ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 7, pp. 1064–1071. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © A.N. Antonov, R.V. Tyurin, K.A. Lysenko, A.F. Smol'yakov, V.V. Mezheritskii, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 7, pp. 1074–1080.

Oxidative Transformatons of 2-Aryl-1,2,3,4,7,8-hexahydroacenaphtho[5,6-*bc*]azepin-4-ones

A. N. Antonov[a], R. V. Tyurin[a], K. A. Lysenko[b], A. F. Smol'yakov[b], and V. V. Mezheritskii[a]

[a]*Research Institute of Physical and Organic Chemistry at the South Federal University, Rostov-on-Don, 344090 Russia*
e-mail: mezher@ipoc.rsu.ru
[b]*Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, Moscow, 119991 Russia*
e-mail: kostya@xrlab.ineos.ac.ru

Received Novemner 19, 2007

Abstract—Reactions of partial (elimination of H_2 from the bimethylene unit) and exhaustive (elimination of $2H_2$ from the bimethylene unit and the seven-membered heterocycle) dehydrogenation of 2-aryl-1,2,3,4,7,8-hexahydroacenaphtho[5,6-*bc*]azepin-4-ones were performed. The effect of the electronic structure of initial and dehydrogenated compounds on their spectral characteristics was discussed. New *peri*-fused heterocyclic systems were obtained.

DOI: 10.1134/S1070428008070208

In the preceding publication [1] we described a preparation method of 2-aryl-1,2,3,4,7,8-hexahydroacenaphtho[5,6-*bc*]-azepin-4-ones **II** bazed on a reaction of acenaphthene *peri*-aminoketone **I** with aromatic aldehydes. These compounds are possible synthons for the preparation of qualitatively new heteroaromatic systems by means of exhaustive dehydrogenation of the saturated carbon-carbon units of the heterocycle and the bimethylene fragment.

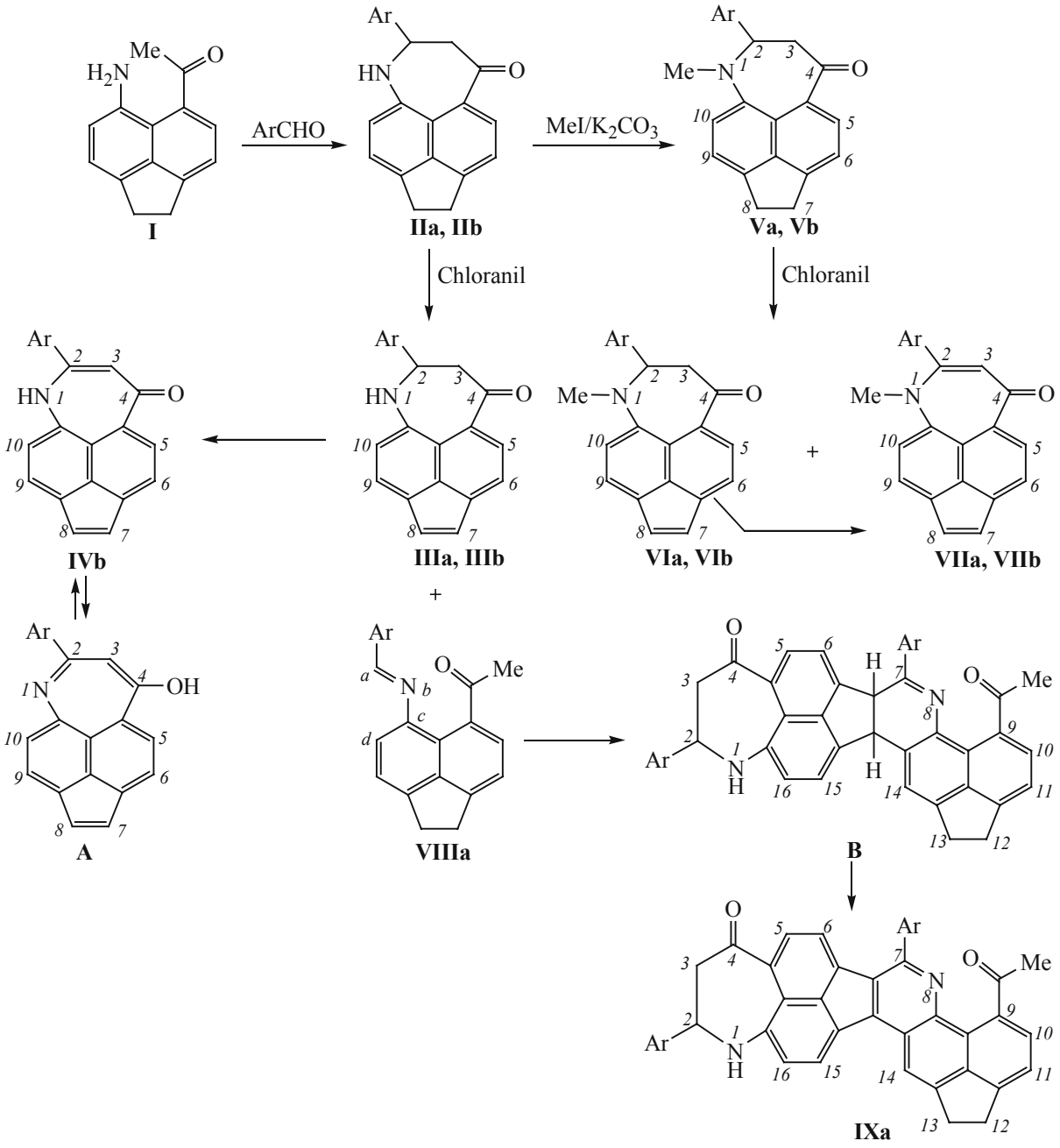
Dehydrogenation of NH-derivatives **IIa** and **IIb** of the said heterocyclic system with chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) in ether or THF resulted in a multicomponent mixture that was subjected to column chromatography to yield several individual compounds. It was observed that the readiness and degree of dehydrogenation depend on the character of the aryl substituent in the position *2* of the heterocycle. For instance, from compound **IIa** with a 2-anisyl substituent only the product of bimethylene unit dehydrogenation **IIIa** was obtained, whereas from 2-veratryl-substituted compound **IIb** formed both products of the partial, **IIIb**, and exhaustive, **IVb**, dehydrogenation. From the reaction products of 2-anisyl derivative **IIa** with chloranil alongside compound **IIIa** trace amount (yield 3%) was isolated of one more compound that based on IR, ^{1}H NMR, and mass spectra was identified as a substance of structure **IXa**.

The key stage in the formation of the new heterocyclic system **IXa** was evidently the [4+2]-cycloaddition of partially dehydrogenated molecules **IIIa** (dienophile) to azomethine **VIIIa** (as diene operated the fragment: *abcd*), the product of a prototropic opening of the azepine heterocycle; subsequently adduct **B** underwent aromatization.

After the reaction with chloranil of N-methyl-substited azepines **Va** and **Vb** (obtained from compounds **IIa** and **IIb** and methyl iodide) products of partial **VIa** and **VIb** and exhaustive dehydrogenation **VIIa** and **VIIb** were isolated; hence a conclusion was possible that the primary act was the dehydrogenation of the bimethylene fragment. The same should be valid for the sequence of azepines dehydrogenation stages in compounds lacking a substituent at the nitrogen atom (**II** → **III** → **IV**).

The structure of compounds synthesized was confirmed by the spectral data. The final proof of the structure of compounds **IIIa** and **Va** was obtained by XRD analysis (Figs. 1 and 2).

The principal geometric parameters of the molecules are close to the values expected for this class compounds. In both structures the acenaphthene and acenaphthylene fragments are planar. The appearance of a double bond in the molecule results in insignificant shortening of the bond distances in the five-membered ring of compound



Ar = 4-MeOC$_6$H$_4$ (**a**), 3,4-(MeO)$_2$C$_6$H$_3$ (**b**).

IIIa compared with compound **Va**. The conformations of the azepine ring in compounds **IIIa** and **Va** are slightly different. For instance, the conformation of the azepine ring in compound **IIIa** may be described as a distorted envelope with the deviation of atom C^{14} from the plane formed by atoms C^{10}, C^{11}, C^{1}, N^{1}, C^{15}, and C^{13}, and that of compound **Va**, as *distorted sofa* with the deviation of atoms C^{14} and C^{15} from the plane formed by atoms C^{1}, C^{11}, C^{10}, N^{1}, and C^{13}. The observed difference in the conformation of the seven-membered heterocycle in these compounds is apparently due to the appearance of a conjugation between the nitrogen heteroatom and the carbonyl group through a system of the multiple bonds of the acenaphthylene framework in molecule **IIIa** and the absence of this conjugation in molecule **Va**.

The bond surrounding of nitrogen atoms in compounds **IIIa** and **Va** is pyramidal: the sum of the bond angles equals 355.5 and 350.9° respectively. The analysis of crystal packing showed that beside the intermolecular hydrogen bond N–H···O [N^{1}–H···O^{1} (–*x*

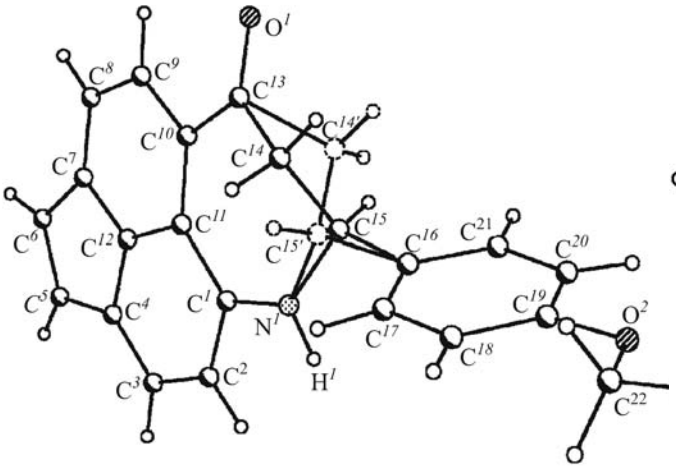


Fig. 1. General view of a molecule of compound **IIIa**. Carbon atoms of the minor component are shown (see EXPERIMENTAL). Main bond distances: C^4–C^5 1.464(2), C^5–C^6 1.355(2), C^6–C^7 1.465(2), O^1–C^{13} 1.221(2), N^1–C^1 1.377(2), N^1–C^{15} 1.450(2) Å.

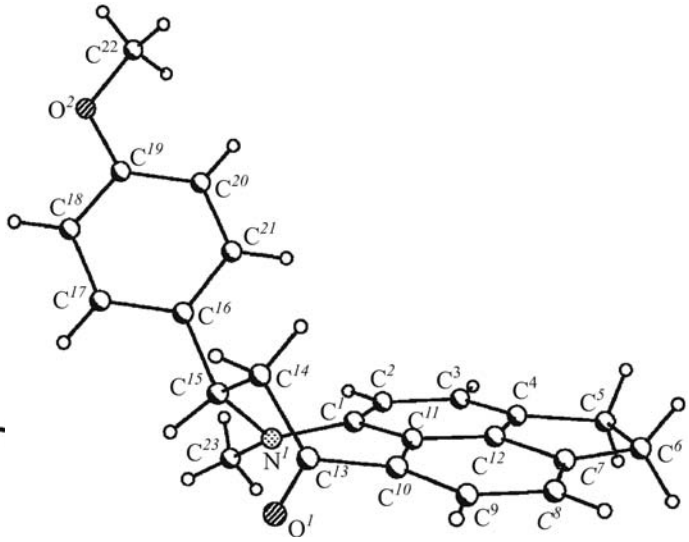


Fig. 2. General view of a molecule of compound **Va**. Main bond distances: C^4–C^5 1.510(3), C^5–C^6 1.538(3), C^6–C^7 1.515(3), O^1–C^{13} 1.218(2), C^1–N^1 1.417(2), N^1–C^{15} 1.470(2), N^1–C^{23} 1.458(2) Å.

+ 2, *y* + 1/2, –*z* + 1/2), $N^1\cdots O^1$ 2.986(2) Å] in compound **IIIa** (Fig. 3) all other contacts in the crystals under study corresponded to the common van der Waals interactions. The mentioned hydrogen bond joined the molecules of compound **IIIa** into chains directed along the crystallographic axis *b*.

Some spectral characteristics of hydrogenated, partially and completely dehydrogenated *peri*-fused heterocyclic systems make it possible to follow clearly the changes in their electronic structure.

To ensure the validity of conclusions the spectra of compounds **IIa** and **IIb** described in [1] were again registered on the same instruments and in the same conditions as the spectra of compounds **III–VII** described in this publication.

Inasmuch as the IR spectra were recorded from mulls in mineral oil the position of the "carbonyl" band ν_{CO} depended on many factors (the presence or absence of hydrogen bonds, type of the crystal lattice etc.) and therefore could not underlie a rigorous conclusion. Nonetheless, the considerable shift of this band from the values 1650–1687 cm^{-1} in hydrogenated (**II, V**) and partially dehydrogenated (**III, VI**) compounds into the low-frequency region (~1600 cm^{-1}) in systems subjected to exhaustive dehydrogenation (**IV, VII**) indicated the aromatization of the latter and the significant contribution of the betaine form **D** into their structure.

In the ^1H NMR spectra the signals of protons H^{10} (upfield) and H^5 (downfield) are the boarder signals of naphthalene framework protons. It is readily observed that in going from hydrogenated to partially and then to completely dehydrogenated compounds these signals gradually shifted downfield. The latter compounds are aromatic despite the presence of 16 π-electrons for they consist of two aromatic fragments: 10π-electron fragment of the naphthalene ring and 14π-electron contour situated on the perimeter of the *peri*-fused heterocyclic system.

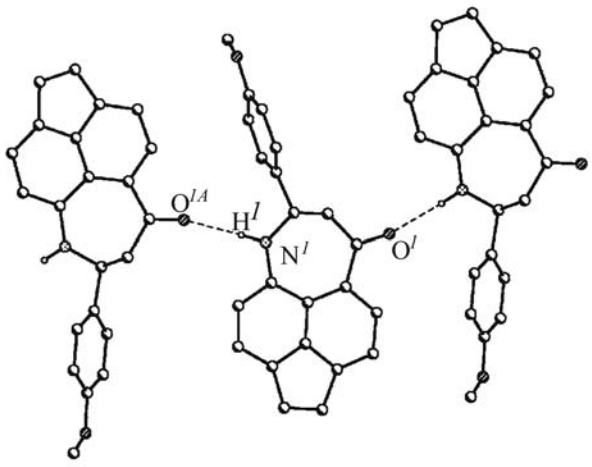
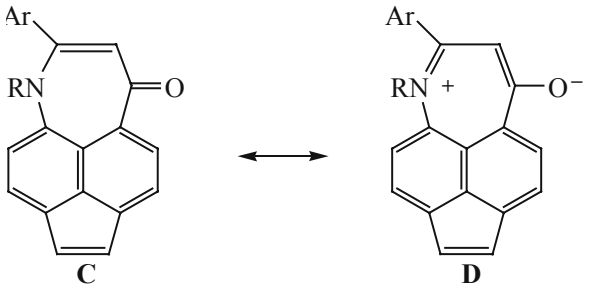


Fig. 3. Intermolecular hydrogen bonds in the crystal of compound **IIIa**. Parameters of the H-bond: $N^1\cdots O^{1A}$ 2.986(3), $N^1H\cdots O^{1A}$ 2.12 Å, angle N^1–$H\cdots O^{1A}$ 163°.

The electronic structure of the new heteroaromatic systems is sufficiently completely and clearly described by presented below resonance structures **C** and **D** whose protons (R = H) or methyl groups (R = Me) at the nitrogen atom also suffer a downfield shift. The signals of protons H^7 and H^8 belonging to the vinyl group appear in the region characteristic of aromatic protons evidencing their involvement into the aromatic conjugation in the 14π-electron peripheral contour. The most upfield signal belonged to atom H^3 of the heteroaromatic system due to the "pumping" of the electron density into this position at the sacrifice of the lone electron pair of nitrogen heteroatom.

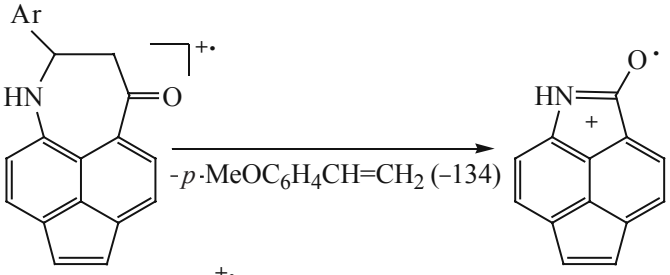


C **D**

The protons of vinyl group of compounds **III, IV, VI**, and **VII** are distinguished from the protons of naphthalene framework by low coupling constant (~5 Hz) in conformity to the characteristic data of the previously obtained [2–5] *peri*-fused heterocyclic systems, acenaphthylene derivatives.

The methylene group protons of azepine heterocycle in compounds **II, III, V**, and **VI** involved into a strongly coupled spin system and located near the asymmetrical center are magnetically nonequivalent and therefore appear in the ^{1}H NMR spectra as one-proton doublets of doublets of dissimilar appearance. The methine proton (ArCH) at the asymmetrical center in the heterocycle of these compounds gives rise in the ^{1}H NMR spectrum to one-proton doublet or doublet of doublets at ~4.8 ppm

In the mass spectrum of compound **IIIa** a molecular ion $[M]^+$ was detected; it underwent fragmentation with ejection of a *p*-vinylanisole molecule giving a fragment ion Φ_1.



IIIa, *m/z* 327 $[M]^{+\bullet}$ Φ_1 *(m/z* 193)

A choice between two tautomeric structures **IVb** and **A** in favor of the former was done based on the comparison of the electronic spectra of compounds **IVb** and **VIIb** (Fig. 4). However the essential difference in the extinction coefficients at the coincidence of the position of the absorption bands in the electronic spectra of the compared compounds and the presence of two singlets of equal intensity (1:1) from the proton in the position *3* in the ^{1}H NMR spectrum of compound **IVb** suggests that both tautomers can exist in solutions.

In the IR spectrum of compound **IXa** appear two carbonyl bands and a band of the NH group. The ^{1}H NMR

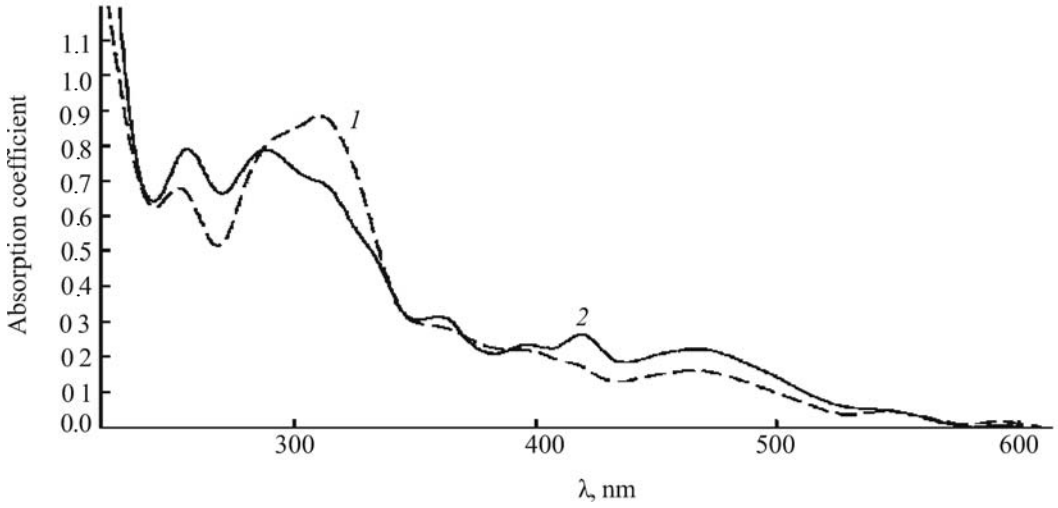


Fig. 4. Electron absorption spectra of compounds **IVb** (*1*) and **VIIb** (*2*) in acetonitrile.

Main crystallographic data and parameters of refinement of compounds **IIIa** and **Va**

Parameters	**IIIa**	**Va**
Empirical formula	$C_{22}H_{17}NO_2$	$C_{23}H_{21}NO_2$
M	327.37	343.41
T, K	100	298
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	*P*-1
Diffractometer	Smart Apex II CCD	Smart 1000 CCD
Z (*Z*′)	4(1)	2(1)
a, Å	11.3760(11)	7.8044 (1)
b, Å	14.1934(14)	10.9472(14)
C, Å	10.2287(11)	11.7491(15)
α, deg	90	103.270(3)
β, deg	103.955(2)	96.889(3)
γ, deg	90	107.871(3)
V, Å^3	1602.8(3)	910.0(2)
d_{calc}, g cm^{-3}	1.357	1.253
μ, cm^{-1}	0.87	0.80
F(000)	688	364
θ_{max}, deg	29.0	27.0
Number of measured reflexions	8449	8750
R_{int}	0.0240	0.0253
Number of independent reflexions	4230	3946
Number of reflexions with $I > 2\sigma(I)$	3254	2730
Number of refined parameters	291	237
R_1	0.0461	0.0519
wR_2	0.1270	0.1357
GOF	1.026	0.945
Residual electron density, *e* Å^{-3} (d_{max}/d_{min})	0.327/–0.280	0.174/–0.155

spectrum corresponds to a structure containing an acetyl group (CH_3C=O), two methoxy groups (two three-proton singlets), a fragment $ArCHCH_2$, a bimethylene "bridge" (CH_2CH_2), a single NH group, and 15 aromatic protons. The mass spectrum contains a peak with a mass 653 $[M + H]^+$ and two fragment ions: Φ_2 arising from ejection of a CO molecule, and Φ_3 formed by elimination of *p*-methoxyphenylethylene from the seven-membered heterocycle of the molecular ion with the closure of a five-membered heterocycle similarly to the process observed in the fragmentation of compound **IIIa**.

The analysis of the mass spectra of compounds **IIIa** and **IXa** leads to a conclusion that this kind molecules are prone to elimination of a neutral vinylaromatic fragment, and therefore this fact may serve as a proof of the presence in their structure of a seven-membered heterocycle. This process resembles the elimination of arylacetylenes that we have observed in the mass spectra of 2-aryl-1,4-dihydroacenaphtho[5,6-*bc*]oxepin-4-ones [6] and 2-aryl-1,4,7,8-tetrahydroacenaphtho[5,6-*bc*]-oxepin-4-ones [7].

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Varian Unity-300 (300 MHz). As internal reference served residual signals of $CHCl_3$ (δ 7.25 ppm) and $(CH_3)_2SO$ (δ 2.50 ppm). Electron absorption spectra were recorded in acetonitrile on a spectrophotometer Specord M-40. Vibrational spectra were measured on a Specord 75IR instrument from mulls in mineral oil. XRD investigation of single crystals of compounds **IIIa** and **Va** was carried out on three-circle diffractometers using MoK_α-radiation, graphite monochromator, and ω-scanning. The structures were solved by the direct method and refined by least-squares procedure in full-matrix anisotropic approximation by F^2_{hkl}. The position of hydrogen atoms in **IIIa** molecule were calculated geometrically, and in **Va** molecule the hydrogen atoms were localized from the difference Fourier syntheses of the electron density and refined isotropically. Analysis of the difference Fourier charts showed that atoms C^{14} and C^{15} in compound **IIIa** are disordered by two positions with occupancy of the positions 0.9 and 0.1. The refinement of the minor component was performed in the isotropic approximation. The main crystallographic data and parameters of the refinement of compounds **IIIa** and **Va** are presented in the table. All calculations were performed by the software complex SHELXTL PLUS [8].

2-(4-Methoxyphenyl)-1,2,3,4,7,8-hexahydroacenaphtho[5,6-*bc*]azepin-4-one (IIa) [1]. IR spectrum, ν, cm^{-1}: 1650 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.80 (H^{10}), 8.15 (H^5), 4.36 (NH).

2-(3,4-Dimethoxyphenyl)-1,2,3,4,7,8-hexahydroacenaphtho[5,6-*bc*]azepin-4-one (IIb) [1]. IR spectrum, ν, cm^{-1}: 1650 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.82 (H^{10}), 8.14 (H^5), 4.36 (NH).

2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroacenaphtho[5,6-*bc*]azepin-4-one (IIIa). To a solution of 100 mg (0.3 mmol) of compound **IIa** [1] in 3 ml of THF was added a solution of 75 mg (0.3 mmol) of chloranil in 5 ml of THF, and the mixture was stirred at room temperature for 1 h. The solution was evaporated, the dry residue was dissolved in chloroform and subjected to column chromatography on aluminum oxide collecting the fraction of the highest chromatographic mobility, whereas the other products were retained "at the start". Yield 52 mg (53%), violet powder, mp 138–139°C. IR spectrum, ν, cm^{-1}: 3407 (NH), 1660 (C=O), 1607. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.20 d.t (1H, HαCHβ, ^2J 16.11, ^3J 1.58 Hz), 3.60 d.d (1H, HαCHβ, ^2J 11.06, ^3J 2.50 Hz), 3.80 s (3H, CH_3O), 4.77 br.d (1H, ArCH, J 11.37 Hz), 5.00 br.s (1H, NH), 6.63 d (1H, H^{10}, $J_{10,9}$ 7.58 Hz), 6.83 d (1H, H^7, $J_{7,8}$ 5.05 Hz), 6.92 d (2H$_{Ar}$, J 8.85 Hz), 7.14 d (1H, H^8, $J_{8,7}$ 5.05 Hz), 7.35 d (2H$_{Ar}$, J 8.53 Hz), 7.45 d (1H, H^9, $J_{9,10}$ 7.58 Hz), 7.78 d (1H, H^6, $J_{6,5}$ 7.27 Hz), 8.34 d (1H, H^5, $J_{5,6}$ 7.59 Hz). Mass spectrum, *m/z* (I_{rel}, %): 327 [M]$^+$ (50), 193 (100). Found, %: C 80.50; H 5.36; N 4.45. $C_{22}H_{17}NO_2$. Calculated, %: C 80.73; H 5.20; N 4.28.

2-(3,4-Dimethoxyphenyl)-1,2,3,4-tetrahydroacenaphtho[5,6-*bc*]azepin-4-one (IIIb) was obtained similarly to compound **IIIa** from 108 mg (0.3 mmol) of compound **IIb** [1], 75 mg (0.3 mmol) of chloranil in 10 ml of THF. Yield 64 mg (60%), violet powder, mp 184–185°C. IR spectrum, ν, cm^{-1}: 3340 (NH), 1650 (C=O), 1600. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.22 d.t (1H, HαCHβ, ^2J 16.01, ^3J 1.57 Hz), 3.60 q (1H, HαCHβ, ^2J 11.30, ^3J 2.50 Hz), 3.85 s (6H, 2CH_3O), 4.75 br.d (1H, ArCH, J 10.99 Hz), 5.03 br.s (1H, NH), 6.65 d (1H, H^{10}, $J_{10,9}$ 7.53 Hz), 6.83 d (1H, H^7, $J_{7,8}$ 5.03 Hz), 6.86 d (1H$_{Ar}$, J 8.17 Hz), 6.92 s (1H$_{Ar}$), 6.98 d (1H$_{Ar}$, J 8.16 Hz), 7.13 d (1H, H^8, $J_{8,7}$ 5.34 Hz), 7.44 d (1H, H^9, $J_{9,10}$ 7.54 Hz), 7.77 d (1H, H^6, $J_{6,5}$ 7.54 Hz), 8.34 d (1H, H^5, $J_{5,6}$ 7.53 Hz). Found, %: C 77.59; H 5.06; N 4.15. $C_{23}H_{19}NO_3$. Calculated, %: C 77.31; H 5.32; N 3.92.

2-(3,4-Dimethoxyphenyl)-1,4-dihydroacenaphtho-[5,6-*bc*]azepin-4-one (IVb). To a solution of 244 mg (0.68 mmol) of compound **IIIb** in 4 ml of THF was added at stirring a solution of 334 mg (1.36 mmol) of chloranil in 6 ml of THF, the mixture was kept for 3 h at room temperature, the solvent was removed in air, the dry residue was dissolved in chloroform and subjected to column chromatography on aluminum oxide (eluent chloroform), collecting the first fraction (R_f 0.35). Yield 40 mg (17%), dark-red powder, mp 208–209°C. UV spectrum, λ_{max}, nm (ε 10^{-4}): 550 (0.063), 468 (0.25), 418 (0.27), 395 (0.35), 360 (0.44), 311 (1.39), 288 (1.28), 253 (1.07). IR spectrum, ν, cm^{-1}: 3350, 3320 (NH), 1620 (C=O), 1590. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.92 s (3H, CH_3O), 3.97 s (3H, CH_3O), 6.28 d (1H, H^3, J 1.91 Hz), 6.95 d (1H, H^{10}, $J_{10,9}$ 8.41 Hz), 7.19–7.32 m (3H$_{Ar}$, H^6, H^7, H^9), 7.45 d (1H, H^8, $J_{8,7}$ 5.35 Hz), 7.90 d (1H$_{Ar}$, J 7.65 Hz), 8.10 d (1H$_{Ar}$, J 7.65 Hz), 8.20 br.s (1H, NH), 8.89 d (1H, H^5, $J_{5,6}$ 7.27 Hz). Found, %: C 77.64; H 5.00; N 4.23. $C_{23}H_{17}NO_3$. Calculated, %: C 77.75; H 4.79; N 3.94.

1-Methyl-2-(4-methoxyphenyl)-1,2,3,4,7,8-hexahydroacenaphtho[5,6-*bc*]azepin-4-one (Va). To a solution of 200 mg (0.61 mmol) of compound **IIa** [1] in 4 ml of acetonitrile was added 200 mg (1.45 mmol) of potassium carbonate, 0.2 ml (3.24 mmol) of methyl iodide, and the mixture was heated at reflux for 10 h. On removing the solvent in air the dry residue was dissolved in chloroform and subjected to column chromatography on aluminum oxide (eluent chloroform), collecting the most mobile fraction (R_f 0.9). Yield 188 mg (90%), yellow crystals, mp 144–145°C. IR spectrum, ν, cm^{-1}: 1680 (C=O), 1650, 1607. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.75 s (3H, CH_3N), 2.94 q (1H, HαCHβ, J_1 5.66, J_2 6.65 Hz), 3.32–3.48 m (5H, HαCHβ, CH_2CH_2), 3.80 s (3H, CH_3O), 4.83 q (1H, ArCH, J_1 5.34, J_2 6.03 Hz), 6.82 d (2H, H$_{Ar}$, J 8.71 Hz), 6.89 d (1H, H^{10}, J 7.27 Hz), 7.19 d (2H$_{Ar}$, J 8.71 Hz), 7.26–7.29 m (2H, H^6, H^9), 7.76 d (1H, H^5, J 7.27 Hz). Found, %: C 80.54; H 5.92; N 4.28. $C_{23}H_{21}NO_2$. Calculated, %: C 80.47; H 6.12; N 4.08.

2-(3,4-Dimethoxyphenyl)-1-methyl-1,2,3,4,7,8-hexahydroacenaphtho[5,6-*bc*]azepin-4-one (Vb) was prepared in the same way as compound **Va** from 450 mg (1.25 mmol) of compound **IIb** [1], 426 mg (3 mmol) of potassium carbonate, 0.4 ml (3.48 mmol) of methyl iodide by boiling in 10 ml of acetonitrile for 15 h. Yield 430 mg (92%), yellow crystals, mp 167–168°C. IR spectrum, ν, cm^{-1}: 1673 (C=O), 1600. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.75 s (3H, CH_3N), 2.95 q (1H, HαCHβ, J_1 5.68, J_2 6.64 Hz), 3.32–3.47 m (5H, HαCHβ, CH_2CH_2), 3.75 s (3H, CH_3O), 3.85 s (3H, CH_3O), 4.81 q (1H, ArCH, J_1 5.37, J_2 6.00 Hz), 6.75–6.87 m (3H, H^{10}, 2H$_{Ar}$), 6.94 d (1H, H^6, $J_{6,5}$ 7.58 Hz), 7.27 br.d (2H, H^9, H$_{Ar}$, J 7.58 Hz), 7.78 d (1H, H^5, $J_{5,6}$ 7.58 Hz). Found, %: C 77.56; H 6.32; N 3.48. $C_{24}H_{23}NO_3$. Calculated, %: C 77.21; H 6.17; N 3.75.

1-Methyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroacenaphtho[5,6-*bc*]azepin-4-one (VIa). A solution of 46 mg (0.134 mmol) of compound **Va** and 33 mg (0.134 mmol) of chloranil in 1 ml of *o*-dichlorobenzene was boiled for 5 min. The solvent was evaporated in air, the dry residue was dissolved in chloroform and subjected to column chromatography on aluminum oxide (eluent chloroform), collecting the first fraction (R_f 0.9). Yield 20 mg (44%), violet powder, mp 94–95°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1590. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.90 s (3H, NCH_3), 3.30 d.d (1H, HαCHβ, ^1J 4.42, ^2J 9.16 Hz), 3.50 d.d (1H, HαCHβ, ^2J 10.11, ^3J 3.48 Hz), 3.75 s (3H, CH_3O), 4.80 d.d (1H, ArCH, J_1 4.58, J_2 5.68 Hz), 6.70 d (1H, H^{10}, $J_{10,9}$ 7.59 Hz), 6.81 d (2H_{Ar}, J 8.84 Hz), 6.82 d (1H, H^7, $J_{7,8}$ 5.06 Hz), 7.08 d (1H, H^8, $J_{8,7}$ 5.05 Hz), 7.10 d (2H_{Ar}, J 8.84 Hz), 7.55 d (1H, H^9, $J_{9,10}$ 7.58 Hz), 7.63 d (1H, H^6, $J_{6,5}$ 7.15 Hz), 7.90 d (1H, H^5, $J_{5,6}$ 7.15 Hz). Found, %: C 80.73; H 5.68; N 3.93. $C_{23}H_{19}NO_2$. Calculated, %: C 80.94; H 5.57; N 4.10.

1-Methyl-2-(3,4-dimethoxyphenyl)-1,2,3,4-tetrahydroacenaphtho[5,6-*bc*]azepin-4-one (VIb) was obtained similarly to compound **VIa** from 50 mg (0.134 mmol) of compound **Vb** and 33 mg (0.134 mmol) of chloranil. Yield 23 mg (46%), violet substance, mp 135–136°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1590. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.95 s (3H, CH_3N), 3.30 d.d (1H, HαCHβ, ^3J 4.18, ^2J 9.11 Hz), 3.52 d.d (1H, HαCHβ, ^2J 10.51, ^3J 2.82 Hz), 3.72 s (3H, CH_3O), 3.83 s (3H, CH_3O), 4.77 d.d (1H, ArCH, J_1 4.39, J_2 5.65 Hz), 6.66 s (1H_{Ar}), 6.73 d (1H, H^{10}, $J_{10,9}$ 7.65 Hz), 6.75 br.s (2H_{Ar}), 6.82 d (1H, H^7, $J_{7,8}$ 5.20 Hz), 7.08 d (1H, H^8, $J_{8,7}$ 5.20 Hz), 7.54 d (1H, H^9, $J_{9,10}$ 7.67 Hz), 7.63 d (1H, H^6, $J_{6,5}$ 7.12 Hz), 7.90 d (1H, H^5, $J_{5,6}$ 7.12 Hz). Found, %: C 77.45; H 5.96; N 3.54. $C_{24}H_{21}NO_3$. Calculated, %: C 77.63; H 6.17; N 3.77.

1-Methyl-2-(4-methoxyphenyl)-1,4-dihydroacenaphtho[5,6-*bc*]azepin-4-one (VIIa). A solution of 46 mg (0.134 mmol) of compound **Va** and 66 mg (0.268 mmol) of chloranil in 1 ml of *o*-dichlorobenzene was boiled for 30 min. The solvent was evaporated in air, the dry residue was dissolved in chloroform and subjected to column chromatography on aluminum oxide (eluent chloroform), collecting the first fraction (R_f 0.5). Yield 22 mg (49%), red powder, mp 177–178°C. IR spectrum, ν, cm^{-1}: 1607, 1600. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.50 s (3H, NCH_3), 3.90 s (3H, CH_3O), 6.15 s (1H, H^3), 6.97 d (2H_{Ar}, J 8.53 Hz), 7.25 d (1H, H^7, $J_{7,8}$ 5.05 Hz), 7.37 d (1H, H^8, $J_{8,7}$ 5.05 Hz), 7.48 d (1H, H^{10}, $J_{10,9}$ 7.75 Hz), 7.53 d (2H_{Ar}, J 8.53 Hz), 7.90 d (1H, H^9, $J_{9,10}$ 7.76 Hz), 8.05 d (1H, H^6, $J_{6,5}$ 7.45 Hz), 8.78 d (1H, H^5, $J_{5,6}$ 7.44 Hz). Found, %: C 81.57; H 5.13; N 4.24. $C_{23}H_{17}NO_2$. Calculated, %: C 81.42; H 5.01; N 4.13.

1-Methyl-2-(3,4-dimethoxyphenyl)-1,4-dihydroacenaphtho[5,6-*bc*]azepin-4-one (VIIb) was obtained similarly to compound **VIIa** from 100 mg (0.268 mmol) of compound **Vb** and 132 mg (0.536 mmol) of chloranil. Yield 46 mg (47%), red substance, mp 166–167°C. UV spectrum, λ_{max}, nm (ε × 10^{-4}): 550 (0.096), 468 (0.41), 420 (0.50), 395 (0.44), 361 (0.61), 311 (1.32), 288 (1.49), 256 (1.51). IR spectrum, ν, cm^{-1}: 1600, 1580. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.50 s (3H, NCH_3), 3.96 br.s (6H, $2CH_3O$), 6.17 s (1H, H^3), 6.93 d (1H, H^{10}, J 8.06 Hz), 7.06 d (1H_{Ar}, J 2.21 Hz), 7.14 d.d (1H_{Ar}, ^1J 8.05, ^2J 2.21 Hz), 7.23 d (1H, H^7, $J_{7,8}$ 5.25 Hz), 7.38 d (1H, H^8, $J_{8,7}$ 5.25 Hz), 7.47 d (1H_{Ar}, J 8.05 Hz), 7.90 d (1H, H^9, $J_{9,10}$ 8.08 Hz), 8.04 d (1H, H^6, $J_{6,5}$ 7.45 Hz), 8.77 d (1H, H^5, $J_{5,6}$ 7.44 Hz). Found, %: C 78.37; H 5.33; N 4.02. $C_{24}H_{19}NO_3$. Calculated, %: C 78.05; H 5.15; N 3.79.

9-Acetyl-2,7-di(4-methoxyphenyl)-1,2,3,4,12,13-hexahydroazepino[2',3',4':5,6]acenaphtho[1,2-*c*]indeno[1,7-*gh*]quinolin-4-one (IXa). To a solution of 438 mg (1.331 mmol) of compound **IIa** in 20 ml of ethyl ether was added at stirring a solution of 327.5 mg (1.331 mmol) of chloranil in 10 ml of ether, the mixture was kept for 1 h at room temperature, and again a solution of 327.5 mg (1.331 mmol) of chloranil in 10 ml of ether was added. The solution obtained was stirred for 2 h. The solvent was evaporated in air, the dry residue was dissolved in chloroform and subjected to column chromatography on aluminum oxide (eluent chloroform), collecting the fraction of R_f 0.25. On removing the solvent yield 26 mg (3%), brown powder, mp > 300°C. IR spectrum, ν, cm^{-1}: 3350, 1660, 1650, 1610. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.50 s (3H, $COCH_3$), 3.15 d (1H, HαCHβ, J 15.18 Hz), 3.40–3.60 m (5H, HαCHβ, CH_2CH_2), 3.80 s (3H, CH_3O), 3.95 s (3H, CH_3O), 4.70 d (1H, ArCH, J 11.69 Hz), 5.23 br.s (1H, NH), 6.78 d (1H_{Ar}, J 7.89 Hz), 6.95 d (2H_{Ar}, J 8.22 Hz), 7.13 d (2H_{Ar}, J 8.85 Hz), 7.25 d (2H_{Ar}, J 9.79 Hz), 7.27 d (1H_{Ar}, J 7.30 Hz), 7.50 d (1H_{Ar}, J 7.28 Hz), 7.85 d (1H_{Ar}, J 8.53 Hz), 7.88 s (1H_{Ar}), 7.92 d (1H_{Ar}, J 6.63 Hz), 8.13–8.25 m (3H_{Ar}). Found, %: C 81.27; H 5.23; N 4.12. $C_{44}H_{32}N_2O_4$. Calculated, %: C 80.96; H 4.94; N 4.29.

REFERENCES

1. Antonov, A.N., Tyurin, R.V., Minyaeva, L.G., and Mezheritskii, V.V., *Zh. Org. Khim.,* 2007, vol. 43, p. 1005.
2. Pozharskii, A.F., Vinokurova, T.I., and Zaletov, V.G., *Khim. Geterotsikl. Soedin.,* 1976, p. 539.
3. Vinokurova, T.I. and Pozharskii, A.F., *Khim. Geterotsikl. Soedin.,* 1976, p. 545.
4. Mezheritskii, V.V., Minyaeva, L.G., Golyanskaya, O.M., Tyurin, R.V., Borbulevich, O.Ya., Borodkin, G.S., and Antonov, A.N., *Zh. Org. Khim*., 2006, vol. 42, p. 293.
5. Mezheritskii, V.V., Minyaeva, L.G., and Tyurin, R.V., *Izv. Akad. Nauk, Ser. Khim.,* 2005, p. 777.
6. Tyurin, R.V., Milov, A.A., Bezuglov, A.N., Antonov, A.N., Minyaeva, L.G., and Mezheritskii, V.V., *Zh. Org. Khim.,* 2007, vol. 43, p. 1474.
7. Mezheritskii, V.V., Pikus, A.L., and Tregub, N.G., *Zh. Org. Khim.,* 1991, vol. 27, p. 2198.
8. Sheldrick, G.M., *SHELXTL-Plus Reference Manual, Version, 5.0*, Siemens Analytical X-ray Instruments Inc.: 1996.