the positions of the long-wavelength bands in the spectra of these compounds are practically coincident with the long-wavelength maxima (λ_{max} approx 360 nm) in the absorption spectra of other β,β -disubstituted derivatives of 1,4-dimethoxyanthraquinone [1]. Removal of the protecting group and reduction of the nitro group causes a bathochromic shift of the long-wavelength absorption band (λ_{max} approx 450 nm) in the spectrum of compound **10**. Annellation of the heterocyclic units with 1,4-dimethoxyanthraquinone (λ_{max} 428 nm [9]) led to a hypsochromic shift of the long-wavelength absorption bands in the spectra of the heterocyclic compounds derivatives **11-14**, with the greatest shift (about 50 nm) with lowest intensities observed in the spectra of derivatives with the acceptor pyrazine ring **13, 14**.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded with a Varian VXR-400 spectrometer (400 and 100 MHz respectively) in DMSO-d_6 (compounds **2, 3, 11-13**) and CDCl_3 solutions (compounds **4-6, 8-10, 14**) with TMS as internal standard. Mass spectra were recorded with Finnigan-MAT (USA) SSQ 710 chromatomass spectrometer, ionizing energy 70 eV, with direct injection of the sample into the ion chamber, heating of the

sample to 350°C, ionizing chamber temperature 150°C. Absorption spectra were recorded on a Hitachi-U2000 spectrometer. The course of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates. Preparative chromatography used Merck 60 silica gel.

5-Acetoxy-2-methyl-4-nitroanthra[2,1-*d*][1,3]oxazole-6,11-dione (2). 2-Amino-3-nitroquinizarine (**1**) (10.0 g, 33.3 mmol) in acetic anhydride (100 ml) was boiled with stirring for 30 min, cooled and poured into water (300 ml). The mixture was stirred for 2-3 h, the precipitate was filtered off, washed with water, and dried. The solid was dissolved in a hot toluene–AcOEt (1:1) mixture, the hot solution was filtered through a layer of SiO₂, and evaporated. The residue was purified chromatographically (silicagel, benzene–AcOEt, 10:0 → 3:1) to anthraoxazole **2** (7.0 g, 58%), light-yellow crystals; mp 214–216°C (benzene). UV spectrum (EtOH), $\lambda_{\max}$, nm (log ϵ): 219 (4.4), 238 (4.2), 260 (4.4), (281), 345 (3.9). ¹H NMR spectrum, δ , ppm: 8.24 (2H, m, H-5,8); 7.84 (2H, m, H-6,7); 2.90 (3H, s, CH₃); 2.51 (3H, s, COCH₃). ¹³C NMR spectrum, δ , ppm: 179.93 (C=O); 179.82 (C=O); 172.82*; 168.15; 147.45; 140.63; 140.06; 137.59; 133.52; 131.98; 121.90; 120.35; 134.96 (CH); 134.42 (CH); 127.54 (CH); 126.81 (CH); 20.61 (CH₃); 15.11 (CH₃). Mass spectrum, m/z (I_{rel} , %): 366 [M]⁺ (12), 324 (100), 282 (26), 252 (18). Found, %: C 59.24; H 2.87; N 7.61. C₁₈H₁₀N₂O₇. Calculated, %: C 59.02; H 2.75; N 7.65.

2-Acetylamino-1,4-dihydroxy-3-nitroanthracene-9,10-dione (3). Anthraoxazole **2** (6.0 g, 16.4 mmol) was boiled while stirring with trifluoroacetic acid (100 ml) and water (2.0 ml) for 10 min, cooled, water (100 ml) was added, the precipitate was filtered off and dried. The solid was recrystallized from 2-methoxyethanol to give red crystals of the acetamide **3**, yield 4.8 g (85%); mp 250°C. UV spectrum (EtOH), $\lambda_{\max}$, nm (log ϵ): 224 (4.3), 255 (4.5), 294 (3.8), (335), 482 (3.9), (530), 571 (3.6). ¹H NMR spectrum, δ , ppm: 13.10 (2H, br. s, 2 OH); 10.51 (1H, br. s, NH); 8.27 (2H, m, H-5,8); 8.02 (2H, m, H-6,7); 2.13 (3H, s, COCH₃). ¹³C NMR spectrum, δ , ppm: 186.41 (C=O); 185.49 (C=O); 168.65 (C=O); 150.17; 148.23; 139.56; 132.61; 132.38; 128.68; 114.25; 111.41; 135.31 (CH); 135.12 (CH); 126.72 (CH); 126.57 (CH); 22.49 (CH₃). Mass spectrum, m/z (I_{rel} , %): 342 [M]⁺ (16), 300 (100), 252 (21). Found, %: C 56.43; H 2.99; N 8.31. C₁₆H₁₀N₂O₇. Calculated, %: C 56.15; H 2.94; N 8.18.

2-[Acetyl(methyl)amino]-1,4-dimethoxy-3-nitroanthracene-9,10-dione (4). A mixture of compound **3** (0.5 g, 1.5 mmol), calcined potassium carbonate (3.0 g, 21.7 mmol), and freshly distilled dimethyl sulfate (0.5 ml, 5.2 mmol) in dry acetone (100 ml) was boiled for 10 h with intense stirring in a stream of argon. The reaction mass was filtered, the filtrate was evaporated in vacuum, the residue was washed with methanol, dried, and purified chromatographically (silicagel, benzene–AcOEt, 10:1 → 2:1) to give the N-methylacetamide **4** (0.38 g, 67%) as yellow crystals; mp 159–161°C (toluene). UV spectrum (EtOH), $\lambda_{\max}$, nm (log ϵ): 219 (4.4), 253 (4.5), 356 (3.7). ¹H NMR spectrum, δ , ppm: 8.22 (2H, m, H-5,8); 7.84 (2H, m, H-6,7); 4.07 (3H, s, OCH₃); 4.00 (3H, s, OCH₃); 3.20 (3H, s, NCH₃); 1.93 (3H, s, COCH₃). Mass spectrum, m/z (I_{rel} , %): 384 [M]⁺ (4), 353 (22), 338 (100), 308 (17), 280 (15). Found, %: C 59.44; H 4.32; N 7.22. C₁₉H₁₆N₂O₇. Calculated, %: C 59.38; H 4.20; N 7.29.

2-[Acetyl(*tert*-butoxycarbonyl)amino]-1,4-dihydroxy-3-nitroanthracene-9,10-dione (5). Anthraquinone **3** (4.0 g, 11.7 mmol) was dissolved on heating in DMF (150 ml), the solution was cooled and Et₃N (4.0 ml, 28.8 mmol), 4-(*N,N*-dimethylamino)pyridine (2.0 g, 16.4 mmol), and Boc-anhydride (3.0 g, 13.8 mmol) were added with stirring. Stirring was continued for 1 h, the mixture was diluted with water (300 ml), extracted with AcOEt, the extract was washed with 1% hydrochloric acid and water, and dried over Na₂SO₄. The solution was filtered through a layer of SiO₂, evaporated, and the residue was crystallized from toluene to give orange crystals of N-Boc-acetamide **5** (4.1 g, 79%); mp 250°C (benzene). UV spectrum (EtOH), $\lambda_{\max}$, nm (log ϵ): 224 (4.5), 253 (4.5), 284 (4.0), (331), 463 (4.0), (530), 572 (3.6). ¹H NMR spectrum, δ , ppm: 13.12 (1H, s, OH); 13.00 (1H, s, OH); 8.40 (2H, m, H-5,8); 7.96 (2H, m, H-6,7); 2.64 (3H, s, COCH₃); 1.42 (9H, s, C(CH₃)₃). Mass spectrum, m/z (I_{rel} , %): 442 [M]⁺ (9), 326 (92), 300 (44), 252 (37). Found, %: C 57.21; H 4.22; N 6.24. C₂₁H₁₈N₂O₉. Calculated, %: C 57.02; H 4.10; N 6.33.

* Here and further all signals without assignment belong to tertiary carbon atoms.

2-[Acetyl(*tert*-butoxycarbonyl)amino]-1,4-dimethoxy-3-nitroanthracene-9,10-dione (6) was prepared analogously to compound **4** from anthraquinone **5**. Yield 76%; mp 170-172°C. UV spectrum (EtOH), $\lambda_{\max}$ nm (log ϵ): 219 (4.4), 253 (4.5), 357 (3.7). ^1H NMR spectrum, δ , ppm: 8.22 (2H, m, H-5,8); 7.84 (2H, m, H-6,7); 4.06 (3H, s, OCH_3); 3.98 (3H, s, OCH_3); 2.65 (3H, s, COCH_3); 1.41 (9H, s, $\text{C}(\text{CH}_3)_3$). Mass spectrum, m/z (I_{rel} , %): 470 $[\text{M}]^+$ (12), 386 (24), 354 (100), 324 (68), 293 (21). Found, %: C 58.61; H 4.82; N 5.77. $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_9$. Calculated, %: C 58.72; H 4.71; N 5.95.

2-Acetylamino-1,4-dimethoxy-3-nitroanthracene-9,10-dione (7). Trifluoroacetic acid (3.0 ml) was added to a solution of anthraquinone **6** (0.4 g, 1.5 mmol) in CH_2Cl_2 (30 ml) and kept for 2 h, water and a solution of NaHCO_3 were added to neutral reaction. The organic phase was separated, washed with water, dried and evaporated. The residue was purified by chromatography (silicagel, benzene–AcOEt, 10:1 $\rightarrow$ 2:1) to give yellow crystals of acetamide **7** (0.25 g, 79%); mp 250°C (toluene). UV spectrum (EtOH), $\lambda_{\max}$ nm (log ϵ): 219 (4.2), 254 (4.4), (286), 363 (3.6). ^1H NMR spectrum, δ , ppm: 10.28 (1H, s, NH); 8.14 (2H, m, H-5,8); 7.91 (2H, m, H-6,7); 3.93 (3H, s, OCH_3); 3.83 (3H, s, OCH_3); 2.11 (3H, s, COCH_3). ^{13}C NMR spectrum, δ , ppm: 181.23 (C=O); 180.28 (C=O); 169.35 (C=O); 151.56; 147.87; 146.48; 133.51; 133.48; 131.33; 129.18; 125.32; 134.26 (CH); 134.23 (CH); 126.33 (CH); 126.31 (CH); 64.26 (CH_3); 62.07 (CH_3); 22.53 (CH_3). Mass spectrum, m/z (I_{rel} , %): 370 $[\text{M}]^+$ (26), 328 (82), 324 (100), 298 (42), 281 (35), 252 (21). Found, %: C 58.44; H 3.76; N 7.31. $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_7$. Calculated, %: C 58.38; H 3.81; N 7.56.

2-(*tert*-Butoxycarbonyl)amino-1,4-dimethoxy-3-nitroanthracene-9,10-dione (8). Anthraquinone **6** (3.0 g, 6.4 mmol) was dissolved on heating in a mixture of MeOH (50 ml) and toluene (50 ml), the solution was cooled and a solution of MeONa (15.0 ml of 2.5 mol/l solution) was added with stirring, the mixture was kept for 4 h, a solution of 1N HCl (40 ml) was added with stirring and cooling, the mixture was extracted with AcOEt, the extract was washed with water, dried over Na_2SO_4 , and evaporated. The residue was purified by chromatography (silicagel, benzene–AcOEt, 10:1 $\rightarrow$ 5:1) to give yellow crystals of carbamate **8** (2.13 g, 78%); mp 164-166°C. UV spectrum (EtOH), $\lambda_{\max}$ nm (log ϵ): 219 (4.2), 253 (4.4), (286), 367 (3.6). ^1H NMR spectrum, δ , ppm: 8.20 (2H, m, H-5,8); 7.80 (2H, m, H-6,7); 7.08 (1H, s, NH); 4.13 (3H, s, OCH_3); 3.99 (3H, s, OCH_3); 1.52 (9H, s, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR spectrum, δ , ppm: 181.66 (C=O); 180.27 (C=O); 155.14; 152.29; 151.52; 148.71; 134.34; 133.76; 133.36; 131.87; 128.22; 88.36; 133.28 (CH); 133.95 (CH); 126.88 (CH); 126.70 (CH); 65.13 (CH_3); 62.68 (CH_3); 27.92 (CH_3). Mass spectrum, m/z (I_{rel} , %): 428 $[\text{M}]^+$ (16), 372 (100), 340 (64), 328 (85), 298 (62), 281 (42). Found, %: C 58.68; H 4.64; N 6.45. $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_8$. Calculated, %: C 58.88; H 4.71; N 6.54.

2-Amino-1,4-dimethoxy-3-nitroanthraquinone (9) was obtained analogously to compound **7** from carbamate **8**. Yield 79%; mp 238-240°C (benzene). UV spectrum (EtOH), $\lambda_{\max}$ nm (log ϵ): 229 (4.4), 247 (4.4), 285 (4.3), 369 (3.7), 423 (3.7). ^1H NMR spectrum, δ , ppm: 8.21 (2H, m, H-5,8); 7.77 (2H, m, H-6,7); 7.71 (2H, br. s, NH_2); 4.09 (3H, s, OCH_3); 3.99 (3H, s, OCH_3). Mass spectrum, m/z (I_{rel} , %): 328 $[\text{M}]^+$ (100), 298 (42), 281 (22), 252 (26). Found, %: C 58.41; H 3.78; N 8.37. $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_6$. Calculated, %: C 58.54; H 3.68; N 8.53.

2,3-Diamino-1,4-dimethoxyanthraquinone (10). A solution of 2-amino-3-nitroanthraquinone **9** (1.5 g, 4.6 mmol) in a mixture of glacial acetic acid (40 ml) and ethanol (40 ml) was heated to 70°C and powdered iron (3.0 g, 53.5 mmol) was added with intense stirring. After 10 min the solution was filtered, evaporated in vacuum to a volume of 5 ml, poured into water, extracted with AcOEt, the extract was washed with Na_2CO_3 solution, water, dried over Na_2SO_4 , and evaporated. The residue was purified by chromatography (silicagel, benzene–AcOEt, 10:1 $\rightarrow$ 1:1) to give brown crystals of diamine **10** (1.1 g, 81%); mp 252-254°C (benzene). UV spectrum (EtOH), $\lambda_{\max}$ nm (log ϵ): 222 (4.2), 240 (4.4), 316 (4.5), 411 (3.6), 450 (3.5), (539). ^1H NMR spectrum, δ , ppm: 8.18 (2H, m, H-5,8); 7.69 (2H, m, H-6,7); 4.18 (4H, br. s, 2 NH_2); 3.94 (6H, s, 2 OCH_3). Mass spectrum, m/z (I_{rel} , %): 298 $[\text{M}]^+$ (100), 283 (52), 255 (36). Found, %: C 64.21; H 4.70; N 9.25. $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$. Calculated, %: C 64.42; H 4.73; N 9.39.

4,11-Dimethoxyanthra[2,3-*d*]imidazole-5,10-dione (11). Diaminoanthraquinone **10** (150 mg, 0.5 mmol) was boiled for 3 h with formic acid (10.0 ml), poured into water (100 ml), and 20% NaOH solution was added with cooling and stirring until weakly basic. The precipitate was filtered off, washed with water,

and dried. It was crystallized from benzene to give yellow crystals of imidazoloanthraquinone **11** (133 mg, 86%); mp >250°C (subl.). UV spectrum (EtOH), $\lambda_{\max}$, nm (log ϵ): 244 (4.3), 270 (4.4), 389 (3.8). ^1H NMR spectrum, δ , ppm: 8.53 (1H, s, H-2); 8.09 (2H, m, H-6,9); 7.84 (2H, m, H-7,8); 4.09 (6H, s, 2 OCH₃). Mass spectrum, m/z (I_{rel} , %): 308 [M]⁺ (100), 293 (56), 279 (31), 279 (36), 265 (41). Found, %: C 66.32; H 3.78; N 9.01. C₁₇H₁₂N₂O₄. Calculated, %: C 66.23; H 3.92; N 9.09.

4,11-Dimethoxyanthra[2,3-*d*][1,2,3]triazole-5,10-dione (12). Diaminoanthraquinone **10** (150 mg, 0.5 mmol) was dissolved in acetic acid (10.0 ml), NaNO₂ (50 mg, 0.7 mmol) in water (0.5 ml) was added, and the mixture was stirred for 1 h. The mixture was poured into water and 20% NaOH solution was added with stirring and cooling until neutral (universal indicator), the precipitate was filtered off, washed with water, and dried to give triazoloanthraquinone **12** as a yellow powder (150 mg, 97%). UV spectrum (EtOH), $\lambda_{\max}$ nm (log ϵ): (215), 251 (4.4), 261 (4.4), 290 (3.7), 398 (3.8). ^1H NMR spectrum, δ , ppm: 8.10 (2H, m, H-6,9); 7.86 (2H, m, H-7,8); 4.31 (6H, s, 2 OCH₃). Mass spectrum, m/z (I_{rel} , %): 309 [M]⁺ (100), 295 (10), 280 (12), 266 (58), 251 (20). Found, %: C 62.26; H 3.36; N 13.32. C₁₆H₁₁N₃O₄. Calculated, %: C 62.14; H 3.58; N 13.59.

5,12-Dimethoxynaphtho[2,3-*g*]quinoxaline-6,11-dione (13). Diaminoanthraquinone **10** (150 mg, 0.5 mmol) and 40% aqueous glyoxal (0.5 ml) in THF (30 ml) were boiled for 2 h, the solvent was evaporated and the residue was crystallized from toluene to give yellow crystals of naphthoquinoxaline **13** (145 mg, 90%); mp >250°C (dec.). UV spectrum (EtOH), $\lambda_{\max}$ nm (log ϵ): (216), 255 (4.3), 295 (4.4), 370 (3.5). ^1H NMR spectrum, δ , ppm: 9.19 (2H, s, H-2,3); 8.16 (2H, m, H-7,10); 7.92 (2H, m, H-8,9); 4.16 (6H, s, 2 OCH₃). Mass spectrum m/z (I_{rel} , %): 320 [M]⁺ (100), 305 (8), 291 (21). Found, %: C 67.42; H 3.88; N 8.81. C₁₈H₁₂N₂O₄. Calculated, %: C 67.50; H 3.78; N 8.75.

5,12-Dimethoxy-2,3-dimethylnaphtho[2,3-*g*]quinoxaline-6,11-dione 14 was obtained analogously to quinoxaline **13** from diamine **10** and butandione. Yield 84%; mp 234-236°C (benzene). UV spectrum (EtOH), $\lambda_{\max}$ nm (log ϵ): 225 (4.2), 254 (4.3), 301 (4.4), 382 (3.5). ^1H NMR spectrum, δ , ppm: 8.25 (2H, m, H-7,10); 7.77 (2H, m, H-8,9); 4.29 (6H, s, 2 OCH₃); 2.85 (6H, s, 2 CH₃). ^{13}C NMR spectrum, δ , ppm: 182.63, 156.09, 154.21, 140.09, 134.87, 124.11: 133.61 (CH), 126.70 (CH), 63.77 (CH₃), 23.55 (CH₃). Mass spectrum, m/z (I_{rel} , %): 348 [M]⁺ (100), 333 (16), 319 (26), 301 (16). Found, %: C 68.76; H 4.60; N 8.15. C₂₀H₁₆N₂O₄. Calculated, %: C 68.96; H 4.63; N 8.04.

REFERENCES

1. A. E. Shchekotikhin, Yu. N. Luzikov, V. N. Buyanov, and M. N. Preobrazhenskaya, *Khim. Geterotsikl. Soedinen.*, 1421 (2006). [*Chem. Heterocycl. Comp.*, **42**, 1236 (2006)].
2. A. E. Shchekotikhin, I. G. Makarov, V. N. Buyanov, and M. N. Preobrazhenskaya, *Khim. Geterotsikl. Soedinen.*, 1081 (2005). [*Chem. Heterocycl. Comp.*, **41**, 914 (2005)].
3. A. E. Shchekotikhin, Yu. N. Lusikov, V. N. Buyanov, and M. N. Preobrazhenskaya, *Khim. Geterotsikl. Soedinen.*, 854 (2006). [*Chem. Heterocycl. Comp.*, **42**, 746 (2006)].
4. C. R. Harrison, P. Hodge, and N. Khan, *J. Chem. Soc., Perkin Trans. 1*, 1592 (1980).
5. T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 2nd Ed. Wiley & Sons, (1991), p. 403.
6. D. L. Flynn, R. E. Zelle, and P. Grieco, *J. Org. Chem.*, **48**, 2424 (1983).
7. D. J. Kempf, *Tetrahedron Lett.*, **30**, 2029 (1989).
8. A. E. Shchekotikhin, D. A. Silaev, E. P. Baberkina, I. G. Makarov, V. N. Buyanov, and N. N. Suvorov, *Khim. Geterotsikl. Soedinen.*, 623 (2002). [*Chem. Heterocycl. Comp.*, **38**, 543 (2002)].
9. V. Ya. Fain, *Electronic Absorption Spectra and Structure of Anthraquinones. Vol. 2. Disubstituted 9,10-Anthraquinones* [in Russian]. Sputnik+. (2003), p.104.