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Comparative Structural Characterization of the Biquaternized N-CH_3 and N-BH_3 Derivatives of the *cis*-Cyclen and *cis*-Cyclam Condensation Products with Glyoxal

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Abstract—The biquaternized N-CH_3 and N-BH_3 derivatives of the *cis*-cyclen (1,4,7,10-tetraazacyclododecane) and *cis*-cyclam (1,4,8,11-tetraazacyclotetradecane) condensation products with glyoxal have been prepared and structurally characterized by NMR spectroscopy and in the case of the BH_3 adducts additionally by X-ray crystallography. A comparison of the structural data between the four compounds and the starting materials permitted: (i) to establish their overall conformation, (ii) to discuss the structural modifications caused by the N-CH_3 and N-BH_3 functional groups and (iii) to understand, why the bialkylated tetraazapolycycles can be reduced to the cross-bridged tetraazamacrocycles, in contrast to the borane adducts.

Introduction

During the last few years one main focus of our research has been directed to the preparation of heterocyclic ring systems via condensation reactions of aminoalcohols[1–6] and aminothiols[7–8] with α-dicarbonyls. Our main objectives in the study of these molecules are related to selective syntheses, stereochemistry, dynamics and reactivity.

In the present contribution we report on the preparation and comparative structural characterization of the biquaternized N-CH_3 (**3**, **7**) and N-BH_3 (**4**, **8**) derivatives of the *cis*-cyclen (**1**) and *cis*-cyclam (**5**) condensation products with glyoxal (**2** and **6**) (Scheme 1).

Cyclen (**1**), cyclam (**5**) and related tetraazamacrocycles have been studied extensively in view of their ligating properties to metal ions.[9–13] Since it has been recognized recently that the condensation products of cyclen and cyclam with glyoxal[14] and their reduced derivatives **9** and **10** ($NaBH_4$ in EtOH, 90%)[15–19] are even more interesting ligands, the interest in the preparation and study of these systems is growing rapidly.

Glyoxal condensation products of cyclen and cyclam derivatives have been prepared for the first time more than 20 years ago,[20–24] but recently new synthetic routes have been developed.[25–27] The tetraazapolycycles can be considered as rigidified cyclic polyamines with four tertiary amino groups. Under most conditions the condensation leads to the thermodynamically most stable products with a maximum of six-membered fused rings in chair conformations and *cis*-configuration[†] of the central two-carbon bridge.[18,21,22,24–31] The *cis*-fusion imposes a folded geometry on the molecule which directs the lone pairs of adjacent nitrogen atoms in two opposite orientations. Two of the four lone pairs are directed to the center of the folded macrocycle and the other two are orientated to the outer sphere. Therefore, these ligands bind metal ions only in a bidentate fashion inside the cavity (Scheme 2).[14]

Complexes with these ligands might be useful in analytical

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[†] In the case of cyclam the *trans*-fused condensation product has been also prepared and it has been argued that it is thermodynamically less stable because of repulsive interactions between the nitrogen lone pairs in each of the aminal groups.

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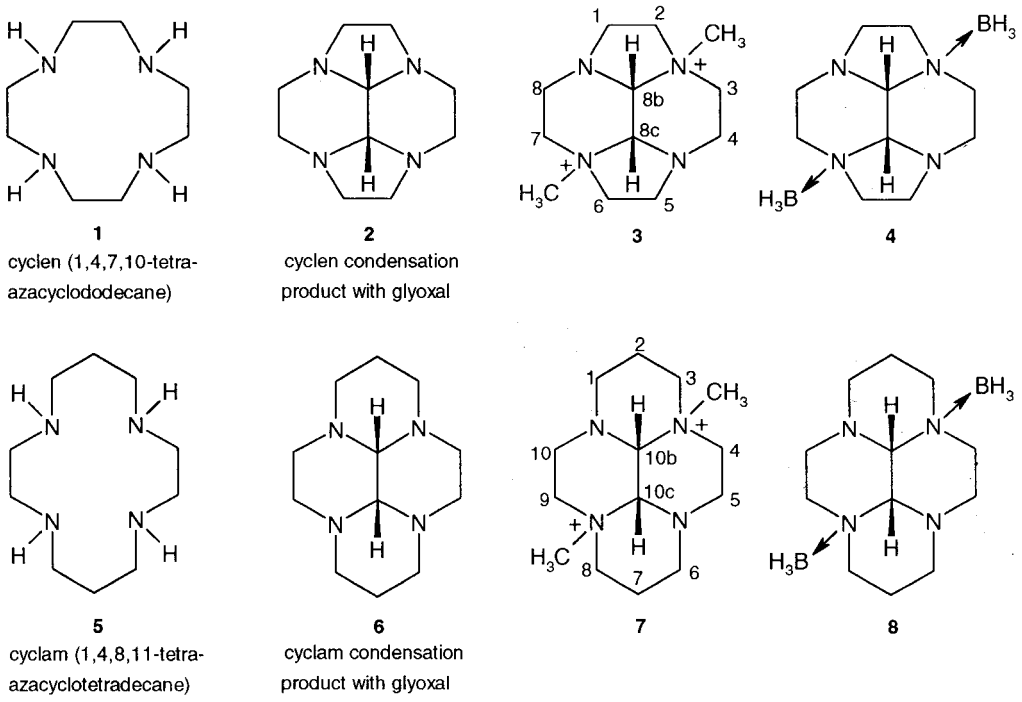
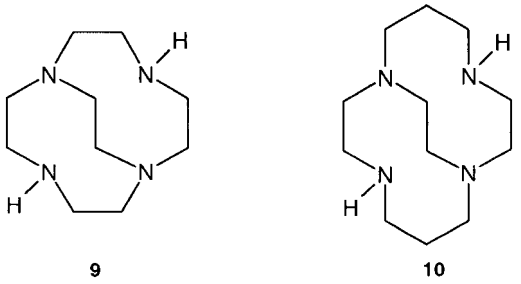


Scheme 1. Compounds involved in the preparation of the N-CH_3 and N-BH_3 derivatives of the *cis*-cyclen and *cis*-cyclam condensation products with glyoxal.

and supramolecular chemistry due to the presence of two non-coordinated nitrogen atoms that are reactive with other functional groups and permit further functionalization. E.g. it is possible to prepare mono- and bis(polyazacrown)s for the selective coordination of one or two metal ions and to develop catalysts with one or more active metal center.[32] In comparison, the complexing properties of the cross-bridged ligands **9** and **10** are different due to the possible coordination of all four nitrogen atoms to the metal ion center.[17–19] Such complexes might be used as models for the study and simulation of enzymes that carry metal ions in the active site.

In what follows we report on the comparative structural characterization of the functionalized *cis*-cyclen and *cis*-cyclam condensation products with glyoxal (**2** and **6**) by methyl iodide and BH_3–THF. The aims of this study were: (i) to determine the overall conformation of the functionalized ligands; (ii) to establish the structural modifications by these functions; and (iii) to understand, why **4** and **8** cannot be reduced by BH_3–THF or $NaBH_4$, in contrast to **3** and **7**.[15,16]



Scheme 2. The condensation products of cyclen and cyclam with glyoxal can be reduced to the cross-bridged ligands **9** and **10**.

During the preparation of this manuscript the X-ray structure of **7** was published by the groups of Busch and Alcock,[18] but the ^1H and ^{13}C NMR data of this molecule have not been reported so far. We have grown crystals of compound **7** in a different crystal system, but no further innermolecular structural differences could be observed.[33]

Results and Discussion

The condensation products of cyclen and cyclam with glyoxal (**2** and **6**) have been obtained according to a method described in the literature.[22] The biquaternized ammonium salts **3** and **7** have been prepared as described for *trans*-**7** by exhaustive alkylation of the bisaminals with methyl iodide (1:10).[30] After recrystallization from EtOH–H_2O the only reaction products obtained were *cis*-**3** and *cis*-**7**, so that under these conditions the introduction of a third methyl group was not possible.

With excess of BH_3–THF the tetraazapolycycles react in a similar manner and the *cis*-fused borane adducts **4** and **8** could be isolated. It may be supposed that the excess of borane could result in a reduction of the bisaminals to the corresponding cross-bridged systems **9** and **10**, but this was not the case.

The molecular structures of compounds **3**, **4**, **7** and **8** have been established by mass spectrometry as well as ^1H, ^{13}C and in the case of the borane adducts additionally by ^{11}B NMR spectroscopy. Furthermore, compounds **7** and **8** have been studied by X-ray crystallography. In all cases the piperazine and hexahydropyrimidine rings adopt all chair conformations and form folded ring systems with a perfect or at least approximate twofold symmetry axis perpendicular to the double bridged ethylene moiety (Fig. 1).

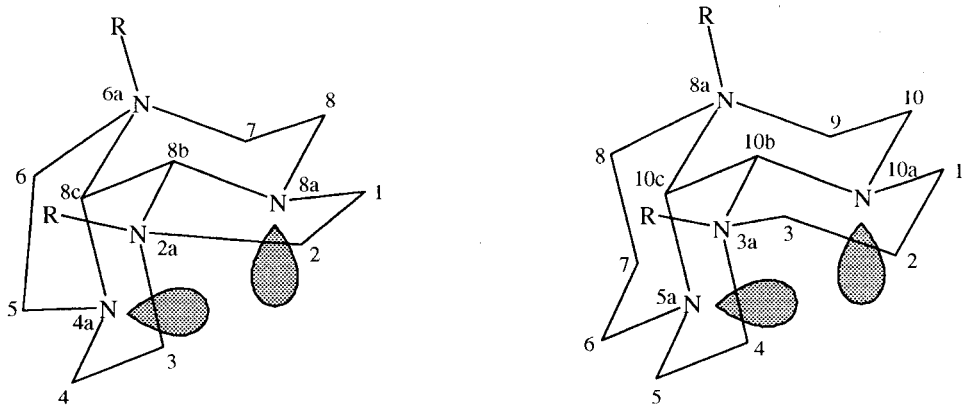


Figure 1. Lateral perspective of the molecular structures of **3**, **4** and **7**, **8** (R=CH_3 for **3** and **7**; R=BH_3 for **4** and **8**).

The NMR spectra could be completely assigned on the basis of the X-ray structures and the following two-dimensional experiments: COSY, HMQC, CHSHF, HMBC and NOESY. Due to the C_2-symmetry expected in solution, the tetraazapolycycles present only five (**3**, **4**) and six (**7**, **8**) carbon signals, respectively, neglecting the CH_3 signal for **3** and **7**. As important starting points for the assignment of the four NCH_2 groups in each case it was considered that quaternary nitrogen atoms cause low field shifts of adjacent methylene groups (in both ^1H and ^{13}C NMR spectra)[34] and that carbons C3 in **3**, **4** and C4 in **7**, **8** should be high field shifted due to a γ-gauche effect caused by N8a and N10a, respectively.[35]

Table 1. ^1H (400 MHz), ^{13}C (100.5 MHz) and ^{11}B NMR (128.3 MHz) data for the cyclen condensation product with glyoxal (**2**) and compounds **3**–**4** (ppm)

	H-1	H-2	H-3	H-4	H-8b	N-CH_3	^{11}B
2[a,b]	2.79 (m)[c]	2.16 (m)[c]	2.29 (m)	2.79 (m)	3.12 (s)	–	–
	3.22 (m)	3.24 (m)	3.05 (d)				
3[d,e]	3.08 (m)	3.90 (ddd)	3.67 (d)	3.14 (m)	4.47 (s)	3.39 (s)	–
	3.61 (ddd)	4.06 (m)	4.04 (m)	3.41 (br)			
4[f]	2.49 (m)	3.20 (m)	3.20 (m)	2.82 (m)	3.47 (s)	–	−13.4
	3.20 (m)	3.27 (m)	2.82 (m)	2.92 (m)			

	C-1	C-2	C-3	C-4	C-8b	N-CH_3
2[a,b]	52.4[c]	50.0[c]	49.2	51.5	77.5	–
3[d,e]	46.6	65.2	59.3	43.2	78.3	46.8
4[f]	47.8	62.5	56.3	45.9	77.9	–

[a] $CDCl_3$; $T=-60°C$.
[b] ^1H and ^{13}C NMR values have been already reported in Ref. 22.
[c] Signals may be interchanged.
[d] ^1H: 600 MHz, ^{13}C: 150 MHz; solvent: D_2O.
[e] See also Ref. 16.
[f] DMSO-d_6.

Table 2. ^1H (400 MHz), ^{13}C (100.5 MHz) and ^{11}B NMR (86.6 MHz) data for the cyclam condensation product with glyoxal (**6**) and compounds **7**–**8** (ppm)

	H-1	H-2	H-3	H-4	H-5	H-10b	N-CH_3	^{11}B
6[a,b,c]	2.86 (m)[d]	1.14 (m)	2.05 (m)[d]	2.25 (m)	2.17 (m)	3.00 (s)	–	–
		2.17 (m)	2.86 (m)	3.45 (m)	2.65 (d)			
7[e,f]	2.67 (ddd)	1.80 (d)	3.55 (ddd)	3.16 (m)	2.96 (m)	4.88 (s)	3.29 (s)	–
	2.96 (m)	2.22 (m)	3.76 (m)	4.24 (ddd)	3.16 (m)			
8[e]	2.22 (m)	1.40 (d)	3.01 (m)	2.28 (m)	2.70 (dd)	4.13 (s)	–	−11.5
	2.84 (m)	2.03 (m)		3.79 (ddd)	3.06 (m)			

	C-1	C-2	C-3	C-4	C-5	C-10	N-CH_3
6[a,b,c]	52.5[d]	19.7	56.1[d]	44.8	54.4	77.1	–
7[e]	51.0	18.8	64.2	49.4	46.3	75.7	48.0
8[e]	53.7	19.1	61.3	47.0	49.1	75.6	–

[a] $CDCl_3$.
[b] ^1H: 300 MHz, ^{13}C: 75.5 MHz.
[c] ^1H and ^{13}C NMR values have been already reported in Refs. 22,23,30.
[d] Signals may be interchanged.
[e] DMSO-d_6.
[f] see also Ref. 15.

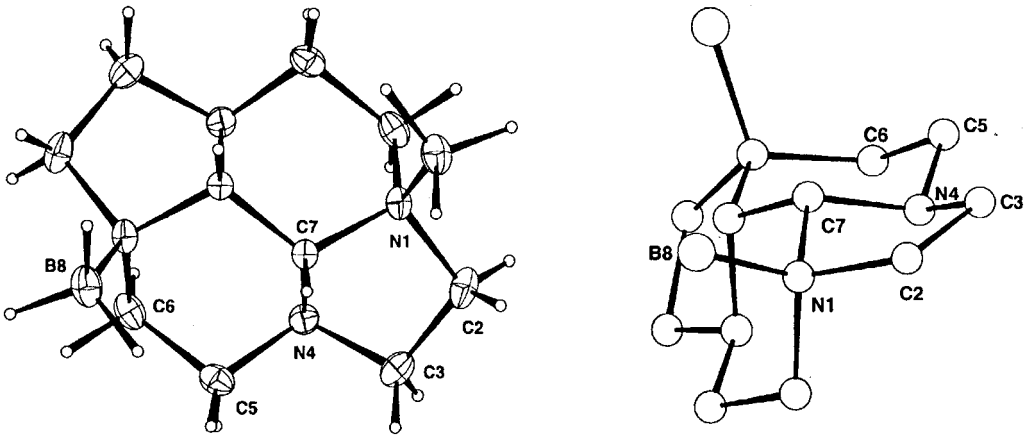


Figure 2. Perspective front and lateral views of the molecular structure of compound **4**.

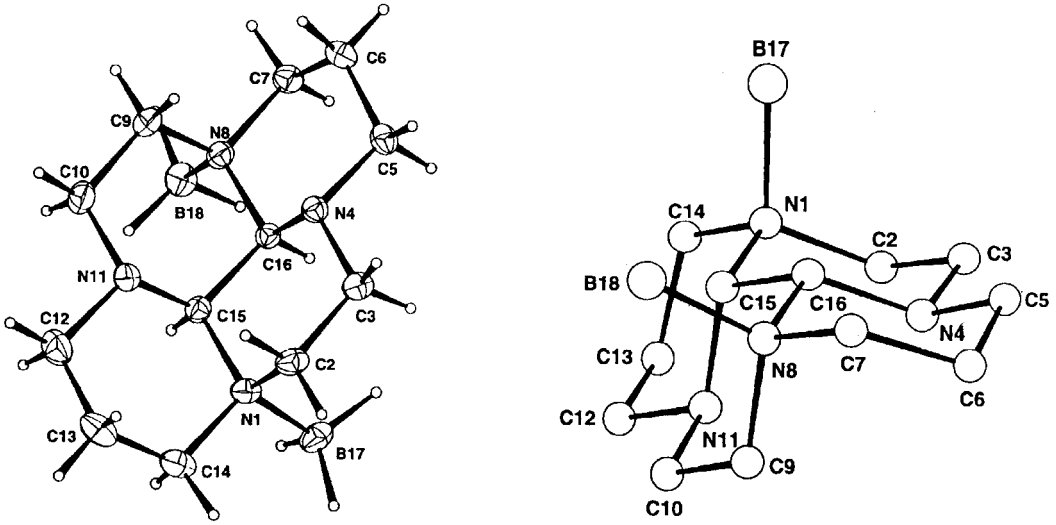


Figure 3. Perspective front and lateral views of the molecular structure of compound **8**.

The NMR spectroscopic data are listed in Tables 1 and 2 together with the chemical shifts of the starting materials. The *cis*-cyclen and *cis*-cyclam condensation products of glyoxal adopt chiral conformations that are not stable in solution, because the two possible enantiomers interconvert by inversion of all four nitrogen atoms.[22,24] The free energy of activation for the inversion process is lower in the case of the cyclen derivative, so that at room temperature only two instead of four signals appear for the NCH_2 carbon atoms. Therefore, all spectra of the cyclen condensation product with glyoxal including the two-dimensional experiments were recorded at −60°C.

All four compounds **3**, **4** and **7**, **8** show ABCD spin systems for the frame ethylene bridges in the ^1H NMR spectra, so that all four molecules are now conformationally

Table 3. Selected bond lengths (Å) of compounds **4** and **8** in comparison to the cyclam condensation product with glyoxal (**6**) and its bimethylated N-CH_3 derivative **7**

	N1–C2	C2–C3	C3–N4	N4–C5	C5–C6	C6–N1	N1–C7	C7–C7′	N4–C7	N1–B8	
4	1.524 (2)	1.524 (3)	1.462 (2)	1.454 (2)	1.513 (2)	1.511 (2)	1.493 (2)	1.503 (3)	1.442 (2)	1.628 (2)	
	N1–C2	C2–C3	C3–N4	N4–C5	C5–C6	C6–C7	C7–N8	N1–C15	C15–C16	N4–C16	N1–C17
6	1.469 (7)	1.496 (7)	1.437 (6)	1.501 (7)	1.521 (9)	1.529 (9)	1.443 (7)	1.461 (6)	1.520 (6)	1.471 (5)	–
7[a,b,c]	1.50 (1)	1.49 (1)	1.47 (1)	1.48 (1)	1.52 (1)	1.50 (1)	1.53 (1)	1.530 (9)	1.53 (1)	1.449 (8)	1.52(1)
8[b]	1.498 (4)	1.503 (4)	1.465 (4)	1.473 (4)	1.500 (5)	1.504 (4)	1.512 (4)	1.502 (3)	1.546 (3)	1.466 (3)	1.652 (4)[d]

[a] Data from Ref. 33.
[b] Average values are indicated for symmetry related bond lengths according to the C_2-symmetry of the molecules in solution.
[c] For the two independent molecules in the asymmetric unit average values have been formed.
[d] N1–B17.

Table 4. Selected bond and torsion angles (°) of compounds **4**, **7** and **8** in comparison to the cyclam condensation product with glyoxal (**6**) and its bimethylated N-CH_3 derivative **7**

	N1–C2–C3	C2–C3–N4	C3–N4–C7	N1–C7–N4	C2–N1–C7	N4–C5–C6	N1–C6–C5	C6–N1–C7′
4	106.2 (1)	103.2 (1)	103.1 (1)	103.0 (1)	100.5 (1)	108.2 (1)	112.4 (1)	110.2 (1)
	N1–C7–C7′	N4–C7–C7′	C5–N4–C7	C2–N1–C6	C2–N1–B8	C6–N1–B8	C7–N1–B8	C3–N4–C5
4	112.7 (1)	111.9 (1)	110.0 (1)	109.4 (1)	111.0 (1)	111.5 (1)	113.7 (1)	118.3 (1)
	N1–C2–C3	C2–C3–N4	C3–N4–C16	N4–C16–C15	N1–C15–C16	C2–N1–C15	N4–C5–C6	C5–C6–C7
6	109.2 (4)	110.5 (4)	109.8 (3)	112.2 (3)	108.8 (4)	111.9 (3)	110.8 (4)	109.7 (5)
7[a,b,c]	110.8 (7)	112.3 (7)	109.8 (6)	112.3 (6)	108.0 (6)	109.5 (6)	109.7 (7)	109.2 (8)
8[b]	111.3 (2)	112.0 (3)	111.3 (2)	111.1 (2)	108.8 (2)	109.1 (2)	110.1 (3)	109.7 (3)
	C6–C7–N8	C7–N8–C16	N4–C16–N8	C5–N4–C16	C2–N1–C14	C2–N1–C17	C14–N1–C17	C15–N1–C17
6	112.3 (4)	111.5 (4)	111.7 (3)	109.7 (3)	113.4 (4)	–	–	–
7[a,b,c]	112.3(7)	110.3(6)	109.3(6)	111.2(6)	110.6(7)	111.7(7)	105.5(6)	109.6(6)
8[b]	113.7(3)	109.2(2)	110.8(2)	111.1(2)	109.3(2)	112.5(2)[d]	105.1(2)[d]	111.6(2)[d]
	C3–N4–C5	N1–C15–C16–N8	N4–C16–C15–N11					
6	110.1 (4)	178.3	69.8					
7[a,b,c]	108.0 (6)	179.4	61.8					
8[b]	108.4 (2)	179.0	63.6					

[a] Data from Ref. 33.
[b] Average values are indicated for symmetry related bond lengths according to the C_2-symmetry of the molecules in solution.
[c] For the two independent molecules in the asymmetric unit average values have been formed.
[d] C2–N1–B17, C14–N1–B17 and C15–N1–B17, respectively.

stable due to the quaternization of two nitrogen atoms. As expected, the NCH_2 groups of the quaternized nitrogen atoms are significantly shifted to lower fields in both the ^1H and ^{13}C NMR spectra. But, it is noteworthy that the chemical shift differences are smaller for the borane adducts **4** and **8** according to the weaker bonding strength of N→B coordinative bonds.[36] The displacements of the methine hydrogen atoms confirm this observation (δ=4.41, 3.47, 4.88 and 4.13 ppm for **3**, **4** and **7**, **8**, respectively). Due to γ-gauche effects the ^{13}C NMR signals for the tertiary NCH_2 carbon atoms are shifted to higher fields. The ^{11}B NMR signals for the borane adducts **4** and **8** are in the expected range for tetracoordinated boranes.[37–39] It has been proposed that there is a correlation between the N→B bond strength and the ^{11}B NMR shifts in structurally related compounds.[36] Under this assumption the N→B bond is stronger in the cyclen derivative **4** than in the cyclam derivative **8** (δ=−13.4 ppm for **4** and δ=−11.5 ppm for **8**).

Compounds **4** and **8** were further characterized by X-ray crystallography (Figs. 2 and 3). The crystallographic data and selected structural data are given in Tables 3–5 together with the previously published structural data of the cyclam condensation product **6**[29] and its bimethylated N-CH_3 derivative **7**.[18,33]

Compound **4** is located at crystallographic C_2-axes in the crystal lattice, while compound **8** has only approximate C_2-symmetry in the solid state. In comparison to the starting material **6** the bond lengths with the largest deviations in compounds **7** and **8** are the elongated nitrogen–methine bonds of the quaternary nitrogen atoms. Thereby, the variations seem to be less significant in the borane adduct **8**, e.g. *d* (N_q–CH)=1.461 (6), 1.530 (9) and 1.502 (3) Å for compounds **6**, **7** and **8**, respectively. The N···N intramolecular distances between the nitrogen atoms with their lone pairs directed into the cavity are smaller in compounds **7** and **8** (2.966 and 2.974 Å, respectively) than in the cyclam condensation product with glyoxal **6** (3.060 Å). As a consequence the bite of the bidentate ligands is changed on

Table 5. Crystallographic data for compounds **4** and **8**

Crystal data	**4**	**8**
Formula	$C_{10}H_{24}B_2N_4$	$C_{12}H_{28}B_2N_4$
Crystal size (mm)	0.2×0.5×0.5	0.3×0.3×0.5
M_W (g mol^{-1})	221.95	250.00
Space group	*C* 2/*c*	*P* 2$_1$ 2$_1$ 2$_1$
Cell parameters		
a (Å)	14.470(1)	8.55(1)
b (Å)	9.747(1)	8.92(1)
c (Å)	9.099(1)	18.75(1)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	1263.6(1)	1429.4(1)
Z	4	4
μ (mm^{-1})	0.066	0.065
ρ_{calcd} (g cm^{-3})	1.17	1.16
Data collection		
Scan range (°)	0.43+0.53 tg θ	0.32+0.45 tg θ
θ limits (°)	2<θ<28	2<θ<28
hkl limits	−19,19;0,12;−12,0	−11,0;−11,0;0,24
No. collected refl.	1707	1983
No. ind. refl. (R_{int})	1523 (0.03)	1983
No. observed refl.	1259	1418
Refinement		
R	0.044	0.037
R_w	0.040	0.033
w	1/σ^2	1/σ^2
No. of variables	111	249
GOOF	4.67	2.63
$\Delta\rho_{min}$ (e Å^{-3})	-0.17	-0.15
$\Delta\rho_{max}$ (e Å^{-3})	0.20	0.16

functionalization of the other two nitrogen atoms. The narrowing of the cavity might be an explanation for the impossibility to methylate more than two of the nitrogen atoms. The N···N intramolecular distance between the nitrogen atoms in compound **4** is 2.924 Å. The N→B bond of compound **4** is shorter than the one of compound **8** (1.628 (2)↔1.652 (4) Å), thus confirming the ^{11}B NMR results that have shown that the N→B bond is stronger in the adduct of the cyclen derivative. Indeed, the lateral view of the X-ray structures of compound **4** in Fig. 2 shows an inclination of the boron atom to the left side, so that repulsive interactions with some of the axial hydrogen atoms are diminished.

Conclusions

From the above discussion it can be concluded that both exhaustive alkylation and reaction with BH_3–THF of the *cis*-cyclen and *cis*-cyclam condensation products with glyoxal leads exclusively to the diammonium salts and borane diadducts described in here. Furthermore (i) the overall all chair conformation of the funtionalized ligands **3**, **4** and **7**, **8** is maintained and the conformational inversion of the fused ring systems is inhibited due to the quaternization of two nitrogen atoms. (ii) The most important structural modifications are the elongations of the N_q–CH bonds and the shortening of the N···N distances, whereby the later variation should influence the metal ion selectivity of these ligands. (iii) The chemical shift displacements of the N_q–CH_2 groups and the N_q–CH bond elongations in the ammonium salts **3** and **7** indicate a weakening of the nitrogen methine bond that is more significant than in the borane adducts **4** and **8**. This observation allows to understand, why **3** and **7** can be reduced to the cross bridged ligands **9** and **10**, whilst this objective could not be realized with **4** and **8**, at least under the conditions used in this work (reduction with BH_3·THF and $NaBH_4$).

Experimental

NMR studies were carried out with Bruker 300, Jeol Eclipse+400 and Jeol 600 equipments. Standards were TMS (^{1}H, ^{13}C) and BF_3·OEt_2 (^{11}B). Chemical shifts are stated in parts per million; they are positive, when the signal is shifted to higher frequencies than the standard. IR spectra have been recorded with a Perkin–Elmer 16F-PC FT-IR spectrophotometer and mass spectra were obtained on an HP 5989 A equipment. Melting points were determined with a Gallenkamp MFB-595 apparatus and have not been corrected. High-resolution mass spectra were obtained with a Jeol 102A spectrometer at the Instituto de Química, UNAM, México.

X-ray diffraction studies of single crystals were determined on an Enraf–Nonius CAD4 diffractometer ($\lambda_{MoK\alpha}$= 0.71069 Å, monochromator: graphite, T=293 K, ω–2θ scan). Crystals were generally mounted in Lindeman tubes. Cell parameters were determined by least squares refinement on diffractometer angles for 24 automatically centered reflections. Absorption correction was not necessary, corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-86) for structure solution and the CRYSTALS (version 9, 1994) software package for refinement and data output. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were determined by difference Fourier maps, their positions and one overall isotropic thermal parameter were refined. $I > 3\sigma(I)$. $(R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum \omega F_o^2]^{1/2}$. In all cases only independent reflections on the basis of Friedel's law have been collected and a reflection-parameter ratio > 5 has been considered sufficient for the type of structural studies performed in here. For compound **4** the molecules are located at special positions (C_2-axis) in the crystal lattice.

Commercial starting materials were used when available. The condensation products of the *cis*-cyclen and *cis*-cyclam with glyoxal were prepared as described in the literature.[22] BH_3–THF was prepared due to the method of Brown.[40] Solvents were dried before use, when anhydrous reaction conditions had to be applied.

***cis*-2a,6a-Dimethyldecahydro-2a,4a,6a,8a-tetraazacyclopent[fg]acenaphtylenium diiodide (3).** A solution of the condensation product of *cis*-cyclen with glyoxal (0.58 mmol, 113 mg) and methyliodide (5.80 mmol, 820 mg) in chloroform (1.5 ml) was stirred for 12 h at 60°C in a sealed glass cylinder. A solid formed that was collected by filtration. The product was recrystallized from EtOH–H_2O (168 mg, 60%), mp 124–126°C. IR (KBr) ν_{max} 3000, 2986, 2972, 2950, 2920, 2848, 1472, 1464, 1458, 1448, 1424, 1420, 1412, 1394, 1334, 1290, 1200, 1178, 1142, 1100, 1036, 1018, 1008 cm^{-1}; MS (DI, 70 eV) *m/z* (%) 224 (M^+, 2), 222 (M^+-H_2, 100), 192 ($M^+-C_2H_6$, 3), 178 (4), 166 (4), 164 (4), 142 (76), 128 (HI, 34), 127 (I, 48), 112 (48), 97 (81), 84 (13), 70 (57), 56 (20), 42 (57). FAB$^+$-HRMS calcd *m/z* for $C_{12}H_{24}N_4$: 224.2001. Found: 224.1989. Error: −5.6 ppm. ^{1}H and ^{13}C NMR data see Table 1.

***cis*-Decahydro-2a,4a,6a,8a-tetraazacyclopent[fg]acenaphtylene-2a,6a-bis(borane) (4).** 1 ml of a 2.2 M solution of BH_3–THF (2.2 mmol) was added dropwise to a stirred solution of the condensation product of *cis*-cyclen with glyoxal (0.5 mmol, 100 mg) in 10 ml of THF. The mixture was kept at reflux for 8 h and allowed to reach room temperature. The solvent was removed and the solid was recrystallized from methanol/acetone, whereby colorless single crystals were isolated that were suitable for X-ray crystallography. Yield 95 mg (86%), mp 253–255°C. IR (KBr) ν_{max} 3000, 2980, 2960, 2922, 2858, 2834, 1506, 1482, 1472, 1460, 1428, 1400, 1382, 1354, 1324, 1314, 1284, 1226, 1190, 1160, 1148, 1126, 1072, 1050, 1004 cm^{-1}; MS (DI, 15 eV) *m/z* (%) 221 (M^+-1, 0.1), 207 (M^+-BH_3, 27), 194 ($M^+-B_2H_6$, 100), 164 (4), 152 (18), 138 (4), 124 (2), 111 (5), 98 (19), 83 (18), 70 (3), 56 (2), 42 (7). FAB$^+$-HRMS calcd *m/z* for $C_{10}H_{20}BN_4$ ($[M+H]^+-H_2-BH_3$): 207.1781. Found: 207.1784. Error: +1.3 ppm. ^{1}H, ^{13}C and ^{11}B NMR data see Table 2.

***cis*-3a,8a-Dimethyldecahydro-1H,6H-3a,5a,8a,10a-tetraazapyrenium diiodide (7).** A solution of the condensation product of *cis*-cyclam with glyoxal (0.13 mmol, 30 mg) and methyliodide (1.33 mmol, 0.80 ml) in chloroform (1.5 ml) was stirred for 12 h at 60°C in a sealed glass cylinder. A

solid formed that was collected by filtration. The product was recrystallized from EtOH/H_2O, whereby colorless single crystals were isolated that were suitable for X-ray crystallography. Yield 44 mg (65%), mp 119–121°C. IR (KBr) ν_{max} 2972, 2958, 2918, 2850, 2808, 1484, 1470, 1460, 1444, 1420, 1352, 1280, 1244, 1206, 1176, 1156, 1148, 1116, 1092, 1080, 1054, 1038, 1004 cm^{-1}; MS (DI, 70 eV) *m/z* (%) 236 (M^+-CH_4, 9), 222 ($M^+-C_2H_6$, 98), 193 (5), 178 (4), 166 (4), 164 (4), 142 (23), 140 (22), 128 (HI, 80), 127 (I, 60), 112 (31), 97 (54), 84 (12), 70 (50), 58 (46), 42 (100). ^1H and ^{13}C NMR data see Table 1.

***cis*-Decahydro-1H,6H-3a,5a,8a,10a-tetraazapyrene-3a, 8a-bis(borane) (8).** 3.6 ml of a 2.2 M solution of BH_3–THF (8.0 mmol) were added dropwise to a stirred solution of the condensation product of *cis*-cyclam with glyoxal (2.0 mmol, 450 mg) in 10 ml of THF. The mixture was kept at reflux for 8 h and allowed to reach room temperature. 12 h later colorless single crystals were isolated that were suitable for X-ray crystallography. Yield 425 mg (84%), mp 228–232°C. IR (KBr) ν_{max} 2958, 2944, 2928, 2902, 1472, 1456, 1448, 1436, 1420, 1358, 1342, 1306, 1278, 1196, 1186, 1156, 1140, 1108 cm^{-1}. MS (DI, 70 eV) *m/z* (%) 249 (M^+-1, 2), 235 (M^+-BH_3, 91), 222 ($M^+-B_2H_6$, 73), 205 (8), 178 (6), 164 (7), 140 (35), 123 (13), 112 (52), 97 (77), 82 (22), 70 (58), 56 (40), 42 (100).). FAB^+-HRMS calcd *m/z* for $C_{12}H_{24}BN_4$ ($[M+H]^+-H_2-BH_3$): 235.2094. Found: 235.2088. Error: −2.4 ppm. ^1H, ^{13}C and ^{11}B NMR data see Table 2.

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