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Tricyclo[7.3.1.0^{2,7}]tridecanes with an Amino Group at the Bridging Carbon. Synthesis and Stereochemistry

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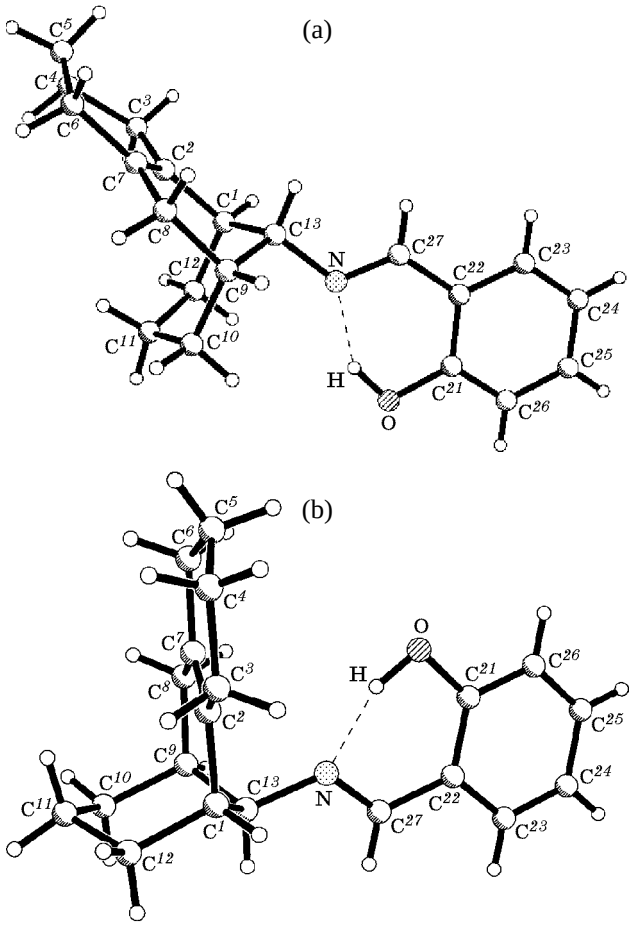
Abstract—Hydroamination of tricyclo[7.3.1.0^{2,7}]tridec-2(7)-en-13-one according to Leukart reaction furnished (tricyclo[7.3.1.0^{2,7}]tridec-2(7)-en-13-yl)methanamides stereoisomeric at C^{13} atom. The corresponding epoxides were prepared therefrom. The unsaturated and epoxidized methanamides were hydrolyzed into amines that were converted into Schiff bases.The configurations of substances were established.

Compounds from the tricyclo[7.3.1.0^{2,7}]tridecane series were first obtained about fifty years ago [1]. They attracted interest when it was established that their skeleton was a key fragment in limonoid molecules [2]. In this connection we studied hydroamination of compound **I** by Leukart procedure in more detail [3].

From the reaction products of enone (**I**) and formamide we separated two stereoisomeric methanamides **IIa, b** that were present in the reaction mixture in 3 : 2 ratio, and a small amount of secondary amine **III**. The hydrolysis of formyl derivatives **IIa, b** with alcoholic alkali yielded amines **IVa, b**. The reactivity of the tetrasubstituted double bond in methanamides **IIa, b** was tested by reaction with monoperphthalic acid that provided the corresponding epoxymethanamides **Va, b**. The latter on hydrolysis afforded epoxyamines **VIa, b**. Amine **IVa** with furfural, *p*-nitrobenzaldehyde, and *p*-dimethylaminobenzaldehyde gave rise to well crystallizable Schiff bases **VII–X** whereas its isomer **IVb** formed crystalline azomethine **XI** only in reaction with salicylaldehyde. Epoxyamine **VIa** formed crystalline azomethine **XII** with *p*-nitrobenzaldehyde; we failed to obtain Schiff bases from its isomer **VIb**.

The structure of compounds obtained was confirmed by spectral data (Table 1); the spatial structure of azomethines **VIII** and **XI** was established by X-ray diffraction study (see the figure).

IR spectra of amides **IIa, b, Va, b** contain the set of absorption bands characteristic of amide groups. The IR spectra of amines **IVa, b, VIa, b** lack the absorption bands of amide groups, and the presence of amino groups is confirmed by two weak bands in the regions 4310–3385 and 3350–3330 cm^{-1}. In the



Structure of Schiff bases: (a) **VIII**; (b), **IX**.

† Deceased.

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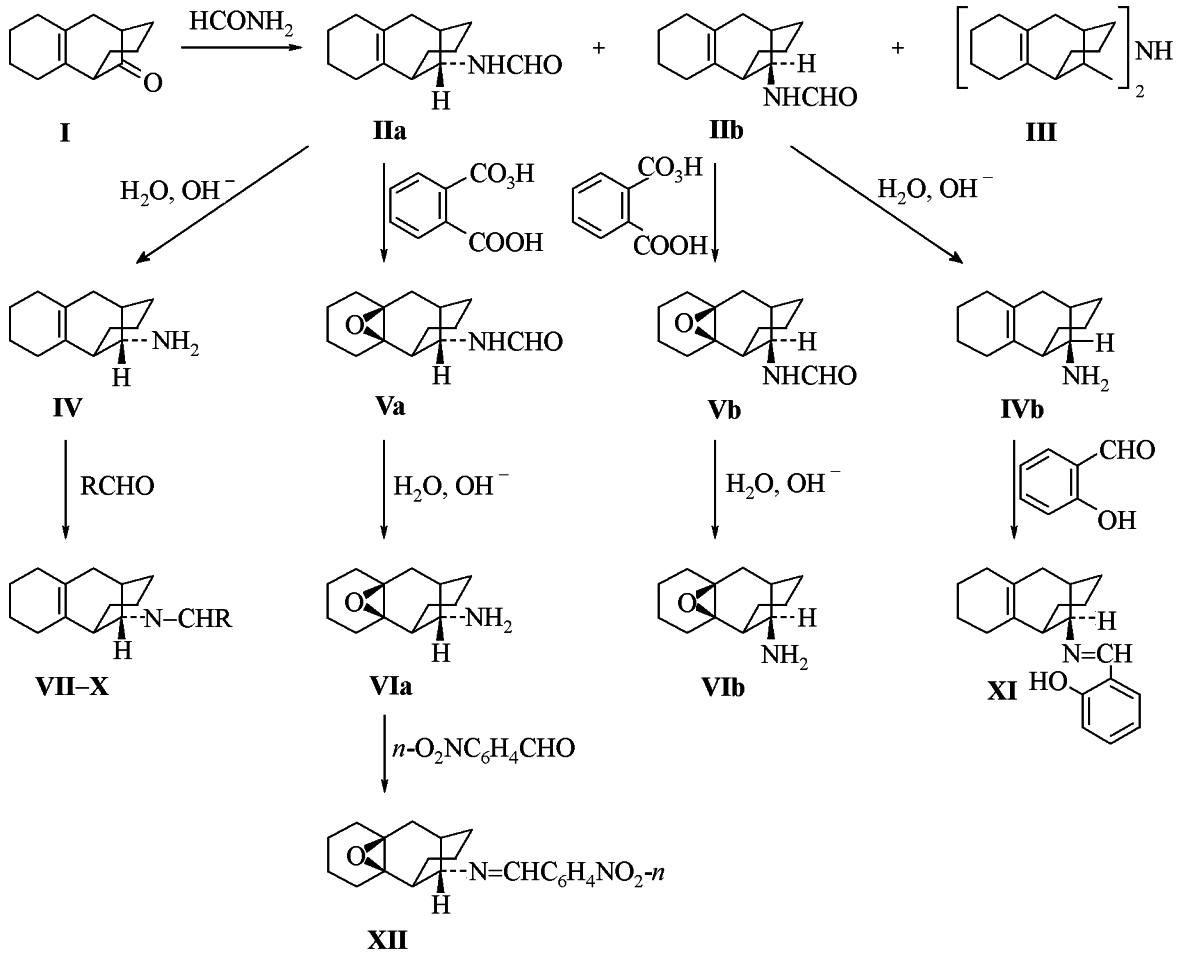
Table 1. ^{13}C NMR spectra, chemical shift values (δ, ppm) of methine and unsaturated carbon atoms (chemical shifts of less intensive signals are given in parentheses)

Compd. no.	C^{1}	C^{2}	C^{7}	C^{9}	C^{13}	C^{14}
IIa	37.83	129.90	129.08	30.85	47.97	160.58
	(40.14)	(130.09)	(129.0)	(32.57)	(51.86)	(164.06)
IIb	40.00	130.85	127.18	31.75	49.38	160.39
	(41.1)	(131.08)	(127.0)	(34.29)	(56.74)	(163.42)
Va	36.84	65.24	61.82	29.41	43.56	160.57
	(39.23)	(65.68)	(62.18)	(31.47)	(47.43)	(164.49)
Vb	37.65	66.20	63.11	31.01	49.30	160.03
	(40.07)	(–)	(–)	(31.82)	(49.40)	(160.4)
VIII	41.46	130.05	129.30	34.24	69.15	162.63
XI	41.87	130.41	126.64	34.56	70.61	161.92



R = α-furyl (**VII**), *o*-C_6H_4OH (**VIII**), *p*-$C_6H_4NO_2$ (**IX**), *p*-$C_6H_4N(CH_3)_2$ (*X*).

IR spectra of Schiff bases **VII–XII** appears absorption around 1630 cm^{-1} typical for imino group. The tetrasubstituted double bond does not show up in any IR spectrum of the compounds under consideration.

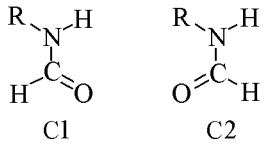
In the ^{1}H NMR spectra of stereoisomeric methanamides **IIa, b** appear signals of amide, formyl, methine, and methylene protons. The protons attached to the bridging atom C^{13} give signals in the

relatively weak field, at δ 4.14 (**IIa**) and 4.08 ppm (**IIb**).

In the ^{1}H NMR spectra of compounds **IIa, b** solutions in $CDCl_3$ additional proton signals are observed indicating that the molecules are present in the solution in two conformational states in 3 : 1 ratio. Similar pattern is observed also in the ^{1}H NMR spectra of epoxymethanamides **Va, b** (conformers ratio 2 : 1).

The analysis of chemical shift values and coupling constants of the characteristic protons shows that the double set of signals may be ascribed to the presence in solution of pairs of stable amide conformations (**IIa, b** and **VIa, b**); the coupling constant of 0.9 Hz between the aldehyde proton and the proton at the bridging carbon C^{13} is due to W-coupling.

^{13}C NMR spectra of methanamides **IIa, b**, epoxymethanamides **Va, b**, azomethines **VIII, XI** are consistent with the assumed structures. In these spectra also appear additional signals (for compounds **IIa, b, Va, b**), same as in the proton spectra. The analysis of the chemical shift values for the characteristic carbon atoms (Table 1) showed that the double set of signals might be attributed to the existence in the solutions of pairs of stable amides conformations that differed from each other as C1 and C2 conformations.



The less intensive peak should be assigned to more spatially strained conformation. A similar pattern in the NMR spectra of methanamides obtained by Leukart reaction already was described [4]. It should be noted that in the ^{13}C NMR spectra of stereoisomers the difference between chemical shifts of C^2 and C^7 may be characteristic: Δδ 0.9 (**IIa**), 3.85 (**IIb**), 0.8 (**VIII**), 3.8 ppm (**XI**).

According to current concepts [5] the mechanism of Leukart reaction includes primary formation of *N*-formylimine A that is subsequently reduced by formic acid to methanamide **IIa** or **IIb**.

When the reduction of intermediate A takes route *a* isomer **IIa** arises with the double bond and the amide group anti-located with respect to the bridge. The reduction along *b* route results in the syn-isomer **IIb**. As shows the ratio of **IIa** and **IIb** isomers in the reaction mixture the reduction of imino group occurs along both ways with comparable rates. The stereochemistry of double bond epoxidation in compounds **IIa, b** was suggested basing on the results of [6] where it had been proved for bridging alcohols.

EXPERIMENTAL

IR spectra were measured on spectrometer Perkin-Elmer Spectrum BX 2 from thin films or solutions of compounds in chloroform. ^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker WM-250 from solutions in $CDCl_3$ with TMS as internal reference. In identification and assignment of peaks was used procedures of *J*-modulation. GC-MS analysis was carried out on HP 5972 MSD/HP instrument. The *m/z* values of molecular ions for all compounds synthesized were in agreement with the calculated molecular weights.

Physical constants and analytical data are presented in Table 2. X-ray diffraction analysis was carried out by A. V. Gerasimenko at the Institute of Chemistry, Far-Eastern Division, Russian Academy of Sciences. The study was performed on an edged single crystal with the use of diffractometer SMART 1000 CCD (MoK_α-radiation, graphite monochromator). Data collection was performed by sets of 906, 660, and 345 exposures at angle values φ 0, 90, and 180° respectively. The ω-scanning was done with a step of

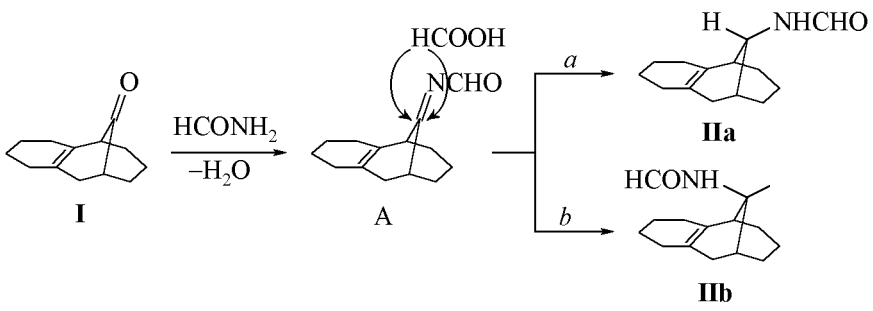


Table 2. Yields, melting points, and elemental analyses of tricyclo[7.3.1.0^{2,7}]tridecane derivatives **II**–**XII**

Compd. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
IIa	57[a]	145–146	76.65	10.27	6.44	$C_{14}H_{21}NO$	76.66	9.65	6.39
IIb	38[a]	126–127	76.86	9.84	6.44	$C_{14}H_{21}NO$	76.66	9.65	6.39
III	4	[b]	86.92	11.31	4.02	$C_{26}H_{39}N$	85.41	10.75	3.83
IVa	70	[c]	81.66	11.32	7.40	$C_{13}H_{21}N$	81.61	11.06	7.33
IVb	70	[d]	81.25	11.56	7.28	$C_{13}H_{21}N$	81.61	11.06	7.33
Va	85	143–144	71.73	9.35	6.06	$C_{14}H_{21}NO_2$	71.45	9.00	5.95
Vb	88	104–105	71.18	8.83	6.18	$C_{14}H_{21}NO_2$	71.45	9.00	5.95
VIa	83	46–47	75.19	9.93	6.71	$C_{13}H_{21}NO$	75.31	10.21	6.76
VIb	60	[e]	75.20	10.67	6.88	$C_{13}H_{21}NO$	75.31	10.21	6.88
VII	90	81–82	80.57	8.60	4.96	$C_{18}H_{23}NO$	80.25	8.61	5.20
VIII	92	86–87	81.31	8.39	5.15	$C_{20}H_{25}NO$	81.31	8.53	4.74
IX	95	139–140	74.02	7.58	8.66	$C_{20}H_{24}N_2O_2$	74.04	7.46	8.64
X	90	127–128	82.33	9.64	8.60	$C_{22}H_{30}N_2$	81.93	9.38	8.69
XI	75	95–96	81.46	8.60	5.04	$C_{20}H_{25}NO$	81.31	8.53	4.74
XII	90	170–171	70.79	7.13	8.82	$C_{20}H_{24}N_2O_3$	70.56	7.11	8.23

[a] According to data of chromatography.
[b] bp 222–223°C (2 mm Hg), n_D^{21} 1.5510.
[c] bp 119–120°C (0.5 mm Hg), n_D^{20} 1.5360.
[d] bp 70°C (0.1 mm Hg), n_D^{22} 1.5310.
[e] bp 81–84°C (0.1 mm Hg), n_D^{21} 1.5235.

Table 3. Crystallographic parameters, conditions of X-ray diffraction experiment and of refining the structures of compounds **VIII** and **XI**

Parameter	(**VIII**)	(**XI**)
Formula	$C_{20}H_{25}NO$	$C_{20}H_{25}NO$
Molecular weight	295.41	295.41
Temperature, K	295 (2)	295 (2)
Wavelength, MoK_α, Å	0.71073	0.71073
Crystal system	Monoclinic	Rhombic
Space group	$P2_1/c$	$Pbca$
a, Å	15.296 (4)	15.077 (2)
b, Å	8.687 (2)	11.517 (2)
c, Å	12.886 (3)	19.009 (3)
β, deg.	95.292 (5)	
V, Å^3	1705.0 (8)	3300.9 (8)
Z	4	8
d_{calc}, g/cm^3	1.151	1.189
μ, mm^{-1}	0.070	0.072
F(000)	640	1280
Crystal habit, mm	Prism (0.12× ×0.19×0.36)	Prism (0.20× ×0.30×0.40)

Table 3. (Contd.)

Parameter	(**VIII**)	(**XI**)
Data collection range of θ, deg.	1.34–21.08	2.14–23.27
Range of reflections indices	$-15 \le h \le 15$, $-5 \le k \le 8$, $-12 \le l \le 12$	$-16 \le h \le 15$, $-12 \le k \le 9$, $-20 \le l \le 21$
Total number of reflections	5568	14485
Number of independent reflections	1836 (R_{int} 0.0518)	2369 (R_{int} 0.0430)
Reflections with $I > 2\sigma$ (**I**)	1199	1744
Refinement method	Full-matrix MHK by F^2	Full-matrix MHK by F^2
Refined parameters	204	203
GooF	0.951	1.033
R-factors for $F^2 > 2\Sigma(F^2)$	$R1$ 0.0502, $wR2$ 0.1294	$R1$ 0.0524, $wR2$ 0.1506
R-factors for all reflections	$R1$ 0.0786, $wR2$ 0.1425	$R1$ 0.071, $wR2$ 0.1665
Extinction factor	0.005 (2)	0.0014 (4)
Residual electron density (min/max), e/Å^3	–0.199/0.276	–0.377/0.354

Table 4. Atom coordinates ($\times 10^3$ for H, $\times 10^4$ for the other atoms) and their isotropic equivalent thermal factors for compound **VIII**

Atom	*x*	*y*	*z*	U_{eq}
O	9076 (1)	3190 (2)	4072 (1)	0.0799 (5)
N	8655 (1)	1229 (2)	2594 (1)	0.0568 (5)
C^1	7293 (1)	–277 (2)	2251 (2)	0.0517 (6)
C^2	6711 (1)	–1057 (2)	1391 (2)	0.0475 (6)
C^3	6231 (2)	–2485 (3)	1688 (2)	0.0710 (8)
C^4	5545 (2)	–3013 (3)	851 (2)	0.1050 (1)
C^5	5794 (2)	–2850 (3)	–186 (2)	0.101 (1)
C^6	6080 (1)	–1263 (3)	–454 (2)	0.0643 (7)
C^7	6629 (1)	–483 (2)	435 (2)	0.0491 (6)
C^8	7097 (1)	953 (2)	139 (2)	0.0599 (7)
C^9	7632 (1)	1779 (3)	1034 (2)	0.0565 (7)
C^{10}	7088 (1)	2912 (3)	1620 (2)	0.0670 (8)
C^{11}	6390 (1)	2146 (3)	2201 (2)	0.0648 (7)
C^{12}	6769 (1)	833 (3)	2885 (2)	0.0628 (7)
C^{13}	8044 (1)	553 (2)	1779 (2)	0.0528 (6)
C^{21}	9860 (1)	2451 (2)	4239 (2)	0.0530 (6)
C^{22}	10052 (1)	1200 (2)	3605 (2)	0.0524 (6)
C^{23}	10861 (1)	498 (3)	3812 (2)	0.0844 (9)
C^{24}	11463 (2)	997 (3)	4588 (2)	0.0960 (1)
C^{25}	11265 (2)	2228 (3)	5192 (2)	0.0772 (8)
C^{26}	10465 (1)	2941 (3)	5022 (2)	0.0670 (8)
C^{27}	9412 (1)	640 (3)	2800 (2)	0.0568 (7)
H	872 (1)	266 (3)	355 (2)	0.0950 (8)

Table 5. Atom coordinates ($\times 10^3$ for H, $\times 10^4$ for the other atoms) and their isotropic equivalent thermal factors for compound **XI**

Atom	*x*	*y*	*z*	U_{eq}
O	–1189 (1)	2866 (1)	6270 (1)	74 (1)
N	490 (1)	2488 (1)	6151 (1)	53 (1)
C^1	1635 (1)	3936 (2)	5849 (1)	50 (1)
C^2	1055 (1)	4946 (2)	6072 (1)	46 (1)
C^3	905 (1)	5873 (2)	5531 (1)	56 (1)
C^4	326 (2)	6833 (2)	5774 (1)	117 (1)
C^5	–147 (2)	6740 (3)	6373 (1)	160 (1)
C^6	110 (1)	5968 (2)	6947 (1)	67 (1)
C^7	721 (1)	4999 (2)	6722 (1)	52 (1)
C^8	896 (1)	4087 (2)	7266 (1)	64 (1)
C^9	1532 (1)	3119 (2)	7047 (1)	60 (1)
C^{10}	2511 (1)	3400 (2)	7181 (1)	72 (1)
C^{11}	2845 (1)	4399 (2)	6725 (1)	71 (1)
C^{12}	2620 (1)	4212 (2)	5955 (1)	63 (1)
C^{13}	1406 (1)	2845 (2)	6270 (1)	53 (1)
C^{21}	–1307 (1)	1739 (2)	6107 (1)	55 (1)
C^{22}	–589 (1)	1020 (2)	5939 (1)	48 (1)
C^{23}	–757 (1)	–134 (2)	5770 (1)	61 (1)
C^{24}	–1600 (2)	–570 (2)	5764 (1)	74 (1)
C^{25}	–2301 (2)	138 (2)	5946 (1)	75 (1)
C^{26}	–2158 (1)	1280 (2)	6114 (1)	72 (1)
C^{27}	315 (1)	1448 (2)	5987 (1)	50 (1)
H	–551 (15)	2951 (18)	6239 (10)	80

0.2° and 10 s for a single exposure, distance from detector to the crystal 50 mm. The absorption of X-rays in the sample was accounted for by equivalent reflections. The structure was solved by the direct method and refined by the least-squares procedure in anisotropic approximation for nonhydrogen atoms. The H hydrogen atom was localized from difference synthesis of the electron density and refined in isotropic approximation. The positions of the other hydrogens were calculated geometrically and were included into refining in the "rider" model.

The collection and processing of data, refining of the unit cell parameters were carried out by SMART and SAINT Plus software [7]. All calculations for solving and refining of the structure were performed by program package SHELXTL/PC [8]. The main crystallographic parameters and results of the structure refining are presented in Table 3. The atom coordinates are listed in Tables 4 and 5.

***N*-[(13-*anti*)-Tricyclo[7.3.1.$0^{2,7}$]tridec-2(7)-en-13-yl]methanamide (IIa) and N-[(13-*syn*)tricyclo-[7.3.1.$0^{2,7}$]tridec-2(7)-en-13-yl]methanamide (IIb).** To 270 g (9 mol) of formamide, heated to 165°C, was added within 2.5 h a mixture of 95 g (0.5 mol) of ketone **I** with 95 ml of 85% formic acid. The reaction mixture was heated to 165–180°C for 5.5 h, cooled, from the crystalline solid the formamide was washed with water, and the residue was dried in air. Thus 104 g of a mixture of compounds **IIa, b** was obtained in 3 : 2 ratio with a small admixture of amine **III**. The mixture was treated with 200 ml of cold petroleum ether (extract no. 1), and then it was boiled in succession with 200 and 500 ml of petroleum ether (extract no.2). The insoluble residue was compound **IIa**, mp 147–149.5°C (publ. bp 145–146.5°C [2]). IR spectrum, cm^{-1}: 3439 (NH), 1687, 1502 (amide). ^1H NMR spectrum, δ, ppm (*J*, Hz): 4.14 ($C^{13}H$, *J* 3.1, 3.1, 8.2, 0.9), 6.19 (NH), 8.21 (CHO, *J* 0.9, 2.0). Signals of lower intensity, δ, ppm (*J*, Hz): 3.64 ($C^{13}H$, *J* 3.4, 3.4, 9.1), 6.48 (NH), 8.14 (CHO). ^{13}C NMR spectrum, δ, ppm: 17.27, 22.03, 22.75, 22.88, 27.66, 28.51, 29.07, 38.16 ($8CH_2$); 30.85, 37.83, 47.97 (3CH); 129.08, 129.90 (C=C); 160.58 (CHO). Signals of lower intensity, δ, ppm: 17.17, 21.65, 22.80, 22.88, 27.89, 28.47, 29.01, 38.04 (CH_2); 32.57, 40.14, 51.86 (CH); 129.0, 130.09 (C=C); 164.06 (CHO).

After cooling extract no.2 30.5 g of the mixture of compounds **IIa, b** precipitated. The filtrate after removing the precipitate was evaporated to 30 ml, and on cooling it the crystals of compound **IIb** precipitated (1.7 g). IR spectrum, cm^{-1}: 3420 (NH), 1683, 1499 (amide). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.08 (C^{13}H, *J* 2.8, 2.8, 9.1), 5.88 (NH), 8.11 (CHO, *J* 2.0). Signals of lower intensity, δ, ppm (*J*, Hz): 3.47 (C^{13}H, *J* 3.1, 3.1, 9.6), 6.05 (NH), 8.11 (CHO). ^{13}C NMR spectrum, δ, ppm: 17.15, 23.07, 23.19, 28.31, 29.13, 29.52, 32.77, 33.13 (8CH_2); 31.75, 40.00, 49.38 (3CH); 127.18, 130.85 (C=C); 160.39 (CHO). Signals of lower intensity, δ, ppm: 16.90, 22.92, 28.39, 29.06, 29.44, 33.08, 33.32 (CH_2); 34.29, 41.10, 53.74 (CH); 127.00, 131.03 (C=C); 163.42 (CHO).

The residue after evaporating extract no. 1 was distilled in a vacuum to afford 1.5 g of amine **III**, bp 222–223°C (2 mm Hg).

13-*anti*-Aminotricyclo[7.3.1.0^{2,7}]tri-dec-2(7)-ene (IVa). In 30 ml of 5% alcoholic solution of sodium hydroxide was dissolved 2.2 g (10 mmol) of amide **IIa**, the solution was boiled for 3 h on a water bath, then 20 ml of alcohol was evaporated, and the residue was diluted with 40 ml of water. The separated amine was extracted into ether, the extract was dried with magnesium sulfate and evaporated. The residue was distilled in a vacuum.

13-*syn*-Aminotricyclo[7.3.1.0^{2,7}]tridec-2(7)-ene (IVb), 14-*anti*-amino-13-oxatetracyclo-[6.4.1.1^{2,6}.0^{1,8}]tetradecene (VIa), and 14-*syn*-amino-13-oxatetracyclo[6.4.1.1^{2,6}.0^{1,8}]tetradecene (VIb) were obtained similarly.

N-[(14-*anti*)-13-Oxatetracyclo[6.4.1.1^{2,6}.0^{1,8}]-tetradec-14-yl]methanamide (Va). Into 340 ml of 0.1 M solution of monoperphthalic acid in chloroform prepared by procedure [9] from sodium perborate was dissolved 5.8 g (26.5 mmol) of amide **IIa**. The solution was kept for a week at 0°C, then washed with water solution of sodium carbonate and with water, dried with magnesium sulfate, and evaporated. The residue was crystallized from hexane to obtain epoxide **Va**. IR spectrum, cm^{-1}: 3438 (NH), 1686, 1503 (amide), 865 (epoxide). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.45 (C^{13}H, *J* 3.0, 3.0, 8.1, 0.9), 6.18 (NH), 8.09 (CHO). Signals of lower intensity, δ, ppm (*J*, Hz): 3.96 (C^{13}H, *J* 3.0, 3.0), 6.96 (NH), 8.14 (CHO). ^{13}C NMR spectrum, δ, ppm: 17.31, 20.04, 20.69, 22.38, 26.90, 27.97, 30.68, 36.41 (8CH_2); 29.41, 36.84, 43.56 (3CH); 61.82, 65.24 (C–O–C); 160.57 (CHO). Signals of lower intensity, δ, ppm: 17.24, 19.98, 20.04, 21.95, 26.75, 27.62, 30.6, 36.56 (CH_2); 31.47, 39.23, 47.43 (CH); 62.18, 65.68 (C–O–C); 164.49 (CHO).

***N*-[(14-*syn*)-13-oxatetracyclo[6.4.1.1^{2,6}.0^{1,8}]tetradec-14-yl]methanamide (Vb)** was obtained in a similar way. IR spectrum, cm^{-1}: 3425 (NH), 1682, 1498 (amide), 865 (epoxide). ^{13}C NMR spectrum, δ, ppm: 17.63, 20.11, 20.89, 27.25, 29.20, 31.19, 33.31; 34.26 (8CH_2); 31.01, 37.65, 49.30 (3CH); 63.11, 66.20 (C–O–C); 160.03 (CHO). Signals of lower intensity, δ, ppm: 17.17, 23.1, 28.33, 29.55, 33.14 (CH_2); 31.82, 40.07, 49.40 (CH); 160.4 (CHO).

Schiff bases **VII–XII** were prepared by mixing in the cold of alcoholic solutions of the corresponding amines and aldehydes. The crystals of reaction products precipitated at standing. Compound **VIII**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.48 (C^{13}H, *J* 3.1, 3.1), 8.40 (N=CH), 14.2 (OH). ^{13}C NMR spectrum, δ, ppm: 18.28, 22.71, 23.17, 23.25, 28.32, 28.78, 29.46, 38.56 (8CH_2); 34.24, 41.46, 69.15 (3CH); 129.30, 130.10 (C=C); 162.63 (C=N); 161.75 (C–OH); 117.08, 118.25, 119.03, 131.05, 132.02 (ArC). Compound XI. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.38 (C^{13}H, *J* 3.0, 3.0, 3.0), 8.40 (N=CH), 14.0 (OH). ^{13}C NMR spectrum, δ, ppm: 17.55, 23.27, 23.42, 27.88, 29.37, 29.60, 33.30, 34.12 (8CH_2); 34.56, 41.87, 70.61 (3CH); 126.64, 130.41 (C=C); 162.02 (C=N); 161.92 (C–OH); 117.24, 117.93, 119.94, 130.91, 131.87 (ArC).

Crystals of compounds **VIII, XI** were grown by procedure [10] from alcoholic solutions.

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