Photochemical Transformations, 83[‡] Proximate, *syn*-Periplanar Bisdiazene Skeletons: Syntheses, Structures, Homoconjugate Reactivity and Photochemistry

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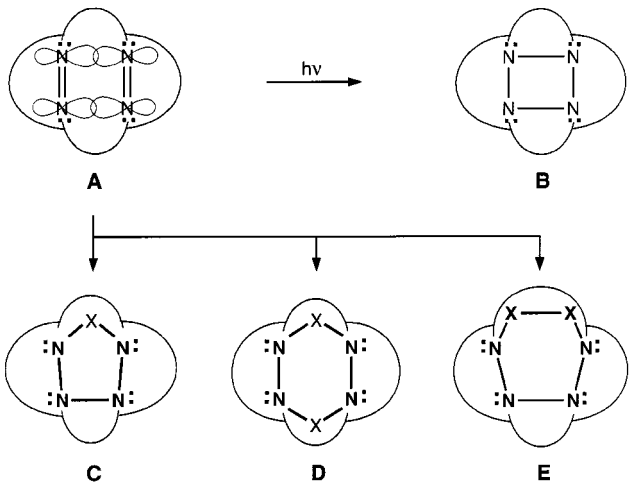
Rigid N=N/N=N (diazene/diazene) systems (**F**) consisting of more or less alkylated DBH and DBO chromophoric units (**1, 2**, X-ray structures), with very short π,π distances [*d* = 2.849 (**1a**, av.), 2.822 Å (**2**)] and almost perfect *syn*-periplanar π,π alignments [ω = 168.6 (**1a**), 174.2° (**2**)] as well as the more flexible, less "proximate" metathesis isomers (**3a**,**c**, **27a,c**, *d* >4.6 Å, ω = 90–100°) have been synthesized. Homoconjugate π,π interaction (in **1**, **2**, not in **3**, **27**) is deduced from UV spectroscopic measurements [$\pi \rightarrow \pi^*$ maxima at 239 (234) nm (sh, 260)], while PE analyses furnished only small interaction parameters (**1a**: <0.3 eV). The potential of the novel *syn*-periplanar N=N/N=N motif in **1** and **2** for the synthesis of somewhat exotic polyheterocycles has been explored by calculation (B3LYP) as well as experimentally: i.a. kinetically stabilized, *all-cis*-peralkylated tetrazolidines (**38**, **44**) and perhydro-1,2,4,5-tetrazines (**41, 47**) have become accessible (i.a. via novel azomethine/diazene and azomethine/azomethine cycloadditions). In **1a** with its unreactive DBO chromophoric subunits, in the "buttressed" derivatives **1b–d**, as well as in the DBH/DBO combination **2**, and likewise in more ″distant″ **27** (differently from the analogous C=C/C=C and N=N/C=C systems), irrespective of the excitation conditions employed (light of λ ≥ 280, 254 nm, low temperature matrix irradiation, acetone sensitization) no [2+2]photocycloaddition was observed. Instead exclusively N_2-elimination took place. It is argued that unproductive N=N/N=N photocycloaddition would have become observable through metathesis isomerization of the respective tetrazetidines.

Introduction – Calculations

The photo[2+2]cycloaddition between two N=N double bonds (diazene, diazene) to give a tetrazetidine ring (**A** → **B**) – still an elusive class of *all*-nitrogen heterocycles[2][3] – is a longstanding topic on our photochemical agenda.[4][5] Obvious obstacles to be faced in the pursuit of photoreactions of type **A** → **B** are relatively strict stereoelectronic prerequisites for through-space interactions due to the tighter N=N π-orbitals and efficient deactivation by denitrogenation, as well as radiative and radiationless processes. From the beginning,[4a] this project was intimately tied to the study of nonclassical through-space electron delocalization between two N=N double bonds (**A**) in ground and excited states. After all, in contrast to the huge variety of more or less proximate and periplanar homoconjugated dienes, no such bisdiazenes were known.[6] Synthetically, such rigidly preorganized bisdiazenes **A** also raised speculations as to their utility for the construction of novel polyheterocyclic ring systems (in part of model character for the tetrazetidines **B**) such as tetrazolidines, oxatetrazolidines, pentazolidines **C** (X = CR_2, O, NR), and perhydro-dioxatetrazines/hexazines **D**/**E** (X = O, NR). These are all forced into the rigid corset provided by their carbon framework, with the special property of 4–6 pairs of *n*-electrons being fixed on the same molecular face. Metal complexation of such bisdiazenes **A** has been pursued as a means of additional corseting.[4i] This paper is an updated full account of our synthetic work directed at structurally preoriented, proximate bisdiazenes of type **A**, and of their structural, chemical, optical and particularly photochemical properties.



In the preceding paper,[1] the arguments have been presented why "isodrin-like" bisdiazenes **F** (Table 1), which are combinations of 1,2-diazabicyclo[2.2.2]octene-(DBO) and 1,2-diazabicyclo[2.2.1]heptene units (DBH, Table 1 in ref.[1]), were the targets of choice in the planning stage of

[‡] Part 82: Ref.[1]

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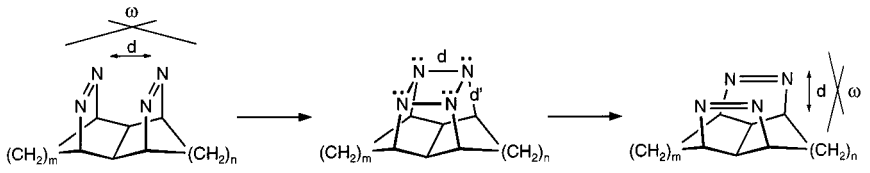
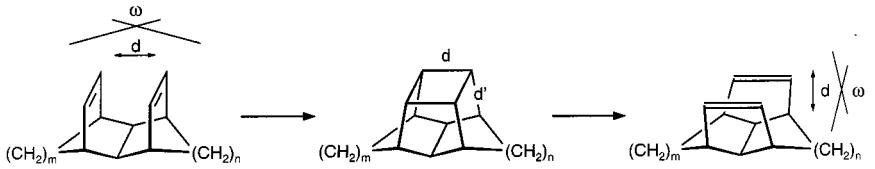
Table 1. B3LYP-31G*-calculated structure and energy data for the homologous diazenes **F**/dienes **I**, the tetrazetidines **G**/cyclobutanes **K** and the metathesis isomers **H/L** (Å,°, kcal mol^{-1})



	d	ω	$\Delta\Delta H_f^\circ$			d'	$\Delta\Delta H_f^\circ$		d	ω
$\mathbf{F_{11}}$	2.77	179.6	26.7	1.50	$\mathbf{G_{11}}$	1.52	-61.3	$\mathbf{H_{11}}$	3.34	142.4
$\mathbf{F_{12}}$	2.87	172.9	34.9	1.50	$\mathbf{G_{12}}$	1.52/1.50	-57.4	$\mathbf{H_{12}}$	3.75/4.05	128.5
$\mathbf{F_{22}}$	2.98	165.2	44.5	1.51	$\mathbf{G_{22}}$	1.52	-59.7	$\mathbf{H_{22}}$	4.87(C_2)	98.1
									4.80(C_s)	95.1



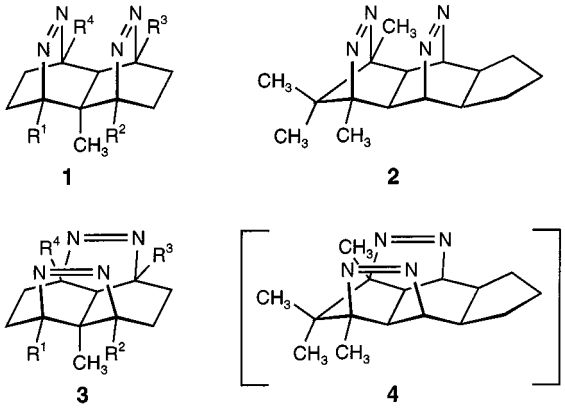
	d	ω	$\Delta\Delta H_f^\circ$			d'	$\Delta\Delta H_f^\circ$		d	ω
$\mathbf{I_{11}}$	3.00	172.7	-40.3	1.56	$\mathbf{K_{11}}$	1.57	3.3	$\mathbf{L_{11}}$	3.45	139.2
$\mathbf{I_{12}}$	3.06	166.5	-30.8	1.56	$\mathbf{K_{12}}$	1.57/1.57	11.7	$\mathbf{L_{12}}$	3.85/4.18	125.2
$\mathbf{I_{22}}$	3.13	160.6	-20.5	1.57	$\mathbf{K_{22}}$	1.57	14.1(C_2)	$\mathbf{L_{22}}$	5.09(C_2)	92.0
							14.5(C_s)		4.93(C_s)	90.4

the project. In summary, the arguments include: (i) High efficiency for cycloaddition in the respective ene/ene systems (**I**). (ii) Very short π,π distances (d) at almost perfect *syn*-periplanar π,π orientation (ω). (iii) Relatively high energy of the substrates. (iv) High skeletal rigidity to suppress radiationless deactivation. (v) Identification of potentially labile tetrazetidines **G** through the metathesis isomers **H**. (vi) Effective *anti*-Bredt protection against azo → hydrazo tautomerization.

The stereoelectronic details ("proximity", "*syn*-periplanarity"), the changes in structure and energy in going from the bisdiazenes **F** to the tetrazetidines **G** to the bisdiazenes **H** have been readdressed with B3LYP methods (Table 1) introduced in the preceeding paper,[1][5g] and proven in their reliability when tested against relevant properties of the DBH and DBO parent units as well as against X-structural data (of i.a. **1a**, **2**, **25c**).[5g] The force-field and semi-empirical calculation methods applied earlier, though reproducing geometric data well and duplicating energy trends closely,[5c–5g] were not applicable to the recent 4*N*-ion projects.[7] For comparison, the corresponding hydrocarbons have been recalculated on the same theoretical level (Table 1, X-ray data for the **I**-dienes cf. ref.[8]). Homologation significant in the case of bisdiazenes $\mathbf{F_{11}}$ – $\mathbf{F_{22}}$ has only minor consequences as to π,π distances (d) and interorbital angles (ω) in the case of the metathesis isomers $\mathbf{H_{11}}$ – $\mathbf{H_{22}}$. These stereoelectronic parameters in $\mathbf{F_{11}}$ – $\mathbf{F_{22}}$ are very similar if not better with respect to [2+2]cycloaddition than in the corresponding dienes $\mathbf{I_{11}}$ – $\mathbf{I_{22}}$.[9] Insignificant as these differences within the **F** series might seem, such small geometrical discrepancies have, in our own experience, been found to totally divert the course of photochemical transformations.[10] The rather modest endothermicity of the steps $\mathbf{F_{11-22}} \rightarrow \mathbf{G_{11-22}}$ reflect the degree of strain inherent in the rigid skeletons **F** and, in principle, should all lie well within the energy range of π → π* and even n → π* excitations.[11] The exothermicity of the isomerizations $\mathbf{G_{11-22}} \rightarrow \mathbf{H_{11-22}}$ with 60–62 kcal mol^{-1}, is indicative of low thermal stability of the tetrazetidine photoproducts. Judged by the geometrical criteria (d, ω) for through-space π → π interactions and the degree of skeletal rigidity as measured against internal deactivation, the $\mathbf{F_{11}}$ system consisting of two DBH units seemed most promising, with the [2+2]photocycloaddition potentially outplaying N_2 elimination (cf. $\Phi_{-N2} \approx 1$ for DBH, Table 1 in ref.[1]). However, the experimental test of this hypothesis is still lacking. Up to now, all attempts to construct such a $\mathbf{F_{11}}$ bisdiazene have failed.[5a][5d][5h] In contrast, for the less proximate, less rigid $\mathbf{H_{11}}$-tetraazatetraquinane and for its cyclopropanated $\mathbf{H_{22}}$-homolog (**27a** in Scheme 3), expeditious syntheses are at hand.[4i][6] Yet, with their N=N double bonds embedded in "closed" and "open" conformations ca. 3.2 Å and ca. 5 Å, respectively, apart, with interorbital angles between 142.4° and 95.1°, respectively, and with steep increases in energy, most probably the $\mathbf{H_{11}}$- and $\mathbf{H_{12}}$-, and certainly the $\mathbf{H_{22}}$-bisdiazenes were unlikely to undergo N=N/N=N cycloaddition. Later, the availability of such **H**-bisdiazenes with varied geometries was highly appreciated.[7]

As first representatives of the $\mathbf{F_{22}}$ and $\mathbf{F_{12}}$ series, the derivatives **1** and **2** are presented in this paper, with the nature and degree of their substitution being necessary by virtue

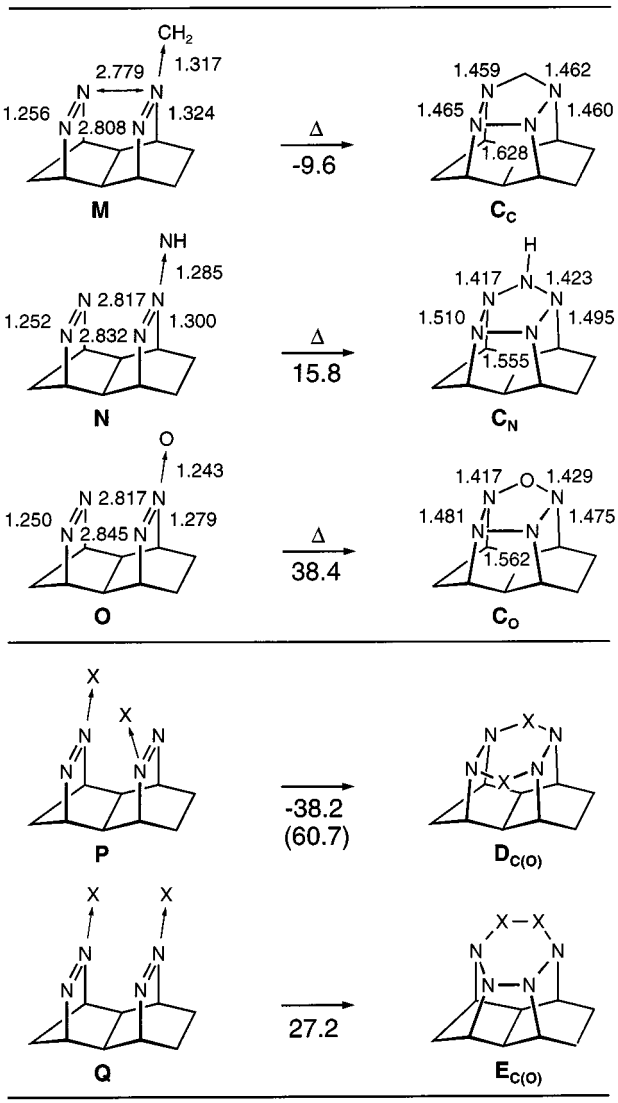
of their synthesis or (bridgehead alkylations, R^1-R^4) intentionally introduced as a means for buttressing the two chromophoric units.[12] Attempts are described to make use of the bisdiazenes **1** and **2** for the preparation of **H**-bisdiazenes. To this end, the point has to be stressed, that in **4** (**27**, see the *N*-oxides in ref.[12]) buttressing by the annelated cyclopentane ring enforces "closed" conformations, with d,ω parameters different from the $\mathbf{H_{12}}$- and closer to the $\mathbf{F_{12}}$ skeletons.



With the N=N/N=N structural motif of bisdiazenes **1** and **2**, the preparative synthetic goals abstracted with the formula **C**-**D** are in principle the ones already formulated for the parallel diazene/ene combinations,[1] implying homoconjugate participation of two N=N double bonds. With the diazene unit as a kinetically poor π_2-component, [3+2]cycloadditions to N=N(X) dipoles, and similarly [3+3]dimerizations of such dipoles are rather scarce.[13][14] DFT calculations for the three types of [3+2]cycloadditions in Table 2 indicated that the diazene/azomethine cycloaddition ($\mathbf{M} \rightarrow \mathbf{C_C}$) was a possibility, whilst the diazene/azimine ($\mathbf{N} \rightarrow \mathbf{C_N}$) and the diazene/diazeneoxy cycloadditions ($\mathbf{O} \rightarrow \mathbf{C_O}$) seemed unlikely. In principle, protonation (alkylation) of the relatively strong bases **C** could be a means of reversing not too unfavourable equilibria. For the [3+3]cycloadditions $\mathbf{P} \rightarrow \mathbf{D}$, minima could be located with X = CH_2 (highly exothermic) and X = O (highly endothermic), but for cycloadditions $\mathbf{Q} \rightarrow \mathbf{E}$, minima could only be found with X = CH_2 and not with X = O.

The photochemistry of the bisdiazenes **A** is directly related to their potential for homoconjugational interaction (through-space, TS and through-bond, TB). According to the B3LYP/6–31G* calculations, HOMO and HOMO-1 of **1** and **2** represent the bonding and antibonding combinations of the n_- N=N orbitals (Figure 1). While for **1a** the weights of the individual n_- contributions are strictly equal, for **2** the n_- DBO (DBH) clearly dominates in the HOMO (HOMO-1), as expected from the respective Ips.[5g] The calculated energy difference corresponds well with PE data of **1a** [$\Delta IP_{vert.}$(HOMO,HOMO-1) = 0.17 eV (calc.), 0.3 eV (exp.)], the bonding combinations of n_- orbitals lying above the antibonding combinations indicating TB interaction. TS interaction is expressed by splitting of the N=N π orbitals, e.g. the LUMO results from in-phase combination of N=N π_- combinations. In view of the orbital ordering in the analogous C=C/C=C (**I**) and C=C/N=N systems,[1]

Table 2. B3LYP/31G* model calculations for selected [3+2] and [3+3]cycloadditions (structural data (A), $\Delta\Delta G_R$ (kcal mol^{-1}); the thermodynamic parameters have been obtained through frequency analyses)



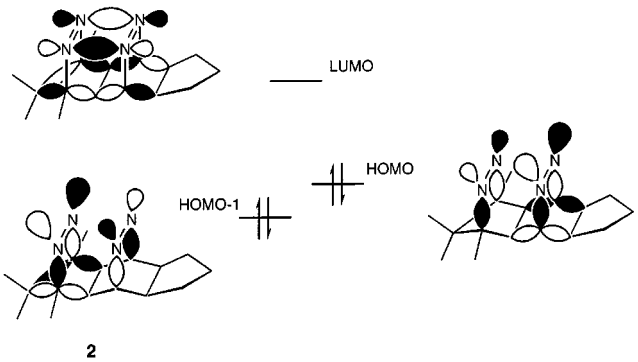
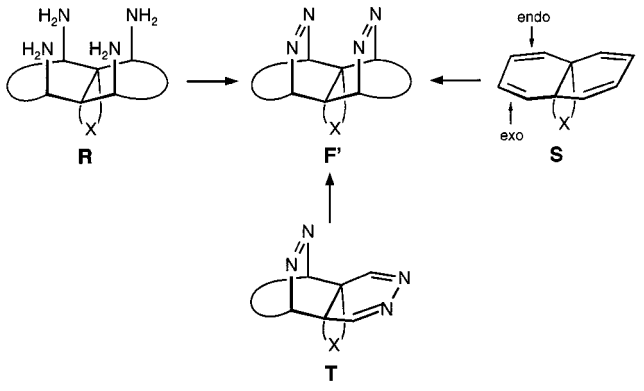


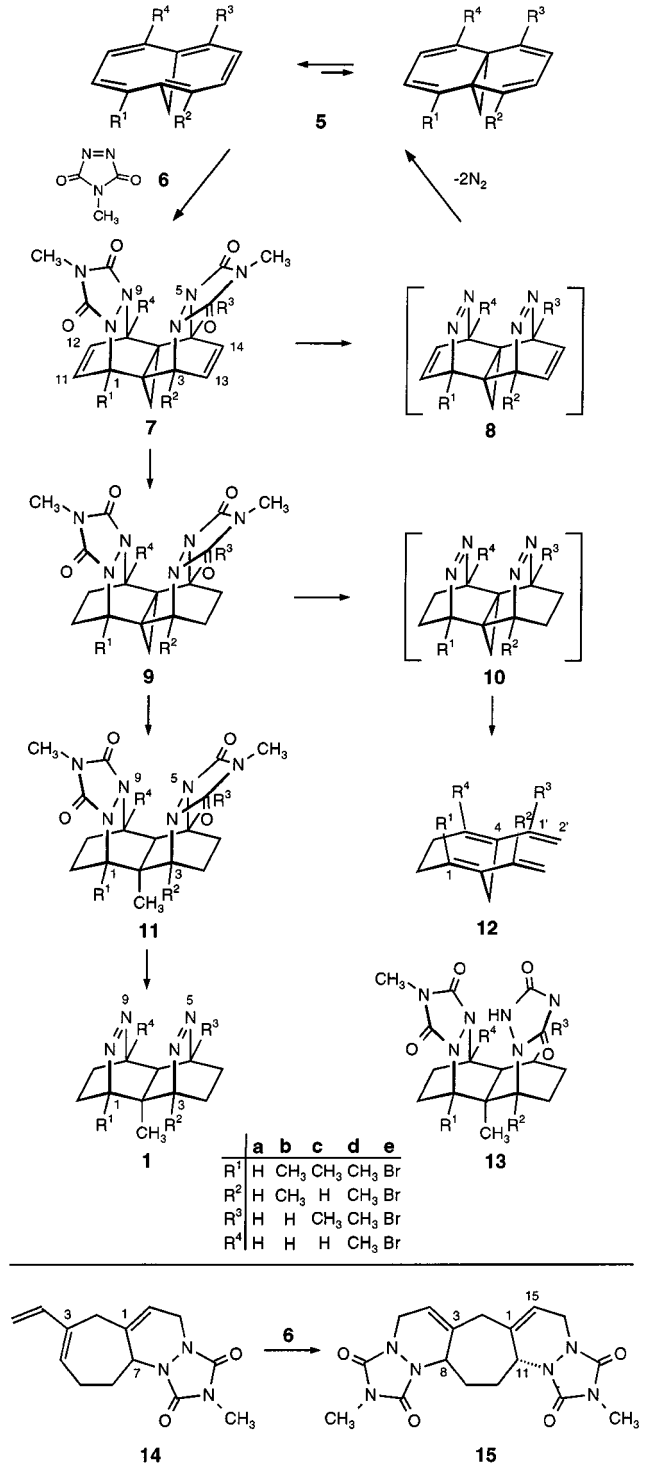
Figure 1. HOMO-1, HOMO and LUMO of bisdiazene **2** according to B3LYP/6–31G* calculations

[2+2]photocycloadditions in the bisdiazenes **F** could be expected. The energy of the highest occupied π orbitals of **1a** and **2** [made up by the out-of-phase combination of the two N=N π_+ orbitals (2.77 and 2.13 eV, respectively, below the HOMO's)] allow for an estimate of the $\pi \rightarrow \pi^*$ transitions occurring at ca. 200 and 230 nm. Particularly for **2**, a confirmation of homoconjugational interaction between the N=N chromophores would lie in energy transfer from a DBH to a DBO unit upon HOMO-1 $\rightarrow \pi^*$-excitation, being manifested in the former's resistance towards N_2 elimination. It has to be emphasized that the PE analysis of **1a** by Heilbronner, supported by model calculations, leave only little room for TS interaction. From PE spectra of the corresponding N=N/C=C systems with their high propensity for [2+2]photocycloaddition,[1] Martin and Hünig had determined significantly higher interaction parameters (–0.56 to –0.80 eV).[15] Clearly, doubts as to any correlation between these parameters and the efficiency of [2+2]photocycloadditions are justified.[4g]

Syntheses

"Proximity", particularly when it comes to through-space distances far below the van der Waals distances as in the **F**(**F'**) skeletons, has its price: besides the costs in energy and strain, it is the intervention of TS bond formation (or here of N_2 elimination) which poses problems all along the synthetic routes. In fact, there are good reasons why no such ″proximate″ bisdiazene had been described before. For the construction of the **F'** skeletons three alternatives had originally been considered: (i) N=N double bond formation through oxidation of *all-syn*-tetramines **R** prepared from the readily available dienes **I**. (ii) Twofold *endo*-[4+2]cycloaddition of an appropriate N=N dienophile to [4.4.X] propellatetraenes **S** in close analogy to the sequence worked out for *syn*-N=N/C=C skeletons.[1] (iii) [4+2] Cycloaddition of an ene-dienophile to diazene/dihydropyrazines of type **T** in analogy to the preparation of ene/diazenes (Hünig).[16] The first approach (**R** → **F'**) was given up when already in early stages the incorporation of four proximate functionalities caused too many complications. In the end, the second alternative (**S** → **F'**) led to the bisdiazenes **1** (**3**, **27**), while the third alternative (**T** → **F'**) provided the bisdiazene **2**.





Scheme 1

F_{22}-bisdiazenes (**1a**–**d**) (Scheme 1). The synthetic potential of the [4.4.X]propellatetraenes **S** turned out to be very limited, when in several such propellanes, even with sterically demanding X-blades, no twofold *endo*-addition of the synthetically required N=N dienophile **6** (*N*-methyl-1,2,4-triazoline-3,5-dione) could be achieved, except with the propellanes with X = CH_2, O, NH. Application of the cyclopropa-propellane **5** (X = CH_2, nearly quantitative

yield of **7a**, Ginsburg[17]), however, meant that intermediate stages such as **8** and **10** would presumably suffer from very rapid, cyclopropane-assisted elimination of N_2 ([2+2+2]).[1][18] In fact, oxidative hydrolysis of the face-to-face fixed urazole rings in **7a** required forcing conditions and led via **8a** neatly back to **5a**; and in the case of **9a** via **10a** to tetraene **12a**. Hydrogenolytic cleavage of the central cyclopropane C–C-bond in **9a** to give the methyl group of **11a** was a self-suggesting way out of this dilemma. Yet, because of the very congested situation, this evolved into a challenging task. It was only after extensive optimization that under very forcing conditions (80 °C, 300 atm H_2, huge excess of catalyst) the desired **11a** could be obtained in a reproducible, acceptable yield (70–75%, g scale); partial hydrogenolytic C–N cleavage to give **13a** (up to 15%) had to be accepted. Subsequent oxidative hydrolysis yielded **1a**, isolated chromatographically in a reproducible 80% yield (g scale).

The reductive opening of the cyclopropane ring meant reduction in symmetry. Attempts to avoid this repeatedly felt drawback, e.g. in the *N*-oxidation study,[12] by making recourse to the bisurazoles of type **9** with an epoxy(aziridine) instead of the cyclopropane ring, proved futile. No means were found for appropriate conversions of the sterically blocked hetero 3-membered rings.[5d]

The oily bisvinyl-cycloheptadiene **12a** was transformed into crystalline derivatives by treatment with **6** to give first the [4+2] adduct **14** which added a second molecule of **6** in an *anti*-fashion to give the C_2 symmetrical bisadduct **15**.

The yellowish crystalline, C_s-symmetrical bisdiazene **1a** survived heating up to its high melting point of 231 °C. N=N stretching absorptions were found at 1525 and 1475 cm^{-1}. In the six (seven) line $^1H(^{13}C)$ NMR spectra (Figure 3), the shifts of the bridgehead protons and carbons, as well as the shift difference for the *syn*/*anti*-CH_2CH_2 protons, are a result of the anisotropic influence of the N=N double bonds. In the UV/VIS spectrum (Figure 2), to be compared with that of the DBO subunit [$n \rightarrow \pi^*$ (CH_3CN) = 376 nm; $\pi \rightarrow \pi^* < 210$ nm, Table 1 in ref.[1]], the $n \rightarrow \pi^*$ transition at 385 nm (CH_3CN, $\varepsilon = 236$) is redshifted by 8 nm; a distinct $\pi \rightarrow \pi^*$ maximum at 239 nm (shoulder at ca. 260 nm) can be taken as evidence for homoconjugational N=N/N=N interaction.

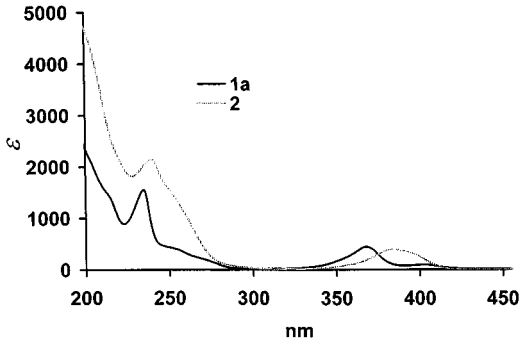
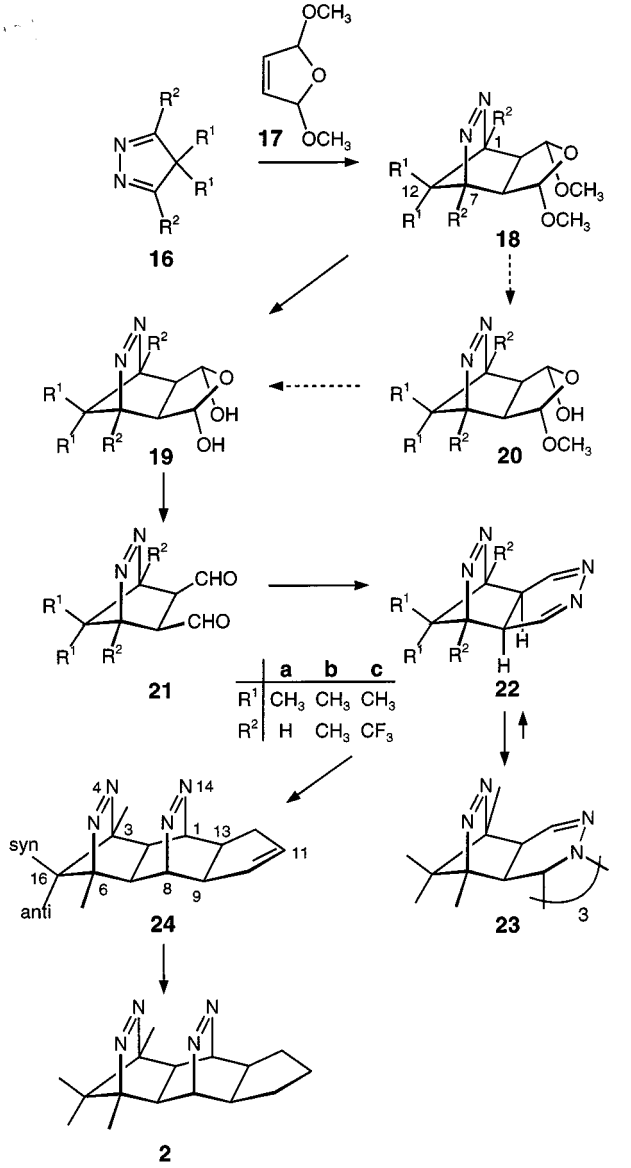


Figure 2. UV/Vis absorption curves of **1a** and **2**

Analogously, with use of the dimethyl- and tetramethylmethanoannulenes **5b–d**[19], the synthesis of the twofold and fourfold bridgehead-methylated bisazo skeletons **1b–d**, respectively, was pursued. Prior attempts to effect e.g. fourfold bridgehead bromination **1a** → **1e** (as practised with homologs of **3** which were not *anti*-Bredt protected [5c]) had not been successful. Originally there was hope that the bridgehead methylation would not only cause a shortening of the transannular π,π distance in **1b–d** and exert a stabilizing influence upon the respective tetrazetidine photoproducts, but would also make the cyclopropane-bisdiazene intermediates **10b–d** manageable. However, after oxidative saponification of the bisurethanes **9b–d**, the bisdiazenes **10b–d**, like **10a**, proved to be kinetically too labile to be isolated, rapidly losing N_2 to give tetraenes **12b–d**. Therefore unavoidable hydrogenolytic scission of the central cyclopropane bonds in **9b–d** (which were sterically even less accessible than in **9a**) allowed only for modest yields of **11b–d** (40, 38, 31%). The transformations **11b–d** → **1b–d** also suffered from increasing alkylation (55, 17, 19%), and the amounts of material at hand were only sufficient for explorative photochemical experiments.

F*$_{12}$*-Bisdiazenes (2) (Scheme 2): Ultimately, the successful route[4k] to **2** meant replacement in the Hünig procedure[15] of cyclopentadiene by 4*H*-pyrazoles **16** with the weakly reactive *cis*-1,4-dimethoxy-dihydrofuran **17** as dienophile. The simplest 4*H*-pyrazole not able to undergo tautomerization to the more stable 1*H*-pyrazole, the 4,4-dimethyl derivative **16a**, trimerizes and hence has to be liberated by acids in order to undergo [$\pi_{4s} + \pi_{2s}$]cycloaddition. For cycloadditions with *cis*-**17** (utilized as a ca. 1:2 mixture with its unreactive *trans*-isomer) **16a** was unsuitable as **17** proved to be too acid-sensitive. The tetramethyl pyrazole **16b** is kinetically stable as a monomer, but is also such a poor diene that it only adds to extremely reactive dienophiles;[20] various catalysts ($LiClO_4$,[21] $MgCl_2$, CuCl) could not induce the addition of **17**. The dimethoxy-bis(trifluoromethyl)-pyrazole **16c**, kindly examined by Seitz and coworkers,[22] delivered the stereochemically uniform adduct **18c** in a nearly quantitative yield based on consumed *cis*-**17**; yet, the given deactivating substitution pattern prohibits hydrolysis to dialdehyde **21c**, and the isolated hemi-acetal **20c** did not react with (anhydrous) hydrazine;[1] presumably strong internal F-HO hydrogen bonds in **20c** are responsible for this resistance. In this situation, recourse was made to the high-pressure reaction of **16b** with **17**. With help by Klärner and Hochstrate, and with optimization on our own, a protocol was worked out (65 °C/13.5 kbar, 12 d) which furnished crystalline **18b** in a reproducible 70–75% yield (g scale, stereochemistry proven by X-ray structural analyses, Figure 3, ref.[12]).[23] Differently from **18c**, the hydrolysis of **18b** into **19b** was complete after boiling in 0.2% aqueous H_2SO_4 for a short time. Treatment of a CH_2Cl_2 solution of **19b** with anhydrous hydrazine in the presence of K_2CO_3 led neatly to a mixture of trimers **23b**, which was directly exposed to a very large excess of cyclopentadiene at +4 °C for 16 h (500 equiv./1.3 equiv. CF_3CO_2H); larger amounts of acid and longer reaction times lowered the 58–

62% yield of **24** by favoring the expulsion (-[4+2]) of pyrazole **16b**. The catalytic hydrogenation **24** → **2** also affected the N=N double bonds; blowing a stream of air into the reaction solution in the presence of the catalyst converted the mixture into pure **2** (in total 52–59% based on **18b**).



Scheme 2

Pure yellowish crystalline **2** decomposed with its melting at 266 °C. In the ^{1}H NMR-analysis (Figure 3) the N=N double bonds are responsible for typical *syn-/anti-* shift differences (e.g. $\delta_{16\text{–Me}syn} = 0.39$ vs. $\delta_{16\text{–Me}anti} = 0.78$). In the UV absorption curve (Figure 2), the $n \rightarrow \pi^*$ maximum at 368 nm ($\varepsilon = 435$) is redshifted by 10 nm vis-à-vis the averaged DBH/DBO maximum (358 nm), the $\pi \rightarrow \pi^*$maximum at 234 nm (shoulder at ca. 260 nm, $\varepsilon = 1580$; cf. DBH/DBO $\lambda_{max} < 210$ nm) is practically that of **1a**, and is suggestive of a comparable degree of N=N/N=N homoconjugation.

H*$_{22}$*-Bisdiazenes (27c) (Scheme 3): For the bis-NMTD-adduct **7a**, but not for its C=C hydrogenated derivative, it had been found that simply by exposure to a 50% aqueous

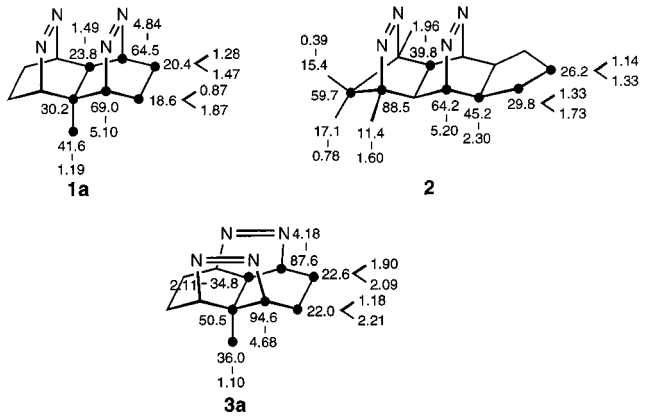
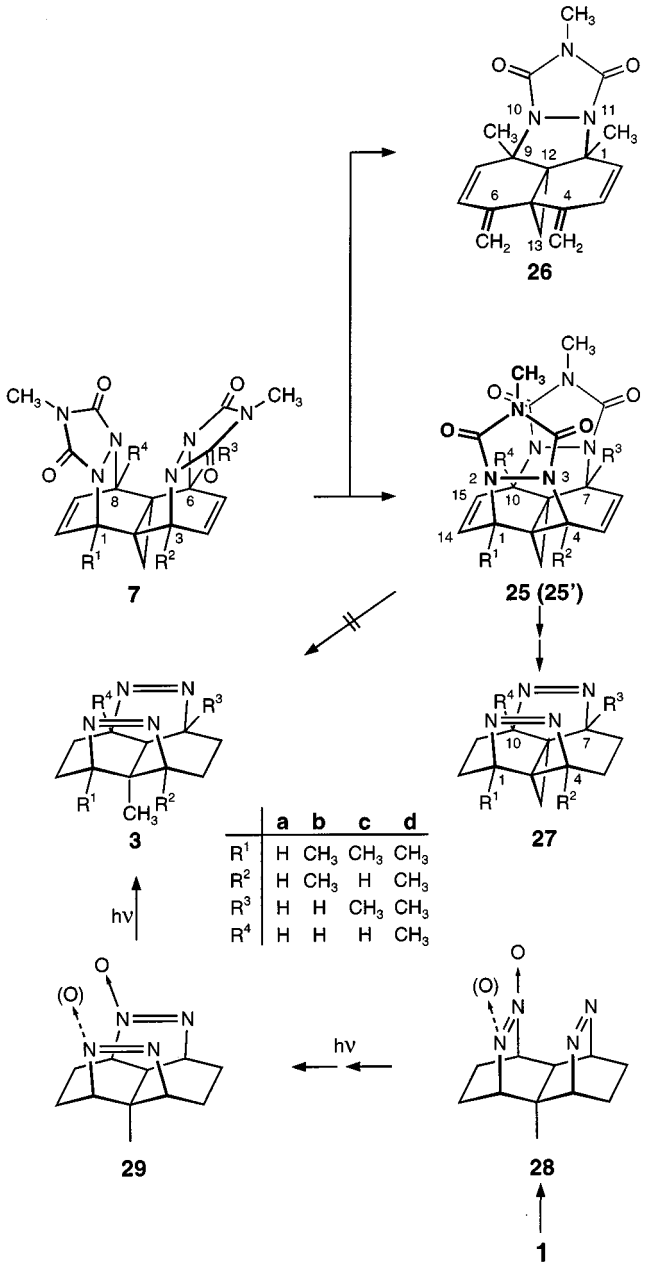


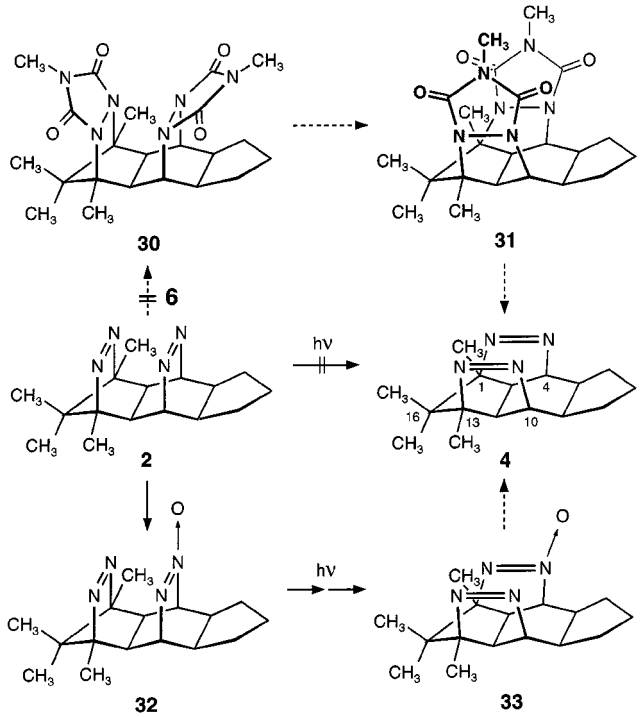
Figure 3. ^{1}H and ^{13}C NMR assignments for **1a**, **2** and **3a** ($CDCl_3$, δ, Hz)



Scheme 3

$H_2SO_4/CHCl_3$ two-phase system, a mechanistically highly complex but nevertheless uniform isomerization into the **H**-isomer **25a** occurs. Thus, subsequent hydrogenation and oxidative hydrolysis had opened a practical access to the cyclopropanated $\mathbf{H_{22}}$-bisdiazene **27a**. Yet, all efforts to transform **25a** into **3a** analogously to **7a** → **9a** → **11a** → **1a** ended in failure.[4i][5b] The attempts to analogously transform **7b**–**d** into the bisdiazenes **27b**–**d** were only partially successful. The response of **7b**–**d** to the two-phase acid system unfolded an influence of the alkylation patterns which was not obvious: **7b** delivered a complex product mixture of at least ten components, which was not further analyzed, **7c** nearly quantitatively the wanted **25c**, and **7d** preferentially (60%) the bismethylene-urazole **26**. Through catalytic hydrogenation (**25c'** in the Experimental section) and oxidative hydrolysis, the 1,7-dimethyl-cyclopropa-bisdiazene **27c** was obtained.

An alternative access to **3a** seemed opened with the finding, to be discussed in the subsequent paper (Scheme 5),[12] that the *N*-oxides of **1a** (**28**) undergo "photometathesis" to **29** and that for the latter, deoxygenation to **3a** is at least a minor pathway (5–7%).[4a] However, the hopefully more productive chemical deoxygenation **29** → **3a** could not be selectively effected in spite of intensive efforts with several reagents successfully applied to diazene oxides lacking α-protons.[24] The UV absorption of **27c** is practically that of unstrained pyrazoline rings[5c][5d] – in line with a π,π distance of >4.8 Å (Table 1, $\mathbf{H_{22}}$); with only a small bathochromic displacement of the $n \rightarrow \pi^*$ absorption vis-à-vis **27a**, the buttressing effect of the bridgehead methyl groups is only marginal.



Scheme 4

H_{12}-Bisdiazenes **(4)** *(Scheme 4):* The efforts to make use of bisdiazene **2** for the construction of its isomer **4** via the bisurazoles **30** and **31** seemed a priori critical in that **30** lacks the (homo) allylic activation of dienes **7**. This pathway ended abruptly when **2**, obviously for steric reasons, did not react with triazolinedione **6** to give **30**. The alternative sequence **2** → **32** → **33** → **4** (Scheme 6 in ref.[12]), patterned after **1a** → **28** → **29** → **3a**, failed again in the deoxigenation step; photochemically (rapid loss of N_2) or chemically[24] competing reactions prevented even mg quantities of **4** from being obtained from **33**.

X-ray Structural Analyses of 1a, 2 and 25c[25]

Crystals of **1a**[4a] and **2**[4k] grown from ether (**1a**) or by diffusion of ether vapor into a $CHCl_3$ solution (**2**) proved thermally and photochemically stable enough for X-ray

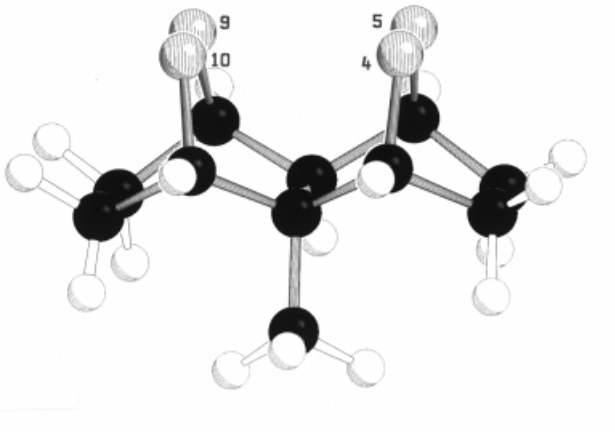


Figure 4. ORTEP plot of **1a**

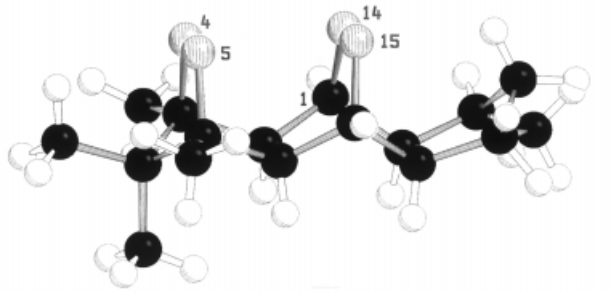


Figure 5. ORTEP plot of **2**

structural analysis. The bond lengths (Figure 4 and Figure 5) were found to be normal; particularly the N=N double bonds (av.: 1.249 and 1.251 Å) are very close to the 1.255(4) Å measured for DBO at –165 °C,[26] and the 1.2553(15) Å determined for **18** (Figure 2 in ref.[12]).[5g] The four nitrogen atoms of **1a** lie within 0.004 Å in a common plane. For **2**, this arrangement is perfect as the molecule is bisected by a crystallographic plane (half a symmetry-independent molecule per unit cell). The π,π distances of **1a** (av. 2.849 Å) and of **2** (2.822 Å) are far below van der Waals contact, with interorbital angles ω of ca. 168.6° (**1a**) and 174.2° (**2**). The π orbitals in **2** are almost perfectly *syn*-periplanar. In **1a** steric compression between the methyl and the 11a(13a)-hydrogens [d = 2.17(2.15) Å] exerting a buttressing effect upon the N=N double bonds is manifested

in a slight shortening of the N4-Nl0 distance (by 0.056 Å). Similarly in **2**, the short H/H distances 2(7)-H/13(9)-H and 16a-H/2(7)-H reflect a buttressing influence of the geminal 16-CH_3 groups.

The X-ray structural data of **1a** and **2** were part of the reliability tests for the B3LYP calculations.[5g] As a demonstration, the experimental data of **2** with those obtained from various calculation methods are listed in Table 3.

Table 3. Comparison of selected experimental distances (Å) and interorbital angles (°) of bisdiazene **2** with the values calculated at different levels of complexity

	Exp.	AM1	PM3	HF/6–31G*	B3LYP/6–31G*
N4–N5	1.248(3)	1.221	1.226	1.216	1.247
C3–N4	1.502(2)	1.529	1.532	1.481	1.505
N14–N15	1.254(2)	1.216	1.223	1.218	1.249
C1–N14	1.482(2)	1.496	1.504	1.469	1.487
N4–N14	2.822	2.856	2.916	2.854	2.827
C11–N14	3.181	3.389	3.409	3.194	3.203
C16–N4	2.907	2.946	2.942	2.891	2.911
C3–N4–N5	108.97(8)	110.01	109.70	109.53	109.13
C1–N14–N15	114.84(7)	115.90	115.86	115.51	115.03
ω	174.2	172.4	170.8	173.2	174.8

Attempts are still underway to obtain crystals of a **H**-bisdiazene (**3**, **27**). So far only for precursor **25c**, crystallized from methanol, can X-ray structural data be presented (Figure 6). The pyramidalization angles of 42–53° at the four nitrogen atoms and the transannular N–N distances of 4.10 (3.95) Å (cf. d = 4.80–4.87 Å for $\mathbf{H_{22}}$-bisdiazene in Table 1) represent the molecular compromise in dealing with destabilizing transannular urazole/urazole interactions.

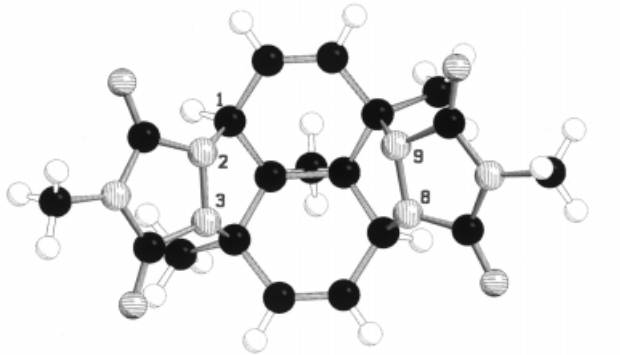
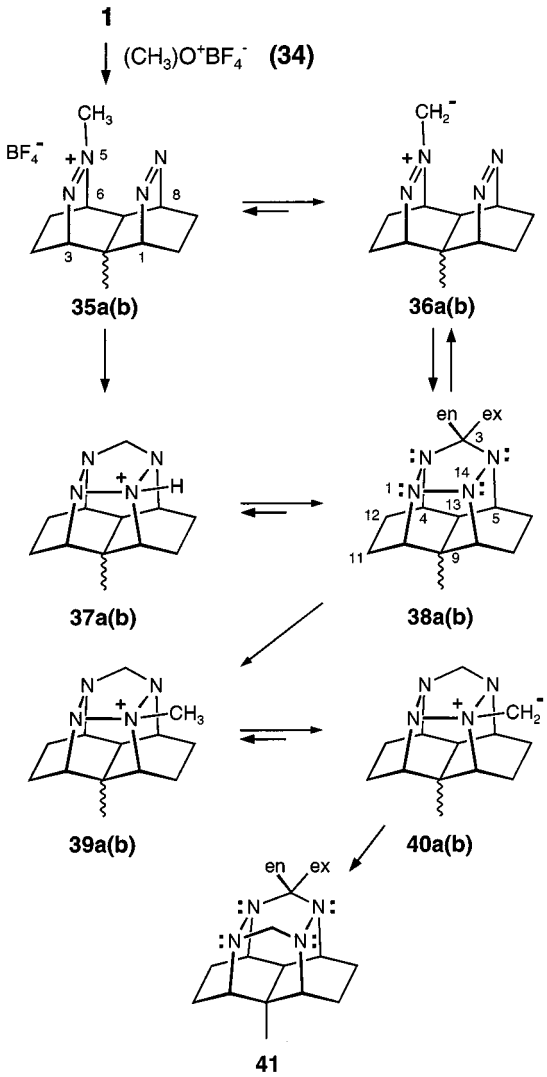


Figure 6. ORTEP plot of **25c**

Homoconjugate Reactivity – Cycloadditions – Metal Complexes

The calculations regarding the formation of the novel heterocycles **C** (Table 2) through internal [3+2]cycloadditions in appropriate derivatives of bisdiazenes **A** were fully confirmed: Tetrazolidines $\mathbf{C_C}$ and perhydro-tetrazolidines $\mathbf{D_C}$ of remarkable stability, (but not, however, pentazolidines $\mathbf{C_D}$, oxatetrazolidines $\mathbf{C_O}$ and terahydro-dioxatetrazines $\mathbf{D_O}$) became accessible. It should be recalled that linear and not specifically substituted tetrazanes readily suffer cleavage of the central N–N bond to hydrazine radicals.[27]

Tetrazolidine **38a** (methyl group in front) [the **b**-isomer (methyl group at the back) is clearly less stable] was approached following the protocol successfully applied to the azomethine/ene cycloaddition[1][28] – by methylation (**35a,b**) and deprotonation (**36a**,**b**) (Scheme 5). In the preparative protocol ultimately followed, bisdiazene **1a** was treated with equimolar amounts of trimethyloxonium tetrafluoroborate (**34**). The crude, complex mixture of salts and **1a** was fractionally crystallized, and the main fraction (50–60%, **37a**) was exposed to the $K_2CO_3/H_2O/CH_2Cl_2$ two-phase system. Isomerically pure, colorless, crystalline **38a** was thus isolated in 90% yield (based on **37a**).[29]



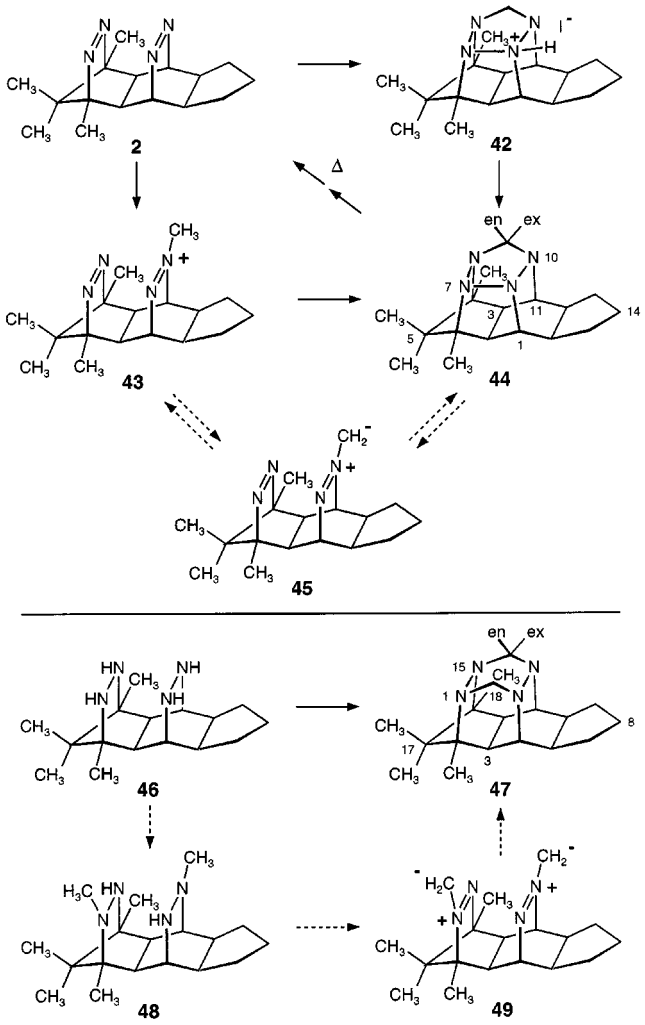
Scheme 5

^{1}H NMR controlled experiments in [D_6]DMSO with an increasing excess of **34** (the yield of **38a** decreasing substantially) revealed a very complex equilibrium scheme between **1**, the protonated **37a**(**b**) (45–50%, ca. 1:10), and the methylated tetrazolidinium salts **39a**(**b**) (12–15%). There is strong evidence that the [3+2] addition **36a** → **38a** is endergonic but becomes exergonic after protonation to give **37a** (contrasting $\Delta\Delta G_R$ = –9.6 kcal mol^{-1} for **M** → $\mathbf{C_C}$ in Table 2). After workup of such mixtures (treatment with base and

chromatography at 0 °C on silica gel, pretreated with triethylamine, or on Alox) only **38a** had survived together with one trace component, presumably perhydro-1,2,4,5-tetrazine **41** (^{1}H NMR).

Colorless, crystalline tetrazolidine **38a**, *all-cis*-alkylated, with four pairs of n-electrons on the same molecular side [cf. the length (1.628 Å) of the central N–N bond of $\mathbf{C_C}$ in Table 2] proved stable enough for isolation but was highly oxygen-sensitive: In acid-free $CDCl_3$-solution the half-life at room temperature is up to ca. 4 d (^{1}H NMR). The UV spectrum (CH_3CN) shows an absorption curve rapidly falling from 200 to ca. 240 nm; the yellowish coloration (λ_{max} ca. 270, 340, 370 nm) developing upon standing in incompletely deoxygenated solution is indicative of rapid oxidation.[30] In all experiments, no bis(methyl-diazenium) salt (cf. $\mathbf{Q_C}$ in Table 2) could be detected; formation of **41** via ylide **40a** is therefore probable. Perhydrotetrazine **41**, of great interest for the 4*N*-ion project as a conformationally immobilized, peralkylated bishydrazine,[7c] turned out to be too labile to be isolated.

For the preparation of tetrazolidine **44** [not for **38a(b)**], methylation of bisdiazene **2** (Scheme 6) with $CH_3I/CHCl_3$/25 °C (**43**) became the first choice when the tetrazolidinium iodide **42**, formed very slowly, after 6 d at 25 °C had nearly quantitatively precipitated without any intermediate diazonium or hydrazonium ion being detectable (NMR).[5g][7c] After treatment with the two-phase base system $K_2CO_3/H_2O/CH_2Cl_2$ the colorless, amorphous tetrazolidine **44** was nearly quantitatively isolated as colorless oil. The NMR probe of **44**, when kept at room temperature showed no change after 4 d; even at 50 °C only very slowly ($t_{1/2}$ ca. 3.5 d) did bisdiazene **2** appear, besides nearly equal amounts of perhydro-1,2,4,5-tetrazine **47**. As in case of **41**, formation via CH_2-transfer (from **45** to **44**) rather than via [3+3]cycloaddition is suggested. Compared with **38a** and **41**, the carbon skeletons of **44** and **47** confer a significantly higher thermal stability. Like **38a**, tetrazolidine **44** is highly oxygen-sensitive; when recording the UV spectrum in CH_3CN which is not totally oxygen-free, long-wavelength maxima of secondary products appeared (340, 364 nm, yellowish color).



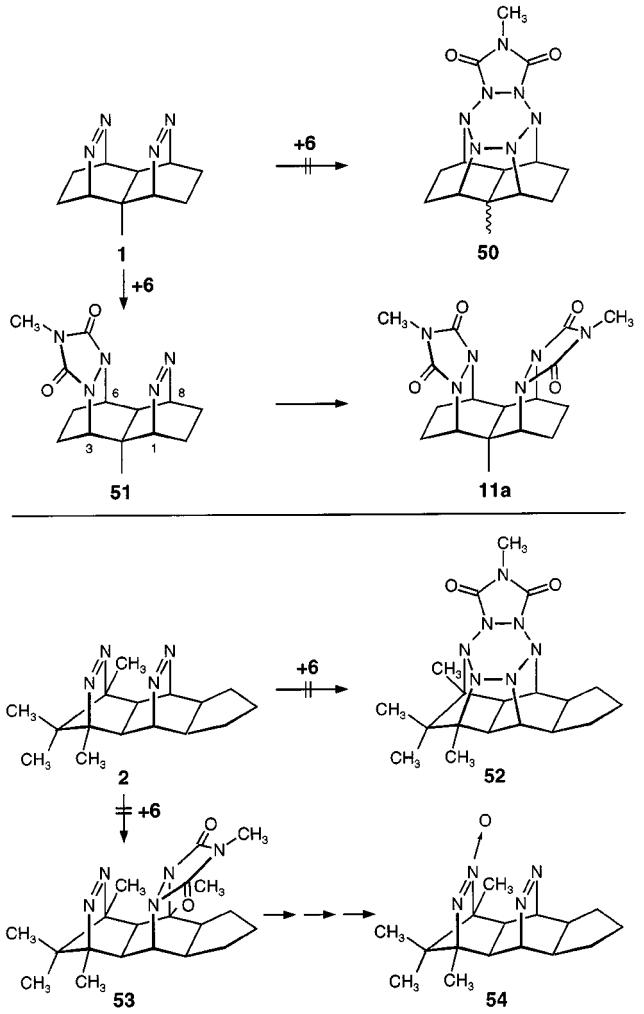
Scheme 6

For the preparation of perhydrotetrazine **47**,[7c] a serendipitously discovered two-step process consists of catalytic hydrogenation (Pt) of **2** to bishydrazine **46** and treatment with the MeI/K_2CO_3/refluxing MeOH system (40%). The oxidation involved presumably occurred in dimethylated bishydrazine **48** by oxygen/traces of Pt metal from the hydrogenation or by I_2 generated by decomposition of MeI. [3+3]Cycloaddition **49** → **47** is probable ($\mathbf{P} \rightarrow \mathbf{D_C}$ in Table 2). In the optimized protocol (up to 80–90%) bishydrazine **46** is treated with a vast excess of CH_2Cl_2/K_2CO_3 (25 °C, 4 d). Pure oily samples of **47** slowly solidified to an amorphous mass that liquefied and decomposed upon heating beyond ca. 130 °C; in air, like the tetrazolidine **44**, it is prone to oxidation.[30]

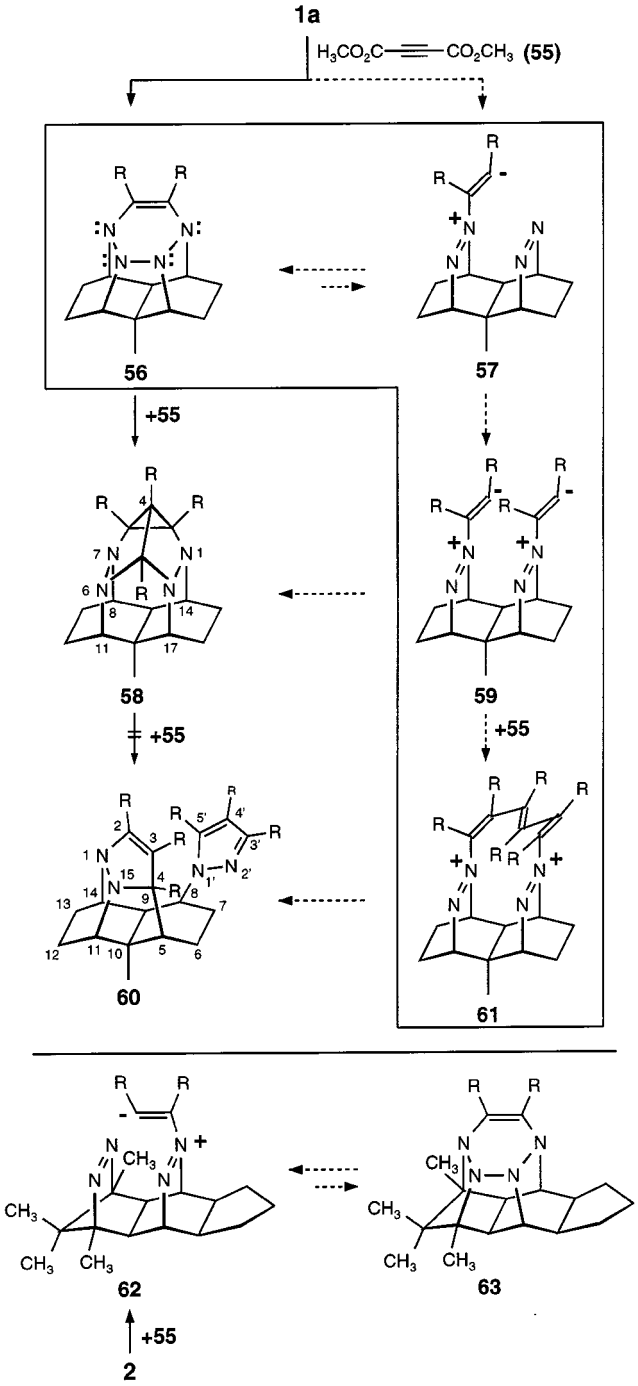
For the CH_2 protons of the rigid envelope-type configuration of the tetrazolidine units in **38** and **44** (cf. the X-ray structure of the related oxadiazolidine in Figure 1 of ref.[1]) the ^{1}H NMR spectra show distinctly different shifts ($\Delta\delta$ = 0.39 and 0.67) with coupling constants of J = 11.5 and 11.0 Hz, respectively. In the case of the boat-like tetrazine ring in **47**, the CH_2 shifts vary even more ($\Delta\delta$ = 1.56) and the coupling constants are expectedly larger (15.5 Hz).[31]

Intensive efforts have been devoted to the construction of N=N/N=NNR systems of type **N** in Table 2 as potential precursors of thus far unknown pentazolidines $\mathbf{C_N}$. To summarize, in line with the calculated endothermicity, no such cycloaddition has been realized;[5a–5h] the corresponding N=N/N=NO systems are presented in the subsequent paper.[12]

With triazolinedione **6** (Scheme 7) as π_2 component, bisdiazene **1a** in boiling $CHCl_3$ reacted smoothly. However, reaction in the [2+2+2] fashion to give the most intriguing perhydrohexazine **50** did not occur, but transamidation took place to give urazole **51**, which changed under more forcing conditions ($CHCl_3$, 100 °C, sealed ampoule) into **11a**, the intermediate in the synthesis of **1a** (Scheme l). This outcome is in full agreement with the behavior of the comparably-structured N=N/C=C substrates.[5a] As a further discrepancy to **1a**, **2** proved resistant towards **6** up to temperatures of total decomposition; the urazole **53** resulting



Scheme 7



Scheme 8

from selective attack of **6** at the DBO unit had been sought after in the pursuit of the "DBH oxide" **54** (isomer of **32**).[12]

With the acetylenic dienophile **55** (DMAD), in contrast to the (formal) [2+2+2]cycloaddition to the model diazene/ene,[1] but in line with a rapid subsequent DMAD addition (cf. **17** → **41** → **43** in Scheme 6 of ref.[1]), the tetrahydro-1,2,3,4-tetrazines **56** and **63** as the (formal) [2+2+2]adducts could also not be obtained. In the case of **1a**, it can only be speculated that **56** functions as the thermodynamically (kinetically) disadvantaged intermediate on the way to the two products isolated (besides mainly oligomers of **55**): The C_s-symmetrical 1:2 adduct **58** and the unsymmetrical l:3 adduct **60**. With the use of one (two) equivalent(s) of DMAD, **58** and **60** were isolated in ca. 1:3(4) ratio in a total 40–60% yield, whereby the major component **60** was shown not to arise from **58** (Scheme 8). From a bisylide such as **59** a reasonable pathway leads to the tetraazasemibullvalene subunit of **58**. Formation of **60** is obscure: In a potential intermediate such as **61** interruption of one acetylenic unit and of a skeletal C–N bond is required.

Differently from **1a**, when bisdiazene **2** was treated even with a very large excess of DMAD at 25 °C (in line with the formulation of **57** as primary intermediate for **1a**) a nearly quantitative yield of the 1:1 ylide **62** was obtained. The latter decomposed upon heating before cyclization to tetrazine **63** could occur. It can be speculated that the absence of higher adducts (cf. **58**, **60**) (with the tetrazine **63** being energetically a more probable equilibrium participant than **56**) is due to the steric resistance of the DBH part in **62** to add **55**. This would be an argument against **56** as an intermediate leading to **58** and **60**.

The $^1H/^{13}C$ NMR analyses for bisadduct **58** (Figure 7) were straightforward, but for trisadduct **60** very extensive H,H, C,H and C,C decoupling experiments and COSY-2D

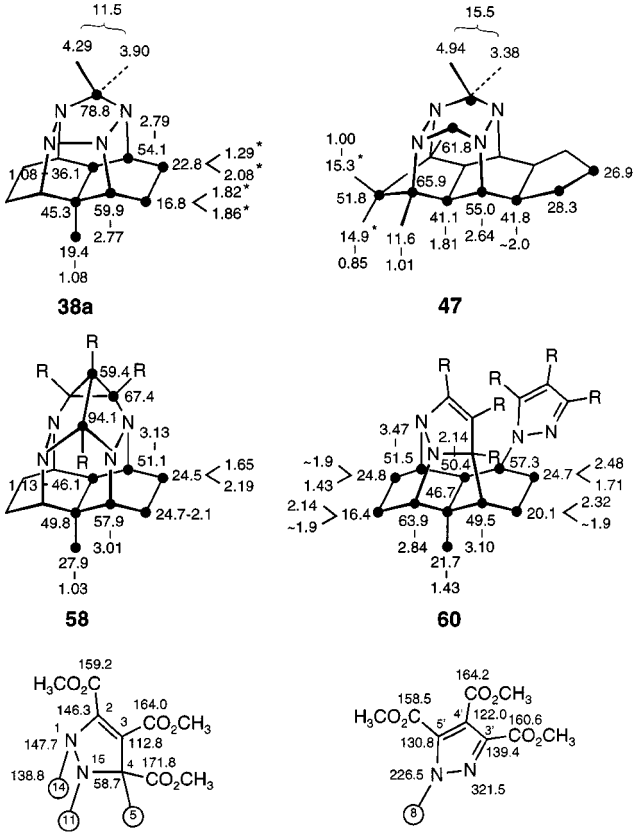
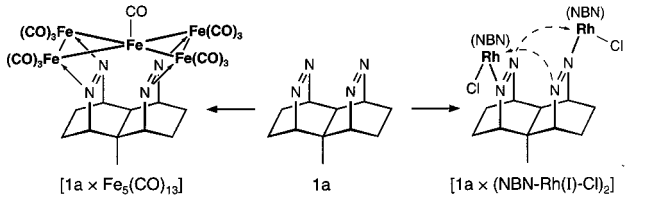


Figure 7. ^{1}H and ^{13}C NMR assignments for **38a**, **47, 58,** and **60** ($CDCl_3$, δ (ppm), J (Hz)).

NMR analyses were needed. Important details for the latter are: the fully established interconnectivities in the perhydronaphthalene part; the scission of a C–N bond with C-5 not being bonded to N any more; and the identification of the pyrazoline/pyrazole rings with their typical ^{15}N shifts.[32] With respect to **58**, an uncertainty had remained as to the position of the methyl group (**a**, **b**). Given the unequivocal assignment for **60**, structure **58** is correct.

Diazenes are known as 2-, 4-, and 6-electron ligands.[33] With the intention to assist N=N/N=N photocycloaddition **A** → **B** by bridging the two diazene units, rigid bisdiazene **1a** – as well as parent $\mathbf{H_{11}}$ diazene and cyclopropanated $\mathbf{H_{22}}$ diazene – were studied for their complexing potential.[4i][5a][5d] Only for **1a** had a bridged complex [**1a*** $\mathbf{Fe_5(CO)_{13}}$] been obtained with the unusual feature of five metal atoms lying in a common plane.[4d] Searching for complexes of **1a** which might be amenable to double bridging[5d] e.g. by internal substitution or thermal activation,[34] an initially promising complex was found when **1a** was treated with norbornadienyl-rhodium(I) chloride dimer in boiling CH_3CN.[5g] From the deeply red solution, black crystals of composition **1a*(NBD-Rh(I)-Cl)$_2$**, suitable for X-ray analysis (Figure 8),[25] deposited upon cooling to room temperature. The geometrical parameters of **1a** are only slightly changed upon complexation; the N=N double bonds are expectedly somewhat larger. Initial attempts to bring about the admittedly critical bridging substitutions have not been successful.



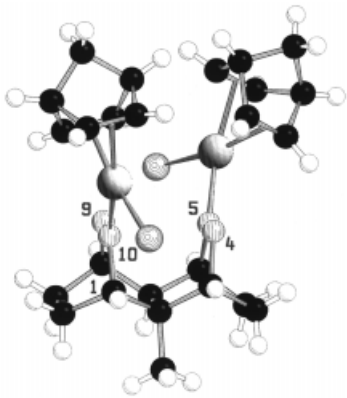
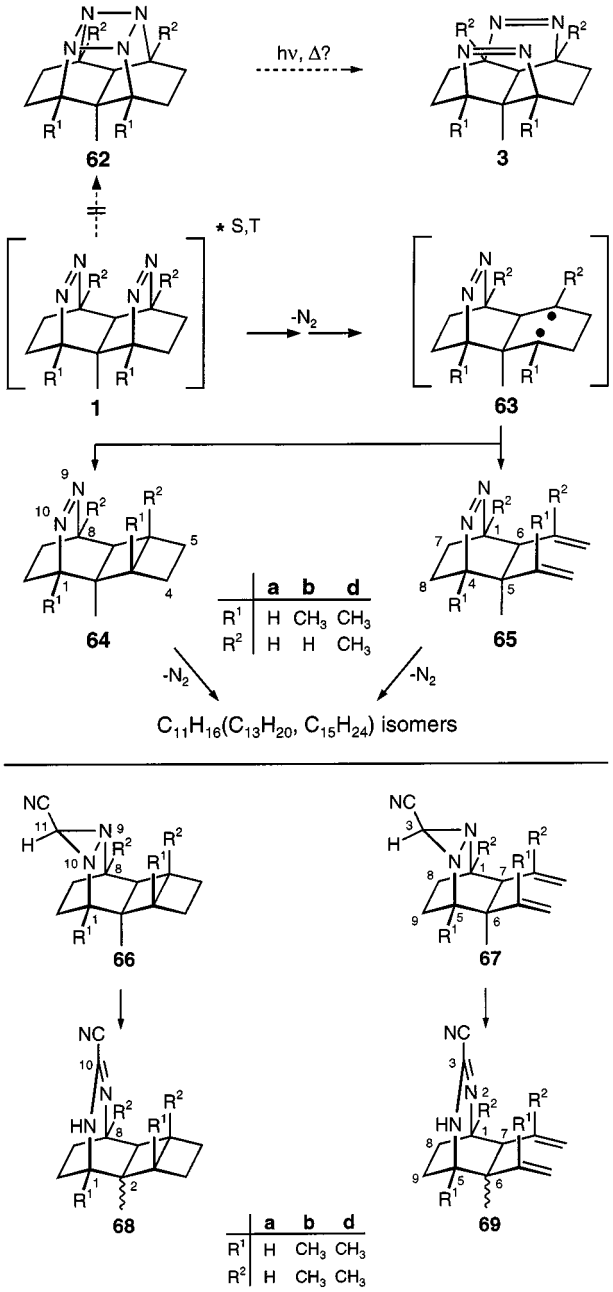


Figure 8. X-ray crystal structure analysis of the **[1a*(NBD-Rh(I)-Cl)$_2$]** complex.

Photochemistry[35,36]

The conditions used are those described in the preceding paper for the N=N/C=C systems:[1] For direct excitation ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$) polychromatic light of λ >280 nm (high pressure Hanau TQ 125 W lamp, Hanovia 450 W lamp, pyrex vessel) or monochromatic light of λ = 254 nm (low pressure Hg lamp, quartz vessel) was used; for sensitized excitation, acetone was used as solvent (λ >280 nm, pyrex vessel). Particularly for the 254 nm irradiations it has to be recalled that Φ_{-N2}(254 nm) for parent DBO and DBH is practically zero.

Bisdiazenes 1 (Scheme 9):[5a] Compound **1a**, as ca. 10^{-3} M degassed solution in CH_3CN, was exposed to the >280 nm and 254 nm light (down to –70 °C) or was irradiated in acetone. Continuous reaction control (TLC, MS, ^{1}H NMR with the CH_3 signal as sensitive probe) confirmed the rapid, initially exclusive, parallel generation of the monodiazenes **64a** and **65a**, which were both comparably rapidly deazatized to a mixture of $C_{11}H_{16}$ hydrocarbons. Small amounts of side-products were identified as the cyanoamidines **68a/69a**. From preparative runs taken to total conversion 50–60% of **64a** and **65a** (constant ratio of 1:1.3) were separated from polymers and, in CH_3CN, from ca. 8% each of the mixtures **68a** and **69a**. In an irradiation experiment (CH_3CN) with pure **65a** besides **69a** the diaziridine intermediate **67a** was secured. For the conversion of the intermediate diradical **63a** into **64a** and **65a** with retention of configuration numerous literature examples can be found.[35][36]

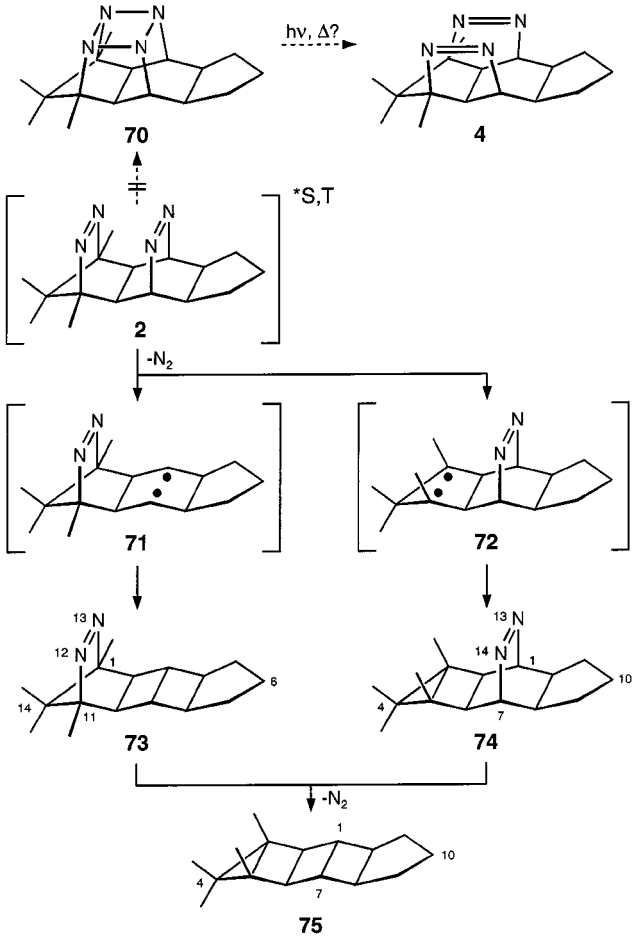


Scheme 9

The formation of diaziridines through formal addition of [CHCN] to N=N double bonds seems to be without precedent.

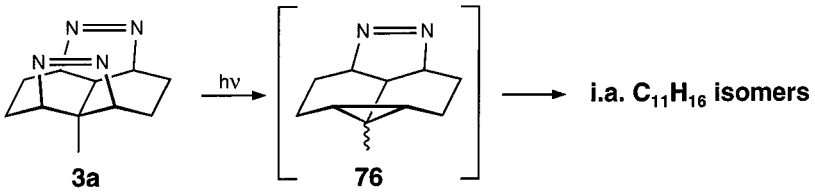
With bisdiazenes **1b** and **1d** only analytical, ^{1}H NMR-controlled experiments were performed. Upon direct as well as sensitized excitation they behaved like **1a**: Up to ca. 20% conversion only loss of N_2 was noted in the case of **1b** to **64b**/**65b** (ratio ca. 2:1) and in the case of **1d** exclusively to **64d** (traces of **65d** in acetone), which simply demonstrates the influence of the CH_3 groups upon the stabilisation pathways of the intermediate diradicals **63b**,**d**.[5e][35][36]

In collaboration with Profs. G. Kaupp (Oldenburg) and J. Wirz (Basel), matrix-irradiation experiments with **1a** were performed. Irradiation in 2-methyltetrahydrofuran at 83 K with monochromatic (λ = 405, 365, 254 nm) and polychromatic light (λ > 280 nm) only proved the stability of **1a** under these conditions. With an excimer laser (λ = 254 nm) as powerful light source, **1a** was slowly converted into a complex mixture of hydrocarbon products with no ^{1}H NMR signal being detectable for **62a** or **3a**. During irradiation of an EPA glass at 77 K with 254 nm light only slow depletion of **1a** was observable.



Scheme 10

Bisdiazene **2** *(Scheme 10):* Also as a test for the relationship between the DBO and DBH subunits in **2** a series of experiments with short and long wavelength light ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$) at various temperatures was conducted (Table 4). The main information: There was once again no hint for [2+2]cycloaddition (tetrazetidine **70**) or metathesis (isomer **4**); according to careful reaction control (TLC, MS, ^{1}H NMR) of the 254 nm experiments, the diazenes **73** and **74** were already at very low conversion of **2** (entries 1, 2) accompanied by the saturated pentacyclic hydrocarbon **75**. After ca. 70% conversion (entry 4), only 18% of **73** and 9% of **74** were left, a ratio clearly not representing the relative tendency for N_2 loss from the DBO and DBH parents. There is an activation barrier for the N_2 elimination from the DBO unit (entries 1, 3):[37] At –75 °C the formation of **74** is highly favored, while at +40 °C the formation of **73** is moderately favored. The >280 nm light (entries 5, 6) causes preferential N_2 elimination from the DBO part, again (cf.



Scheme 11

entry 4) evidence that the two N=N chromophoric units are not independent.

Table 4. Irradiations of **2** with 254 and > 280 nm light between –75 and +40 °C. Relative yields (%) based on conversion

Entry	*T* [°]	λ [nm]	Conv. [%]	**73** [%]	**74** [%]	**75** [%]
1	–75	254	33	13	83	traces
2	18	254	31	28	41	27
3	40	254	26	52	32	13
4	21	254	70	18	9	
5	21	>280	13	73	traces	20
6	21	>280	34	24	traces	71

*Bisdiazene **3a**:* The experiments with "distant" bisdiazene **3a** (>280 nm, 254 nm, DC, ^{1}H NMR, MS control) showed only the "parallel" appearance of several deazatization products (structure **76** being a possibility) and also of i.a. $C_{11}H_{16}$ hydrocarbons, besides mainly polymers (Scheme 11).

The NMR analyses of the photoproducts **64**, **65**, **73**, **74** and **75** (Figure 9) were much aided by the σ-symmetry be-

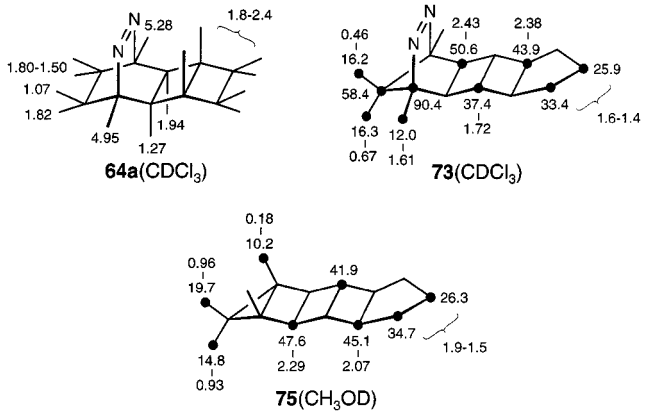


Figure 9. ^{1}H and ^{13}C NMR assignments for **64a**, **73** and **75** [$CDCl_3$, δ, *J* (Hz)]

ing retained. The *anti*-configuration around the central cyclobutane ring in **64a**, and hence retention of configuration in diradical **63a** at C-3(6), was based i.a. on the small vicinal coupling constant $J_{6,7} \leq 2.5$ Hz, but for **64b**,**c** the configuration was assumed for steric reasons. The point is stressed that in the UV spectra of these monodiazenes, between 210 and 250 nm no maximum (π → π*) is registered; the *n* → π* maxima are practically that of the DBO/DBH subunits. Typical of the *N*,*N*-dialkyl-cyano-diaziridine part in **67a** is the 3-H singlet signal at δ = 3.98 with the ^{13}C satellites ca. 190 Hz apart; the shown configuration was chosen for minimal steric demand. In the case of the isomers **69a**, differentiation was made by assuming a lower ^{1}H-shift for H–C=N than for H–C–N(H) and a ^3J coupling between the allylic (7-H) and the lower bridgehead hydrogen (l-H) only posssible for the isomer with the methyl substituent "in front".

Remarks

The $\mathbf{F_{22}}$ (**1**) and particularly the $\mathbf{F_{12}}$ (**2**) bisdiazenes, seemingly near to optimal substrates for N=N/N=N (2+2)photocycloaddition, have been constructed. The failure to observe the respective tetrazetidines (**62**, **70**) or the corresponding metathesis isomers (**3**, **4**) upon direct [*n* → π*, π → π*, down to 77 K (matrix)] and sensitized excitation is most probably not due to photochemical or thermal reversion of the photocycloaddition step – with the argument that these tetrazetidines, certainly transparent toward light of λ >280 nm, thermally should have undergone the kinetically- as well as the thermodynamically-favorable metathesis cleavage. This argument finds support in the photochemistry of the oxides derived from **1a** and **2,** which is detailed in the following paper.[12] As a prelude to the subject of *N*-oxidized tetrazetidines, reference is made to the fate of the 1,2-diazetidine-*N*-ylides pictured in Scheme 11 of ref.[1] and to our earlier, futile approach to tetrazetidines: When kinetically stabilized, *all-cis* alkylated triaziridines were treated with a nitrene (X = NCO_2CH_3), neither the N_3-*N* ylides nor the tetrazetidines were observable, with the former as the more probable intermediates en route to the isolated N=N/N=NR bisdiazenes. Similarly the formation of N_3-oxides (X = O) and N_3–C ylides (X = CH_2) had to be indirectly assessed through their N=N/N=O and N=N/N=CH_2 fragments.[38]

Of the initial goals defined with the polyazaheterocycles **C** – **E**, a few could be realized – in good agreement with the calculational explorations. Specifically the *all-cis* alkylated, corsetted tetrazolidines (**38**, **44**) (probably the first representatives of their type generated by N=N/N=NC cycloaddition) and perhydro-1,2,4,5-tetrazines (**47**) have become very valuable testing compounds in the "4*N*-ion" project (Summary and outlook in the following paper).[5c] The application of the bisdiazenes **1a** and **2**, and generally of bisdiazenes **A**, for the construction of special synthetic building blocks (e.g. *all-cis* tetramines, cf. the original synthetic approach **R** → **F'**) and of novel preoriented polyaza-ligands is being explored.[39]

Experimental Section

General: Melting points were determined on a Monoskop IV (Fa. Bock) and are uncorrected. – Elemental analyses were performed by 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 were measured with a Bruker AC 250, AM 400 and ^{13}C NMR spectra with a Bruker AM 400 or DRX 500 spectrometer. Chemical shifts are given relative to TMS (δ = 0), coupling constants are reported in Hz. Unless otherwise specified, the 250 MHz-^{1}H and 100.6 MHz-^{13}C spectra recorded in $CDCl_3$ are given; assignments marked with an asterisk are interchangeable. Assignments have been confirmed by homo- and hetero-nuclear decoupling experiments, H'H, H'X correlating spectroscopy, and if necessary by GIAO/B3LYP/6–31G* calculations. – Mass spectra were run on a Finnigan MAT 44S spectrometer (EI 70 eV, unless otherwise specified). – For TLC silica gel plates 60 F_{254} (Merck, Darmstadt) were used. The silica gel used for column chromatography was Merck (0.040–0.063 mm) or ICN, Biomedicals GmbH (0.032–0.063 mm). The irradiation experiments were generally performed in carefully-purified, dried and deoxygenated solvents.

(1*R,2*R**,3*S**)-1,3-Dimethyl-4,5,9,10-tetraazapentacyclo-[6.2.2.2^{3,6}.1^{2,7}.0^{2,7}]pentadeca-11,13-diene-4,5;9,10-bis(methyldicarboximide) (7b):** A solution of **5b** (0.12 g, 0.74 mmol) and **6** (0.174 g, 1.54 mmol) in dry diethyl ether (10 mL) was stirred under N_2 at room temp. for 2 h. The precipitate was washed with dry diethyl ether (ca. 30 mL) and dried in vacuo. Colorless crystals (0.250 g, 87%), m.p. 214 °C (dec.). – IR (KBr): $\tilde{\nu}$ = i.a. 1771 cm^{-1} (C=O). – ^{1}H NMR: δ = 6.15 (dd, 12-, 14-H), 5.86 (dd, 11-, 13-H), 5.35 (dd, 6-, 8-H), 2.93 (s, NCH_3), 2.28 (s, 2 CH_3) 0.98 (s, 15-H); $J_{6,14}$ = $J_{8,12}$ = 6.0, $J_{6,12}$ = $J_{8,11}$ = 1.5, $J_{11,12}$ = $J_{13,14}$ = 8.25 Hz. – ^{13}C NMR: δ =155.2 (2 CO), 155.2 (2 CO), 135.4 (C-12 -14)*, 125.6 (C-11, -13)*, 64.6 (C-1, -3), 53.7 (C-6, -8), 29.6 (C-7)**, 22.9 (2 CH_3), 22.2 (NCH_3), 20.9 (C-2)**, 18.0 (C-15). – $C_{19}H_{20}N_6O_4$ (396.4): calcd. C 57.57, H 5.09, N 21.20; found C 57.29, H 5.00, N 20.95.

(±)-(1*R,2*R**,3*S**)-1,6-Dimethyl-4,5,9,10-tetraazapentacyclo-[6.2.2.2^{3,6}.1^{2,7}.0^{2,7}] pentadeca-11,13-diene-4,5;9,10-bis(methyldimethyldicarboximide) (7c):** A solution of **5c** (586 mg, 3.44 mmol) and **6** (818 mg, 7.24 mmol) in dry diethyl ether (20 mL) was stirred at room temp. for 1 h. The slightly pink precipitate was washed with diethyl ether, dried in high vacuum: **7c** (1.25 g, 92%), crystallized from methanol (ca. 1 mL), colorless solid, m.p. 207 °C (dec.). – IR (KBr): $\tilde{\nu}$ = i.a. 1759 cm^{-1} (C=O), 1693 (N–CO–N). – ^{1}H NMR: δ = 6.14 (dd, 12-, 13-H); 5.98 (dd, 11-, 14-H), 5.47 (dd, 3-, 8-H), 2.94 (s, NCH_3), 2.19 (s, -CH_3), 0.90 (s, 15-H), $J_{3,14}$ = $J_{8,11}$ = 1.0, $J_{3,13}$ = $J_{8,12}$ = 6.0, $J_{11,12}$ = $J_{13,14}$ = 8.3 Hz. – ^{13}C NMR: δ = 155.8 (2 C=O), 155.6 (2 C=O), 133.1 (C-12, -13), 125.6 (C-11, -14), 62.9 (C-1, -6), 51.0 (C-3, -8), 25.2 (C-2 -7), 21.1 (CH_3), 19.1 (NCH_3), 18.9 (C-15). – $C_{19}H_{20}N_6O_4$ (396.4): calcd. C 57.57, H 5.09, N 21.20; found: C 57.77, H 5.14, N 21.61.

(1*R,2*R**,3*S**)-1,3,6,8-Tetramethyl-4,5,9,10-tetraazapentacyclo-[6.2.2.2^{3,6}.1^{2,7}.0^{2,7}]pentadeca-11,13-diene-4,5;9,10-bis(methyldicarboximide) (7d):** To a solution of **5d** (1.76 g, 8.89 mmol) in CH_2Cl_2 (50 mL), **6** (2.1 g, 18 mmol) was added in portions and the mixture stirred to total conversion (ca. 15 min, TLC, ethyl acetate, R_f = 0.12). The precipitate was isolated by filtration and washed with ether. Additional product can be precipitated from the mother liquor by addition of ether. 3.71 g, 98%, m.p. 195 °C (dec.). – IR (KBr): $\tilde{\nu}$ = i.a. 1763 cm^{-1} (C=O), 1721 (N–CO–N). – ^{1}H NMR: δ = 5.76 (s, 11-, 12-, 13-, 14-H), 2.86 (s, 2 NCH_3), 2.27 (s, 4 CH_3), 1.00 (s, 15-H). – ^{1}H NMR (C_6D_6): δ = 5.01 (s, 11-, 12-, 13-, 14-H), 2.61 (s, 2 NCH_3), 2.10 (s, 4 CH_3), 1.22 (s, 15-H). – ^{13}C NMR: δ = 152.8 (4 CO), 134.7 (C-11, -12, -13, -14), 63.1 (C-1, -3, -6, -8), 25.9 (C-2, -7), 24.8 (C-15), 23.7 (2 NCH_3), 23.2 (4 CH_3). – $C_{21}H_{24}N_6O_4$ (424.5): calcd. C 59.42, H 5.70, N 19.80; found C 59.81, H 5.56, N 19.46.

(1*R,2*R**,3*S**)-4,5,9,10-Tetraazapentacyclo[6.2.2.2^{3,6}.1^{2,7}.0^{2,7}]-pentadecane-4,5;9,10-bis(methyldicarboximide) (9a):**[29] A suspension of **7a** (2.5 g, 6.8 mmol) and catalyst (Pd/C 10%, 200 mg) in ethyl acetate (500 mL) was stirred vigorously in a hydrogenation apparatus at 50 °C (1 atm. H_2). After ca. 6 h, H_2 uptake had stopped (315 mL). After concentration in vacuo, extraction of the residue with CH_2Cl_2 (12 h, Soxhlet) and evaporation, colorless crystals were obtained (2.4 g, 96%), m.p. 269 °C.

(1*R,2*R**,3*S**)-1,3-Dimethyl-4,5,9,10-tetraazapentacyclo-[6.2.2.2^{3,6}.1^{2,7}.0^{2,7}]pentadecane-4,5;9,10-bis(methyldicarboximide) (9b):** A solution of **7b** (0.15 g, 0.38 mmol) in ethyl acetate was hydrogenated (1 atm H_2, Pd/C, 10%, 25 mg, ultrasound) at 60 °C for 5 h. After addition of $CHCl_3$ at room temp. the catalyst was removed by filtration and the filtrate concentrated in vacuo. Colorless crystals (methanol) (135 mg, 89 %). – IR (KBr): $\tilde{\nu}$ = i.a. 1762 cm^{-1} (C=O), 1705 (N–CO–N). – ^{1}H NMR: δ = 4.72 (m, 6-, 8-H), 2.96 (s, NCH_3), 2.08 (s, 2 CH_3), 1.95–1.61 (m, 11-, 12-, 13-, 14-H), 1.39 (s, 15-H).

(±)-(1*R,2*R**,3*S**)-1,6-Dimethyl-4,5,9,10-tetraazapentacyclo-[6.2.2.2^{3,6}.1^{2,7}.0^{2,7}]pentadecane-4,5;9,10-bis(methyldicarboximide) (9c):** A solution of **7c** (50 mg, 0.13 mmol) in dry ethyl acetate (10 mL) was hydrogenated (1 atm. H_2, Pd/C, 10%, 15 mg, ultrasound) at 60 °C for 90 min (TLC control, ethyl acetate, R_f = 0.03). After addition of CH_2Cl_2 at room temp, the mixture was stirred for 5 min, and the catalyst removed by filtration. Concentration in vacuo gave colorless crystalline **9c** (46 mg, 91%), m.p. 225 °C (dec.), R_f (CH_2Cl_2/methanol, 9:1) = 0.52. – IR (KBr): $\tilde{\nu}$ = i.a. 1803 cm^{-1}, 1758, 1748 (C=O), 1694 (N–CO–N). – ^{1}H NMR: δ = 4.87 (m, 3-, 8-H). 2.94 (s, 2 NCH_3), 1.98 (s, 2 CH_3), 2.03–1.56 (m, 11-, 12-, 13-, 14-H), 1.37 (s, 15-H). – $C_{19}H_{24}N_6O_4$ (400.4): calcd. C 57.00, H 6.04, N 20.99; found C 57.31, H 6.05, N 20.83.

(1*R,2*R**,3*S**)-1,3,6,8-Tetramethyl-4,5,9,10-tetraazapentacyclo-[6.2.2.2^{3,6}.1^{2,7}.0^{2,7}]pentadecane-4,5;9,10-bis(methyldicarboximide) (9d):** A suspension of **7d** (3.60 g, 8.40 mmol) in methanol (150 mL) was hydrogenated (1 atm. H_2, Pd/C, 10%, 0.10 g, ultrasound) to total conversion (ca. 7 h, TLC, ethyl acetate, R_f = 0.06). The catalyst was removed by filtration over Celite and the filter washed with methanol and CH_2Cl_2 (20 mL each). Concentration in vacuo and washing of the solid residue with acetone left analytically-pure **9d** (3.31 g, 92%), m.p. 270 °C (subl.). – IR (KBr): $\tilde{\nu}$ = i.a. 1751 cm^{-1} (C=O), 1702. – ^{1}H NMR: δ = 2.93 (s, 2 NCH_3), 2.14 (s, 4 CH_3), 1.78 (ps, 11-, 12-, 13-, 14-H), 1.43 (15-H). – ^{1}H NMR ([D_6]DMSO): δ = 2.71 (s, 2 NCH_3), 2.08 (ps, 4 CH_3), 1.95 (s, 11-, 12-, 13-, 14-H), 1.49 (s, 15-H). – ^{13}C NMR: δ = 151.4 (4 CO), 61.0 (C-1, -3, -6, -8), 37.4 (C-11, -12, -13, -14), 33.8 (C-2, -7), 25.2 (4 CH_3), 24.7 (2 NCH_3), 19.7 (C-15). – MS; *m*/*z* (%): i.a. 313 [$M^+ - C_3H_5N_3O_2$], 298 (12), 257 (8), 246 (8), 244 (19), 230 (6), 215 (8), 201 (7), 200 (18), [$M^+ - C_3H_3N_3O_2 - C_3H_5N_3O_2$], 199 (83) [$C_3H_7N_3O_4^+$], 198 (13), [$C_6H_6N_4O_4^+$], 194 (20). – $C_{21}H_{28}N_6O_4$ (428.5): calcd. C 58.82, H 6.58, N 19.68; found C 57.66, H 6.44, N 19.10.

(1*R,2*R**,3*S**)-2-Methyl-4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]-tetradecane-4,5;9,10-bis (methyldicarboximide) (11a):** With heating **7a** (9.0 g, 24.4 mmol) was dissolved in freshly-distilled acetic acid. Catalyst (Pd/C, 10%, 1.0 g) was added and the suspension hydro-

genated (80 °C, 300 atm. H_2) in an autoclave, with shaking. After 5 h, with ^{1}H NMR- and TLC control ($CHCl_3/CH_3OH$, 12:1), total conversion into mainly **9a** besides **11a** (R_f = 0.32) and **13a** (R_f = 0.53) was observed; after 30 h **9a** was converted completely. Filtering off the catalyst and removing the volatile components in vacuo left a brown–red residue, consisting only of **11a** and **13a** (TLC). Since **13a** decomposed upon contact with silica gel during chromatography, separation was accomplished by fractional crystallization from methanol. First **11a** (6.9 g, 75%), then **13a** crystallized (1.4 g, 15%). – **11a**: Colorless needles, m.p. 340 °C. – IR (KBr): $\tilde{\nu}$ = i.a. 1700 (C=O). – UV (CH_3OH): ε_{220} = 9850. – ^{1}H NMR: δ = 4.45 (m, 6-, 8-H), 4.26 (pt, 1-, 3-H), 3.00 (s, NCH_3), 2.31 (m_c, 12s-, 13s-H), 2.14 (m, 11s-, 14s-H), 1.90 (t, 7-H), 1.83 (m_c, 12a-, 13a-H), 1.76 (m_c, 11a-, 14a-H), 1.36 (s, CH_3); $J_{3,14s}$ = $J_{3,14a}$ = 2.5, $J_{6,13s}$ =5.0, $J_{6,13a}$ = 1.0, $J_{6,7}$ = 2.0 Hz. – $C_{17}H_{22}N_6O_4$ (374.4): calcd. C 54.54, H 5.92, N 22.45; found C 54.50, H 5.80, N 22.28.

(1*R,2*R**,3*S**)-1,2,3-Trimethyl-4,5,9,10-tetraazatetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradecane-4,5;9,10-bis(methyldicarboximide) (11b):** A suspension of **7b** (210 mg, 0.53 mmol) in freshly-distilled acetic acid (90 mL) was hydrogenated (300 bar H_2) with highly active Pd/C (10%, 0.2 g) at 170 °C for 48 h. Purification by flash chromatography (ethyl acetate, then CH_2Cl_2/methanol, 20:1, R_f = 0.12) gave a colorless solid (65 mg, 40%), m.p. 250 °C (subl.). – IR (KBr): $\tilde{\nu}$ = i.a. 1759 cm^{-1} (C=O), 1699 (N–CO–N). – ^{1}H NMR (400 MHz): δ = 4.43 (m, 6-, 8-H), 2.93 (s, 2 NCH_3), 2.35–2.24 (m, 12a-, 14a-H), 2.13–2.02 (m, 11a- 13a-H), 1.95 (t, 7-H), 1.91 (s, 1-, 3-CH_3), 1.88–1.68 (m, 11s-, 12s-, 13s-, 14s-H), 1.31 (s, 2-CH_3). – ^{13}C NMR: δ = 150.4 (C=O), 62.7 (C-1, –3), 49.4 (C-7), 49.3 (C-6, –8), 36.1 (C-2), 34.6 (C-12, -14), 25.8 (C-11, -13), 24.9 (2 NCH_3), 21.7 (2-CH_3), 20.0 (1-, 3-CH_3). – MS; *m/z* (%): i.a. 404 (5), 403 (9), 402 (38) [M^+], 388 (6) [$M^+ - CH_3$], 222 (7), 182 (6), 181 (14), 180 (100) [$M^+ - 2\ C_3H_5N_3O_2$], 179 (20). – $C_{19}H_{26}N_6O_4$ (402.5): calcd. C 56.70, H 6.50, N 20.88; found C 56.55, H 6.73, N 18.67.

(±)-(1*R,2*R**,3*S**)-1,2,6-Trimethyl-4,5,9,10-tetraazatetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradecane-4,5;9,10-bis(methyldicarboximide) (11c):** A suspension of **7c** (2.27 g, 5.73 mmol) in freshly-distilled acetic acid (90 mL) was hydrogenated (300 bar H_2) with highly active Pd/C (10%, 625 mg) at 170 °C for 72 h. Purification by chromatography (CH_2Cl_2/methanol 20:1, R_f = 0.37) gave colorless crystals (882 mg, 38%). – IR (KBr): $\tilde{\nu}$ = i.a. 1757 cm^{-1} (C=O), 1688 (N–CO–N). – ^{1}H NMR: δ = 5.20 (m, 8-H)*, 4.56 (m, 3-H)* 3.08 (s, NCH_3), 2.96 (s, NCH_3), 2.08 (m, 7-H), 1.85 (s, 6-CH_3), 1.78 (s, 1-CH_3), 1.23 (s, 2-CH_3). – ^{13}C NMR: δ = 64.41 (C-1), 53.89 (C-3, -8), 47.97 (C-7), 43.70 (C-2), 32.58 (C-11), 26.63 (C-13), 25.37 (NCH_3), 25.19 (NCH_3), 24.13 (C-14), 23.11 (2-CH_3), 22.54 (C-12), 19.22 (1-CH_3), 16.38 (9-, 3-CH_3). – MS; *m/z* (%): i.a. 403 (6), 402 (25) [M^+], 289 (12), 288 (61) [M^+ – MTAD], 172 (21), [M^+ – 2 MTAD]. – $C_{19}H_{26}N_6O_4$ (402.5): calcd. C 56.70, H 6.48, N 20.88; found C 56.58, H 6.51, N 20.88.

(1*R,2*R**,3*S**)-1,2,3,6,8-Pentamethyl-4,5,9,10-tetraazatetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradecane-4,5;9,10-bis(methyldicarboximide) (11d):** A suspension of **7d** (745 mg, 1.74 mmol) in freshly-distilled acetic acid (90 mL) was hydrogenated (300 bar H_2) with highly active Pd/C (10%, 0.2 g) at 170 °C for 5 d. Purification by flash chromatography (ethyl acetate, then CH_2Cl_2/methanol, 20:1) gave a colorless solid (230 mg, 31%), m.p. 280 °C (subl.). – IR (KBr): $\tilde{\nu}$ = i.a. 1743 cm^{-1} (C=O), 1688 (N–CO–N). – ^{1}H NMR: δ = 2.94 (s, 2 NCH_3), 2.28–2.10 (m, 11a-, 12a-, 13a-, 14a-H), 1.99 (s, 6-, 8-CH_3), 1.92 (s, 1-, 3-CH_3), 1.83–1.67 (m, 11s-, 12s-, 13s-, 14s-H), 1.58 (s, 7-H), 1.30 (s, 2-CH_3). – ^{13}C NMR: δ = 148.8 (2 CO), 148.6 (2 CO), 61.8 (C-1, -3), 60.5 (C-7), 58.4 (C-6, -8), 48.8 (C-2), 37.2 (C-12, -14), 34.8 (C-11, -13), 25.0 (1-, 3-CH_3), 24.8 (2 NCH_3), 21.4 (2-CH_3), 20.8 (6-, 8-CH_3). – MS; *m/z* (%): i.a. 431 (9), 430 (35) [M^+], 201 (7) [$M^+ - 2\ C_3H_5N_3O_2$], 195 (13), 194 (100), 116 (9) [$C_3H_6N_3O_2^+$].

(1*R,2*R**,3*S**)-2-Methyl-4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]-tetradeca-4,9-diene(1a): 11a** (1.2 g, 3.2 mmol), 2-propanol (120 mL) and KOH (1.5 g, 37.5 mmol) were heated for 5 h at reflux. The mixture was cooled to room temp. and then acidified with 2 N HCl. An aqueous solution (450 mL) of $CuCl_2$ (15 g) was added, the mixture stirred at room temp. for 2 h, then conc. aqueous NH_3 solution (ca. 12 mL) was added until the mixture was deeply blue-colored. After extraction with CH_2Cl_2 (3 × 250 mL), the organic phase was washed with water (200 mL) and dried ($MgSO_4$), the solvent evaporated in vacuo and the remaining brown–red solid purified by chromatography on silica gel (20 g, 20 × 2 cm, $CHCl_3$/CH_3OH, 12:1) to yield **1a** (520 mg, 80%). Crystallization from ether gave colorless, transparent platelets, m.p. 231 °C (dec.), which proved suitable for an X-ray structural analysis (Table 5). – IR (KBr): $\tilde{\nu}$ = i.a. 1525 cm^{-1}, 1475 (N=N). – UV (CH_3CN): λ_{max} (ε) = 385 nm (236), 260 (sh, 260), 239 (610), 225 (sh, 615). – ^{1}H NMR: δ = 5.10 (dt, 6-, 8-H), 4.84 (pt, 1-, 3-H), 1.87 (m, 14a-H), 1.49 t, 7-H), 1.47 (m, 13a-H), 1.28 (m, 13s-H), 1.19 (s, CH_3), 0.87 (dddd, 14s-H), $J_{1,14s}$ = 3.0, $J_{6,13s}$ = 4.5, $J_{6,13a}$ = $J_{6,7}$ = 1.0, $J_{14a,14s}$ = 14.0, $J_{13s,13a}$ = 13.5, $J_{13s,14s}$ = 12.0, $J_{13a,14a}$ = 10.0, $J_{13s,14a}$ = 3.0, $J_{13a,14s}$ = 7.0, $J_{1,14a}$ = 2.5 Hz. – ^{13}C NMR: δ = 69.0, 64.5 (C-1, -3, -6, -8), 41.6 (CH_3), 30.2 (C-2), 23.8 (C-7), 20.4, 18.6 (C-11, -12, -13, -14). – MS; *m/z* (%): i.a. 204 (8) [M^+], 133 (10), 105 (37), 94 (11), 92 (14), 91 (77) [$C_7H_7^+$], 83 (100). – $C_{11}H_{16}N_4$ (204.2): calcd. C 64.68, H 7.85, N 27.43; found C 64.39, H 7.80, N 27.66.

Table 5. X-ray structural analysis of **1a**

Empirical formula	$C_{11}H_{16}N_4$
Formula mass	204.2
Temperature	298 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P1\ 2_1/c1$
Unit cell dimensions	a = 1.870 Å, α = 90° b = 8.385 Å, β = 118.79° c = 11.582 Å, γ = 90°
Volume	1010 Å^3
Z	4
Density (calculated)	1.343 g cm^{-3}
Crystal size	0.39 × 0.9 × 0.11 mm
Theta range for data collection	6 to 48°
Reflections collected	1920
Reflections scaled	1523
Reflections observed	1113
Refinement method	Full-matrix least-squares on F
Final R indices [I>2σ(I)]	$R1$ = 0.058

(1*R,2*R**,3*S**)-1,2,3-Trimethyl-4,5,9,10-tetraazatetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene (1b):** cf. **1a**. A solution of **11b** (31 mg, 0.08 mmol) in 2-propanol (4 mL), and KOH (95 mg, 1.70 mmol), was heated at reflux for 11 h. Oxidation with satd. aqueous $CuCl_2$ (2 mL) was carried out. Workup with conc. NH_3, purification by flash-chromatography (CH_2Cl_2/methanol, 9:1, R_f = 0.29) gave yellowish crystals (10 mg, 55%). – IR (KBr): $\tilde{\nu}$ = i.a. 1518 cm^{-1} (N=N), 1464 (N=N). – ^{1}H NMR: δ = 5.06 (m_c, 6-, 8-H), 1.91 (s, 1-, 3-CH_3), 2.00–1.83 (m, 11a-, 13a-H), 1.57–1.41 (m, 12a-, 14a-H), 1.26 (s, 2-CH_3), 1.38–1.18 (m, 12s-, 14s-H), 0.5–0.65 (m, 11s-, 13s-H) – ^{13}C NMR: δ = 69.1 (C-1, –3), 65.7 (C-6, –8), 44.4 (C-7), 49.3 (C-2), 28.5 (C-11, –13), 23.6 (1-, 3-CH_3), 22.0 (C-12, –14), 21.3 (2-CH_3). – MS (CI, NH_3); *m/z* (%): i.a. 250 (82) [M

+ H^+ + NH_3], 249 (5), 236 (26), 234 (7), 233 (41) [M + H^+], 221 (9), 219 (8), 205 (18) [M – N_2 + H^+], 98 (8), 97 (100).

(±)-(1*R,2*R**,3*S**)-1,2,6-Trimethyl-4,5,9,10-tetraazatetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene (1c):** cf. **1a**. Compound **11c** (228 mg, 0.57 mmol) and KOH (544 mg, 9.7 mmol) in 2-propanol (12 mL), were heated at reflux for 8 h, followed by oxidation with satd. aqueous $CuCl_2$, and workup with conc. aqueous NH_3. Flash-chromatography (CH_2Cl_2/methanol, 20:1, R_f = 0.18) gave a yellowish solid (10 mg, 7%). – ^{1}H NMR: δ = 4.93 (m, 8-H)*^{2}, 4.51 (m, 3-H)*^{2}, 2.01(s, 7-H), 1.83 (s, 6-CH_3)*, 1.78 (s, 1-CH_3)*, 2.29–1.26 (m, 11-, 12-, 13-, 14-H), 1.19 (s, 2-CH_3).

(1*R,2*R**,3*S**)-1,2,3,6,8-Pentamethyl-4,5,9,10-tetraazatetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene (1d):** To a solution of **11d** (45 mg, 0.10 mmol) in dry THF (15 mL) was added $LiAlH_4$ (26.6 mg, 0.70 mmol) and the mixture was stirred at room temp. under N_2 for 48 h (TLC, CH_2Cl_2/methanol, 9:1, R_f = 0.14, detection with aqueous $CuCl_2$). This was followed by oxidation with satd. aqueous $CuCl_2$ (2 mL) and workup with NH_3 as for **1a**. Chromatography over silica gel (ethyl acetate, R_f = 0.14) gave yellowish crystals (5 mg, 19%). – IR (KBr): ṽ = i.a. 1521 cm^{-1} (N=N), 1479 (N=N). – UV (CH_3CN): λ_{max} (ε) = 383 nm (160), 200 (1490). – ^{1}H NMR: δ = 2.01 (s, 6-, 8-CH_3), 1.92 (s, 1-, 3-CH_3), 1.80 (ddd, 11a-13a-H), 1.57 (ddd, 12a-, 14a-H), 1.36 (s, 7-H), 1.23 (s, 2-CH_3), 0.98 (ddd, 12s-, 14s-H), 0.65 (ddd, 11s-, 13s-H); $J_{11a,11s}$ = $J_{13a,13s}$ = 13.5, $J_{11a,12a}$ = $J_{13a,14a}$ = 7.0, $J_{11a,12s}$ = $J_{13a,14s}$ = 3.3, $J_{11s,12a}$ = $J_{13s,14a}$ = 6.75, $J_{12a,12s}$ = $J_{14a,14s}$ = 9.75, $J_{11s,12s}$ = $J_{13s,14s}$ = 12.0 Hz. – ^{1}H NMR ([D$_6$]acetone): δ = 1.91 (s, 6-, 8-CH_3), 1.87 (s, 1-, 3-CH_3), 1.83 (ddd, 11a-, 13a-H), 1.66 (ddd, 12a-, 14a-H), 1.26 (s, 2-CH_3), 0.88 (ddd, 12s-, 14s-H), 0.52 (ddd, 11s-, 13s-H). – $J_{11a,11s}$ = $J_{14a,14s}$ = 14.0, $J_{11a,12a}$ = $J_{13a,14a}$ = 12.0, $J_{11a,12s}$ = $J_{13s,14a}$ = 7.0, $J_{11s,12a}$ = $J_{13a,14s}$ = 3.5, $J_{11s,12s}$ = $J_{13s,14s}$ = 11.0, $J_{12a,12s}$ = $J_{13a,13s}$ = 14.0 Hz. – ^{1}H NMR (CD_3CN): δ = 1.90 (s, 6-, 8-CH_3), 1.85 (s, 1-, 3-CH_3), 1.65 (ddd, 11a-, 13a-H), 1.61 (ddd, 12a-, 14a-H), 1.20 (s, 2-CH_3), 0.88 (ddd, 12s-, 14s-H), 0.52 (ddd, 11s-, 13s-H). – $J_{11a,11s}$ = $J_{14a,14s}$ = 11.0, $J_{11a,12a}$ = $J_{13a,14a}$ = 10.5, $J_{11a,12s}$ = $J_{13s,14a}$ = 7.0, $J_{11s,12a}$ = $J_{13a,14s}$ = 3.5, $J_{11s,12s}$ = $J_{13s,14s}$ = 10.0, $J_{12a,12s}$ = $J_{13a,13s}$ = 11.0 Hz. – ^{13}C NMR: δ = 69.0 (C-1, -3), 66.3 (C-6, -8), 55.5 (C-7), 42.4 (C-2), 31.8 (C-11, -13), 29.4 (C-12, -14), 27.6 (1-, 3-CH_3), 24.4 (6-, 8-CH_3), 22.0 (2-CH_3). – MS (CI, NH_3, 170 eV); *m/z* (%): i.a. 279 (7), 278 (6) [M + H^+ + NH_3] 261 (8) [M + H^+], 234 (18), 233 (100) [M^+ – N_2], 123 (5).

2,4-Divinylcyclohepta-1,4-diene (12a): To a suspension of **9a** (1.2 g, 3.2 mmol) in 2-propanol (120 mL) was added KOH (1.5 g, 37.5 mmol) and the mixture was heated at reflux under N_2 until total conversion of **9a** (5 h, TLC). After cooling, the mixture was acidified with 2 N HCl (ca. 18 mL) and stirred for 2 h after a solution of $CuCl_2$ (15 g) in water (450 mL) had been added. Concentrated aqueous NH_3 (12 mL) was added until the solution remained deeply blue. The solution was extracted with CH_2Cl_2 (3 × 250 mL), the combined organic phases were washed with water (200 mL) and dried ($MgSO_4$). After removing the solvent in vacuo, chromatography (silica gel, petroleum ether, R_f = 0.70) furnished a colorless oil (395 mg, 85%) with a tendency to polymerize rapidly. – IR (CCl_4): ṽ = i.a. 3090, 3010 cm^{-1} (=C–H). – UV (CH_3CN: λ_{max} (ε) = 223 nm (36900). – ^{1}H NMR: δ = 6.32 (dd, 1-H), 5.83 (m, 1-, 5-H), 5.21 (d, 2b-H), 4.96 (d, 2a-H), 3.19 (s, 3-H), 2.36 (br. s, 6-, 7-H); $J_{1,2b}$ = 18.0, $J_{1,2a}$ = 10.5 Hz. – $C_{11}H_{14}$ (146.2).

(±)-(1*R,2*R**,3*S**)-2-Methyl-3-(4'-methyltriazolyl)-9,10-diazatricyclo[6.2.2.0^{2,7}]dodecane-9,10-methyldicarboximide (13a):** Colorless, spheric crystals, m.p. 312–314 °C. – IR (KBr): ṽ = i.a. 3440 cm^{-1} (NH), 1600 (C=O). – ^{1}H NMR: δ = 8.56 (br. m, NH), 4.27 (pt, 3-H), 4.21 (pt, 1-H), 4.18 (m, 8-H), 3.16 (s, NCH_3), 3.12 (s, N-CH_3), 2.2–1.4 (m_c, CH_2, 7-H), 1.34 (s, CH_3). – MS; *m/z* (%): i.a. 377 (10) [M^+ + 1], 376 (52) [M^+], 275 (31), 263 (14), 262 (90) [M^+-$C_3H_4N_3O_2$], 168 (39), 166 (83), 154 (63), 147 (80), 116 (100). – $C_{17}H_{24}N_6O_4$ (376.4): calcd. C 54.25, H 6.43, N 22.23; found C 54.26, H 5.97, N 22.57.

(±)-3-Vinyl-8,9-diazabicyclo[5.4.0]undeca-1(11),3-diene-8,9-methyldicarboximide (14) and (±)-(8*R,11*R**)-6,7,12,13-tetraazatricyclo-[9.4.0.0^{3,8}]pentadeca-1(15),3-diene-6,7;12,13-bis(methyldicarboximide) (15):** To a stirred solution of **12a** (295 mg, 2.0 mmol) in CH_2Cl_2 (10 mL), a solution of **6** (225 mg, 2.0 mmol) in CH_2Cl_2 (15 mL) was added dropwise at 0 °C over 20 min. The solution was stirred for another 10 min, then the solvent evaporated in vacuo. The colorless residue was worked up chromatographically (silica gel, CH_2Cl_2/acetone, 4:1) to give bisadduct **15** (145 mg, 28% based on **6**, R_f = 0.35), monoadduct **14** (225 mg, 61% based on **6**, R_f = 0.62) and residual **12a** (120 mg, R_f = 0.90). **14**: M.p. 130–131 °C (ethyl acetate). – IR (KBr): ṽ = i.a. 1695 cm^{-1} (br, C=O). – UV (CH_3OH): λ_{max} (ε) = 227 nm (23850). – ^{1}H NMR: δ = 6.32 (dd, 1-H), 5.85 (m, 4-H), 5.60 (br. s, 11-H), 5.22 (d, 2b-H), 5.03 (d, 2a-H), 4.46 (m, 7-H), 4.15 (dd, 10b-H), 3.88 (dddd, 10a-H), 3.30 (BA, 2b-H), 3.08 (s, NCH_3), 2.80 (AB, 2a-H), 2.31 (m_c, 5b-*, 6a-, 6b-H), 1.51 (m, 5a-H*); $J_{2a,2b}$ =14.0, $J_{1,2a}$ = 10.5, $J_{1,2b}$ = 17.5, $J_{10a,10b}$ 16.0, $J_{10a,11}$ = 2.5, $J_{10b,11}$ = 4.0, $J_{2b,10a}$ = 1.0 Hz. – $C_{14}H_{17}N_3O_2$ (259.3): calcd. C 64.85, H 6.61, N 16.20; found C 64.41, H 6.60, N 16.09. – **15**: M.p. 240 °C (ethyl acetate). – IR (KBr): ṽ = i.a. 1705 cm^{-1} (br, C=O). – UV (CH_3OH): ε_{235} = 4900. – ^{1}H NMR: δ = 5.73 (br. s, 1-, 15-H), 4.31 (d, 5-, 14-H)*, 4.21 (m, 8-, 11-H), 3.92 (d, 5-, 14-H)*, 3.38 (br. s, 2-, 2-H), 3.09 (s, NCH_3), 2.08, 1.81 (m, 9-, 9-, 10-, 10-H), $J_{5,5'}$ = $J_{14,14'}$ = 16.0 Hz. – $C_{17}H_{20}N_6O_4$ (372.4): calcd. C 54.83, H 5.41, N 22.57; found C 54.79, H 5.43, N 22.48.

(1*R,2*R**,3*S**,5*R**,6*S**,7*S**)-3,5,10,10-Tetramethoxy-1,7-bis(trifluoromethyl)-4-oxa-8,9-diazatricyclo[5.2.1.0^{2,6}]dec-8-ene (18c):**[40] A solution of **16b** was prepared by heating 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine (440 mg, 2.2 mmol) and 1,2,3,4-tetrachloro-7,7-dimethoxy-5-phenylbicyclo[2.2.1]hepta-2,5-diene (1.10 g, 3.0 mmol) in chlorobenzene (10 mL) to reflux, until the red color of the tetrazine had disappeared and the solution became orange. Then **17** (781 mg, 6.00 mmol) was added and heating continued until the color had changed to yellow. Concentration in vacuo and chromatography on silica gel (*n*-hexane, then *n*-hexane/CH_2Cl_2, 1:1) gave colorless crystals (260 mg, 30%), m.p. 121 °C, R_f (cyclohexane/ethyl acetate 1:1) = 0.56. – IR (KBr): ṽ = i.a. 3004 (CH) cm^{-1}, 2962 (CH), 2848 (CH), 1455. – UV (CH_3CN): λ_{max}(ε) = 343 (348), 217 (1189). – ^{1}H NMR: δ = 5.02 (s, 3-, 5-H), 3.48 (s, 2-, 6-H), 3.41 (s, 10a-OCH_3), 3.36 (s, 3-, 5-OCH_3), 3.29 (s, 10s-OCH_3). – ^{1}H NMR (C_6D_6): δ = 5.23 (s, 3-, 5-H), 3.61 (s, 2-, 6-H), 3.06 (s, 3-, 5-OCH_3), 2.74 (s, 10a-OCH_3), 2.66 (s, 10s-OCH_3). – ^{13}C NMR: δ = 123.3 (q, $^1J_{C,F}$ = 278.8, CF_3), 121.0 (s, c-10), 104.3 (s, C-3, -5), 90.0 (q, $^2J_{C,F}$ = 30.2, C-1, -7), 55.6 (s, 3-, 5-OCH_3), 53.3 (s, 10-OCH_3), 53.0 (s, 10-OCH_3), 51.0 (s, C-2, -6). – MS; *m/z* (%): = i.a. 394 (1) [M^+], 363 (32) [M^+ – OCH_3], 75 (100). – $C_{13}H_{16}F_6N_2O_5$ (394.3): calc. C 39.60, H 4.10, N 7.11; found C 39.44, H 4.19, N 7.02.

(±)-(1*R,2*R**,3*S**,5*R**,6*S**,7*S**)-5,10,10-Trimethoxy-1,7-bis(trifluoromethyl)-4-oxa-8,9-diazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3-ol (20c):** A solution of **18c** (20 mg, 0.05 mmol) in trifluoroacetic acid/water, 5:1, was stirred at room temp. for 12 h. Concentration in vacuo gave a colorless oil (19 mg, 100%), R_f (cyclohexane/ethyl acetate, 1:1) = 0.58. – IR (KBr): ṽ = i.a. 1749 cm^{-1} (C=O). – UV (CH_3CN): λ_{max}(ε) = 342 nm (300). – ^{1}H NMR ($CDCl_3$/D_2O): δ = 5.23 (d, 3-H), 5.08 (s, 5-H), 3.78 (s, 5-OCH_3), 3.63 (dd, 2-H), 3.49 (s, 10-OCH_3), 3.42 (s, 10-OCH_3), 3.11 (d, 6-H); $J_{2,6}$ = 7.5, $J_{2,3}$ = 4.7 Hz. – MS (CI, NH_3); *m/z* (%): i.a. 398 (100) [M^+ + NH_4], 349 (80) [M^+ – OCH_3], 334 (90). – $C_{12}H_{14}F_6N_2O_5$ (380.3)

(1*R,2*R**,3*S**,5*R**,6*S**,7*S**)-3,5-Dimethoxy-1,7,10,10-tetramethyl-4-oxa-8,9-diazatricyclo[5.2.1.0^{2,6}]dec-8-ene (18b):**[41] A solution of **16b** (2.0 g 16 mmol) and **17** (*cis*/*trans* mixture, 1:2, 9.2 mL, 9.9 g, 76 mmol) in NEt_3 (4.0 mL) was sealed in a Teflon tube (pretreated with NEt_3) and pressurized at 13.5 kbar/65 °C for 12 d. Concentration in vacuo and crystallization of the solid residue from *n*-hexane gave colorless crystals (3.0 g, 74%), m.p. 94 °C (*n*-hexane), R_f = 0.19 (cyclohexane/ethyl acetate, 3:1; $CuCl_2/\Delta$). – IR: (KBr): $\tilde{\nu}$ = i.a., 2977 cm^{-1}, 2959, 2907, 1502, 1471. – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 358 nm (195), 197 (1335). –^{1}H NMR: δ = 4.92 (s, 3-, 5-H), 3.38 (s, 3-, 5-OCH_3), 2.78 (s, 2-, 6-H), 1.72 (s, 1-, 7-CH_3), 0.85 (s, 10a-CH_3), 0.48 (s, 10s-CH_3). – ^{13}C NMR: δ = 105.4 (C-3, -5), 90.2 (C-1, -7), 59.7 (C-10), 56.6 (C-2, -6), 54.9 (3-, 5-OCH_3), 16.9 (10a-CH_3), 15.4 (10s-CH_3), 11.9 (1-, 7-CH_3). – MS; *m*/*z* (%): i.a. 233 [M^+ – OCH_3] (18), 151 (100), 125 [tetramethyl-4-*H*-pyrazole + H^+] (40), 119(5). – $C_{13}H_{22}N_2O_3$(254.4): calc. C 61.37, H 8.73, N 11.01; found C 61.23, H 8.65, N 10.90.

(±)-(1*R,2*R**,3*S**,5*R**,6*S**,7*S**)-5-Methoxy-1,7,10,10-tetramethyl-4-oxa-8,9-diazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3-ol (20b):** A suspension of **18b** (100 mg, 0.394 mmol) in H_2O (15 mL), after addition of conc. H_2SO_4 (30 mg), was briefly heated at reflux (TLC control, $CHCl_3$/methanol, 10:1, **18b**: R_f = 0.78; **20b**: 0.47**; 19b**: 0.27). After cooling to room temperature the solution was saturated with NaCl and extracted with CH_2Cl_2. (6 × 10 mL). The organic phase was dried (K_2CO_3) concentrated in vacuo and purified chromatographically (silica gel, $CHCl_3$/acetone, 7:1, R_f = 0.26) to give a colorless oil (ca. 30 mg, 32%, not optimized), R_f = 0.47 ($CHCl_3$/MeOH, 10:1, anisaldehyde). – IR: (KBr): $\tilde{\nu}$ = i.a. 3285 cm^{-1} (br., OH), 1384. – ^{1}H NMR: δ = 5.33 (d, $J_{5,OH}$ = 6.41 Hz, 1 H, 3-H), 4.90 (s, 1 H, 5-H), 3.35 (s, 3 H, 5-OCH_3), 2.95 (d, $J_{OH,5}$ = 6.41 Hz, 3-OH), 2.80 (*A*B, J_{AB} = 8.55 Hz, 6-H*), 2.76 (A*B*, J_{AB} = 8.55 Hz, 2-H*), 1.73 (s, 3 H, 7-CH_3**), 1.72 (s, 1-CH_3**), 0.83 (s, 10a-H), 0.45 (s, 10s-H). – ^{13}C NMR: δ = 105.7 (C-3), 99.3 (C-3), 90.5/90.4 (C1/C7), 60.0 (C-10), 57.8/56.8 (C-2/C-6), 55.0 (3-OCH_3), 17.1 (10a-CH_3), 15.5 (10a-CH_3), 12.08/12.05 (1-CH_3, 7-CH_3). – MS *m*/*z* (%): i.a. 223 [M^+ – OH] (18), 209 [M^+ – OCH_3] (11), 195 [M^+ – OH – N_2] (3), 181 [M^+ –OCH_3 – N_2] (1), 166 (16), 151 (48), 137 (46), 125 (100); MS (CI, isobutane); *m*/*z* (%): i.a. 241 [M^+ + H^+] (82), 223 [M^+] (80), 209 [M^+ – OCH_3] (21), 195 [M^+ – OH – N_2] (100), 181 [M^+ – OCH_3 – N_2] (54), 125 (33). – $C_{11}H_{18}N_2O_3$ (240.31).

(1*R,2*R**,3*S**,5*R**,6*S**,7*S**)-1,7,10,10-Tetramethyl-4-oxa-8,9-diazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-diol (19b):** A suspension of **18b** (100 mg, 0.40 mmol) in H_2O (15 mL) after addition of conc. H_2SO_4 (30 mg) was heated to reflux for 10 min. Workup as with **20b** and chromatography (silica gel, $CHCl_3$/acetone, 5:3, R_f = 0.22) gave a colorless oil (80 mg, 90%), R_f = 0.27 ($CHCl_3$/MeOH 10:1, anisaldehyde). – IR: (KBr): $\tilde{\nu}$ = i.a. 3335 cm^{-1} (s, br. OH). – ^{1}H NMR: δ = 5.34 (s, 3-, 5-H), 4.83 (br. s, 2 OH), 2.81 (s, 2-, 6-H), 1.71 (s, 1-, 7-CH_3), 0.82 (s, 10a-CH_3), 0.43 (s, 10s-CH_3). – ^{13}C NMR: δ = 99.0 (C-3, -5), 90.6 (C-1, -7), 60.1 (C-10), 57.9 (C-2, -6), 17.1 (10a-CH_3), 15.5 (10s-CH_3), 11.9 (1-, 7-CH_3). – MS; *m*/*z* (%): i.a., 180 [M^+ – H_2O – N_2] (1), 165 (6), 152 (8), 137 (64), 123 (58), 109 (100). – MS (CI, isobutane); *m*/*z* (%): 227 (31) [M + H^+], 209 (92) [M – H_2O + H^+] 181 (26), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (100). – $C_{11}H_{18}N_2O_3$ (226.3).

(±)-(1*R,2*S**,3*R**,6*S**,7*R**,8*S**,9*S**,13*R**)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,10,14-triene (24):** (cf. **19b**) To a CH_2Cl_2 solution of **19b** (from 1.20 g, 4.72 mmol **18b**, 90 mL H_2O, 200 mg conc. H_2SO_4, continuous extraction with 250 mL CH_2Cl_2) at 0 °C, anhydrous K_2CO_3 (30.0 g) and then anhydrous N_2H_4 (2.0 mL) were added. After stirring at 0 °C for 20 min, filtration and concentration in vacuo at 35 °C, excess hydrazine was evaporated at room temp. under high vacuum. To the suspension of the yellowish residue in CH_2Cl_2 (30.0 mL), freshly-distilled cyclopentadiene (70 mL) was added. To the vigorously-stirred solution at –78 °C, a cooled (–78 °C) solution of CF_3CO_2H (0.40 mL, 590 mg, 5.2 mmol) in CH_2Cl_2 (40.0 mL) was added and the repeatedly shaken solution kept at 4 °C for 16 h. After extraction with satd. aqueous $NaHCO_3$ solution (50 mL), the aqueous phase was reextracted with CH_2Cl_2 (50 mL), the combined organic phases dried (K_2CO_3), and concentrated in vacuo. Purification was carried out by chromatography on silica gel ($CHCl_3$/MeOH 30:1) or by the dissolution of the residue in $CHCl_3$ (ca. 5 mL) and precipitation of the product by slow addition of diethyl ether (ca. 50 mL). Impurities precipitated with the product could be separated by dissolution of the product in MeOH, the impurities remaining insoluble. Additional product could be obtained by chromatography of the residue (ca. 10%). Yellowish crystals (0.74–0.79 g, 58–62%), m.p. 273 °C (dec.) ($CHCl_3$/Et_2O). R_f ($CHCl_3$/MeOH, 30:1; UV, $CuCl_2/\Delta$, red-brown→dark brown) = 0.13. – UV (CH_3CN): λ_{max} (ε) = 367 nm (433), 233 (1782), 213 (3141). – IR: (KBr): $\tilde{\nu}$ = i.a. 3053 cm^{-1}, 2961, 2926, 2870, 1525, 1495, 1459, 1449. – ^{1}H NMR: (400 MHz): δ = 5.48 (m, 10-, 11-H), 5.25 (br. s, 1-H), 5.20 (br. s, 8-H), 2.94 (dddd, 9-H, *J* = 1.9, *J* = 1.9 Hz), 2.51 (dddd, 13-H, *J* = 4.0, *J* = 1.9 Hz), 2.43 (m, 12-H), 2.27 (m, 12-H), 2.04 (2-, 7-H), 1.62 (s, 3-CH_3), 1.61 (s, 6-CH_3), 0.80 (s, 16$_a$-CH_3), 0.40 (s, 16$_s$-CH_3). $J_{2,7}$ = 10.4, $J_{9,10}$ = 3.7, $J_{9,13}$ = 9.1, $J_{10,11}$ = 5.6, $J_{12,13}$ = 10.4 Hz. – ^{1}H NMR (CD_3CN, 400 MHz): δ = 5.45 (m, 10-, 11-H), 5.15 (br. s, 1-H), 5.10 (app. dd, *J* = 1.6 Hz, *J* = 1.6 Hz, 8-H), 2.95 (dddd, *J* = 1.9, *J* = 1.9 Hz, 9-H), 2.55 (dddd, *J* = 4.3, *J* = 1.9 Hz, 13-H), 2.39 (dddd, *J* = 1.9, *J* = 1.9 Hz, 12$_a$-H), 1.54 (s, 3-CH_3), 1.53 (s, 6-CH_3), 0.78 (s, 16$_a$-CH_3), 0.31 (s, 16$_s$-CH_3). $J_{9,10}$ = 3.5, $J_{9,13}$ = 9.1, $J_{12,12}$ = 17.4, $J_{12,13}$ = 10.4 Hz. The 12-H$_s$ signal is hidden by the solvent. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 5.33 (m, 10-H, 11-H), 4.92 (m, 1-H, 8-H), 2.31 (ddd, *J* = 1.9 Hz, 9-H), 2.18 (m, 12$_a$-H), 2.09 (m 12$_s$-H), 1.80 (m 13-H), 1.35 (s, 3-CH_3), 1.38 (m, i. a. AB, J_{AB} = 8.9 Hz, 2-H, 7-H), 1.34 (s, 6-CH_3), 0.25 (s, 16$_a$-CH_3), 0.17 (s, 16$_s$-CH_3). $J_{9,10}$ = 3.7, $J_{9,13}$ = 9.4 Hz. – ^{13}C NMR: δ = 132.9 (C-10*), 129.1 (C-11*), 88.6 (C-3, C-6), 64.9 (C-8**), 62.9 (C-1**), 59.5 (C-16), 52.3 (C-9), 40.3 (C-13), 39.6 (C-2, C-7), 36.9 (C-12), 17.1 (16-CH_{3a}), 15.4 (16-CH_{3s}), 11.4 (1-CH_3***), 11.4 (8-CH_3***). – MS; *m*/*z* (%): 271 [M + H^+] (1), 270 [M^+] (0.8), 199 [M^+ – 2 N_2 – CH_3] (35), 133 [M^+ – N_2 – CH_3 – cyclopentadiene] (100). – MS (CI, NH_3); *m*/*z* (%): 395 [M + 3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (5), 288 [M + NH_4^+] (33), 271 [M + H^+] (100), 270 [M^+] (17), 243 [M – N_2 + H^+] (18), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (7). – $C_{16}H_{22}N_4$ (270.4)

(1*R,2*S**,3*R**,6*S**,7*R**,8*S**,9*S**,13*R**)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,14-diene (2):** A solution of **24** (1.00 g, 3.70 mmol) in MeOH (30.0 mL) after addition of Pd/C (10%, 100 mg) was hydrogenated (1 atm. H_2) to total conversion [TLC, $CHCl_3$/MeOH 10:1; UV, $KMnO_4$, $CuCl_2$, R_f = 0.46 (**24**), 0.48 (**2**), 0.42 (monohydrazines), 0.09 (bishydrazine)]. The hydrazines were reoxidized by bubbling air through the solution. Concentration in vacuo and chromatography (silica gel, $CHCl_3$/MeOH, 30:1) or crystallization ($CHCl_3$/diethyl ether) furnished yellowish crystals (0.91–0.96 g, 90–95%), m.p. 266 °C (dec.). Single crystals suitable for X-ray analysis were obtained at 25 °C by isothermal diffusion of diethyl ether vapor into a solution of **2** in $CHCl_3$ (Table 6). – UV (CH_3CN): λ_{max} (ε) = 368 nm (436), 234 (1578), 212 (1500). – IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1}, 2867, 1445. – ^{1}H NMR (400 MHz): δ = 5.20 (s, 1-, 8-H), 2.20 (m, 9-H, 13-H), 1.96 (s, 2-H, 7-H), 1.73 (m, 10-H$_a$, 12-H$_a$), 1.60 (s, 3-CH_3, 6-CH_3), 1.33 (m, 10$_s$-H, 11$_a$-H, 12$_s$-H), 1.14 (m, 11$_s$-H), 0.78 (s, 16$_a$-CH_3), 0.39 (s, 16$_s$-CH_3). – ^{1}H NMR (CD_3CN, 400 MHz): δ = 5.10 (s, 1-H, 8-

H), 2.25 (m, 9-H, 13-H), 2.07 (s, 2-H, 7-H), 1.69 (m, 10_a-H, 12_a-H), 1.53 (s, 3-CH_3, 6-CH_3), 1.40–0.80 (br. m, 10_s-H, 11_s-H, 11_a-H, 12_s-H), 1.14 (m, 11_s-H), 0.77 (s, 16_a-CH_3), 0.31 (s, 16_s-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 88.4 (C-3, C-6), 64.2 (C-1, C-8), 59.7 (C-16), 45.2 (C-9, C-13), 39.8 (C-2, C-7), 29.8 (C-10, C-12), 26.2 (C-11), 17.1 (16_a-CH_3), 15.4 (16_s-CH_3), 11.4 (3-CH_3, 6-CH_3). – MS; *m/z* (%): 201 [M^+ – 2 N_2 – CH_3] (33), 133 (100). – MS (CI, NH_3); *m/z* (%): 397 [M + 3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (4), 290 [M + NH_4^+] (19), 273 [M + H^+] (100), 245 [M – N_2 + H^+] (59), 125 [3,4,4,5-tetramethy-4*H*-pyrazole + H^+] (93). – $C_{16}H_{24}N_4$ (272) calcd. C 70.55, H 8.88, N 20.57; found C 70.54 H 8.79 N 20.47

Table 6. X-ray structural analysis of **2**

Empirical formula	$C_{16}H_{24}N_4$
Formula mass	272.39
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	*P*1 2_1/*m*1
Unit cell dimensions	*a* = 6.1041(4) Å, α = 90° *b* = 10.8204(8) Å, β = 98.052(3)° *c* = 11.4023(8) Å, γ = 90°
Volume	745.68(9) Å^3
Z	2
Density (calculated)	1.213 g cm^{-3}
Absorption coefficient	0.576 mm^{-1}
F(000)	296
Crystal size	0.22 × 0.2 × 0.1 mm
Theta range for data collection	3.92 to 72.93°
Index ranges	–7*h*7, 0*k*13, 0*l*14
Reflections collected	1652
Independent reflections	1576 [*R*(int) = 0.0967]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1573/0/156
Goodness-of-fit on F^2	1.453
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0503, *wR*2 = 0.1691
R indices (all data)	*R*1 = 0.0579, *wR*2 = 0.1863
Extinction coefficient	0.009(3)
Largest diff. peak and hole	0.251 and –0.165 eÅ^{-3}

(1*S,9*R**,12*R**)-1,9-Dimethyl-4,6-bismethylene-10,11-diazatetracyclo[7.2.1.15,12.05,12]trideca-2,7-diene-10,11-methyldicarboximide (26):** To a solution of **7d** (73 mg, 0.17 mmol) in $CHCl_3$ (2 mL), half conc. H_2SO_4 (0.6 mL) was added and the mixture stirred at room temp. until total conversion of **7d** (ca. 4 h, TLC, cyclohexane/ethyl acetate, 1:1, R_f = 0.26). Then it was poured into H_2O (10 mL, 0 °C) and extracted thoroughly with $CHCl_3$. The organic phase was washed with satd. $NaHCO_3$ solution and H_2O (10 mL each). Concentration in vacuo and chromatography (silica gel, cyclohexane/ethyl acetate, 1:1) gave a pure (TLC) colorless solid (44 mg, 60%). – IR (KBr): ṽ = 1776 cm^{-1} (C=O), 1700 (N–CO–N). – ^1H NMR: δ = 6.23 (d, 2-, 8-H), 5.91 (ddd, 3-, 7-H), 5.51 (dd, R_2C=C–H_z), 5.38 (dd, R_2C=C–H_a), 3.04 (s, NCH_3), 1.61 (s, CH_3), 1.19 (s, 13-H); $J_{2,3}$ = $J_{7,8}$ = 9.75, $J_{3,1'a}$ = $J_{7,1''a}$ = –1.0, $J_{3,1'z}$ = $J_{7,1''z}$ = –1.0, $J_{1'a,1'z}$ = $J_{1''a,1''z}$ = 0.5 Hz. – MS *m/z* (%): i.a. 310 (18) [M + H^+], 309 (74) [M^+], 295 (7), 294 (32) [M^+ – CH_3], 197 (6), 196 (22) [M^+ – MTAD], 195 (38), 194 (8) [M^+ – $C_3H_5N_2O_3$], 182 (18), 182 (18), 181 (100).

(±)-(1*S,4*R**,13*R**)-1,7-Dimethyl-2,3,8,9-tetraazapentacyclo[8.3.2.0^{4,13}.0^{7,11}.0^{11,13}]pentadeca-5,14-diene-2,3,8,9-bis(methyldicarboximide) (25c):** A solution of **7c** (100 mg,) in $CHCl_3$ was stirred at 0 °C vigorously with half conc. H_2SO_4 (2 mL) to total conversion (TLC, ethyl acetate), then poured into H_2O (20 mL, 0 °C) and extracted thoroughly with $CHCl_3$. The organic phase was washed with satd. $NaHCO_3$ solution and H_2O, dried ($MgSO_4$) and concentrated in vacuo to give a colorless solid (97 mg, 97%), m.p. 282 °C (methanol). (Table 7). – IR (KBr): ṽ = 1761 cm^{-1} (C=O), 1689 (N–CO–N). – ^1H NMR: δ = 6.18 (ps, 5-, 6-, 14-, 15-H), 4.65 (mc, 4-, 10-H), 3.04 (s, NCH_3), 1.49 (s, 2 CH_3), 0.94 (s, 12-H). – ^{13}C NMR: δ = 153.3 (CO), 153.2 (CO), 128.8 (C-6, -15)*, 121.2 (C-5, -14)*, 58.9 (C-1, -7), 51.2 (C-4, -10), 33.5 (C-11, -13), 25.4 (NCH_3), 20.7 (CH_3), 8.3 (C-12). – MS *m/z* (%): i.a. 397 (19) [M + H^+], 396 (85) [M^+], 283 (9) [M^+ – MTAD], 169 (100).

Table 7. X-ray structural analysis of **25c**

Empirical formula	$C_{19}H_{20}N_6O_4$
Formula mass	396.4
Temperature	298 K
Wavelength	1.54184 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	*a* = 6.9696(9) Å, α = 90° *b* = 21.832(2) Å, β = 98.871(3)° *c* = 12.403(1) Å, γ = 90°
Volume	1864 Å^3
Z	4
Calculated density	1.412 g cm^{-3}
Extinction coefficient (isotropic)	4.517 × 10^{-6}
Crystal size	0.45 × 0.32 × 0.3 mm
Reflections collected/unique	7419/3648
Absorption correction	Ψ-scans
Parameters	343
Final *R* index	*R*1 = 0.037

(±)-(1*S,4*R**,13*R**)-1,7-Dimethyl-2,3,8,9-tetraazapentacyclo[8.3.2.0^{4,13}.0^{7,11}.0^{11,13}]pentadecane-2,3,8,9-bis(methyldicarboximide) (25c'):** A suspension of **25c** (135 mg, 0.34 mmol) in ethyl acetate (10 mL) was hydrogenated (1 atm. H_2/Pd/C,10%, 10 mg/ultrasound) for 2 h at 60 °C. Then $CHCl_3$ (10 mL) was added, the mixture filtered over Celite and concentrated in vacuo. The colorless solid was crystallized from warm methanol (10 mL) by addition of diethyl ether: 132 mg, 97%, m.p. 225 °C (dec). – IR (KBr): ṽ = 1748 cm^{-1} (C=O), 1694 (N–CO–N). – ^1H NMR: δ = 4.90 (m, 4-, 10-H), 2.94 (NCH_3), 1.98 (s, CH_3), 2.11–1.65 (5-, 6-, 14-, 15-H), 1.39 (12-H). – ^{13}C NMR: δ = 152.1 (CO), 151.6 (CO), 60.5 (C-1, –7), 54.1 (C-4, –10), 36.4 (C-11, –13), 28.3 (C-5, –15), 25.1 (NCH_3), 22.0 (C-6, –14), 20.4 (1-, 7-CH_3), 12.5 (C-12). – MS; *m/z* (%): i.a. 401 (18) [M + H^+], 400 (78) [M^+], 386 (6), 385 (22) [M^+ – CH_3], 116 (100).

(±)-(1*S,4*R**,13*R**)-1,7-Dimethyl-2,3,8,9-tetraazapentacyclo[8.3.2.0^{4,13}.0^{7,11}.0^{11,13}]pentadeca-2,8-diene (27c):** A mixture of **25c'** (100 mg, 0.25 mmol) and hydrazine hydrate (100%, 6 mL) was heated under N_2 at reflux for 6 d (TLC, CH_2Cl_2/methanol, 9:1, R_f = 0.18). The excess hydrazine was removed at room temp. under high vacuum. The residue was dissolved in ethanol (4 mL), diluted with H_2O (15 mL), acidified with 1N HCl. Then satd. aqueous $CuCl_2$ solution was added to give a red–brown solution, which was stirred at room temp. for 3 h. After addition of conc. NH_3 until a homogenous, intense blue colored solution was obtained, the mixture was extracted thoroughly with CH_2Cl_2. The combined organic phases were washed (H_2O), dried ($MgSO_4$), concentrated in vacuo, and purified by chromatography to give a slightly beige solid (33 mg, 57%). – IR (KBr): ṽ = 2960 cm^{-1} (C–C–H), 1958, 1088. – ^1H NMR: δ = 4.30 (4-, 10-H), 2.13–1.53 (5-, 6-, 14-, 15-H), 1.17 (s, 1-, 7-CH_3), 0.80 (s, 12-H); ^{13}C NMR: δ = 86.1 (C-1, -7), 84.6 (C-4, -10), 28.8 (C-6, -14), 25.5 (C-11, -13), 22.1 (C-5, -15), 20.5 (1-, 7-CH_3), 10.5 (C-12). – MS; *m/z* (%): i.a. 248 (23) [M + H^+ + NH_3], 232 (18), 231 (100) [M + H^+], 203 (23) [M^+ + H^+ – N_2].

9(10)-Methyl-1,2,4,15-tetraazahexacyclo[6.6.1.0^{2,11}.0^{4,15}. 0^{5,10}.0^{9,14}]-pentadecan-1-ium Tetrafluoroborate (37a/37b) and 1,9(10)-Dimethyl1,2,4,15-tetraazahexacyclo[6.6.1.0^{2,11}.0^{4,15}. 0^{5,10}.0^{9,14}]pentadecan1-ium Tetrafluoroborate (39a/39b): To a solution of **34** (370 mg, 2.50 mmol) in CH_2Cl_2 (5 mL) under N_2 was added a solution of **1a** (500 mg, 2.45 mmol) in CH_2Cl_2 (5 mL) at room temp. over 1 h. After stirring for another 1 h, the solution was filtered through a G4 frit and concentrated in vacuo. The residue was crystallized from methanol to give a mixture of **37a** (43%), **37b** (31%), **39a** (9%), **39b** (12%), and **1a** (5%) as yellowish spherical crystals (250 mg, ca 34%), m.p. 170–200 °C. An analogous reaction of **1a** (500 mg, 2.45 mmol) with 2 equiv. **34** (740 mg, 5.00 mmol) provided a mixture of **37a** (8%), **37b** (5%), **39a** (53%) and, **39b** (34%) as brown-yellow crystals (500 mg, ca. 57%), m.p. >160 °C (dec.). **37a:** ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 5.97 (d, 3ex-H), 3.63 (mc, 8-, 14-H), 3.60 (d, 3en-H) 3.57 (mc, 5-, 11-H), 1.90 (mc, 7-, 13-H), 1.87 (mc, 10-H), 1.40 (mc, 6-, 12-H), 1.08 (s, CH_3); $J_{3en,3ex}$ = 10.5, $J_{5,10}$ $J_{10,11}$ 3 Hz. – ^{13}C NMR ([D$_6$]DMSO): δ = 94.0 (C-3), 60.2 (C-9), ca.57.5 (br., C-8, –14), 54.1 (br., C-5, –11), 52.7 (C-10), 20.2 (CH_3), 19.5 (C-7, -13), 15.3 (C-6, -12). **37b:** ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.23 (d, 3ex-H), 4.06 (mc, 8-, 14-H), 3.57 (mc, 5-, 11-H), 2.50 (t, 9-H), 1.90 (mc, 12-, 13-H), 1.40 (mc, 6-, 7-H); $J_{3en,3ex}$ = 10.0, $J_{5,10}$ $J_{10,11}$ 3 Hz. – ^{13}C NMR ([D$_6$]DMSO): δ = 97.3 (C-3), 69.1 (C-9), 59.0 (br., C-5, –11), 55.1 (br., C-8, –14), 52.1 (C-10), 21.05 (CH_3), 17.5 (C-12, –13), 14.2 (C-6, –7). **39a:** ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.09 (d, 3ex-H), 4.26 (d, 3en-H), 4.09 (t, 8-H)*, 3.39 (t, 14-H)*, 3.81 (mc, 11-H)**, 3.48 (ddd, 5-H)**, 3.03 (s, 1-CH_3), 1.91 (mc, 10-H), 1.90 (mc, 7-, 13-H), 1.40 (mc, 6-, 12-H), 1.09 (s, 9-CH_3); $J_{3en,3ex}$ = 11.0, $J_{7;8s}$ $J_{7,8a}$ $J_{3s,14}$ $J_{13a,14}$ 2.5 Hz. – ^{13}C NMR ([D6]DMSO): δ = 93.2 (C-3), 62.4 (C-14)*, 60.6 (C-8)*, 59.8 (C-9), 56.4 (C-11)**, 54.4 (C-5)**, 52.6 (C-10), 42.8 (1-CH_3), 20.2 (9-CH_3), 20.0 (C-7)***, 18.7 (C-13)***, 14.7 (C-6)****, 14.1 (C-12)****. **39b:** ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.25 (d, 3ex-H), 4.53 (mc, 14-H), 4.18 (d, 3en-H), 3.81 (mc, 8-H), 3.63 (mc, 5-H)*, 3.34 (mc, 11-H)*, 2.98 (s, 1-CH_3), 1–90 (mc, 12-, 13-H), 1.40 (mc, 6-, 7-H), 0.96 (s, 10-CH_3); $J_{3en,3ex}$ = 10.5 Hz. – ^{13}C NMR ([D$_6$]DMSO): δ = 95.0 (C-3), 67.3 (C-9), 61.2 (C-8)*, 60.8 (C-14)*, 58.3 (C-5)**, 56.9 (C-11)**, 50.7 (C-10), 42.0 (1-CH_3), 20.7 (10-CH_3), 17.0 (C-6)***, 16.2 (C-7)***, 16.2 (C-12)****, 15.2 (C-13)****.

9-Methyl-1,2,4,15-tetraazahexacyclo[6.6.1.0^{2,11}.0^{4,15}. 0^{5,10}.0^{9,14}]pentadecane (38a(b)) and 9-Methyl-1,2,4,16-tetraazahexacyclo-[6.6.2.02,11.04,15.05,10.09,14]hexadecane (41): a): To a suspension of **34** (370 mg, 2.5 mmol) in CH_2Cl_2 (5 mL) a solution of **1a** (510 mg, 2.5 mmol) in CH_2Cl_2 (15 mL) was added dropwise with stirring. After stirring for 2.5 h at room temp. the mixture was filtered and the filtrate concentrated in vacuo. Fractional crystallization of the residue from methanol yielded first **39a** as yellow crystals, m.p. 170 °C (dec.), then starting material **1a** (50 mg, 10%). A solution of **39a** (420 mg, 1.37 mmol) in CH_2Cl_2 (40 mL) and satd. aqueous K_2CO_3 solution (20 mL) were stirred at room temp. for 30 min. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic phases were dried and volatile components evaporated in vacuo. The residue was filtered through silica gel ($CHCl_3$/CH_3OH, 12:1) to give **38a** (270 mg, 90%). From methanol/ether, 5:1, yellowish crystals were obtained, m.p. 160 °C (dec.). – IR (KBr): $\tilde{\nu}$ = i.a. 500 cm^{-1}. – UV (CH_3CN): unstructured absorption reaching beyond 300 nm; upon standing maxima at ca. 340 and 270 nm developed. – ^{1}H NMR: δ = 4.29 (d, 3ex-H), 3.90 (dd, 3en-H), 2.79 (m, 5-, 11-H), 2.77 (m, 8-, 14-H), 2.08 (m, 6a-, 12a-H)*, 1.86 (m, 7a-, 13a-H)**, 1.82 (m, 7s-, 13s-H)**, 1.53 (mc, 10-H), 1.29 (m, 6s, 12s-H)*, 1.08 (s, CH_3); $J_{3en,3ex}$ = 11.5, $J_{3ex,10}$ = 1.0 Hz. – ^{13}C NMR: δ = 78.8 (C-3), 59.9 (C-8, –14), 54.1 (C-5, –11), 46.1 (C-10), 45.3 (C-9), 22.8 (C-6, –12), 19.4 (CH_3), 16.0 (C-7, –13); $J_{C-3,Hen}$ = 150*, $J_{C-3,Hex}$ = 160*, $J_{C-5,H}$ = $J_{C-11,H}$ = 141, $J_{C-6,H}$ = $J_{C-7,H}$ = $J_{C-10,H}$ = $J_{C-12,H}$ = $J_{C-13,H}$ = 130, $J_{C-8,H}$ = 130, $J_{C-14,H}$ = 148, $J_{CH3,H}$ = 126 Hz. – MS; *m/z* (%): i.a. 218 (55) [M$^+$], 135 (28), 108 (28). – $C_{12}H_{18}N_4$ (218.3): calcd. C 66.02, H 8.31, N 25.67; found C 65.85, H 8.05, N 25.72. – b): To the brown–yellow product mixture of the reaction of **1a** with 2 equiv. of **34** (50 mg, 0.23 mmol), dissolved in CH_2Cl_2 (10 mL), a solution of satd. aqueous K_2CO_3 (5 mL) was added under N_2. The mixture was stirred vigorously at room temp. for 8 h and then extracted with CH_2Cl_2 (5 × 10 mL), the organic phase dried (K_2CO_3) and concentrated in vacuo to give a mixture of unstable **38a(b)** and **41**. The ^{1}H NMR spectrum was registered without further manipulation within 10 min. – **38a**: ^{1}H NMR: δ = 4.30 (d, 3ex-H), 3.91 (dd, 3en-H), 2.78 (mc, 5-, 8-, 11-, 14-H), 1.07 (s, CH_3); $J_{3en,3ex}$ = 11.0, $J_{3ex,10}$ = 1.0 Hz. – **38b**: ^{1}H NMR: δ = 4.11 (d, 3ex-H), 3.59 (dd, 3en-H); $J_{3en,3ex}$ = 13.5 Hz. – **41**: ^{1}H NMR: δ = 5.05 (d, 3ex-H)*, 4.99 (dd, 15en-H)*, 3.30 (d, 15en-H)**, 3.22 (d, 3en-H)**, 2.59 (m, 5-, 11-H)***, 2.33 (m, 8-, 14-H)***, 1.18 (s, CH_3); $J_{3en,3ex}$ = 15.0, $J_{15en,15ex}$ = 14.5 Hz.

(±)-(1*R,2*S**,3*R**,4*S**,6*R**,11*S**,12*S**,16*R**)-4,5,5,6-Tetramethyl-7,8,10,17-tetraazaheptacyclo[8.6.1.0^{2,6}.0^{3,11}.0^{4,8}.0^{7,17}.0^{12,16}]-heptadecane hydroiodide (42):** To a solution of **2** (11 mg, 0.040 mmol) in $CDCl_3$ (0.6 mL) was added CH_3I (7.5 μL, 17 mg, 0.12 mmol, 3.0 equiv.). NMR control showed (after 5–6 d) no more starting material, and slightly yellow crystals were precipitated (quantitatively). After concentration in vacuo the residue gave a homogeneous solution in CD_3CN suitable for spectroscopic characterization. The crystals decomposed without m.p. above 100 °C. – IR (KBr): $\tilde{\nu}$ = i.a. 2954 cm^{-1}, 2835, 1439. – ^{1}H NMR (CD_3CN): δ = 5.87 [d, 9-H$_{ex}$], 4.07 [dd, 1-H], 3.64 [dd, 9-H$_{en}$], 3.60 [dd, 11-H], 3.06 [d, 2-H], 2.50 [ddd, 3-H], 2.41–2.38 [m, 1 H], 2.20 [br. s, HI], 2.10–1.40 [m, hidden, 7 H], 1.57 [s, CH_3], 1.39 [s, CH_3], 1.01 [s, CH_3], 0.86 [s, CH_3]. $J_{1,2}$ $J_{1,16}$ 2.4, $J_{2,3}$ = 11.6, $J_{3,9en}$ = 1.8, $J_{3,11}$ = 2.4, $J_{9en,3}$ = 1.2, $J_{9ex,9en}$ = 11.3, $J_{11,3}$ $J_{11,12}$ 1.8 Hz. – ^{1}H NMR ($CDCl_3$): δ = 10.81 [br. s, HI], 5.88 [d, 9-H$_{ex}$], 4.16 [s, 1-H], 3.89 [d, 9-H$_{en}$], 3.62 [s, 1 H, 11-H], 3.06 [d, 2-H], 2.47 [d, 3-H], 2.41–2.38 [m, 1 H], 2.10–1.40 [m, hidden, 7 H], 1.63 [s, CH_3], 1.45 [s, CH_3], 1.07 [s, CH_3], 0.90 [s, CH_3]. – ^{13}C NMR (CD_3CN): δ = 89.2, 72.0, 61.2, 54.5, 54.4, 39.5, 36.5, 31.9, 30.3, 27.2, 16.1, 15.6, 11.5, 10.4; 3 signals are not observed. – $C_{18}H_{24}N_4$*HI (424.3).

(±)-(1*R,2*S**,3*R**,4*S**,6*R**,11*S**,12*S**,16*R**)-4,5,5,6-Tetramethyl-7,8,10,17-tetraazaheptacyclo[8.6.1.0^{2,6}.0^{3,11}.0^{4,8}.0^{7,17}.0^{12,16}]heptadecane (44):** Hydroiodide **42** (30 mg) was treated with a mixture of H_2O and $CHCl_3$ (6 mL each), the aqueous phase was made alkaline with K_2CO_3, extracted with $CHCl_3$ (4 × 9 mL), the combined organic phases dried (K_2CO_3), filtered and concentrated in vacuo to give solid, amorphous **44** quantitatively and analytically-pure (^{1}H NMR). – R_f = 0.28 ($CHCl_3$/MeOH, 10:1; $CuCl_2$: brown). – IR (KBr): $\tilde{\nu}$ = i.a. 2941 cm^{-1}, 2865, 1468, 1444. – UV (CH_3CN): $\lambda_{max}(\varepsilon_{rel})$ = 364 nm (13), 340 (12), 212 (100); ε_{rel}(254) = 26. Absorptions at 364 and 340 nm are supposedly due to decomposition products. – ^{1}H NMR: δ = 4.24 [d, 9-H$_{ex}$], 3.77 [dd, 9-H$_{en}$], 3.65 [br. m, 1-H], 2.64 [br. s, 11-H], 2.35–2.18 [m, 2 H], 2.23 [dd, 2-H], 2.00–1.65 [m, 6 H], 1.50–1.25 [m, 1 H], 1.25 [s, 6- CH_3], 1.13 [s, 5-CH_{3s}], 1.07 [s, 4- CH_3], 0.86 [s, 5- CH_{3a}]; $J_{1,2}$ = 1.8, $J_{1,16}$ 2.4, $J_{2,3}$ = 10.4, $J_{3,9en}$ = 1.22 Hz, $J_{9en,9ex}$ = 11.0 Hz. – ^{13}C NMR: δ = 75.5 (C-6*), 72.0 (NCH_2N), 67.3 (C-4*), 64.2 (C-5), 56.3 (CH), 55.0 (CH), 53.6 (CH), 44.2 (CH), 37.3 (CH), 39.7 (CH), 30.3 (CH_2), 29.1 (CH_2), 26.9 (CH_2), 17.4 (CH_3), 16.6 (CH_3), 12.9 (CH_3), 12.0 (CH_3). – ^{13}C NMR (CD_3CN): δ = 76.2 (C-6*), 72.9 (NCH_2N), 68.0 (C-4*), 65.3 (C-5), 57.2 (CH), 55.4 (CH), 54.1 (CH), 44.6 (CH), 40.2 (CH), 38.0 (CH), 31.0 (CH_2), 29.9 (CH_2), 27.1 (CH_2),

17.6 (CH_3), 16.8 (CH_3), 13.1 (CH_3), 12.0 (CH_3). – MS; *m/z* (%): 286 [M^+] (16), 243 (8), 138 (39), 97 (100). – HRMS: found 286.2169 (error 3.9 ppm).

(2*R,3*S**,5*S**,6*S**)-2,16,17,17-Tetramethyl-1,12,13,15-tetraazaheptacyclo [10.5.1.0^{1,15}.0^{3,11}.0^{4,16}.0^{5,13}.0^{6,10}]octadecane (47):** A solution of **2** (270 mg, 0.99 mmol) in CH_3OH (30 mL) was hydrogenated (1 atm H_2, Pt, 10 mg) until total conversion (**46**, TLC control, $CHCl_3/CH_3OH$, 10:1, $CuCl_2$). The solvent was evaporated in vacuo and the residue dissolved under argon in a carefully deoxygenated mixture of CH_3CN/CH_2Cl_2 (5 mL each). After addition of K_2CO_3 (5.0 g), the mixture was stirred under argon at room temp. for 4 d. After filtration, the solvents were evaporated in vacuo and the oily residue purified by chromatography (silica gel, $CHCl_3/CH_3OH$, 10/1, R_f = 0.18, $CuCl_2$) to give 240–270 mg (80–90%) of a colorless solid, m.p. 130–140 °C (dec.). – IR (KBr): $\tilde{\nu}$ = i.a. 2992 cm^{-1}, 2951, 2925, 2904, 2862, 1491, 1466, 1450. – UV (CH_3CN): unstructured absorption reaching beyond 300 nm; upon standing, maxima at ca. 340 and 270 nm developed. – ^{1}H NMR (400 MHz): δ = 4.94 (d, 14-H_{en}, 18-H_{en}), 3.38 (dd, *J* 1 Hz, 14-H_{ex}, 18-H_{ex}), 2.64 (d, *J* 1 Hz, 5-H, 11-H), 2.02–1.95 (m, 6-H, 10-H), 1.98–1.83 (m, 7-H_a*, 8-H_a*, 9-H_a*), 1.81 (s, 3-H, 4-H), 1.76–1.66 (m, 7-H_s*, 9-H_s*), 1.50–1.39 (m, 8-H_s*), 1.01 (s, 2-CH_3, 16- CH_3), 1.00 (s, 17- CH_{3s}), 0.85 (s, 17- CH_{3a}); $J_{14en,14ex}$ = $J_{18en,18ex}$ = 15.5 Hz. – ^{13}C NMR: δ = 65.9 (C-2, -16), 61.8 (C-14, -18), 6.04 (C-5, -11), 51.8 (C-17), 41.8 (C-6*, -10*), 41.1 (C-3*, -4*), 28.3 (C-7, -9), 26.9 (C-8), 15.3 (17-CH_3), 14.9 (17-CH_3), 11.6 (2-, 16-CH_3). – MS (EI) *m/z* (%): i.a. 300 [M^+] (96), 272 [M^+ – 28] (17), 257 (9), 244 (10), 125 (100), 91 (43). – HRMS; *m/z* (%): 300.2325 (calcd. 300.2314, +3.6 ppm). – $C_{18}H_{28}N_4$ (300.5).

Tetramethyl 12-Methyl-1,6,7,18-tetraazaoctacyclo[12.4.0.0^{2,4}.0^{3,7}.0^{5,18}.0^{6,11}.0^{8,13}0^{12,17}]octadeca-2,3,4,5-tetracarboxylate (58) and Trimethyl 8-[3,4,5-Tris-(methoxycarbonyl)-pyrazolyl]-10-methyl-1,15-diazapentacyclo[9.3.1.04,15.05,10.09,14]pentadec-2-ene-2,3,4-tricarboxylate (60): To a solution of **1a** (408 mg, 2.0 mmol) in CH_2Cl_2 (10 mL), freshly distilled ADM (284 mg, 2.0 mmol) was added. While the solution was stirred (2 h, 20 °C, N_2 atmosphere) the color changed first to yellow, then to green, and was finally to a deep violet. After total consumption of ADM (10 h, TLC control), the volatile components were removed in vacuo and the residue was separated chromatographically on silica gel. First **60** (ethyl acetate, R_f = 0.67, 175 mg) was eluted, then **58** (ethyl acetate, R_f = 0.35, 42 mg) – both of them containing ADM oligomers and by-products (< 5%, ^{1}H NMR). The last fraction consisted of starting material **1a** ($CHCl_3/CH_3OH$ 12/1, R_f = 0.47, 303 mg, 75%). The fractions were purified by chromatography again (silica gel, ether), yielding firstly spectroscopically-pure **60** (155 mg, 12%, R_f = 0.35; 50% based on conversion), then **58** (ethyl acetate/ether, 3/1, R_f = 0.27, 36 mg, 3.6%; 15% based on conversion), the latter containing an inseparable by-product. Total yield based on ADM: 44%. With an excess of ADM: **1a** (408 mg, 2.0 mmol), ADM (freshly distilled, 2.9 g, 20.4 mmol), CH_2Cl_2 (10 mL), 20 °C, stirring (5 h, N_2 atmosphere, TLC control). Workup as described above yielded **60** (500 mg, 41%) and **58** (114 mg, 12%). **58:** Colorless crystals, m.p. 192 °C (ethyl acetate/$CHCl_3$, 10:1). – IR (KBr): $\tilde{\nu}$ = i.a. 2950, 1740 cm^{-1} (C=O). – UV (CH_3CN): λ_{max} (ε) = 220 (9100) nm. – ^{1}H NMR (400 MHz): δ = 3.76 (s, 2 OCH_3), 3.75 (s, OCH_3), 3.74 (s, OCH_3), 3.13 (m, 8-, 14-H), 3.01 (″t″, *J* = 3.0 Hz, 11-, 17-H), 2.19 (m, 9a-, 15a-H)*, 2.11–1.95 (m, 10a-, 10s-, 16a-, 16s-H), 1.65 (m, 9s-, 15s-H)*, 1.03 (s, CH_3), 1.00 (t, 13-H); $J_{8,13}$ = $J_{13,14}$ = 1.5 Hz. – ^{13}C NMR: δ = 166.2 (C_2-*C*O, C_3–*C*O), 165.4 (C_4–*C*O)*, 162.7 (C_5–*C*O)*, 94.1 (C-5), 67.4 (C-2, –3), 59.0 (C-4), 59.7 (C-11, –17), 52.9 (OCH_3), 52.8 (OCH_3), 52.7 (OCH_3), 51.1 (C-8, -14), 44.8 (C-12), 36.1 (C-13), 27.9 (CH_3), 24.7 (C-10, -16), 24.5 (C-9, –15). – MS; *m/z* (%): 488 (59) [M^+], 429 (11) [M^+–CO_2CH_3], 313 (35), 281 (73), 211 (35), 91 (100). – MS (170 eV, CI, NH_3); *m/z* (%): 490 (54) [M^+ + 2], 489 (100) [M^++1], 588 (31) [M^+], 445 (12). **60:** Yellowish crystals, m.p. 100 °C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = i.a. 1730 (C=O) cm^{-1}. – ^{1}H NMR (400 MHz): δ = 3.76 (s, 2OCH_3), 3.75 (s, OCH_3), 3.74 (s, OCH_3), 3.13 (m, 8-, 14-H), 3.01 (″t″, *J* 3.0 Hz, 11-, 17-H), 2.19 (m, 9a-, 15a-H)*, 2.11–1.95 (m, 10a-, 10s-, 16a-, 16s-H), 1.65 (m, 9s-, 15s-H)*, 1.03 (s, CH_3), 1.00 (t, 13-H); $J_{8,13}$ = $J_{13,14}$ 1.5 Hz. – ^{1}H NMR ($CDCl_3/C_6D_6$ 1:1, 400 MHz): δ = 5.29 (td, 8-H), 3.85 (s, OCH_3), 3.76 (s, OCH_3), 3.65 (s, OCH_3), 3.61 (s, OCH_3), 3.59 (s, 2 OCH_3), 3.48 (t, 14-H), 3.11 (br. d, 5-H), 2.74 (s, 11-H), 2.54 (dq, 7s-H), 2.37 (md, 6s-H), 2.10 (br. d, 9-H), 1.87 (m_c, 2s-H)*, 1.90–1.70 (m, 6a-**, 12a-H**), 1.70–1.50 (m, 7a-, 13s-H), 1.28 (s, CH_3), 1.09 (tt, 13a-H**). – ^{13}C NMR: δ = 171.8 (C_4–*C*O), 164.2 (C_4–*C*O), 164.0 (C_3–*C*O), 160.6 (C_3–*C*O), 159.2 (C_2–CO), 158.5 (C_5–*C*O), 146.3 (C-2), 139.4 (C-3'), 130.8 (C-5'), 122.0 (C-4'), 112.8 (C-3), 85.7 (C-4), 63.9 (C-11), 57.3 (C-8), 53.3, 53.0, 52.9, 52.8, 52.3, 51.6 (6 OCH_3), 51.5 (C-14), 50.4 (C-9), 49.5 (C-5), 46.7 (C-10), 29.8 (C-13), 24.1 (C-7), 21.7 (CH_3), 20.1 (C-6)*, 16.4 (C-12)*; $J_{C-5,H}$ = 131, $J_{C-8,H}$ = 140, $J_{C-9,H}$ = 130, $J_{C-11,H}$ = 144, J_{OCH3} = 146, $J_{C-2,C-3}$ = 75.2, $J_{C-2,C2-CO'}$ = 88.6, $J_{C-3,C-4}$ = 46.7, $J_{C-3,C3-CO'}$ = 88.3, $J_{C-4,C4-CO}$ = 67.7, $J_{C-4,C-5}$ = 31.9, $J_{C-3,C3'-CO}$ = 93.0, $J_{C-3',C-4'}$ = 57.4, $J_{C-4',C4'-CO}$ = 88.2, $J_{C-4',C-5'}$ = 70.2, $J_{C-5',C5'-CO}$ = 89.2 Hz. – ^{15}N NMR (44.55 MHz, natural abundance): δ = 321.5 (d, $J_{N-2',8-H}$ = 3.2 Hz, N-2'), 226.5 (s, N-1'), 147.7 (m, N-1)*, 138.8 (m, N-15)*. – MS; *m/z* (%): i.a., 630 (6) [M], 571 (69) [M – CO_2CH_3], 297 (40), 237 (31), 211 (100), 179 (41), 145 (39), 131 (59), 105 (40). – $C_{29}H_{34}N_4O_{12}$ (630.6): calcd. C 55.24, H 5.43 N 8.88; found C 55.28, H 5.21, N 8.71.

(±)-(1*R,2*S**,3*R**,6*S**,7*R**,8*S**,9*S**,13*R**)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,14-dien-14-ylium-1'2'-dimethoxycarbonyl-2'-ide (62):** Compound **2** (20 mg, 0.074 mmol) was dissolved in dry benzene (5.0 mL). Freshly distilled ADM (0.30 mL, 34 equiv.) was added under N_2. The solution immediately turned yellow; **2** was completely consumed after one week. The product could not be crystallized; when purified by flash-chromatography ($CHCl_3$/MeOH = 30/1; R_f = 0.22), substantial decomposition had to be accepted. After purifying twice by chromatography, 3 mg (10%) of a red, glassy solid was obtained. – UV (CH_3CN): λ_{max}(ε) = 418 nm (5600), 368 (4800), 257 (3500), 212 (4600). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.57 (s, 1-H), 4.95 (s, 8-H), 3.83 (s, OCH_3), 3.71 (s, OCH_3), 2.43 (ddd, 13-H), 2.32 (dd, 9-H), 2.31 (s, 2-H, 7-H), 2.17 (s, 3-CH_3*), 1.81 (s, 6-CH_3*), 1.87–1.72 (m, 1 H), 1.70–1.55 (m, 2 H), 1.55–1.45 (m, 1 H), 1.45–1.32 (m, 1 H), 1.32–1.20 (m, 1 H), 0.81 (s, 16-CH_{3a}), 0.44 (s, 16-CH_{3s}); $J_{9,10a}$ = 8.6, $J_{9,13}$ = 16.0, $J_{12s,13}$ 1.0, $J_{12a,13}$ 8.0 Hz. – MS (CI, NH_3); *m/z* (%): 431 [M^+ + NH_3] (100), 403 [M^+ + NH_3 – N_2] (6), 361 (10), 345 (11), 306 (9), 290 [M + NH_4^+ – ADM] (5), 273 [M + H^+ – ADM] (14), 245 [M + H^+ – N_2 – ADM] (15), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (36). – $C_{22}H_{30}N_4O_4$ (414.5).

(±)-(1*R,2*S**,3*R**)-2-Methyl-9,10-diazatetracyclo[8.2.2.2^{2,7}.0^{3,6}]-dodec-9-ene (64a) and (±)-*endo*,*endo*-5-Methyl-5,6-divinyl--2,3-diazabicyclo[2.2.2]oct-2-ene (65a):** A solution of **1a** (500 mg, 2.45 mmol) in pure CH_3CN (400 mL) was irradiated (Hg-high-pressure lamp Hanovia G 79A, 450 W, pyrex) at –20 °C to total conversion (26 h, TLC). The yellowish solution was concentrated in vacuo, and the residue was filtered through a short column of silica gel ($CHCl_3/CH_3OH$, 12:1). The monomeric components were separated from polymers by preparative TLC (silica gel, CH_2Cl_2/ether 6:1) to give **64a** (130 mg, 30%, R_f = 0.52) as a colorless, slowly-crystallizing oil (at room temperature) and **65a** (100 mg, 23%, R_f = 0.73) as a bright red oil. **64a:** m.p. 42–43 °C. – UV (CH_3CN): λ_{max}

(ε) = 380 nm (115), 371 (75), 341 (sh, 15). – ^{1}H NMR: δ = 5.28 (m, 8-H), 4.95 (pt, 1-H), 2.40, 2.24, 2.01, 1.82 (m_c, cyclobutane-H), 1.94 (s, 7-H), 1.82 (m_c, 11a-H), 1.50–1.20 (m_c, 12s-, 12a-H), 1.27 (s, CH_3), 1.07 (11s-H); $J_{1,11s} = J_{1,11a} = 2.0$, $J_{6,7} < 2.5$, $J_{7,8} = 3.0$ Hz. – ^{1}H NMR (C_6D_6): δ = 5.00 (m, 8-H), 4.71 (pt, 1-H), 2.38, 2.24, 2.02, 1.82, 1.57 (m_c, cyclobutane-H), 1.46 (s, 7-H), 1.29 (m_c, 11a-H), 1.00–0.80 (m_c, 12s-, 12a-H), 0.88 (s, CH_3), 0.71 (11s-H); $J_{1,11s} = J_{1,11a} = 2.0$, $J_{6,7} < 2.5$, $J_{7,8} = 3.0$ Hz. – PE: eV = 8.2$_0$, 9.5. – $C_{11}H_{16}N_2$ (176.3): calcd. C 74.96, H 9.15, N 15.89; found C 74.70, H 9.45, N 16.09. – **65a:** oil. – IR (film): $\tilde{\nu}$ = i.a. 1635 cm^{-1} (C=C), 1525, 1500 (N=N). – UV (CH_3CN): λ_{max} (ε) = 377 (75), 367 (sh, 65), 339 (sh, 40) nm. – ^{1}H NMR: δ = 5.43 (dd, 1''-H), 5.40 (ddd, 1'-H), 5.20 (dd, 2d''-H), 5.17 (m, 1-H), 5.10 (m, 4-H), 5.03 (dd, 2b'-H), 4.96 (dd, 2a'-H), 4.94 (dd, 2c''-H), 3.17 (d, 6-H), 1.87 (m, 8a-H), 1.58 (m, 7a-H), 1.32 (m, 7s-H), 1.20 (s, CH_3), 1.14 (m, 8s-H); $J_{1',2b'} = J_{1'',2c''} = 17.0$, $J_{2a',2b'} = J_{2c'',2d''} = 1.5$, $J_{1',2a'} = J_{1'',2d''} = 10.0$, $J_{1',6} = 9.5$, $J_{1,6} = 1.0$ Hz. – $C_{11}H_{16}N_2$ (176.3): calcd. C 74.96, H 9.15, N 15.89; found C 74.41, H 9.23, N 15.95.

(±)-(1*R,2*R**,3*R**)-1,2,3-Trimethyl-9,10-diazatetracyclo-[8.2.2.2^{2,7}.0^{3,6}]dodec-9-ene (64b)** and **(±)-*endo*,*endo*-4,5,1'-Trimethyl-5,6-divinyl--2,3-diazabicyclo[2.2.2]oct-2-ene (65b):** A ca. 2 mM solution of **1b** in CD_3CN was irradiated in a NMR tube (Hg high pressure lamp, 150 W) for 6 h to give a mixture of **64b**/**65b** (3.2:1) as new products. – ^{1}H NMR (CD_3CN): **64b:** i.a. δ = 4.90 (m, 8-H)*, 2.02–1.05 (m, 4-, 5-, 6-, 7-H, CH_3), 0.40–0.90 (m, 11-, 12-H); **65b:** i.a. δ = 5.52 (m, 5-, 6-Vinyl-H), 5.11 (m, 4-H)*, 2.02–1.05 (m, 5-H, CH_3), 0.90–0.40 (m, 7-, 8-H).

(±)-(1*R,2*R**,3*R**)-1,2,3,6,8-Pentamethyl-9,10-diazatetracyclo-[8.2.2.2^{2,7}.0^{3,6}]dodec-9-ene (64c):** A ca. 2 mM solution of **1c** in CD_3CN was irradiated in a NMR tube (Hg high pressure lamp, 150 W) for 6 h (78% conversion) to give exclusively **64c**. – ^{1}H NMR (CD_3CN): δ = 1.66 (s, 8-CH_3)*, 1.62 (s, 1-CH_3)*, 1.75–1.52 (m, 11-, 12a-H), 1.33–1.05 (m, 4-, 5-H), 1.06 (s, 6-CH_3), 0.99 (s, 3-CH_3)**, 0.98 (s, 2-CH_3)**, 0.90–0.62 (m, 11-, 12s-H).

(1*R,2*R**,3*S**,4*R**)-1,11,14,14-Tetramethyl-12,13-diazapentacyclo[9.2.1.0^{2,10}.0^{3,9}.0^{4,8}]tetradec-12-ene (73) and (1*R**,2*R**,3*R**,12*R**)-3,4,4,5-Tetramethyl-13,14-diazapentacyclo-[5.5.2.02,6.03,5.08,12]tetradec-13-ene (74):** A solution of 2 (90 mg) in CH_3CN (5.0 mL), purged with Ar for 30 min, was irradiated in a sealed quartz tube (= 1.4 cm) in a Rayonet reactor (253.7 nm) for 200 min (70% conversion, ^{1}H NMR) to give a mixture of **73**, **74** and **75**. Traces of polymers were removed by filtration. Chromatography on silica gel (cyclohexane/ethyl acetate, 10:1) gave **73** (10 mg, 18% on conversion, R_f = 0.22) and **74** (5 mg, 9% on conversion, R_f = 0.16). Compound **75** (R_f = 0.72) is volatile with the solvent. It could be obtained more conveniently by a photolysis carried to complete conversion. – **73:** UV (CH_3CN): λ_{max} = 358 nm. – ^{1}H NMR: δ = 2.43 (app t, J_{app} = 1.2 Hz, 2-H, 10-H), 2.38 (app. d, $J_{app.}$ = 5.2 Hz, 4-H, 8-H), 1.72 (br. s, 3-H, 9-H), 1.61 (s, 1-CH_3, 11-CH_3), 1.60–1.43 (5-H_s, 5-H_a, 6-H_s, 6-H_a, 7-H_s, 7-H_a), 0.67 (s, 14-CH_{3a}), 0.46 (s, 14-H_s). – ^{13}C NMR: δ = 90.4 (C-1, C-11), 58.5 (C-14), 50.6 (CH), 43.9 (CH), 37.4 (CH), 33.4 (C-5, C-7), 25.0 (C-6), 16.3 (14-CH_{3a}), 16.2 (14-CH_{3s}), 12.0 (1-CH_3, 11-CH_3). – MS (CI, NH_3); *m/z* (%): 489 [2M + H^+] (2), 369 [M + tetramethyl-4*H*-pyrazole + H^+] (1), 262 [M + NH_4^+] (2), 245 [M + H^+] (93), 125 [tetramethyl-4*H*-pyrazole + H^+] (100). – $C_{16}H_{24}N_2$ (244.38). – **74:** UV (CH_3CN): λ_{max} = 384 nm. – ^{1}H NMR: (400 MHz): δ = 5.40 (br. s, 1-H, 7-H), 2.20–2.16 (m, 8-H, 12-H), 1.88 (app t, J_{app} = 1.6 Hz, 2-H, 6-H), 1.83–1.72 (m, 9-H_a, 11-H_a), 1.46–1.34 (m, 9-H_s, 10-H_a, 11-H_s), 1.19–1.08 (m, 10-H_s), 1.02 (s, 4-CH_{3a}), 0.95 (s, 3-CH_3, 5-CH_3), 0.81 (s, 4-CH_{3s}). – ^{13}C NMR: δ = 69.2 (C-1, C-7), 42.5 (C-8, C-12), 42.0 (C-2, C-6), 31.8 (C-3, C-5), 31.0 (C-9, C-11), 25.8 (C-10), 24.8 (C-4), 19.2 (4-CH_{3s}), 14.8 (4-CH_{3a}), 10.1 (3-CH_3, 5-CH_3). – MS; *m/z* (%): 133 (100), 107 (37), 77 (51). – MS (CI, NH_3); *m/z* (%): 245 [M + H^+] (100). – $C_{16}H_{24}N_2$ (244.38).

(1*R,2*S**,3*S**,5*R**,6*R**,7*S**)-3,4,4,5-Tetramethyl-pentacyclo-[5.5.0.0^{2,6}.0^{3,5}.0^{8,12}]tetradecane (75):** From a solution of **2** (10 mg, 0.037 mmol) in CD_3OD (1.0 mL), dissolved O_2 was removed by three *freeze-pump-thaw* cycles and the NMR tube sealed in vacuo. The solution was irradiated at 25 °C with a 150 W Hg high pressure lamp for 2.5 h (complete conversion) to give **75** (90–95% by integration, solvent as internal standard). – ^{1}H NMR (CD_3OD): δ = 2.29 (app. t, $J_{app.}$ = 1.1 Hz, 2-H, 6-H), 2.07 (app. quint., $J_{app.}$ = 0.9 Hz 8-H, 12-H), 1.90–1.50 (m, 8 H), 0.98 (s, 3-CH_3, 5-CH_3), 0.96 (s, 4-CH_3), 0.93 (s, 4-CH_3). – ^{13}C NMR (CD_3OD): δ = 47.6 (C-2, C-6), 45.1 (C-8, C-12), 41.9 (C-1, C-7), 34.7 (C-9, C-11), 26.3 (C-10), 19.7 (4-CH_{3s}), 14.8 (4-CH_{3a}), 8.0 (3-CH_3, 5-CH_3); signals of the quaternary C atoms were not observed. – MS; *m/z* (%): 133 (100), 122 (72), 107 (90). – MS (CI, isobutane); *m/z* (%): 273 [M + H^+ + isobutene] (4), 217 [M + H^+] (30), 216 [M^+] (31), 215 [M^+ – H] (100), 214 [M^+ – 2 H] (18), 201 [M^+ – CH_3] (8), 142 [M^+ – cyclopentene] (66). – $C_{16}H_{24}$ (216.4).

(±)-(1*R,2*S**,3*S**,6*R**,7*R**,8*S**)-2-Methyl-4,5,9,10-tetraaza-tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene-4,9-bis(norbornadiene-rhodium(I) Chloride):** The deeply red solution of **1a** (10 mg, 0.049 mmol) and norbornadiene-rhodium(I)-chloride dimer (22 mg, 0.048 mmol) in CH_3CN (2.0 mL) was heated at reflux for 2 min. Upon cooling to room temp. single crystals of the complex were obtained as small black cubes (Table 8).

Table 8. X-ray structural analysis of **1a** (NBD-Rh(I)-Cl)$_2$

Empirical formula	$C_{27}H_{35}Cl_2N_5Rh_2$
Formula mass	706.32
Temperature	293(2) K
Wavelength	0.71074 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 10.7395(3) Å, α = 90° b = 19.8793(6) Å, β = 110.3160(16)° c = 13.7400(4) Å, γ = 90°
Volume	2750.92(14) Å^3
Z	4
Calculated density	1.705 g cm^{-3}
Absorption coefficient	1.420 mm^{-1}
F(000)	1424
Crystal size	0.2 × 0.2 × 0.1 mm
Theta range for data collection	2.93 to 30.52°
Index ranges	0h15, 0k27, –19l18
Reflections collected/unique	17330/7990 [R(int) = 0.050]
Completeness to 2θ	30.52 92.5%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7990/0/337
Goodness-of-fit on F^2	0.582
Final R indices [I>2σ(I)]	R1 = 0.0339, wR2 = 0.0927
R indices (all data)	R1 = 0.0664, wR2 = 0.1030
Largest diff. peak and hole	0.894 and –0.490 eÅ^{-3}

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