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3-Azabicyclo[3.3.1]nonane Derivatives: IX.* Synthesis and Molecular Structure of 3-Azabicyclo[3.3.1]nonane-1,5-diamines in Solution and in Solid State

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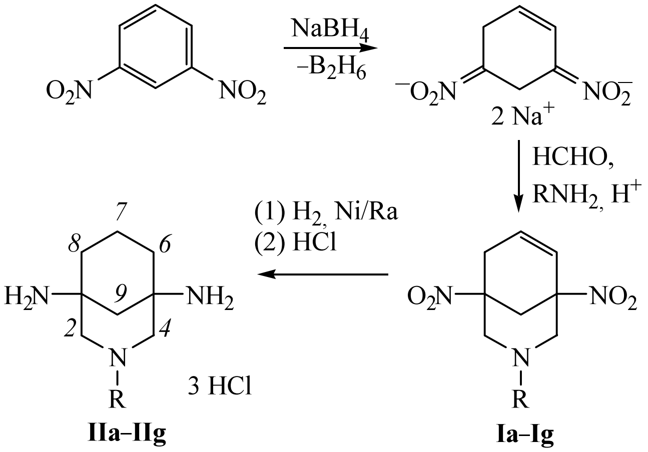
Abstract—During catalytic reduction with hydrogen on nickel of a series of 3-substituted 1,5-dinitro-3-azabicyclo-[3.3.1]non-6-enes alongside nitro groups reduction occurred also hydrogenation of the double bond. New diamines of the 3-azabicyclo[3.3.1]nonane series were synthesized, and their structure was established by means of IR, ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction study.

Heteroanalogs of bicyclo[3.3.1]nonane possess a variety of unique properties. Aza derivatives of bicyclo[3.3.1]nonane are convenient models for investigating conformational analysis problems, mechanisms of reactions and stereochemistry, transfer of electronic effects [2], and they also are applied as physiologically active substances [3]. One nontrivial way of 3-azabicyclo[3.3.1]nonanes preparation is selective reduction of aromatic dinitro compounds with alkali metal complex hydrides to provide cycloaliphatic dinitro compounds that then are used as a CH-acid component in the Mannich reaction with formaldehyde and primary amines [4–9]. 1,5-Dinitro-3-azabicyclo[3.3.1]non-6-enes thus obtained can be used for preparation of bicyclic amines, aminoalcohols, aminocarboxylic acids, and their derivatives, promising synthons for organic synthesis. The aim of this work was development of a preparation method for 3-azabicyclo[3.3.1]nonane-1,5-diamines by catalytic reduction with hydrogen in the presence of nickel of corresponding dinitro compounds **Ia–Ig** that we had synthesized before [6, 8] from 1,3-dinitrobenzene. Raney nickel catalyst is widely used for reduction of cycloaliphatic and unsaturated nitro compounds [10, 11].



R = Me (**a**), Et (**b**), CH$_2$Ph (**c**), (CH$_2$)$_2$ OH (**d**), CH(C$_2$H$_5$)CH$_2$OH (**e**), CH$_2$CO$_2$H (**f**), (CH$_2$)$_2$CO$_2$H (**g**).

The formerly performed reduction of 3-methyl-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]nonane with tributyltin hydride SnBu$_3$H afforded a mixture of isomeric nitrohydroxylamines in 9–12% yield [12]. We did not find any published data on catalytic hydrogenation of nitro derivatives of 3-azabicyclo[3.3.1]nonane. Preliminary results of our studies were published earlier [13, 14]. Already after completion of this research appeared a

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* For Communication VIII see [1].

Table 1. Characteristics of decomposition stages (*1–3*) of compounds **IIa–g** studied by thermogravimetry under dynamic conditions

Compd. no.	*1*		*2*		*3*	
	T, °C	Δ*m*, %	*T*, °C	Δ*m*, %	*T*, °C	Δ*m*, %
IIa	262–312	12.2	323–353	42.2	360–380	68.9
Iib	252–285	12.5	300–320	22.3	330–392	74
IIc	261–297	12.7	330–360	42.6	375–385	70.5
IId	275–289	11.2	310–340	29.2	340–367	60.7
IIe	205–242	12.4	268–290	35.2	290–308	57.2
IIf	213–239	48.2	350–422	72.4	–	–
IIg	238–268	18	313–345	65	–	–

publication [15] treating a reduction of 2-(1,5-dinitro-3-azabicyclo[3.3.1]non-6-en-3-yl)-1-ethanol **Id** where was demonstrated that the hydrogenation of nitro compound **Id** by hydrogen in the presence of Raney nickel or palladium on carbon resulted in 2-(1,5-diamino-3-azabicyclo[3.3.1]non-3-yl)-1-ethanol **IId**, whereas at the use of hydrazine as reductant alongside the saturated diamine **IId** formed also unsaturated compound, 2-(1,5-diamino-3-azabicyclo[3.3.1]non-6-en-3-yl)-1-ethanol.

We carried out a reduction of 3-R-1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes **Ia–Ig** with molecular hydrogen on Raney nickel in methanol. The variation of temperature and hydrogen pressure permitted establishing of the optimal conditions of the reaction (20°C, 20 at). Compounds containing a carboxy group **If, Ig**, were hydrogenated in the presence of ammonia for the respective ammonium salts of the dinitrocarboxylic acids were better soluble in methanol and did not react with the catalyst. As a result of dinitro compounds **Ia–Ig** reduction we obtained the corresponding 3-azabicyclo[3.3.1]-nonane-1,5-diamines **IIa–g** in 65–93% yield. Compounds **IIa–IIe** are oily noncrystallizable fluids, and therefore they were isolated as hydrochlorides containing according to elemental analysis data three HCl molecules per each diamine molecule. Aminoacids **IIf, g** being intra-molecular salts are crystalline substances and were isolated in an individual state.

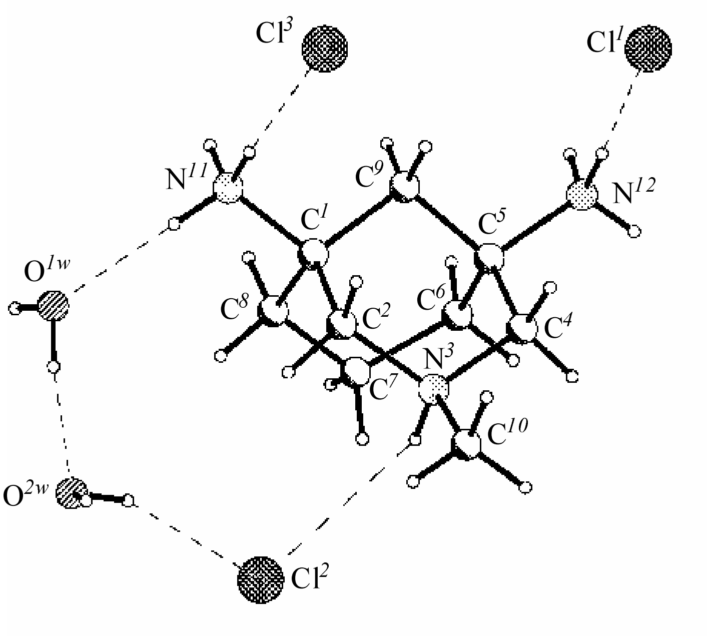
The obtained trihydrochlorides of 3-azabicyclo-[3.3.1]-nonane-1,5-diamines **IIa–e** are heat resistant compounds. By means of thermogravimetry on the curves of heating the substances three endoeffects were observed (Table 1). The two former ones in the temperature range from 200 to 360°C corresponded to the stepwise elimination of HCl molecules. The structure of obtained 3-azabicyclo[3.3.1]nonane-1,5-diamines **IIa–g** was proved by IR, ^{1}H and ^{13}C NMR spectroscopy. As the starting point in assignment of the signals in the NMR spectra was applied the simplest compound of the series **IIa**. In the ^{1}H NMR spectrum of the compound the resonance of protons of the NCH_3 group appeared as a singlet at δ 2.85 ppm. The signals of equatorial and axial protons $H^{2,4}$ were observed as two doublets (*AA*') at δ 3.65 and 3.21 ppm. Among the upfield signals in the region 1.65–2.12 ppm two doublets (δ 2.02 and 2.12 ppm) corresponded judging from the multiplicity and integral intensity (2H) to the bridging protons H^9. The chemical shifts in the ^{13}C NMR spectrum of the carbons C^{10}, C^9, and $C^{2,4}$ were unambiguously determined from the two-dimensional spectrum of the heteronuclear $^{13}C–^1H$ correlation by the cross-peaks with the corresponding protons (NCH_3, H^9, and $H^{2,4}$). The chemical shifts of the components constituting the multiplet of protons $H^{6,8}$ were determined from the cross-peaks in the HSQC spectrum with the remaining methylene carbon atoms and from their integral intensity (4H) in the ^{1}H NMR spectrum. The second multiplet from this group signals belonged to the protons H^7, and thereto corresponds a cross-peak with the respective signal of C^7 atom. A signal that had no cross-peaks in the HSQC spectrum (δ_C 51.72 ppm) originated from the quaternary carbon atoms $C^{1,5}$ linked to NH_2 groups. Inasmuch as these atoms are equivalent, and the signals in the region δ_C 120–130 ppm are lacking it is clear that the reduction of the nitro compounds under the conditions of our experiment is accompanied by hydrogenation of the C=C bond in agreement with the data of [15]. The assignment of signals in the ^{13}C NMR spectra of compounds **IIb–g** was done by analogy with compound **IIa** and also by comparison of coupling constants $^{13}C–^1H$ measured in the ^{13}C NMR spectra registered without decoupling from protons with the published value of the corresponding constants [16]. The relative location of signals corresponding to the 3-azabicyclo[3.3.1]nonane fragment did not change in the ^{1}H NMR spectra on variation of the substituents R at the nitrogen atom. The of proton signals of the substituents were easily assignable by their multiplicity and chemical shifts.

The conformation of compound **IIa** dissolved in D_2O was established by means of two-dimensional NOE spectroscopy. No cross-peaks in the NOESY spectrum corresponding to contacts between the bridging protons H^9 and protons H^7 and those of NCH_3 group shows unambiguously that compound **IIa** is present in the solution in the *chair-chair* conformation that is common for 3-azabicyclo[3.3.1]-nonane derivatives [2].

An additional confirmation of the structure of the synthesized 3-azabicyclo[3.3.1]nonane-1,5-diamines provide the data of X-ray diffraction analysis of compound **IIa** (see figure and Table 2). The molecule of compound **IIa** $[C_9H_{22}N_3]Cl_3{\cdot}2H_2O$ is composed of a cation $C_9H_{22}N_3$, three chloride anions, and two coordinat-ed water molecules. The azabicyclo[3.3.1]nonane cage-like structure of the triple-charged cation in the solid state as also in the solution possesses the *chair-chair* conformation. The atoms C^9 and N^3 deviate from the plane $C^1C^2C^4C^5$ by +0.764(1) and –0.573(1) Å respectively; the deviation of atoms C^9 and C^7 from the plane $C^1C^8C^6C^5$ amounts to +0.767(1) and –0.516(2) Å. The angle between the planar parts of the rings is equal to 114.79(6)°. The lengths of bonds C^6–C^7 [1.538(2) Å] and C^7–C^8 [1.534(2) Å] correspond to the length of an ordinary bond {for comparison, the length of the double bond C^6–C^7 in nitro compound **Ia** is 1.341(5) Å [17]}, and the lengths of the N–C bonds vary in the range 1.501(2)–1.510(2) Å characteristic of C_{sp^3}–$N_{sp^3}^+$ bonds [18].

In the crystal the cation, chloride anions, and water molecules take part in a ramified system of intermolecular hydrogen bonds N–H···O, O–H···O, N–H···Cl, O–H···Cl and contacts Cl···Cl (Table 3); therewith all hydrogen atoms of ammonium groups are involved in hydrogen bonds. The packing consists of layers parallel to the crystallographic plane (001). Part of chloride ions (Cl^1 and Cl^3) is located between $C_9H_{22}N_3$ molecules within the layer whereas the chloride anions Cl^2 and water molecules form an interlayer between (001) layers.

Thus a convenient preparative method was developed for the synthesis of diamino derivatives of the 3-azabicyclo[3.3.1]nonane series containing amino groups in the nodal positions. The structure of compounds synthesized was confirmed, and their conformation in solution and in the solid state was established.



General view of the molecule of compound $[C_9H_{22}N_3]Cl_3{\cdot}2H_2O$ (**IIa**). The dashed lines show the hydrogen bonds.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-300 [300.13 (^{1}H) and 75.47 (^{13}C) MHz] from solutions in D_2O, internal refernce TMS. IR spectra were recorded on spectrophotometer

Table 2. Some bond (*d*) and bond angles (ω) in compound $[C_9H_{22}N_3]Cl_3{\cdot}2H_2O$ (**IIa**)

Bond	*d*, Å	Bond	*d*, Å
C^1–N^{11}	1.501(2)	C^4–C^5	1.539(2)
C^1–C^9	1.532(2)	C^5–N^{12}	1.505(2)
C^1–C^8	1.534(2)	C^5–C^9	1.528(2)
C^1–C^2	1.536(2)	C^5–C^6	1.533(2)
C^2–N^3	1.501(2)	C^6–C^7	1.538(2)
N^3–C^{10}	1.505(2)	C^7–C^8	1.534(2)
N^3–C^4	1.510(2)		
Angle	ω, deg	Angle	ω, deg
$N^{11}C^1C^9$	109.20(9)	$N^{12}C^5C^9$	108.84(9)
$N^{11}C^1C^8$	107.23(9)	$N^{12}C^5C^6$	106.95(9)
$C^9C^1C^8$	110.31(9)	$C^9C^5C^6$	110.28(9)
$N^{11}C^1C^2$	105.43(9)	$N^{12}C^5C^4$	106.18(9)
$C^9C^1C^2$	109.68(9)	$C^9C^5C^4$	109.62(9)
$C^8C^1C^2$	114.74(9)	$C^6C^5C^4$	114.72(9)
$N^3C^2C^1$	112.26(9)	$C^5C^6C^7$	113.66(9)
$C^2N^3C^{10}$	109.65(9)	$C^8C^7C^6$	113.63(9)

Table 3. Parameters of hydrogen bonds and intermolecular contacts Cl–Cl in compound $[C_9H_{22}N_3]Cl_3{\cdot}2H_2O$ (**IIa**)

D–H···A[a]	*d*(D–H), Å	*d*(H···A), Å	*d*(D···A), Å	ω(DHA), deg
$N^{11}–H^{11A}\cdots O^{1W}$	0.87(2)	1.91(2)	2.766(2)	170(2)
$N^{11}–H^{11B}\cdots Cl^{3}$	0.85(2)	2.28(2)	3.124(2)	172(2)
$N^{11}–H^{11C}\cdots Cl^{1\ \#3}$	0.89(2)	2.28(2)	3.170(2)	178(2)
$N^{12}–H^{12A}\cdots Cl^{1\ \#4}$	0.85(2)	2.41(2)	3.222(2)	161(2)
$N^{12}–H^{12B}\cdots Cl^{3\ \#3}$	0.87(2)	2.45(2)	3.277(2)	161(2)
$N^{12}–H^{12C}\cdots Cl^{1}$	0.91(5)	2.24(2)	3.141(2)	179(2)
$N^{3}–H^{3N}\cdots Cl^{2}$	0.91(2)	2.73 (2)	3.403(2)	132(2)
$O^{1W}–H^{1WA}\cdots Cl^{2\ \#1}$	0.82(2)	2.35(2)	3.160(2)	169(2)
$O^{1W}–H^{1WB}\cdots O^{2W}$	0.87(2)	1.87(2)	2.733(2)	172(2)
$O^{2W}–H^{2WA}\cdots Cl^{2\ \#2}$	0.84(2)	2.36(2)	3.193(2)	170(2)
$O^{2W}–H^{2WB}\cdots Cl^{2}$	0.84(2)	2.39(2)	3.190(2)	160(3)
$Cl^{3}\cdots Cl^{3\ \#5}$			3.571(2)	

[a] Symmetry transformations to reveal equivalent atoms: #1 $-x + 1, -y, -z + 1$; #2 $-x, -y, -z + 1$; #3$-x + 1, -y + 1, -z$; #4 $-x, -y + 2, -z$; #5 $-x + 1, -y, -z$.

Specord IR-75 (from mulls in mineral oil). The decomposition temperature of compounds was measured by thermogravimetry on Q-1500 D instrument (MOM, Hungary) in a labirinth crucible in air, heating rate 1.25 deg/min in the temperature range 20–500°C, sample weight 100 mg.

The crystals of compound **IIa** were obtained by slow isothermal evaporation of the substance solution in 50% aqueous MeOH. The X-ray diffraction study of compound **IIa** was carried out on a colorless single crystal of crystal habit 0.70×0.50×0.40 mm. At 300 K crystals of the composition $[C_9H_{22}N_3]Cl_3{\cdot}2H_2O$ triclinic: *a* 8.024(4), *b* 8.241(4), *c* 12.949(7) Å, α 72.80(4), β 80.72(4), γ 67.96(4)°, *V* 757.0(7) Å^3, d_{calc} 1.381 g cm^{-3}, absorption factor μ 0.602 mm^{-1}, space group $P\bar{1}$, *Z* 2. Intensities of 4438 independent reflections (R_{int} 0.018) were measured on a four-circle automatic diffractometer Siemens P3/PC (MoK_α-radiation, Å 0.71093 , graphite monochromator, θ/2θ scanning, $2\theta_{max}$ 60°).

The structure was solved by the direct method with the use of a software package SHELXTL PLUS 5.0 [19]. The nonhydrogen atoms were refined by the full-matrix least-squares method (along F^2) in anisotropic approximation. The positions of hydrogen atoms were revealed from the difference Fourier synthesis and were refined in isotropic approximation, the O–H bond length in the water molecules was fixed at 0.89(2) Å. The final values of divergence factors $R_1(F)$ 0.031 for 4018 reflections with $I > 2\sigma(I)$, $wR_2(F^2)$ 0.095, and GOOF 1.09 using all independent reflections involved into the final stage of refinement. The atoms coordinates are deposited into the Cambridge Structural Database. The main bond lengths and bond angles of compound **IIa** are listed in Table 2.

The initial 1,5-dinitro-3-azabicyclo[3.3.1]non-6- enes **Ia–g** were prepared by procedures we had described before [6, 8].

Hydrogenation of 1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes (Ia–g). A mixture of 3 mmol of nitro compound, 20 ml of CH_3OH. and 0.5 g of Raney nickel was charged into a cylindrical laboratory pressure reactor (*V* 150 cm^3) of stainless nonmagnetic steel equipped with a jacket connected to a thermostat. The stirrer was magnetically operated. The hydrogenation was carried out at room temperature and initial hydrogen pressure 20 at till the end of hydrogen consumption. On completion of the process the catalyst was separated and washed with a little of methanol. The filtrate was added dropwise to a concn. HCl solution. The separated precipitate of the diamine hydrochloride was filtered off, and on evaporation of the mother liquor additional amount of the product was isolated

The hydrogenation of nitrocarboxylic acids **If, Ig** was carried out in methanol saturated with ammonia to avoid dissolution of the catalyst. The obtained diamines **IIf, IIg** were isolated as bases by adding to the filtrate after separating the catalyst of 2 ml of water followed by evaporating the solution on a rotary evaporator at 60°C.

The reaction products were recrystallized from methanol and dried in a vacuum-desiccator at 50°C till constant weight.

3-Methyl-3-azabicyclo[3.3.1]nonane-1,5-biamine trihydrochloride (IIa). Yield 65%. Colorless crystals. IR spectrum, cm^{-1}: 2400–3000 br.s (ν NH_3^+), 1610 (δ NH_3^+). ^{1}H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 1.65 m (2H, H_a^6, H_a^8), 1.76 m (1H, H_a^7), 1.87 m (1H, H_e^7), 1.94 δ (2H, H_e^6, H_e^8, 12.0), 2.02 δ (1H, H_a^9, 11.85), 2.12 δ (1H, H_e^9, 11.85), 2.85 s (3H, NMe), 3.21 δ (2H, H_a^2, H_a^4, 13), 3.65 d (2H, H_e^2, H_a^4, 13.0). ^{13}C NMR spectrum (D_2O), δ, ppm: 17.39 (C^7), 30.93 ($C^{6,8}$), 36.45 (C^9), 45.99 (NMe), 51.72 ($C^{1,5}$), 56.63 ($C^{2,4}$). Found, %: C 38.84; H 8.04; Cl 38.02; N 14.91. $C_9H_{19}N_3{\cdot}3HCl$. Calculated, %: C 38.79; H 7.9; Cl 38.24; N 15.08.

3-Ethyl-3-azabicyclo[3.3.1]nonane-1,5-diamine trihydrochloride (IIb). Yield 85%. Colorless crystals.

IR spectrum, cm^{-1}: 2410–3000 br.s (ν NH_3^+), 1610 (δ NH_3^+). ^1H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 1.31 t (3H, $NCH_2C\underline{H}_3$, 8.1), 1.84 m (2H, H_a^6, H_a^8), 1.91 m (1H, H_a^7), 2.04 m (1H, H_e^7), 2.10 δ (2H, H_e^6, H_e^8, 13.7), 2.15 δ (1H, H_a^9, 13.1), 2.30 δ (1H, H_e^9, 13.1), 3.33 q (2H, $NC\underline{H}_2CH_3$, 8.1), 3.35 δ (2H, H_a^2, H_a^4, 11.9), 3.71 δ (2H, H_e^2, H_e^4, 11.9). ^{13}C NMR spectrum (D_2O), δ, ppm: 11.39 ($NCH_2\underline{C}H_3$), 19.82 (C^7), 33.95 ($C^{6,8}$), 38.77 (C^9), 54.32 ($C^{1,5}$), 56.93 ($C^{2,4}$), 58.68 ($N\underline{C}H_2CH_3$). Found, %: C 41.38; H 8.77; Cl 36.90; N 14.44. $C_{10}H_{21}N_3 \cdot 3HCl$. Calculated, %: C 41.03; H 8.21; Cl 36.41; N 14.36.

3-Benzyl-3-azabicyclo[3.3.1]nonane-1,5-biamine trihydrochloride (IIc). Yield 70%. Colorless crystals. IR spectrum, cm^{-1}: 3105 (ν CH_{arom}), 2400–3000 br.s (ν NH_3^+), 1610 (δ NH_3^+). ^1H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 1.76 m (2H, H_a^7, H_e^7), 2.02 m (4H, H_a^6, H_e^6, H_a^8, H_e^8), 2.10 δ (1H, H_a^9, 12.5), 2.23 δ (1H, H_e^9, 12.5), 3.28 δ (2H, H_a^2, H_a^4, 12.2), 3.53 δ (2H, H_e^2, H_e^4, 12.2), 4.33 br.s (2H, $NC\underline{H}_2Ph$), 7.47 m (5H, Ph). ^{13}C NMR spectrum (D_2O), δ, ppm: 18.04 (C^7), 32.11 ($C^{6,8}$), 36.97 (C^9), 52.37 ($C^{1,5}$), 55.28 ($C^{2,4}$), 62.45 ($N\underline{C}H_2Ph$), 128.81, 129.60, 130.66, 131.72 (Ph). Found, %: C 49.85; H 7.46; Cl 29.92; N 11.92. $C_{15}H_{23}N_3 \cdot 3HCl$. Calculated, %: C 50.78; H 7.33; Cl 30.04; N 11.85.

2-(1,5-Diamino-3-azabicyclo[3.3.1]nonan-3-yl)-1-ethanol trihydrochloride (IId). Yield 75%. Colorless crystalls. IR spectrum, cm^{-1}: 3360 (ν OH), 2350–3000 br.s (ν NH_3^+), 1610 (δ NH_3^+). ^1H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 1.81 m (2H, H_a^7, H_e^7), 2.09 m (4H, H_a^6, H_e^6, H_a^8, H_e^8), 2.14 d (1H, H_a^9, 12.5), 2.26 d (1H, H_a^9 12.5), 3.22 t (2H, $NC\underline{H}_2CH_2OH$, 5.3), 3.25 δ (2H, H_a^2, H_a^4, 11.6), 3.60 δ (2H, H_e^2, H_e^4, 11.6), 3.88 t (2H, $NCH_2C\underline{H}_2OH$, 5.3). ^{13}C NMR spectrum (D_2O), δ, ppm: 20.20 (C^7), 34.17 ($C^{6,8}$), 38.91 (C^9), 54.45 ($C^{1,5}$), 57.78 ($C^{2,4}$), 58.04 ($N\underline{C}H_2CH_2OH$), 62.89 ($NCH_2\underline{C}H_2OH$). Found, %: C 38.72; H 8.01; Cl 34.56; N 13.4. $C_{10}H_{21}N_3O \cdot 3HCl$. Calculated, %: C 38.9; H 7.78; Cl 34.12; N 13.61.

2-(1,5-Diamino-3-azabicyclo-[3.3.1]nonane-3-yl)-1-butanol trihydrochloride (IId). Yield 65%. Colorless crystals. IR spectrum, cm^{-1}: 3350 (ν OH), 2300–3000 br.s (ν NH_3^+), 1620 (δ NH_3^+). ^1H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 0.92 δ.δ [1H, $NCH(CH_2C\underline{H}_3)CH_2OH$, 12.6, 5.6], 1.63 and 1.90 m [on 1H, $NCH(C\underline{H}_2CH_3)CH_2OH$], 1.84 μ (2H, $H_a{}^6$, $H_a{}^8$), 1.87 μ (1H, $H_a{}^7$), 2.05 m (1H, $H_e{}^7$), 2.12 μ (2H, $H_e{}^6$, $H_e{}^8$), 2.14 d (1H, H_a^9, 11.6), 2.38 d (1H, H_e^9, 11.6), 3.44 d (2H, H_a^2, H_a^4, 11.2), 3.51 m [1H, $NC\underline{H}(CH_2CH_3)CH_2OH$], 3.59 δ (2H, H_e^2, H_e^4, 11.2), 3.75 and 3.98 d.t [1H, $NCH(CH_2CH_3)C\underline{H}_2OH$, 14.1, 5.4]. ^{13}C NMR spectrum (D_2O), δ, ppm: 9.59 [$NCH(CH_2\underline{C}H_3)CH_2OH$], 17.66 ($C^7$), 31.38 ($C^{6,8}$), 36.12 ($C^9$), 51.21 [$NCH \cdot (\underline{C}H_2CH_3)CH_2OH$], 51.59 ($C^{1,5}$), 52.52 [$N\underline{C}H(CH_2CH_3) \cdot CH_2OH$], 56.99 ($C^{2,4}$), 69.96 [$NCH(C_2H_5)\underline{C}H_2OH$]. Found, %: C 42.31; H 8.37; Cl 31.12; N 12.29. $C_{12}H_{25}N_3O \cdot 3HCl$. Calculated, %: C 42.79; H 8.32; Cl 31.65; N 12.48.

(1,5-Diamine-3-azabicyclo[3.3.1]nonan-3-yl)-ethanoic acid (IIe). Yield 72%. Colorless crystals. IR spectrum, cm^{-1}: 3300 (ν OH), 2400–3000 br.s (ν $NH_3{}^+$), 1725 (ν C=O), 1610 (δ $NH_3{}^+$). ^1H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 1.41 μ (1H, H_a^7), 1.47 d.d (2H, H_a^6, H_a^8, 12.5, 5.5), 1.50 δ (1H, H_a^9, 10.4), 1.62 δ (1H, H_e^9, 10.4), 1.81 d.d (2H, H_e^6, H_e^8, 12.5, 5.5), 2.11 δ (2H, H_a^2, H_a^4, 10.1), 2.64 m (1H, $H_e{}^7$), 2.86 d (2H, H_e^2, H_e^4, 10.1), 3.26 br.s (2H, $NC\underline{H}_2COOH$). ^{13}C NMR spectrum (D_2O), δ, ppm: 19.75 (C^7), 34.55 ($C^{6,8}$), 43.95 (C^9), 51.27 ($C^{1,5}$), 61.19 ($C^{2,4}$), 61.94 ($N\underline{C}H_2COOH$), 178.09 (COOH). Found, %: C 56.18; H 9.3; N 19.32. $C_{10}H_{19}N_3O_2$. Calculated, %: C 56.34; H 8.92; N 19.42.

3-(1,5-Diamine-3-azabicyclo[3.3.1]nonan-3-yl) propanoic acid (IIg). Yield 82%. Colorless crystals. IR spectrum, cm^{-1}: 3300 (ν OH), 2400–3000 br.s (ν NH_3^+), 1726 (ν C=O), 1610 (δ $NH_3{}^+$). ^1H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 1.40 m (1H, $H_a{}^7$), 1.45 d.d (2H, H_a^6, H_a^8, 10.9, 6.0), 1.49 d (1H, H_a^9, 11.5), 1.60 d (1H, H_e^9, 11.5), 1.77 d.d (2H, H_e^6, H_e^8, 10.9, 6.0), 2.05 d (2H, H_a^2, H_a^4, 10.2), 2.29 t (2H, $NCH_2C\underline{H}_2COOH$, 6.4), 2.46 m (1H, $H_e{}^7$), 2.54 t (2H, $NC\underline{H}_2CH_2COOH$, 6.4), 2.93 d (2H, H_e^2, H_e^4, 10.2). ^{13}C NMR spectrum (D_2O), δ, ppm: 19.04 (C^7), 30.60 ($C^{6,8}$), 32.36 ($NCH_2\underline{C}H_2COOH$), 38.93 ($C^9$), 54.93 ($C^{1,5}$), 55.70 ($C^{2,4}$), 57.51 ($N\underline{C}H_2CH_2COOH$), 176.58 (COOH). Found, %: C 58.62; H 9.0; N 19.16. $C_{11}H_{21}N_3O_2$. Calculated, %: C 58.15; H 9.25; N 18.5.

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