# Towards In-Plane Delocalized 4N/7e Radical Cations and 4N/6e Dications – One-/Two-Electron Oxidation of Proximate-Parallel Bis(*N*,*N'*-bicyclic)-bishydrazines

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*Dedicated to Christoph Rüchardt on the occasion of his 75th birthday*

**Keywords:** Heterocycles / Cage compounds / Density functional calculations / Cyclic voltammetry / Homoaromaticity

In the pursuit of novel bishomoconjugated (σ-bishomoaromatic) 4N/7(6)e bonding motifs, (bisseco)pagodane/isopagodane and dodecahedrane-like, caged, proximate-parallel bishydrazines have been designed as suitable host skeletons. The derived radical cations and dications are characterized by calculations as cyclically in-plane delocalized (σ-bishomoaromatic) species (4N/7(6)e). However, the synthetic approaches based on a pool of half-caged proximate-parallel bisdiazenes/bishydrazines and on strategies in part elaborated in the pagodane area have not led to the target structures. Half-caged, rather flexible bis(*N*,*N'*-bicyclic) bishydrazines (**9**,**10**) evolved as the structurally closest synthetically accessible model compounds. Whilst CV (PE, ESR)measurements were not suggestive of significant through-space interaction in the respective radical cations and dications, DFT calculations (B3LYP/6-31G*) identified a singlet dication ($\mathbf{10}^{2+}$) as proximate, cyclically in-plane delocalized species, which, however, relaxed into a more stable, more distant triplet. In an Appendix, selected examples are presented for the synthetic utilization of proximate-parallel bisdiazenes (bishydrazines) in the area of more or less preorganized, semi- to fully caged tetra(hexa)azapolycyclic molecules.

## Introduction

The unique, perfectly in-plane delocalized, four-center three-electron radical cations and σ-bishomoaromatic two-electron dications **A** [4C/3(2)e][1] owe their existence and, in part, impressive kinetic stability to their very special molecular architecture, polycyclic pagodane-/dodecahedrane-type cages.[2–5] Thus, when the project centered on the in-plane bishomoconjugated four-center five(six)-electron radical anions/dianions **B** [4N/5(6)e][6] was extended to the 4N/7(6)e radical cations/dications **C** and **D**,[7] fully cagedtetraazapolycycles such as **1**, **2**, and **3** emerged as first choice host skeletons:[8] The C=C double bonds of the carbocyclic models **4**–**6**[1–5] are replaced by hydrazine units, which are held strictly parallel at relatively short transannular distances (*d*) and in a plane made up of the four nitrogen atoms. As for **1** and **2**, there had been good reasons to assume that the skeletons would be flexible enough to respond to their one-/two electron-oxidation by increasing inward pyramidalization of the four N-atoms, thus bringing the nitrogen lone-pairs close enough to allow for increasing cyclic in-plane electron delocalization. As an additional bonus, these skeletons should provide the evolving **C**-type cations with appreciable kinetic stabilization, showing little tendency for β-elimination ("anti-Bredt-protection"). Tetraazadodecahedrane **3** was a priori considered as limiting case as its very rigid spherical skeleton would be expected to resist geometrical changes of the degree needed for efficient transannular delocalization in the $\mathbf{3}^{\cdot+(2+)}$ ions. In making this choice, it was helpful to know that the radical cations generated from 1,5-diazabicyclo[3.3.0]octanes, subunits of **1**, **2**, and **3**, were stable at room temperature and had been subjected toextensive structural,[9] ESR,[10] PE,[10a,11] CV[10a,12], as well as computational investigations.[13,14] In addition, hydrogenolytic N–N cleavages in **1**–**3** would pave the way to highly preoriented tetramines, potential precursors of **D**-type cations.

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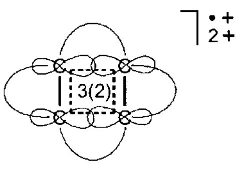
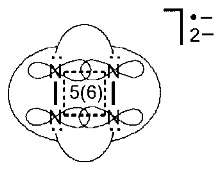
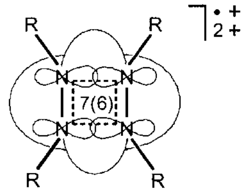
DOI: 10.1002/ejoc.200400647



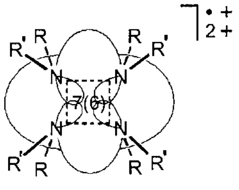
**A**
4C/3(2)e



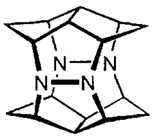
**B**
4N/5(6)e



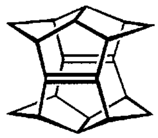
**C**
4N/7(6)e



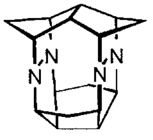
**D**
4N/7(6)e



**1**



**4**



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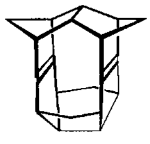

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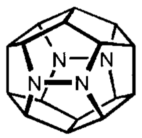

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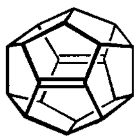


**6**

To put the bonding motifs **C** and **D** into perspective, through-space (TS) 2N/3e homoconjugation[15,16] and through-bond (TB) intramolecular electron transfer in bis(hydrazyl) radical cations are well documented.[10,17] For the generation of TS 4N/7(6)e cations, urotropin homologues such as the [$1^4.2^2$] (TTD[18])/[$2^4.3^2$]/[$3^6$]adamanzanes[19] seemed promising candidates, since they readily offer conformations with all four n-lobes pointing into the cage.[20] In fact, for the TTD radical cation, a very recent reinvestigation established three-dimensional TS/TB delocalization of seven electrons over four equivalent nitrogen atoms.[21] Still, the statement that "this extensive delocalization in a completely saturated system is a unique feature of the TTD radical cation"[21] remains a questionable one. Extended TS/TB delocalization had been reported for deeply colored cations resulting from γ-irradiation of an all-*cis*-alkylated tetrazolidine at 77 K[22a] and chemical/electrochemical oxidation of an all-*cis*-peralkylated perhydrotetrazine at room temperature (cf. **33**, Figure 6).[22b]

Not to nourish false expectations, when our activities had to be brought to an end,[23] none of the target structures had yielded to long lasting efforts.[6,8] In this paper we report the most relevant results: **C**-type cations generated "on paper" from **1**, **2**, and **3**, the synthesis and one-/two-electron oxidation (CV) of two proximate-parallel bis(*N*,*N'*-bicyclic)-bishydrazines (**9**,**10**) as the closest accessible approximations to **1** and **2**, and the computational characterization of the derived ions. In an Appendix examples are presented that show our attempts to construct semicaged and more or less preorganized tetra(hexa)azapolycycles, alternatives to **1**–**3** as potential hosts of novel bonding motifs.

## Results and Discussion

### C-type 4N/7e Radical Cations and 4N/6e Dications

#### *Calculations*

As in the case of the counterion-free 4N/5(6)e anions **B**,[6] the 6-31G* basis set and the B3LYP functional were applied to the neutral compounds **1**–**3** and to the ions resulting from their one-/two-electron oxidation.[24,25] Selected features − energies, N– bond lengths (*d'*), N···N distances (d), CCN/CNC angles, and NICS values − are presented in Figure 1. Most notably, for all three neutral compounds high-symmetry conformations ($D_{2h}$, $C_{2v}$) surfaced as energy minima[26], and for their radical cations as well as dications, the symmetry was retained. Loss of the electrons enforces appreciable shortening of the N···N distances (*d*) and N–N bond lengths (*d'*): for **1** ($\rightarrow \mathbf{1}^{\cdot+} \rightarrow \mathbf{1}^{2+}$), by ca. 0.48 (0.08) and ca. 0.41 (0.06) Å; for **2** ($\rightarrow \mathbf{2}^{\cdot+} \rightarrow \mathbf{2}^{2+}$), by ca. 0.90 (0.10) and ca. 0.46 (0.06) Å; the two dications feature similarly short homoconjugate distances (*d*) of 2.23 and 2.26 Å. For $\mathbf{3} \rightarrow \mathbf{3}^{\cdot+} \rightarrow \mathbf{3}^{2+}$, the changes in transannular distance (ca. 0.17 Å) are expectedly much smaller; N···N distances of 3.72 and 3.54 Å in the cations undoubtedly mark limits for through-space interaction. Are these calculations reliable in view of the tendency of the DFT functional to favor delocalization?[27,28] For comparison, the changes in energy and geometry associated with the oxidation of the reference dienes **4**–**6**, calculated on the same theoretical level, are listed in Figure 1. In-plane bishomoconjugation/σ-bishomoaromaticity for $\mathbf{4}^{\cdot+/2+}$, $\mathbf{5}^{\cdot+/2+-}$ and even $\mathbf{6}^{\cdot+}$ is well established.[1–5,29,30] It should be noted, (i) for the 4N-ions, the increase in energy is generally significantly smaller than for their 4C-analogues; (ii) the homoconjugate distances (*d*) in the radical cations $\mathbf{1}^{\cdot+}/\mathbf{2}^{\cdot+}$ hardly differ from those in $\mathbf{4}^{\cdot+}/\mathbf{5}^{\cdot+}$ and are shorter in the dications $\mathbf{1}^{2+}/\mathbf{2}^{2+}$ (significantly) than in $\mathbf{4}^{2+}/\mathbf{5}^{2+}$. For $\mathbf{3}^{\cdot+}/\mathbf{3}^{2+}$, these distances are significantly longer than for dodecahedral $\mathbf{6}^{\cdot+}/\mathbf{6}^{2+}$, for which only the radical cation has been observed in a Freon matrix.[5a]

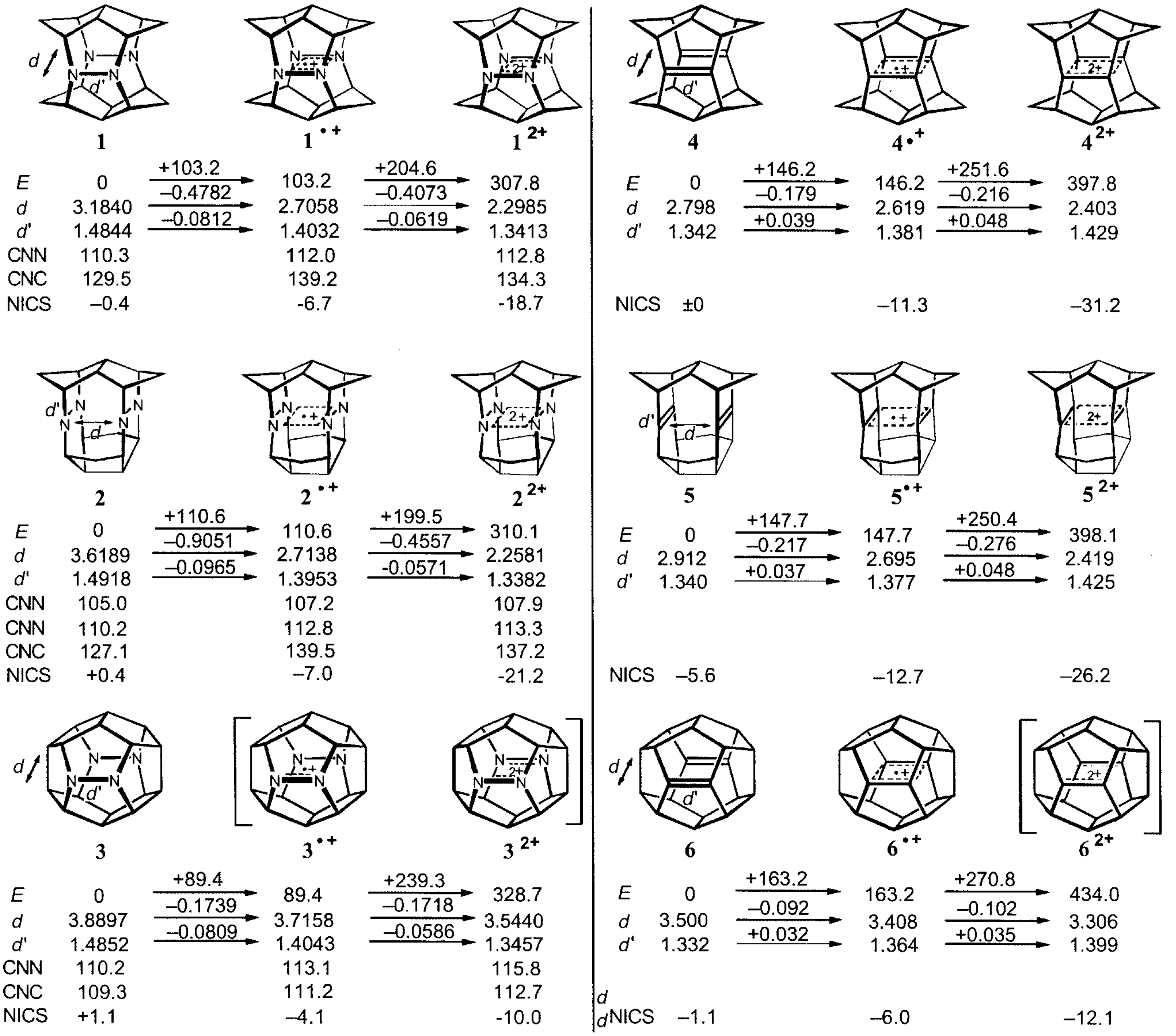
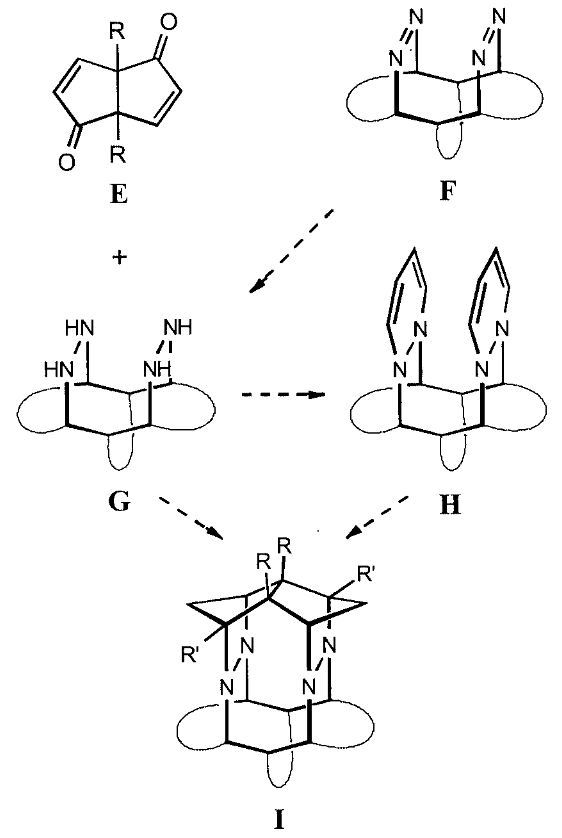


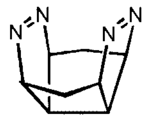
Figure 1. Calculated (B3LYP/6-31G*) structures, relative energies (*E*, kcal mol$^{-1}$), bond lengths (*d'*, Å), distances (*d*, Å), angles (°), and NICS values of the caged bishydrazines **1**–**3**, the derived 4N/7(6)e cations, the (iso)pagodadienes **4**(**5**), dodecahedradiene **6**, and the derived 4C/3(2)e cations.

### *Synthetic Concepts*

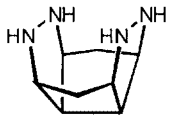
For structures as complex as the caged bishydrazines **1** and **2**, a one-pot assembly of two readily accessible parts such as the reaction of dienediones **E** with bishydrazines **G** to give tetraaza cages **I** appeared to be a tempting gamble even if the prospects of success seemed rather small. Still, parent hydrazine had added to diones **E** exclusively from the concave side (see Scheme 1 in ref.[6c]), and even small yields of **I** would have been welcomed. Alternative strategies had been closely patterned after the highly optimized protocols for (iso)pagodanes/dodecahedranes[31] and implied "face-to-face" bisdihydropyridazines **H** as central intermediates. When in explorative experiments with several of the available bisdiazenes **F** and with the derived bishydrazines **G**, "proximity" severely complicated if not prohibited even standard transformations; systematic experimentation was restricted to the most distant, most mobile, and also most readily accessible bisdiazene/bishydrazine **7**/**8**. The outcome along these two strategies can be shortly summarized.[8c,d] When bishydrazine **8** was smoothly added to parent dienedione **E** (R = H), at an understandably slower rate than parent hydrazine,[6,8c] even traces of the monomers (**I**, R' = OH) did not form (polymers instead). Twofold anellations of functionalized six-membered rings to **8** could be achieved but the ultimate transformation into the respective bisdihydropyridazines **H** (**17**, Schemes 3, 4) failed primarily due to adverse "proximity" effects. It was at this stage that we had to settle for more modest goals – the half-caged bis(*N*,*N'*-bicyclic)-bis-hydrazines **9** and **10** represent experimentally accessible "models" of **2**.



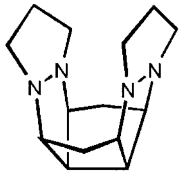
Scheme 1.



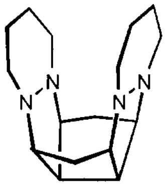
**7**



**8**



**9**



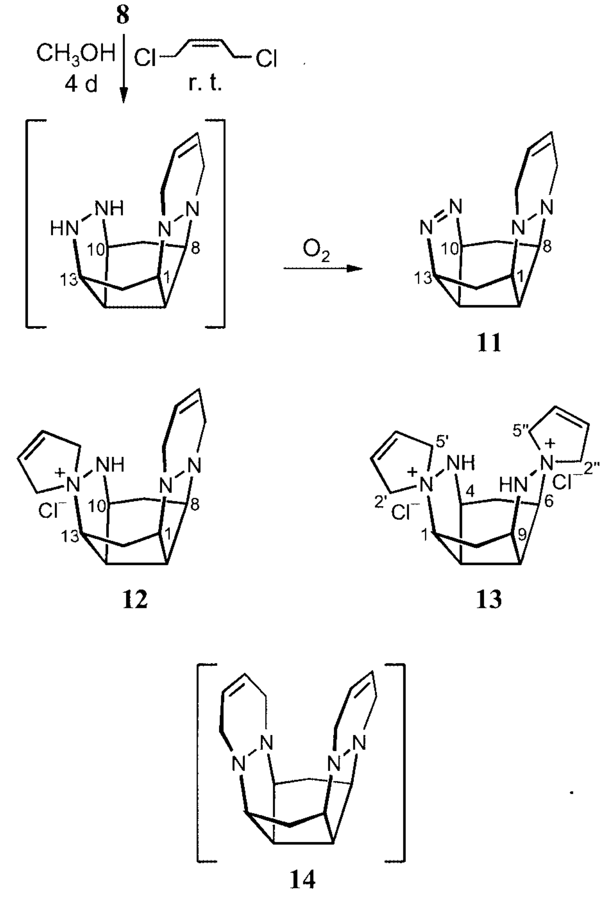
**10**

### Half-Caged, Proximate-Parallel bis(*N*,*N'*-bicyclic)-Bishydrazines (9, 10)

#### *Syntheses*

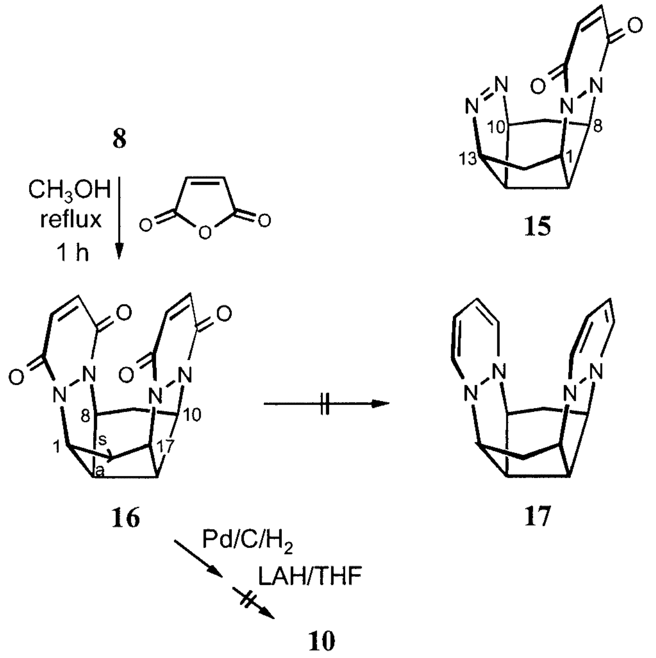
Waxy-solid, highly oxygen-sensitive bishydrazine **8** as starting material was nearly quantitatively accessible through controlled catalytic hydrogenation of bisdiazene **7**. N–N hydrogenolysis ensued only under forced conditions. The $^1$H- and $^{13}$C-NMR spectra ($CD_3OD$) display the (averaged) symmetry of **7** and, judging by the H/H coupling constants, a preference for similarly "closed" conformations.

For twofold 5-ring and even more for 6-ring anellations to **8** through *N*,*N'*-bridging dialkylation with 1,3-/1,4-difunctionalized alkanes, *N*,*N*-dialkylation was thought to be the major competing pathway.[32] Aiming at kinetic preferences needed for efficient twofold alkylation and ring closure, the behaviour of **8** to various bifunctional reagents was explored (e.g. 1,3-dibromo(dichloro)propane, 1,4-dibromo(dichloro)butane, epichlorohydrin,[33]DL-1,3-diepoxybutane,[34] succindialdehyde, *meso*-1,4-dibromo-2,3-butane-diol and its dimethyl acetal[35]). As it turned out, anellation, particularly the second one, was generally not as significant (if at all) as quarternization and polymerization.[8d,8i] Details are provided in the Experimental Section for the surprisingly neat reaction with *cis*-1,4-dichloro-but-2-ene,[36] which furnished nearly quantitatively monomeric products with **11** (up to 10%) and the water-soluble salts **12** (25%) and **13** (60%), but not even a trace of the desired **14**. For **11**, the NMR spectra exhibit $C_s$ symmetry (with presumably a *trans*-anellated tetrahydropyridazine ring[9b]), and for **13**, $C_2$ symmetry (Scheme 2).



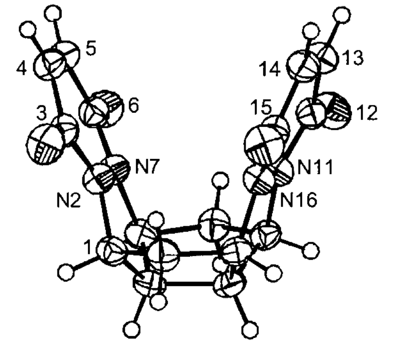
Scheme 2.

With the compact and rigid maleic anhydride as standard bisacylating reagent, 6-ring anellation faced no complication (Scheme 3). The slightly yellowish bis(tetrahydropyridazinedione) **16** deposited, nearly quantitatively, from a boiling methanolic solution of **8** and 2 equiv. reagent. Although **16** is practically insoluble in common organic solvents, it is readily soluble in water, aqueous methanol, organic, and inorganic acids. Incomplete exclusion of oxygen was manifested by the appearance of the monoanellated diazene **15**. However, no methods were found to convert **16** into bis(dihydropyridazine) **17** (cf. **H**, Scheme 1); the X-ray crystal structure (Figure 2)[37,38] helps to comprehend the many possibilities for neighboring-group complications. To minimize steric interactions, the conformation of the parent skeleton is slightly extended, the pyridazinedione rings are slightly tilted outwards, with a C=C/C=C distance of ca. 5 Å. The UV absorption band [$\lambda_{max}$, nm ($\varepsilon$) = 240 (2760), 339 (3390)] was practically that of the isolated chromophores, and cage formation through photo[2+2]cycloaddition was excluded. After hydrogenation of both C=C double bonds, fourfold C=O → $CH_2$ reduction to access target **10** was inhibited by transannular C–O–C bond formation.[39]



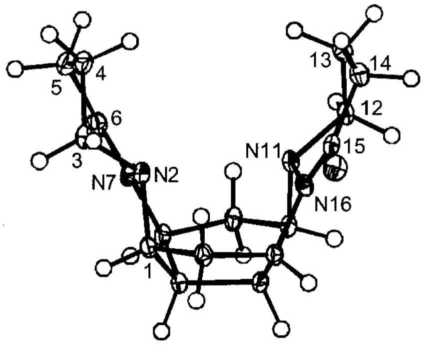
Scheme 3.

Methyl 3,4-epoxy-butanoate[40] (Scheme 4) offered the advantages that the rates of twofold *N*-alkylation (epoxide opening) and subsequent *N*-acylation differed significantly, and that higher alkylation was sterically retarded. With 2.2 equiv. reagent and $SiO_2$ as the weakly electrophilic catalyst, *anti*-(2,7)-dialkylated **18** was predominantly formed, and comparable amounts of polymers were also formed (traces of trisubstitution – NMR spectroscopy, TLC, MS). After concentration of the solution, the residue was heated in vacuo to 140 °C, which effected twofold cyclization to the three bis(hydroxyhexahydropyridazinone)s **19a** (*RR*:*SS*:*RS*, ca. 1:1:1), isolated in up to 36% yield. Occasionally the monoanellated diazenes **20** were minor byproducts. When the mixture of diols **19a** were bismesylated (73% **19b**), gentle elimination conditions (triethylamine, 60 °C, 2 d) neatly



**16**

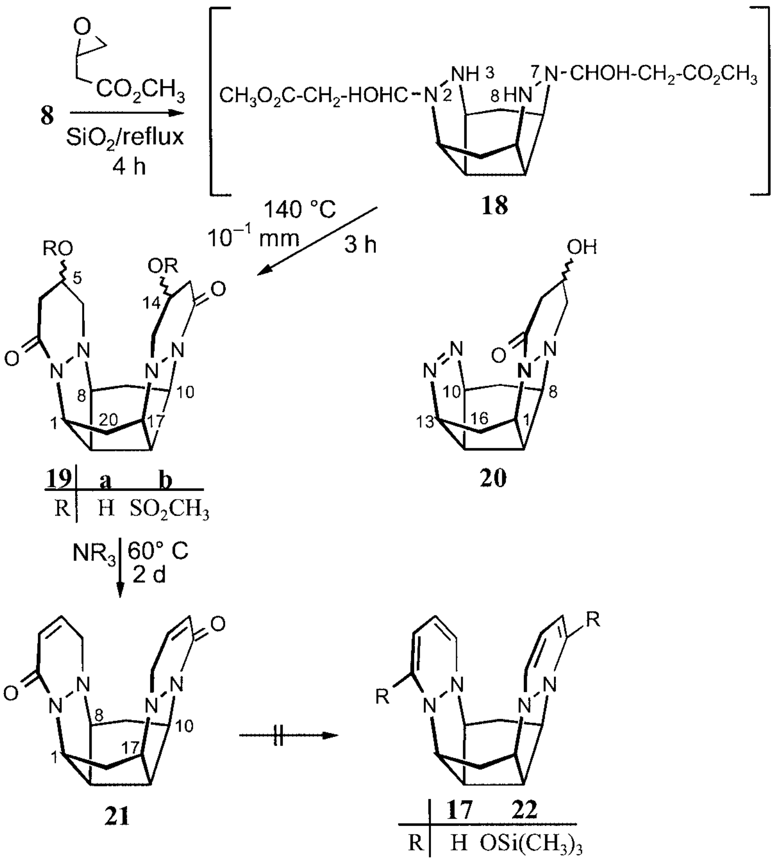
| | |
|---|---|
| N2-N7 (N11-N16) | 1.3973(15) |
| N2 ... N16 | 3.140(2) |
| N7 ... N11 | 3.206(2) |
| C3 ... C15 | 4.114(2) |
| C6 ... C12 | 4.253(2) |
| C4 ... C14 | 4.963(3) |
| C5 ... C13 | 5.059(3) |
| (C3,N2,N7,C6)/(C1,N2,N7,C8) | 10.81(9) |



**26a**

| | |
|---|---|
| N2-N7 (N11-N16) | 1.442(2) |
| N2 ... N16 | 3.1598(17) |
| N7 ... N11 | 3.1598(17) |
| N2 ... N11 | 2.971(2) |
| N7 ... N16 | 3.881(2) |

Figure 2. ORTEP plots of the X-ray structures of **16** and **26a**, selected bond lengths [Å], distances [Å], and angles [°].

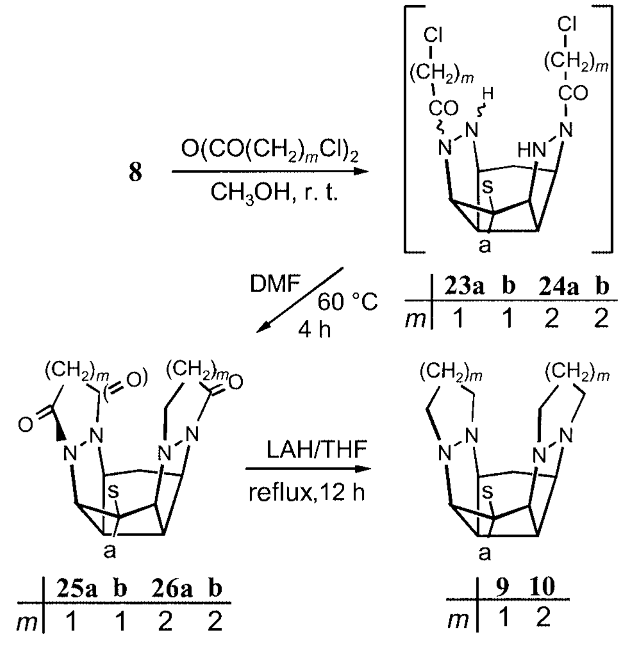


Scheme 4.

provided crystalline bis(tetrahydropyridazinone) **21**. As with **16**, attempts to transform **21** into **17** or its derivative **22** were not successful.

With 3-chloropropanoic and 4-chlorobutanoic anhydride (Scheme 5),[41] and notably not with the respective 3(4)-bromides, acylation and subsequent alkylation (cyclization) steps could be controlled well. To this end, **8** was treated in methanol at room temperature with 2 equiv. reagents, and the rapidly formed mixtures of mainly 2,7- and 3,7-bisamides (**23**, **24**, NMR, MS) were, after the change to DMF/NEt$_3$ as solvent, kept at 60 °C for two days (higher temperature favored intermolecular reactions). Mixtures of the $C_2$/$C_s$ symmetrical (NMR spectroscopy, room temperature) bis(imidazolidinones) **25a**,**b** (ca. 2:1)/bis(tetrahydropyridazinones) **26a**,**b** (ca. 3:1) were separated chromatographically in 76% and 84% yields, respectively, from polymers. For analytical purposes, individual, high-melting samples were secured chromatographically. For **26a**, a well-resolved X-ray structure was obtained at –140 °C (Figure 2)[37] – a "frozen" conformation of a rather closed skeleton. When subjected to reduction conditions (LAH/THF), mixtures of **25a**,**b** and **26a**,**b** delivered **9** and **10**, respectively, nearly quantitatively.

The waxy solids **9** (m.p. 77–80 °C) and **10** (m.p. 74–77 °C), in common with **8**, are highly sensitive to oxygen, decomposing on air within minutes (brown-reddish tar); however, they can be stored under nitrogen below –10 °C. The NMR spectra of **9** exhibit five $^{13}$C and eight $^{1}$H signals at room temperature; for **10**, $C_{2v}$ symmetry is averaged only at higher temperatures (ca. 140 °C). This stereodynamic difference, with particularly noticeable consequences for the 8(18)-Hs(a)/9(19)-Hs(a) chemical shifts, reflects the confor-



Scheme 5.

mational behavior of the known subunits, *cis*-fused, rapidly interconverting 1,5-diazabicyclo[3.3.0]octane (**27**) and *trans*-fused (*ee*), relatively rigid 1,5-diazabicyclo[4.3.0]nonane (**28**).[10a] For **9**, as lowest-energy conformations, B3LYP/6-31G* calculations (Figure 5) proposed an extended, somewhat distorted structure ($C_1$) with the *cis*-fused five-membered rings oriented inside/outside; for **10**, two comparably stable, extended forms ($C_s$, $C_2$) with *trans*-fused six-membered rings were proposed. The intensity of the [M$^+$] peak in the MS spectra attested to a remarkable stability of the respective radical cations. On the other hand, no [M$^{2+}$] signals of significant intensity were recorded.

### *One-/Two-Electron Oxidation*

For the cyclic voltammetric (CV) study with **9** and **10**, bis(*N*,*N'*-diethyl)-bishydrazine **35** (Scheme 6) and the bishydrazines **27**–**31** served as reference systems (Figure 3). Thanks primarily to the Nelsen group, the anodic behavior of these compounds and the structural and spectral properties of the respective (radical) cations were well documented.[9,10,12–14]

The CV measurements were generally carried out at different scan rates and temperatures.[42a] Representative cyclic voltammograms recorded for **9** and **10** are shown in Figure 4. Experimental voltammograms of **35** are presented as Supporting Information. For **9**, with its *cis*-anellated diazabicyclo[3.3.0]-subunits (cf. **27**), a first reversible oxidation step was expected. In the voltammograms recorded between 0.2 and 2.0 V s$^{-1}$ and 298 to 233 K, the first and the second electron transfer wave were, however, not resolved. At lower temperatures, the anodic waves were shifted to more positive and the cathodic waves to more negative potentials. Such behavior is indicative of a two-step $E_iE$ process with an electron transfer which is slow even at room temperature and with very similar oxidation potentials. The simulations[43] indeed resulted in practically equal oxidation potentials of $E_{1/2} \cong -0.03$ V ($\Delta E_{1/2}$ smaller than 100 mV) and equal activation enthalpies of $\Delta H^{\#} \cong 10 \pm 2$ kcal mol$^{-1}$; the oxidation potential is close to that of the bicyclic reference **27**. For **10**, with its *trans*-anellated diazabicyclo[4.3.0] subunits (cf. **28**) at 298 K and low scan rates (0.1–1 V), two reversible electron transfers were observed ($E_{1/2}{}^1 = -0.10$ V s$^{-1}$, $E_{1/2}{}^2 = +0.05$ V s$^{-1}$). At higher scan rates and

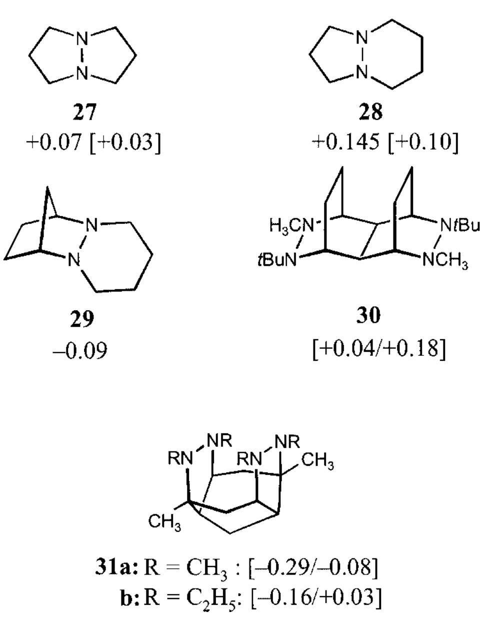


Figure 3. Oxidation potentials of reference compounds **27**–**31** {$E_{1/2}$, V s$^{-1}$, vs. Ag/AgCl [SCE], $CH_3CN$ (ACN), $CH_3(CH_2)_2CN$ (PrCN)}.

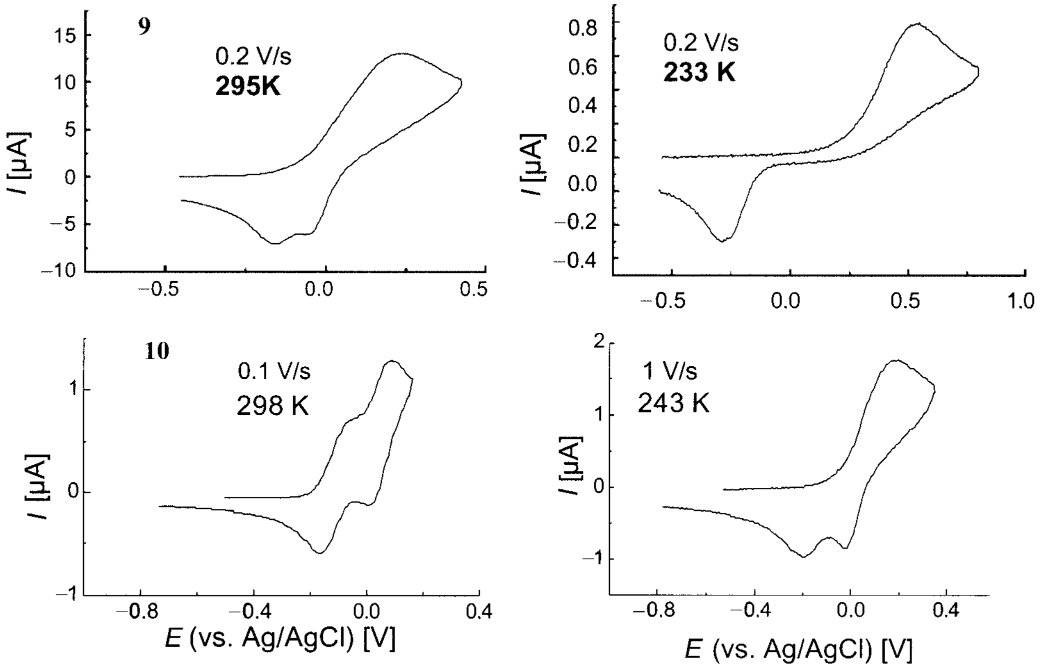


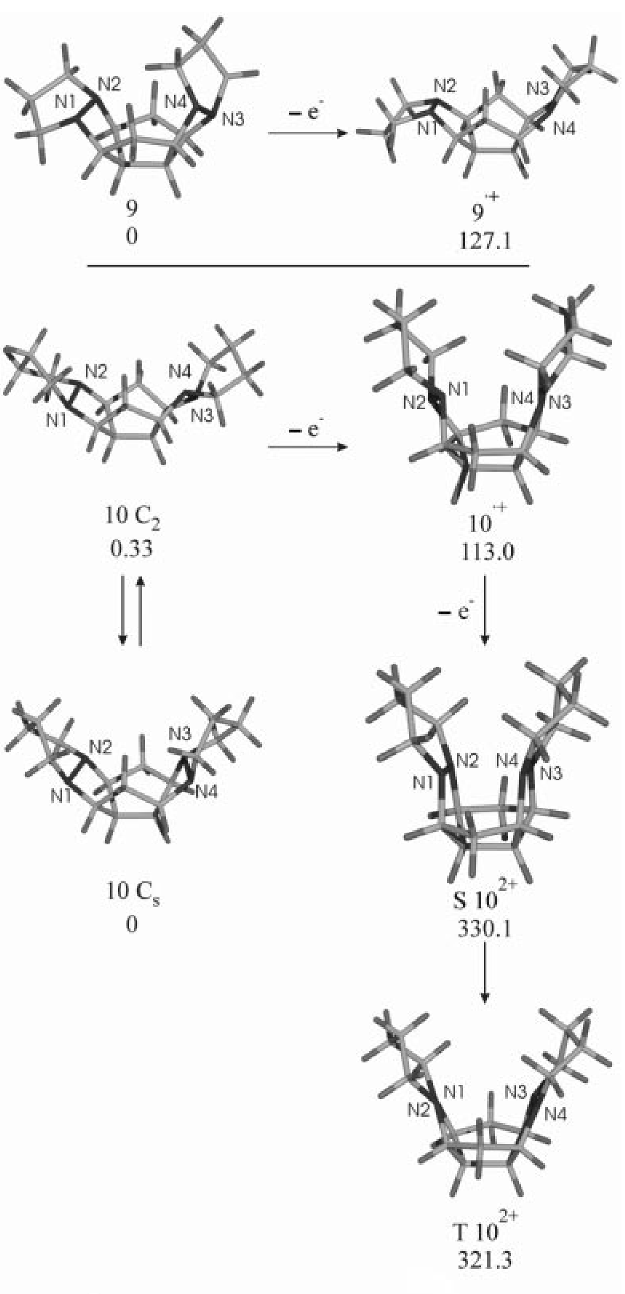
Figure 4. Exemplary cyclic voltammograms of **9** (PCN/TBAPF$_6$) and **10** (ACN/TBAPF$_6$).

lower temperatures, the first redox step coalesced with the second one. In this $E_iE$ process, the first oxidation is somewhat easier, the second slightly more difficult than for **9**; $\Delta E_{1/2}$ = 150 mV is close to $\Delta E_{1/2}$ = 140 mV for the "distant" bishydrazine **30** which had been attributed to the formation of a through-bond interacting bis(radical cation).[14a]$E_{1/2}{}^2$ and $\Delta E_{1/2}$ were practically independent of temperature and scan rate; this excludes the double oxidation of one hydrazine unit. The activation enthalpy for the first, slower step ($\Delta H^{\#1}$ = 8.3, $\Delta H^{\#2}$ = 4.9 kcal mol$^{-1}$) was comparable to that of **9**. As to the ease of the first oxidation, there is a better correspondence to tricyclic **29** than to bicyclic **28**. For **35**, with its sterically interacting pairs of vicinal *N*-ethyl groups (NMR spectroscopy), the low-scan-rate curves are similar in shape and temperature-dependence to those of **9**, yet simulation furnished two oxidation potentials ($E_{1/2}{}^1$ =–0.16 V, $E_{1/2}{}^2$ = –0.04 V), which are close to those of **10** and reference **31b**.[14b] In case of the radical cations **31a**$^{\cdot+}$ and **31b**$^{\cdot+}$, conformational differences (*cis*-closed versus *trans*-open) had been held responsible for the former's thermodynamic advantage of 0.13 V s$^{-1}$.[14] In contrast with **9** and **10**, the first electron transfer step was the faster one ($\Delta H^{\#1}$ = 5.2 kcal mol$^{-1}$, $\Delta H^{\#2}$ = 9.8 kcal mol$^{-1}$).

Only very preliminary PE[44] and ESR[45] data are available. For **10**, of the four ionization potentials – 6.97, 7.58, 9.28, 9.70 eV – the lowest one (IP$^1$ = 6.97 eV) is not far from IP$^1$ = 7.19 eV for **29**, and the differences IP$^3$ – IP$^1$ = 2.31 eV and IP$^4$ – IP$^2$ = 2.12 eV are indicative of a *trans* lone-pair orientation.[9,10] ESR spectra could be measured between –70 and +25 °C ($CH_2Cl_2/CF_3CO_2H$). Simulation of the high-temperature spectra shows two kinds of equivalent, strongly pyramidalized N-atoms [*g*-factor 2.0038 ± 0.0004, *a*(2N) ca. 2.1 mT], in line with spin localization on one hydrazine unit.[9,10,14] The low-temperature spectra could not be simulated in a satisfactory manner.

What are the lessons? (i) The radical cations and dications generated from **9**, **10** and **35** are long-livedon the time scale of the CV experiments. Localization of both charges on one hydrazine unit, a priori highly unlikely yet established for sesquibicyclic tetraalkylhydrazines inter alia by $\Delta E_{1/2}$ = 0.7–1.2 V,[9,10] is not compatible with the persistence of the dications and with the comparably small $\Delta E_{1/2}$ values. (ii) In *cis*-anellated **9**, as well as in **35**, the geometrical changes due to the first electron transfer have a smaller influence upon the second transfer than in *trans*-anellated **10** with its high barrier for conformational equilibration (NMR spectroscopy). (iii) As had been argued for **31a**,**b**,[14] the anodic behaviors of **9**, **10**, and **35** reflect primarily conformational differences and are not suggestive of significant stabilization of the respective radical cations and dications through charge delocalization between the two hydrazine units.

DFT calculations provide more details (Figure 5). Since the hypersurfaces of **9**, **10**, and of the respective radical cations and dications allowed the molecules to exist in a number of energetically very similar conformations, several plausible starting geometries with different symmetries ($C_1$, $C_2$, $C_s$) were chosen in each case and optimized using B3LYP/6-31G*. The loss of an electron from the energetically most favorable conformation of **9** ($C_1$) led to a $C_s$ symmetrical structure extended by ca. 0.4/0.5 Å, with the charge largely localized in the formerly inside-bicyclo[3.3.0]



| | 9 | $9^{\cdot+}$ | 10 $C_2$ | 10 $C_s$ | $10^{\cdot+}$ | S $10^{2+}$ | T $10^{2+}$ |
|---|---|---|---|---|---|---|---|
| N1–N2 | 1.453 | 1.486 | 1.487 | 1.486 | 1.478 | 1.345 | 1.345 |
| N3–N4 | 1.454 | 1.352 | 1.487 | 1.486 | 1.341 | 1.345 | 1.345 |
| N1___N4 | 4.232 | 4.658 | 4.722 | 4.802 | 3.132 | 2.470 | 3.487 |
| N2___N3 | 4.158 | 4.659 | 4.723 | 3.895 | 3.631 | 2.471 | 3.486 |
| N1___N3 | 4.891 | 4.869 | 5.240 | 4.572 | 3.175 | 2.809 | 3.526 |
| N2___N4 | 3.812 | 4.870 | 4.522 | 4.573 | 4.055 | 2.816 | 3.929 |

Figure 5. Calculated (B3LYP-6/31 G*) lowest-energy structures (the N numeration is arbitrary), energies [kcal mol$^{-1}$], selected bond lengths [Å] and distances [Å] of **9** and **10**, radical cations **9**$^{\cdot+}$ and **10**$^{\cdot+}$, and singlet/triplet dications **10**$^{2+}$.

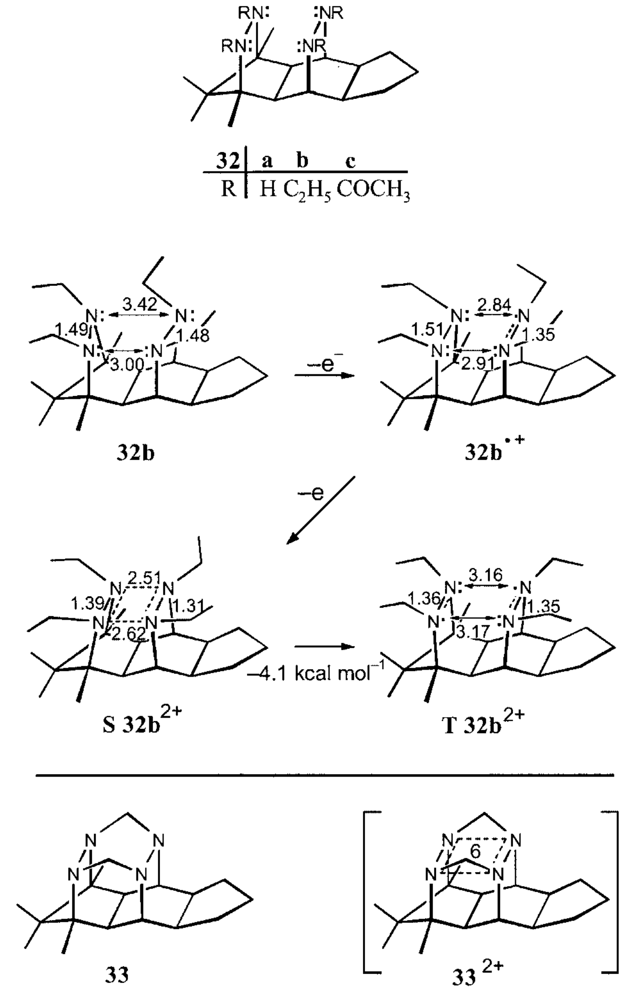


Figure 6. Selected calculated (B3LYP-6/31G*) bond lengths and distances [Å] of bishydrazine **32b,** radical cation $\mathbf{32b}^{\cdot+}$, and singlet/triplet dications $\mathbf{32b}^{2+}$.

subunit [$a_{\mathrm{N3(4)}}$ is about 1.3(2) mT, $a_{\mathrm{N1(2)}}$ is about 0.3 mT] and with geometrical consequences similar to that in the reference compound **27**[9,10] – shortening of the N3–N4 bond by ca. 0.1 Å and considerable flattening around the N3/N4 atoms. In contrast, loss of an electron from the two practically isoenergetic conformations of **10** causes significant tightening (by ca. 1.6/1.1 and ca. 1.7/0.3 Å, respectively). In line with charge localization comparable to $\mathbf{9}^{\cdot+}$, the N3–N4 bond is shortened (1.341 Å), pyramidalization for N3(4) reduced. Yet, even the shortest N···N distance in $\mathbf{10}^{\cdot+}$ (ca. 3.1 Å) is much larger than that in fully caged, cyclically delocalized $\mathbf{3}^{\cdot+}$ (ca. 2.7 Å, Figure 1). For dication $\mathbf{10}^{2+}$, the outcome was on first sight pleasing, in that within the singlet manifold, a closed structure [$d_{\mathrm{N1–N2(N3–N4)}}$ = 1.345 Å, $d_{\mathrm{N1\cdots N4(N2\cdots N3)}}$ = 2.470(1) Å] proved energetically favorable by ca. 10 kcal mol$^{-1}$ versus its extended, ground-state-like $C_2/C_s$ isomers. The lengths of the homoconjugate bonds between the quite coplanar N–N units (ca. 2.5 Å) are similar to those of $\mathbf{1}(\mathbf{2})^{2+}$ (ca. 2.3 Å) and $\mathbf{4}(\mathbf{5})^{2+}$ (ca. 2.4 Å, Figure 1). This presumably σ-bishomoaromatic singlet, however, relaxed to the significantly more extended($d_{\mathrm{N1\cdots N4(N2\cdots N3)}}$ is about 3.5 Å) and more stable (by ca. 10 kcal mol$^{-1}$) triplet. Clearly, if the two highest energy electrons of the 4N/6e$^{2+}$ system were forced to reside in the same orbital that has bonding character between the two N–N units, a cyclically delocalized singlet structure must result (cf. $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$). However, for S $\mathbf{10}^{2+}$, the gain in delocalization energy (σ-bishomoaromaticity, roughly 10 kcal mol$^{-1}$ based on the energies of the extended/tight conformations) could not sufficiently compensate for the implied charge–charge repulsion and conformational strain.[46]

Could a tighter and less mobile skeletal corset as, for example, that of the bis(*N*,*N*′-diethyl)-bishydrazine **32b** (Figure 6), derived from the most proximate and rigid bisdiazene available ($d_{\mathrm{N..N}}$ = 2.827 Å, $\omega$ = 174.2°),[6b] prohibit the singlet → triplet relaxation? According to calculations, oxidation has, in principle, the same consequences as for **10** – shortening of the N···N distances (by ca. 0.6/0.1 Å) for the radical cation $\mathbf{32b}^{\cdot+}$ (charge largely localized on the diazabicyclooctene part[47]), further shortening (by ca. 0.3/0.3 Å) for the singlet dication S $\mathbf{32b}^{2+}$, and relaxation into the triplet T $\mathbf{32b}^{2+}$. For S $\mathbf{32b}^{2+}$, the dimensions of the 4N core are practically that of S $\mathbf{10}^{2+}$, in line with cyclic in-plane electron delocalization. Compared to S $\mathbf{10}^{2+}$/T $\mathbf{10}^{2+}$, the less extended triplet was, however, only 4.1 kcal mol$^{-1}$ more stable than the singlet. The tighter half-cage of **32b** prohibited any experimental test. Synthesis of **32b** from **32c** in analogy to **35** (Scheme 6) did not prove to be possible; when forced, acetylation of bishydrazine **32a** ended in polymers.

In this context, the response of **33** (the above-cited[22b] semicaged perhydrotetrazine derivative of **32a**) to oxidation should be recalled. For its dication, CV measurements had attested to strong hydrazine–hydrazine interaction, according to the B3LYP/6-31G* calculations predominantly of the through-bond type. Still, a highly negative NICS value for a model dication (with –20.6 compared to –18.7/–21.2 for $\mathbf{1}^{2+}/\mathbf{2}^{2+}$) suggests additional cyclic through-space interactions ($\mathbf{33}^{2+}$).

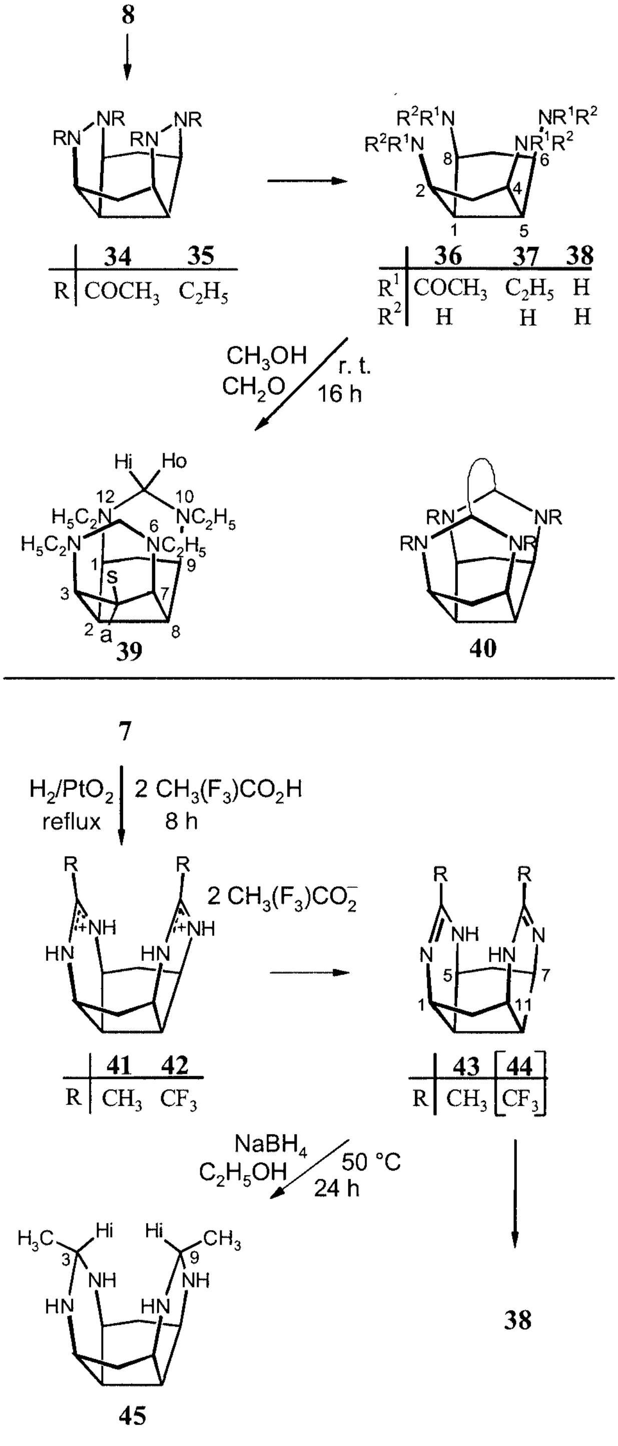
## Conclusions

It was in the context of our early interest in photochemical C=C/C=C cycloadditions as entry to synthetically versatile, high-energy cage compounds[48] that in-plane N=N/N=N interactions and their photochemical exploitation had become an opportune project. As long ago as 1982, the synthesis and PE analysis of a first, truly proximate-parallel bisdiazene/bishydrazine was presented,[49] and over the years, a pool of structurally modified planar-parallel bisdiazenes has been added.[6b,50] The photochemistry proved very disappointing, though, when even under seemingly very favorable circumstances, no [2+2] cycloaddition could be effected.[50] Still, photometathesis in variably N-oxidized derivatives suggested the existence of tetrazetidine *N*-oxides as short-lived [2+2] cycloadducts.[51] A major reward for the synthetic investment came with the transfer of electrons to these bisdiazenes, with the demonstration of σ-bishomoconjugation/σ-bishomoaromaticity in the form of the unique 4N/5e radical anions and 4N/6e dianions **B**.[6] The very recently determined crystal structures of $Na_4B_2$ aggregates, in good agreement with the calculations, visualize perfect in-plane delocalization.[52] The attempts to further improve our prior work, particularly the activities directed towards the tetraazacages **1**–**3** and the derived **C**-type 4N/7(6)e cations, were not nearly as rewarding. Thus, even the seemingly most promising of the synthetic routes abstracted in Scheme 1 (**G** → **H** → **I**) came to an early end [**16** (**21**) → **17**]. Still, experiments and calculations with the half-cages **9**, **10**, **32**, and **35**, deepened the understanding of the stereoelectronic and structural prerequisites that have to be met to make **C**-type 4N/7(6)e cations observable.[53] For the time being, the fully caged, (iso)pagodane-like radical cations/dications $\mathbf{1}^{\cdot+/2+}$ and $\mathbf{2}^{\cdot+/2+}$, with dodecahedrane-like $\mathbf{3}^{\cdot+/2+}$ as borderline cases, serve as representatives of these novel bonding motifs; they have to share their existence as "paper molecules" with prominent, in part structurally very close, examples of unusual bonding.[8n,8o,54,55]

## Appendix

Faced with some early failures in our quest for the bishydrazine cages **1**–**3** (Scheme 1), less risky utilizations of the available pool of proximate-parallel bisdiazenes[6c,41] were explored in the ballpark of preorganized, semi- and fully caged polyazapolycycles. Selected examples, in part closely patterned after the study of Mellor et al.,[56] are presented in the Schemes 6–9.

Scheme 6 traces our intention to build tetraaza cages such as **40** from bishydrazine **8** viathe all-cis-tetramines **37** (**38**), themselves versatile building blocks. When both the weakly strained **8** and **35** resisted even after protonation, very vigorous hydrogenolysis conditions [Pd/C(10%)/300 bar $H_2$/80 °C/30h][49] as well as several alternative procedures ($BH_3$-THF, Raney-Ni, $SnCl_2$/HCl or Al-Ni/KOH), N–N cleavage was attempted through electron/proton transfer to **34**. Fourfold acetylation of **8** was achieved at room temperature. Treatment of **34** with $Na/NH_3$ at –33 °C uniformly provided the all-*cis*-bicyclo[3.3.0]octane-2,4,6,8-tetrakis(acetamide) **36**. Forcing LAH reduction of **34** delivered waxy-solid **35** (95%, $C_{2v}$ in [D$_5$]pyridine at 80 °C), of **36**, the oily all-*cis*-tetrakis(ethylamine) **37** (83%). The highly unstable tetramines were stored as hydrochlorides, which deposited upon introduction of HCl gas into the ethanolic solutions. Somewhat surprising, and different from bishydrazine **8**, conformationally mobile tetramine **37** reacted with $CH_2O$ to give a single bisaminal (90%). NOE measurements [inter alia 5(11)-Hi versus 13(14)-Hs] unequivocally differentiated the 4,6,10,12-tetraaza[7.3.1.1$^{3,7}$.0$^{2,8}$]tetradecane structure **39** (with boatlike perhydropyrimidine rings) from the isomer arising from N2–N8/N4–N6 bridging. Yet, the scope of this reaction proved limited. With sterically more demanding reagents (acetaldehyde, benzaldehyde), the condensation needed catalytic assistance and generally ended in complex mixtures of monomers and polymers. Most disappointing was several attempts to build completely caged, admittedly highly strained skeletons of type **40** from **37** through condensation with bifunctional reagents such as glyoxal or 2,3-butanedione, which led exclusively to polymers.

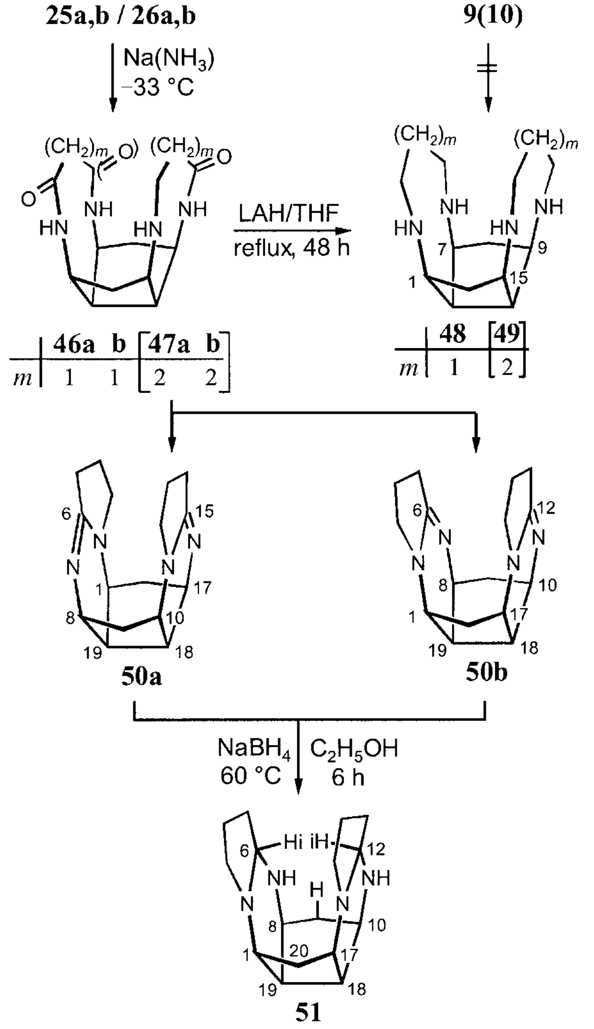


Scheme 6.

In contrast, NC2–NC8/NC4–NC6 bridging resulted when catalytic hydrogenation of bisdiazene **7** was pursued in boiling acetic acid. The nearly quantitatively obtained bisamidinium diacetate **41** was additionally characterized as a dichloride. Mildly basic conditions converted **41** into $C_2$-symmetrical bisamidine **43**, which, when searching for unambiguous structural proof, was reduced with $NaBH_4$. The NOE effects measured for the 3(9)-Hi-isomer **45**, the major isomer (41%) of the 1:1:2 mixture of the three isomers (oo, oi, ii), and chromatographically separated, confirmed the 2,4,8,10-tetraaza[9.2.1.0$^{5,13}$.0$^{7,12}$]tetradecane skeleton. Still in need of a useful protocol for the preparation of the parent tetramine **38**,[57,58] hydrolysis of the four amide groups of **36** had been found to be impractical, and its preparation through hydrolysis of the "activated" bis(trifluoroamidinium)-bistrifluoroacetate **42** was checked. Indeed, the latter, neatly available through hydrogenation of **7** in trifluoroacetic acid, was under forced conditions hydrolyzed to **38** (under reflux in aqueous KOH for 20 h, via **44**, 92%). The latter, which like **37** rapidly decomposed, was utilized as crude material of ca. 85% purity. There remain questions as to the detailed reaction course leading from **7** to **41** and **42**, especially since control experiments excluded bishydrazine **8** and the bispyrazoline arising from **7** in $CH_3CO_2H$ or $CF_3CO_2H$[6c] as intermediates.

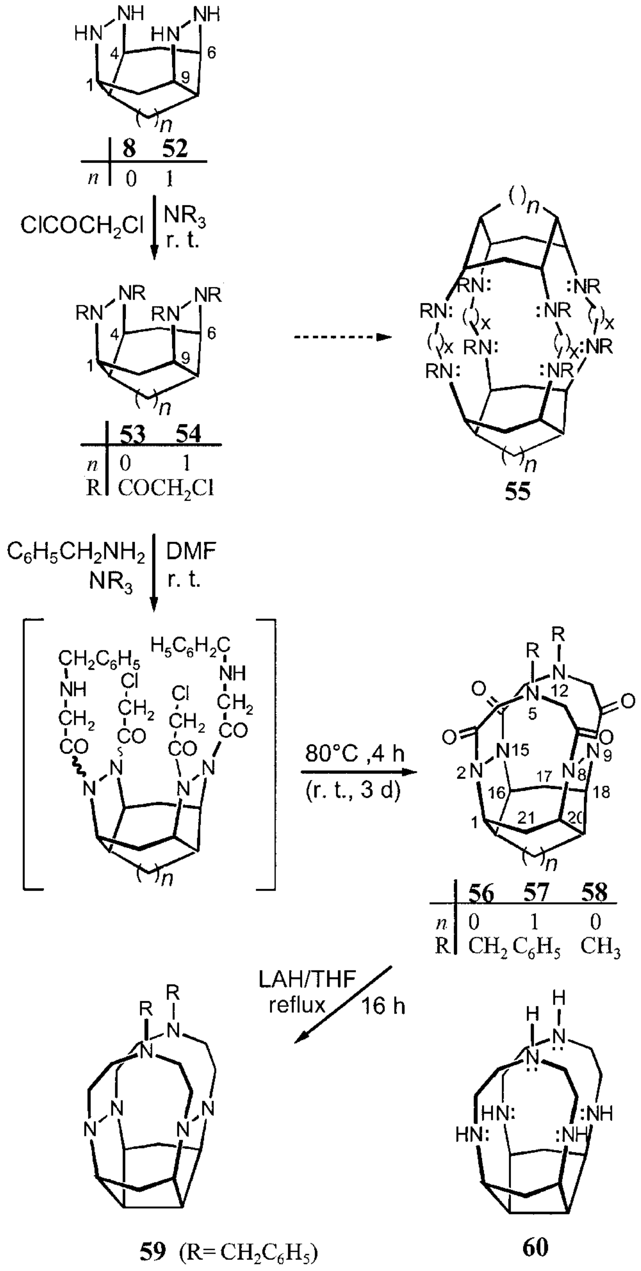
The half-caged tetramines **48** and **49** – doubly bridged 1,5,9(10),13(14)-tetraazacyclohexa(octa)decanes and, like **39**(**40**), potential precursors of **D**-type ions – were primary targets in Scheme 7. Since N–N hydrogenolysis in **9**(**10**) proved impossible, cleavage through electron/proton transfer to the monoacetylated N–N units in **25a**,**b** and **26a**,**b** was pursued. In practice, under conditions similar to the neat conversion **34** → **36**, the 1:1 mixture of 5-ring anellated **25a**,**b** delivered practically quantitatively **46a**,**b** (1:1), which was spectroscopically analyzed as a mixture and subjected as such to reduction. The common, oily and extremely oxygen-sensitive tetramine **48** (90%) was stabilized and analyzed as tetrakishydrochloride. The outcome with the individual 6-ring anellated **26a** and **26b** differed in that transannular cyclizations in intermediates such as **47a** and **47b** led uniformly to the bisamidines **50a** ($C_2$) and **50b** ($C_s$), respectively. Reduction with $NaBH_4$ proceeded, as in the case of **43**, non-stereospecifically. The main product (52%) in the reaction with **50b**, the crystalline, in solution $C_s$-symmetrical 6(12)-Hi isomer **51**, was separated and spectroscopically characterized.

For tetrakis(chloroacetamide) **53** and the less-mobile homologue **54** (Scheme 8), both nearly quantitatively produced under controlled conditions from the bishydrazines **8**/**52** and chloroacetylchloride/triethylamine, a considerable synthetic potential was seen, as, for example, for the possibly template-assisted construction of octaaza cages of type **55**. Highly oxygen-sensitive bishydrazine **52** had been quantitatively obtained, like **8**, through catalytic hydrogenation of the corresponding bisdiazene.[6b] In experiments directed at hexaaza cage **60**, the tetrakisamides **53** and **54** were treated with 2 equiv. benzylamine in dilute trimethylamine/DMF solution to give the transannularly bridged, in solution $C_{2v}$ symmetrical hexacycles **56** and **57**, respectively (72%, 76% besides polymers). This selectivity for transannular bridging, hence for ten- versus seven-membered ring formation, was found exceptional. Under similar conditions with methylamine only 10–15% of **58** was formed, besides polymers. Forcing LAH reduction of **56** provided the low-melting, air-sensitive 2,5,8,9,12,15-hexaazahexacyclo[14.5.1.0$^{2,15}$.0$^{8,20}$,0$^{9,18}$.0$^{19,22}$]docosane **59** nearly quantitatively. There were observations that **56**, under the conditions of the transformation **25a**,**b** → **48** (Na/$NH_3$; LAH/THF), allows access to target **60**. Could the tetra(hexa)aza skeletons **39**, **48**, and **59** serve as more or less rigid, specifically preorganized tetra(hexa)dentate ligands?[59] From anhydrous ethanolic solutions of **59**, after addition of $FeCl_3$, $CoCl_2$, or $Ni(ClO_4)_2$, a yellowish, a blueish, or a greenish solid, respectively, all with 1:1 composition (MS), deposited (82–94%).[60]



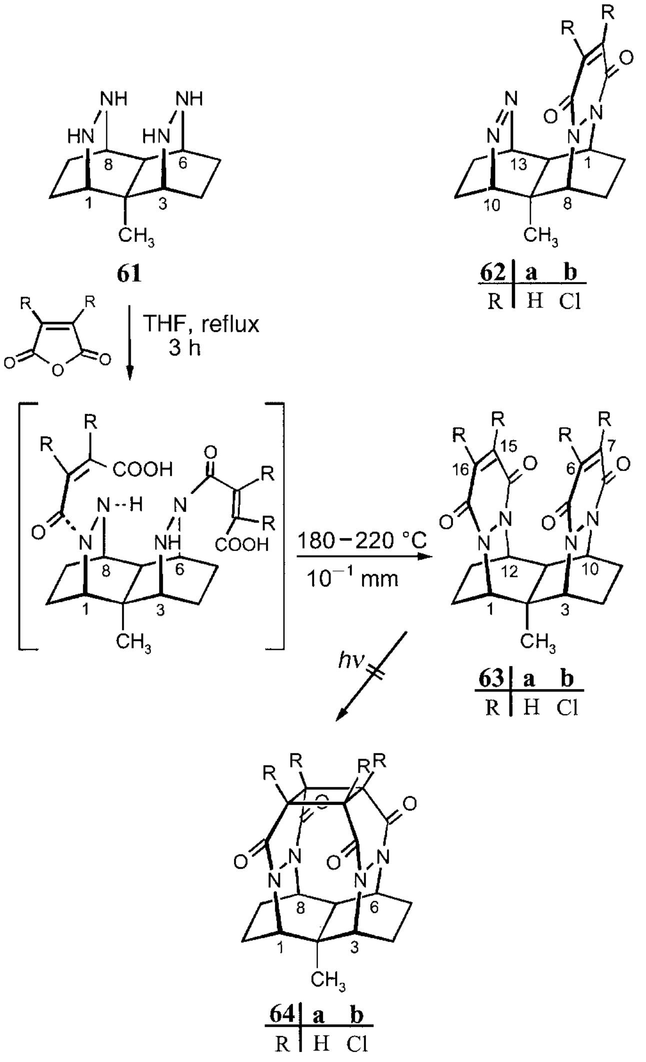
Scheme 7.

Better prospects for cage formation through photo[2+2] cycloaddition[61] could be expected for the corresponding derivatives of the more proximate and more rigid bishydrazine **61** (Scheme 9) than for the bis(dihydropyridazinedione) **16** (Scheme 3, Figure 2) and bis(tetrahydropyridazinone) **21**. Controlled twofold acylation with (dichloro)maleic an-



Scheme 8.

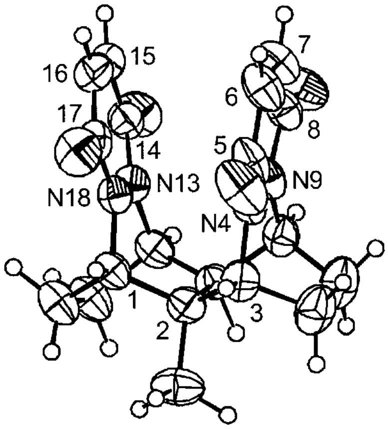
hydride, followed by heating to 180–220 °C under reduced pressure provided **63a**(**b**) in up to 80% yields. The monoanellated **62a**(**b**) were once again unavoidable side products. The crystal structure of **63a** (Figure 7)[37] discloses a slight distortion as consequence of $CH_2$/$CH_3$ steric compressions and presumably electronic C=O/C=O repulsions. In line with the skeletal rigidity, the N···N distances of 2.789/2.881 Å hardly differed from that of the parent bisdiazene (2.821/2.877 Å).[6c] Yet, with a distance of ca. 3.8 Å between the nearly coplanar C=C bonds, **63a** still constitutes a borderline case for photo[2+2]cycloaddition; the UV absorption suggests considerable (through-space?) interaction [$\lambda_{max}$, nm ($\varepsilon$) = 284 (2900), 361 (3250), compared with **16** (red-shifted by 38 nm)]. In practice, neither direct (monochromatic light, 254 nm; pyrex-filtered polychromatic light, $\lambda$ >280 nm) nor sensitized excitation (acetone, benzene[62]) notably caused formation of tetraaza cage **64** (too highly strained?[63])



Scheme 9.

## Experimental Section

**General Remarks:** Melting points were determined on a Monoskop IV (Fa. Bock) and are uncorrected. Elemental analyses were performed by the Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. IR spectra were measured with a Perkin–Elmer 457 or a Philips PU 9706, $^1$H NMR spectra with a Bruker AC 250, AM 400, and $^{13}$C NMR spectra with a Bruker AM 400 instrument. When necessary, assignments were confirmed by homo- and heteronuclear decoupling and by H,H- and H,X-correlation experiments. Chemical shifts are given relative to TMS ($\delta$ = 0 ppm), coupling constants in Hz; unless otherwise specified, the 250 MHz ($^1$H) and 100.6 MHz ($^{13}$C) spectra recorded in $CDCl_3$ are given; values marked with an asterisk are interchangeable. Mass spectra were recorded with a Finnigan MAT 44S spectrometer (EI, 70 eV, unless specified differently). All reactions with hydrazines and polyamines



**63a**

| | |
|---|---|
| N4-N9 | 1.408(2) |
| N13-N18 | 1.403(2) |
| N4 ... N18 | 2.789(2) |
| N9 ... N13 | 2.881(2) |
| C5 ... C17 | 3.331(3) |
| C8 ... C14 | 3.428(3) |
| C6 ... C16 | 3.727(4) |
| C7 ... C15 | 3.772(4) |
| (C5,N4,N9,C8)/(C3,N4,N9,C10) | 12.29(19) |
| (C14,N13,N18,C17)/(C12,N13,N18,C1) | 6.82(14) |

Figure 7. ORTEP plot of the X-ray structure of **63a**, selected bond lengths [Å], distances [Å], and angles [°].

were performed with careful exclusion of air. For TLC, silica gel plates 60 $F_{254}$ (Merck, Darmstadt) were used. The silica gel used for column chromatography was purchased from Merck (0.040–0.063 mm) or ICN, Biomedicals GmbH (0.032–0.063 mm).

The cyclic voltammetric measurements were performed in a cell developed by H. Kiesele.[42b] The cell contained an internal drying column with highly activated alumina, with a typical three-electrode-arrangement. A Pt disk (diameter 1 mm, area 0.785 $mm^2$) sealed in a soft glass rod was used as the working electrode, polished with diamond polishing paste (0.25 mm) and then rinsed thoroughly with ethanol and acetone. Pt and Ag wires were used as counter and quasireference electrodes, respectively. Potentials versus the Ag quasireference electrode were then rescaled by Ag/AgCl, calibrated with the ferrocene/ferrocenium redox couple (0.35 V vs. Ag/AgCl). An EG & G Potentiostat/Galvanostat Model 273 and a Kipp & Zonen Delft BV BD 92 recorder were used for electrochemical control and data recording. For digital simulations see ref.[43].

**2,3,7,8-Tetraazatetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodecane (8):** A solution of **7** (100 mg, 0.64 mmol) in $CH_3OH$ (20 mL) was stirred in the presence of $PtO_2$ (20 mg) under $H_2$ for 2 h (total conversion, single product, TLC). After filtration and concentration in vacuo, the extremely oxygen-sensitive solid was utilized without further purification. In air, **8** was rapidly oxidized back to **7**. $^1H$ NMR ($CD_3OD$): $\delta$ = 3.82 (m, 1-,4-,6-,9-H), 3.47 (m, 10-,11-H), 2.31 (dt, 5-,12-Ha), 2.06 (d, 5-,12-Hs) ppm; $J_{1,10(4,10;6,11;9,11)}$ = 5.6, $J_{1,11(4,11;6,10;9,10)}$ = $J_{1,12a(4,5a;5a,6;9,12a)}$ = 7.5, $J_{5a,5s(12a,12s)}$ = 15.8 Hz. $^{13}C$ NMR ($CD_3OD$): $\delta$ = 68.2 (C-1,-4,-6,-9), 59.2 (C-10,-11), 29.4 (C-5, -12) ppm. HRMS: $C_8H_{14}N_4$ calcd. 166.1218; found 166.1224.

With the use of Pd/C hydrogenation was impeded by complexation with **7**.

**2,7,11,12-Tetraazapentacyclo[11.2.1.$0^{2,7}$.$0^{8,15}$.$0^{10,14}$]hexadeca-4,11-diene (11), 2,7,11,12-Triaazapentayclo[11.2.1.$0^{2,7}$.$0^{8,15}$.$0^{10,14}$]hexadec-4-ene-11-spiropyrrolinium Chloride (12) and 3,8-Diazatetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodecane-2,7-bis(spiropyrrolinium chloride) (13):** A solution of **8** (281 mg, 1.71 mmol) in anhydrous $CH_3OH$ (30 mL) was added to a stirred mixture of *cis*-1,4-dichloro-but-2-ene and $Na_2CO_3$ (240 mg, 6.40 mmol). After 4 days, a second batch of $Na_2CO_3$ (240 mg, 6.40 mmol) was added to the now yellowish solution, and stirring was continued for 1 day (no further change in product composition, TLC, up to 10% **11**, 25% **12**, 60% **13**, $^1H$ NMR, [D4]methanol). After concentration in vacuo, the two main components were extracted with water (5 mL), and the residue (**11**) was filtered through silica gel ($CHCl_3$) and isolated as a waxy solid. Through repeated chromatography of the water-soluble material on neutral $Al_2O_3$ (nearly) pure **12** (ca. 90%) and **13** were secured. **11**: UV ($CH_3CN$): $\lambda_{max}$, nm ($\varepsilon$): = 323 (510). $^1H$ NMR (400 MHz): $\delta$ = 5.64 (t, 4-,5-H), 5.02 (m, 10-,13-H), 3.40 (m, 1-,8-H), 3.35 (dd, 3-,6-Ha), 3.32 (m, 14-H), 2.91 (dd, 3-,6-Hs), 2.82(m, 15-H), 2.73 (d, 9-,16-Hs), 2.22 (m, 9-,16-Ha) ppm; $J_{1,14(8,14)}$ = 0.4, $J_{1,15(8,15)}$ = 7.9, $J_{1,16a(8,9a)}$ = 6.9, $J_{1,16s(8,9s)}$ = 1.0, $J_{3a,3s(6a,6s)}$ = 11.1, $J_{9a,9s(16a,16s)}$ = 15.6, $J_{9a,10(13,16a)}$ = 9.3, $J_{10,16s(13,16s)}$ = 1.1, $J_{10,14((13,14)}$ = 8.1, $J_{14,15}$ = 9.8 Hz. $^{13}C$ NMR: $\delta$ = 123.2 (C-4,-5), 97.0 (C-10,-13), 68.7 (C-3,-6), 57.8 (C-1,-8), 49.1 (C-15), 46.0 (C-14), 34.6 (C-9,-16) ppm. MS: *m*/*z* (%) = 217 (5), 216 (30) [$M^+$], 121(78), 105 (31) [$M^+ - C_4H_6N_2 - N_2 - 1$], 91 (100), 54 (23) [$C_4H_6$]. HRMS: $C_{12}H_{16}N_4$ calcd. 216.1375; found 216.1360. **12**: $^1H$ NMR (400 MHz): $\delta$ = 7.20 (d, NH), 5.99 (s, 3′-,4′-H), 5.80 (d, 4-H), 5.78 (d, 5-H), 5.60 (m, 10-H), 5.18 (m, 2′-Ha), 5.12 (m, 5′-Ha), 4.45 (d, 5′-Hs), 4.06 (m, 13-H), 4.00 (m, 2′-H s), 3.84 (m, 1-H), 3.80 (m, 14-H), 3.60 (m, 8-,15-H), 3.40 (m, 3-,6-Ha), 3.18 (m, 3-,6-Hs), 2.60 (m, 8-,15-H), 2.20 (m, 16-H) ppm; $J_{6a,6s}$ = 16.5, $J_{8,15}$ = $J_{10,14}$ = 7.5, $J_{14,15}$ = 9.8, $J_{17a,17s}$ = 13.5, $J_{20a,20s}$ = 14.3 Hz. $^{13}C$ NMR: $\delta$ = 125.2 (C-4′), 123.8 (C-3′), 123.3 (C-4), 122.1 (C-5), 83.9 (C-10), 71.0 (C-5′), 70.7 (C-2′), 67.9 (C-3,-6), 64.9(C-14), 57.0 (C-15), 56.8 (C-8), 47.6 (C-13), 35.6 (C-1), 33.1 (C-9), 29. 8 (C-16) ppm. GC/MS: *m*/*z* (%) = 271 (48), 270 (10) [$M^+ - HCl$], 269 (42), 217(100) [$M^+ - C_4H_6 - HCl - 1$]. HRMS: ($C_{16}H_{23}ClN_4$)/$C_{16}H_{22}N_4$ calcd. 216.1375; found 216.1342. **13**: Colorless solid, m.p. 150 °C (dec.). $^1H$ NMR (400 MHz): $\delta$ = 6.10 (m, 4′-,4′′-H), 6.02 (m, 3′-,3′′-H), 4.93 (m, 1-, 6-H), 4.76 (m, 2′-,2′′-Ha), 4.68 (m, 5′,-5′′-Ha), 4.52 (m, 5′,-5′′-Hs), 4.48 (m, 2′-,2′′-Hs), 4.30 (m, 4-,9-H), 3.99 (m, 10-,11-H), 2.71 (m, 5-,12-Ha), 2.52 (m, 6-,12-Hs) ppm; $J_{1,10(6,11)}$ = 3.4, $J_{1,11((6,10)}$ = 6.8, $J_{1,12a(5a,6)}$ = 9.2, $J_{1,12s(5s,6)}$ = 2.3, $J_{4,5a(9,12a)}$ = 6.8, $J_{4,5s(9,12s)}$ = 1.5, $J_{4,10(9,11)}$ = 2.9, $J_{4,11(9,10)}$ = 5.5, $J_{5a,5s(12a,12s)}$ = 17.3 Hz. $^{13}C$ NMR: $\delta$ = 125.8 (C-4′,-4′′), 125.4 (C-3′,-3′′), 84.8 (C-1,-6), 73.3 (C-5′,-5′′), 67.8 (C-2′-2′′), 63.6 (C-4,-9), 58.0 (C-10,-11), 36.3 (C-5,-12) ppm. MS: *m*/*z* (%) = 271 (40), 270 (16) [$M^+ - 2\ HCl$], 118 (63) [$C_4H_7N_2Cl$], 80 (50) [$C_4H_4N_2$], 68 (100). HRMS: ($C_{16}H_{24}Cl_2N_4$)/$C_{16}H_{22}N_4$ calcd. 216.1375; found 216.1358.

**2,7,11,16-Tetraazahexacyclo[15.2.1.$0^{2,7}$.$0^{8,19}$.$0^{10,18}$.$0^{11,16}$]icosa-4,13-diene-3,6,12,15-tetrone (16):** A yellowish solution of **8** (166 mg, 1.00 mmol) and freshly sublimed maleic anhydride (220 mg, 2.20 mmol)) in anhydrous methanol (30 mL) were stirred at 50 °C.

After ca. 1 h, a uniform product had deposited (TLC, 316 mg, 96%), which was filtered and thoroughly washed with methanol. Colorless crystals ($H_2O$), m.p. >320 °C. Practically insoluble in organic solvents, **16** proved soluble in water and mineral acids. UV ($CHCl_3$): $\lambda_{max}$, nm ($\varepsilon$): 339 (3390), 240 (2760). IR (KBr): $\tilde{\nu}$ = 3042, 2930, 1848, 1707, 1671, 1636, 1562 cm$^{-1}$. $^1$H NMR (400 MHz, $D_2O$): $\delta$ = 6.97 (s, 4-,5-,13-,14-H), 5.07 (dd, 1-,8-,10-,17-H), 4.13 (18-,19-H), 3.74 (d, 9-,20-Hs), 2.52 (dt, 9-,20-Ha) ppm; $J_{1,19(8,19;10,18;17,18)}$ = 6.0, $J_{1,20a(8,9a;9a,10;17,20a)}$ = 5.5, $J_{1,20s(8,9s;9s,10;17,20s)}$ = 1.0, $J_{9s,9a(20s,20a)}$ = 15.8 Hz. $^{13}$C NMR ($D_2SO_4$): $\delta$ = 161.7 (C-3,-6,-12,-15), 138.4 (C-4,-5,-13,-14), 77.6 (C-1,-8,-10,-17), 55.8 (C-18,-19), 39.7 (C-9,-20) ppm. MS: *m*/*z* (%) = 326 (33) [M$^+$], 244 (10) [(M – COCH=CHCO)$^+$], 214 [(M – NCOCH=CHCON)$^+$], 106 (100) [(M – 2 NCOCH=CHCON)$^+$], 82 (35) [$C_4H_2O_2$]. $C_{16}H_{14}N_4O_4$ (326.3): calcd. C 58.89, H 4.32, N 11.17; found C 58.50, H 4.62, N 10.89. Crystals for an X-ray crystal structure analysis have been obtained from a concentrated aqueous solution. From reactions performed with even less than one equivalent of maleic anhydride, **16** still surfaced as the major product besides **15**.

**2,7,11,12-Tetraazapentacyclo[11.2.1.0$^{2,7}$.0$^{8,15}$.0$^{10,14}$]hexadeca-4,11-diene-3,6-dione (15):** Yellowish crystals, m.p. 275 °C (dec.). UV ($CHCl_3$): $\lambda_{max}$, nm ($\varepsilon$): 334 (2790), 241 (2690). IR (KBr): $\tilde{\nu}$ = 1724, 1638, 1564 cm$^{-1}$. $^1$H NMR: $\delta$ = 6.78 (s, 4-,5-H), 5.07 (dd, 10-,13-H), 4.66 (dd, 1-,8-H), 3.83 (d, 9-,16-Hs), 3.57 (dt, 15-H), 3.13 (dt, 14-H), 2.50 (m, 9-,16-Ha) ppm; $J_{1,15(8,15)}$ = 8.3 $J_{1,16a(8,9a)}$ = 6.0, $J_{9a,9s(16a,16s)}$ = 15.8; $J_{9a,10(13,16a)}$ = $J_{10,14(13,14)}$ = 7.5 Hz. $^{13}$C NMR: $\delta$ = 154.9 (C-3,-6), 145.6 (C-4,-5), 95.7 (C-10,-13), 64.3 (C-1,-8), 51.7 (C-15), 47.2 (C-14), 37.7 (C-9,-16) ppm. MS: *m*/*z* (%) = 244 (38) [M$^+$], 216 (160) [(M – $N_2$)$^+$], 135 (31) [(M – NCOCH=CHCON)$^+$], 82 (100) [$C_4H_2O_2$]. $C_{12}H_{12}N_4O_2$ (244.3): calcd. C 59.01, H 4.95, N 22.94; found C 58.79, H 4.62, N 22.59.

**5,14-Dihydroxy-2,7,11,16-tetraazahexacyclo[15.2.1.0$^{2,7}$.0$^{8,19}$.0$^{10,18}$.0$^{11,16}$]icosane-3,12-diones (19a):** Upon addition of silica gel (50 mg, ICN Silica 32–63, 60 Å) to a solution of **8** (200 mg, 1.20 mmol) and methyl 3,4-epoxybutanoate (306 mg, 2.64 mmol), two main products evolved slowly (TLC, $^1$H NMR). After refluxing for 4 h (total conversion of **8**), filtration and concentration in vacuo, the oily material (mainly **18**, $^1$H NMR, MS) was heated at 140 °C for 3 h in vacuo (10$^{-1}$ mm). Chromatography of the brownish oily residue ($SiO_2/CH_3OH/CHCl_3$, 1:5) afforded up to 160 mg (36%) of a ca. 1:1:1 mixture of the three diols besides polymers. $^1$H NMR (400 MHz, $CD_3OD$): $\delta$ = 4.8–4.7 (m, 1-,10-H), 4.15–4.05 (m, 5-,14-H), 3.3–3.2 (m, 6 H), 2.7–2.1 (m, 10 H) ppm. $^{13}$C NMR ($CD_3OD$): $\delta$ = 162.8, 161.9, 161.3, 72.7, 71.7, 69.4, 63.4, 63.2, 62.3, 61.6, 61.5, 60.1, 59.3, 56.8, 54.0, 53.6, 53.4, 39.0, 38.9, 38.8, 38.5, 38.1 ppm. MS: *m*/*z* (%) = 334 (73) [M$^+$], 333 (5), 317 (10), 316 (29) [(M – $H_2O$)$^+$], 315 (7), 298 (30) [(M – 2 $H_2O$)$^+$], 288 (16), 263 (28), 192 (21), 191 (28), 122 (40), 109 (44), 107 (29), 94 (57). HRMS: $C_{16}H_{22}N_4O_4$ calcd. 334.1641; found 334.1635. Small amounts of an occasionally isolated byproduct were identified as a ca. 1:1 mixture of **20** and **20′**.

**5-Hydroxy-2,7,11,12-tetraazapentacyclo[11.2.1.0$^{2,7}$.0$^{8,15}$.0$^{10,14}$]-hexadec-11-en-3-ones (20, 20′):** These compounds were separated chromatographically ($SiO_2$,$CHCl_3$/MeOH, 9:1) and crystallized ($CHCl_3$). **20**: Colorless crystals, m.p. 217–219 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3305 (OH), 1674 (C=O), 1447 (N=N) cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 5.0–5.1 (m, 10-,13-H), 4.67 (t, 1-H), 4.09 (br. s, 5-H), 3.31 (dd, 6-H), 3.28, (dd, 8-H), 3.26 (m, 15-H), 3.14 (d, 16-Hs), 2.93 (dd, 14-H), 2.90 (d, 9-Hs), 2.67 (m, 16-Ha), 2.46 (dd, 6-H′), 2.44, (m, 4-H), 2.14 (m, 9-Ha) ppm; $J_{1,15}$ = $J_{1,16a}$ = 7.5, $J_{4,4'}$ = 12.4, $J_{4,5}$ = 7.5, $J_{4',5}$ = 4.2, $J_{5,6}$ = 5.2, $J_{5,6'}$ = 3.6, $J_{6,6'}$ = 11.2, $J_{8,9a}$ = 7.5, $J_{8,15}$ = 4.5, $J_{9a,10}$ = 7.5, $J_{10,14}$ = 7.5, $J_{13,16a}$ = 7.5 Hz. $^{13}$C NMR: $\delta$ = 162.8 (C-3), 96.3 (C-13), 96.2 (C-10), 69.8 (C-8), 63.0 (C-5), 59.6 (C-1), 55.3 (C-6), 54.1 (C-15), 46.2 (C-14), 40.7 (C-16), 38.6 (C-4), 35.5 (C-9) ppm. MS: *m*/*z* (%) = 248 (100) [M$^+$], 153 (35), 138 (9), 135 (92). **20′**: Colorless crystals, m.p. 210–213 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3307 (OH), 1453 (N=N) cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 5.0–5.1 (m, 10-,13-H), 4.66 (t, 1-H), 4.02 (m, 5-H), 3.38(m, 6-H), 3.28 (m, 15-H), 3.14 (dd, 8-H), 2.94 (d, 16-Hs), 2.91 (dt, 14-H), 2.85 (d, 9-Hs), 2.69 (m, 16-Ha), 2.67 (m, 4-H), 2.27 (dd, 4′-H), 2.26 (t, 6′-H), 2.11 (m, 9-Ha) ppm; $J_{1,4'}$ <1, $J_{1,15}$ = 8.4, $J_{1,16a}$ = 7.5, $J_{1,16s}$ <1, $J_{4,4'}$ = 17.4, $J_{4,5}$ = 6.3, $J_{4',5}$ = 10.0, $J_{4,6}$ = 2.1, $J_{5,6}$ = 4.2, $J_{5,6'}$ = 10.5, $J_{6,6'}$ = 10.5, $J_{8,9a}$ = 4.5, $J_{8,15}$ = 7.5, $J_{9a,9s}$ = 15.0, $J_{9a,10}$ = 8.1, $J_{10,14}$ = $J_{13,14}$ = $J_{13,16a}$ = 7.5, $J_{13,16s}$ <0.5, $J_{14,15}$ = 10.5, $J_{16a,16s}$ = 15.7 Hz. $^{13}$C NMR: $\delta$ = 161.4 (C-3), 96.3 (C-10)*, 96.3 (C-13)*, 71.2 (C-8), 63.6 (C-5), 58.9 (C-1), 57.5 (C-6), 54.6 (C-15), 46.3 (C-14), 40.6 (C-16), 39.1 (C-4), 35.3 (C-9) ppm. MS (EI): *m*/*z* (%) = 248 (100) [M$^+$], 230 (12) [(M – $H_2O$)$^+$], 153 (23), 138 (10), 133 (6), 110 (13), 105 (12), 94 (21). HRMS: $C_{12}H_{16}N_4O_2$ calcd. 248.1273; found 248.1728.

**5,14-Bis(methylsulfonyloxy)-2,7,11,16-tetraazahexacyclo[15.2.1.0$^{2,7}$.0$^{8,19}$.0$^{10,18}$.0$^{11,16}$]icosane-3,12-diones (19b):** A solution of **19a** (100 mg, 0.30 mmol) and methanesulfonic anhydride (156 mg, 0.93 mmol) in pyridine (5 mL) was stirred for 48 h. After concentration in vacuo, the residue was dissolved in aqueous NaOH (10%, 5 mL), and the solution was extracted with $CHCl_3$ (8 × 5 mL). After standard chromatographical ($SiO_2$,$CHCl_3$/MeOH, 9:1) workup, colorless crystals (108 mg, 73%) were isolated (1:1 mixture). $^1$H NMR (400 MHz): $\delta$ = 5.09 (m, 1-,10-H), 4.68 (m, 5-,14-H), 3.6–3.3 (m, 6 H), 3.07 (s, 6 H), 3.02 (dd, 1 H), 2.79 (dd, 1 H), 2.6–2.5 (m, 6 H), 2.1–2.0 (m, 2 H) ppm. $^{13}$C NMR:$\delta$ = 164.4, 163.7, 159.5, 158.8, 73.9, 72.7, 71.6, 71.0, 61.7, 61.1, 53.6, 53.4, 38.9, 38.8, 38.5, 38.4, 36.1, 35.0 ppm. MS: *m*/*z* (%) = 394 (14) [(M – $CH_3SO_3H$)$^+$], 334 (7), 316 (4), 299 (8), 298 (12) [(M – 2 $CH_3SO_3H$)$^+$], 297 (10), 285 (5), 281 (11), 218 (7), 205 (9), 175 (10), 135 (12), 105 (23), 97 (10), 96 (100) $CH_3SO_3H$), 81 (41), 79 (74), 65 (18). MS [Fab (Nba)]: *m*/*z* (%) = 491 (71) [(M + 1)$^+$], 490 (52) [M$^+$]. HRMS: $C_{18}H_{26}N_4O_8S_2$ calcd. 490.1192; found 490.1184.

**2,7,11,16-Tetraazahexacyclo[15.2.1.0$^{2,7}$.0$^{8,19}$.0$^{10,18}$.0$^{11,16}$]icosa-4,13-diene-3,12-dione (21):** A suspension of **19b** (100 mg, 0.20 mmol) in dry triethylamine (5 mL) was stirred at 60 °C for 3 days. After concentration in vacuo, the solid uniform residue (TLC) was treated with aqueous NaOH (10%, 5 mL), and the residue was extracted with $CHCl_3$ (8 × 5 mL). After standard workup, filtration (silica gel, $CHCl_3/CH_3OH$, 5:1), and crystallization ($CHCl_3$), colorless crystals (55 mg, 92%) were collected. M.p. 287 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1760 (C=O) cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 6.42 (m, 5-,14-H), 5.87 (m, 4-,13-H), 4.71 (m, 1-,10-H), 3.60 (dd, 6-,15-H), 3.47 (m, 18-,19-H), 3.28 (dd, 8-,17-H), 3.13 (dt, 6-,15-H′), 2.69 (d, 9-,20-Hs), 1.96 (ddd, 9-,20-Ha) ppm; $J_{1,19(10,18)}$ = 7.0, $J_{1,20a(9a,10)}$ = 5.0, $J_{4,5(13,14)}$ = 9.9, $J_{5,6(14,15)}$ = 5.9, $J_{5,6'(14,15')}$ = 2.6, $J_{6',8(15',17)}$ = 2.7, $J_{6,6'(15,15')}$ = 15.0, $J_{8,9a(17,20a)}$ = 5.0, $J_{8,19(17,18)}$ = 2.9, $J_{9a,9s(20a,20s)}$ = 15.1 Hz. $^{13}$C NMR (400 MHz): $\delta$ = 161.0 (C-3,-12), 136.2 (C-5,-14), 124.7 (C-4,-13), 71.7 (C-8,-17), 62.0 (C-1,-10), 54.2 (C-18,-19), 51.5 (C-6,-15), 37.4 (C-9,-20) ppm. $C_{16}H_{18}N_4O_2$ (298.3): calcd. C 64.41, H 6.08, N 18.78; found C 64.10, H 5.82, N 18.60.

**2,6,10,14-Tetraazahexacyclo[13.2.1.0$^{2,6}$.0$^{7,17}$.0$^{9,16}$.0$^{10}$,$^{14}$]octadecane-3,11-/3,13-diones (25a,b):** A solution of **8** (100 mg, 0.62 mmol) and 3-chloropropanoic anhydride (275 mg, 1.34 mmol) in anhydrous methanol (30 mL) was stirred until total consumption of **8** and formation of two main products (TLC, ca. 3 h). After concentration in vacuo, the oily residue (two main components, TLC, **23a** and **23b**) was dissolved in dry DMF (30 mL), and triethylamine

(4 mL) was added. After stirring for 4 h at 60 °C and concentration in vacuo, the solid residue was chromatographed ($SiO_2$, $CHCl_3$/$CH_3OH$, 10:1) to give a 1.8:1 ($^1H$ NMR) mixture (129 mg, 76%) of crystalline **25a** and **25b**, separated by preparative TLC (silica gel, 6% $CH_3OH/CHCl_3$, 1:15, $R_f$ 0.28, 0.25). **25a**: M.p. 238–240 °C ($CHCl_3$, dec.). IR (KBr): $\tilde{\nu}$ = 1712 (C=O) $cm^{-1}$. $^1H$ NMR (400 MHz): $\delta$ = 4.67 (m, 1-,9-H), 3.68 (m, 5-,13-H), 3.50 (m, 7-,15-H), 3.10 (m, 16-,17-H), 2.82 (m, 4-,12-H), 2.68 (m, 5-,13-H′), 2.24 (d, 8-,18-Hs), 2.06 (m, 8-,18-Ha) ppm; $J_{1,17(9,16)} = 2.6$, $J_{1,18a(8a,9)} = 7.6$, $J_{4,5(12,13)} = 7.9$, $J_{4',5'(12',13')} = 7.9$, $J_{5,5'(13,13')} = 13.4$, $J_{7,8a(15,18a)} = 5.4$, $J_{7,17(15,16)} = 2.6$, $J_{8a,8s(18a,18s)} = 15.0$ Hz.- $^{13}C$ NMR ($CD_3OD$): $\delta$ = 169.2 (C-3,-11), 74.0 (C-7,15), 61.0 (C-1,-9), 60.1 (C-16,-17), 52.7 (C-5,-13), 40.0 (C-4,-12), 35.4 (C-8,-18) ppm. MS: *m/z* (%) = 275 (20) [$(M + 1)^+$], 274 (100) [$M^+$], 218 (9) [$(M - CH_2CH_2CO)^+$], 163 (29) [$(M - 2\ CH_2CH_2CO + 1)^+$]. **25b**: M.p. 224–227 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1724 (C=O) $cm^{-1}$.- $^1H$ NMR (400 MHz): $\delta$ = 4.65 (m, 1-,15-H), 3.74 (dt, 5-,11-H), 3.44 (dt, 16-,17-H), 3.34 (m, 7-,9-H), 2.98 (m, 5-,11-H′), 2.74 (d, 18-Hs), 2.66 (m, 4-,12-H), 2.16 (d, 8-Hs), 2.04 (dt, 18-Ha), 1.79 (dt, 8-Ha) ppm; $J_{1,18a(15,18a)} = 5.8$, $J_{1,17(15,16)} = 2.6$, $J_{4,5(11,12)} = J_{4',5'(11',12')} = 8.4$, $J_{5,5'(11,11')} = 11.2$, $J_{7,8a(8a,9)} = 6.3$, $J_{7,17(9,16)} = 2.6$, $J_{8a,8s} = 14.9$, $J_{18a,18s} = 15.4$ Hz. $^{13}C$ NMR: $\delta$ = 168.8 (C-3,-13), 74.9 (C-7,-9), 58.8 (C-1,-15), 58.6 (C-16,-17), 48.4 (C-5,-11), 38.3 (C-4,-12), 35.1 (C-18), 32.2 (C-8) ppm. MS: *m/z* (%) = 275 (19) [$(M + 1)^+$], 274 (100) [$M^+$], 218 (11) [$(M - CH_2CH_2CO)^+$], 163 (26) [$(M - 2\ CH_2CH_2CO + 1)^+$]. HRMS: $C_{14}H_{18}N_4O_2$ calcd. 274.1430; found 274.1437.

**2,7,11,16-Tetraazahexacyclo[15.2.1.0$^{2,7}$.0$^{8,19}$.0$^{10,18}$.0$^{11,16}$]icosane-3,12-/3,15-diones (26a,b):** Cf. **25a,b** with compound **8** (166 mg, 1.0 mmol)/4-chlorobutanoic anhydride (226 mg, 2.0 mmol)/$CH_3OH$ (80 mL). After concentration in vacuo, the oily residue (two main components, TLC, **24a** and **24b**) was dissolved in dry DMF (30 mL), and triethylamine (4 mL) was added. After stirring for 4 h at 60 °C and concentration in vacuo, the solid residue was chromatographed ($SiO_2$, $CHCl_3$/$CH_3OH$, 10:1). **26a**: Colorless crystals (181 mg, 60%), m.p. 223–225 °C ($CHCl_3$). $^1H$ NMR (400 MHz): $\delta$ = 4.79 (m, 1-,10-H), 3.32 (dt, 18-,19-H), 3.26–3.22 (m, 8-,17-,6-,15-H), 2.44 (d, 9-,20-Hs), 2.36–2.32 (m, 6 H, 6′-,15′-,4-,13-H), 2.01 (m, 9-,20-Ha), 1.90–1.76 (m, 4 H, 5-,14-H) ppm; $J_{1,19(10,18)} = 2.7$, $J_{1,20a(9a,10)} = 4.8$, $J_{4,5(13,14)} = 2.9$, $J_{5,6(14,15)} = 3.7$, $J_{6,6',15,15'} = 14.7$, $J_{8,9a(17,20a)} = 5.4$, $J_{8,19(17,18)} = 2.7$, $J_{9a,9s(20a,20s)} = 15.0$ Hz. $^{13}C$ NMR: $\delta$ = 162.7 (C-3,-12), 71.7 (C-8,-17), 61.5 (C-1,-10), 53.4 (C-18,-19), 51.2 (C-6,-15), 39.1 (C-9,-20), 29.4 (C-4,-13), 21.5 (C-5,-14) ppm. MS: *m/z* (%) = 303 (20) [$(M + 1)^+$], 302 (100) [$M^+$]. **26b**: Colorless crystals (72 mg, 24%), m.p. 214–216 °C ($CHCl_3$). $^1H$ NMR (400 MHz): $\delta$ = 4.82 (m, 1-,17-H), 3.43 (m, 8-,10-H), 3.3–3.2 (m, 6, 12-,18-,19-H), 2.80 (m, 20-Hs), 2.49 (m, 6′-,12′-H), 2.32 (m, 4-,14-H), 2.26 (dt, 20-Ha), 2.07 (d, 9-Hs), 1.92 (m, 5-,13-H), 1.81 (m, 9-Ha) ppm; $J_{1,20a(17,20a)} = 4.6$, $J_{1,19(17,18)} = 6.2$, $J_{5,6'(12',13)} = 2.4$, $J_{4,5(13,14)} = 2.9$, $J_{5,6,(12,13)} = 4.6$, $J_{6,6'(12,12')} = 14.5$, $J_{6,9s(12,9s)} = 1.1$, $J_{8,9a(9a,10)} = 6.2$, $J_{8,19(10,18)} = 2.7$, $J_{9a,9s} = 14.7$, $J_{20a,20s} = 15.3$ Hz. $^{13}C$ NMR: $\delta$ = 163.4 (C-3,-15), 74.2 (C-8,-10), 61.0 (C-1,-17), 53.3 (C-18,-19), 50.9 (C-6,-12), 41.0 (C-20), 35.3 (C-9), 29.3 (C-4,-14), 21.0 (C-5,-13) ppm. MS: *m/z* (%) = 303 (20) [$(M + 1)^+$], 302 (100) [$M^+$], 301 (80) [$(M - 1)^+$]. HRMS: $C_{16}H_{22}N_4O_2$ calcd. 302.1743; found 302.1744.

**2,6,10,14-Tetraazahexacyclo[13.2.1.0$^{2,6}$.0$^{7,17}$.0$^{9,16}$.0$^{10,14}$]octadecane (9):** A degassed suspension of **25a,b** (150 mg, 0.55 mmol) and LAH (167 mg, 4.40 mmol) in THF (10 mL) was refluxed for 12 h (one product, TLC). After concentration in vacuo and hydrolysis, it was extracted with $CH_2Cl_2$ (8 × 30 mL). After standard workup, the oily, highly oxygen-sensitive residue was filtered through silica gel {$NH_3$ (9%)/$H_2O$ (25%)/$CH_3OH$}; a waxy, oxygen-sensitive solid (135 mg, 97%) was isolated. M.p. 77–80 °C ($CHCl_3$). $^1H$ NMR ([$D_5$]pyridine): $\delta$ = 4.04 (m, 1-,7-,9-,15-H), 3.73 (m, 16-,17-H), 3.43 (m, 3-,5-,11-,13-H), 3.16 (m, 3′-,5′-,11′-,13′-H), 2.51 (dd, 8-,18-Hs), 2.28 (m, 4-,12-H, 8-,18-Ha), 1.99 (m, 4′-,12′-H) ppm; $J_{1,18s(7,8s;8s,9;15,18s)} = 9.5$, $J_{8a,8s(18a,18s)} = 15.9$ Hz. $^{13}C$ NMR ([$D_5$]pyridine): $\delta$ = 71.3 (C-1,-7,-9,-15), 58.0 (C-16,-17), 51.8 (C-3,-5,-11,-13), 38.4 (C-8,-18), 24.4 (C-4,-12) ppm. MS: *m/z* (%) = 247 (15) [$(M + 1)^+$], 246 (89) [$M^+$], 149 (100), 109 (27). HRMS: $C_{14}H_{22}N_4$ calcd. 246.1845; found 246.1851.

**2,7,11,16-Tetraazahexacyclo[15.2.1.0$^{2,7}$.0$^{8,19}$.0$^{10,18}$.0$^{11,16}$]icosane (10)*:*** Cf. **9** with compound **26a,b** (194 mg, 0.64 mmol)/LAH (730 mg, 19.2 mmol)/THF (20 mL)/12 h reflux. After workup and filtration, a colorless, oxygen-sensitive waxy solid (170 mg, 97%) was isolated. M.p. 74–77 °C ($CHCl_3$). $^1H$ NMR (400 MHz, $C_6D_5Br$, 140 °C): $\delta$ = 3.42 (m, 1-,8-,10-,17-H), 3.08 (m, 18-,19-H), 2.90 (m, 3-,6-,12-,15-H), 2.56 (m, 3-,6-,12-,15-H′), 2.41 (dt, 9-,20-Ha), 1.62 (dt, 9-,20-Hs), 1.59 (m, 4-,5-,13-,14-H); 1.48 (m, 4-,5-,13-,14-H′) ppm; $J_{1,20a(17,20a;8,9a;9a,10)} = 7.5$, $J_{1,20s(17,20s;8,9s;9s,10)} = 4.5$, $J_{1,19(8,19;10,18;17,18)} = 7.5$, $J_{1,18(8,18;10,19;17,19)} = 2.3$, $J_{9a,9s(20a,20s)} = 13.5$, $J_{3,3'(6,6';12,12';15,15')} = 10.5$, $J_{3,4(5,6;12,13;14,15)} = 3.0$, $J_{3,4'(5',6;12,13';14',15)} = J_{3',4(5',6';12',13;14,15')} = 4.5$, $J_{3',4'(5',6';12',13';14',15')} = 3.0$, $J_{4,4'(5,5';13,13';14,14')} = 9.5$ Hz. $^{13}C$ NMR ($C_6D_5Br$, 140 °C): $\delta$ = 72.3 (C-1,-8,-10,-17), 53.2 (C-18,-19), 52.1 (C-3,-6,-12,-15), 41.5 (C-9,-20), 24.7 (C-4,-5,-13,-14) ppm. $C_{16}H_{26}N_4$ (274.4): calcd. C 70.03, H 9.55, N 20.42; found C 69.61, H 9.62, N 20.89.

**2,3,7,8-Tetraacetyl-2,3,7,8-tetraazatetracyclo[7.2.1.0$^{4,11}$.0$^{6,10}$]dodecane (34):** Asolution of **8** (166 mg, 1.0 mmol) in acetic anhydride (4 mL) was stirred for 3 h (one product, TLC). After concentration in vacuo, the uniform solid (TLC) was filtered through silica gel ($CHCl_3$/$CH_3OH$, 5:1). Colorless crystals (296 mg, 98%) were isolated, m.p. 295–297 °C ($CHCl_3$). IR (KBr): $\tilde{\nu}$ = 1697 (C=O) $cm^{-1}$. $^1H$ NMR: $\delta$ = 4.86 (br.s, 1-,6-H)*, 4.30 (br. m, 4-,9-H)*, 3.20 (m, 10-,11-H), 2.83 (dt, 5-,12-Ha), 2.32 (br., 5-,12-Hs), 2.10 (s, 2 $CH_3$), 1.97 (s, 2 $CH_3$) ppm; $J_{1,12a(4,5a;5a,6;9,12a)} = 7.3$, $J_{5a,5s(12a,12s)} = 15.3$ Hz. $^{13}C$ NMR: $\delta$ = 174.5 (C=O), 66.3 (C-1,-4,-6,-9), 52.9 (C-10,-11), 36.8 (C-5,-12), 22.2 ($CH_3$) ppm. MS (CI, isobutane): *m/z* (%) = 336 (24), 335 (100) [$(M + 1)^+$], 334 (47) [$M^+$], 293 (51), 275 (37). $C_{16}H_{22}N_4O_4$ (334.4): calcd. C 57.47, H 6.63, N 16.76; found C 57.20, H 6.62, N 17.11.

**2,3,7,8-Tetraethyl-2,3,7,8-tetraazatetracyclo[7.2.1.0$^{4,11}$.0$^{6,10}$]dodecane (35):** A solution of **34** (100 mg, 0.30 mmol) and LAH (40 mg, 1.06 mmol) in THF (20 mL) was refluxed for 14 h. After standard workup, a colorless-waxy, air-sensitive solid (79 mg, 95%) was isolated, m.p. 42–44 °C ($CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3388, 2972, 2876, 2851, 1633, 1453, 1388, 1237 $cm^{-1}$. $^1H$ NMR (400 MHz, [$D_5$]pyridine, 80 °C): $\delta$ = 3.86 (m, 1-,4-,6-,9-H), 3.43 (m, 10-,11-H), 2.94 (m, 4 $CH_2$), 2.31 (dt, 5-,12-Hs), 2.14 (dt, 5-,12-Ha), 1.11 (t, 4 $CH_3$) ppm; $J_{1,12a(4,5a;5a,6;9,12a)} = 7.5$, $J_{1,12s(4,5s;5s,6;9,12s)} = 2.7$, $J_{1,11(4,11;6,10;9,10)} = 8.0$, $J_{5a,5s(12a,12s)} = 15.5$ Hz. $^1H$ NMR (400 MHz, $CF_3CO_2D$): $\delta$ = 4.46 (m, 1-,4-,6-,9-H), 3.96 (m, 10-,11-H), 3.42 (m, 4 $CH_2$), 2.62 (m, 5-,12-Ha, 5-,12-Hs), 1.43 (t, 4 $CH_3$) ppm.$^{13}C$ NMR ([$D_5$]pyridine, 80 °C): $\delta$ = 68.6 (C-1,-4,-6,-9), 53.7 (C-10,-11), 43.2 ($CH_2$), 33.6 (C-5,-12), 11.2 ($CH_3$) ppm.MS: *m/z* (%) = 278 (85) [$M^+$], 263 (26) [$(M - CH_3)^+$], 249 (89) [$(M - C_2H_5)^+$], 191 (40) [$(M - 3\ C_2H_5)^+$], 162 (72) [$(M - 4\ C_2H_5)^+$], 148 (34), 134 (100) [$(M - 4C_2H_5 - N_2)^+$]. UV ($CH_3OH$): $\lambda_{max}$, nm (lg $\varepsilon$) = 300 (2.9), 236 (3.3). $C_{16}H_{30}N_4$ (278.4): calcd. C 69.01, H 10.80, N 20.14; found: C68.58, H9.95, N 19.97.

Reduction of **34** (390 mg, 1.16 mmol) with $BH_3$/THF (20 mmol, room temp.) provided **35** (249 mg, 76%). Some material was lost, possibly because of N–N cleavage.

**2,4,6,8-Tetrakis(acetylamino)-bicyclo[3.3.0]octane (36):** In a 100-mL Schlenk tube, **34** (420 mg, 1.25 mmol) was dissolved in dry, liquid ammonia (30 mL). Sodium (171 mg, 7.5 mmol) was added in small portions over 1 h; stirring continued for 1 h. After addition of $NH_4Cl$ (300 mg), the mixture was warmed to room temperature. The crystalline residue was dissolved in methanol (5 mL), then filtered through silica gel (2-propanol/water). Colorless crystals (404 mg, 96%) were isolated; m.p. >280 °C ($CHCl_3$). IR(KBr): $\tilde{\nu}$ = 1752 (C=O) cm$^{-1}$. $^{1}$H NMR ($CD_3OD$): $\delta$ = 4.19 (m, 2-,4-,6-,8-H), 2.95 (dd, 1-,5-H), 2.21 (dd, 3-,7-Hs)*, 2.01 (dd, 3-,7-Ha)*, 1.99 (s, 4 $CH_3$) ppm; $J_{1,2(4,5;5,6;8,1)}$ = 7.2, $J_{2,3a(3a,4;6,7a;7a,8)}$ = 7.5, $J_{2,3s(3s,4;6,7s;7s,8)}$ = 5.1, $J_{3a,3s(7a,7s)}$ = 7.3 Hz. $^{13}$C NMR (400 MHz, $CD_3OD$): $\delta$ = 173.3 (CO), 60.7 (C-2,-4,-6,-8), 46.8 (C-1,-5), 38.4 (C-3,-7), 22.9 ($CH_3$) ppm. MS: *m*/*z* (%) = 338 (100) [M$^+$], 329 (29), 321 (19), 282 (21) [(M – $CH_3CON$)$^+$], 280 (14), 279 (58). HRMS: $C_{16}H_{26}N_4O_4$ calcd. 338.1954; found 338.1940.

**2,4,6,8-Tetrakis(ethylamino)-bicyclo[3.3.0]octane (37):** Cf. **35**, with compound **36** (306 mg, 0.90 mmol)/LAH (406 mg, 10.7 mmol)/THF (50 mL)/48 h reflux. Upon workup with filtration through silica gel (2-propanol/water/ammonia, 8:1:1), a yellowish, uniform (TLC), extremely oxygen-sensitive oil (210 mg, 83%) was isolated and used as such. IR: $\tilde{\nu}$ = 3230 (NH) cm$^{-1}$. $^{1}$H NMR (400 MHz): $\delta$ = 4.65 (br., 4 NH), 3.54 (m, 2-,4-,6-,8-H), 2.68 (m, 2 $CH_2$), 2.63 (dt, 1-,5-H), 2.56 (m, 2 $CH_2$), 1.92 (dt, 3-,7-Ha), 1.70 (dt, 3-,7-Hs), 1.11 (t, 4 $CH_3$) ppm; $J_{1,2(4,5;5,6;8,1)}$ = 7.5, $J_{2,3a(3a,4;6,7a;7a,8)}$ = 6.4, $J_{2,3s(3s,4;6,7s;7s,8)}$ <0.5, $J_{3a,3s(7a,7s)}$ = 12.3 Hz. $^{13}$C NMR: $\delta$ = 60.9 (C-2,-4,-6,-8), 46.9 (C-1,-5), 42.3 ($CH_2$), 37.4 (C-3,-7), 15.4 ($CH_3$) ppm. MS: *m*/*z* (%) = 282 (10) [M$^+$], 281 (6), 267 (10) [(M – $CH_3$)$^+$], 238 (25) [(M – $CH_2CH_3$ – $CH_3$)$^+$], 224 (3) [(M – 2 $CH_2CH_3$)$^+$], 197 (8), 195 (59) [(M – 3 $CH_2CH_3$)$^+$], 167 (30), 166 (12), 165 (13), 153 (35), 151 (20), 140 (25), 123 (29), 122 (100). HRMS: $C_{16}H_{34}N_4$ calcd. 282.2783; found 282.2790. **37**·HCl: A solution of **37** in ethanol (5 mL) was saturated with gaseous HCl, and the colorless, uniform precipitate was filtered. M.p. 248 °C. $^{13}$C NMR ($D_2O$): $\delta$ = 63.9 (C-2,-4,-6,-8), 52.8 ($CH_2$), 52.4 (C-1,-5), 40.7 (C-3,-7), 19.3 ($CH_3$) ppm.

**2,4,6,8-Tetraamino-bicyclo[3.3.0]octane (38):** A solution of **42** (165 mg, 0.50 mol) in aqueous KOH (30%, 5 mL) was refluxed for 20 h. After concentration in vacuo, the residue was extracted with $CHCl_3$ (8 × 5 mL), and the dried ($MgSO_4$) organic phase was concentrated in vacuo. The oily, extremely oxygen-sensitive residue (78 mg, 92%) consisted largely (>85%) of **38** and was utilized as such. $^{1}$H NMR ($CD_3OD$): $\delta$ = 3.74 (m, 2-,4-,6-,8-H), 2.65 (m, 1-,5-H), 2.03 (dt, 3-,7-Hs), 1.72 (dt, 3-,7-Ha) ppm; $J_{1,2(4,5;5,6;8,1)}$ = 2.3, $J_{2,3a(3a,4;6,7a;7a,8)}$ = 6.5, $J_{2,3s(3s,4;6,7s;7s,8)}$ = 6.3, $J_{3a,3s(7a,7s)}$ = 12.8 Hz. $^{13}$C NMR: $\delta$ = 54.4 (C-2,-4,-6,-8), 50.0 (C-1,-5), 43.6 (C-3,-7) ppm. MS: *m*/*z* (%) = 170 (14) [M$^+$], 169 (92), 168 (26), 153 (9), 137 (17), 119 (6), 104 (18), 89 (12), 77 (35). HRMS: $C_8H_{18}N_4$ calcd. 170.1531; found 170.1524.

**4,6,10,12-Tetraethyl-4,6,10,12-tetraazatetracyclo[7.3.1.1$^{3,7}$.0$^{2,8}$]tetradecane (39):** A solutionof **37** (112 mg, 0.40 mmol) and formaldehyde (24 mg, 0.80 mmol) in methanol (5 mL) was stirred for 16 h (single monomeric product, TLC). After concentration in vacuo, the oily uniform residue (TLC, 120 mg) was bulb-to-bulb distilled (104–120 °C, 10$^{-1}$ mm). A colorless uniform oil (110 mg, 90%) was isolated. IR: $\tilde{\nu}$ = 2978, 2947, 2854, 1380, 1078 cm$^{-1}$. $^{1}$H NMR (400 MHz): $\delta$ = 3.43 (d, 5-,11-Ho), 3.22 (d, 5-,11-Hi), 3.18 (m, 1-,3-,7-,9-H), 2.59 (dd, 2-,8-H), 2.55 (m, 2 $CH_2$), 2.46 (m, 2 $CH_2$), 1.82 (dt, 13-,14-Hs), 1.40 (dt, 13-,14-Ha), 1.02 (t, 4 $CH_3$) ppm; $J_{1,2(2,3;7,8;8,9)}$ = 6.1, $J_{1,13a(3,14a;7,14a;9,13a)}$ = 6.2, $J_{1,13s(3,14s;7,14s;9,13s)}$ = 2.0, $J_{5i,5o(11i,11o)}$ = 10.8, $J_{13a,13s(14a,14s)}$ = 12.1 Hz. $^{13}$C NMR ([$D_5$]pyridine): $\delta$ = 59.3 (C-5,-11), 58.5 (C-1,-3,-7,-9), 47.8 ($CH_2$), 35.8 (C-2,-8), 25.5 (C-13,-14), 12.8 ($CH_3$) ppm. MS: *m*/*z* (%) = 307 (7), 306 (32) [M$^+$], 277 (100) [(M – $C_2H_5$)$^+$], 261 (21), 248 (29) [(M – 2 $C_2H_5$)$^+$], 206 (55), 178 (80), 152 (96), 127 (30). HRMS: $C_{18}H_{34}N_4$ calcd. 306.2784; found 306.2788.

**3,9-Dimethyl-2,4,8,10-tetraazatetracyclo[9.2.1.0$^{5,13}$.0$^{7,12}$]tetradeca-2,8-dienylium Diacetate (41):** A suspension of **7** (162 mg, 1.0 mmol) and $PtO_2$ (10 mg) in acetic acid (2 mL) was refluxed under a hydrogen atmosphere for 8 h. After filtration and concentration in vacuo, the solid residue was dried in vacuo at 50 °C for 4 h (310 mg practically pure **41**) and utilized as such.$^{1}$H NMR:$\delta$ = 12.01 (br., 4 NH), 3.88 (m, 1-,5-,7-,11-H), 3.34 (m, 12-,13-H), 3.10 (d, 6-,14-Hs), 2.19 (s, 2 $CH_3$), 2.11 (dt, 6-,14-Ha), 2.00 (s, 2 $CH_3$) ppm; $J_{1,13(5,13;7,12;11,12)}$ = 7.3, $J_{1,14a(5,6a;6a,7;11,14a)}$ = 5.3, $J_{6a,6s(14a,14s)}$ = 14.5 Hz. $^{13}$C NMR: $\delta$= 178.4 (CO), 160.1 (C-3,-9), 48.7 (C-1,-5,-7,-11), 44.7 (C-12,-13), 40.7 (C-6,-14), 24.8 ($CH_3$), 18.6 ($CH_3$) ppm. $^{1}$H NMR ($CD_3OD$): $\delta$ = 4.02 (dt, 1-,5-,7-,11-H), 3.14 (m, 12-,13-H), 2.51 (dt, 6-,14-Hs), 2.21 (s, 2 $CH_3$), 1.91 (s, 2 $CH_3CO_2$ H), 1.86 (dt, 6-,14-Ha) ppm; $J_{1,13(5,13;7,12;11,12)}$ = 6.1, $J_{1,14a(5,6a;6a,7;11,14a)}$ = 9.5, $J_{1,14s(5,6s;6s,7;11,14s)}$ = 6.7, $J_{6a,6s(14a,14s)}$ = 14.5 Hz. **Dichloride**: HCl gas was bubbled through a solution of **41** (170 mg) in $CH_3OH$ (5 mL) at 0 °C with stirring for 10 min. After concentration in vacuo, the residue [colorless crystals(148 mg)] was dried in vacuo at 40 °C for 6 h. $^{1}$H NMR (400 MHz, $CD_3OD$): $\delta$ = 4.03 (dt, 1-,5-,7-,11-H), 3.14 (m, 12, 13-H), 2.58 (dt, 6-,14-Hs), 2.20 (s, 2 $CH_3$), 1.83 (dt, 6-,14-Ha) ppm; $J_{1,13(5,13;7,12;11,12)}$ = 6.2, $J_{1,14a(5,6a;6a,7;11,14a)}$ = 8.4, $J_{1,14s(5,6s;6s,7;11,14s)}$ = 6.7, $J_{6a,6s(14a,14s)}$ = 15.2 Hz. $^{13}$C NMR ($CD_3OD/D_2O$): $\delta$ = 160.6 (C-3,-9), 49.8 (C-1,-5,-7,-11), 41.6 (C-12,-13), 39.0 (C-6,-14), 19.1 ($CH_3$) ppm. $C_{12}H_{20}Cl_2N_4$: calcd. C 49.50, H 6.88, N 19.25; found C 49.09, H 7.04, N 18.84.

**3,9-Bis(trifluoromethyl)-2,4,8,10-tetraazatetracyclo[9.2.1.0$^{5,13}$.0$^{7,12}$]tetradeca-2,8-dienylium Bis(trifluoroacetate) (42):** Cf. **41** with compound **7** (162 mg, 1.0 mmol)/$PtO_2$ (10 mg)/$CF_3CO_2H$ (2 mL)/10 h reflux. After filtration and concentration, the highly hygroscopic material (ca. 300 mg) consisted of >90% **42** and was utilized as such. $^{1}$H NMR ($CD_3OD$): $\delta$ = 4.24 (br., 1-,5-,7-,11-H), 3.22 (br., 12-,13-H), 2.61 (br., 6-,14-Ha), 2.00 (br., 6-,14-Hs) ppm. $^{13}$C NMR ($CD_3OD$): $\delta$ = 164.3 ($CF_3CO_2$), 150.0 (C-3,-9), 119.3 ($CF_3CO_2$), 116.5 ($CF_3$), 51.1 (C-1,-5,-7,-11), 40.7 (C-12,-13), 39.2 (C-6,-14) ppm; $^{1}J_{C,F}$ = 279.1, $^{2}J_{C,F}$ = 39.0 Hz. MS (41): *m*/*z* (%) = 327 (8), 326 (100) [M$^+$], 325 (5), 257 (9) [(M – $CF_3$)$^+$], 164 (20), 163 (54), 149 (18), 137 (26), 69 (54) [$CF_3$].

**3,9-Dimethyl-2,4,8,10-tetraazatetracyclo[9.2.1.0$^{5,13}$.0$^{7,12}$]tetradeca-2,8-diene (43):** Asolution of **41** (160 mg, 0.50 mmol) and NaOH (40 mg, 1.0 mmol) in water (5 mL) was stirred at 5 °C for 30 min, then concentrated in vacuo. The solid residue was extracted with $CHCl_3$ (5 × 5 mL). After workup the colorless solid was crystallized from $CHCl_3$. The crystals (99 mg, 91%) were isolated, m.p. 176–179 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2937, 2873, 1678, 1652, 1431, 1016 cm$^{-1}$. $^{1}$H NMR (400 MHz, $CD_3OD$): $\delta$ = 3.75 (m, 1-,5-,7-,11-H), 2.52 (m, 12-,13-H), 2.42 (dt, 6-,14-Ha), 1.88 (s, 2 $CH_3$), 1.31 (m, 6-,14-Hs) ppm; $J_{1,13(5,13;7,12;11,12)}$ = 7.0, $J_{1,14a(5,6a;6a,7;11,14a)}$ = 6.4, $J_{6a,6s(14a,14s)}$ = 12.3 Hz. $^{13}$C NMR ($CD_3OD$): $\delta$ = 154.7 (C-3, -9), 52.3 (C-1,-5,-7,-11), 45.4 (C-6,-14), 38.6 (C-12,-13), 22.4 ($CH_3$) ppm. MS:*m*/*z* (%) = 218 (100) [M$^+$], 217 (12), 177 (19) [(M – $CH_3CN$)$^+$], 160 (12), 133 (25), 123 (5), 109 (62), 95 (22), 83 (30), 69 (18). $C_{12}H_{18}N_4$ (218.3): calcd. C 66.02, H 8.31, N 25.66; found C 65.79, H 8.52, N 25.32.

**3,9-Dimethyl-2,4,8,10-tetraazatetracyclo[9.2.1.0$^{5,13}$.0$^{7,12}$]tetradecane (45) and Stereoismers:** $NaBH_4$ (136 mg, 3.6 mmol) was added at 0 °C to a solution of **43** (130 mg, 0.60 mmol) in anhydrous ethanol (15 mL). After stirring at 50 °C for 24 h (three products, TLC) and evaporation in vacuo, the residue was filtered through $Al_2O_3$ (neutral, $CHCl_3/CH_3OH$, 30:1) giving a solid mixture of three isomers (135 mg, 1:1:2, $^1H$ NMR, MS). The major 3(9)-Hi-component was chromatographically separated ($Al_2O_3$, $CHCl_3/CH_3OH$, 30:1, $R_f$ = 0.27). A waxy solid (55 mg, 41%) was obtained, m.p. ca. 40 °C. $^1H$ NMR (400 MHz): $\delta$ = 3.55 (m, 1-,5-,7-,11-H), 3.37 (q, 3-,9-Hi), 2.81 (br., 4 NH)), 2.40 (m, 12-,13-H), 2.01 (dt, 6-,14-Hs), 1.93 (d, 6-,14-Ha), 1.14 (d, 2 $CH_3$) ppm; $J_{1,13(5,13;7,12;11,12)}$ = 6.7, $J_{1,14a(5,6a;6a,7;11,14a)}$ = 2.3, $J_{1,14s(5,6s;6s,7;11,14s)}$ = 4.5, $J_{3,CH3(9,CH3)}$ = 5.9, $J_{6a,6s(14a,14s)}$ = 13.7 Hz.- $^{13}C$ NMR: $\delta$ = 64.2 (C-3,-9), 55.5 (C-1,-5,-7,-11), 45.1 (C-12,-13), 44.9 (C-6,-14), 23.6 ($CH_3$) ppm. MS: *m*/*z* (%) = 223 (7), 222 (31) [$M^+$], 221 (30), 208 (10), 207 (45) [$(M - CH_3)^+$], 206 (9), 193 (13), 180 (7), 179 (88) [$(M - C_2H_5N)^+$], 164 (13), 163 (49) [$(M - C_2H_5N - CH_4)^+$], 151 (8), 150 (2), 137 (20), 136 (76) [$(M - 2\ C_2H_5N)^+$], 121 (36), 120 (100) [$(M - C_2H_6N_2 - C_2H_6N)^+$], 110 (7), 109 (19), 108 (39) [$(M - 2\ C_2H_5N_2)^+$], 94(81). HRMS: $C_{12}H_{22}N_4$ calcd. 222.1845; found 222.1835.

**2,6,10,14-Tetraazahexacyclo[13.2.1.0$^{7,17}$.0$^{9,16}$]octadecane-3,11/3,13-diones (46a,b):** Cf. **36** with compound **25a,b** (100 mg, 0.36 mmol)/liq. $NH_3$/(50 mL)/Na (50 mg, 2.17 mmol)/1.5 h reflux at –33 °C. After workup including filtration through silica gel ($CH_3OH$/aqueous $NH_3$), a ca. 1:1 mixture (97 mg, 96%) of solids **46a** and **46b** was isolated and utilized as such. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ = 4.18–4.05 (m, 2 H, **46a**: 1-,15-H; **46b**: 1-,9-H), 3.50–3.39 (m, 2 H, **46a**: 16-,17-H; **46b**: 16-,17-H), 3.26–3.15 (m, 6 H, **46a**: 7-,9-,5-,11-H; **46b**: 7-,15-,5-,13-H), 2.50–2.22 (m, 6 H, **46a**: 4-,12-H, 8-,18-Hs; **46b**: 4-,12-H, 8-,18-Hs), 2.05–1.84 (m, 2 H, **46a**: 8-,18-Ha, **46b**: 8-,18-Ha) ppm.$^{13}C$ NMR ($CD_3OD$): $\delta$ = 177.8, 177.3, 60.4, 60.3, 54.9, 54.7, 50.6, 49.4, 48.6, 48.4, 45.8, 44.2, 43.4, 36.6, 36.0 ppm. MS: *m*/*z* (%) = 279 (24), 278 (41) [$M^+$]. HRMS: $C_{14}H_{22}N_4O_2$ calcd. 278.1742; found 278.1730.

**2,6,10,14-Tetraazatetracyclo[13.2.1.0$^{7,17}$.0$^{9,16}$]octadecane (48):** Cf. **35** with compound **46a,b** (100 mg, 0.35 mmol)/LAH (110 mg, 2.89 mmol)/THF (5 mL)/48 h reflux. After workup, an extremely oxygen-sensitive oil (81 mg, 90%) was isolated. MS: *m*/*z* (%) = 252 (17), 251 (100), 250 (10) [$M^+$]. HRMS: $C_{14}H_{26}N_4$calcd. 250.2157; found 250.2160. From the solution in $CH_3OH$ (1 mL) saturated with HCl gas, **48**·4HCl deposited as colorless solid, m.p. 257–263 °C ($CHCl_3$, dec.). $^1H$ NMR (400 MHz, $D_2O$): $\delta$ = 3.79 (m, 1-,7-,9-,15-H), 3.48 (m, 3-,5-,10-,13-H), 3.30 (dd, 3-,5-,10-,13-H′), 3.15 (m, 16-,17-H), 2.34 (d, 8-,18-Hs), 2.32 (m, 4-,12-H), 2.20 (m, 4-,12-H′), 1.70 (dt, 8-,18-Ha) ppm; $J_{1,18a(7,8a;8a,9;15,18a)}$ = 4.8, $J_{1,17(7,17;9,16;15,16)}$ = 6.7, $J_{3,4'(4',5;11,12;12',13)}$ = 4.8, $J_{3,4(4,5;11,12;12,13)}$ = 4.6, $J_{3,3'(5,5;11,11';13,13')}$ = 13.1, $J_{3',4(4,5';11',12;12,13')}$ = 5.4, $J_{3',4'(4',5';11',12';12',13')}$ = 4.4, $J_{8a,8s(18a,18s)}$ = 15.4 Hz. $^{13}C$ NMR ($D_2O$): $\delta$ = 57.9 (C-1,-7,-9,-15), 52.4 (C-3,-5,-11,-13), 38.5 (C-16,-17), 32,8 (C-8,-18), 128.4 (C-4,-12) ppm. $C_{14}H_{26}Cl_4N_4$ (392.2): calcd. C 42.87, H 6.68; found C 42.50, H 6.49.

**2,7,11,16-Tetraazahexacyclo[15.2.1.0$^{2,6}$.0$^{8,19}$.0$^{10,18}$.0$^{11,15}$]icosa-6,15-diene (50a):** Cf. **48** with compound **26a** (50 mg, 0.17 mmol)/liq. $NH_3$ (25 mL)/Na(23 mg, 1.0 mmol)/1.5 h reflux at –33 °C. After workup and crystallization ($CHCl_3$), colorless crystals (42 mg, 94%) were isolated. M.p. 182–186 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1685 (C=N) cm$^{-1}$. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ = 4.1 (m, 8-,17-H), 4.15 (m, 1-,10-H), 3.92 (m, 3-,12-H), 3.69 (m, 3-,12-H′), 3.23 (m, 18-,19-H), 2.97 (dd, 4 H, 5-,14-H), 2.67 (dt, 9-,20-Hs), 2.22 (m, 4 H, 4-,13-H), 1.90 (dt, 9-,20-Ha) ppm; $J_{1,20a(9a,10)} = J_{8,9a(17,20a)}$ = 10.4, $J_{1,20s(9s,10)} = J_{8,9s(17,20s)}$ = 6.6, $J_{3,3'(12,12')}$ = 10.2, $J_{3,4'(12,13')}$ = 7.7, $J_{3,4(12,13)}$ = 6.5, $J_{3',4(12,13')}$ = 8.0, $J_{3',4'(12',13')}$ = 6.7, $J_{9a,9s(20a,20s)}$ = 12.9 Hz. $^{13}C$ NMR ($CD_3OD$): $\delta$ = 164.5 (C-6,-15), 54.5 (C-8,-17), 54.4 (C-3,-12), 50.7 (C-1,-10), 40.5 (C-18,-19), 39.4 (C-9,-20), 31.7 (C-5,-14), 19.5 (C-4,-13) ppm. MS: *m*/*z* (%) = 271 (11), 270 (55) [$M^+$], 269 (13), 189 (12), 188 (15), 136 (10), 135 (26), 134 (12), 122 (11), 121 (33), 109 (15), 84 (100).HRMS: $C_{16}H_{22}N_4$ calcd. 270.1844; found 270.1864.

**2,7,11,16-Tetraazahexacyclo[15.2.1.0$^{2,6}$.0$^{8,19}$.0$^{10,18}$.0$^{12,16}$]icosa-6,11-diene (50b):** Cf. **50a**with compound **26b** (100 mg, 0.34 mmol)/liq. $NH_3$(50 mL)/Na(46 mg, 2.0 mmol)/1.5 h reflux at –33 °C. After workup, colorless crystals (82 mg, 92%) were isolated, m.p. 178–182 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1685 (C=N) cm$^{-1}$. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ = 4.1 (m, 8-,10-H), 4.2 (m, 1-,17-H), 3.88 (m, 3-,15-H), 3.72 (m, 3-,15-H′), 3.17 (m, 18-,19-H), 2.97 (m, 4 H, 5-,13-H), 2.89 (dt, 9-Hs), 2.54 (dt, 20-Hs), 2.21 (m, 4 H, 4-,14-H), 1.76 (dd, 9-Ha), 1.74 (dd, 20-Ha) ppm; $J_{1,19(17,18)}$ = 5.4, $J_{1,20a(17,20a)}$ = 6.9, $J_{1,20s(17,20s)}$ = 5.9, $J_{3,4'(14',15)}$ = 4.3, $J_{3',4(14,15')}$ = 6.7, $J_{4,4'(14,14')}$ = 14.5, $J_{8,9a(9a,10)}$ = 7.1, $J_{8,9s(9s,10)}$ = 6.7, $J_{9a,9s=}$ 12.6, $J_{20a,20s}$ = 12.3 Hz. $^{13}C$ NMR ($CD_3OD$): $\delta$ = 164.6 (C-6,-12), 54.6 (C-3,-15), 54.3 (C-8,-10), 50.7 (C-1,-17), 41.4 (C-5.-13), 39.5 (C-18,-19), 37.4(C-9), 31.5 (C-20), 19.5 (C-4,-14) ppm. MS: *m*/*z* (%) = 271 (32), 270 (98) [$M^+$], 269 (29), 188 (22), 162 (100), 111 (64), 84 (69). HRMS: $C_{16}H_{22}N_4$ calcd. 270.1844; found 270.1838.

**2,7,11,16-Tetraazahexacyclo[15.2.1.0$^{2,6}$.0$^{8,19}$.0$^{10,18}$.0$^{12,16}$]icosane (51):** Cf. **45** with compound **50a,b** (54 mg, 0.30 mmol)/$NaBH_4$ (15 mg, 0.4 mmol)/ethanol (5 mL)/0 °C/stirring at 60 °C/6 h. After workup, the solid mixture of at least three components (TLC) was chromatographed ($Al_2O_3$, $CHCl_3/CH_3OH$, 30:1); the major component ($R_f$ = 0.35) was isolated and crystallized. Colorless crystals (28 mg, 52%) were obtained, m.p. 154–158 °C ($CHCl_3$, dec.). $^1H$ NMR (400 MHz): $\delta$ = 3.81 (t, 6-,12-H), 3.54 (m, 1-,17-H), 3.46 (m, 8-,10-H), 2.96 (dt, 3-,15-H), 2.60 (dt, 3-,15-H′), 2.42 (m, 18-,19-H), 2.11 (d, 20-Hs), 2.08 (m, 4 H, 5-,13-H), 1.86 (d, 9-Hs), 1.82 (m, 4-,14-H), 1.78 (dt, 20-Ha), 1.72 (dt, 9-Ha), 1.39 (m, 4-,14-H′) ppm; $J_{1,19(17,18)}$ = 4.7, $J_{1,20a(17,20a)}$ = 6.5, $J_{1,20s(17,20s)}$ = 1.9, $J_{3,3'(15,15')}$ = 10.2, $J_{5,5'(13,13')}$ = 12.6, $J_{5,6(12,13)} = J_{5',6(12,13')}$ = 6.5, $J_{8,9a(9a,10)}$ = 7.1, $J_{8,9s(9s,10)}$ = 1.5, $J_{8,19(10,18)}$ = 5.3, $J_{9a,9s}$ = 12.1, $J_{20a,20s)}$ = 12.9 Hz. $^{13}C$ NMR: $\delta$ = 62.8 (C-6,-12), 57.7 (C-1,-17), 54.1 (C-8,-10), 48.9 (C-3,-15), 37.0 (C-18,-19), 34.3 (C-20), 30.8 (C-5,-13), 24.0 (C-9), 19.5 (C-4,-14) ppm. MS: *m*/*z* (%) = 275 (3), 274 (7) [$M^+$], 273 (11), 231 (2), 190 (7), 189 (6), 163 (8), 162 (38), 161 (16), 136 (10). $C_{16}H_{26}N_4$ (274.4): calcd. C 70.03, H 9.55, N 20.42; found C 69.66, H 9.62, N 20.89.

**2,3,7,8-Tetraazatetracyclo[7.3.1.0$^{4,12}$.0$^{6,10}$]tridecane (52):** Cf. **8** with 2,3,7,8-tetraazatetracyclo[7.3.1.0$^{4,12}$.0$^{6,10}$]trideca-2,7-diene[6b] (110 mg, 0.62 mmol)/$CH_3OH$ (5 mL)/$PtO_2$ (10 mg)/3 h. The waxy, highly air-sensitive solid (110 mg, 98%) was used as such. $^1H$ NMR (400 MHz, $CD_3OD$): $\delta$ = 3.40 (m, 1-,4-,6-,9-H), 2.47 (m, 10-,12-H), 1.95 (dt, 5-,13-Hs), 1.64 (m, 5-,13-Ha, 11-H) ppm; $J_{1,13a(4,5a;5a,6;9,13a)} \leq 1$, $J_{1,13s(4,5s;5s,6;9,13s)}$ = 6.4, $J_{5a,5s(13a,13s)}$ = 16.1, $J_{1,12(4,12;6,10;9,10)}$ = 9.9, $J_{10,11(11,12)}$ = 3.2 Hz.$^{13}C$ NMR: $\delta$ = 69.0 (C-1,-4,-6,-9), 36.4 (C-10,-12), 29.7 (C-5,-13), 20.1 (C-11) ppm. HRMS: $C_9H_{16}N_4$ calcd. 180.1375; found 180.1381.

**2,3,7,8-Tetrakis(chloroacetyl)-2,3,7,8-tetraazatetracyclo[7.2.1.0$^{4,12}$.0$^{6,10}$]dodecane (53):** To an anhydrous solution of **8** (300 mg, 1.80 mmol) and trietylamine (5 mL) in acetonitrile (50 mL) at –10 °C, chloroacetyl chloride (2.8 g, 25 mmol) was added dropwise. After stirring for 30 min, keeping at room temperature for 2 h (single product, TLC), and concentration in vacuo, the solid, uniform (TLC) residue was filtered and washed thoroughly with $CHCl_3$. The solid material (800 mg, 95%), m.p. 270 °C (dec.), proved hardly soluble in $CHCl_3$, $CH_2Cl_2$, MeOH, THF, $H_2O$, but soluble in $CF_3CO_2$ H, DMF, DMSO. $^1H$ NMR (400 MHz, $CF_3CO_2D$): $\delta$ = 5.33 (br., 1-,6-H)*, 4.87 (br., 4-,9-H)*, 4.32 (br., 2 $CH_2Cl$), 4.18 (br., 2 $CH_2Cl$), 3.69 (br., 10-,11-H), 3.37 (br., 5-,12-Hs), 2.22 (br., 5-,12-Ha) ppm. $^{13}C$ NMR ($CF_3CO_2D$): $\delta$ = 171.7 (C=O), 70.2 (C-1,-6)*, 66.9 (C-4,-9)*, 53.6 (C-10,-11), 42.1 ($CH_2Cl$), 38.1 (C-5,

-12) ppm. MS: *m*/*z* (%) = 472 (2), 470 (2) [$M^+$], 393 (47) [$(M - COCH_2Cl)^+$], 319 (74) [$(M - 2\ COCH_2Cl)^+$], 241 (100) [$(M - 3\ COCH_2Cl)^+$], 163 (10) [$(M - 4\ COCH_2Cl)^+$]. HRMS: $C_{16}H_{18}Cl^{35}{}_4N_4O_4$ calcd. 470.0082; found 470.0088.

**2,3,7,8-Tetrakis(chloroacetyl)-2,3,7,8-tetraazatetracyclo[7.3.1.0$^{4,12}$.0$^{6,10}$]tridecane (54):** Cf. **53** with compound **52** (320 mg, 1.70 mmol)/chloroacetylchloride (5.6 g, 50 mmol)/trietylamine (5 ml)/$CH_3CN$ (40 mL)/-10 °C (1 h)/room temp. (2 h). The colorless product (760 mg, 93%), m.p. >320 °C, was only slightly more soluble than **53**. $^1$H NMR (400 MHz, $CF_3COOD$): $\delta$ = 4.71 (br., 1-,4-,6-,9-H), 4.3 (br., 4 $CH_2$), 2.95 (br., 4 H, 5-,13-H), 2.15 (br., 4 H, 10-,11-,12-H) ppm. MS: (CI, isobutane): *m*/*z* (%) = 488 (4), 444 (100), 408 (34), 406 (10), 374 (8), 366 (8), 126 (34). HRMS: $C_{17}H_{20}Cl^{35}{}_4N_4O_4$ calcd. 484.0239; found 484.0244.

**5,12-Dibenzyl-2,5,8,9,12,15-hexaazahexacyclo[14.5.1.0$^{2,15}$.0$^{8,20}$.0$^{9,18}$.0$^{19,22}$]docosane-3,7,10,14-tetrone (56):** An anhydrous solution of **53** (80 mg, 0.17 mmol), benzylamine (36 mg, 0.34 mmol), and trimethylamine (0.5 mL) in DMF (10 mL) was stirred for 2 h at room temperature (two new components, TLC), then at 80 °C for 4 h (a single monomeric product, TLC). After concentration in vacuo and filtration through silica gel ($CHCl_3/CH_3OH$, 9:1), a single product was eluted and crystallized from $CHCl_3$. Colorless needles (66 mg, 72%) were isolated, m.p.: 242–243 °C. IR (KBr): $\tilde{\nu}$ = 3402, 3017, 2956, 2857, 1698, 1270 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 7.3–7.2 (m, 10 H, phenyl), 4.73 (m, 1-,16-,18-,20-H), 3.67 (s, 2 $CH_2$), 3.49 (m, 19-,22-H), 3.35 (dt, 17-,21-Hs), 3.32 (m, 4-,6-,11-,13-H), 3.30 (m, 4-,6-,11-,13-H′), 2.49 (dt, 17-,21-Ha) ppm; $J_{1,21a(16,17a;17a,18;20,21a)}$ = 7.2, $J_{1,21s(16,17s;17s,18;20,21s)}$ = 2.3, $J_{1,22(16,22;18,19;19,20)}$ = 5.6, $J_{4,4'(6,6';11,11';13,13')}$ = 12.3, $J_{17a,17s(21a,21s)}$ = 16.2 Hz. $^{13}$C NMR ($CDCl_3$/[$D_5$]pyridine, 2:3): $\delta$ = 167.2 (CO), 136.7, 129.5, 128.8, 127.9 (phenyl), 63.7 (C-1,-16,-18,-20), 61.4 ($CH_2$), 56.7 (C-4,-6,-11,-13), 55.3 (C-19,-22), 37.6 (C-17,-21) ppm. MS: *m*/*z* (%): = 541 (3), 540 (10) [$M^+$], 449 (4) [$(M - CH_2C_6H_5)^+$], 421 (18) [$(M - CH_2NCH_2C_6H_5)^+$], 274 (6), 134 (19), 91 (100) [$CH_2C_6H_5$]. $C_{30}H_{32}N_6O_4$ (540.6): calcd. C 66.65, H 5.97, N 15.55, found C 66.24, H 5.68, N 15.67.

**5,12-Dibenzyl-2,5,8,9,12,15-hexaazahexacyclo[14.5.1.1$^{19,22}$.0$^{2,15}$.0$^{8,20}$.0$^{9,18}$]tricosane-3,7,10,14-tetrone (57):** Cf. **56** with compound **54** (100 mg, 0.2 mmol)/benzylamine (45 mg, 0.4 mmol)/triethylamine (0.5 mL)/DMF (100 mL). After stirring at room temperature for 3 days (one product, TLC), chromatography (silica gel, $CHCl_3/CH_3OH$, 5:1), and crystallization ($CHCl_3$), colorless crystals (84 mg, (76%) were isolated, m.p. 262–265 °C. $^1$H NMR: $\delta$ = 7.3–7.2 (m, 10 H, phenyl), 4.61 (m, 1-,16-,18-,20-H), 3.66 (s, 2 $CH_2$), 3.45 (d, 17-,21-Hs), 3.33 (d, 4-,6-,11-,13-H), 3.24 (d, 4-,6-,11-,13-H′), 2.87 (dt, 19-,22-H), 1.94(dt, 17-,21-Ha), 1.72 (m, 2 H, 23-H) ppm; $J_{1,21a(21a,20;16,17a;17a,18)}$ = 6.4, $J_{1,22(22,16;,18,19;19,20)}$ = 10.7, $J_{19,23(23,22)}$ = 3.2, $J_{17a,17s(21a,21s)}$ = 16.8 Hz. $^{13}$C NMR: $\delta$ = 167.1 (CO), 136.8, 129.2, 128.5, 127.7 (phenyl), 61.3 ($CH_2$), 56.3 (C-4,-6,-11,-13), 52.6 (C-1,-16,-18,-20), 31.5 (C-19,-22), 24.9 (C-17,-21), 18.7 (C-23) ppm. MS: *m*/*z* (%) = 554 (55) [$M^+$], 497 (16), 495 (15), 463 (55) [$(M - CH_2C_6H_5)^+$], 435 (85) [$(M - CH_2NCH_2C_6H_5)^+$], 152 (100) [$(M - 2\ \{(COCH_2)_2NCH_2C_6H_5\} - N_2)^+$], 124 (43) [$(M - 2\ \{(COCH_2)_2NCH_2C_6H_5\} - 2\ N_2)^+$], 91 (83) [$CH_2C_6H_5$], 81(53). HRMS: $C_{31}H_{34}N_6O_4$ calcd. 554.2642; found 554.2640.

**5,12-Dibenzyl-2,5,8,9,12,15-hexaazahexacyclo[14.5.1.0$^{2,15}$.0$^{8,20}$.0$^{9,18}$.0$^{19,22}$]docosane (59):** Cf. **35** with compound **56** (100 mg, 0.18 mmol)/LAH (70 mg, 1.8 mmol)/THF (10 mL)/16 h reflux (one single product). After workup, colorless, highly oxygen-sensitive crystals (85 mg, 96%) were isolated, m.p. 47–50 °C ($CHCl_3$). $^1$H NMR (400 MHz): $\delta$ = 7.35–7.20 (m, 10 H, phenyl), 3.67 (s, 2 $CH_2$), 3.43 (m, 1-,16-,18-,20-H), 3.15 (m, 19-,22-H), 2.93 (m, 3-,7-,10-,14-H), 2.83(m, 8 H, 4-,6-,11-,13-H), 2.77 (m, 3-,7-,10-,14-H′), 2.22 (dt, 17-,21-Hs), 1.70 (dt, 17-,21-Ha) ppm; $J_{1,21a(16,17a;17a,18;20,21a)}$ = 7.5, $J_{1,21s(16,17s;17s,18;20,21s)}$ = 4.8, $J_{1,22(16,22;18,19;19,20)}$ = 5.4, $J_{17a,17s(21a,21s)}$ = 13.7 Hz. $^{13}$C NMR ($CDCl_3$/[$D_5$]pyridine, 2:3): $\delta$ = 139.4, 129.0, 128.2, 126.9 (phenyl), 73.4 (C-1,-16,-18,-20), 62.7 ($CH_2$), 53.7 (C-19,-22), 53.6 (C-4,-6,-11,-13)*, 53.0 (C-3,-7,-10-,-14)*, 31.6 (C-17,-21) ppm. MS: *m*/*z* (%) = 484 (13) [$M^+$], 393 (24) [$(M - CH_2C_6H_5)^+$], 272 (33), 91 (100) [$CH_2C_6H_5$]. $C_{30}H_{40}N_6$ (484.7): calcd. C 74.34, H 8.32, N 17.34; found C 73.95, H 8.62, N 17.00.

**2-Methyl-4,9,13,18-tetraazahexacyclo[10.6.2.2$^{3,10}$.0$^{2,11}$.0$^{4,9}$.0$^{13,18}$]-docosa-6,15-diene-5,8,14,17-tetrone (63a):** (Cf. **16**.) A degassed suspension of freshly prepared **61** (104 mg, 0.50 mmol) and maleic anhydride (110 mg, 1.1 mmol) in dry THF (30 mL) was refluxed for 3 h. After concentration in vacuo, the colorless residue (mostly bisacylated **28**, TLC, MS) was heated at 180 °C in vacuo (10$^{-1}$ mm) for 3 h. The now yellowish solid was chromatographed ($SiO_2$, $CH_3OH/CHCl_3$, 1:20) to give **63a** (152 mg, (83%) ($R_f$ = 0.41) and **9-methyl-2,7,11,12-tetraazapentacyclo[6.6.2.2$^{10,13}$.0$^{2,7}$.0$^{9,14}$]octadeca-4,11-diene-3,6-dione (62a)** (16 mg, 12%) ($R_f$ = 0.45). **63a**: Yellow crystals, m.p. >320 °C. UV ($CH_3CN$): $\lambda_{max}$, nm ($\varepsilon$) = 361 (3250), 284 (2900). IR (KBr): $\tilde{\nu}$ = 2948, 2754, 1686, 1463, 1156, 848 cm$^{-1}$. $^1$H NMR ($CD_3OD$, 400 MHz): $\delta$ = 6.78 (s, 6-,7-,15-,16-H), 5.18 (ddd, 10-,12-H), 5.00 (dd, 1-,3-H), 2.48 (dddd, 19-,21-Ha), 2.36 (t, 11-H), 2.07 (dddd, 20-,22-Ha), 1.97 (dddd, 20-,22-Hs), 1.77 (dddd, 19-,21-Hs), 1.51 (s, $CH_3$) ppm; $J_{1,19a(3,21a)}$ = 4.6, $J_{1,19s(3,21s)}$ = 3.0, $J_{10,11(11,12)}$ = 1.6, $J_{10,22a(12,20a)}$ = 4.6, $J_{10,22s(12,20s)}$ = 4.5, $J_{19a,19s(21a,21s)}$ = 14.3, $J_{19a,20a(21a,22a)}$ = 10.5, $J_{19a,20s(21a,22s)}$ = 3.8, $J_{19s,20a(21s,22a)}$ = 6.8, $J_{19s,20s(21s,22s)}$ = 11.3, $J_{20a,20s(22a,22s)}$ = 13.5 Hz. $^{13}$C NMR: $\delta$ = 153.6 (C-5,-17)*, 153.5 (C-8,-14)*, 133.8 (C-6,-16)**, 133.7 (C-7,-15)**, 52.6 (C-1,-3), 48.8 (C-10,-12), 46.6 (C-11), 38.7 (C-2), 24.4 ($CH_3$), 24.3 (C-20,-22), 23.2 (C-19,-21) ppm. MS (CI, isobutane): *m*/*z* (%) = 370 (43) 369 (100) [$(M + 1)^+$], 368 (32) [$M^+$], 366 (6). $C_{19}H_{20}N_4O_4$ (368.4): calcd. C 62.03, H 5.48, N 15.34; found C 61.77, H 5.28 N 14.39. For X-ray measurements, crystals were grown by diffusing the vapor of **63a** slowly into $CHCl_3/Et_2O$, 1:1. **62a**: Pale-yellowish crystals, m.p. 214 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3046, 2948, 1624, 1635, 1466, 1452, 1324, 1156, 839 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 6.81 (s, 4-,5-H), 5.18 (ddd, 13-H), 5.14 (ddd, 1-H), 4.94 (dd, 10-H), 4.88 (dd, 8-H), 2.21 (mc, 16-Ha), 1.98 (mc, 15-Hs), 1.90 (dd, 14-H), 1.88 (mc, 17-Ha), 1.80 (mc, 16-Hs), 1.77 (mc, 15-Ha), 1.50 (mc, 18-Ha), 1.32 (mc, 18-Hs), 1.26 (s, $CH_3$), 1.01 (dddd, 17-Hs) ppm; $J_{1,15a}$ = 5.2, $J_{1,15s}$ = $J_{8,16s}$ = 3.0, $J_{8,16a}$ = 5.6, $J_{10,17a}$ = 4.5, $J_{10,17s}$ = 1.9, $J_{13,18a}$ = 4.6, $J_{13,18s}$ = 1.5, $J_{15a,15s}$ = 14.3, $J_{15s,16a}$ = 6.8, $J_{15s,16s}$ = 10.5, $J_{16a,16s}$ = 13.5, $J_{15a,16s}$ = 3.0, $J_{15a,16a}$ = 9.8, $J_{17a,17s}$ = 14.3, $J_{17a,18s}$ = 5.3, $J_{17a,18a}$ = 11.3, $J_{17s,18s}$ = 11.3, $J_{17s,18a}$ = 10.5, $J_{18a,18s}$ = 13.5 Hz. $^{13}$C NMR: $\delta$ = 154.6 (C-3*), 154.1 (C-6*), 134.0 (C-4,-5), 67.9 (C-10**), 63.9 (C-13**), 52.0 (C-1***), 51.8 (C-8***), 48.7 (C-14), 42.5 (C-9), 24.7, 22.6, 21.5, 19.1, 17.9 ppm. MS: *m*/*z* (%) = 288 (4), 287 (23), 286 (53) [$M^+$], 285 (14), 259 (2), 258 (27) [$(M - N_2)^+$], 229(8), 177 (3), 176 (36) [$(M - N_2 - C_4H_2O_2)^+$], 175 (9), 149 (4), 148 (21) [$(M - N_2 - C_4H_2N_2O_2)^+$], 91(84). $C_{15}H_{18}N_4O_2$ (286.3): calcd. C 62.92, H 6.34, N 19.57; found C 62.70, H 6.22, N 19.11.

**6,7,15,16-Tetrachloro-2-methyl-4,9,13,18-tetraazahexacyclo[10.6.2.2$^{3,10}$.0$^{2,11}$.0$^{4,9}$.0$^{13,18}$]docosa-6,15-diene-5,8,4,17-tetrone (63b):** Cf. **63a/62a** with compound **61** (104 mg, 0.50 mmol)/dichloromaleic anhydride (185 mg, 1.1 mmol)/THF (50 mL)/4 h reflux. The residue was heated at 200 °C/10$^{-1}$ mm/4 h. Compounds **63b** (208 mg, 81%) ($R_f$ = 0.38) and **4,5-dichloro-9-methyl-2,7,11,12-tetraazapentacyclo[6.6.2.2$^{10,13}$.0$^{2,7}$.0$^{9,14}$]octadeca-4,11-diene-3,6-dione (62b)** (8 mg, 5%) ($R_f$ = 0.47) were obtained chromatographically (MeOH/$CHCl_3$, 1:2). **63b**: Yellow crystals, m.p. >320 °C; hardly soluble in $CHCl_3$, $CH_2Cl_2$, slightly soluble in methanol, well soluble in

$CF_3CO_2H$. $^{1}$H NMR (400 MHz, $CF_3CO_2D$): $\delta$ = 5.70 (dt, 10-,12-H), 5.02 (dd, 1-,3-H), 2.68 (mc, 19-, 21-Hs), 2.57 (dt, 11-H), 2.21 (m, 20-,22-Ha,s), 2.05 (mc, 19-,21-Ha), 1.71 (s, $CH_3$) ppm. $^{13}$C NMR ($CF_3CO_2D$): $\delta$ = 171.5 (C-5,-8,-14,-17), 143.9 (C-6,-7,-15, -16), 58.7 (C-1,-3), 55.1 (C-10,-12), 48.6 (C-11), 47.6 (C-2), 25.0 (C-19,-21*), 24.7 (C-20,-22*), 24.1 ($CH_3$) ppm. MS:*m*/*z* (%) = 511 (3), 510 (11), 509 (11), 508 (50), 506 (100) [$M^+$], 504 (17), 207 (7), 206 (9), 205 (8), 204 (12), 203 (5), 202 (2), 183 (16), 181 (24), 179 (3). $C_{19}H_{16}Cl_4N_4O_4$ (506.2): calcd. C 45.09, H 3.19; found C 44.79, H 3.01. **62b**: Pale-yellowish crystals, m.p. 276–279 °C (dec.). $^{1}$H NMR (400 MHz): $\delta$ = 5.18 (ddd, 13-H), 5.14 (ddd, 1-H), 4.95 (dd, 10-H), 4.88 (dd, 8-H), 2.20 (mc, 16-Ha), 1.95 (mc, 15-Hs), 1.93 (dd, 14-H), 1.92 (mc, 18-H), 1.90 (mc, 17-Ha), 1.81 (mc, 16-Hs), 1.70 (mc, 15-Ha), 1.30 (mc, 18-Hs), 1.20 (s, $CH_3$), 0.98 (mc, 17-Hs) ppm; $J_{1,15a}$ = 5.2, $J_{1,15s}$ = $J_{8,16s}$ = 3.0, $J_{8,16a}$ = 5.6, $J_{10,17a}$ = 4.5, $J_{10,17s}$ = 1.9, $J_{13,18a}$ = 4.6, $J_{13,18s}$ = 1.5, $J_{15a,15s}$ = 14.3, $J_{15s,16a}$ = 6.8, $J_{15s,16s}$ = 10.5, $J_{16a,16s}$ = 13.5, $J_{15a,16s}$ = 3.0, $J_{15a,16a}$ = 9.8, $J_{17a,17s}$ = 14.3, $J_{17a,18s}$ = 5.3, $J_{17a,18a}$ = 11.3, $J_{17s,18s}$ = 10.3, $J_{17s,18a}$ = 10.5, $J_{18a,18s}$ = 13.3 Hz. $^{13}$C NMR: $\delta$ = 154.6 (C-3*), 154.1 (C-6*), 134.0 (C-4, -5), 67.9 (C-10**), 63.9 (C-13**), 52.0 (C-1***), 51.8 (C-8***), 48.7 (C-14), 42.5 (C-9), 24.7, 22.6, 21.5, 19.1, 17.9 ppm. MS (CI, isobutane): *m*/*z* (%) = 358 (4), 357 (23), 356 (12), 355 (100) [$(M + 1)^+$], 354 (13) [$M^+$], 353 (5). $C_{15}H_{16}Cl_2N_4O_2$ (355.2): calcd. C 50.72, H 4.54; found C 50.28, H 4.17.

**Supporting Information** (see also footnote on the first page of this article)**:** Experimental voltammograms and simulations of **9**, **10**, and **35** in PrCN (ACN)/ $TBAPF_6$ at varied temperatures and rates, selected kinetic parameters. Calculated (B3LYP-6/31 G*) lowest energy structures, energies, selected distances, and angles of the tetramine derived from **1** (**65**) through twofold N–N hydrogenolysis, its radical cation and singlet/triplet dications.

## Acknowledgments

Thanks go to Dr. D. Hunkler, Dr. J. Wörth and C. Warth for NMR and MS analyses, to Prof. Dr. R. Schwesinger and Dr. H.-D. Beckhaus for force-field calculations, to Dr. P. R. Spurr for help with the manuscript, to G. Fehrenbach for artwork, to the Deutsche Forschungsgemeinschaft and the Fonds der ChemischenIndustrie for generous financial support. We cordially thank Prof. Dr. E. Vogel for repeated supply of methanocyclodecapentaene. The correspondence author would like to express his sincere thanks to his many coworkers involved in the "bisdiazene" projects, to the colleagues – E. Heilbronner, G. Rihs, G. Gescheidt, J. Wirz, T. Bally, J. Heinze, H. Irngartinger, H. Fritz, H.-D. Martin, B. Mayer, H. Bock, P. Rademacher, A. Schweiger, H. Vahrenkamp, G. Huttner, H.-J. Grützmacher – who have contributed their expertise at various stages along the long road.

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[1] a) H. Prinzbach, K. Weber, *Angew. Chem.* **1994**, *106*, 2329–2348; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2239–2257; b) G. A. Olah, in *Cage Hydrocarbons* (Ed.: G. A. Olah), Wiley, New York, **1990**, pp. 103–153; c) H. Prinzbach, G. Gescheidt, H.-D. Martin, R. Herges, J. Heinze, G. K. S. Prakash, G. A. Olah, *Pure Appl. Chem.* **1995**, *67*, 673–682; d) G. K. S. Prakash, in: *Stable Carbocation Chemistry* (Eds.: G. K. S. Prakash, P. v. R. Schleyer), Wiley, New York, **1997**, pp. 137–163; e) G. Gescheidt, H. Prinzbach, A. G. Davies, R. Herges, *Acta Chem. Scand.* **1997**, *51*, 174–180; f) R. V. Williams, *Chem. Rev.* **2001**, *101*, 1185–1204.

[2] Oxidation of (iso)[1.1.1.1]pagodanes/pagodadienes: a) G. K. S. Prakash, V. V. Krishnamurthy, R. Herges, R. Bau, H. Yuan, G. A. Olah, W.-D. Fessner, H. Prinzbach, *J. Am. Chem. Soc.* **1986**, *108*, 836–838; b) H. Prinzbach, B. A. R. C. Murty, W.-D. Fessner, J. Mortensen, J. Heinze, G. Gescheidt, F. Gerson, *Angew. Chem.* **1987**, *99*, 488–490; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 457–458; c) G. K. S. Prakash, V. V. Krishnamurthy, R. Herges, R. Bau, H. Yuan, G. A. Olah, W.-D. Fessner, H. Prinzbach, *J. Am. Chem. Soc.* **1988**, *110*, 7764–7772; d) R. Herges, P. v. R. Schleyer, M. Schindler, W.-D. Fessner, *J. Am. Chem. Soc.* **1991**, *113*, 3649–3656; e) A. Trifunac, D. Werst, R. Herges, H. Neumann, H. Prinzbach, M. Etzkorn, *J. Am. Chem. Soc.* **1996**, *118*, 9444–9445.

[3] Oxidation of (iso)[2.2.1.1]pagodanes/pagodadienes: a) G. Gescheidt, R. Herges, H. Neumann, J. Heinze, M. Wollenweber, M. Etzkorn, H. Prinzbach, *Angew. Chem.* **1995**, *107*, 1109–1112; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1016–1019; b) G. K. S. Prakash, K. Weber, G. A. Olah, H. Prinzbach, M. Wollenweber, M. Etzkorn, T. Voss, R. Herges, *Chem. Commun.* **1999**, 1029–1030; Cf. c) W. Grimme, H. Geich, J. Lex, J. Heinze, *J. Chem. Soc., Perkin 2* **1997**, 1955–1958.

[4] Oxidation of (iso)[2.2.2.2]pagodanes/pagodadienes: M. Etzkorn, F. Wahl, M. Keller, H. Prinzbach, F. Barbosa, V. Peron, G. Gescheidt, J. Heinze, R. Herges, *J. Org. Chem.* **1998**, *63*, 6080–6081.

[5] Oxidation of (seco-, homo-)dodecahedradienes: a) K. Weber, H. Prinzbach, R. Schmidlin, F. Gerson, G. Gescheidt, *Angew. Chem.* **1993**, *105*, 907–909; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 875–877; b) A. Weiler, E. Quennet, M. Keller, K. Exner, H. Prinzbach, *Tetrahedron Lett.* **2000**, *41*, 4763–4767; c) J. Reinbold, M. Bertau, T. Voss, D. Hunkler, L. Knothe, H. Prinzbach, D. Neschadin, G. Gescheidt, B. Mayer, H.-D. Martin, J. Heinze, G. K. S. Prakash, G. A. Olah, *Helv. Chim. Acta* **2001**, *84*, 1518–1560.

[6] a) K. Exner, O. Cullmann, M. Vögtle, H. Prinzbach, B. Großmann, J. Heinze, L. Liesum, R. Bachmann, A. Schweiger, G. Gescheidt, *J. Am. Chem. Soc.* **2000**, *122*, 10650–10660; b) J. Geier, K. Exner, M. Vögtle, M. Kegel, F. Yang, D. Hunkler, O. Cullmann, H. Prinzbach, *Tetrahedron* **2002**, *58*, 1137–1145; c) E. Beckmann, N. Bahr, O. Cullmann, F. Yang, M. Kegel, M. Vögtle, K. Exner, M. Keller, L. Knothe, H. Prinzbach, *Eur. J. Org. Chem.* **2003**, 4248–4264.

[7] Cf. the one-/two-electron oxidation of bisdiazene N-oxides: K. Exner, H. Prinzbach, G. Gescheidt, B. Großmann, J. Heinze, *J. Am. Chem. Soc.* **1999**, *121*, 1964–1965.

[8] **1**: 1,10,11,20-Tetraazanonacyclo$[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]$icosane. **2**: 1,10,11,20-Tetraazanonacyclo$[12.6.0.0^{2,6}.0^{4,20}.0^{5,9}.0^{7,11}.0^{10,17}.0^{12,16}.0^{15,19}]$icosane: Dissertations, University of Freiburg: a) E. Beckmann, **1991**; b) N. Bahr, **1994**; c) M. Lugan, **1994**; d) M. Heitzmann, **1996**; e) O. Cullmann, **1997**; f) K. Exner, **1998**; g) M. Vögtle, **2000**; h) M. Kegel, **2001**; i) Research reports of Dr. F. Yang (Humboldt Fellow **1993–1999**); j) J. Geier, Diplomarbeit, **2000**. **3**: 1,2,16,17-Tetraazaundecacyclo$[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]$icosane: Dissertations, University of Freiburg: k) C. Grund, **1990**; l) R. Thiergardt, **1992**; Cf. m) T. Mathew, M. Keller, D. Hunkler, H. Prinzbach, *Tetrahedron Lett.* **1996**, *37*, 4491–4494; n) For calculations on all-azadodecahedrane ($C_{20}N_{20}$) see: I. Alkorta, J. Elguero, I. Rozas, *Theochem* **1992**, *228*, 47–60; for a $T_h$ symmetrical $C_{12}N_8$ and its $C_{12}H_{12}N_8$ derivative see: o) R. W. Alder, J. N. Harvey, P. v. R. Schleyer, D. Moran, *Org. Lett.* **2001**, *3*, 3233–3236.

[9] a) Review: S. F. Nelsen, in *Acyclic Organonitrogen Stereodynamics* (Eds.:J. B. Lambert, Y. Takeuchi), VCH, Weinheim, **1992**, chapters 3 and 7; b) . S. F. Nelsen, E. L. Clennan, *J. Am. Chem. Soc.* **1978**, *100*, 4004–4012,. and cit. ref.

[10] Reviews: a) S. F. Nelsen, *Acc. Chem. Res.* **1981**,*14*, 131–138; b) S. F. Nelsen, in *The Chemistry of the Hydrazo, Azo and Azoxy Groups* (Ed.: S. Patai), Wiley, New York, **1997**, chapter 6; c) *Electron SpinResonance Spectroscopy of Organic Radicals* (Eds.: F. Gerson, W. Huber), Wiley-VCH,Weinheim, **2003**, p. 193 ff.

[11] Review: a) I. Novak, B. Kovaĉ in ref. [10b], chapter 7; b) P. Rademacher, H. Koopmann, *Chem. Ber.* **1975**, *108*, 1557–1569.

[12] Review: J. Simonet, N. Gueguen-Simonet in ref.[10b], chapter 12.

[13] For a comparison of experimental geometries with molecular mechanics (MM2), semiempirical MO (AM1) and DFT (6-31G*) calculations see: S. F. Nelsen, Y. Wang, D. R. Powell, R. Hayashi, *J. Am. Chem. Soc.* **1993**, *115*, 5246–5253.

[14] a) S. F. Nelsen, *J. Am. Chem. Soc.* **1993**, *115*, 12276–12289; b) S. F. Nelsen, M. R. Willi, J. M. Mellor, N. S. Smith, *J. Org. Chem.* **1986**, *51*. 2081–2089.

[15] a) R. W. Alder, *Chem. Rev.* **1996**, *96*, 2097–2111; b) R. W. Alder, *Tetrahedron* **1990**, *46*, 683–713.

[16] S. F. Nelsen, F. Gerson, G. Gescheidt, J. Knoebel, W. B. J. Martin, L. Neumann, E. Vogel, *J. Am. Chem. Soc.* **1992**, *114*, 7107–7115.

[17] S. F. Nelsen, *J. Am. Chem. Soc.* **1996**, *117*, 2047–2058, and cit. ref.

[18] TTD: 1,3,6,8-Tetraazatricyclo[4.4.1.$1^{3,8}$]dodecane; a) S. F. Nelsen, E. Haselbach, R. Geschwind, U. Klemm, S. J. Lanyova, *J. Am. Chem. Soc.* **1978**, *100*, 4367–4368; b) S. F. Nelsen, J. M. Buschek, *J. Am. Chem. Soc.* **1974**, *96*, 6424–6428.

[19] J. Springborg, B. Nielsen, C. E. Olsen, I. Sotofte, *J. Am. Chem. Soc.* **2002**, *124*, 5084–5090, and cit. ref.

[20] For DFT calculations see: V. Galasso, *Chem. Phys.* **2001**, *279*, 79.

[21] J. M. Zwier, A. M. Brouwer, T. Keszhelyi, G. Balakrishnan, J. F. Offersgaard, R. Wilbrandt, F. Barbosa, U. Buser, J. Amaudrut, G. Gescheidt, S. F. Nelsen, C. D. Little, *J. Am. Chem. Soc.* **2002**, *124*, 159–167, and cit. ref.

[22] a) K. Exner, B. Großmann, G. Gescheidt, J. Heinze, M. Keller, T. Bally, P. Bednarek, H. Prinzbach, *Angew. Chem.* **2000**, *112*, 1514–1517; *Angew. Chem. Int. Ed.* **2000**, *39*, 1455–1458; b) K. Exner, G. Gescheidt, B. Großmann, J. Heinze, P. Bednarek, T. Bally, H. Prinzbach, *Tetrahedron Lett.* **2000**, *41*, 9595–9600.

[23] The correspondence author (H. P.) has retired in **1999** and had to close his laboratories in **2001**.

[24] a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94*, Revision E.2, Gaussian Inc., Pittsburgh PA, **1995** B3LYP; Cf. b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; d) W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory: an Introduction and Practical Guide to DFT Calculations*, Wiley-VCH, Weinheim, **2000**; e) For nucleus independent chemical shift (NICS) see: P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

[25] Oxidation of the tetramine derived from **1** through N–N hydrogenolysis was part of the calculational search for **D**-type ions (see Supporting Information, Figure S4, for lowest-energy structures of the neutral $C_{16}H_{24}N_4$ (**65**), its radical cation and S/T dications).

[26] Early force-field calculations (MM3) for **1** and **2** proposed somewhat tilted conformations of lower symmetry.[8d,8i].

[27] The performance of the DFT methods in their application to bis(hydrazines)and their localized radical cations has been discussed: a) F. Blomgren, S. Larson, S. F. Nelsen, *J. Comput. Chem.* **2001**, *22*, 655–664; b) S. F. Nelsen, F. Blomgren. *J. Org. Chem.* **2001**, *66*, 6551–6559; c) J. M. Zwier, J.-W. Hoeth, A. M. Brouwer, *J. Org. Chem.* **2001**, 66, 466–473.

[28] a) T. Bally; G. N. Sastry, *J. Phys. Chem. A* **1997**, *101*, 7923–7225; b) T. Clark, *Acta Chem. Scand.* **1997**, *51*, 646–652.

[29] a) K. Weber, G. Lutz, L. Knothe, J. Mortensen, J. Heinze, H. Prinzbach, *J. Chem. Soc., Perkin Trans. 2* **1995**, 1991–1997; b) H.-D. Martin, B. Mayer, K. Weber, F. Wahl, H. Prinzbach, *Liebigs. Ann.* **1995**, 2019–2025.

[30] a) In practice, the dication $\mathbf{5}^{2+}$ has not been generated from diene **5** but from the valence-isomeric, more stable iso[1.1.1.1]-pagodane; the radical cation produced by γ-irradiation in a Freon matrix ($^{60}$Co, 77 K)[1e] was identified as the "tight" isomer of "extended" $\mathbf{5}^{\cdot+}$[30b] (for the experimental "tight"/"extended" distinction (FDMR) in case of the ions derived from [1.1.1.1]pagodane/diene **4** see: A. Trifunac, D. Werst, R. Herges, H. Neumann, H. Prinzbach, M. Etzkorn, *J. Am. Chem. Soc.* **1996**, *118*, 9444–9445; b) H. Prinzbach, M. Wollenweber, R. Herges, H. Neumann, G. Gescheidt, R. Schmidlin, *J. Am. Chem. Soc.* **1995**, *117*, 1439–1440; c) Ref.[10c], p. 383 ff.

[31] a) W.-D. Fessner, G. Sedelmeier, P. R. Spurr, G. Rihs, H. Prinzbach, *J. Am. Chem. Soc.* **1987**, *109*, 4626–4642; b) M. Wollenweber, M. Etzkorn, J. Reinbold, F. Wahl, T. Voss, J.-P. Melder, C. Grund, R. Pinkos, D. Hunkler, M. Keller, J. Wörth, L. Knothe, H. Prinzbach, *Eur. J. Org. Chem.* **2000**, 3855–3886.

[32] U. Jensen-Kloster, M. Müller, in *Methoden der Organischen Chemie* (*Houben-Weyl*), vol. E16a, part 1, Thieme, Stuttgart, **1990**, pp. 503, 551.

[33] M. J. Kornet, R. Daniels, *J. Heterocycl. Chem.* **1979**, *16*, 1485–1486.

[34] H. R. Meyer, R. Gabler, *Helv. Chim. Acta* **1963**, *46*, 2685–2697.

[35] a) M. S. Malinovskii, V. G. Dryuk, A. G. Yudasina, N. N. Maksimenko, *Zh. Org. Khim.* **1966**, *2*, 2129–2132; Cf. b) M. F. Semmelhack, J. S. Foos, S. Katz, *J. Am. Chem. Soc.* **1973**, *95*, 7325–7336.

[36] a) A. E. Blood, C. R. Noller, *J. Org. Chem.* **1957**, *22*, 873–876; b) B. Junge, Diplomarbeit, University of Heidelberg (H. A. Staab), **1966**.

[37] CCDC-244101 (**16**), -244103 (**26a**) and -244102 (**63a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[38] Cf. the structure of 1,2-dimethyl-3,6-pyridazinone: T. Ottersen, *Acta Chem. Scand.* **1973**, *27*, 835–845.

[39] Cf., e.g., the formation of oxadodecahedranes from seco-dodecahedrane-diones: T. Voss, H. Prinzbach, *Tetrahedron Lett.* **1994**, *35*, 1535–1538.

[40] J. Muggee, O. Vogl, *J. Polym. Sci. Polym. Chem. Ed.* **1984**, *22*, 2501.

[41] T. Sakai, K. Iwata, M. Utaka, A. Takeda, *Bull.Chem. Soc. Jpn.* **1987**, *60*, 1161–1162.

[42] a) B. Großmann, Dissertation, University of Freiburg, **1999**; b) H. Kiesele, *Anal. Chem.* **1981**, *53*, 1952–1954.

[43] The kinetic parameters ($k_{\text{het}}$)and the activation enthalpies ($\Delta H^{\#}$) for the heterogeneous electron transfers were determined by digital simulation of the experimental voltammograms using DIGISIM® (Vers. 2.0). S. W. Feldberg, in *Electroanalytical Chemistry,* vol.3 (Ed.:A. J. Bard), Marcel Dekker, New York, **1969**, p. 199 (see Supporting Information).

[44] We thank Prof. Dr. H. Bock and Dr. B. Soluki, University of Frankfurt, for these measurements.

[45] We thank Prof. Dr. G. Gescheidt, University of Graz, for these measurements.

[46] A comparable situation had been encountered with the σ-bishomoaromatic dianions **B** when the presence of counterions proved necessary to make the singlet state to the ground state[8f]; In these cases, the predictions made by the B3LYP/6-31G* calculations were experimentally corroborated by a dramatic dependence of the stability of the dianions on the nature of the counterion.[6a]

[47] a) The ionization potential of 2,3-diazabicyclo[2.2.1]heptene is significantly higher than that of 2,3-diazabicyclo[2.2.3]octene (8.96 vs. 8.32 eV): R. J. Boyd, J. C. Bünzli, J. P. Snyder, M. L. Heyman, *J. Am. Chem. Soc.* **1973**, *42*, 6478–6480. For a correlation with oxidation potentials: b) W. M. Nau, W. Adam, D.

Klapstein, C. Sahin, H. Walther, *J. Org. Chem.* **1997**, *62*, 5128–5132.

[48] a) H. Prinzbach, *Pure Appl. Chem.* **1968**, *16*, 17–46; b) H. Prinzbach, W. Eberbach, H. Hagemann, G. Philippossian, *Chem. Ber.* **1974**, *107*, 1957–1970; c) H. Prinzbach, G. Sedelmeier, C. Krüger, R. Goddard, H.-D. Martin, R. Gleiter, *Angew. Chem.* **1978**, *90*, 297–305; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 271–273; d) K.-H. Lehr, R. Hildebrand, H. Fritz, L. Knothe, C. Krüger, H. Prinzbach, *Chem. Ber.* **1982**, *115*, 1875–1901.

[49] H. Prinzbach, G. Fischer, G. Rihs, G. Sedelmeier, E. Heilbronner, Z.-Z. Yang, *Tetrahedron Lett.* **1982**, *23*, 1251–1254.

[50] K. Exner, G. Fischer, N. Bahr, E. Beckmann, M. Lugan, F. Yang, G. Rihs, M. Keller, D. Hunkler, L. Knothe, H. Prinzbach, *Eur. J. Org. Chem.* **2000**, 763–785.

[51] K. Exner, G. Fischer, M. Lugan, H. Fritz, D. Hunkler, M. Keller, L. Knothe, H. Prinzbach, *Eur. J. Org. Chem.* **2000**, 787–806.

[52] J. Geier, H.-J. Grützmacher, K. Exner, H. Prinzbach, *Angew. Chem.*, in press.

[53] Recently, for a 4S/7e radical cation (counterion $SbCl_6^-$, 2,3,5,6-tetrathiabicyclo[2.2.2]oct-7-ene skeleton) with transannular electron delocalization over two disulfide units a transannular distance [$d_{S..S}$ = 2.794(3) Å] very close to $d_{N..N}$ of the 4N/7e radical cations $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ (Figure 1) – and of the **B**-type 4N/5e radical anions – has been reported: A. Wakamiya, T. Nishinaga, K. Komatsu, *J. Am. Chem. Soc.* **2002**, *124*, 15038–15050.

[54] a) J. F. Lyons, D. R. Rasmussen, M. P. McGrath, R. H. Nobes, L. Radom, *Angew. Chem.* **1994**, *106*, 1722–1724; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1667–1668; b) L. Radom, D. R. Rasmussen, *Pure Appl. Chem.* **1998**, *70*, 1977–1984.

[55] a) K. Exner, P. v. R. Schleyer, *Science* **2000**, *290*, 1937–1939; b) Z.-X. Wang, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2002**, *124*, 11979–11982; c) Z: Chen, H. Jiao, A. Hirsch, P. v. R. Schleyer, *Angew. Chem.* **2002**, *114*, 4485–4488; *Angew. Chem. Int. Ed.* **2002**, *41*, 4309–4312; d) F. Stahl, P. v. R. Schleyer, H. Jiao, H. F. Schaefer III, K.-H. Chen, N. L. Allinger, *J. Org. Chem.* **2002**, *67*, 6599–6611.

[56] a) R. Mellor, R. Pathirana, J. H. A. Stibbard, *J. Chem. Soc., Perkin Trans. 1* **1988**, 2541–2544; b) R. Mellor, R. Pathirana, N. M. Smith, *J. Chem. Soc., Perkin Trans. 1* **1983**, 2545–2549.

[57] Early attempts to prepare **38** as potential precursor of **8** from the all-*cis* bicyclo[3.3.0]octane-2,4,6,8-tetracarboxylic acid[58] had not been successful (G. Fischer, Dissertation, University of Freiburg, **1987**).

[58] a) K. Stille, R. J. Sevenich, D. D. Whithurst, *J. Org. Chem.* **1965**, *30*, 938–940; b) N. Sugiyama, K. Yamada, H. Aoyama, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1988–1990.

[59] a) R. M. Izatt, K. Pawlak, J. S. Bradshaw, *Chem. Rev.* **1995**, *95*, 2529–2586; b) P. Comba, *Coord. Chem. Rev.* **2000**, 202–217.

[60] M. Kegel, Diplomarbeit, University of Freiburg, **1997**.

[61] H. Meier, in *Methoden der Organischen Chemie* (*Houben-Weyl*), *Photochemie 1*, vol. IV/5a, Thieme, Stuttgart, **1975**, p. 222.

[62] Cf. the photocycloaddition **30** → **31** in ref.[3b]

[63] E. Osawa, K. Aigami, Y. Inamoto, *J. Org. Chem.* **1977**, *42*, 2621–2626.

Received September 15, 2004