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Synthesis and Molecular Structure of Bis(areno)piperidinoaza-14(17)-crowns-4(5)

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Abstract—The condensation of dialkyl ketones with α,ω-bis(2-formylphenoxy)- or α,ω-bis(1-formylnaphthalen-2-yloxy)-3-oxapentane and -3,6-dioxaoctane in the presence of ammonium acetate according to Petrenko–Kritchenko gave 14–41% of new bis(areno) aza crowns, bis(areno)piperidinoaza-14-crown-4 and bis(benzo)-piperidinoaza-17-crown-5, having functional substituents in the piperidine fragment. The yield of the aza crown ether appreciably decreases upon extension of the polyether chain in the aldehyde component. The molecular structure of two of the obtained macrocyclic compounds and the relative configuration of asymmetric carbon atoms in the piperidine ring were determined by X-ray analysis, and the size of their internal cavities was estimated.

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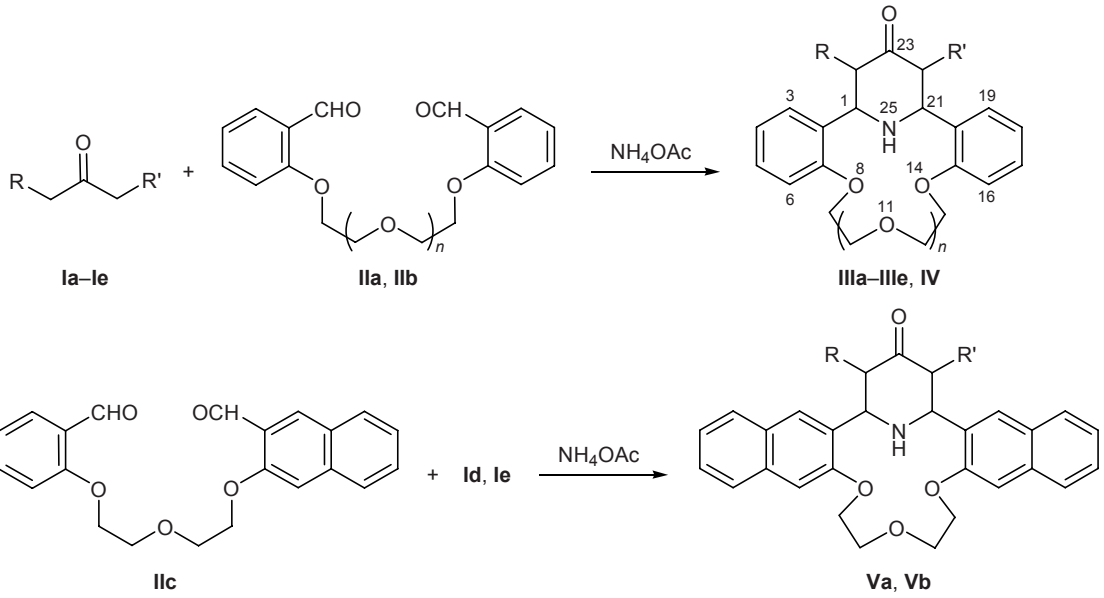
Crown ethers constitute one of the most important classes of macrocyclic compounds. In the past 2–3 decades, crown ethers attracted researchers' attention due to their ability to act as effective complexing agents, catalysts, ion carriers, and other active components [1]. Introduction of a nitrogen atom into classical crown ether molecules endows them with a number of specific properties, enhances their activity as ligands, and increases the selectivity of formation and stability of complexes based thereon [2]. As far as we know, aza crown ethers in which the nitrogen atom is incorporated into piperidine ring were not reported. However, the presence of a crown ether moiety and a functionalized piperidine ring in a single macrocyclic molecule could diversify and increase the potential of biological activity of such derivatives. In addition, a combination of the above fragments could affect to an appreciable extent the reactivity of the piperidine fragment and change the size of the internal cavity and its template activity in complex formation with metal ions. While performing systematic studies in the field of chemistry and biological activity of functionalized piperidine derivatives [3], we have developed procedures for the synthesis of aza crown ethers consisting of a 2,6-diarylpiperidine fragment where the aryl groups are linked through a polyether chain. The present article describes in detail (for preliminary communication, see [4]) the synthesis, spectral parameters, and molecular structure of first representatives of a new family of macrocyclic aza crownophanes, bis(areno)aza-14(17)-crowns-4(5) **IIIa**–**IIIe**, **IV**, **Va**, and **Vb**, containing a 4-oxopiperidine fragment.

As starting compounds for the synthesis of aza crowns **IIIa**–**IIIe**, **IV**, **Va**, and **Vb** we used relatively accessible [5] oligoethers: 2-{2-[2-(2-formylphenoxy)-ethoxy]ethoxy}benzaldehyde (**IIa**), its analog **IIb**, and 2-{2-[2-(1-formylnaphthalen-2-yloxy)ethoxy]ethoxy}-naphthalene-1-carbaldehyde (**IIc**). Oligoethers **II** were brought into condensation at the terminal formyl groups with activated methyl or methylene groups of dialkyl ketones **Ia**–**Ie** and ammonia. The reactions were carried out at 80°C in a mixture of ethanol with acetic acid, i.e., under the conditions corresponding to the Petrenko–Kritchenko synthesis of piperidin-4-ones [6], and they led to the formation of macrocyclic compounds **III**–**V**. After appropriate treatment of the reaction mixtures and chromatographic purification, compounds **III**–**V** were isolated in 22–40% yield. The

Scheme 1.



IIa, **III**, n = 1; **IIb**, **IV**, n = 2; **I**, **III**, R = H, R′ = Me (**a**), Ph (**b**), EtOCO (**c**); R = R′ = $EtOCOCH_2$ (**d**), Me (**e**); **IV**, R = R′ = Me; **V**, R = Me (**a**), $EtOCOCH_2$ (**b**).

yields of aza crowns **IIIa**, **IIIb**, and **IIIe** were approximately similar (about 40%). Introduction of electron-withdrawing substituents into the initial ketone molecule, as well as extension of the oligoether chain appreciably reduced the product yield (to 24–26%).

In the ^{1}H NMR spectra of monosubstituted aza crownophanes **IIIa**–**IIIc** ($CDCl_3$), only the signal from the equatorial 24-H_{eq} proton in the piperidine ring is readily identified. It appears as a doublet of doublets at δ 2.57–2.72 ppm with a large geminal coupling constant (^2J = 13.5–14.2 Hz) and small vicinal coupling constant with the axial proton on C^1 (^3J = 2.0–2.6 Hz). No such signal is present in the spectra of 22,24-disubstituted derivatives **IIId**, **IIIe**, **IV**, and **V** where all bulky substituents in the piperidine ring are equatorial while all CH protons are axial; the latter resonate in a weaker field, at δ 3–4 ppm. These data indicate deshielding effect of the crown ether fragment on the axially oriented 22-H and 24-H protons. As shown in [7], all analogous equatorial and axial β-protons in 2,6-diarylpiperidin-4-ones resonate in the region δ 2.56–2.76 ppm. The observed effect is likely to result from magnetic fields created by the phenoxy fragments. The assignment of signals from the axial methine protons in the $MeCH_{ax}COCH_{ax}Me$ fragments of **IIIe**, **IV**, and **V** is facilitated due to their interaction with the methyl protons. These protons resonate as octet-like multiplets at δ 3.36 ppm for aza-14-crown-4 **IIIe**, and their signals shift upfield as the oligoether chain becomes longer: Δδ = 0.55 ppm for aza-17-crown-5 **IV**. Greater conformational mobility of the crown ether fragment in molecule **IV** reduces deshielding effect of the phenoxy fragments on 22-H and 24-H. The other methine and methylene protons in the macrocycle (CHNHCH and OCH_2CH_2O fragments) are difficult to assign; their signals overlap each other, giving rise to a complicated pattern in the region δ 3.3–4.4 ppm.

With a view to unambiguously confirm the product structure, determine their configurational and conformational parameters, and estimate the size of their internal cavities, we performed X-ray analysis of single crystals of compounds **IIIe** and **IV**. Figures 1 and 3 show the structures of their molecules, and the conformations of the piperidine and crown ether fragments (without benzene rings) are shown in Figs. 2 and 4.

Compound **IIIe** is a 14-membered aza crownophane. According to the X-ray diffraction data, the size of the internal cavity therein, estimated as the double average distance between the cyclic n-electron-donor heteroatoms and the centroid of the $N^1O^1O^2O^{1A}$ tetragon, is equal to 4.02 Å. The conformation of the polyether fragment $C^6O^1C^{11}C^{12}O^2C^{12A}C^{11A}O^{1A}C^{6A}$ is t-$g^{(+)}$-t-t-$g^{(-)}$-t where t stands for *trans* (±180°) and g stands for *gauche* (±60°). Molecule **IIIe** has an idealized $C_s(m)$ symmetry which is exactly reproduced in crystal (the molecule occupies a partial position on the m plane). It involves two symmetric intramolecular hydrogen bonds N^1–$H^1\cdots O^1$ and N^1–$H^1\cdots O^{1A}$ (Fig. 1) with the

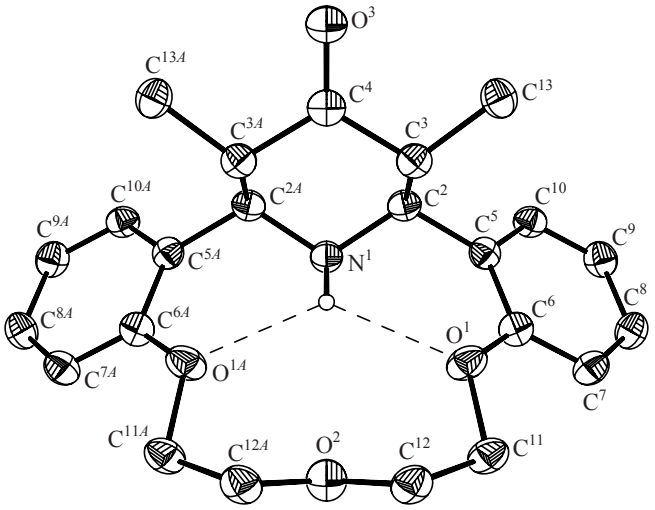


Fig. 1. Structure of the molecule of compound **IIIe** according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal ellipsoids with a probability of 50%; intramolecular hydrogen bonds are shown with dashed lines.

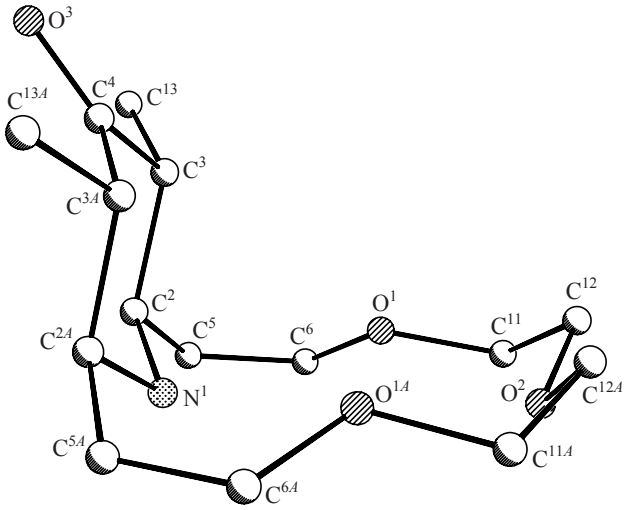


Fig. 2. Conformations of the heterocyclic fragments and spatial arrangement of substituents in the piperidine ring of molecule **IIIe** according to the X-ray diffraction data.

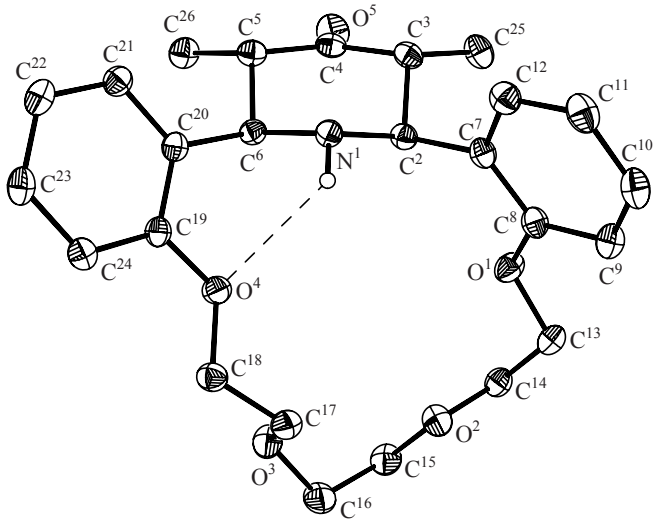


Fig. 3. Structure of the molecule of compound **IV** according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal ellipsoids with a probability of 50%; intramolecular hydrogen bond is shown with a dashed line.

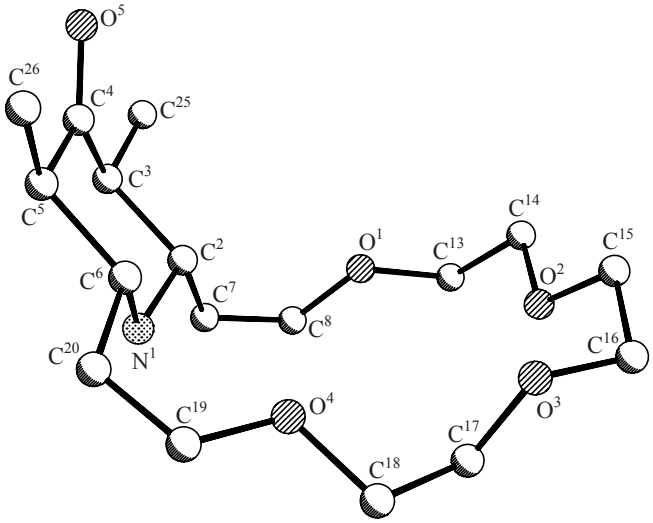


Fig. 4. Conformations of the heterocyclic fragments and spatial arrangement of substituents in the piperidine ring of molecule **IV** according to the X-ray diffraction data.

following parameters: N···O 2.993(2), H···O 2.45(2) Å, ∠NHO 122(1)°. The formation of intramolecular hydrogen bonds is responsible for deviation of the N^1, O^1, O^2, and O^{1A} donor atoms from planar arrangement: the mean-square deviation is 0.174 Å.

Molecule **IIIe** contains four asymmetric centers (C^2, C^3, C^{3A}, and C^{2A}). Compound **IIIe** in crystal is a racemate with the relative configuration *rac*-(2*S**,3*R**,3*AS**,2*AR**). The dihedral angle between the benzene ring planes is 56.3°. The piperidine ring adopts an almost ideal *chair* conformation characterized by torsion angles ranging from 50.3(2) to 57.9(2)° in absolute values. The dihedral angles between the benzene rings and the average piperidine ring plane ($C^2C^3C^{3A}C^{2A}$) are equal to 104.4°. The two aryl and two methyl groups in the piperidine ring occupy equatorial positions. Figures 1 and 2 show that the phenoxy fragments are turned in such a way that the oxygen atoms face the axial H^3 and H^{3A} protons and are fixed by intramolecular hydrogen bond. This configuration is consistent with the observed deshielding of the H^3 and H^{3A} protons in the ^{1}H NMR spectrum of **IIIe**.

Compound **IV** is a 17-membered aza crownophane; the size of the internal cavity therein, estimated as the double average distance between the cyclic *n*-electron-donor heteroatoms and the centroid of the $N^1O^1O^2O^3O^4$ pentagon, is equal to 5.30 Å. The conformation of the $C^8O^1C^{13}C^{14}O^2C^{15}C^{16}O^3C^{17}C^{18}O^4C^{19}$ polyether fragment in molecule **IV** is *t*-$g^{(-)}$-*t*-*t*-$g^{(+)}$-*c*-*t*-*g*-$t^{(-)}$ where *t* stands for *trans* (±180°), *g* stands for *gauche* (±60°), and *c* stands for *clinal* (±90°). Molecule **IV** has an idealized $C_s(m)$ symmetry; however, the presence of only one intramolecular hydrogen bond $N^1H^1\cdots O^4$ [N···O 3.033(2), H···O 2.49(2) Å, ∠NHO 122(1)°] (Fig. 3) distorts the symmetry. The O^4 atom involved in intramolecular hydrogen bond deviates by 0.338(8) Å from the plane formed by the other donor atoms of the macroring. Compound **IV** possesses four chiral centers: C^2, C^3, C^5, and C^6; it is a racemic mixture of diastereoisomers with the relative configuration *rac*-(2*S**,3*R**,5*S**,6*R**). The benzene rings are almost orthogonal to each other: the dihedral angle between their planes is 88.3°. The piperidine ring has a slightly distorted *chair* conformation (Fig. 4); the torsion angles therein range from 48.0(2) to 67.4(2)° in absolute values. The dihedral angles between the benzene ring planes and the average plane of the piperidine ring ($C^2C^3C^5C^6$) are 41.6° for the phenoxy fragment involved in intramolecular hydrogen bond and 101.0° for the other. The aryl and methyl substituents in the piperidine ring are equatorial.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker WP-400 spectrometer at 400 MHz using $CDCl_3$ as solvent. The mass spectra (70 eV, electron impact) were obtained on a Finnigan MAT INCOS-50 mass spectrometer with direct sample admission into the ion source. The IR spectra were measured in KBr on a Specord 75IR instrument. Preparative column chromatography was performed on aluminum oxide (100–160 μm). The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates. Ketones **Ia**–**Id** were commercial products; dialdehydes **II** were synthesized according to the procedure described in [5].

X-Ray analysis of compounds IIIe and IV. The unit cell parameters and reflection intensities were measured on a Bruker SMART 1000 CCD automatic diffractometer at 120 K (MoK_α irradiation, graphite monochromator, φ- and ω-scanning). The principal crystallographic data and refinement parameters are given in table. The structures of both compounds were solved by the direct methods and were refined by the full-matrix least-square procedure in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were localized objectively by Fourier difference syntheses, and their positions were refined in isotropic approximation. All calculations were performed using SHELXTL PLUS software package [8]. The complete sets of crystallographic data (coordinate of atoms, bond lengths, bond angles, and anisotropic temperature parameters) for compounds **IIIe** and **IV** were deposited to the Cambridge Crystallographic Data Center.

Principal crystallographic data and refinement parameters for compounds **IIIe** and **IV**

Parameter	**IIIe**	**IV**
Formula	$C_{23}H_{27}NO_4$	$C_{25}H_{31}NO_5$
Molecular weight	381.46	425.51
Temperature, K	120	120
Crystal system	Rhombic	Triclinic
Space group	*Pnma*	*P*-1
a, Å	7.9988(15)	9.6546(8)
b, Å	20.662(4)	10.4316(8)
c, Å	11.626(2)	11.9408(9)
α, deg	90	69.988(1)
β, deg	90	84.617(2)
γ, deg	90	85.347(2)
V, Å^3	1921.3(6)	1123.45(15)
Z	4	2
d_{calc}, g cm^{-3}	1.319	1.258
F(000)	816	456
μ, mm^{-1}	0.090	0.087
$2\theta_{max}$, deg	54	54
Total number of reflections	15566	10811
Number of independent reflections	2144	4881
Number of reflections with $I > 2\sigma(I)$	1582	3419
Number of refined parameters	404	188
R_1 [$I > 2\sigma(I)$]	0.057	0.056
wR_2 (all reflections)	0.145	0.153
Goodness of fit	1.037	1.018

Aza crownophanes IIIa–IIIe, IV, Va, and Vb (*general procedure*). A solution of 16 mmol of oligoether **IIa**–**IIc**, 16 mmol of ketone **Ia**–**Ie**, and 1.57 g

(20 mmol) of ammonium acetate in a mixture of 15 ml of ethanol and 3 ml of acetic acid was heated for 5 h under reflux. The solvent was removed under reduced pressure, 50 ml of a saturated solution of sodium carbonate was added to the residue, and the mixture was extracted with chloroform (3×30 ml). The extracts were combined, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was subjected to column chromatography on alumogel using ethyl acetate–hexane (1:1) as eluent. The product was additionally purified by recrystallization from ethanol. Compounds **IIIa**–**IIIe**, **IV**, **Va**, and **Vb** were isolated as colorless crystalline substances.

22-Methyl-8,11,14-trioxa-25-azatetracyclo-[19.3.1.$0^{2,7}$.$0^{15,20}$]pentacosa-2,4,6,15(20),16,18-hexaen-23-one (IIIa). Yield 2.35 g (40%), mp 232–233°C (from alcohol). IR spectrum, ν, cm^{-1}: 3302 (NH), 1696 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.82 d (3H, Me, J = 5.7 Hz), 2.57 d.d (1H, 24-H_{eq}, ^2J = 13.5, ^3J = 2.2 Hz), 3.10 br.s (1H, NH), 3.30 m (1H, 22-H), 3.35–4.25 m (11H, 1-H, 9-H, 10-H, 12-H, 13-H, 21-H, 24-H), 6.77 d (2H, 6-H, 16-H, J = 8.14 Hz), 6.85 br.s (2H, 4-H, 18-H), 7.09–7.20 m (4H, 3-H, 5-H, 17-H, 19-H). Mass spectrum, m/z (I_{rel}, %): 367 (56) $[M]^+$, 352 (5), 339 (7), 310 (25), 297 (20), 279 (12), 251 (31), 180 (14), 148 (27), 131 (61), 211 (52), 105 (37), 91 (100), 77 (78). Found, %: C 71.57; H 7.01; N 3.68. $C_{22}H_{25}NO_4$. Calculated, %: C 71.91; H 6.86; N 3.81.

22-Phenyl-8,11,14-trioxa-25-azatetracyclo-[19.3.1.$0^{2,7}$.$0^{15,20}$]pentacosa-2,4,6,15(20),16,18-hexaen-23-one (IIIb). Yield 2.4 g (35%), mp 210–212°C (from alcohol). IR spectrum, ν, cm^{-1}: 3325 (NH), 1700 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.70 d.d (1H, 24-H_{eq}, ^2J = 13.6, ^3J = 2.2 Hz), 3.47 br.m (1H, 22-H), 3.93 d.d (1H, 24-H, ^2J = 13.6, ^3J = 1.0 Hz), 3.90–4.45 m (11H, H_{aliph}, NH), 6.57–7.25 m (13H). Mass spectrum, m/z (I_{rel}, %): 429 (100) $[M]^+$, 310 (71), 297 (44), 131 (62), 121 (80), 119 (90), 118 (81), 91 (89). Found, %: C 75.37; H 6.45; N 3.68. $C_{27}H_{27}NO_4$. Calculated, %: C 75.50; H 6.34; N 3.26.

Ethyl 23-oxo-8,11,14-trioxa-25-azatetracyclo-[19.3.1.$0^{2,7}$.$0^{15,20}$]pentacosa-2,4,6,15(20),16,18-hexaene-22-carboxylate (IIIc). Yield 1.63 g (24%), mp 200–201°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 3325 (NH), 1743 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.06 t (3H, $CH_2C\mathbf{H}_3$, ^3J = 7.1 Hz), 2.62 d.d (1H, 24-H_{eq}, ^2J = 14.1, ^3J = 2.02 Hz), 3.29 br.s (1H, NH), 3.80–4.28 m (12H, H_{aliph}, NH), 4.37 q (2H, $C\mathbf{H}_2CH_3$, ^3J = 7.1 Hz), 6.76–7.61 m (8H, H_{arom}). Mass spectrum, m/z (I_{rel}, %): 425 (9) $[M]^+$, 310 (10), 247 (23), 131 (52), 121 (43), 91 (69), 77 (34), 43 (100). Found, %: C 67.57; H 6.67; N 3.18. $C_{24}H_{27}NO_6$. Calculated, %: C 67.75; H 6.40; N 3.29.

Ethyl 2-{24-ethoxycarbonylmethyl-23-oxo-8,11,14-trioxa-25-azatetracyclo[19.3.1.$0^{2,7}$.$0^{15,20}$]-pentacosa-2(7),3,5,15,17,19-hexaen-22-yl}acetate (IIId). Yield 2.26 g (27%), mp 176–178°C (from ethyl acetate–hexane). IR spectrum, ν, cm^{-1}: 3319 (NH); 1734, 1700 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.12 t (6H, $CH_2C\mathbf{H}_3$, ^3J = 7.12 Hz), 1.97 d.d (2H, CH_2CO, ^2J = 16.7, ^3J = 4.94 Hz), 2.58 d.d (2H, CH_2CO, ^2J = 16.7, ^3J = 6.8 Hz), 3.71–4.50 m (16H, H_{aliph}, NH), 6.77 d (2H, 6-H, 16-H, ^3J = 8.17 Hz), 6.82 br.t (2H, 4-H, 18-H, ^3J = 7.42 Hz), 7.08 d.d (2H, 3-H, 19-H, ^3J = 7.45, ^4J = 1.5 Hz), 7.17 t.t (2H, 5-H, 17-H, ^3J = 8.16, 7.5, ^4J = 1.5 Hz). Mass spectrum, m/z (I_{rel}, %): 525 (100) $[M]^+$, 497 (41), 480 (79), 452 (68), 438 (52), 396 (53), 297 (91), 131 (34), 119 (23). Found, %: C 65.98; H 7.04; N 2.34. $C_{29}H_{35}NO_8$. Calculated, %: C 66.27; H 6.71; N 2.66.

22,24-Dimethyl-8,11,14-trioxa-25-azatetracyclo-[19.3.1.$0^{2,7}$.$0^{15,20}$]pentacosa-2,4,6,15(20),16,18-hexaen-23-one (IIIe). Yield 2.5 g (41%), mp 248–249°C. IR spectrum, ν, cm^{-1}: 3319 (NH), 1693 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.81 d (6H, Me, ^3J = 6.26 Hz), 3.36 m (2H, 22-H, 24-H), 3.48 t (2H, CH_2O, ^3J = 12.0, 11.3 Hz), 3.84 m (2H, CH_2O), 4.04 d (2H, 1-H, 21-H, J = 10.7 Hz), 4.10–4.35 m (5H, H_{aliph}, NH), 6.76 d (2H, 6-H, 16-H, ^3J = 8.16 Hz), 6.85 t (2H, 4-H, 18-H, J = 7.41 Hz), 7.08 br.d (2H, 3-H, 19-H, ^3J = 7.36 Hz), 7.16 t.t (2H, 5-H, 17-H, ^3J = 7.75, ^4J = 1.4 Hz). Mass spectrum, m/z (I_{rel}, %): 381 (89) $[M]^+$, 353 (51), 324 (76), 297 (100), 296 (53), 293 (27), 265 (25), 149 (44), 134 (54), 121 (50), 119 (52), 91 (22). Found, %: C 72.11; H 7.22; N 3.58. $C_{23}H_{27}NO_4$. Calculated, %: C 72.42; H 7.13; N 3.67.

25,27-Dimethyl-8,11,14,17-tetraoxa-28-azatetracyclo[22.3.1.$0^{2,7}$.$0^{18,23}$]octacosa-2,4,6,18(23),19,21-hexaen-26-one (IV). Yield 1.76 g (26%), mp 165–167°C. IR spectrum, ν, cm^{-1}: 3321 (NH), 1711 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.88 d (6H, Me, J = 6.53 Hz), 2.81 m (2H, 25-H, 27-H), 3.50 br.s (1H, NH), 3.61–3.85 m (8H, 10-H, 12-H, 13-H, 15-H), 4.01–4.11 m (4H, 9-H, 16-H), 4.39 d (2H, 1-H, 24-H, J = 10.9 Hz), 6.76 d (2H, 6-H, 16-H, J = 8.0 Hz), 6.94 t (2H, 4-H, 21-H, J = 7.56), 7.14 t (2H, 5-H, 20-H, ^3J = 8.0, 7.52 Hz), 7.53 d (2H, 3-H, 22-H, J = 7.56 Hz). Mass spectrum, m/z (I_{rel}, %): 425 (91) $[M]^+$, 424 (7), 410 (8), 397 (35), 383 (19), 368 (64), 340

(57), 310 (24), 264 (25), 161 (46), 149 (48), 131 (68), 121 (100), 119 (42), 91 (57), 77 (40). Found, %: C 70.13; H 7.53; N 3.05. $C_{25}H_{31}NO_5$. Calculated, %: C 70.57; H 7.34; N 3.29.

30,32-Dimethyl-12,15,18-trioxa-33-azahexacyclo-[27.3.1.$0^{2,11}$.$0^{3,8}$.$0^{19,28}$.$0^{22,27}$]tritriaconta-2,4,6,8,10,-19(28),20,22(27),24-nonaen-31-one (Va). Yield 1.3 g (17%), mp 253–255°C. IR spectrum, ν, cm^{-1}: 3348 (NH), 1698 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.70 d (6H, Me, ^3J = 6.1 Hz), 1.10 t (1H, NH, J = 6.0 Hz), 3.68 m (2H, 30-H, 32-H), 3.90–4.45 m (8H, CH_2O, NCH), 4.84 t (2H, CH_2O, J = 12.0 Hz), 7.30 t (2H, H_{arom}, J = 9.0, 6.0 Hz), 7.37 d (2H, H_{arom}, J = 9.0 Hz), 7.47 t (2H, H_{arom}, J = 9.0, 6.0 Hz), 7.81 d (2H, H_{arom}, J = 9.0 Hz), 7.86 d (2H, H_{arom}, J = 9.0 Hz), 8.33 d (2H, H_{arom}, J = 9.0 Hz). Mass spectrum, m/z (I_{rel}, %): 481 (18) $[M]^+$, 466 (5), 453 (4), 365 (12), 228 (21), 195 (28), 181 (63), 169 (100), 168 (51), 152 (31), 141 (56), 115 (52). Found, %: C 77.18; H 6.57; N 2.98. $C_{31}H_{31}NO_4$. Calculated, %: C 77.31; H 6.49; N 2.91.

Ethyl 2-{32-ethoxycarbonylmethyl-31-oxo-12,15,18-trioxa-33-azahexacyclo-[27.3.1.$0^{2,11}$.$0^{3,8}$.$0^{19,28}$.$0^{22,27}$]tritriaconta-2(11),3(8),5,-9,19,21,23,25,27-nonaen-30-yl}acetate (Vb). Yield 1.4 g (14%), mp 235–237°C. IR spectrum, ν, cm^{-1}: 3329 (NH); 1738, 1703 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.96 t (6H, $CH_2C\mathbf{H}_3$, ^3J = 7.2 Hz), 1.69 d.d (2H, CH_2CO, ^2J = 16.5, ^3J = 4.8 Hz), 2.55 d.d (2H, CH_2CO, ^2J = 16.5, ^3J = 4.8 Hz), 3.75 q (4H, $C\mathbf{H}_2CH_3$, ^3J = 7.2 Hz), 3.95–4.62 m (11H, H_{aliph}, NH), 5.51 t (2H, H_{aliph}, J = 12.0 Hz), 7.32 t (2H, H_{arom}, J = 9.0, 6.0 Hz), 7.40 d (2H, H_{arom}, J = 9.0 Hz), 7.50 t (2H, H_{arom}, J = 9.0, 6.0 Hz), 7.82 d (2H, H_{arom}, J = 9.0 Hz), 7.89 d (2H, H_{arom}, J = 9.0 Hz), 8.28 d (2H, H_{arom}, J = 9.0 Hz). Mass spectrum, m/z (I_{rel}, %): 625 (7) $[M]^+$, 509 (10), 397 (22), 228 (20), 199 (21), 182 (81), 181 (100), 169 (90), 153 (23), 141 (48), 115 (37). Found, %: C 70.91; H 6.35; N 2.12. $C_{37}H_{39}NO_8$. Calculated, %: C 71.02; H 6.28; N 2.24.

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