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AMINO- AND HYDROXYMETHYLATION OF HYDRIDE ADDUCTS OF 2-HYDROXY-3,5-DINITROPYRIDINE

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A series of 1,5-dinitro-3,3-diazabicyclo[3.3.1]nonan-2-one derivatives has been synthesized by Mannich condensation of the hydride adduct of 2-hydroxy-3,5-dinitropyridine with formaldehyde and primary amines. The structure of the obtained compounds was proved by NMR spectroscopy.

Keywords: 3,7-diazabicyclo[3.3.1]nonanes, 2-hydroxy-3,5-dinitropyridine, Mannich reaction.

Considerable interest in the study of 3,7-diazabicyclo[3.3.1]nonane derivatives is caused by their high physiological activity over a wide spectrum of actions [1, 2]. Various methods of obtaining compounds of such type exist, for example by the interaction of 1,3-dinitropropanes [3], aliphatic ketones [4], piperidin-4-ones [4] with primary amines and formaldehyde under Mannich reaction conditions. Previously we carried out the synthesis of 3-azabicyclo[3.3.1]nonanes by the Mannich reaction involving anionic adducts of dinitroarenes [5, 6]. In a continuation of these investigations, it is proposed to use 2-hydroxy-3,5-dinitropyridine (**1**) as substrate for the synthesis of 3,7-diazabicyclic systems.

The synthesis of 7-substituted 1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-ones **3a-p** was effected in two stages. In the first stage, reduction of the C=C bonds of the aromatic ring occurred by the action of $NaBH_4$ on a solution of 2-hydroxy-3,5-dinitropyridine (**1**) with the formation of hydride adduct **2**. It is known from literature sources that 3-cyanopyridine and 3,5-dicyanopyridine form the corresponding 1,2- and 1,4-dihydro-pyridines under the action of such reducing agents as $NaBH_4$ [7]. The obtained adduct **2**, without isolation from solution, on cooling to 5-10°C reacts by Mannich condensation with formaldehyde and primary amine as an aqueous ethanolic solution. On acidifying the reaction mixture to pH 4, the solid desired products **3a-p** were precipitated (52-82% yield).

The structure of the obtained compounds **3a-p** was proved by IR and NMR spectroscopy. In the IR spectra of the compounds being analyzed, broad bands were observed for the stretching vibrations of the C=O bond (1690-1703 cm^{-1}). Intense bands at 1552-1559 and 1345-1351 cm^{-1} were assigned to the asymmetric and symmetric vibrations of the nitro groups.

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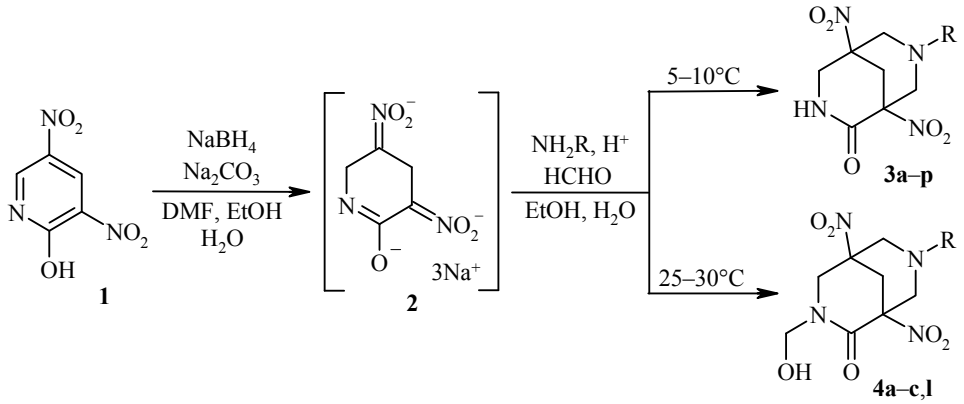

a R = Me, **b** R = Et, **c** R = allyl, **d** R = Bu, **e** R = *i*-Bu, **f** R = *s*-Bu, **g** R = $(CH_2)_2OMe$, **h** R = C_5H_{11}, **i** R = *i*-C_5H_{11}, **j** R = $(CH_2)_3OMe$, **k** R = $(CH_2)_3OEt$, **l** R = Bn, **m** R = 3-methylbenzyl, **n** R = CH(Me)Ph, **o** R = 2-(2-thienyl)ethyl, **p** R = 5-bromo-2-methoxybenzyl

More convincing evidence of the synthesized compound structure was obtained by NMR spectroscopy. In the ^{1}H NMR spectrum of 7-methyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (**3a**) in DMSO-d_6, the broad signal of the NH proton was observed at lowest field at 8.44 ppm, then two doublet signals (^2J = 12.1 Hz) for the equatorial and axial protons at the C-4 atom with chemical shifts of 3.88 and 3.60 ppm, respectively. The protons of the methylene groups of the piperidine ring (6,8,9-CH_2) were diastereotropic, consequently their signals formed a group of doublets (^2J = 10.5-11.3 Hz) in the 2.52-3.41 ppm region. The singlet signal at high field at 2.36 ppm corresponds to the protons of the NCH_3 group.

For a more reliable assignment of the signals in the NMR spectrum of 7-methyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (**3a**), two-dimentional homo- (COSY) and heteronuclear (HMBC, HSQS) correlation spectroscopy was used. The conformation of this compound in solution was established with the aid of the nuclear Overhauser effect (NOESY). The signals of atoms C-4 (δ_C 47.4 ppm), C-6 (δ_C 62.6 ppm), C-8 (δ_C 57.1 ppm), and C-9 (δ_C 34.2 ppm) may be determined from the two-dimensional HSQC spectrum (Table 1). These are linked with the protons of the piperidine ring by direct coupling constants J_{CH}. The signals at 86.5 and 81.6 ppm, having no correlation peaks in the HSQC spectrum, were assigned to the quaternary carbon atoms C-1 and C-5, respectively. The signals of the 6,8,9-CH_2 protons were determined from the corresponding cross peaks with carbon atoms C-1,4,5 in the HMBC spectrum. The cross peaks corresponding to the geminal coupling constants (H-4*a*/H-4*e*, H-6*a*/H-6*e*, H-8*a*/H-8*e*, H-9*a*,/H-9*e*) were the most intense in the COSY spectrum of the compound being investigated. The absence of correlation peaks from the NOESY spectrum of compound **3a,** corresponding to the interaction of the bridge proton with the NH and NCH_3 groups, indicates a twin "chair" conformation for the compound under investigation.

Further confirmation of the structure of the synthesized 3,7-diazabicyclo[3.3.1]nonanes was obtained by X-ray structural analysis of a crystal of 7-methyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (**3a**) (Fig. 1).

The bicyclic fragment in the crystal has the conformation characteristic of compounds of a similar group. The six-membered ring containing the substituted N(7) nitrogen atom has the "chair" conformation, but the second ring containing the ketone fragment has a distorted "sofa" conformation. The torsion angles C(1)–C(2)–N(3)–C(4) and C(5)–C(4)–N(3)–C(2), showing the extent of flattening of the five-membered fragment, were -6.3(1) and 13.1(1)°, respectively. The bonds at the N(3) nitrogen atom are in one plane (sum of angles was 359.6°) due to the conjugation of the lone electron pair with the π-system of the carbonyl fragment. The geometric parameters of the molecule in the crystal did not differ significantly from those for analogous compounds investigated previously.

On carrying out the aminomethylation of diadduct **2** at 25-30°C, instead of compounds **3a-c**,**l**, compounds **4a-c**,**l** were isolated by extraction with toluene. These are products not only of aminomethylation but also of hydroxymethylation at the nitrogen atom of the pyridine ring (60-65% yields). A further increase in temperature led to a reduction in yield of products, probably due to the instability of diadduct **2** at elevated temperature.

The structures of the obtained compounds **4a-c**,**l** were also proved by IR and NMR spectroscopy. In difference to compounds **3a-p**, the characteristic signals of an OH group, coordinated by an intramolecular hydrogen bond with the carbonyl group, were displayed at 3395 cm^{-1} in the IR spectra of compounds **4a-c**,**l.** The amide proton signal was absent.

TABLE 1. Correlation Peaks in the 2D NMR Spectra of 3,7-Diazabicyclo[3.3.1]nonanes **3a** and **4c**

Atom number	δ_H, ppm	δ_C, ppm	HSQC	HMBC	COSY	NOESY
Compound **3a**						
1	—	86.5	—	H-8*a*,*e* / C-1, H-9*a*,*e* / C-1, NCH_3 / C-1	—	—
2	—	163.9	—	—	—	—
4	3.88 d, 3.60 d	47.4	H-4 / C-4	H-9*a*,*e* / C-4, H-6*a* / C-4	H-4*a* / H-4*e*	H-4*a* / H-4*e*, H-4*a*,*e* / NH
5	—	81.6	—	H-4*a*,*e* / C-5, H-6*a* / C-5, H-9*a*,*e* / C-5, NCH_3 / C-5	—	—
6	3.32 d, 2.52 d	62.6	H-6 / C-6	H-4*a* / C-6, H-8*a* / C-6, H-9*a*,*e* / C-6, $NC\underline{H}_3$ / C-6	H-6*a* / H-6*e*	H-6*a* / H-6*e* H-6*a* / $NC\underline{H}_3$ H-6*e* / H-9*a*
8	3.41 d, 2.61 d	57.1	H-8 / C-8	H-6*e* / C-8, H-9*a* / C-8, NCH_3 / C-8	H-8*a* / H-8*e*	H-8*a* / H-8*e*
9	3.37 d, 2.84 d	34.2	H-9 / C-9	H-6*e* / C-9, H-8*a*,*e* / C-9	H-9*a* / H-9*e*	H-9*a* / H-9*e*, H-9*a* / H-6*e*
NH	8.44 br. s	—	—	—	—	NH / H-4*a*,*e*
NCH_3	2.36 s	44.4	$NC\underline{H}_3$ / $N\underline{C}H_3$	H-8*a* / $N\underline{C}H_3$	—	$NC\underline{H}_3$ / H-6*a*
Compound **4c**						
1	—	87.0	—	H-8*a*,*e* / C-1, H-9*a*,*e* / C-1	—	—
2	—	162.9	—	H-α / C-2, H-4*a*,*e* / C-2	—	—
4	4.07 d, 3.80 d	50.9	H-4 / C-4	H-α / C-4, H-9*a* / C-4, H-6*a* / C-4	H-4*a* / H-4*e*, H-6*a* / H-4*a*, H-9*a* / H-4*e*	H-4*a* / H-4*e*, H-9*e* / H-4*a*,*e* H-α / H-4*a*,*e*
5	—	81.3	—	H-α / C-5, H-4*a*,*e* C-5, H-6*a* / C-5, H-9*a*,*e* / C-5	—	—
6	3.38 d, 2.65 d	60.4	H-6 / C-6	H-4*a*,*e* / C-6, H-8*a*,*e* / C-6, H-9*a* / C-6, H-α / C-6	H-4*a* / H-6*a*, H-6*a* / H-6*e*	H-6*a* / H-6*e*, H-8*e* / H-6*a*, H-α / H-6*a*, H-9*a* / H-6*a*, H-α / H-6*a*,*e*
8	3.48 d, 2.74 d	55.0	H-8 / C-8	H-6*e* / C-8	H-8*a* / H-8*e*, H-9*a* / H-8*a*	H-8*a* / H-8*e*, H-9*a* / H-8*a*, H-6*a* / H-8*e*
9	3.34 d, 2.95 d	34.5	H-9 / C-9	H-4*e* / C-9, H-6*e* / C-9, H-8*a*,*e* / C-9	H-9*a* / H-9*e*, H-4*e* / H-9*a*, H-8*a* / H-9*a*	H-9*a* / H-9*e*, H-4*a*,*e* / H-9*e*, H-6*a* / H-9*a*, H-8*a* / H-9*a*
α ($\underline{C}H_2OH$)	4.84 d, 4.65 d	68.8	H-α / C-α	—	H-α / H-α	H-α / H-α, H-4*a*,*e* / H-α

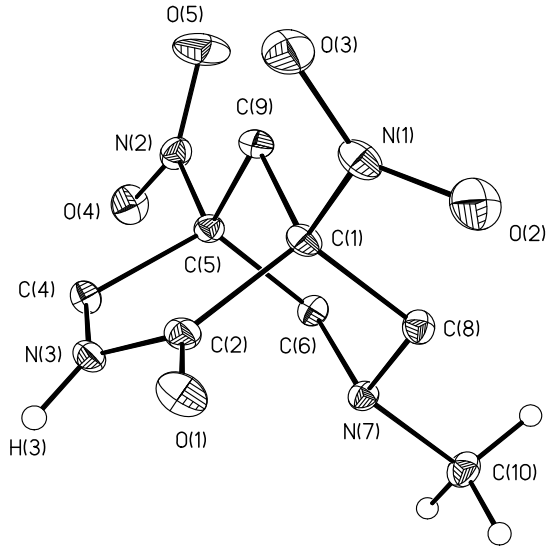

Fig. 1. Molecular structure of compound **3a** with atoms represented by thermal vibration ellipsoids of 50% probability.

The signals of the C-4 (δ_C 50.9 ppm), C-6 (δ_C 60.4 ppm), C-8 (δ_C 55.0 ppm), and C-9 (δ_C 34.5 ppm) atoms may be determined from the two-dimensional HSQC spectrum of 7-allyl-3-hydroxymethyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (**4c**) linked with the protons of the piperidine ring by direct coupling constants J_{CH}. The signals at 87.0 and 81.3 ppm, having no correlation peaks in the HSQC spectrum, were assigned to the quaternary carbon atoms C-1,5, respectively. The signals of the 4,6,8,9-CH_2 protons were determined from the corresponding cross peaks with carbon atoms C-1,4,5 and C-α in the HMBC spectrum.

The most intense cross peaks in the COSY spectrum of the investigated compound were those corresponding to geminal (H-4*a*/H-4*e*, H-6*a*/H-6*e*, H-8*a*/H-8*e*, H-9*a*/H-9*e*) and allyl (H-6*a*/H-4*a*, H-9*a*/ H-4*e*, H-9*a*/H-8*a*) coupling constants.

The presence in the NOESY spectrum of compound **4c** of correlation peaks corresponding to the interaction of the spatially adjacent H-6*a*, H-8*a*, and H-9*a* axial atoms, and also the absence from the spectrum of contact of the bridge proton with the protons of the $NC\underline{H}_2OH$ (H-α) and NCH_3 groups indicates that the investigated compound takes up a twin "chair" conformation in solution.

A simple one-pot method is therefore proposed for the synthesis of 7-R-1,5-dinitro-3,7-diaza-bicyclo[3.3.1]nonan-2-one derivatives from 2-hydroxy-3,5-dinitropyridine.

EXPERIMENTAL

The IR spectra were recorded on a FSM 1201 Fourier spectrometer in KBr pellets. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 and 75 MHz, respectively) in DMSO-d_6, internal standard was HMDS (0.05 ppm). Mixing time in the NOESY experiments was 120 msec. Elemental analysis was carried out on a Carlo Erba 1100 CHN analyzer. Melting points were determined on a Boetius Kofler hot stage. The purity of the obtained compounds was checked by TLC on Sorbfil UV-254 plates, eluent was PhMe–acetone–heptane, 4:1:1, visualization was by UV light or iodine vapor.

2-Hydroxy-3,5-dinitropyridine (**1**) was synthesized by the nitration of 2-hydroxypyridine [8], mp 176-178ºC.

Synthesis of 7-Substituted 1,5-Dinitro-3,7-diazabicyclo[3.3.1]nonan-2-ones 3a-p (General Method). Na_2CO_3 (0.53 g, 5 mmol) in water (10 ml) was added to a solution of 2-hydroxy-3,5-dinitropyridine

(**1**) (1.00 g, 5 mmol) in a mixture (10 ml) of DMF and EtOH, 1:1. $NaBH_4$ (0.76 g, 20 mmol) was added during 5 min in portions with stirring and cooling with ice; then the mixture was stirred for several minutes more. After the end of the reduction, as indicated by a decrease in the intensity of the color, a cooled solution of 32% formaldehyde (2.5 ml, 30 mmol) and the corresponding amine hydrochloride (15 mmol) (for compound **3a**) or free amine (15 mmol) (for the remaining compounds) was added in a mixture of EtOH–H_2O, 1:1 (8 ml). The temperature of the reaction mixture was maintained at 5-10°C. The pH of the reaction mixture was brought to 4 with the aid of 20% H_3PO_4 solution, the precipitated solid was filtered off, and washed with H_2O. Compounds **3a-p** were recrystallized from 2-PrOH. The compounds obtained were crystalline solids with a bright-yellow color.

7-Methyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3a). Yield 1.00 g (82%), mp 195-196°C, R_f 0.27. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.36 (3H, s, NCH_3); 2.52 (1H, d, ^2J = 10.5, H-6*a*); 2.61 (1H, d, ^2J = 10.5, H-8*a*); 2.84 (1H, d, ^2J = 11.3, H-9*a*); 3.32 (1H, d, ^2J = 10.5, H-6*e*); 3.37 (1H, d, ^2J = 11.3, H-9*e*); 3.41 (1H, d, ^2J = 10.5, H-8*e*); 3.60 (1H, d, ^2J = 12.1, H-4*e*); 3.88 (1H, d, ^2J = 12.1, H-4*a*); 8.44 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 34.2 (C-9); 44.4 (NCH_3); 47.4 (C-4); 57.1 (C-8); 62.6 (C-6); 81.6 (C-5); 86.5 (C-1); 163.9 (C-2). Found, %: C 39.41; H 4.94; N 22.98. $C_8H_{12}N_4O_5$. Calculated, %: C 39.35; H 4.95; N 22.94.

7-Ethyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3b). Yield 0.99 g (77%), mp 183-184°C, R_f 0.35. IR spectrum, ν, cm^{-1}: 3398 (N–H), 2981, 2950, 2908 (C–H aliph), 1690 (C=O), 1552 (NO_2 *asym*), 1460 δ(CH_2/CH_3), 1349 (NO_2 *sym*), 935, 909, 846, 830 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.00 (3H, t, ^3J = 7.0, $NCH_2C\underline{H}_3$); 2.57-2.62 (2H, m, $NC\underline{H}_2CH_3$); 2.61 (1H, d, ^2J = 10.2, H-6*a*); 2.68 (1H, d, ^2J = 10.5, H-8*a*); 2.88 (1H, d, ^2J = 11.3, H-9*a*); 3.35 (1H, d, ^2J = 10.2, H-6*e*); 3.38 (1H, d, ^2J = 11.3, H-9*e*); 3.45 (1H, d, ^2J = 10.5, H-8*e*); 3.57 (1H, d, ^2J = 12.1, H-4*e*); 3.90 (1H, d, ^2J = 12.1, H-4*a*); 8.46 (1H, br. s, NH). Found, %: C 41.80; H 5.47; N 21.63. $C_9H_{14}N_4O_5$. Calculated, %: C 41.86; H 5.46; N 21.70.

7-Allyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3c). Yield 1.05 g (78%), mp 124-125°C, R_f 0.24. IR spectrum, ν, cm^{-1}: 3395 (N–H), 2913 (C–H aliph), 1703 (C=O), 1646 (C=C), 1562 (NO_2 *asym*), 1462 δ(CH_2/CH_3), 1348 (NO_2 *sym*), 933 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.62 (1H, d, ^2J = 10.5, H-6*a*); 2.67 (1H, d, ^2J = 10.5, H-8*a*); 2.89 (1H, d, ^2J = 11.3, H-9*a*); 3.21 (2H, d, ^3J = 7.3, $NC\underline{H}_2CH{=}CH_2$); 3.33 (1H, d, ^2J = 10.5, H-6*e*); 3.38 (1H, d, ^2J = 11.3, H-9*e*); 3.47 (1H, d, ^2J = 10.5, H-8*e*); 3.57 (1H, d, ^2J = 12.1, H-4*e*); 3.91 (1H, d, ^2J = 12.1, H-4*a*); 5.21 (1H, d, ^3J = 9.1) and 5.25 (1H, d, ^3J =17.2, $NCH_2CH{=}C\underline{H}_2$); 5.77 (1H, ddt, ^3J = 17.2, ^3J = 9.1, ^3J = 7.3, $NCH_2C\underline{H}{=}CH_2$); 8.49 (1H, br. s, NH). Found, %: C 44.60; H 5.27; N 20.71. $C_{10}H_{14}N_4O_5$. Calculated, %: C 44.45; H 5.22; N 20.73.

7-Butyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3d). Yield 1.00 g (70%), mp 151-152°C, R_f 0.46. IR spectrum, ν, cm^{-1}: 3401 (N–H), 2961, 2935 (C–H aliph), 1701 (C=O), 1558 (NO_2 *asym*), 1457 δ(CH_2/CH_3), 1348 (NO_2 *sym*), 933, 903, 885 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.86 (3H, t, ^3J = 7.0, $N(CH_2)_3C\underline{H}_3$); 1.21-1.30 (2H, m, $NCH_2CH_2C\underline{H}_2CH_3$); 1.37-1.44 (2H, m, $NCH_2C\underline{H}_2CH_2CH_3$); 2.51-2.54 (2H, m, $NC\underline{H}_2CH_2CH_2CH_3$); 2.59 (1H, d, ^2J = 10.7, H-6*a*); 2.66 (1H, d, ^2J = 10.5, H-8*a*); 2.88 (1H, d, ^2J = 11.3, H-9*a*); 3.33 (1H, d, ^2J = 10.7, H-6*e*); 3.37 (1H, d, ^2J = 11.3, H-9*e*); 3.44 (1H, d, ^2J = 10.5, H-8*e*); 3.54 (1H, d, ^2J = 12.1, H-4*e*); 3.89 (1H, d, ^2J = 12.1, H-4*a*); 8.48 (1H, br. s, NH). Found, %: C 46.12; H 6.31; N 19.54. $C_{11}H_{18}N_4O_5$. Calculated, %: C 46.15; H 6.34; N 19.57.

7-Isobutyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3e). Yield 0.97 g (68%), mp 126-127°C, R_f 0.52. IR spectrum, ν, cm^{-1}: 3361 (N–H), 2962 (C–H aliph), 1693 (C=O), 1559 (NO_2 *asym*), 1465, 1391 δ(CH_2/CH_3), 1345 (NO_2 *sym*), 905, 880 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.82 (6H, t, ^3J = 7.0, $NCH_2CH(C\underline{H}_3)_2$)); 1.72-1.82 (1H, m, $NCH_2C\underline{H}Me_2$); 2.22-2.32 (2H, m, $NC\underline{H}_2CHMe_2$); 2.62 (1H, d, ^2J = 10.5, H-6*a*); 2.67 (1H, d, ^2J = 10.5, H-8*a*); 2.89 (1H, d, ^2J = 11.3, H-9*a*); 3.32 (1H, d, ^2J = 10.5, H-6*e*); 3.38 (1H, d, ^2J = 11.3, H-9*e*); 3.42 (1H, d, ^2J = 10.5, H-8*e*); 3.54 (1H, d, ^2J = 12.4, H-4*e*); 3.92 (1H, d, ^2J = 12.4, H-4*a*); 8.52 (1H, br. s, NH). Found, %: C 46.16; H 6.31; N 19.53. $C_{11}H_{18}N_4O_5$. Calculated, %: C 46.15; H 6.34; N 19.57.

7-*sec*-Butyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3f). Yield 0.86 g (60%), mp 169-170°C, R_f 0.41. IR spectrum, ν, cm^{-1}: 2971, 2935 (C–H aliph), 1703 (C=O), 1558 (NO_2 *asym*), 1445 δ(CH_2/CH_3), 1349

(NO_2 *sym*), 854, 903 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.80 (1.5H, t, ^3J = 7.0) and 0.83 (1.5H, t, ^3J = 7.0, NCH(Me)$CH_2C\underline{H}_3$); 0.91 (1.5H, d, ^3J = 7.0) and 0.93 (1.5H, d, ^3J = 7.0, NCH(Et)$C\underline{H}_3$); 1.22-1.33 (1H, m) and 1.35-1.53 (1H, m, NCH(Me)$C\underline{H}_2CH_3$); 2.66-2.73 (1H, m, N$C\underline{H}$(Me)Et); 2.73 (0.5H, d, ^2J = 10.7) and 2.76 (0.5H, d, ^2J = 10.7, H-6*a*); 2.87 (1H, d, ^2J = 11.3, H-8*a*); 2.94 (0.5H, d, ^2J = 10.7) and 3.01 (0.5H, d, ^2J = 10.7, H-9*a*); 3.21 (0.5H, d, ^2J = 10.7) and 3.24 (0.5H, d, ^2J = 10.7, H-6*e*); 3.32 (0.5H, d, ^2J = 10.7) and 3.35 (0.5H, d, ^2J = 10.7, H-9*e*); 3.38 (1H, d, ^2J = 11.3, H-8*e*); 3.49 (0.5H, d, ^2J = 12.4) and 3.56 (0.5H, d, ^2J = 12.4, H-4*e*); 3.88 (0.5H, d, ^2J = 12.4) and 3.91 (0.5H, d, ^2J = 12.4, H-4*a*); 8.46 (1H, br. s, NH). Found, %: C 46.17; H 6.38; N 19.58. $C_{11}H_{18}N_4O_5$. Calculated, %: C 46.15; H 6.34; N 19.57.

7-(2-Methoxyethyl)-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3g). Yield 0.91 g (63%), mp 160-161°C, R_f 0.36. IR spectrum, ν, cm^{-1}: 3380 (N–H), 2949, 2909 (C–H aliph), 1697 (C=O), 1559 (NO_2 *asym*), 1473, 1376 δ(CH_2/CH_3), 1351 (NO_2 *sym*), 1110, 1071 (C–O–C), 904, 872, 843, 831 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.71 (1H, d, ^2J = 10.5, H-6*a*); 2.74 (1H, d, ^2J = 10.7, H-8*a*); 2.77-2.81 (2H, m, N$C\underline{H}_2CH_2$OMe); 2.86 (1H, d, ^2J = 11.3, H-9*a*); 3.23 (3H, br. s, $NCH_2CH_2OC\underline{H}_3$); 3.37 (1H, d, ^2J = 10.5, H-6*e*); 3.41 (1H, d, ^2J = 11.3, H-9*e*); 3.44 (2H, t, ^3J = 5.4, $NCH_2C\underline{H}_2$OMe); 3.51 (1H, d, ^2J = 10.7, H-8*e*); 3.58 (1H, d, ^2J = 12.1, H-4*e*); 3.89 (1H, d, ^2J = 12.1, H-4*a*); 8.45 (1H, br. s, NH). Found, %: C 41.67; H 5.44; N 19.46. $C_{10}H_{16}N_4O_6$. Calculated, %: C 41.67; H 5.59; N 19.44.

1,5-Dinitro-7-pentyl-3,7-diazabicyclo[3.3.1]nonan-2-one (3h). Yield 0.98 g (65%), mp 90-91°C, R_f 0.47. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.86 (3H, t, ^3J = 7.3, $N(CH_2)_4C\underline{H}_3$); 1.19-1.30 (4H, m, $NCH_2CH_2C\underline{H}_2C\underline{H}_2CH_3$); 1.38-1.45 (2H, m, $NCH_2C\underline{H}_2CH_2CH_2CH_3$); 2.52-2.54 (2H, m, N$C\underline{H}_2CH_2CH_2CH_2CH_3$); 2.59 (1H, d, ^2J = 10.5, H-6*a*); 2.67 (1H, d, ^2J = 10.5, H-8*a*); 2.88 (1H, d, ^2J = 11.3, H-9*a*); 3.35 (1H, d, ^2J = 10.5, H-6*e*); 3.38 (1H, d, ^2J = 11.3, H-9*e*); 3.44 (1H, d, ^2J = 10.5, H-8*e*); 3.54 (1H, d, ^2J = 12.4, H-4*e*); 3.90 (1H, d, ^2J = 12.4, H-4*a*); 8.48 (1H, br. s, NH). Found, %: C 46.92; H 6.68; N 18.68. $C_{12}H_{20}N_4O_5$. Calculated, %: C 47.99; H 6.71; N 18.66.

1,5-Dinitro-7-isopentyl-3,7-diazabicyclo[3.3.1]nonan-2-one (3i). Yield 1.01 g (67%), mp 117-119°C, R_f 0.58. IR spectrum, ν, cm^{-1}: 3395 (N–H), 2957 (C–H aliph), 1696 (C=O), 1553 (NO_2 *asym*), 1468 δ(CH_2/CH_3), 1348 (NO_2 *sym*), 846 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.86 (6H, t, ^3J = 6.4, $N(CH_2)_2CH(C\underline{H}_3)_2$)); 1.29-1.34 (2H, m, $NCH_2C\underline{H}_2CHMe_2$); 1.49-1.59 (1H, m, $NCH_2CH_2C\underline{H}Me_2$); 2.51-2.56 (2H, m, N$C\underline{H}_2CH_2CHMe_2$); 2.59 (1H, d, ^2J = 10.2, H-6*a*); 2.66 (1H, d, ^2J = 10.5, H-8*a*); 2.88 (1H, d, ^2J = 11.8, H-9*a*); 3.36 (1H, d, ^2J = 10.2, H-6*e*); 3.38 (1H, d, ^2J = 11.8, H-9*e*); 3.45 (1H, d, ^2J = 10.5, H-8*e*); 3.55 (1H, d, ^2J = 12.1, H-4*e*); 3.90 (1H, d, ^2J = 12.1, H-4*a*); 8.47 (1H, br. s, NH). Found, %: C 46.86; H 6.55; N 18.68. $C_{12}H_{20}N_4O_5$. Calculated, %: C 47.99; H 6.71; N 18.66.

7-(3-Methoxypropyl)-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3j). Yield 1.06 g (70%), mp 95-97°C, R_f 0.47. IR spectrum, ν, cm^{-1}: 3399 (N–H), 2953 (C–H aliph), 1639 (C=O), 1559 (NO_2 *asym*), 1456 δ(CH_2/CH_3), 1350 (NO_2 *sym*), 1131, 1109 (C–O–C), 936, 908, 879 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.61-1.68 (2H, m, $NCH_2C\underline{H}_2CH_2$OMe); 2.55-2.59 (2H, m, N$C\underline{H}_2CH_2CH_2$OMe); 2.62 (1H, d, ^2J = 10.2, H-6*a*); 2.70 (1H, d, ^2J = 10.5, H-8*a*); 2.88 (1H, d, ^2J = 11.3, H-9*a*); 3.21 (3H, br. s, $NCH_2CH_2CH_2OC\underline{H}_3$); 3.30 (2H, t, ^3J = 6.4, $NCH_2CH_2C\underline{H}_2$OMe); 3.33 (1H, d, ^2J = 10.2, H-6*e*); 3.38 (1H, d, ^2J = 11.3, H-9*e*); 3.43 (1H, d, ^2J = 10.5, H-8*e*); 3.56 (1H, d, ^2J = 12.4, H-4*e*); 3.90 (1H, d, ^2J = 12.4, H-4*a*); 8.49 (1H, br. s, NH). Found, %: C 43.75; H 6.06; N 18.53. $C_{11}H_{18}N_4O_6$. Calculated, %: C 43.71; H 6.00; N 18.53.

7-(3-Ethoxypropyl)-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3k). Yield 1.06 g (67%), mp 123-124°C, R_f 0.31. IR spectrum, ν, cm^{-1}: 3418 (N–H), 2991, 2972 (C–H aliph), 1697 (C=O), 1559 (NO_2 *asym*), 1453, 1381 δ(CH_2/CH_3), 1346 (NO_2 *sym*), 1140 (C–O–C), 836 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.09 (3H, t, ^3J = 7.0, $N(CH_2)_3OCH_2C\underline{H}_3$); 1.61-1.67 (2H, m, $NCH_2C\underline{H}_2CH_2$OEt); 2.57 (1H, d, ^2J = 10.7, H-6*a*); 2.55-2.60 (2H, m, N$C\underline{H}_2CH_2CH_2$OEt); 2.70 (1H, d, ^2J = 10.7, H-8*a*); 2.88 (1H, d, ^2J = 11.6, H-9*a*); 3.33 (1H, d, ^2J = 10.7, H-6*e*); 3.34-3.37 (2H, m, $NCH_2CH_2C\underline{H}_2$OEt); 3.38 (1H, d, ^2J = 11.6, H-9*e*); 3.39-3.41 (2H, m, ^3J = 6.4, $N(CH_2)_3OC\underline{H}_2CH_3$); 3.43 (1H, d, ^2J = 10.7, H-8*e*); 3.56 (1H, d, ^2J = 12.1, H-4*e*); 3.90 (1H, d, ^2J = 12.1, H-4*a*); 8.49 (1H, br. s, NH). Found, %: C 45.83; H 6.46; N 17.64. $C_{12}H_{20}N_4O_6$. Calculated, %: C 45.57; H 6.37; N 17.71.

7-Benzyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3l). Yield 0.86 g (54%), mp 152-153°C, R_f 0.24. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.65 (1H, d, ^2J = 10.2, H-6*a*); 2.68 (1H, d, ^2J = 10.5, H-8*a*); 2.90 (1H, d, ^2J = 11.6, H-9*a*); 3.34 (1H, d, ^2J = 10.2, H-6*e*); 3.39 (1H, d, ^2J = 11.6, H-9*e*); 3.45 (1H, d, ^2J = 10.5, H-8*e*); 3.57 (1H, d, ^2J = 12.1, H-4*e*); 3.73 (1H, d, ^2J = 13.7) and 3.80 (1H, d, ^2J = 13.7, NC$\underline{H}_2$Ph); 3.92 (1H, d, ^2J = 12.1, H-4*a*); 7.33 (2H, d, ^3J = 7.0, H-2,6 Ph); 7.36 (1H, t, ^3J = 7.0, H-4 Ph); 7.39 (2H, t, ^3J = 7.0, H-3,5 Ph); 8.40 (1H, br. s, NH). Found, %: C 52.53; H 5.08; N 17.44. $C_{14}H_{16}N_4O_5$. Calculated, %: C 52.50; H 5.04; N 17.49.

7-(3-Methylbenzyl)-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3m). Yield 1.07 g (64%), mp 165-167°C, R_f 0.45. IR spectrum, ν, cm^{-1}: 3425 (N–H), 2915 (C–H aliph), 1693 (C=O), 1609 (C–H Ar), 1553 (NO_2 *asym*), 1458 δ(CH_2/CH_3), 1347 (NO_2 *sym*), 838 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.30 (3H, br. s, CH_3); 2.65 (1H, d, ^2J = 10.7, H-6*a*); 2.68 (1H, d, ^2J = 10.5, H-8*a*); 2.90 (1H, d, ^2J = 11.3, H-9*a*); 3.35 (1H, d, ^2J = 10.7, H-6*e*); 3.39 (1H, d, ^2J = 11.3, H-9*e*); 3.45 (1H, d, ^2J = 10.5, H-8*e*); 3.56 (1H, d, ^2J = 12.1, H-4*e*); 3.69 (1H, d, ^2J = 14.0) and 3.75 (1H, d, ^2J = 14.0, NC$\underline{H}_2$Ar); 3.92 (1H, d, ^2J = 12.1, H-4*a*); 7.05-7.11 (3H, m, H-2,4,6 Ar); 7.23 (1H, t, ^3J = 7.5, H-5 Ar); 8.60 (1H, br. s, NH). Found, %: C 53.81; H 5.47; N 16.78. $C_{15}H_{18}N_4O_5$. Calculated, %: C 53.89; H 5.43; N 16.76.

1,5-Dinitro-7-(1-phenylethyl)-3,7-diazabicyclo[3.3.1]nonan-2-one (3n). Yield 1.00 g (60%), mp 79-81°C, R_f 0.40. IR spectrum, ν, cm^{-1}: 3382 (N–H), 3086, 2972 (C–H aliph), 1700 (C=O), 1602 ν(C–H aliph), 1554 (NO_2 *asym*), 1454 δ(CH_2/CH_3), 1347 (NO_2 *sym*), 934, 904 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.33 (1.5H, d, ^3J = 7.0) and 1.35 (1.5H, d, ^3J = 7.0, NCH(C$\underline{H}_3$)Ph); 2.58 (1H, d, ^2J = 10.5, H-6*a*); 2.64 (0.5H, d, ^2J = 10.5) and 2.67 (0.5H, d, ^2J = 10.5, H-8*a*); 2.86 (1H, d, ^2J = 11.3, H-9*a*); 3.35 (1H, d, ^2J = 10.5, H-6*e*); 3.38 (1H, d, ^2J = 11.3, H-9*e*); 3.44 (0.5H, d, ^2J = 10.5) and 3.48 (0.5H, d, ^2J = 10.5, H-8*e*); 3.55 (1H, d, ^2J = 12.1, H-4*e*); 3.87-3.93 (1H, m, NC$\underline{H}$(Me)Ph); 3.95 (1H, d, ^2J = 12.1, H-4*a*); 7.27-7.36 (5H, m, H Ph); 8.55 (0.5H, br. s) and 8.58 (0.5H, br. s, NH). Found, %: C 53.83; H 5.44; N 16.72. $C_{15}H_{18}N_4O_5$. Calculated, %: C 53.89; H 5.43; N 16.76.

1,5-Dinitro-7-[2-(2-thienyl)ethyl]-3,7-diazabicyclo[3.3.1]nonan-2-one (3o). Yield 0.88 g (52%), mp 144-146°C, R_f 0.41. IR spectrum, ν, cm^{-1}: 3402 (N–H), 3091 (C–H thiophene), 2924 (C–H aliph), 1698 (C=O), 1553 (NO_2 *asym*), 1461 δ(CH_2/CH_3), 1346 (NO_2 *sym*), 841 (C–N), 706 (thiophene). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.69 (1H, d, ^2J = 10.2, H-6*a*); 2.80 (1H, d, ^2J = 10.5, H-8*a*); 2.90 (1H, d, ^2J = 11.3, H-9*a*); 2.94-3.00 (4H, m, NC$\underline{H}_2$C$\underline{H}_2$Ar); 3.33 (1H, d, ^2J = 10.2, H-6*e*); 3.39 (1H, d, ^2J = 11.3, H-9*e*); 3.44 (1H, d, ^2J = 10.5, H-8*e*); 3.56 (1H, d, ^2J = 12.1, H-4*e*); 3.90 (1H, d, ^2J = 12.1, H-4*a*); 6.89 (1H, d, ^3J = 3.2, H-3 thiophene); 6.92–6.94 (1H, m, H-4 thiophene); 7.30 (1H, d, ^3J = 5.1, H-5 thiophene); 8.48 (1H, br. s, NH). Found, %: C 45.90; H 4.83; N 16.39. $C_{13}H_{16}N_4O_5S$. Calculated, %: C 45.88; H 4.74; N 16.46.

7-(5-Bromo-2-methoxybenzyl)-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (3p). Yield 1.33 g (62%), mp 83-85°C, R_f 0.37. IR spectrum, ν, cm^{-1}: 3407 (N–H), 2942 (C–H aliph), 1697 (C=O), 1593 (C–H Ar), 1553 (NO_2 *asym*), 1489 δ(CH_2/CH_3), 1347 (NO_2 *sym*), 1116 (C–O–C), 1077, 1026 (C–Br), 820 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.68 (1H, d, ^2J = 10.5, H-6*a*); 2.70 (1H, d, ^2J = 10.7, H-8*a*); 2.87 (1H, d, ^2J = 11.3, H-9*a*); 3.18 (3H, br. s, OCH_3); 3.36 (1H, d, ^2J = 10.5, H-6*e*); 3.39 (1H, d, ^2J = 11.3, H-9*e*); 3.45 (1H, d, ^2J = 10.7, H-8*e*); 3.56 (1H, d, ^2J = 12.4, H-4*e*); 3.77 (2H, d, ^2J = 5.6, NC$\underline{H}_2$Ar); 3.91 (1H, d, ^2J = 12.4, H-4*a*); 7.00 (1H, d, ^3J = 8.6, H-3 Ar); 7.40 (1H, d, ^4J = 2.4, H-6 Ar); 7.44 (1H, d. d, ^3J = 8.6, ^4J = 2.4, H-4 Ar); 8.57 (1H, br. s, NH). Found, %: C 41.93; H 3.95; N 13.08. $C_{15}H_{17}BrN_4O_6$. Calculated, %: C 41.97; H 3.99; N 13.05.

7-R-3-(hydroxymethyl)-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-ones 4a-c,l were obtained by the procedure described for compounds **3a-p**, the only difference being that the temperature of the reaction mixture was maintained within the limits 25-30°C. Products **4a-c**,**l** were extracted with toluene, and the extract was dried with anhydrous calcium chloride. The solvent was then distilled off in vacuum, and the residue recrystallized from 2-PrOH. The compounds obtained were light-yellow crystalline solids.

3-(Hydroxymethyl)-7-methyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (4a). Yield 0.89 g (65%), mp 197-198°C, R_f 0.33. IR spectrum, ν, cm^{-1}: 3424 (O–H), 2958, 2894 (C–H aliph), 1687 (C=O), 1559 (NO_2 *asym*), 1400, 1385 δ(CH_2/CH_3), 1351 (NO_2 *sym*), 929, 839 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.34 (3H, s, NCH_3); 2.55 (1H, d, ^2J = 10.5, H-6*a*); 2.65 (1H, d, ^2J = 10.7, H-8*a*); 2.90 (1H, d, ^2J = 11.3, H-9*a*); 3.34

(1H, d, ^2J = 11.3, H-9*e*); 3.37 (1H, d, ^2J = 10.5, H-6*e*); 3.41 (1H, d, ^2J = 10.7, H-8*e*); 3.80 (1H, d, ^2J = 12.1, H-4*e*); 4.08 (1H, d, ^2J = 12.1, H-4*a*); 4.72 (1H, d, ^2J = 10.2) and 4.77 (1H, d, ^2J = 10.2, NC$\underline{H}_2$OH); 6.31 (1H, br. s, NCH$_2$O$\underline{H}$). Found, %: C 39.47; H 5.18; N 20.39. $C_9H_{14}N_4O_6$. Calculated, %: C 39.42; H 5.15; N 20.43.

7-Ethyl-3-(hydroxymethyl)-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (4b). Yield 0.86 g (60%), mp 150-151°C, R_f 0.47. IR spectrum, ν, cm^{-1}: 3395 ν(O–H), 2989, 2958, 2921, 2850 (C–H aliph), 1697 (C=O), 1559 (NO_2 *asym*), 1460, 1451 δ(CH_2/CH_3), 1349 (NO_2 *sym*), 928, 898, 863 (C–N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.99 (3H, t, ^3J = 7.0, NCH$_2$C$\underline{H}_3$); 2.59 (2H, m, NC$\underline{H}_2$CH$_3$); 2.62 (1H, d, ^2J = 10.7, H-6*a*); 2.74 (1H, d, ^2J = 10.5, H-8*a*); 2.93 (1H, d, ^2J = 11.3, H-9*a*); 3.36 (1H, d, ^2J = 11.3, H-9*e*); 3.38 (1H, d, ^2J = 10.7, H-6*e*); 3.45 (1H, d, ^2J = 10.5, H-8*e*); 3.77 (1H, d, ^2J= 12.1, H-4*e*); 4.07 (1H, d, ^2J = 12.1, H-4*a*); 4.67 (1H, d, ^2J = 10.2) and 4.80 (1H, d, ^2J = 10.2, NC$\underline{H}_2$OH); 6.26 (1H, br. s, NCH$_2$O$\underline{H}$). Found, %: C 41.61; H 5.63; N 19.45. $C_{10}H_{16}N_4O_6$. Calculated, %: C 41.67; H 5.59; N 19.44.

7-Allyl-3-(hydroxymethyl)-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (4c). Yield 0.95 g (63%), mp 129-131°C, R_f 0.50. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.65 (1H, d, ^2J = 10.5, H-6*a*); 2.74 (1H, d, ^2J = 10.5, H-8*a*); 2.95 (1H, d, ^2J = 11.3, H-9*a*); 3.18 (2H, d, ^3J = 6.7, NC$\underline{H}_2$CH=CH$_2$); 3.34 (1H, d, ^2J = 11.3, H-9*e*); 3.38 (1H, d, ^2J = 10.5, H-6*e*); 3.48 (1H, d, ^2J = 10.5, H-8*e*); 3.80 (1H, d, ^2J = 12.1, H-4*e*); 4.07 (1H, d, ^2J = 12.1, H-4*a*); 4.65 (1H, d, ^2J = 10.2) and 4.84 (1H, d, ^2J = 10.2, NC$\underline{H}_2$OH); 5.19 (1H, d, ^3J = 10.5) and 5.24 (1H, d, ^3J = 17.2, NCH$_2$CH=C$\underline{H}_2$); 5.75 (1H, ddt, ^3J = 17.2, ^3J = 10.5, ^3J = 6.7, NCH$_2$C$\underline{H}$=CH$_2$). ^{13}C NMR spectrum, δ, ppm: 34.5 (C-9); 50.9 (C-4); 55.0 (C-8); 58.6 (N$\underline{C}$H$_2$CH=CH$_2$); 60.4 (C-6); 68.8 (N$\underline{C}$H$_2$OH); 81.3 (C-5); 87.0 (C-1); 118.7 (NCH$_2$CH=$\underline{C}$H$_2$); 133.8 (NCH$_2\underline{C}$H=CH$_2$); 162.9 (C-2). Found, %: C 44.06; H 5.34; N 18.68. $C_{11}H_{16}N_4O_6$. Calculated, %: C 44.00; H 5.37; N 18.66.

7-Benzyl-3-(hydroxymethyl)-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonan-2-one (4l). Yield 1.07 g (61%), mp 154-155°C, R_f 0.44. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.67 (1H, d, ^2J = 10.5, H-6*a*); 2.77 (1H, d, ^2J = 10.5, H-8*a*); 2.97 (1H, d, ^2J = 11.3, H-9*a*); 3.33 (1H, d, ^2J = 11.3, H-9*e*); 3.38 (1H, d, ^2J = 10.5, H-6*e*); 3.47 (1H, d, ^2J = 10.5, H-8*e*); 3.71 (1H, d, ^2J = 13.7) and 3.76 (1H, d, ^2J = 13.7, NC$\underline{H}_2$Ph); 3.79 (1H, d, ^2J = 12.1, H-4*e*); 4.07 (1H, d, ^2J = 12.1, H-4*a*); 4.63 (1H, d, ^2J = 10.2) and 4.98 (1H, d, ^2J 10.2, NC$\underline{H}_2$OH); 7.26-7.35 (5H, m, H Ph). Found, %: C 51.41; H 5.21; N 15.92. $C_{15}H_{18}N_4O_6$. Calculated, %: C 51.43; H 5.18; N 15.99.

X-Ray structural investigation of compound 3a was carried out on a Bruker Apex II automatic diffractometer (graphite monochromator, λ(MoKα) 0.71073 Å, ω-scanning). A well-formed crystal having the shape of a trigonal pyramid was chosen for carrying out the investigation. The colorless crystals ($C_8H_{12}N_4O_5$, *M* 244.22); at 100 K it was monoclinic, space group $P2_1/n$; *a* 7.6100(4), *b* 9.7784(6), *c* 13.8124(9) Å; β 92.540(1)°; *V* 1026.8(1) Å^3; *Z* 4 (*Z*' 1); d_{calc} 1.580 g/cm^3. In a series of three scannings 13179 reflections were selected. An empirical calculation of the absorption and correlation of systematic errors was carried out with the SADABS program. The structure was solved by the direct method and refined with the full-matrix least-squares method on F^2_{hkl} with anisotropic thermal parameters for all the non-hydrogen atoms. The position of the hydrogen atom on the amino group was found from a Fourier difference synthesis, the positions of hydrogen atoms on carbon atoms were calculated. All the hydrogen atoms were refined by the "rider" model. Final probability factors were R_1 0.0311, wR_2 0.0698, *GOOF* 1.005 for 2769 independent reflections with $I > 2\sigma(I)$ and $5.1 < 2\theta < 60^o$. The deciphering and refinement were carried out using the SHELX set of programs version 2009-9.13 [9]. The complete crystallographic information on compound **3a** has been deposited at the Cambridge Crystallographic Data Center (deposit CCDC 903890).

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REFERENCES

1. N. S. Zefirov and S. V. Rogozina, *Usp. Khim.*, **42**, 423 (1973).

2. V. Kogel, T. Christoph, E. Frederichs, N.-N. Hennies, T. Matthiesen, J. Schneider, and U. Holzgrabe, *CNS Drug Rev.*, **4**, 54 (1998).
3. N. N. Yarmukhamedov, N. Z. Baibulatova, V. A. Dokichev, Yu. V. Tomilov, and M. S. Yunusov, *Izv. Akad. Nauk*, *Ser. Khim.*, **4**, 721 (2001).
4. R. Jejaraman and S. Avila, *Chem. Rev.*, **81**, 149 (1981).
5. I. E. Yakunina, I. V. Shahkeldyan, Yu. M. Atroshchenko, A. S. Rybakova, N. A. Troitskii, and E. V. Shuvalova, *Zh. Org. Khim.*, **41**, 1259 (2005).
6. I. E. Yakunina, I. V. Shahkeldyan, Yu. M. Atroshchenko, O. Ya. Borbulevich, V. V. Nesterov, M. V. Kopyshev, N. A. Troitskii, Yu. M. Efremov, E. N. Alifanova, and V. A. Subbotin, *Zh. Org. Khim.*, **40**, 266 (2004).
7. U. Eisner and J. Kuthan, *Chem. Rev*., **72,** 5 (1972).
8. R. P. Lastovskii (editor), *Methods of Obtaining Chemical Reagents and Preparations* [in Russian], sec. 23, NIITEKhIM, Moscow (1971), p. 150.
9. G. M. Sheldrick, *Acta Crystallogr*., *Sect. A: Found. Crystallogr.*, **A64**, 112 (2007).