*Chemistry of Heterocyclic Compounds, Vol. 49, No. 7, October, 2013 (Russian Original Vol. 49, No. 7, July, 2013)*

# 6(7)-ACYLPERIMIDINES NITRATION AND METHODS OF *peri*-ANNELATION ON THIS BASE

**A. V. Aksenov[1]*, N. A. Aksenov[1], A. S. Lyakhovnenko[1], A. N. Smirnov[1], I. I. Levina[2], and I. V. Aksenova[1]**

*A method has been developed for the nitration of 6(7)-acylperimidines using sodium nitrite in formic acid. The reaction gives a mixture of 4(9)-, 9(4)-, and 7(6)-nitro-6(7)-acylperimidines from which the latter can be separated by extraction with chloroform. Reduction of the 6(7)-acyl-7(6)-nitro-perimidines yields 1H-1,5,7-triazacyclopenta[cd]phenalenes. Subsequent Schmidt reaction and reduction give 1,3,6,8-tetraazapyrenes.*

**Keywords:** formic acid, perimidines, polyphosphoric acid, sodium azide, sodium nitrite, 1,3,6,8-tetra-azapyrenes, 1*H*-1,5,7-triazacyclopenta[*cd*]phenalenes, zinc, nitration, Schmidt reaction.

*peri*-Annelated polynuclear aromatic and heteroaromatic compounds have a series of useful properties. Their derivatives include many organic luminophores, dyes [1-4], and effective medications [5-10], which behave, in first place, as luminescent intercalators [11-14]. So called molecular machines have been built based on such compounds [15, 16].

Despite the diversity of possible structures for azapyrenes and other *peri*-annelated heterocycles, only a few have been synthesized at this time and these do not generally contain functional groups [17, 18]. This is firstly connected to the absence of convenient methods for the *peri*-annelation of heterocyclic nuclei to phenalenes and azaphenalenes, that is partly explained by the lack of methods for the introduction of a nitrogen atom into azophenalene molecules. All this fully applies to perimidine derivatives. Despite a recently developed series of methods for the introduction of an amino group into the *peri* position of perimidine [19-23] they all have significant drawbacks, *viz*. the difficulty associated with the work up of large amounts of material when using polyphosphoric acid (PPA) and the possible formation of hydrazoic acid.

The nitration of arenes is the most widely used method for the introduction of a nitrogen atom into the target molecule [19]. This is due to the simplicity of carrying out the reaction and the ease of the subsequent reduction of the nitro to an amino group. It is important that the reduction can be combined with other reactions, e.g., the acylation of the amines formed.

*To whom correspondence should be addressed, e-mail: alexaks05@rambler.ru.

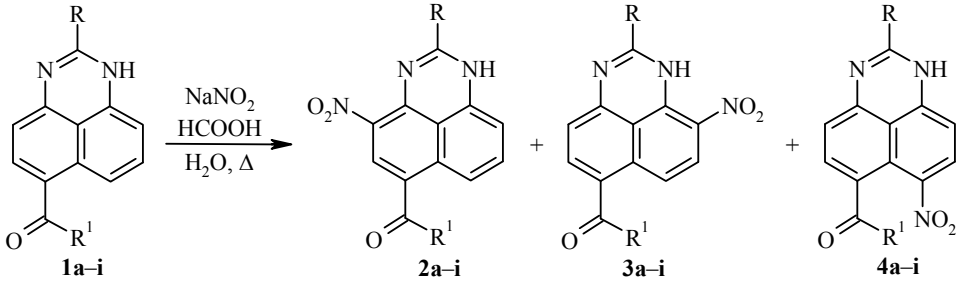
[1]North Caucasus Federal University, 1 Pushkin St., Stavropol 355009, Russia.
[2]N. M. Emanuel Institute of Biochemical Physics, 4 Kosygin St., Moscow 119991, Russia; e-mail: iilevina@rambler.ru.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1052-1059, July, 2013. Original article submitted July 1, 2012.

We have previously reported a method for the nitration of perimidines using nitric acid in acetic acid [24]. The main drawback of this method is the low yield of the nitro derivative and the poor selectivity. Thus, the main reaction products are 4(9)-nitroperimidines. The more efficient system for the preparation of nitro derivatives turned out to be sodium nitrite in acetic acid [25].

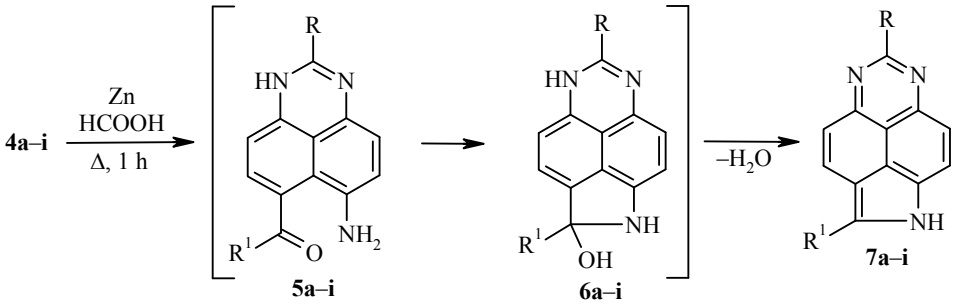
While a series of nitroperimidines was known at the beginning of our studies the nitro derivatives of the perimidine series aldehydes and ketones **2-4** have not been reported. We decided to apply the method of perimidine nitration to the nitration of the carbonyl compounds **1a-i**. It was found that nitration of these compounds with sodium nitrite in formic acid led to a mixture of the nitro derivatives **2a-i**, **3a-i**, and **4a-i** in a ratio close, in all cases, to 1:3:6 (as judged by $^1$H NMR spectroscopy). The main products are the 6(7)-nitro derivatives **4a-i** in 46-62% yields.




**a** R = R$^1$ = H; **b** R = Me, R$^1$ = H; **c** R = Ph, R$^1$ = H; **d** R = H, R$^1$ = Me; **e** R = R$^1$ = Me; **f** R = Ph, R$^1$ = Me; **g** R = H, R$^1$ = Ph; **h** R = Me, R$^1$ = Ph; **i** R = R$^1$ = Ph

Compounds **4a-i** can be readily purified from the *o*-isomers **2a-i** and **3a-i** by extraction with chloroform. The latter compounds are extracted by the chloroform but the 6(7)-nitro derivatives **4a-i** remain in the aqueous formic acid. Compounds **3d**,**f-h** can be separated from compounds **2d**,**f-h** by treating the residue with acetone after distillation of the chloroform. The residue contains almost pure nitro derivatives **3d**,**f-h**. In some examples, compounds **2** can be isolated by flash chromatography in pure from the remaining mixture of nitro derivatives but, in most cases, they could not be separated due to the close chromatographic mobilities of compounds **3a-i** and **2a-i** as well as the low yield of the latter. Using this method the nitro derivatives **2e**,**g**,**i** were obtained, but compounds **2a-d**,**f**,**h** and **3a-c** could not be isolated in a pure state.

We have further studied the reduction of the nitro derivatives **4a-i**. It was found that the reaction of these compounds with zinc dust in acetic or formic acids gave a quantitative yield of the 1*H*-1,5,7-triazacyclopenta[*cd*]phenalenes **7a-i**.



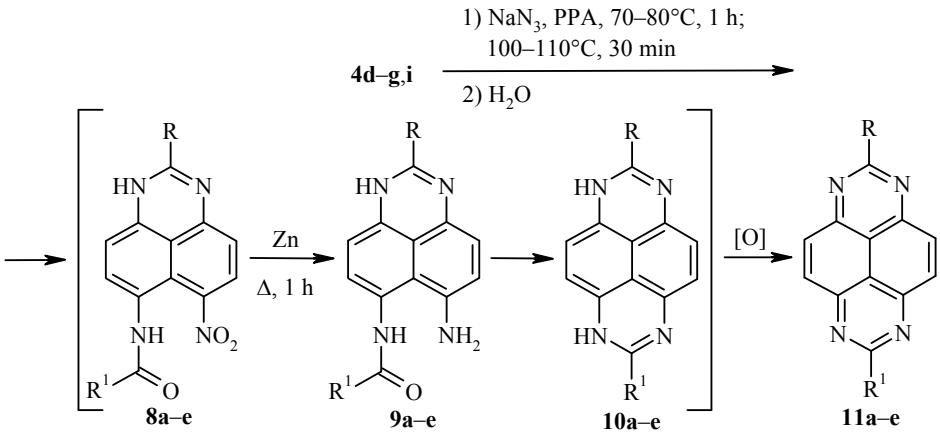

**a** R = R$^1$ = H; **b** R = Me, R$^1$ = H; **c** R = Ph, R$^1$ = H; **d** R = H, R$^1$ = Me; **e** R = R$^1$ = Me; **f** R = Ph, R$^1$ = Me; **g** R = H, R$^1$ = Ph; **h** R = Me, R$^1$ = Ph; **i** R = R$^1$ = Ph

It seems likely that the amines **5a-i** formed in the course of reduction can undergo nucleophilic attack by the amino group at the carbonyl function to give the intermediate compounds **6a-i** which can lose a molecule of water to give the indoles **7a-i**.

This reaction can be carried out as a one-pot procedure. In this case, the carbonyl compounds **1a-i** are first nitrated using sodium nitrite in formic acid, and the zinc dust is then added to the reaction mixture and stirred for 1 h.

The indoles **7a-i** were quite readily separated from by-products but it proved no less convenient to separate the mixture after the nitration. Compounds **2a-i** and **3a-i** were separated by extraction from the aqueous formic acid solution. The nitro compounds **4a-i** remaining in the solution were not separated but could be converted to the corresponding indoles **7a-i**. The yields calculated on the starting ketones **1a-i** are not significantly changed.

Use of the Schmidt reaction and subsequent reduction of the nitro group allows the nitro ketones **4d-g**,**i** to be converted to the 1,3,6,8-tetraazapyrenes **11a-e**. The reagent used was the sodium azide in PPA developed previously in our laboratory. The reaction mixture from treatment of the Schmidt reaction products 6(7)-(acylamino)-7(6)-nitroperimidines **8a-f** with water can be reduced by zinc dust in phosphoric acid to give the intermediates **9a-e** which spontaneously cyclize to the dihydrotetraazapyrene derivatives **10a-e**. Oxidation of the latter, likely by atmospheric oxygen, forms the tetraazapyrenes **11a-e**.




**8–11 a** R = H, $R^1$ = Me; **b** R = H, $R^1$ = Ph; **c** R = $R^1$ = Me; **d** R = $R^1$ = Ph; **e** R = Ph, $R^1$ = Me

Thus, a synthetic method has been developed for the preparation of 6(7)-acylperimidine nitro derivatives, 1*H*-1,5,7-triazacyclopenta[*cd*]phenalenes, and 1,3,6,8-tetraazapyrenes based on 6(7)-acylperimidines.

## EXPERIMENTAL

IR spectra were recorded on a Hitachi 215 spectrometer for KBr pellets. $^1$H and $^{13}$C NMR spectra were recorded on a JNM-ECX400 spectrometer (400 and 100 MHz, respectively) using DMSO-$d_6$ with TMS as internal standard. Elemental analysis was performed on a KOVO CHN-1 analyzer. Melting points were determined on a Chimlaborpribor PTP-M apparatus. Monitoring of the reaction course and the purity of the products was carried out by TLC on Silufol UV-254 plates using EtOAc as eluent. Column chromatography was carried out on L 40/100 silica gel with EtOAc as eluent. In the experiments the PPA used was prepared by method [26] and had an 86% $P_2O_5$ content.

**Nitration of Acylperimidines 1a-i (General Method)**. $NaNO_2$ (0.104 g, 1.5 mmol) in water (0.2 ml) was added in one aliquot to a stirred solution of the corresponding formyl- or acetyl(benzoyl)perimidines **1a-i** (1 mmol) in HCOOH (10 ml). The product was left for 5 min at room temperature, after which it was heated to reflux and immediately cooled. The solution was diluted with water (10 ml), forming a precipitate, and extracted with chloroform (5×30 ml). The aqueous formic acid layer with the precipitate was diluted with more water (10 ml), neutralized with sodium carbonate solution, and extracted with ethyl acetate (5×50 ml). The extract was evaporated to give the pure 6(7)-nitroperimidines **4a-i** as dark-red crystals. The chloroform extracts were combined and evaporated to give a mixture of the carbonyl compounds **2a-i** and **3a-i** with a small amount of the 6(7)-isomers of compounds **4a-i**. The latter can be separated by flash chromatography. Virtually pure compounds **3d**,**f-h** can be isolated by treating the residue with acetone. The compounds **3d**,**f-h** remain as the residue and can be filtered off and recrystallized. Compounds **3d-i** and **2e**,**g**,**i** are brick-red crystals. Compounds **2e**,**g**,**i** and **3e**,**g**,**i** could be partially separated by flash chromatography, but compounds **2a-d**,**f**,**h** and **3a-c** could not be prepared in a pure state.

**7(6)-Acetyl-2-methyl-9(4)-nitroperimidine (2e)**. Yield 0.008 g (3%). Mp 165-170°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1636 (C=O), 3845 (NH). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 2.53 (3H, s, 2-$CH_3$); 2.64 (3H, s, $COCH_3$); 7.36 (1H, d, *J* = 8.0, H-4(9)); 7.85 (1H, dd, *J* = 8.4, *J* = 8.0, H-5(8)); 8.54 (1H, s, H-8(5)); 8.64 (1H, d, *J* = 8.4, H-6(7)); 12.61 (1H, br. s, NH). Found, %: C 62.54; H 4.07; N 15.54. $C_{14}H_{11}N_3O_3$. Calculated, %: C 62.45; H 4.12; N 15.61.

**7(6)-Benzoyl-9(4)-nitroperimidine (2g)**. Yield 0.023 g (7%). Mp 196-198°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1643 (C=O), 3849 (NH). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 7.46 (1H, d, *J* = 8.0, H-4(9)); 7.61-7.63 (3H, m, H-3,4,5 Ph); 7.80-7.84 (3H, m, H-5(8), H-2,6 Ph); 8.07 (1H, s, H-2); 8.54 (1H, s, H-8(5)); 8.76 (1H, d, *J* = 8.4, H-6(7)); 12.60 (1H, br. s, NH). Found, %: C 68.28; H 3.43; N 13.21. $C_{18}H_{11}N_3O_3$. Calculated, %: C 68.14; H 3.49; N 13.24.

**7(6)-Benzoyl-9(4)-nitro-2-phenylperimidine (2i)**. Yield 0.006 g (1.5%). Mp 221-223°C (EtOAc – petroleum ether). IR spectrum, ν, $cm^{-1}$: 1643 (C=O), 3850 (NH). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 7.43 (1H, d, *J* = 8.0, H-4(9)); 7.60-7.64 (6H, m, H-3,4,5 Ph, H-3,4,5 COPh); 7.82 (2H, d, *J* = 7.5, H-2,6 COPh); 7.84 (1H, dd, *J* = 8.4, *J* = 8.0, H-5(8)); 8.12 (2H, d, *J* = 8.0, H-2,6 Ph); 8.54 (1H, s, H-8(5)); 8.76 (1H, d, *J* = 8.4, H-6(7)); 12.60 (1H, br. s, NH). Found, %: C 73.47; H 3.74; N 10.62. $C_{24}H_{15}N_3O_3$. Calculated, %: C 73.27; H 3.84; N 10.68.

**6(7)-Acetyl-9(4)-nitroperimidine (3d)**. Yield 0.053 g (21%). Mp 234-236°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1645 (C=O), 3848 (NH). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 2.63 (3H, s, $COCH_3$); 7.21 (1H, d, *J* = 8.5, H-4(9)); 8.06 (1H, d, *J* = 9.9, H-7(6)); 8.12 (1H, s, H-2); 8.25 (1H, d, *J* = 9.9, H-8(5)); 8.34 (1H, d, *J* = 8.5, H-5(8)); 12.49 (1H, br. s, NH). Found, %: C 61.36; H 3.49; N 16.41. $C_{13}H_9N_3O_3$. Calculated, %: C 61.18; H 3.55; N 16.46.

**6(7)-Acetyl-2-methyl-9(4)-nitroperimidine (3e)**. Yield 0.012 g (4.5%). Mp 202-203°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1644 (C=O), 3843 (NH). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 2.46 (3H, s, 2-$CH_3$); 2.63 (3H, s, $COCH_3$); 7.21 (1H, d, *J* = 8.5, H-4(9)); 8.06 (1H, d, *J* = 9.9, H-7(6)); 8.22 (1H, d, *J* = 9.9, H-8(5)); 8.31 (1H, d, *J* = 8.5, H-5(8)); 12.46 (1H, br. s, NH). Found, %: C 62.58; H 4.05; N 15.53. $C_{14}H_{11}N_3O_3$. Calculated, %: C 62.45; H 4.12; N 15.61.

**6(7)-Acetyl-9(4)-nitro-2-phenylperimidine (3f)**. Yield 0.041 g (12%). Mp 212-214°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1636 (C=O), 3842 (NH). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 2.58 (3H, s, $COCH_3$); 7.21 (1H, d, *J* = 8.5, H-4(9)); 7.59-7.63 (3H, m, H-3,4,5 Ph); 8.09-8.12 (3H, m, H-7(6), H-2,6 Ph); 8.22 (1H, d, *J* = 9.9, H-8(5)); 8.31 (1H, d, *J* = 8.5, H-5(8)); 12.46 (1H, br. s, NH). Found, %: C 69.06; H 3.87; N 12.55. $C_{19}H_{13}N_3O_3$. Calculated, %: C 68.88; H 3.95; N 12.68.

**6(7)-Benzoyl-9(4)-nitroperimidine (3g)**. Yield 0.067 g (21%). Mp 257-258°C (EtOAc). IR spectrum, ν, $cm^{-1}$: 1638 (C=O), 3847 (NH). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 7.25 (1H, d, *J* = 8.5, H-4(9)); 7.58 (2H, dd, *J* = 7.5, *J* = 7.1, H-3,5 Ph); 7.69 (1H, t, *J* = 7.1, H-4 Ph); 7.81 (2H, d, *J* = 7.5, H-2,6 Ph); 8.06 (1H, s, H-2);

8.09 (1H, d, *J* = 9.8, H-7(6)); 8.17 (1H, d, *J* = 9.8, H-8(5)); 8.31 (1H, d, *J* = 8.5, H-5(8)); 12.42 (1H, br. s, NH). Found, %: C 68.26; H 3.42; N 13.22. $C_{18}H_{11}N_3O_3$. Calculated, %: C 68.14; H 3.49; N 13.24.

**6(7)-Benzoyl-2-methyl-9(4)-nitroperimidine (3h)**. Yield 0.028 g (8.5%). Mp 276-278°C (EtOAc). IR spectrum, ν, $cm^{-1}$: 1642 (C=O), 3767 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.54 (3H, s, $CH_3$); 7.32 (1H, d, *J* = 8.5, H-4(9)); 7.57 (2H, dd, *J* = 7.4, *J* = 7.3, H-3,5 Ph); 7.70 (1H, t, *J* = 7.4, H-4 Ph); 7.79-7.84 (3H, m, H-7(6), H-2,6 Ph); 8.02-8.03 (2H, m, H-5,8); 12.04 (1H, br. s, NH). Found, %: C 69.03; H 3.88; N 12.59. $C_{19}H_{13}N_3O_3$. Calculated, %: C 68.88; H 3.95; N 12.68.

**6(7)-Benzoyl-9(4)-nitro-2-phenylperimidine (3i)**. Yield 0.018 g (5%). Mp 184-186°C (EtOAc – petroleum ether). IR spectrum, ν, $cm^{-1}$: 1638 (C=O), 3847 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 7.23 (1H, d, *J* = 8.5, H-4(9)); 7.61-7.63 (6H, m, H-3,4,5 Ph, H-3,4,5 COPh); 7.82 (2H, d, *J* = 7.5, H-2,6 COPh); 8.11-8.12 (3H, m, H-7(6), H-2,6 Ph); 8.19 (1H, d, *J* = 9.8, H-8(5)); 8.34 (1H, d, *J* = 8.5, H-5(8)); 12.42 (1H, br. s, NH). Found, %: C 73.43; H 3.76; N 10.64. $C_{24}H_{15}N_3O_3$. Calculated, %: C 73.27; H 3.84; N 10.68.

**7(6)-Formyl-6(7)-nitroperimidine (4a)**. Yield 0.118 g (49%). Mp 257-259°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1652 (C=O), 3167 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 6.95 (1H, d, *J* = 8.5, H-4(9)); 7.01 (1H, d, *J* = 8.1, H-9(4)); 8.08 (1H, s, H-2); 8.14 (1H, d, *J* = 8.1, H-8(5)); 8.17 (1H, d, *J* = 8.5, H-5(8)); 9.76 (1H, s, CHO); 12.28 (1H, br. s, NH). Found, %: C 59.93; H 2.88; N 17.49. $C_{12}H_7N_3O_3$. Calculated, %: C 59.76; H 2.93; N 17.42.

**7(6)-Formyl-2-methyl-6(7)-nitroperimidine (4b)**. Yield 0.130 g (51%). Mp 241-243°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1651 (C=O), 3211 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.29 (3H, s, $CH_3$); 6.74 (1H, d, *J* = 8.5, H-4(9)); 6.88 (1H, d, *J* = 8.1, H-9(4)); 8.01 (1H, d, *J* = 8.1, H-8(5)); 8.08 (1H, d, *J* = 8.5, H-5(8)); 9.74 (1H, s, CHO); 12.14 (1H, br. s, NH). Found, %: C 61.31; H 3.49; N 16.41. $C_{13}H_9N_3O_3$. Calculated, %: C 61.18; H 3.55; N 16.46.

**7(6)-Formyl-6(7)-nitro-2-phenylperimidine (4c)**. Yield 0.146 g (46%). Mp 255-257°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1658 (C=O), 3170 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 6.83 (1H, d, *J* = 8.5, H-4(9)); 7.03 (1H, d, *J* = 8.1, H-9(4)); 7.60-7.62 (3H, m, H-3,4,5 Ph); 8.08 (1H, d, *J* = 8.1, H-8(5)); 8.13-7.15 (3H, m, H-5(8), H-2,6 Ph); 9.77 (1H, s, CHO); 12.27 (1H, br. s, NH). Found, %: C 68.31; H 3.45; N 13.28. $C_{18}H_{11}N_3O_3$. Calculated, %: C 68.14; H 3.49; N 13.24.

**7(6)-Acetyl-6(7)-nitroperimidine (4d)**. Yield 0.150 g (59%). Mp 296-298°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1638 (C=O), 3429 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.51 (3H, s, $COCH_3$); 6.77 (1H, d, *J* = 8.5, H-4(9)); 6.92 (1H, d, *J* = 8.1, H-9(4)); 7.94 (1H, s, H-2); 8.02 (1H, d, *J* = 8.1, H-8(5)); 8.08 (1H, d, *J* = 8.5, H-5(8)); 12.22 (1H, br. s, NH). $^{13}$C NMR spectrum, δ, ppm: 27.7; 108.0; 111.1; 122.5; 123.4; 126.7 (2C); 129.9; 132.9 (2C); 138.1; 147.1; 198.7. Found, %: C 61.33; H 3.51; N 16.47. $C_{13}H_9N_3O_3$. Calculated, %: C 61.18; H 3.55; N 16.46.

**7(6)-Acetyl-2-methyl-6(7)-nitroperimidine (4e)**. Yield 0.167 g (62%). Mp 279-281°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1636 (C=O), 3428 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.28 (3H, s, 2-$CH_3$); 2.51 (3H, s, $COCH_3$); 6.74 (1H, d, *J* = 8.5, H-4(9)); 6.88 (1H, d, *J* = 8.1, H-9(4)); 8.01 (1H, d, *J* = 8.1, H-8(5)); 8.08 (1H, d, *J* = 8.5, H-5(8)); 12.11 (1H, br. s, NH). $^{13}$C NMR spectrum, δ, ppm: 22.3; 27.7; 108.0; 111.2; 122.5; 123.3; 126.8 (2C); 130.0; 132.9 (2C); 138.1; 147.1; 198.8. Found, %: C 62.63; H 4.04; N 15.55. $C_{14}H_{11}N_3O_3$. Calculated, %: C 62.45; H 4.12; N 15.61.

**7(6)-Acetyl-6(7)-nitro-2-phenylperimidine (4f)**. Yield 0.182 g (55%). Mp 261-262°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1633 (C=O), 3431 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.52 (3H, s, $COCH_3$); 6.97 (1H, d, *J* = 8.4, H-4(9)); 7.11 (1H, d, *J* = 8.1, H-9(4)); 7.61 (2H, dd, *J* = 7.6, *J* = 7.1, H-3,5 Ph); 7.66 (1H, t, *J* = 7.1, H-4 Ph); 8.07 (1H, d, *J* = 8.1, H-8(5)); 8.12-8.13 (3H, m, H-5(8), H-2,6 Ph); 12.09 (1H, br. s, NH). Found, %: C 69.04; H 3.89; N 12.57. $C_{19}H_{13}N_3O_3$. Calculated, %: C 68.88; H 3.95; N 12.68.

**7(6)-Benzoyl-6(7)-nitroperimidine (4g)**. Yield 0.196 g (62%). Mp 206-207°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1638 (C=O), 3427 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 6.79 (1H, d, *J* = 8.3, H-4(9)); 6.92 (1H, d, *J* = 7.7, H-9(4)); 7.56-7.58 (3H, m, H-8(5), H-3,5 Ph); 7.67 (1H, t, *J* = 7.0, H-4 Ph); 7.84 (2H, d,

*J* = 7.2, H-2,6 Ph); 7.99 (1H, s, H-2); 8.10 (1H, d, *J* = 8.3, H-5(8)); 12.10 (1H, br. s, NH). Found, %: C 68.22; H 3.43; N 13.21. $C_{18}H_{11}N_3O_3$. Calculated, %: C 68.14; H 3.49; N 13.24.

**7(6)-Benzoyl-2-methyl-6(7)-nitroperimidine (4h)**. Yield 0.162 g (49%). Mp 171-173°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1634 (C=O), 3428 (NH). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 2.31 (3H, s, $CH_3$); 6.77 (1H, d, *J* = 8.5, H-4(9)); 6.88 (1H, d, *J* = 8.0, H-9(4)); 7.55 (2H, dd, *J* = 7.6, *J* = 7.1, H-3,5 Ph); 7.56 (1H, d, *J* = 8.0, H-8(5)); 7.67 (1H, t, *J* = 7.5, H-4 Ph); 7.83 (2H, d, *J* = 7.0, H-2,6 Ph); 8.10 (1H, d, *J* = 8.5, H-5(8)); 12.12 (1H, br. s, NH). Found, %: C 69.01; H 3.90; N 12.56. $C_{19}H_{13}N_3O_3$. Calculated, %: C 68.88; H 3.95; N 12.68.

**7(6)-Benzoyl-6(7)-nitro-2-phenylperimidine (4i)**. Yield 0.189 g (48%). Mp 174-176°C (EtOH–$H_2O$). IR spectrum, ν, $cm^{-1}$: 1632 (C=O), 3429 (NH). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 6.98 (1H, d, *J* = 8.5, H-4(9)); 7.11 (1H, d, *J* = 8.1, H-9(4)); 7.54-7.71 (7H, m, H-8(5), H-3,4,5 Ph, H-3,4,5 COPh); 7.85 (2H, dd, *J* = 7.1, *J* = 1.3, H-2,6 COPh); 8.14 (1H, d, *J* = 8.5, H-5(8)); 8.17 (2H, dd, *J* = 7.0, *J* = 1.5, H-2,6 Ph); 12.18 (1H, br. s, NH). Found, %: C 73.44; H 3.77; N 10.61. $C_{24}H_{15}N_3O_3$. Calculated, %: C 73.27; H 3.84; N 10.68.

**Preparation of 1*H*-1,5,7-Triazacyclopenta[*cd*]phenalenes 7a-i (General Method)**. A. $NaNO_2$ (0.104 g, 1.5 mmol) in water (0.2 ml) was added in one aliquot to a stirred solution of the corresponding acylperimidine **1a-i** (1 mmol) in HCOOH (10 ml) and left for 5 min at room temperature. The solution was diluted with water (10 ml) with formation of a precipitate and extracted with $CHCl_3$ (5×30 ml). Zinc dust (0.320 g, 5.0 mmol) was added to the aqueous formic acid layer, stirred for 1 h at room temperature, and then refluxed for a further 1 h. The product was diluted with water (10 ml), neutralized with ammonia solution, and extracted with toluene (10×50 ml). The toluene extracts were combined, the solvent was evaporated, and the residue was purified by recrystallization.

B. $NaNO_2$ (0.104 g, 1.5 mmol) in water (0.2 ml) was added in one aliquot to a stirred solution of the corresponding acylperimidine **1a-i** (1 mmol) in HCOOH (10 ml) and left for 5 min at room temperature. Zinc dust (0.320 g, 5.0 mmol) was added, and the reaction mixture was stirred for 1 h at room temperature and then refluxed for a further 1 h. The product was diluted with water (10 ml), neutralized with ammonia solution, and extracted with toluene (10×50 ml). The toluene extracts were combined, the solvent was evaporated, and the residue was purified by recrystallization.

**1*H*-1,5,7-Triazacyclopenta[*cd*]phenalene (7a)**. Yield 0.091 g (47%, method A), 0.089 g (46%, method B). Mp 207-209°C (PhH) (mp 207-209°C [22, 27]). $^1H$ NMR spectrum identical to that given in the work [22].

**6-Methyl-1*H*-1,5,7-triazacyclopenta[*cd*]phenalene (7b)**. Yield 0.101 g (49%, method A), 0.097 g (47%, method B). Mp 237-238°C (PhH) (mp 227-238°C [27]). $^1H$ NMR spectrum identical to that given in the work [27].

**6-Phenyl-1*H*-1,5,7-triazacyclopenta[*cd*]phenalene (7c)**. Yield 0.121 g (45%, method A), 0.121 g (45%, method B). Mp 201-203°C (PhH) (mp 201-203°C [22, 27]). $^1H$ NMR spectrum identical to that given in the work [22].

**2-Methyl-1*H*-1,5,7-triazacyclopenta[*cd*]phenalene (7d)**. Yield 0.116 g (56%, method A), 0.110 g (53%, method B). Mp 259-260°C (PhH) (mp 259-260°C [22]). $^1H$ NMR spectrum identical to that given in the work [22].

**2,6-Dimethyl-1*H*-1,5,7-triazacyclopenta[*cd*]phenalene (7e)**. Yield 0.157 g (71%, method A), 0.150 g (68%, method B). Mp 271-272°C (PhH) (mp 271-272°C [22]). $^1H$ NMR spectrum identical to that given in the work [22].

**2-Methyl-6-phenyl-1*H*-1,5,7-triazacyclopenta[*cd*]phenalene (7f)**. Yield 0.150 g (53%, method A), 0.150 g (53%, method B). Mp 245-246°C (PhH–hexane) (mp 245-246°C [22, 27]). $^1H$ NMR spectrum identical to that given in the work [22].

**2-Phenyl-1*H*-1,5,7-triazacyclopenta[*cd*]phenalene (7g)**. Yield 0.164 g (61%, method A), 0.160 g (60%, method B). Mp 263-265°C (PhH) (mp 263-265°C [22, 27]). $^1H$ NMR spectrum identical to that given in the work [22].

**6-Methyl-2-phenyl-1*H*-1,5,7-triazacyclopenta[*cd*]phenalene (7h)**. Yield 0.133 g (47%, method A), 0.127 g (45%, method B). Mp 291-292°C (PhH) (mp 291-292°C [22, 27]). $^1$H NMR spectrum identical to that given in the work [22].

**2,6-Diphenyl-1*H*-1,5,7-triazacyclopenta[*cd*]phenalene (7i)**. Yield 0.159 g (46%, method A), 0.145 g (42%, method B). Mp 169-171°C (PhH–hexane) (mp 169-171°C [22, 27]). $^1$H NMR spectrum identical to that given in the work [22].

**Preparation of 1,3,6,8-Tetraazapyrenes 11a-e (General Method)**. A mixture of the nitroacylperimidine **4d-g**,**i** (1 mmol) and $NaN_3$ (0.07 g, 1.07 mmol) in 86% PPA (2-3 g) was heated at 70-80ºC with vigorous stirring for 1 h, and the temperature was then increased to 100-110ºC. The reaction mixture was heated at this temperature for 0.5 h. The reaction mixture was diluted with water (50 ml), and zinc dust (0.45 g, 7.00 mmol) was added. The product was refluxed for 1 h, cooled, and neutralized with ammonia solution. The product was then extracted with BuOH (3×50 ml), solvent was evaporated, and the compounds were purified by recrystallization.

**2-Methyl-1,3,6,8-tetraazapyrene (11a)**. Yield 0.191 g (87%). Mp >300°C (EtOH) (mp >300°C [28]). $^1$H NMR spectrum identical to that given in the work [28].

**2-Phenyl-1,3,6,8-tetraazapyrene (11b)**. Yield 0.237 g (84%). Mp >300°C (BuOH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 7.50-7.52 (3H, m, H-3,4,5 Ph); 8.41-8.42 (2H, m, *J* = 9.4, H-5,9); 8.51 (2H, d, *J* = 9.4, H-4,10); 8.88-8.89 (2H, m, H-2,6 Ph); 9.94 (1H, s, H-7). Found, %: C 76.73; H 3.54; N 19.73. $C_{18}H_{10}N_4$. Calculated, %: C 76.58; H 3.57; N 19.85.

**2,7-Dimethyl-1,3,6,8-tetraazapyrene (11c)**. Yield 0.213 g (91%). Mp >300°C (EtOH) (mp >300°C [28]). $^1$H NMR spectrum identical to that given in the work [28].

**2,7-Diphenyl-1,3,6,8-tetraazapyrene (11d)**. Yield 0.315 g (88%). Mp >300°C (EtOH) (mp >300°C [29]). $^1$H NMR spectrum identical to that given in the work [29].

**2-Methyl-7-phenyl-1,3,6,8-tetraazapyrene (11e)**. Yield 0.258 g (87%). Mp >300°C (EtOH) (mp >300°C [29]). $^1$H NMR spectrum identical to that given in the work [29].

This work was carried out with the financial support of the Russian Foundation for Basic Research (grant 12-03-31646mol_a)

## REFERENCES

1. S. C. Martens, U. Zschieschang, H. Wadepohl, H. Klauk, and L. H. Gade, *Chem.-Eur. J.*, **18**, 3498 (2012).
2. N. Leventis, I. A. Elder, D. R. Rolison, M. L. Anderson, and C. I. Merzbacher, *Chem. Mater.*, **11**, 2837 (1999).
3. H. E. Katz, J. Johnson, A. J. Lovinger, and W. Li, *J. Am. Chem. Soc.*, **122**, 7787 (2000).
4. S. Alp, Ş. Erten, C. Karapire, B. Köz, A. O. Doroshenko, and S. İçli, *J. Photochem. Photobiol.*, *A*, **135**, 103 (2000).
5. S. K. Abilev, I. K. Lyubimova, and G. I. Migachev, *Genetika*, **28**, 52 (1992).
6. A. D. Andricopolo, L. A. Muller, V. C. Filho, G.-N. R. J. Cani, and R. A. Yunes, *Farmaco*, **55**, 319 (2000).
7. A. E. S. Fairfull, D. A. Peak, W. F. Short, and T. I. Watkins, *J. Chem. Soc.*, 4700 (1952).
8. S. Roknic, L. Glavas-Obrovac, I. Karner, I. Piantanida, M. Zinic, and K. Pavelic, *Chemotherapy*, **46**, 143 (2000).
9. I. Piantanida, B. S. Palm, M. Zinic, and H.-J. Schneider, *J. Chem. Soc*., *Perkin Trans. 2*, 1808 (2001).
10. I. Steiner-Biocic, L. Glavas-Obrovac, I. Karner, I. Piantanida, M. Zinic, K. Pavelic, and J. Pavelic, *Anticancer Res.*, **16**, 3705 (1996).

11. H.-C. Becker and B. Norden, *J. Am. Chem. Soc.*, **119**, 5798 (1997).
12. A. M. Brun and A. Harriman, *J. Am. Chem. Soc.*, **113**, 8153 (1991).
13. A. M. Brun and A. Harriman, *J. Am. Chem. Soc.*, **114**, 3656 (1992).
14. H. Ikeda, K. Fuji, and K. Tanaka, *Bioorg. Med. Chem. Lett.*, **6**, 101 (1996).
15. V. Balzani, A. Credi, S. J. Langford, F. M. Raymo, J. F. Stoddart, and M. Venturi, *J. Am. Chem. Soc.*, **122**, 3542 (2000).
16. S. Geib, S. C. Martens, U. Zschieschang, F. Lombeck, H. Wadepohl, H. L. Klauk, and H. Gade, *J. Org. Chem.*, **77**, 6107 (2012).
17. A. V. Aksenov, A. S. Lyakhovnenko, N. A. Aksenov, and I. V. Aksenova, *Obzor. Zh. Po Khimii*, **2**, 242 (2012).
18. A. V. Aksenov and I. V. Aksenova, *Khim. Geterotsikl. Soedin.*, 167 (2009). [*Chem. Heterocycl. Compd.*, **45**, 130 (2009)].
19. A. V. Aksenov, N. A. Aksenov, O. N. Nadein, and Yu. I. Smushkevich, *Obzor. Zh. Po Khimii*, **1**, 350 (2011).
20. A. V. Aksenov, A. S. Lyakhovnenko, and N. Ts. Karaivanov, *Khim. Geterotsikl. Soedin.*, 1091 (2009). [*Chem. Heterocycl. Compd.*, **45**, 871 (2009)].
21. A. V. Aksenov, A. S. Lyakhovnenko, N. Ts. Karaivanov, and I. I. Levina, *Khim. Geterotsikl. Soedin.*, 591 (2010). [*Chem. Heterocycl. Compd.*, **46**, 468 (2010)].
22. A. V. Aksenov, A. S. Lyakhovnenko, A. V. Andrienko, and I. I. Levina, *Tetrahedron Lett.*, **51**, 2406 (2010).
23. A. V. Aksenov, A. S. Lyakhovnenko, and N. Ts. Karaivanov, *Khim. Geterotsikl. Soedin.*, 146 (2010). [*Chem. Heterocycl. Compd.*, **46**, 127 (2010)].
24. A. F. Pozharskii and V. N. Koroleva, *Khim. Geterotsikl. Soedin.*, 550 (1975). [*Chem. Heterocycl. Compd.*, **11**, 486 (1975)].
25. A. F. Pozharskii, V. N. Koroleva, I. F. Grekova, and I. S. Kashparov, *Khim. Geterotsikl. Soedin.*, 557 (1975). [*Chem. Heterocycl. Compd.*, **11**, 492 (1975)].
26. F. Uhlig, *Angew. Chem.*, **66**, 435 (1954).
27. A. V. Aksenov, A. S. Lyakhovnenko, and A. V. Andrienko, *Khim. Geterotsikl. Soedin.*, 1563 (2010). [*Chem. Heterocycl. Compd.*, **46**, 1266 (2010)].
28. A. V. Aksenov, A. S. Lyakhovnenko, A. N. Spitsyn, and I. V. Aksenova, *Khim. Geterotsikl. Soedin.*, 1429 (2011). [*Chem. Heterocycl. Compd.*, **47**, 1180 (2011)].
29. A. V. Aksenov, A. S. Lyakhovnenko, N. Ts. Karaivanov, and I. V. Aksenova, *Khim. Geterotsikl. Soedin.*, 1418 (2010). [*Chem. Heterocycl. Compd.*, **46**, 1146 (2010)].