1,8-Diazabicyclo[6.6.6]eicosane, 1,8-Diazabicyclo[6.6.5]nonadecane and 1,8-Diazabicyclo[6.6.4]octadecane and Their Diprotonated Forms

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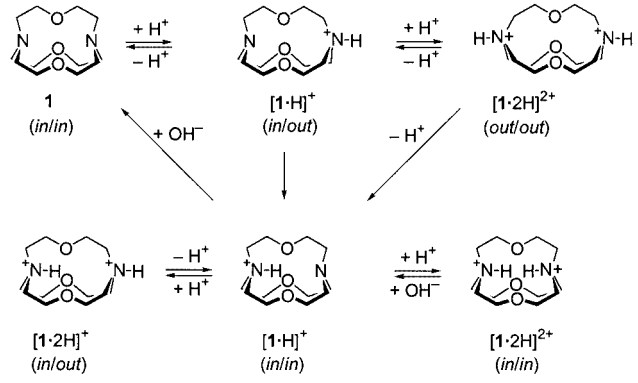
Dedicated to Professor Zvonimir B. Maksić on the occasion of his 65th birthday

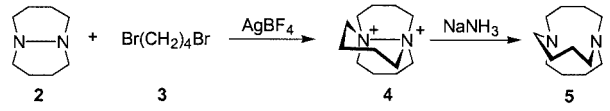
Keywords: Alkynes / Medium-ring compounds / Protonation

The preparation of the title compounds **9**–**11** was achieved by catalytic hydrogenation of 1,8-diazabicyclo[6.6.6]eicosa-4,11-diyne (**13**), 1,8-diazabicyclo[6.6.5]nonadeca-4,11-diyne (**14**), and 1,8-diazabicyclo[6.6.4]octadeca-4,11-diyne (**15**), respectively. As catalyst we used $Pd(OH)_2$ on carbon. NMR studies on **9**–**11** revealed an *in*/*in* conformation at the bridgehead positions. Treatment of **9**–**11** with an excess of trifluoroacetic acid yielded, in a kinetically controlled reaction, mixtures of the *out*/*out* and *in*/*out* diprotonated species $[\mathbf{9}\cdot 2H]^{2+}$, $[\mathbf{10}\cdot 2H]^{2+}$ and $[\mathbf{11}\cdot 2H]^{2+}$. The thermodynamically controlled species, the corresponding *in*/*in* conformers, are formed at higher temperatures and longer reaction times. The experimental observations are supported by AM1 calculations.

1,(k+2)-Diazabicyclo[$k.l.m$]alkanes are model systems for studying the interactions between bridgeheads[1] and, moreover, they are of interest with respect to their conformations[2] and basicities.[3−5] The first 1,(k+2)-diazabicyclo[$k.l.m$]alkanes with k, l and m between six and ten were reported by Simmons and Park.[6] Recently, the molecular structure of 1,12-diazabicyclo[10.10.10]dotriacontane was reported.[7] Detailed investigations of the macrobicyclic [1.1.1]cryptand **1** (Scheme 1) revealed that protonation with trifluoroacetic acid yields first a monoprotonated species with the *in*/*out* conformation at the bridgeheads.[8] The *in*/*in* monoprotonated isomer is formed from this species in a slow process. Upon decreasing the pH value of the solution the diprotonated species $[\mathbf{1}\cdot 2H]^{2+}$ in the *out*/*out*, *in*/*out* and *in*/*in* conformations was also detected.[8] It was found that *in* protonation occurs rather slowly, but that $[\mathbf{1}\cdot 2H]^{2+}$ in its *in*/*in* conformation is the thermodynamically most stable isomer of all.[8]



Scheme 1



Scheme 2

To investigate the conformations and chemistry of those bridgehead diazaalkanes with k, l, $m < 6$ Alder et al. developed two routes to synthesize medium-sized bicyclic systems. The first route uses reductive cleavage of propellane-type hydrazinium dications (Scheme 2).[9]

This route provided five bicyclic compounds ranging from [3.3.2] to [4.4.4] systems. This path is limited in that only five- and six-membered rings were closed efficiently. The second route[10] involves the cleavage of α-ammonium ions (Scheme 3), which provided eleven bicyclic diaza species ranging from [4.3.2] to [6.5.3] systems.[10]

In this paper we report an alternative method to those summarized in Schemes 2 and 3. Our path starts with bicyclic systems in which two bridges originate from alkynes. This limits it to macrobicyclic species. As examples we re-

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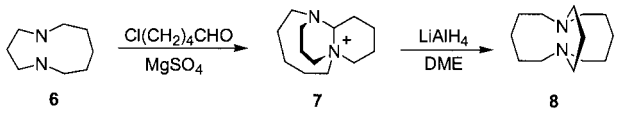
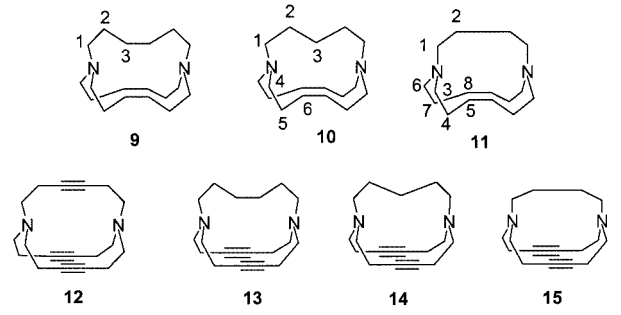


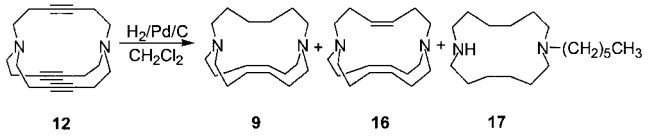
Scheme 3

port the syntheses of 1,8-diazabicyclo[6.6.6]eicosane (**9**), 1,8-diazabicyclo[6.6.5]nonadecane (**10**), and 1,8-diazabicyclo[6.6.4]octadecane (**11**). We also disclose the NMR spectroscopic data of the diprotonated species of **9**−**11**. The NMR spectra of **9**−**11** show a plane of symmetry perpendicular to the N···N axis. In the case of **11** the two hexamethylene chains are non-equivalent at low temperatures.



Synthesis and Structures of 9−11

To achieve our goal we first tried, in vain, a three-component reaction between 1,6-diaminohexane and 2 equiv. of 1,6-dibromohexane. A second effort started by hydrogenation of **12** with Pd^0 on carbon in dichloromethane at room temperature. After 24 h, we observed a mixture (GC) of **9**, together with the monoene **16** and 1-hexyl-1,8-diazacyclotetradecane (**17**; Scheme 4). With the exception of **9**, the side products **16** and **17** were only identified by mass spectrometry (FAB^+) and NMR spectroscopy (**16**). The diazabicycloalkane **9** was separated from the mixture by sublimation in vacuo as a waxy colorless solid, in a yield of only 30%. When we carried out the hydrogenation reaction of either **13**,[11] **14**[11] or **15**[11] with $Pd(OH)_2$ on carbon[12] in methanol, only one main product (**9**, **10** or **11**, respectively) was found.



Scheme 4

The ^1H and ^{13}C NMR spectra of **9** proved to be rather simple due to symmetry reasons. The three signals observed in the ^1H NMR spectrum correspond to the three non-equivalent CH_2 groups at C-1, C-2 and C-3 (see numbering scheme above). At 183 K the lower field signals reveal different shifts as expected for diastereotopic hydrogen atoms. The relevant data is collected in Table 1.

Table 1. ^1H and ^{13}C NMR chemical shifts (δ) of **9** in CD_2Cl_2; see text for the atom numbering

1-H	2-H	3-H	*T* [K]
2.22	1.43	1.57	298
2.51	1.43	1.16	183
1.62	1.24		
C-1	C-2	C-3	*T* [K]
50.9	22.8	21.0	298

Due to the lower symmetry of **10** relative to **9** its ^1H NMR spectrum is more complex (Table 2). In Figure 1 we notice six signals between $\delta = 1.3$ and 2.4 ppm in the ^1H NMR spectrum of **10**. The three multiplets at $\delta = 2.37$, 2.28 (2 H) and 2.23 (2 H) were assigned to the hydrogen atoms of the methylene groups in the α-position to the nitrogen atoms at C-1 and C-4 (1-H, 4-H), respectively. The assignment of the other signals was made possible using correlation techniques (COSY, HMQC, TOCSY).

Table 2. ^1H and ^{13}C NMR chemical shifts (δ) of **10** in CD_2Cl_2; see numbering scheme shown earlier

1-H	2-H	3-H	4-H	5-H	6-H	*T* [K]
ca. 2.23	1.36	1.62	2.37 2.28	ca. 1.36	ca. 1.36 1.84	298
C-1	C-2	C-3	C-4	C-5	C-6	*T* [K]
53.8	27.7	22.7	55.6	27.8[a]	28.4[a]	298

[a] Assignment exchangeable.

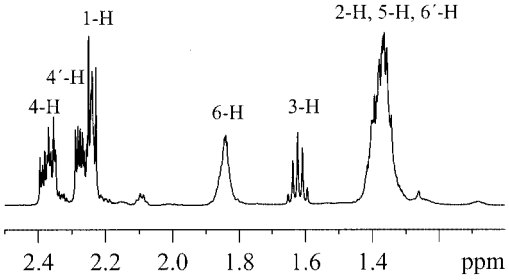


Figure 1. ^1H NMR spectrum of **10** (298 K) in CD_2Cl_2

The ^1H NMR spectrum of **11** at 298 K is relatively simple due to the equivalence of the two C_6 bridges (Figure 2a). At 183 K we encounter a mixture of two isomers, **11a** and **11b**, with a large surplus of **11a**. In both isomers both C_6 bridges are no longer equivalent and all CH_2 protons are diastereotopic (Table 3). The assignment of the strongly shifted signals of the protons at the positions α to the nitrogen centers at $\delta = 2.73$, 2.47 ppm of **11a** is straightforward.

For the assignment of all the other protons of the mixture we had to use HMQC-TOCSY experiments. In Figure 3 we show a two dimensional C−H correlation for the protons in the α-position to the nitrogen atom (Figure 3) and for the protons at the carbon atoms C-2, C-4, C-5, C-6 and C-7 of **11a** and **11b**.

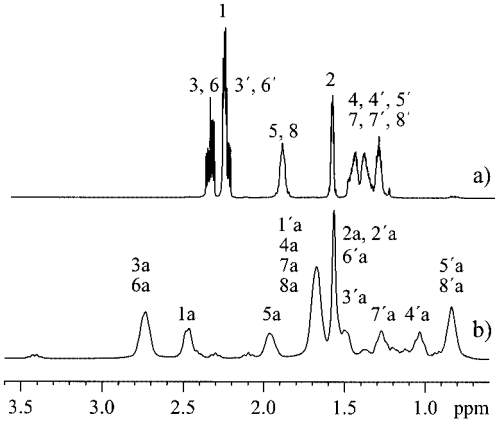


Figure 2. a) ^{1}H NMR spectrum of **11** at 298 K in CD_2Cl_2; b) ^{1}H NMR spectrum of **11** at 183 K in CD_2Cl_2

Table 3. ^{1}H and ^{13}C NMR chemical shifts (δ) of **11** in CD_2Cl_2; see numbering scheme shown earlier

	1-H	2-H	3-H	4-H	5-H	6-H	7-H	8-H	*T* [K]
11	2.28	1.60	2.39	1.48	1.92	2.39	1.48	1.92	298
			2.25	1.92	1.34	2.25	1.42	1.34	
11a	2.47	1.55	2.73	1.68	1.96	2.73	1.68	1.68	183
	1.68		1.50	1.03	0.83	1.55	1.27	0.83	
11b	2.41	1.37	2.28	1.36	3.41	2.76	1.22	1.68	183
	1.97	1.14	2.09	1.15	0.83	2.30	1.10	0.92	
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	*T* [K]
11	57.08	29.18	55.49	26.71	25.24	55.49	26.71	25.25	298
11a	53.49	27.69	48.19	24.15	20.28	51.27	24.03	19.98	183
11b	54.36	29.02	58.36	27.72	25.08	64.83	26.24	31.56	183

Protonation Experiments

The bicyclic saturated diaza compounds **9**−**11** show the anticipated basic properties. Protonation of **9**−**11** in CD_2Cl_2 with an excess of trifluoroacetic acid at temperatures of 233 K (**9**) and 273 K (**10** and **11**) yielded a mixture of two isomers in solution which convert into a third one in a slow reaction at 298 K.

For the assignment of the signals in the ^{1}H NMR spectra we assumed, in analogy to the work of Simmons and Park,[4] that the *out*/*out* conformer of the diprotonated forms of $[\mathbf{9}\cdot 2H]^{2+}$, $[\mathbf{10}\cdot 2H]^{2+}$ and $[\mathbf{11}\cdot 2H]^{2+}$ is formed first, accompanied by the corresponding *in*/*out* conformers.

As an example we show in Figure 4 the ^{1}H NMR spectra recorded for $[\mathbf{9}\cdot 2H]^{2+}$. At 233 K a mixture of the *out*/*out* and *in*/*out* conformation of $[\mathbf{9}\cdot 2H]^{2+}$ was observed immediately after addition of trifluoroacetic acid (Figure 4a). The

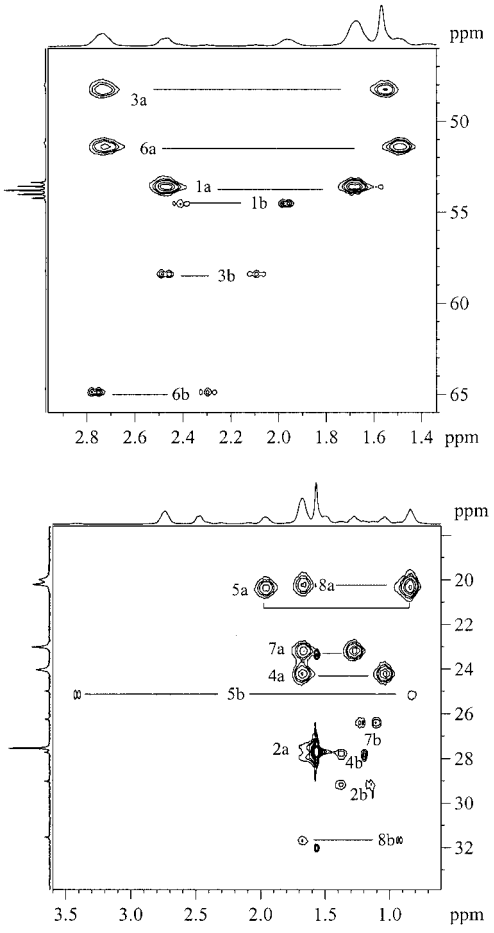


Figure 3. Two-dimensional H,C-correlated spectrum of the mixture **11a/11b** at 193 K

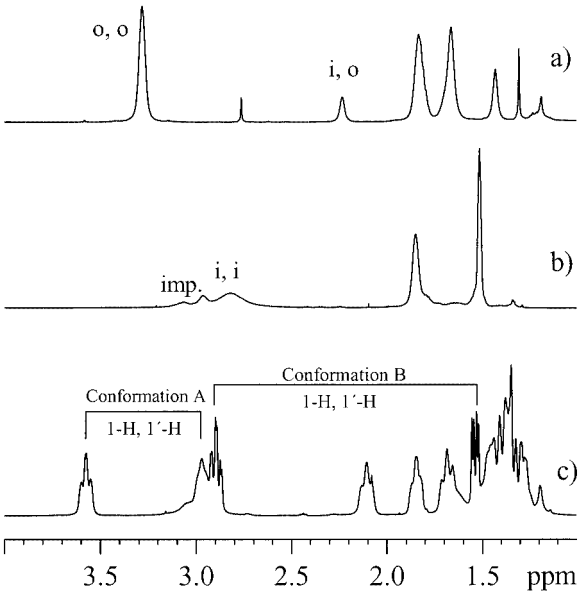


Figure 4. ^{1}H NMR spectra of $[\mathbf{9}\cdot 2H]^{2+}$ in CD_2Cl_2 at 233 K (a), after 4 h at 298 K (b), and after lowering the temperature to 213 K (c)

presence of a mixture is best seen from the two singlets at δ = 3.28 and 2.23 ppm with different intensities. The stronger peak was assigned to the *out*/*out* conformation and the weaker one to the *in*/*out* isomer. All other assignments (Table 4) are based on COSY and TOCSY experiments. The assumption of a mixture of two isomers is also supported by the peaks at δ = 1.83 and 1.66 ppm which were assigned to the hydrogen atoms at positions 2 and 3 of the *out*/*out* isomer. The singlet at δ = 1.43 ppm is due to the protons at positions 2 and 3 of the *in*/*out* isomer. Raising the temperature of the solution to 298 K allowed us to observe after 4 h (Figure 4b) only the *in*/*in* isomer. The ^{1}H NMR spectrum in Figure 4c was recorded after cooling the *in*/*in* conformer of [**9**·2H]$^{2+}$ to 213 K. It can be understood by assuming interconverting conformers in the ratio of 1:1 with the assignments given in Table 4.

In the ^{1}H NMR spectrum of [**10**·2H]$^{2+}$ (Table 5) we had to discriminate the resonances of the C_5 chain from those of the C_6 chains. This was possible by taking into account the intensities of the signals as well as COSY, HMQC and especially TOCSY experiments. The assignment of the signals for the CH_2 groups α to the nitrogen centers is unequivocal, as given in Table 5, whereas an exact assignment of the signals of the remaining groups is not always clear-cut due to a strong overlap of the peaks at higher fields. For the *out*/*out* isomer of [**10**·2H]$^{2+}$ the signals at δ = 3.49/3.33 and 3.42 ppm were significant. The same protons of the *in*/*out* isomer resonate at δ = 2.26 and 2.20 ppm. After leaving the solution at 298 K for 24 h, only the *in*/*in* isomer was present. Most pronounced are the low-field signals for 4-H at δ = 2.87 ppm and 1-H at δ = 2.81 ppm.

The bicyclic species **11** was protonated with trifluoroacetic acid at 273 K. Its ^{1}H NMR spectroscopic data (Table 6) show the presence of the *out*/*out* and the *in*/*out* conformations in a ratio of about 1:1. In both isomers the C_6 chains are equivalent and the protons at the carbon atoms next to the nitrogen (C-1, C-3, C-6) absorb at δ = 3.79/3.27 and δ = 2.45/2.36, 2.26 ppm (Table 6). Both isomers converted into the *in*/*in* conformer when the solution was left at 298 K for 27 h. Cooling of this solution to 183 K gives the spectrum of the *in*/*in* isomer. The two C_6 chains are also non-equivalent in this case and all signals for the CH_2 groups, with the exception of C-2, are diastereotopic (Table 6). Due to the strong overlap of the signals the $\Delta G^{\neq}$ value for **11** could only be roughly estimated (9 kcal/mol).

Table 4. ^{1}H and ^{13}C NMR chemical shifts (δ) of [**9**·2H]$^{2+}$ in CD_2Cl_2 and CF_3CO_2H; see numbering scheme shown earlier

	1-H	2-H	3-H	NH	*T* [K]
[**9**·2H]$^{2+}$ (*out*/*out*)	3.28	1.83	1.66	12.8	233
[**9**·2H]$^{2+}$ (*in*/*out*)	2.23	1.43	1.43	11.0	233
[**9**·2H]$^{2+}$ (*in*/*in*)	2.85	1.85	1.49	11.7	
[**9**·2H]$^{2+}$ (*in*/*in*)[a]	3.58 2.98	2.12 1.69	ca. 1.38	10.5	213
[**9**·2H]$^{2+}$ (*in*/*in*)[b]	2.91 1.54	1.86 1.35	ca. 1.31	10.5	213
	C-1	C-2	C-3		
[**9**·2H]$^{2+}$ (*out*/*out*)[c]	56.6	26.4[d]	23.9[d]		233
[**9**·2H]$^{2+}$ (*in*/*out*)[c]	50.1	27.1[d]	25.7[d]		233
[**9**·2H]$^{2+}$ (*in*/*in*)	50.3	22.4	20.6		298
[**9**·2H]$^{2+}$ (*in*/*in*)[a]	50.0	20.8	19.9		213
[**9**·2H]$^{2+}$ (*in*/*in*)[b]	49.1	22.5	18.9		213

[a] Conformation **A**. [b] Conformation **B**. [c] In $CDCl_3/CF_3CO_2H$. [d] Assignment interchangeable.

Model Calculations

To obtain more information on the geometrical parameters of **9**−**11** as well as on their diprotonated species we carried out quantum chemical calculations on these molecules considering *in*/*out* isomerization of the bridgeheads and the protons. The geometrical parameters were optimized by a conformational search using the MMFF force field in Macro Model.[13] The resulting total and local minima were further optimized by the AM1 method[14] to be consistent within the model. In Scheme 5 we have outlined the different isomers for **9**. In Table 7 we list the relative energies of **9**−**11** and their diprotonated derivatives in their *out*/*out*, *in*/*out* and *in*/*in* conformations.

These calculations reveal that for **9**−**11**, as well as for the diprotonated forms, the respective *in*/*in* conformation is the

Table 5. ^{1}H and ^{13}C NMR chemical shifts (δ) of [**10**·2H]$^{2+}$ in CD_2Cl_2 and CF_3CO_2H; see numbering scheme shown earlier

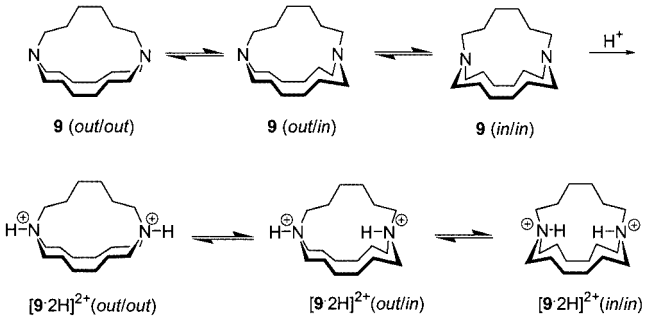
	1-H	2-H	3-H	4-H	5-H	6-H	NH	*T* [K]
[**10**·2H]$^{2+}$ (*out*/*out*)	3.49	ca. 1.80	1.62 1.52	3.33 3.24	ca. 1.83	ca. 1.52	9.5[a]	273
[**10**·2H]$^{2+}$ (*in*/*out*)	2.26	ca. 1.82	ca. 1.62	ca. 2.20	1.52	1.52	9.5[b]	273
[**10**·2H]$^{2+}$ (*in*/*in*)	2.81	1.76 1.83	1.76 1.83	2.87	1.72	1.51	9.6	298
	C-1	C-2	C-3	C-4	C-5	C-6		*T* [K]
[**10**·2H]$^{2+}$ (*out*/*out*)	51.3	24.7	28.2	51.8	25.8	27.9		273
[**10**·2H]$^{2+}$ (*in*/*out*)	58.5	26.1	25.2	56.2	23.5	27.9		273
[**10**·2H]$^{2+}$ (*in*/*in*)	53.5	23.0	23.5	53.4	23.0	21.7		298

[a] δ = 13.4 ppm at 233 K. [b] δ = 10.7 ppm at 233 K.

Table 6. ^1H and ^{13}C NMR chemical shifts (δ) of $[\mathbf{11}\cdot 2H]^{2+}$ in CD_2Cl_2 and CF_3CO_2H; see numbering scheme shown earlier

	1-H	2-H	3-H	4-H	5-H	6-H	7-H	8-H	NH	*T* [K]
$[\mathbf{11}\cdot 2H]^{2+}$ (*out*/*out*)	3.71	1.82 1.60	3.27	2.12 1.87	1.76 1.64	3.27	2.12 1.87	1.76 1.64	12.0	273
$[\mathbf{11}\cdot 2H]^{2+}$ (*in*/*out*)	2.45	1.60	2.36 2.26	1.51	1.61	2.36 2.26	1.51	1.61	[a]	273
$[\mathbf{11}\cdot 2H]^{2+}$ (*in*/*in*)	2.79	1.93	3.01 2.82	1.96 1.73	1.53	3.01 2.82	1.96 1.73	1.53	9.58	298
$[\mathbf{11}\cdot 2H]^{2+}$ (*in*/*in*)	3.00 2.42	1.70	3.33 2.35	1.99 1.47	1.47 1.29	2.82 2.42	1.95 1.64	1.48 1.29	9.74	183
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8		*T* [K]
$[\mathbf{11}\cdot 2H]^{2+}$ (*out*/*out*)	51.33	23.69	52.23	23.78	26.13	52.23	23.78	26.13		273
$[\mathbf{11}\cdot 2H]^{2+}$ (*in*/*out*)	54.54	23.23	53.50	25.28	26.34	53.50	25.28	26.34		273
$[\mathbf{11}\cdot 2H]^{2+}$ (*in*/*in*)	55.57	25.56	52.79	23.10	21.28	52.79	23.10	21.28		298
$[\mathbf{11}\cdot 2H]^{2+}$ (*in*/*in*)	49.53	21.24	52.60	22.45	21.65	54.03	24.38	18.18		183

[a] Could not be found.



Scheme 5

Table 7. Relative energies [kcal/mol] of **9**−**11** and their diprotonated congeners $[\mathbf{9}\cdot 2H]^{2+}$, $[\mathbf{10}\cdot 2H]^{2+}$ $[\mathbf{11}\cdot 2H]^{2+}$ in the *in*/*in*, *in*/*out* and *out*/*out* conformations, as derived by a combined MMFF force field/AM1 calculation

	in/*in*	*in*/*out*	*out*/*out*		*in*/*in*	*in*/*out*	*out*/*out*
9	0	3.2	1.08	$[\mathbf{9}\cdot 2H]^{2+}$	0	13.2	17.9
10	0	1.0	2.44	$[\mathbf{10}\cdot 2H]^{2+}$	0	13.3	25.3
11	0	[a]	[a]	$[\mathbf{11}\cdot 2H]^{2+}$	0	10.6	19.4

[a] No minimum could be found.

most stable one. In the cases of the neutral species **9** and **10** the energy differences between the *in*/*out* and *out*/*out* conformations are small. For **11** no minima were found for the *in*/*out* and *out*/*out* conformations. This, and the relatively small differences mentioned in the cases of **9** and **10**, are due to the fact that the CH_2 groups in the α position to the bridgeheads are situated almost in plane with the nitrogen atoms. For the diprotonated species the energy differences between the minima (*in*/*in*) and the other two respective conformations are larger than in the unprotonated species (Table 7).

Conclusions

We found a new way of preparing diazabicyclic macrocycles by hydrogenation of partially hydrogenated bicyclic diynes. This method should also be extended to the *N*,*N*′-bridged 1,10-diazacyclooctadeca-5,14-diynes.[15] Our investigations of **9**−**11** reveal that diprotonation occurs first from outside and that the *in*/*in* conformer of the neutral and the diprotonated species is the most stable isomer.

Experimental Section

General Methods: ^1H and ^{13}C NMR spectra were recorded with a Bruker 500 MHz spectrometer (^1H at 500 MHz and ^{13}C at 125 MHz). The chemical shifts are quoted in ppm on the δ scale using the residual protonated solvent as the internal standard. Mass spectrometry (high resolution) was performed using a JEOL JMS-700 spectrometer. Elemental analyses were carried out by Mikroanalytisches Labor der Chemischen Institute der Universität Heidelberg.

General Procedure for the Preparation of 9−11: The 1,8-diazabicyclodialkyne (**13**−**15**) was dissolved in 10 mL of methanol/ethyl acetate (1:1). $Pd(OH)_2$ on carbon was added and the mixture was stirred under H_2 (1 atm) for 5 h.[12] The catalyst was then removed by filtration through Celite and the solvent was removed under reduced pressure. Column chromatography on basic ALOX III with petroleum ethers as the eluent yielded the pure compound.

1,8-Diazabicyclo[6.6.6]eicosane (9): 1,8-Diazabicyclo[6.6.6]eicosa-4,11-diyne[11] (0.08 g) and $Pd(OH)_2$ on carbon (0.08 g) were used to obtain **9** as a clear waxy solid (0.056 g, 67%). ^1H and ^{13}C NMR: see Table 1. HRMS (EI): calcd. for $C_{18}H_{36}N_2$ 280.2878; found 280.2890. $C_{18}H_{36}N_2$ (280.49): calcd. C 77.07, H 12.94, N 9.99; found C 76.92, H 13.04, N 9.88.

1,8-Diazabicyclo[6.6.5]nonadecane (10): 1,8-Diazabicyclo[6.6.5]nonadeca-4,11-diyne[11] (0.11 g) and $Pd(OH)_2$ on carbon (0.04 g) were used to obtain **10** as a clear waxy solid (0.060 g, 54%). ^1H and ^{13}C NMR: see Table 2. HRMS (EI): calcd. for $C_{17}H_{34}N_2$ 266.2722;

found 266.2712. $C_{17}H_{34}N_2$ (266.46): calcd. C 76.62, H 12.86, N 10.52; found C 76.86, H 12.91, N 10.30.

1,8-Diazabicyclo[6.6.4]octadecane (11): 1,8-Diazabicyclo[6.6.4]octadeca-4,11-diyne (0.10 g) and $Pd(OH)_2$ on carbon (0.06 g) were used to obtain **11** as a clear waxy solid (0.02 g, 15%). ^1H and ^{13}C NMR: see Table 3. HRMS (EI): calcd. for $C_{16}H_{32}N_2$ 280.2878; found 280.2890. $C_{16}H_{32}N_2$ (280.49): calcd. C 76.12, H 12.78, N 11.10; found C 75.94, H 12.64, N 11.01.

Protonation of 9−11: A sample of the 1,8-diazabicycloalkane **9**−**11** was dissolved in CD_2Cl_2 (0.8 mL) and placed in an NMR tube. This solution was then cooled within the spectrometer to the initial temperature for the NMR experiments (233 K for **9**, 273 K for **10** and **11**). A solution of trifluoroacetic acid (2.5 equiv.) in CD_2Cl_2 (0.1 mL) was added, the tube was shaken and then returned to the spectrometer for the commencement of the NMR experiments.

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