SYNTHESIS AND PROPERTIES OF DIISOPROPYLTETRAAZABIS-(TROPOCORONAND)S AND RELATED PODANDS[1]

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Abstract - The reaction of 8-isopropylbenzo[*b*]cyclohept[*e*][1,4]oxazine (**3b**) with a 1.2 equivalent of α,ω-alkanediamines (**2**, n=3-12) afforded diisopropyltropocoronands (**4**, n,n'=3-12) in a one-pot procedure, while the reaction of **3b** with an excess of **2** mainly gave isopropyltropopodands (**8**)(n,n'=4-6). The reactions of **3b** with ω-aminoalcohol afforded the corresponding dihydroxy podands **11**. A single-crystal X-ray diffraction analysis of the nickel (II)-complex (**12b**) obtained from **4** (n,n'=5) was made.

Tetraazabis(tropocoronand)s (**1**, R=H) were first synthesized by one of us (T.N) and his co-workers from the reaction of reactive troponoid and α,ω-alkanediamines (**2**) *via* dimeric diaminotropones and then dimeric 2-alkoxytroponeimine under high dilution condition.[2] Recently, we reported a very convenient one pot synthesis of **1** and related tropopodands[3] by the reaction of benzo[*b*]cyclohept[*e*][1,4]oxazine (**3a**)[4] with **2** through an intermolecular heterocycle exchange reaction[5] in high yields. We then reported the synthesis of

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Dedicated to Professor Rolf Huisgen.

tropocoronands having heteroatom-containing linker chains[6] and tris- and tetrakis(tropocoronand)s having three or four aminotroponeimine moieties.[7]

We wish to report here the synthesis of various diisopropyltetraaza(tropocoronand)s and related podands to examine the general utility of afore-mentioned method[3] and to increase lipophilic properties of the tropocoronands.

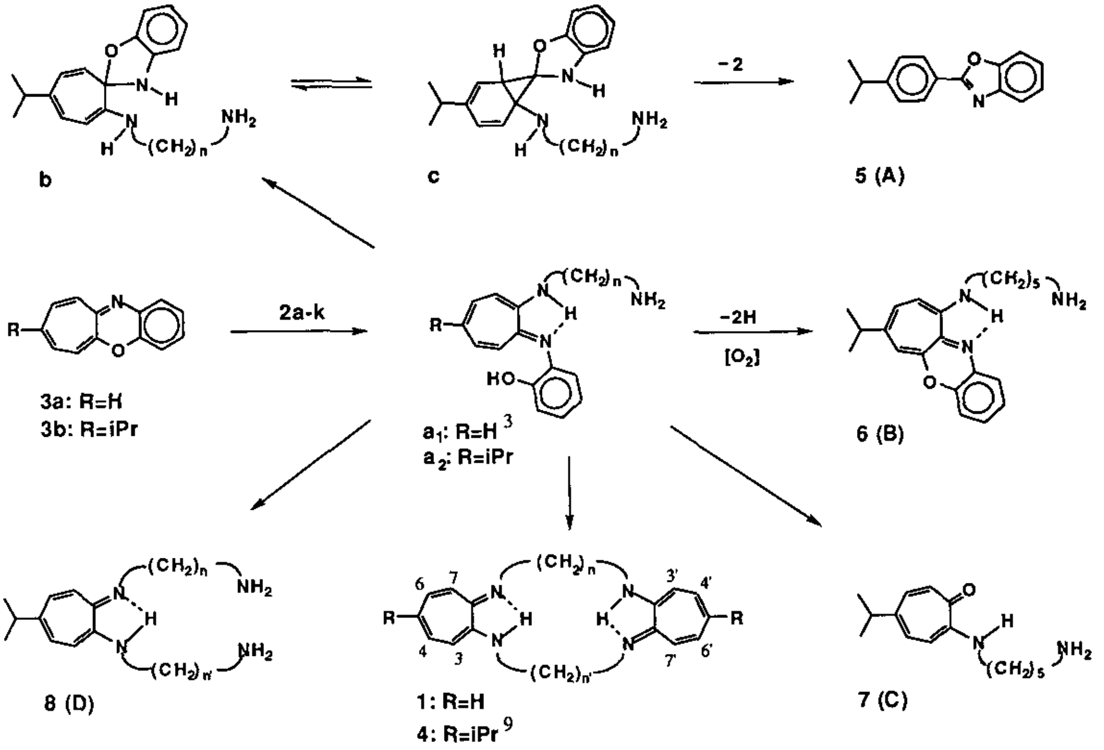
Results and Discussion

Treatment of a solution of 8-isopropylbenzo[*b*]cyclohept[*e*][1,4]oxazine (**3b**)[4] with **2** in a 1:1.2 ratio in absolute ethanol at 80 °C under an inert atomosphere[8] yielded orange crystals of diisopropyltropocoronands (**4**) as the main products, except for the reaction with short-chain diamines (**2a,b**)(n=2,3). These compounds showed similar uv absorption maxima to the previously known tropocoronands[2,3] and the structures were determined on the basis of nmr, mass spectra and elemental analysis. By this one-pot synthesis, we could obtain diisopropyltropocoronands (**4**) in 62-85% yield (for n,n'=4-12) and 8% yield (for n,n'=3) (Table 1).

Table 1. Synthesis of Tropocoronands (**4b-k**) by the Reaction of **3b** with **2b-k**.

Reagents	Products	Yield (%)	mp (°C)	Color - shape
2a (n=2)	**4a**	0	–	–
2b (n=3)	**4b**	8	>300	Yellow scales
2c (n=4)	**4c**	67	175-176	Yellow scales
2d (n=5)	**4d**	68	214-215	Yellow scales
2e (n=6)	**4e**	81	120-121	Orange prisms
2f (n=7)	**4f**	62	160-161	Orange needles
2g (n=8)	**4g**	66	91-92	Orange prisms
2h (n=9)	**4h**	70	176-177	Yellow needles
2i (n=10)	**4i**	66	73-74	Orange prisms
2j (n=11)	**4j**	70	161-162	Yellow needles
2k (n=12)	**4k**	85	74-75	Orange prisms

The by-products formed by the reaction of **3b** with **2d** (n=5) were closely examined. The mixtures of the mother liquor were separated by silica gel column chromatography into **A** to **D**. A colorless compound **A**, a red compound **B** and a yellow compound **C** were obtained from a benzene-methanol eluant, and high absorptive compound of yellow **D** was obtained from the eluant of methanol containing saturated aqueous solution of NaCl.



Scheme I

Compound **A** (colorless needles, mp 72-73 °C) was assigned to have the structure of 2-(4-isopropylphenyl)benzoxazol (**5**, 1%) based on uv, nmr, and mass spectra. The ring contraction of **3b** to **5** is considered to proceed *via* intermediate **a**$_2$ followed by **b** and norcaradiene type **c** as shown in Scheme 1. The structures of **B** (red scales, mp 48-46 °C) and **C** (yellow oil) were identified spectroscopically as 10-(5-aminopentylamino)-7-isopropylbenzo[*b*]cyclohept[*e*][1,4]oxazine (**6**, 2%) and 2-(5-aminopentylamino)-5-isopropyltropone (**7**, 7%), respectively, the former was a dehydrocyclized product of key intermediate **a**$_2$, while the latter was partially hydrolyzed aminotropone.[3]

Both the uv and ^{1}H-nmr spectra of compound **D** (yellow scales, mp 92-93 °C) resembled those of tropocoronand[3] except for a 4:20 proton ratio (instead of 4:10) of ring protons to methylene protons of side chains (linker chains) indicating a structure of tropopodand (**8d**, n,n'=5, 15%).

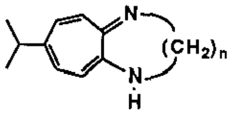
The reactions of **3b** with short chain diamines (**2a**) (n=2) and (**2b**) (n=3) gave 7-isopropyl-2,3-dihydro-1*H*-cyclohepta[*b*]pyrazine (**9a**) and 7-isopropyl-1,2,3,4-tetrahydrocyclohept[*b*][1,4]azepine (**9b**) mainly, respectively. No compound (**4a**)(n,n'=2,2) was produced and **4b** (n,n'=3,3) was only 8% yield. The structures of **9a** and **9b** were confirmed in comparison with 2,3-dihydro-1*H*-cyclohexapyrazine[10] and 1,2,3,4-tetrahydrocyclohept[*b*][1,4]azepine.[3]

Table 2. Synthesis of Tropopodands (**8**) and (**11**) by the Reaction of **3b** with **2** and **10.**

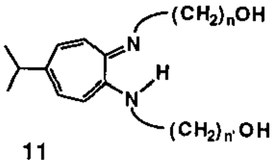
Reagents		Products	Yield (%)	mp (°C)	Color - shape
2a	(n=2)	**8a**	—	—	
2b	(n=3)	**8b**	—	—	
2c	(n=4)	**8c**	57	88-89	Yellow scales
2d	(n=5)	**8d**	67	92-93	Yellow scales
2e	(n=6)	**8e**	75	93-94	Yellow scales
10a	(n=2)	**11a**	53	90-91	Yellow pismes
10b	(n=3)	**11b**	67	52-53	Yellow prismes
10c	(n=4)	**11c**	65	46-47	Yellow prismes
10d	(n=5)	**11d**	83	95-94	Yellow prismes
10e	(n=6)	**11e**	76	73-76	Yellow prismse

We then tried to synthesize tropopodands by the reaction of **3b** with an excess of diamines (**2**). The reactions of **3b** with **2a-e** (n=2-6) in a 1:5 ratio at 80 °C gave podands (**8c-e**)(n,n'=4,-6) in 57-75% yield, while those of **3b** with **2a,b** (n=2,3) yielded **9a** and **9b**. The reactions of **3b** with ω-aminoalcohol (**10a-e**) (n=2-6)(1:6) under the above conditions afforded **11a-e** (n,n'=2-6) in 53-83% yield (Table 2). The structure of **8c-e** and **11a-e** were also confirmed from spectral analysis.

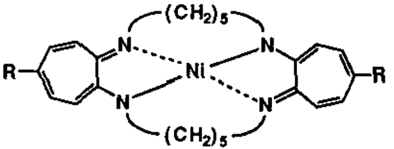
Possible pathways for the formation of these tropocoronands and podands are the same in the case of the parent compounds.[3]



9a: n=2
9b: n=3



11



12a: R=H
12b: R=iPr

One pot synthesis method of **4** and **8** by the reaction of **3b** with **2** was useful in a similar manner as the reaction of **3a** with **2**.[3] The effect of isopropyl group was small increment in the lipophilic properties qualitatively. We then tried to synthesize metal complexes from ligand (**4d**, n,n'=5,5) with nickel acetate tetrahydrate. ORTEP drawing of **12b** elucidated by the X-ray diffraction analysis is shown in Figure 1.[11] Average bond distance between N-Ni is 1.959(4) Å and dihederal angle between N1-Ni-N2 and N3-Ni-N4 is 69.5°(2). Both average bond angles (N-Ni-N) within the troponiminato chelate ring and between two troponiminato rings are 81.9°(2) and 114.8°(2), respectively. These selected structure features of **12b** bear a close resemblance to those of **12a**.[2]

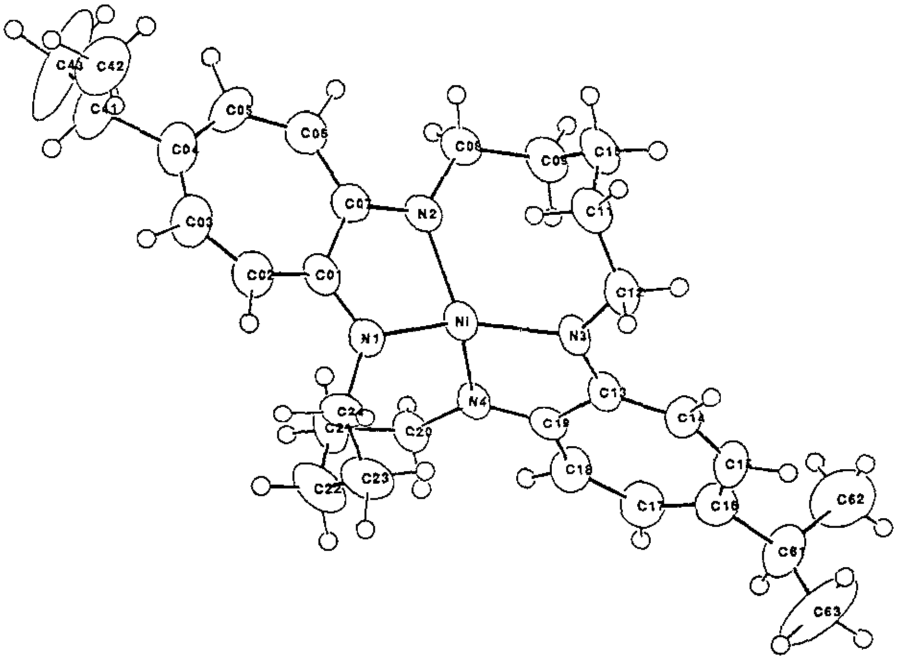


Figure. 1 ORTEP Drawing of **12b**.

EXPERIMENTAL

The melting points were determined with a Yanagimoto MP-35 melting-point apparatus and were uncorrected. The ir and electronic spectra were measured by using a Shimadzu IR-435 and a Shimadzu UV-265FS spectrometer, respectively. The nmr spectra were measured in $CDCl_3$ with a JEOL JNM-GX270 (270 MHz for ^1H and 67.8 MHz for ^{13}C) spectrometer using TMS as an internal standard. The assiggnments of all signals were made by employing a first-order analysis with the aid of a decoupling technique. The mass spectra were taken on a JEOL JMS-DX300 mass spectometer at 70 eV. The tlc analyses and column chromatoography were carried out with Merck Kieselgel 60 F-254 plates and Wako gel C-200 using MeOH-satulated NaCl aq (1:1) as an eluent.

The Equimolar Reaction of 3b with 2d. A solution of **3b** (237 mg, 1.0 mmol) and **2d** (12 mg, 1.2 mmol) in absolute ethanol (3 ml) was heated at 80 °C for 30 h under an argon atmosphere. After having been set aside overnight at room temperature, the orange precipitates which formed was collected and washed with cold methanol to give, upon recrystallization ($CHCl_3$-MeOH), **4d** as yellow scales (157 mg, 68% yield). The filtrate was concentrated in *vacuo*. The residue was dissolved in chloroform and passed through a silica gel column. A colorless needles (**5**)(2 mg, 1%)(**A**), a red compound (**6**)(7 mg, 2%)(**B**) and a yellow compound (**7**)(17 mg, 7%)(**C**) were obtained from the benzene-methanol (10:1) eluant and a high absorptive yellow compound (**8d**)(49 mg, 15%)(**D**) was obtained from the methanol-satulated NaCl aq (1:1) eluant.

3,15-Diisopropyl-6,7,8,9,10,11,18,19,20,21,22,23-dodecahydrodicyclohepta[*b*,*k*][1,4,10,13]tetraazacyclooctadecine (4d, n,n'=5): Yellow needles; mp 214-215 °C ($CHCl_3$-MeOH); uv λ max (MeOH) 265 (log ε 4.72), 352 (4.44), 383 (4.18, sh), 415 (4.30), 439 (3.89, sh), 470 nm (3.34, sh); ir (KBr) ν: 3240, 2900, 2850, 1580 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.16 (12H, d, J=6.7 Hz, iPr-CH_3), 1.80 (12H, m, CH_2), 2.62 (2H, sept, J=6.7 Hz, iPr-CH), 3.32 (8H, m, N-CH_2), 6.25 (4H, d, J=11.7 Hz, H-3,3',7,7'), 6.66 (4H, d, J=11.7 Hz, H-4,4',6,6'); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 23.81 (q, CH_3), 26.37 (t, CH_2), 30.26 (t, CH_2), 36.35 (d, CH), 45.99 (t, CH_2), 110.10 (d, C-3,7), 131.30 (d, C-4,6), 136.99 (s, C-5), 152.11 (s, C-1,2); ms (70 eV) m/z 460 (M^+, 66%), 298 (48%), 280 (100%). Anal. Calcd for $C_3H_{44}N_4$: C,78.21; H,9.62; N,12.16. Found: C,78.19; H,9.60; N,12.18.

2-(4-Isopropylphenyl)benzoxazol (5); Colorless needles; mp 72-73 °C (EtOH); uv λ max (MeOH) 239 (log ε 4.48), 346 nm (4.60); ^1H nmr (270 MHz, $CDCl_3$) δ 1.29 (6H, d, J=7.0 Hz, iPr-CH_3), 2.98 (1H, sept, J=7.0 Hz, iPr-CH), 7.33 (2H, m, J=7.5, 7.9, 2.5, 2.2 Hz, H-5,6), 7.37 (2H, d, J=8.5 Hz, H-3',5'), 7.55 (2H, dd, J=7.5 and 2.5 Hz, H-4), 7.76 (2H, dd, J=7.9 and 2.2 Hz, H-7), and 8.18 (2H, d, J=8.5 Hz, H-2',6'); ms (70 eV) m/z 237 (M^+, 50%), 222 (100%). Found: M^+, 237.1167. Calcd for $C_{16}H_{15}NO$: M, 237.1157.

10-[(5-Aminopentyl)amino]-7-isopropylbenzo[*b*]cyclohepta[*e*][1,4]oxazine (6): Red scales; mp 48-49 °C (benzene); uv λ max (MeOH) 266 (log ε 3.88), 488 nm (3.49); ir (neat) ν: 3300, 2900, 2850, 1580 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.10 (6H, d, J=7.0 Hz, iPr-CH_3), 1.49 (4H, quin, J=7.3 Hz, CH_2), 1.73 (2H, quin, J=7.3 Hz, CH_2), 2.15 (2H, br, NH_2), 2.64 (1H, sept, J=7.0 Hz, iPr-CH), 2.72 (2H, t, J=7.3 Hz, N-CH_2), 3.21 (2H, t, J=7.3 Hz, N-CH_2), 5.81 (1H, d, J=9.9 Hz, H-9), 5.96 (1H, d, J=1.8 Hz, H-6), 6.16 (1H, dd, J=9.9 and 1.8 Hz, H-8), 6.38 (1H, m, H-4), 6.68 (2H, m, H-2,3), 6.76 (1H, m, H-1); ms (70 eV) m/z 337 (M^+, 8%), 321 (46%), 307 (18%), 289 (13%), 154 (100%). Found M^+, 337.2154. Calcd for $C_{21}H_{27}N_3O$: M, 337.2132.

2-[(5-Aminopentyl)amino]-5-isopropyltropone (7): Yellow oil; uv λ max (MeOH) 249 (log ε 4.26), 339 (4.04), 410 nm (3.88); ir (neat) ν: 3300, 2900, 2850, 1635 cm^{-1}; ^1H nmr (270 MHz, CD_3OD) δ 1.22 (6H, d, J=7.0 Hz, iPr-CH_3), 1.49 (4H, quin, J=7.3 Hz, CH_2), 1.75 (2H, quin, J=7.3 Hz, CH_2), 1.96 (2H, t, J=7.3 Hz, NH_2), 2.70 (2H, t, J=7.3 Hz, CH_2), 2.80 (1H, sept, J=7.0 Hz, iPr-CH), 3.29 (2H, t , J=7.3 Hz, N-CH_2), 6.51 (1H, d, J=10.7 Hz, H-3), 7.04 (1H, br, NH), 7.13 (1H, dd, J=10.6 and 1.8 Hz, H-4), 7.14 (1H, d, J=12.1 Hz, H-7), 7.22 (1H, dd, J=12.1 and 1.8 Hz, H-6); ms (70 eV) m/z 248 (M^+, 5%), 84 (100%). Found: M^+, 248.1872. Calcd for $C_{20}H_{36}N_4$: M, 248.1853.

***N*-[2-[(5-Aminopentyl)amino]-5-isopropyl-2,4,6-cycloheptatrien-1-ylidene]-1,5-pentanediamine (8d, n,n'=5):** Yellow scales; mp 92-93 °C (benzene-MeOH); uv λ max (MeOH) 255 (log ε 4.05), 346 (3.78), 413 nm (3.70); ir (neat) ν: 3300, 2900, 2850, 1580 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.16 (6H, d, J=7.0 Hz, iPr-CH_3), 1.49 (8H, quin, J=7.3 Hz, CH_2), 1.74 (4H, quin, J=7.3 Hz, CH_2), 2.64 (1H, sept, J=7.0 Hz, iPr-CH), 2.65 (4H, t, J=7.3 Hz, N-CH_2), 3.30 (4H, t, J=7.3 Hz, N-CH_2), 6.27 (2H, d, J=11.7 Hz, H-3,3',7,7'), 6.68 (2H, d, J=11.7 Hz, H-4,4',6,6'); ms (70 eV) m/z 332 (M^+, 2%), 260 (100%), 248 (81%), 175 (56%), 163 (79%), 84 (89%). Found: M^+, 332.2906. Calcd for $C_{20}H_{36}N_4$: M, 332.2906.

Synthesis of Other Tropocoronands. The reactions of **3b** with α,ω-alkanediamines (n=3,4,6-12) (mole ratio, 1:1.2) as described above gave **4b,c** and **4d-k**. The yields and melting points are shown in Table 1.

3,13-Diisopropyl-6,7,8,9,16,17,18,19-octahydrodicyclohepta[*b,i*][1,4,8,11]tetraazacyclotetradecine (4b, n,n'=3): Yellow scales; mp > 300 °C ($CHCl_3$-MeOH); uv λ max (MeOH) 267 (log ε 4.61), 360 (4.39), 395 (4.23), 412 (4.20, sh), 442 (3.89, sh), 464 nm (3.53, sh); ir (KBr) ν: 3280, 2950, 2938, 1578, 1504, 1502 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.15 (12H, d, J=6.7 Hz, iPr-CH_3), 2.26 (4H, m, CH_2), 2.62 (2H, sept, J=6.7 Hz, iPr-CH), 3.48 (8H, m, N-CH_2), 6.24 (4H, d, J=11.7 Hz, H-3,3',7,7'), 6.70 (4H, d, J=11.7 Hz, H-4,4',6,6'), 8.62 (2H, br, NH); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 23.85 (q, CH_3), 29.14 (t, CH_2), 36.55 (d, CH), 48.45 (t, CH_2), 110.28 (d, C-3,6), 131.86 (d, C-4,6), 136.96 (s, C-5), 152.81 (s, C-1,2); ms (70 eV) m/z 404 (M^+, 100%), 389 (28%). Anal. Calcd for $C_{26}H_{36}N_4$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.31; H, 8.77; N, 13.92.

3,14-Diisopropyl-6,7,8,9,10,17,18,19,20,21-decahydrodicyclohepta[*b,j*][1,4,9,12]tetraazacyclohexadecine (4c, n,n'=4): Yellow scales; mp 175-176 °C ($CHCl_3$-MeOH); uv λ max (MeOH) 269 (log ε 4.64), 340 (4.37, sh), 360 (4.42), 377 (4.13, sh), 410 (4.15), 472 nm (3.42, sh); ir (KBr) ν: 3200, 2950, 2850, 1610, 1585 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.17 (12H, d, J=7.0 Hz, iPr-CH_3), 1.96 (8H, m, CH_2), 2.64 (2H, sept, J=7.0 Hz, iPr-CH), 3.27 (8H, m, N-CH_2), 6.27 (4H, d, J=11.7 Hz, H-3,3',7,7'), 6.68 (4H, d, J=11.7 Hz, H-4,4',6,6'); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 23.89 (q, CH_3), 28.13 (t, CH_2), 36.76 (d, CH), 45.25 (t, CH_2), 109.99 (d, C-3,7), 131.35 (d, C-4,6), 136.72 (s, C-5), 152.17 (s, C-1,2); ms (70 eV) m/z 432 (M^+, 63%), 269 (67%), 255 (100%). Anal. Calcd for $C_{28}H_{40}N_4$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.92; H, 9.40; N, 13.00.

3,16-Diisopropyl-6,7,8,9,10,11,12,19,20,22,23,24,25-tetradecahydrodicyclohepta[*b,i*]-[1,4,11,14]tetraazacycloeicosine (4e, n,n'=6): Orange prisms; mp 120-121 °C (toluene-MeOH); uv λ max (MeOH) 264 (log ε 4.56), 290 (4.24, sh), 352 (4.28), 360 (4.29), 382 (4.08, sh), 419 (4.16), 438 (4.02, sh), and 471 nm (3.71, sh); ir (KBr) ν: 3200, 2930, 2850, 1585 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.15

(12H, d, J=7.0 Hz, iPr-CH$_3$), 1.48 (8H, m, CH$_2$), 1.73 (8H, m, CH$_2$), 2.61 (2H, sept, J=7.0 Hz, iPr-CH), 3.27 (8H, m, N-CH$_2$), 6.24 (4H, d, J=11.5 Hz, H-3,3',7,7'), 6.64 (4H, d, J=11.5 Hz, H-4,4',6,6'); ^{13}C nmr (67.8 MHz, CDCl$_3$) δ 23.87 (q, CH$_3$), 27.44 (t, CH$_2$), 30.08 (t, CH$_2$), 36.64 (d, CH), 46.19 (t, CH$_2$), 110.09 (d, C-3,7), 131.15 (d, C-4,6), 137.02 (s, C-5), and 151.99 (s, C-1,2); ms (70 eV) m/z 488 (M$^+$, 3%), 105 (100%). Anal. Calcd for $C_{32}H_{48}N_4$: C, 78.63; H, 9.90; N, 11.46. Found: C, 78.70; H, 10.23; N, 11.09.

3,17-Diisopropyl-6,7,8,9,10,11,12,13,20,21,22,23,24,25,26,27-hexadecahydrodicyclohepta[*b,m*][1,4,12,15]tetraazacyclodocosine (4f, n,n'=7): Yellow needles; mp 160-160 °C (CHCl$_3$-MeOH); uv λ max (MeOH): 264 (log ε 4.72), 350 (4.42), 359 (4.36), 379 (4.36, sh), 415 (4.31), 471 nm (3.14, sh) ; ir (KBr) ν: 3200, 2900, 2850, 1590 cm^{-1}; ^{1}H nmr (270 MHz, CDCl$_3$) δ 1.16 (12H, d, J=7.0 Hz, iPr-CH$_3$), 1.46 (4H, m, CH$_2$), 1.51 (8H, m, CH$_2$), 1.74 (8H, m, CH$_2$), 2.62 (2H, sept, J=7.0 Hz, iPr-CH), 3.28 (8H, m, N-CH$_2$), 6.25 (4H, d, J=11.7 Hz, H-3,3',7,7'), 6.64 (4H, d, J=11.7 Hz, H-4,4',6,6'); ^{13}C nmr (67.8 MHz, CDCl$_3$) δ 23.82 (q, CH$_3$), 27.99 (t, CH$_2$), 30.13 (t, CH$_2$), 30.18 (t, CH$_2$), 36.68 (d, CH), 45.96 (t, CH$_2$), 110.04 (d, C-3,7), 131.22 (d, C-4,7), 136.97 (s, C-5), 151.96 (s, C-1,2); ms (70 eV) m/z 516 (M$^+$, 88%), 501 (36%), 473 (100%). Anal. Calcd for $C_{34}H_{52}N_4$: C, 79.02; H, 10.14; N, 10.84. Found: C, 79.10; H, 10.00; N, 10.60.

3,18-Diisopropyl-6,7,8,9,10,11,12,13,14,21,22,23,24,25,26,27,28,29-octadecahydrodicyclohepta[*b,n*][1,4,13,16]tetracosine (4g, n,n'=8): Orange prisms; mp 91-92 °C (toluene-MeOH); uv λ max (MeOH) 241 (log ε 4.04 sh), 250 (4.15, sh), 260 (4.20), 286 (3.80, sh), 345 (3.85), 355 (3.83), 410 (3.83), 457 (3.32), 495 nm (2.46); ir (KBr) ν: 3400-3200, 2930, 1615, 1590 cm^{-1}; ^{1}H nmr (270 MHz, CDCl$_3$) δ 1.15 (12H, d, J=7.0 Hz, iPr-CH$_3$), 1.38 (8H, m, CH$_2$), 1.42 (8H, m, CH$_2$), 1.71 (8H, m, CH$_2$), 2.61 (2H, sept, J=7.0 Hz, iPr-CH), 3.27 (8H, t, J=7.3 Hz, CH$_2$), 6.24 (4H, d, J=11.4 Hz, H-3,3',7,7'), 6.64 (2H, d, J=11.4 Hz, H-4,4',6,6'); ms (70 eV) m/z 544 (M$^+$, 3%). Found: M$^+$, 544.4530. Calcd for $C_{36}H_{56}N_4$: M, 544,4492.

3,19-Diisopropyl-6,7,8,9,10,11,12,13,14,15,22,23,24,25,26,27,28,29,30,31-eicosahydrodicyclohepta[*b,o*][1,4,14,17]tetraazacyclohexacosine (4h, n,n'=9): Yellow needles; mp 176-177 °C (CHCl$_3$); uv λ max (MeOH) 263 (log ε 4.73), 350 (4.43), 358 (4.36, sh), 417 nm (4.34); ir (KBr) ν: 3225, 2900, 2850, 1685 cm^{-1}; ^{1}H nmr (270 MHz, CDCl$_3$) δ 1.16 (12H, d, J=6.9 Hz, iPr-CH$_3$), 1.35 (12H, m, CH$_2$), 1.46 (8H, m, CH$_2$), 1.72 (8H, m, CH$_2$), 2.62 (2H, sept, J=6.9 Hz, iPr-CH), 3.27 (8H, m, N-CH$_2$), 6.25 (4H, d, J=11.7 Hz, H-3,3',7,7'), 6.65 (4H, d, J=11.7 Hz, H-4,4',6,6'); ^{13}C nmr (67.8 MHz, CDCl$_3$) δ 23.82 (q, CH$_3$), 27.85 (t, CH$_2$), 29.50 (t, CH$_2$), 29.89 (t, CH$_2$), 30.04 (t, CH$_2$), 36.68 (d, CH), 45.91 (t, CH$_2$), 110.02 (d, C-3,7), 131.18 (d, C-4,6), 136.93 (s, C-5), 151.94 (s, C-1,2); ms (70 eV) m/z 572 (M$^+$, 100%), 558 (43%), 557 (34%). Anal. Calcd for $C_{38}H_{60}N_4$: C, 79.67; H, 10.56; N, 9.78. Found: C, 79.48; H, 10.57; N, 9.82.

3,20-Diisopropyl-6,7,8,9,10,11,12,13,14,15,16,23,24,25,26,27,28,29,30,31,32,33-docosahydrodicyclohepta[*b,p*][1,4,15,18]tetraazacyclooctacosine (4i, n,n'=10): Orange prisms; mp 73-74 °C (toluene-MeOH); uv λ max (MeOH) 264 (log ε 4.72), 350 (4.42), 359 (4.36), 379 (4.36, sh), 415 (4.31), 471 nm (3.14); ir (KBr) ν: 3250, 2925, 2850, 1585 cm^{-1}; ^{1}H nmr (270 MHz, CDCl$_3$) δ 1.15 (12H, d, J=6.6 Hz, iPr-CH$_3$), 1.31 (16H, m, CH$_2$), 1.40 (8H, m, CH$_2$), 1.71 (8H, m, CH$_2$), 2.61 (2H, sept, J=6.6 Hz, iPr-CH), 3.26 (8H, m, CH$_2$), 6.24 (4H, d, J=11.7 Hz, H-3,3',7,7'), 6.64 (4H, d, J=11.7 Hz, H-4,4',6,6'); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 23.82 (q, CH_3), 27.62 (t, CH_2), 29.53 (t, CH_2), 29.68 (t, CH_2), 30.08 (t, CH_2), 36.65 (d, CH), 46.29 (t, CH_2), 110.09 (d, C-3,7), 131.15 (d, C-4,6), 137.04 (s, C-5), 152.02 (s, C-1,2); ms (70 eV) m/z 600 (M^+, 4%), 472 (8%), 453 (12%). Found: M^+, 600.5139. Calcd for $C_{40}H_{64}N_4$: M, 600.5116.

3,21-Diisopropyl-6,7,8,9,19,11,12,13,14,15,16,17,24,25,26,27,28,29,30,31,32,33,34,35-tetracosahydrodicyclohepta[*b*,*q*][1,4,16,19]triacontine (4j, n,n'=11): Yellow needles, mp 161-162 °C ($CHCl_3$-MeOH); uv λ max (MeOH) 262 (log ε 4.76), 351 (4.42), 419 (4.35), 476 nm (3.22); ir (KBr) ν: 3225, 2900, 2850, 1590 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.16 (12H, d, J=7.0 Hz, iPr-CH_3), 1.32 (12H, br, CH_2), 1.36 (8H, m, CH_2), 1.47 (8H, m, CH_2), 1.73 (8H, m, CH_2), 2.62 (2H, sept, J=7.0 Hz, iPr-CH), 3.27 (8H, t, J=6.3 Hz, CH_2), 6.25 (4H, d, J=11.4 Hz, H-3,3',7,7'), 6.66 (4H, d, J=11.4 Hz, H-4,4',6,6'); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 23.82 (q, CH_3), 27.62 (t, CH_2), 29.53 (t, CH_2), 29.68 (t, CH_2), 30.08 (t, CH_2), 36.65 (d, CH), 46.29 (t, CH_2), 110.09 (d, C-3,7), 131.15 (d, C-4,6), 137.04 (s, C-5), 152.02 (s, C-1,2); ms (70 eV) m/z 628 (M^+, 100%), 585 (77%), 501 (82%). Anal. Calcd for $C_{42}H_{68}N_4$: C, 80.20; H, 10.90; N, 8.90. Found: C, 80.45; H, 10.80; N, 9.01.

3,22-Diisopropyl-6,7,8,9,10,11,12,13,14,15,16,17,18,25,26,27,28,29,30,31,32,33,34,35, 36,37-hexaeicosahydrodicyclohepta [*b*,*r*][1,4,17,20]tetraazacyclocontine (4k, n,n'=12): Orange prisms; mp 74-75 °C (toluene-MeOH); uv λ max (MeOH) 257 (log ε 4.60), 351 (4.25), 361 (4.26), 382 (4.08), 418 (4.13), 430 (3.98 sh), 470 nm (3.76); ir (KBr) ν: 3200, 2900, 2850, 1585 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.15 (12H, d, J=7.0 Hz, iPr-CH_3), 1.29 (24H, m, CH_2), 1.42 (8H, m, CH_2), 1.71 (8H, m, CH_2), 2.61 (2H, sept, J=7.0 Hz, iPr-CH), 3.27 (8H, t, J=7.0 Hz, CH_2), 6.25 (4H, d, J=11.4 Hz, H-3,3',7,7'), 6.64 (4H, d, J=11.4 Hz, H-4,4',6,6'); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 23.82 (q, CH_3), 27.62 (t, CH_2), 29.53 (t, CH_2), 29.68 (t, CH_2), 30.08 (t, CH_2), 36.65 (d, CH), 46.29 (t, CH_2), 110.09 (d, C-3,7), 131.15 (d, C-4,6), 137.04 (s, C-5), 152.02 (s, C-1,2); ms (70 eV) m/z 654 (M^+, 3%), 472 (8%), 453 (12%). Found: M^+, 654.5552. Calcd for $C_{44}H_{70}N_4$: M, 654.5584.

2,3-Dihydro-1*H*-7-isopropylcyclohepta[*b*]pyrazine (9a): A mixture of **3b** (237 mg, mmol) and **2a** (72 mg, 1.2 mmol) in absolute ethanol (3 ml) was treated as above to give, after chromatography, **9a** (169 mg, 90%): Yellow prisms, mp 110-111 °C (benzene-MeOH); uv λ max (MeOH) 264, 359, 399, 430 nm; ir (neat) ν: 3200, 2950 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.12 (6H, d, J=7.0 Hz, iPr-CH_3), 2.56 (1H, sept J=7.0 Hz, iPr-CH), 3.48 (4H, s, CH_2), 6.57 (4H, s, H-3,7,4,6); ms (70 eV) m/z 188 (M^+, 70%), 173 (100%). Found: M^+, 188.1326 . Calcd for $C_{12}H_{16}N_2$: M, 188.1308.

8-Isopropyl-1,2,3,4-tetrahydrocyclohepta[*b*][1,4]diazepine (9b): A mixture of **3b** (237 mg, 1.0 mmol) and **2b** (89 mg, 1.2mmol) in absolute ethanol (3 ml) was treated as above to give **9b** (122 mg, 60%) and **4b** (13 mg, 8%). **9b**: Yield 121 mg (60%), Yellow oil; uv λ max (MeOH) 275 (log ε 3.14), 307 (2.88), 337 (2.14), 386 (2.72), 399 (2.75), 406 (2.78), 475 (2.20), 508 nm (2.14); ir (neat) ν: 3255, 2950 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.13 (6H, d, J=7.0 Hz, iPr-CH_3), 1.80 (2H, sept, J=6.0 Hz, CH_2), 2.75 (1H, sept, J=7.0 Hz, iPr-CH), 3.45 (4H, t, J=6.0 Hz, CH_2), 7.17 (2H, m, H-3,7), 7.59 (2H, m, H-4,6); ms (70 eV) m/z 202 (M^+, 100%). Found: M^+, 202.1458. Calcd for $C_{13}H_{18}N_2$: M, 202.1466.

Synthesis of 8d by the Reaction of 3b with 2d: A mixture of **3b** (237 mg, 1 mmol) and 1,5-hexanediamine (**2d**, 510 mg, 5 mmol) in absolute ethanol (3 ml) was heated at 80 °C for 30 h under an argon atmosphere. After concentration in vacuo, the residue dissolved in chloroform was washed with 10% NaOH and water, and then purified through a silica-gel column with MeOH-satulated NaCl aq (1:1) as an eluent, giving **8d** (223 mg, 67% yield).

Synthesis of Other Tropopodands. The reactions of **3b** with α,ω-alkanediamine **2c,e** (n=2-6) (mole ratio 1: 5) and ω-aminoalcohol **10a-e** (n=2-6) (mol ratio 1:6), as descrived above, gave **8c-e** and **11a-e**, respectively. The yields and melting points are given in Table 2.

***N*-[2-[(4-Aminobutyl)amino]-5-isopropyl-2,4,6-cycloheptatrien-1-ylidene]-1,4-butanediamine (8c, n,n'=4):** Yellow scales, mp 88-89 °C (benzene-MeOH); uv λ max (MeOH) 252 (log ε 4.32), 345 (4.05), 411 nm (3.95); ir (neat) ν: 3300, 2900, 2850, 1580 cm^{-1}; ^{1}H nmr (270 MHz, CDCl$_3$) δ 1.16 (6H, d, J=7.0 Hz, iPr-CH$_3$), 1.59 (4H, quin, J=7.3 Hz, CH$_2$), 1.76 (4H, quin, J=7.3 Hz, CH$_2$), 1.89 (1H, br), 2.64 (1H, sept, J=7.0 Hz, iPr-CH), 2.75 (4H, t, J=7.3 Hz, N-CH$_2$), 3.32 (4H, t, J=7.3 Hz, N-CH$_2$), 6,30 (2H, d, J=11.7 Hz, H-3,7), 6.71 (2H, d, J=11.7 Hz, H-4,6); ms (70 eV) m/z 304 (M$^+$, 2%), 246 (100%), 234 (81%), 175 (56%), 163 (79%), 72 (89%). Found: M$^+$, 304.2945. Calcd for $C_{20}H_{36}N_4$: M, 332.2932.

***N*-[2-[(6-Aminohexyl)amino]-5-isopropyl-2,4,6-cycloheptatrien-1-ylidene]-1,6-hexanediamine (8e, n,n'=6):** Yellow scales, mp 93-94 °C (benzene-MeOH); uv λ max (MeOH): 257 (log ε 4.15), 350 (3.86), 415 nm (3.78); ir (neat) ν: 3300, 2900, 2850, 1580 cm^{-1}; ^{1}H nmr (270 MHz, CDCl$_3$) δ 1.16 (6H, d, J=7.0 Hz, iPr-CH$_3$), 1.36 (4H, m, CH$_2$), 1.44 (8H, m , CH$_2$), 1.74 (4H, m, CH$_2$), 2.64 (1H, sept, J=7.0 Hz, iPr-CH), 2.65 (4H, m, N-CH$_2$), 3.30 (4H, t, J=6.9 Hz, N-CH$_2$), 6,27 (2H, d, J=11.4 Hz, H-3,7), 6.67 (2H, d, J=11.4 Hz, H-4,6); ms (70 eV) m/z 360 (M$^+$, 2%), 274 (100%), 262 (10%), 175 (11%), 163 (20%), 98 (25%). Found: M$^+$, 360.3242. Calcd for $C_{22}H_{40}N_4$: M, 360.3244.

2-[[2-[(3-Hydroxyethyl)amino]-5-isopropyl-2,4,6-cycloheptatrien-1-ylidene]amino]-1-ethanol (11a, n,n'=2): Yellow prisms, mp 90-91 °C (benzene-MeOH); uv λ max (MeOH) 264 (log ε 4.43), 360 (4.09), 417 nm (4.04); ir (neat) ν: 3200, 2950 cm^{-1}; ^{1}H nmr (270 MHz, CDCl$_3$) δ 1.29 (6H, d, J=7.3 Hz, iPr-CH$_3$), 2.94 (1H, sept, J=7.3 Hz, iPr-CH), 3.55 (4H, m, CH$_2$), 4.18 (4H, m, CH$_2$), 7.05 (2H, d, J=11.7 Hz, H-3,7), 7.54 (2H, d, J=12.0 Hz, H-4,6); ms (70 eV) m/z 250 (M$^+$, 18%), 219 (100%). Found: M$^+$, 250.1696. Calcd for $C_{14}H_{22}N_2O_2$: M, 250.1676.

3-[[2-[(3-Hydroxypropyl)amino]-5-isopropyl-2,4,6-cycloheptatrien-1-ylidene]amino]-1-propanol (11b, n=3): Yellow prisms; mp 52-53 °C (benzene-MeOH); uv λ max (MeOH) 264 (log ε 4.43), 360 (4.09), 417 nm (4.04); ir (neat) ν: 3350, 3150, 2950, 2870, 1580 cm^{-1}; ^{1}H nmr (270 MHz, CDCl$_3$) δ 1.27 (6H, d, J=7.0 Hz, iPr-CH$_3$), 1.97 (4H, quin, J=5.3 Hz, CH$_2$), 2.87 (1H, sept, J=7.0 Hz, iPr-CH), 3.69 (4H, t, J=5.3 Hz, N-CH$_2$), 3.73 (4H, t, J=5.3 Hz, O-CH$_2$), 6.37 (3H, br, NH, OH), 6.98 (2H, d, J=12.0 Hz, H-3,7), 7.40 (2H, d, J=12.0 Hz, H-4,6); ^{13}C nmr (67.8 MHz, CDCl$_3$) δ 23.82 (q, CH$_3$), 30.00 (t, CH$_2$), 36.80 (d, CH), 41.76 (t, CH$_2$), 59.16 (t, CH$_2$), 116.65 (d, C-3,7), 139.79 (d, C-4,6), 146.49 (s, C-5), 151.20 (s, C-1,2); ms (70 eV) m/z 278 (M$^+$, 44%), 233 (90%), 219 (100%). Anal. Calcd for $C_{16}H_{26}N_2O_2$: C, 69.03; H, 9.14; N, 10.06. Found: C, 69.25; H, 9.01; N, 10.06.

4-[[2-[(4-Hydroxybutyl)amino]-5-isopropyl-2,4,6-cycloheptatrien-1-ylidene]amino]-1-butanol (11c, n=4): Yellow prisms, mp 46-47 °C (benzene-MeOH); uv λ max (MeOH) 264 (log ε 4.33), 350 (4.00), 418 nm (4.33); ir (neat) ν: 3300, 3150, 2950, 1620, 1575 cm^{-1}; ^{1}H nmr (270 MHz, CDCl$_3$) δ 1.26 (6H, d, J=7.0 Hz, iPr-CH$_3$), 1.75 (4H, quin, J=6.0 Hz, CH$_2$), 2.02 (4H, quin, J=6.0 Hz, CH$_2$), 2.91 (1H, sept, J=7.0 Hz, iPr-CH), 3.60 (4H, t, J=6.0 Hz, N-CH$_2$), 3.70 (4H, t, J=6.0 Hz, O-CH$_2$), 7.05 (2H, d, J=11.5 Hz, H-3,7), 7.50 (2H, d, J=11.5 Hz, H-4,6), 9.36 (1H, br, NH); ^{13}C nmr (67.8 MHz, CDCl$_3$) δ

23.89, 24.18, 29.95, 36.85, 44.81, 61.89, 117.71, 138.69, 147.95, 150.69; ms (70e V) m/z 306 (M^+, 10%), 235 (84%), 176 (100%). Found: M^+, 306.2325. Calcd for $C_{18}H_{30}N_2O_2$: M, 306.2300.

5-[[2-[(5-Hydroxypentyl)amino]-5-isopropyl-2,4,6-cycloheptatrien-1-ylidene]amino]-1-pentanol (11d, n,n'=5): Yellow prisms, mp 94-95 °C (benzene-MeOH); uv λ max (MeOH) 264 (log ε 4.39), 350 (4.03), 416 nm (4.01); ir (neat) ν: 3300, 3150, 2950, 2850, 1620, 1575 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.28 (6H, d, J=7.0 Hz, iPr-CH_3), 1.62 (8H, m, CH_2), 1.92 (4H, m, CH_2), 2.91 (1H, sept, J=7.0 Hz, iPr-CH), 3.58 (4H, t, J=6.5 Hz, N-CH_2), 3.65 (4H, t, J=6.5 Hz, O-CH_2), 7.01 (2H, d, J=11.6 Hz, H-3,7), 7.48 (2H, d, J=11.6 Hz, H-4,6); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 23.21 (q, CH_2), 23.87 (q, CH_3), 26.65 (t, CH_2), 31.92 (t, CH_2), 36.81 (d, CH), 44.62 (t, CH_2), 61.51 (t, CH_2), 117.43 (d, C-3,7), 138.37 (d, C-4,6), 147.55 (s, C-5), 150.71 (s, C-1,2); ms (70 eV) m/z 334 (M^+, 16%), 261 (79%), 229 (100%). Found: M^+, 334.2636. Calcd for $C_{20}H_{34}N_2O_2$: M, 334.2612.

6-[[2-[(6-Hydroxyhexyl)amino]-5-isopropyl-2,4,6-cycloheptatrien-1-ylidene]amino]-1-hexanol (11e, n,n'=6): Yellow prisms, mp 73-76 °C (benzene-MeOH); uv λ max (MeOH) 264 (log ε 4.42), 350 (4.08), 418 nm (4.06); ir (neat) ν: 3430, 3220, 2940, 2850, 1610, 1585 cm^{-1}; ^1H nmr (270 MHz, $CDCl_3$) δ 1.18 (6H, d, J=7.0 Hz, iPr-CH_3), 1.47 (8H, m, CH_2), 1.60 (4H, m, CH_2), 1.78 (4H, m, CH_2), 2.65 (2H, sept, J=7.0 Hz, iPr-CH), 3.31 (4H, m, N-CH_2), 3.64 (4H, t, J=6.5 Hz, O-CH_2), 6.28 (2H, br, H-3,7), 6.68 (2H, br, H-4,6); ^{13}C nmr (67.8 MHz, $CDCl_3$) δ 23.84, 25.61, 27.34, 29.91, 32.73, 36.67, 45.95, 62.71, 110.26, 131.35, 137.50, 151.99; ms (70 eV) m/z 362 (M^+, 29%), 275 (100). Found: M^+, 362.2947. Calcd for $C_{22}H_{38}N_2O_2$: M. 362.2924.

3,15-Diisopropyl-6,7,8,9,10,11,18,19,20,21,22,23-dodecahydrodicyclohepta[*b*,*k*][1,4,10,13]-tetraazacyclooctadecinato(2-)-N^6,N^{12},N^{18},N^{24}]nickel (II) (12): To **4d** (n,n'=5) (100 mg, 0.22 mmol) in dichloromethane (50 ml) was added nickel (II) acetate tetrahydrate (77 mg, 0.31 mmol) in ethanol (25 ml), and the mixture was stirred for 10 min. After most of the dichloromethane had been removed on awater bath, the solution was set aside overnight at room temperature, resulting in the formation of black precipitates. These were collected and recrystallized from dichloromethane-methanol to give **12b** (91 mg, 80 % yield) as black needles; mp >300 °C; Anal. Calcd for $C_{30}H_{42}N_4Ni$: C, 69.64; H, 8.18; N, 10.83. Found: C, 69.26; H, 8.51; N, 10.66.

Data collection: A dark blue crystal with dimensions ca. 0.5 × 0.2 × 0.2 mm^3 was used for data collection, using graphite-monochromated Cu Kα radiation (λ=1.5418 Å). 5090 reflection (2θ<130°; h-12->0, k-14->15, 1-13->13) were observed of which 3119 unique reflections with $|F| \geq 4\sigma(|F|)$ were used for structure determination. Intensities were corrected for Lorentz and polarization effects but not for absorption and extinction. Unit cell dimensions were obtained from least-squares fit of 20 2θ values (27<2θ<32°). Crysral data: $C_{30}H_{42}N_4Ni$; space group, P1; a=10.961(2), b=12.921(2), c=11.050(1)Å, α=111.43(1), β=91.70(1), γ=107.24(1)°, V=1374.5(4)$Å^3$, Z=2, dx=1.250 g cm^{-3}, μ(Cu Kα)=1.16 mm^{-1}, F(000)=556.

Structure determination: Structure has been solved by direct method using MULTAN 78[12] on a FACOM M-770 computer. Coordinates of Ni atom and a six membered chelating part of macrocycle were obtained from E map. From succesive Fourier maps all other non-H atoms could be located. Parameters for H-atoms were obtained from calculation. Atomic scattering factors used were from literature.[13] Structure reffinement and characterzation were carried out using XTAL program system[14] on a SUN470 Work-station at Jorsai University. Observed and calculated structure amplitudes, final atomic coordinates, anisotropic thermal parameters, parameters for H-atoms, and bond distances and angles not given in the paper will be obtained from the author (HM) on request.

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REFERENCES

1. L.C. Zhang, K. Shindo, H. Wakabayashi, S. Ishikawa, and T. Nozoe, presented at the 63th Annual Meeting of Chem. Soc. of Japan, Osaka, 1992, Abstr., No. 2B137.
2. a) S. Imajo, K. Nakanishi, M. Roberts, S. J. Lippard, and T. Nozoe, *J. Am. Chem. Soc.*, 1983, **105**, 2071; b) A. Zask, N. Gonnella, K. Nakanishi, C. J. Turner, S. Imajo, and T. Nozoe, *Inorg.Chem.*, 1986, **25**, 3400.
3. a) T. Nozoe, K. Shindo, H. Wakabayashi, and S. Ishikawa, *Heteroctcles*, 1992, **34**, 881; b) K. Shindo, H. Wakabayashi. S. Ishikawa, and T. Nozoe, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2941.
4. T. Nozoe, H. Okai, and T. Someya, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2185.
5. a) T. Nozoe, H. Okai, H. Wakabayashi, and S. Ishikawa, *Chem. Lett.*, **1988**, 1589; b) T. Nozoe, K. Shindo, and S. Ishikawa, *Chem. Lett.*, **1988**, 1593.
6. K. Shindo, H. Wakabayashi, H. Miyamae, S. Ishikawa, and T. Nozoe, *Heterocycles*, 1994, **37**, 943.
7. K. Shindo, H. Wakabayashi, L. C. Zhang, S. Ishikawa, and T. Nozoe, *Heterocycles*, 1994, **39** in press.
8. The sample was sealed in a small tube while refluxing under an argon atmosphere to avoid a contact with oxygen. A stoppered bottle can also be more conveniently.
9. For convenience, numbering of the seven-memberd ring of **4** on the nmr assignments are shown in the formulas.
10. T. Nozoe, S. Ishikawa, and K. Shindo, *Heterocycles*, 1989, **28**, 733.
11. C. K. Johnson, ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1956.
12. *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. P. Main, S.E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, M.M. Woolfson, Univs. of York, England, and Louvain, Belgium, 1978.
13. *International Tables for X-ray Crystallography*, Birmingham, Kynoch Press, 1974, Vol. IV, p. 72.
14. S.R. Hall and J.M. Stewart, XTAL3.2 Users Manual, Univ. of Western Australia, Australia, and Maryland, USA, 1992.

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