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Synthesis and Structure of Derivatives of 9-(2-Oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicylo[3.3.1]non-7-en-6-ones

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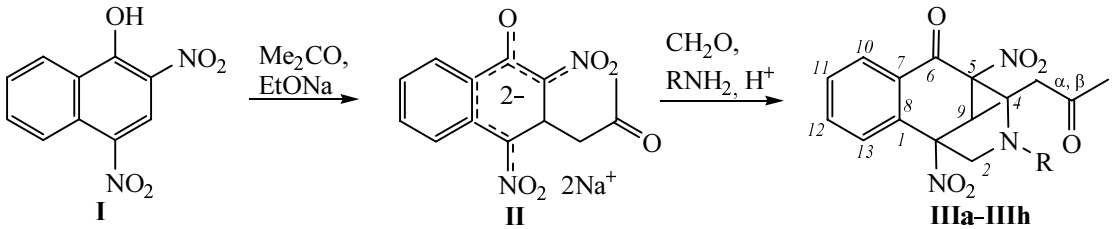
Abstract—A number of 3-R-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azsbicyclo[3.3.1]non-7-en-6-ones was synthesized by Mannich reaction involving Yanovsky adduct of 2,4-dinitronaphthol. It was established by molecular spectroscopy and X-ray diffraction analysis that the piperidine ring in these compounds was in the *chair* conformation with a diequatorial position of the substituent attached to the heteroatom and 2-oxo-propyl group, and the cyclohexenone fragment was in *sofa* form. By an example of 3-methyl-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azsbicyclo[3.3.1]non-7-en-6-one the dissociative ionization of bicyclononanes under the electron impact was investigated.

This study was carried out in extension of research aimed at preparation of 3-azabicyclo[3.3.1]nonanes by aminoalkylation of anionic adducts of 1,3-dinitrobenzene derivatives [1–4]. 3-Azabicyclo[3.3.1]nonane fragment is present in the structure of many natural alkaloids [5] and therefore the studies on the synthesis and properties of this class compounds are urgent. A procedure for preparation of 3-azabicyclo[3.3.1]nonanes was formerly developed [6] based on Mannich condensation of formaldehyde and primary amines with Yanovsky adduct of 2,4-dinitrophenol An extension of the reaction to other dinitrohydroxyaromatic systems, in particular, to 2,4-dinitronaphthol, would permit preparation of biologically active substances with elevated solubility in media of low polarity and thus would enable the compounds to transit through lipid membranes of cells.

The synthesis of heterocyclic compounds from 2,4-dinitronaphthol **I** was performed in two stages (Scheme 1). In the first stage disodium salt of Yanovsky σ-adduct **II** was obtained by treating with sodium ethoxide an acetone solution of 2,4-dinitronaphthol. The anionic intermediate **II** was isolated from the reaction mixture in an individual state, but because of its high lability it was at once used in further reactions.

In the second stage of the reaction the obtained disodium salt **II** was introduced into an aminomethylating mixture consisting of formaldehyde and an appropriate amine hydrochloride. On acidifying the reaction mixture with orthophosphoric acid azabicyclononanes **IIIa–IIIh** separate as crystalline precipitates. The characteristics of compounds obtained and the results of elemental analyses are compiled in Table 1. At the use in

Scheme 1.



I **II** **IIIa–IIIh**

R = Me (**a**), Et (**b**), Bu (**c**), $(CH_2)_2OH$ (**d**), $(CH_2)_2Br$ (**e**), CH_2CO_2H (**f**), $(CH_2)_2CO_2H$ (**g**), Bz (**h**).

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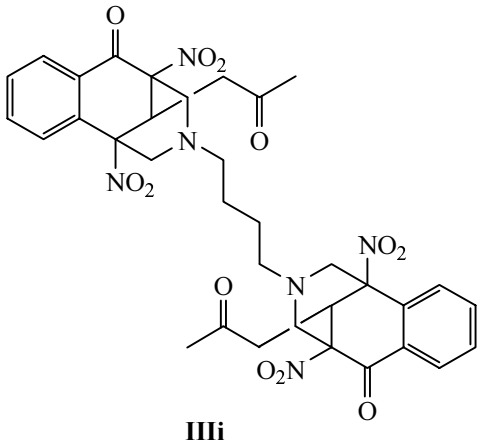
Table 1. Yields, melting points, retention factors, IR spectra, and elemental analyses of 3-R-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-ones (**IIIa–i**)

Compd. no.	Yield, %	mp, °C	R_f	IR spectra, ν, cm^{-1}			Found, %			Formula	Calculated, %		
				C=C	C=O	NO_2	C	H	N		C	H	N
IIIa	46	186–188 (C decomp.)	0.57	1601	1689, 1710	1335, 1375, 1543	55.73, 55.63	5.02, 4.90	12.19, 11.78	$C_{16}H_{17}N_3O_6$	55.33	4.90	12.10
IIIb	57	173–174 (C decomp.)	0.62	1600	1711, 1725	1337, 1362, ,1544	56.69, 56.93	5.35, 5.39	11.84, 12.01	$C_{17}H_{19}N_3O_6$	56.51	5.26	11.63
IIIc	53	126–127 (C decomp.)	0.68	1593	1687, 1712	1331 1352, 1537	58.69, 58.67	5.43, 5.60	10.74, 10.81	$C_{19}H_{23}N_3O_6$	58.61	5.91	10.80
IIId[a]	50	162–163	0.19	1587	1695, 1710	1325, 1350, 1551	54.74, 54.72	5.12, 5.08	11.10, 11.12	$C_{17}H_{19}N_3O_7$	54.11	5.04	11.14
IIIe[b]	63	165–166	0.59	1588	1697, 1715	1332, 1351,1549	46.61, 46.27	4.14, 4.02	9.48, 9.40	$_{17}H_{18}BrN_3O_6$	46.36	4.09	9.54
IIIf[c]	44	202–203 (C decomp.)	0.14	1601	1708, 1726	1336, 1548, 1363	52.12, 51.85	4.27, 4.11	10.64, 10.81	$C_{17}H_{17}N_3O_8$	52.17	4.35	10.74
IIIg[c]	30	204–205	0.18	1590	1710, 1737	1335, 1543, 1350	53.55, 53.60	4.91, 5.18	10.34, 10.56	$C_{18}H_{19}N_3O_8$	53.33	4.69	10.37
IIIh	54	136–137	0.73	1611	1700,1710	1345, 1365, 1570	62.98, 63.17	5.22, 5.16	12.61, 12.31	$C_{22}H_{21}N_3O_6$	62.41	4.96	9.93
IIIi	29	220–221	0.60	1600	1700, 1725	1340, 1361, 1541	55.92, 56.45	4.87, 4.81	11.83, 11.65	$C_{34}H_{36}N_6O_{12}$	56.66	5.00	11.66

[a] ν(OH) 3537–3425 cm^{-1}. [b] Found, %: Br 18.25, 18.32. Calculated, %: Br 18.18. [c] ν(OH) 3580–2825 cm^{-1}.

condensation of 1,4-butanediamine dimer **IIIi** was obtained.



IIIi

Compounds synthesized were studied using IR and NMR spectroscopy, mass spectrometry, and X-ray diffraction analysis (Tables 1 and 2). The results obtained are discussed by an example of 3-methyl-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-one (**IIIa**).

In the IR spectrum of the compound in question is observed a broad band of the stretching vibrations of C=O bond that is split in two maxima due to the presence in the molecule of two nonequivalent carbonyl groups (Table 1). Therewith the component at lower frequency (1689 cm^{-1}) corresponds to the absorption of the cyclic carbonyl conjugated with the fused aromatic ring [7]. The strong bands at при 1543, 1375, and 1335 cm^{-1} belong to symmetric and antisymmetric nitro groups vibrations, and the C=C bond is revealed by the absorption at 1601 cm^{-1}.

More compelling proof of the structure of compound synthesized was obtained by NMR spectroscopy. In the ^{1}H NMR spectrum of 3-methyl-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-one (**IIIa**) in the downfield region (δ 7.45–8.05 ppm) two doublets and two triplets (^3J 7.93 Hz) from four protons of the fused ring were observed (Table 2). The doublet resonance of the H^{10} proton is the most downfield signal (δ 8.05 ppm) because of the anisotropic effect of the C=O bond in the *peri*-position. The assignment of signals from the other aromatic protons is based on their multiplicity. Each component of the doublet belonging to proton H^{10} and to triplet from proton H^{12} is additionally split (^4J 1.49 Hz). The chemical shifts in the ^{13}C NMR spec-

Table 2. Data of ^{1}H NMR spectra of 3-R-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-ones (**IIIa–i**) (DMSO-d_6–CCl_4, 1:3), δ, ppm (*J*, Hz)

Compd. no.	H arom				Piperidine ring					Oxopropyl[a]		R
	H^{10}	H^{11}	H^{12}	H^{13}	H^{9}	H_e^4	H_a^4	H_a^2	H_e^2	H^{α}	H^{β}	
IIIa	8.05 d.d (7.94, 1.49)	7.66 t (7.93)	7.82 t.d (7.93, 1.49)	7.45 d (7.93)	3.95 d.d (5.50, 3.66)	3.45 d.d (10.98, 1.22)	3.19 d (10.98)	3.31 d (10.98)	3.21 d.d (10.98, 1.22)	2.87 d.d (19.23, 5.49)	2.73 d.d (19.23, 3.66)	2.22 s
IIIb	8.04 d.d (7.93, 1.41)	7.66 t (7.93)	7.82 t (7.93, 1.41)	7.46 d (7.93)	3.97 d.d (5.50, 3.05)	3.50 d.d (10.38, 1.22)	3.24 d (10.38)	3.37 d (10.99)	3.26 d.d (10.99, 1.22)	2.86 d.d (19.53, 5.50)	2.72 d.d (19.53, 3.06)	2.45 q (7.02), 0.76 t (7.02)
IIIc	8.04 d.d (7.93, 1.42)	7.65 t (7.93)	7.81 t.d (7.93, 1.42)	7.46 d (7.93)	3.97 d.d (5.49, 3.66)	3.49 d.d (10.98, 1.22)	3.25 d (10.98)	3.35 d (10.98)	3.23 d.d (10.98, 1.22)	2.88 d.d (19.53, 5.49)	2.73 d.d (19.53, 3.66)	2.34 m, 1.12 m, 0.74 m, 0.56 t (7.32)
IIId	8.05 d.d (7.93, 1.42)	7.66 t (7.93)	7.82 t.d (7.93, 1.42)	7.45 d (7.93)	3.95 d.d (5.49, 3.66)	3.64 d.d (10.99, 1.22)	3.4 d (10.99)	3.54 d (10.99)	3.3 d.d (10.99, 1.22)	2.85 d.d (18.92, 5.49)	2.73 d.d (18.92, 3.66)	3.24 m, 3.10 m
IIIe	8.04 d.d (7.93, 1.4)	7.65 t (7.93)	7.82 t.d (7.93, 1.4)	7.45 d (7.94)	3.97 d.d (5.50, 3.66)	3.63 d.d (10.98, 1.22)	3.43 d (10.98)	3.56 d (10.99)	3.36 d.d (10.99, 1.22)	2.90 d.d (19.23, 5.50)	2.73 d.d (19.23, 3.66)	3.23 m, 2.80 m
IIIf	8.05 br.d (7.93)	7.66 t (7.93)	7.82 br.t (7.93)	7.45 d (7.93)	3.92 d.d (5.50, 3.66)	3.76 d.d (10.99, 1.22)	3.59 d (10.99)	3.67 d (10.99)	3.36 d.d (10.99, 1.22)	2.90 d.d (19.53, 5.49)	2.74 d.d (19.53, 3.66)	12.29 br.s, 3.29 d (17.37), 3.18 d (17.37)
IIIg	8.09 br.d (7.33)	7.66 t (7.33)	7.80 br.t (7.33)	7.44 d (7.33)	4.03 d.d (5.5, 3.66)	3.58 d.d (10.98, 1.22)	3.38 d (10.98)	3.50 d (10.98)	3.2 d.d (10.98, 1.22)	2.89 d.d (19.23, 5.5)	2.75 d.d (19.23, 3.06)	11.5 br.s, 2.74 m, 2.15 m
IIIh	8.22 br.d (7.33)	7.52 t (7.33)	7.83 br.t (7.33)	7.37 d (7.33)	4.10 d.d (5.5, 3.66)	3.6 br.d (10.38)	3.19 d (10.38)	3.46 d (11.3)	3.41 br.d (11.3)	2.97 d.d (19.23, 4.88)	2.82 d.d (19.23, 2.75)	7.14 m, 6.69 d (6.71), 3.73 d (14.03), 3.64 d (14.03)
IIIi	7.99 br.d (7.33)	7.64 t (7.33)	7.82 br.t (7.33)	7.45 d (7.33)	3.93 d.d (5.49, 3.66)	3.35 br.d (10.38)	3.01 d (10.38)	3.21 d (10.38)	3.12 br.d (10.38)	2.79 d.d.d (18.92, 6.11, 3.06)	2.70 d.d (18.92, 3.66)	3.30 m, 0.49 m

[a] δ(COMe) 2.00–2.09 ppm.

trum belonging to the carbons of the benzene ring [δ 126.3 (C^{13}), 126.5 (C^{10}), 129.5 (C^{11}) и 135.3 (C^{12}) ppm] were unambiguously assigned with the use of two-dimensional spectrum of heteronuclear ^{13}C–^1H correlation HSQC from the cross-peaks with the corresponding protons H^{10}–H^{13}. The signals at δ 131.9 and 136.7 ppm that have no correlation peaks in the HSQC spectrum of compound **IIIa** belong to the quaternary carbon atoms C^7 and C^8 respectively. These signals were distinguished with the help of coupling constants $^3J(H^{11}, C^7)$, (H^{13}, C^7), (H^{10}, C^8) and (H^{12}, C^8) revealed through the corresponding correlation peaks in the HMBC spectrum. The downfield position of signals at δ 186.8 and 203.4 ppm in the ^{13}C NMR spectrum suggests that the peaks correspond to the carbon atoms of two carbonyl groups. In the HMBC spectrum the signal at δ 186.8 ppm has cross-peaks due to coupling through three bonds with protons H^4, H^9, H^{10}, and therefore it corresponds to C^6 carbon of the endocyclic carbonyl.

The assignment of signals of alicyclic protons from the piperidine ring was done taking into consideration the published data [8] indicating that the majority of heterocyclic derivatives of bicyclo[3.3.1]nonanes existed in the *chair-chair* conformation. The signals of the

bridging proton H^9 and of methylene protons from the 2-oxopropyl group form in the ^1H NMR spectrum of compound **IIIa** an *ABX* system. The resonance of H^9 proton appears as a doublet of doublets (^3J 5.5, 3.66 Hz) at δ 3.95 ppm, and the *AB* part consists of two doublets of doublets (^2J 19.23, ^3J 5.5, 3.66 Hz) from two diastereotopic protons $H^{\alpha,\beta}$ of CH_2 group at δ 2.87 and 2.73 ppm The equatorial and axial protons H^2 and H^4 appear as doublets (^2J ~11 Hz) in the region δ 3.2–3.5 ppm; therewith the doublets of the equatorial protons are additionally split into doublets with an allylic coupling constant ^4J 1.22 Hz. Two upfield singlets at δ 2.01 and 2.22 ppm belong to the protons of COMe and NMe groups (Table 2). In the ^{13}C NMR spectrum of compound **IIIa** the quaternary carbons C^1 and C^5 attached to electron-withdrawing NO_2 groups appear as peaks at δ 91.08 and 92.41 ppm These signals were distinguished by the correlation peaks H^4/C^5 and H^2/C^1 in the HMBC spectrum. The signals of carbons neighboring to the heteroatom C^2, C^4 , and of NMe group are observed at δ 61.04, 60.01 and 43.92 ppm and are readily assigned by the intense cross-peaks of the corresponding couplings through one bond in HSQC spectrum. The signal at δ 43.54 ppm corresponds to the bridging atom C^9, and to the carbon atoms of the methylene and methyl groups from the acetone rest belong the signals at δ 41.04 and 29.13 ppm

The conformation of 3-methyl-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-one (**IIIa**) in solution was established with the use of homonuclear spectroscopy COSY and nuclear Overhauser effect In the COSY spectrum of compound **IIIa** the strongest cross-peaks correspond to geminal (H_a^2/H_e^2, H_a^4/H_e^4, H^α/H^β), vicinal (H^9/H^α, H^9/H^β), and allylic (H_e^2/H_e^4) couplings. The remote constant ^4J appears because of coplanar location of bonds (*W*-coupling). The absence of *W*-coupling through four bonds between proton H^9 and equatorial protons H^2 and H^4 evidences the axial orientation of the bridging proton with respect to the nitrogen-containing ring and consequently the equatorial position of the oxopropyl group. The presence in the NOESY spectrum of compound **IIIa** of correlation peaks corresponding to the 1,3-coupling of the spatially close axial atoms H^9, H_a^2, and H_a^4, and also the lack in the spectrum of a contact between the bridging proton and the NMe group unambiguously proves the *chair* conformation of the nitrogen-containing ring in the molecule of the compound under study in solution. The equatorial position of the substituent attached to heteroatom follows from the observed in the NOESY spectrum its contacts with equatorial protons H^2 and H^4. Hence according to NMR data the piperidine ring of compound **IIIa** in solution exists predominantly in the *chair* conformation with diequatorial position of the N-methyl and oxopropyl groups.

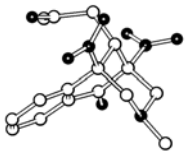
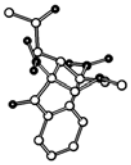
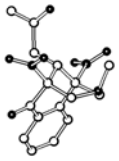
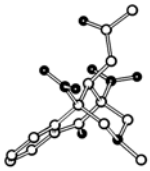
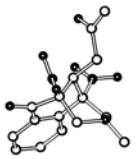
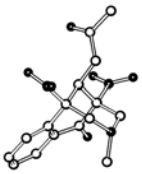
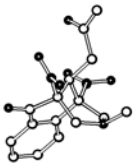
The comparative estimation of stability of various conformations of 3-methyl-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-one (**IIIa**) was carried out by quantim-chemical calculation of their enthalpy of formation by semiempirical methods PM3 and AM1. These methods were formerly applied to calculation of azabicyclo[3.3.1]nonanes [9–12] but among the derivatives studied were lacking nitro compounds and azabicyclo compounds with and endocyclic double bond. As mentioned above, the saturated 3-heteroanalogs of bicyclo[3.3.1]nonane are mostly present in the *chair-chair* conformation [8]. Itroducing a nitrogen atom into position *3* of bicyclo[3.3.1]nonane results in the stabilization of this form due to decrease in the 3,7-repulsion. The presence of a double bond and a trigonal atom of the *endo*-carbonyl group in the skeleton of compounds **III** causes a strong flattening of the cyclohexenone fragment that becomes incapable of inversion and thus also reduces the 3,7-repulsion. The calculation results show (Table 3) that the cyclohexenone fragmant of compound **IIIa** has a *sofa* conformation, and the piperidine ring takes a form of *chair* or *boat.* At equatorial position of the substituents at the bridging atom C^9 the *boat* conformation is more stable, and at the axial orientation of the oxopropyl group the *chair* form is more favored. According to PM3 calculations in the most stable conformation the piperidine ring is in the *chair* form, the substituents at the nitrogen atom is in the equatorial position, and the 2-oxopropyl group is axially oriented (ΔH_f –201.60 kJ mol^{-1}). The nitro groups in the molecule of compound **IIIa** are located in the equatorial plane, therefore the axial position of the bulky oxopropyl substituents becomes more favorable by energy. The analysis of data compiled in Table 3 shows that the calculation results of different procedures are qualitatively alike. However the difference also exists. For instance, according to AM1 data the most stable conformation is 3*a*, 9*e* where the nitrogen-containing ring is in the *boat* form (ΔH_f –79.96 kJ mol^{-1}). Consequently, the results obtained by PM3 method fit better to the experimental data since these calculations predict a higher stability for the *chair* conformation of the piperidine ring in the molecule of compound **IIIa**.

An additional information on the structure of compounds synthesized can be derived from the mass spectra. The decomposition under the electron impact was investigated by an example 3-methyl-9-(2-

oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-one **IIIa** (Scheme 2). In the mass spectrum was detected the peak of an unstable molecular ion $[M]^+$(*m/z* 347, I_{rel} 3.2%) that was easily cleaved with the loss of nitro groups as evidenced by the presence in the spectrum of fragment ion peaks $[M - NO_2^{\cdot}]^+$ (*m/z* 301), $[M - NO^{\cdot}, OH^{\cdot}]^+$ (*m/z* 300), $[M - 2NO_2^{\cdot}]^+$ (*m/z* 255), $[M - NO^{\cdot}, OH^{\cdot}, NO_2^{\cdot}]^+$ (*m/z* 254). The maximum intensity of the fragment ion peak with *m/z* 254 indicated that this path of the molecule fragmentation dominated. This conclusion is consistent with the published data on the mass spectrometry of the nitro compounds [13]. Further fragmentation of the primary fragment ions occurred by ejection of the rest of 2-oxopropyl group resulting in appearance in the spectrum of secondary fragment ions peaks with *m/z* 244, 198, 197, 196. At the deeper stages of fragmentation the nitrogen-containing ring got decomposed. Hence the presence in the mass spectrum of peaks belonging to the molecular ion (*m/z* 347) and to fragment ions permits a reliable identification of the compound under study and a description of its dissociative ionization under electron impact in the following scheme.

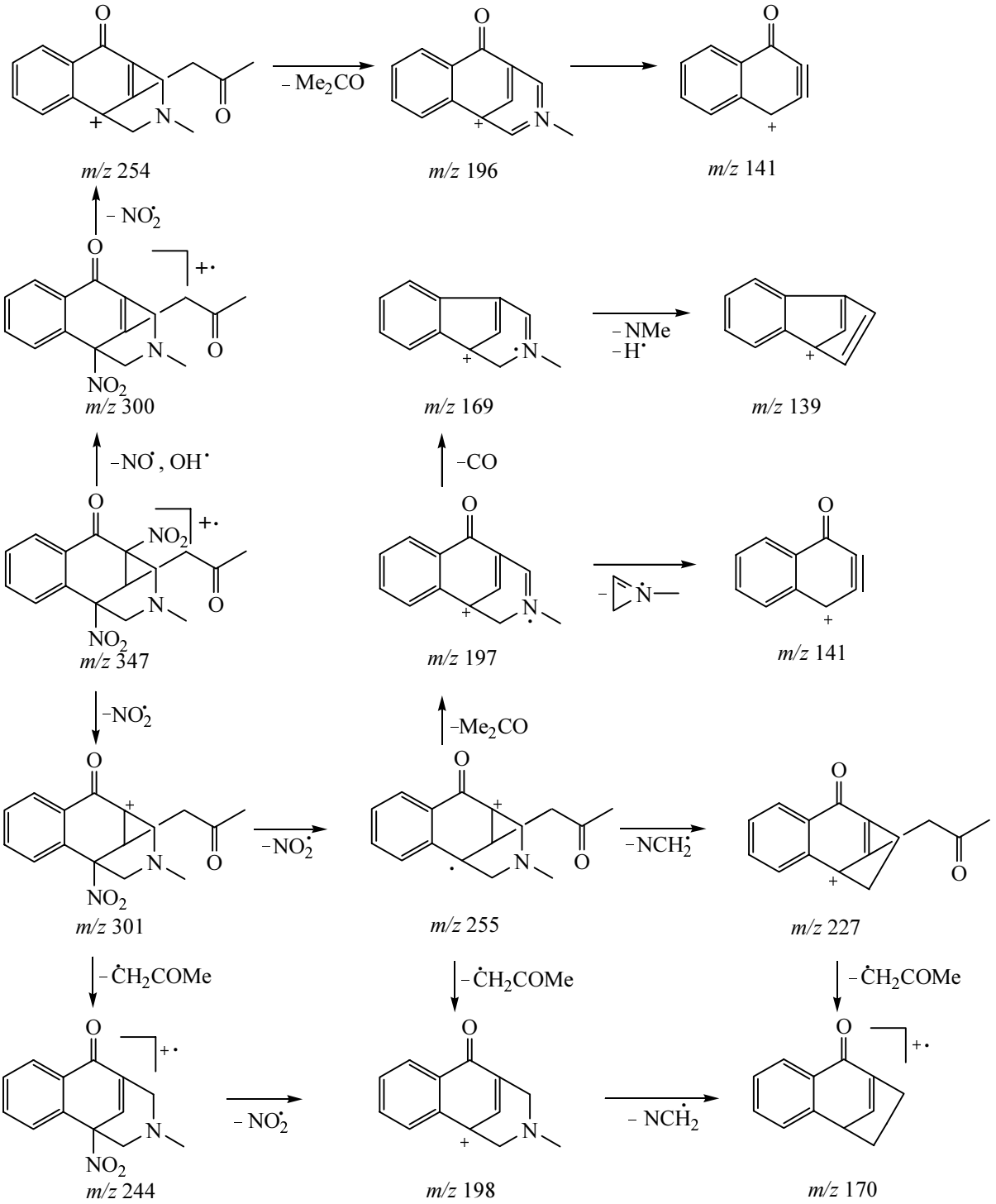
The final confirmation of the structure of the synthesized 3-azabicyclononanes was obtained by X-ray diffraction study on a single crystal of 3-methyl-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-

Table 3. Results of quantum-chemical calculations by PM3 and AM1 procedures of conformations of 3-methyl-9-(2-oxopropyl) -1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-one (**IIIa**)

Orientation of substituents[a]	Conformation of piperidinr ring ($-\Delta H_f$, kJ mol^{-1}[b])	
	chair	*boat*
3*e*, 9*e*		
	167.70 (47.48)	181.66 (67.21)
3*a*, 9*e*		
	156.07 (51.91)	188.14 (79.96)
3*e*, 9*a*		
	201.60 (79.37)	183.92 (64.37)
3*a*, 9*a*		
	197.46 (73.19)	181.24 (65.83)

[a] With respect to piperidine ring. [b] The values of ΔH_f in parentheses are calculated by AM1 procedure.

7-en-6-one (**IIIa**) (see figure and Table 4). The piperidine ring in the molecule of the compound in question is in the *chair* conformation. The deviations of N^3 and C^9 atoms from the plane through the other atoms of the ring amount to –0.709(2) and 0.736(2) Å respectively. The cyclohexenone ring $C^1C^8C^7C^6C^5C^9$ is in the *sofa* conformation with the deviation of 0.812(2) Å of atom C^9 from the plane where are located the other atoms of the ring. The conformation of the eight-membered C^1–C^8 is approximately *boat-boat* one and possesses the follow-



ing Zefirov–Palyulin folding parameters [14]: S_2 = 1.234, S_3 = 0.537, S_4 = –0.470, φ_2 = 1.67, φ_3= 0.48. The nitro groups at C^1 and C^5 atoms are in equatorial positions [torsion angles $N^1C^1C^9C^5$ and $N^2C^5C^9C^1$ are equal respectively to –174.9(1) and 173.4(1)°] and are considerably turned with respect to the flattened fragment of the cyclohexenone ring [torsion angles $O^2N^1C^1C^8$ and $O^4N^2C^5C^6$ are equal to 41.3(2) and 68.5(2)° respectively]. The nitrogen atom N^3 has a trigonal-pyramidal configuration. Its deviation from the plane going through the three atoms bonded thereto is –0.462(2) Å, and the sum of the corresponding bond angles equals to 331.4(4)°. 2-Oxopropyl substituent at C^9 atom has an equatorial orientation with respect to the piperidine ring, and the torsion angle $C^{14}C^9C^5C^6$ is equal to 56.7(2)°. The MeC(O) group is significantly turned with respect to the C^{15}–C^{14} bond [torsion angle $O^6C^{15}C^{14}C^9$ 30.5(2)°].

Thus the structural data obtained for the crystalline compound **IIIa** are in full agreement with the results of spectral studies of the conformations in solution, and also are close to the X-ray diffraction data for other nitro derivatives of azabicyclo[3.3.1]nonanes [1–3, 15–17]. The developed two-stage method of preparation of 3-azabicyclo[3.3.1]nonane derivatives from 2,4-dinitronaphthol affords new compounds interesting both as synthons for organic syntheses and as potential biologically active compounds.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord 75IR from films prepared from solutions in acetone. NMR spectra were registered on spectrometer Bruker AC-300 (^{1}H, 300.13 MHz; ^{13}C, 75.47 MHz) from solutions in a mixture CCl_4–DMSO-d_6, 3:1, internal reference HMDS. Retention factors R_f were measured on Silufol UV-254 plates, eluent toluene–acetone–hexane, 4:1:1, development under UV irradiation. Mass spectrum of compound **IIIa** was measured on Varian MAT-311 instrument at ionizing radiation energy 70eV. Quantum-chemical calculations were carried out on PC (550 MHz) using a software package HyperChem 6.0.

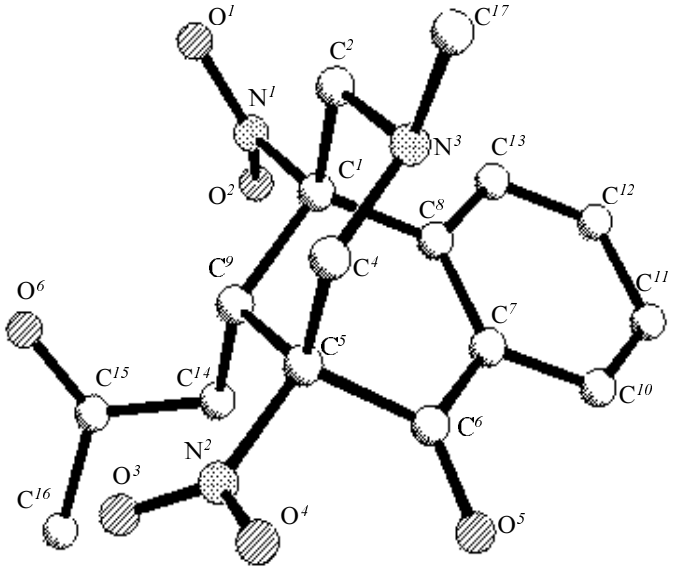
The crystals of compound **IIIa** were obtained by slow isothermal evaporation of the substance solution in toluene. Crystals of $C_{16}H_{17}N_3O_6$ at 110(2) K triclinic: *a* 8.024(2) Å, *b* 9.651(2) Å, *c* 11.509(2) Å, α 76.825(5)°, β 70.273(5)°, γ 72.164(5)°, *V* 790.9(3)Å^3, crystal habit 0.4×0.4×0.3 mm, space group *P* 1, *Z* 2, d_{calc} 1.459 g/cm^3, *F*(000) 364, μ 0.113 mm^{-1}. Intensities of 5501 reflections (3568 independent, R_{int} 0.027) were measured on an automatic diffractometer Bruker 1K SMART CCD (graphite monochromator, MoK_α radiation, φ and ω scanning, $2\theta_{max}$ 55°).

Table 4. Coordinates (×10^4) and equivalent isotropic thermal parameters (E^2×10^3) of nonhydrogen atoms in 3-methyl-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-one (**IIIa**)

Atom	*x*	*y*	*z*	*U*(eq)
N^1	3011(2)	1681(2)	9550(1)	24(1)
N^2	730(2)	6019(2)	6694(1)	25(1)
N^3	379(2)	2116(2)	7271(1)	21(1)
O^1	1827(2)	1366(2)	10478(1)	40(1)
O^2	4543(2)	1665(1)	9555(1)	29(1)
O^3	922(2)	6775(1)	7339(1)	32(1)
O^4	–21(2)	6503(1)	5864(1)	36(1)
O^5	3288(2)	4584(1)	4774(1)	28(1)
O^6	2301(2)	5207(2)	10013(1)	34(1)
C^1	2526(2)	2187(2)	8313(2)	18(1)
C^2	847(2)	1649(2)	8444(2)	23(1)
C^4	–171(2)	3725(2)	7040(2)	22(1)
C^5	1435(2)	4344(2)	6932(2)	19(1)
C^6	3069(2)	3837(2)	5792(2)	20(1)
C^7	4329(2)	2381(2)	6046(2)	20(1)
C^8	4119(2)	1569(2)	7240(2)	20(1)
C^9	2081(2)	3896(2)	8107(2)	19(1)
C^{10}	5730(2)	1802(2)	5024(2)	25(1)
C^{11}	6901(2)	421(2)	5199(2)	30(1)
C^{12}	6674(2)	–379(2)	6379(2)	28(1)
C^{13}	5305(2)	183(2)	7400(2)	23(1)
C^{14}	3694(2)	4518(2)	7974(2)	21(1)
C^{15}	3313(2)	5452(2)	8977(2)	24(1)
C^{16}	4259(4)	6670(2)	8621(2)	38(1)
C^{17}	–1069(3)	1493(2)	7281(2)	30(1)

The diffraction data were processed with the use of SAINT routine [18]. The structure was solved by the direct method applying the program SHELXTL-97 [19]. The hydrogen atoms positions were revealed from the difference synthesis of the electron density. The refinement along F^2 in anisotropic approximation (isotropic for hydrogen atoms) was performed by the full-matrix least-squares method (294 parameters) using 3568 reflections till $R1$=0.060 [for 2653 reflections with $F > 4\sigma(F)$], $wR2$ = 0.175, S = 0.99. The coordinates of nonhydrogen atoms are listed in Table 4.

3-(2-Oxopropyl)-2,4-bis-(*aci*-nitro)-5,6-benzocyclohex-5-en-1-one (II). To a solution of 2,4-dinitronaphthol (0.64 g, 3 mmol) in a mixture of anhydrous



Molecular structure of 3-methyl-9-(2-oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-one (**IIIa**) (hydrogen atoms are not shown).

acetone (7 ml) and anhydrous ethanol (13 ml) was slowly added at stirring a solution of sodium ethoxide prepared from sodium metal (0.13 g, 5.4 mmol) and ethanol (12 ml). The reaction mixture was stirred for 1 h at 18–20°C, then ethyl ether was added, the precipitate was separated, washed with ethanol and ether, and dried in a vacuumdesiccator. We obtained 0.84 g (91%) of compound **II** that was at once used in further synthesis.

3-R-9-(2-Oxopropyl)-1,5-dinitro-7,8-benzo-3-azabicyclo[3.3.1]non-7-en-6-ones (IIIa–i). To a mixture of 9 mmol of an appropriate amine hydrochloride, 30% formaldehyde water solution (1.65 ml, 18 mmol), and 20 ml of water was added by small portions at stirring adduct **II** (1.01 g, 3 mmol). In 1 h the reaction mixture was acidified with 20% orthophosphoric acid (2 ml), the reaction products were extracted into toluene (3×10 ml), the extract was dried with calcium chloride, evaporated in a vacuum to a volume of 5 ml, and passed through a column packed with silica gel (ASKG, eluent toluene). The solution obtained was evaporated in a vacuum to a volume of 20 ml, compounds **III** were precipitated with hexane and recrystallized from ethanol.

Yields, melting points, retention factors (R_f), and elemental analyses of compounds **III** are compiled in Table 1, and the spectral data in Tables 1 and 2.

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