Proximate, "Parallel-In-Plane" Preoriented Bis(diazenes) − In-Plane Delocalized Bis(homoconjugated) 4N/5(6)e Anions

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Synthetic details are presented for a series of more or less rigid, "parallel-in-plane" preoriented bis(diazenes), with N=N/N=N distances (*d*) of 3.3–2.9 Å and interorbital angles (ω) of 142–164° (X-ray crystal structures). DFT calculations (B3LYP/6–31G*) and one-/two-electron reduction experiments with the two least preoriented, most "distant" bis(diazenes) ($d_{N=N/N=N}$ ca. 3.3 Å; ω 142–146°) provide more insight into the structural prerequisites for bis(homoconjugative) in-plane electron delocalization in 4N/5e radical anions and 4N/6e dianions.

Introduction

Bis(diazenes) of type **A**−**D** (Figure 1) had provided the playing ground for our partly long-lasting[1,2] attempts to effect photochemical N=N/N=N ([2+2]) cycloaddition[3] as a route to the still unknown[4] tetrazetidines. Judged by the degree of preorientation between the N=N/N=N chromophores − as defined by N=N/N=N distance (*d*) and π-orbital alignment (ω), originally calculated by force-field (MMX)[5] and semiempirical (AM1) techniques[6] and recently by DFT methods (B3LYP/6−31G*, Figure 1)[7] − cycloaddition seemed to have a good chance. After all, for the geometrically closely related C=C/C=C[8] and N=N/C=C[9] systems, [2+2] cycloaddition had been established as highly efficient if not exclusive photochemical pathway. In the end, though, in no case was N=N/N=N photocycloaddition observed. Arguments have been put forward for why cycloaddition could not compete with more or less rapid N_2 elimination even in the most promising, near to perfectly *syn*-periplanar, **A**-systems.[10,11] One such argument was based on the fact that exothermic metathetical isomerization into the **B**-type isomers, via the respective tetrazetidine *N*-Oxides as vibrationally excited transients,[12] might become a highly competitive process after *N*-oxidation of **A**-type bis(diazenes).[1,13] In contrast, various **B**-,[13] **C**-,[14] and **D**-type *N*-Oxides,[15] in which metathesisis significantly endothermic, underwent only standard photoprocesses (deoxygenation, oxaziridine formation).[2c−2e]

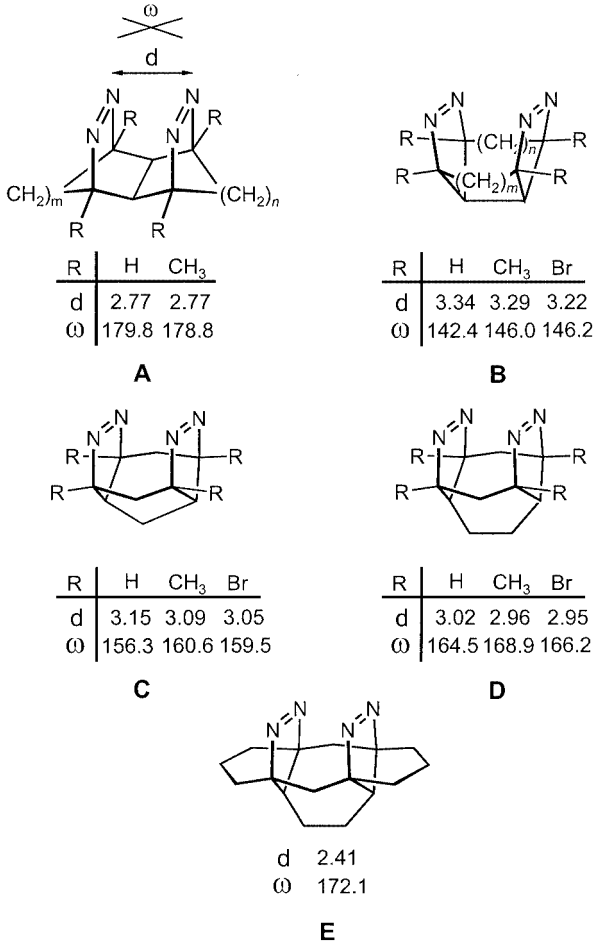

Figure 1. Calculated (B3LYP/6−31G*) N=N/N=N-distances (*d*, Å) and interorbital angles (ω,°) of bis(diazenes) **A**−**E** (for R = H, $m = n = 1$)

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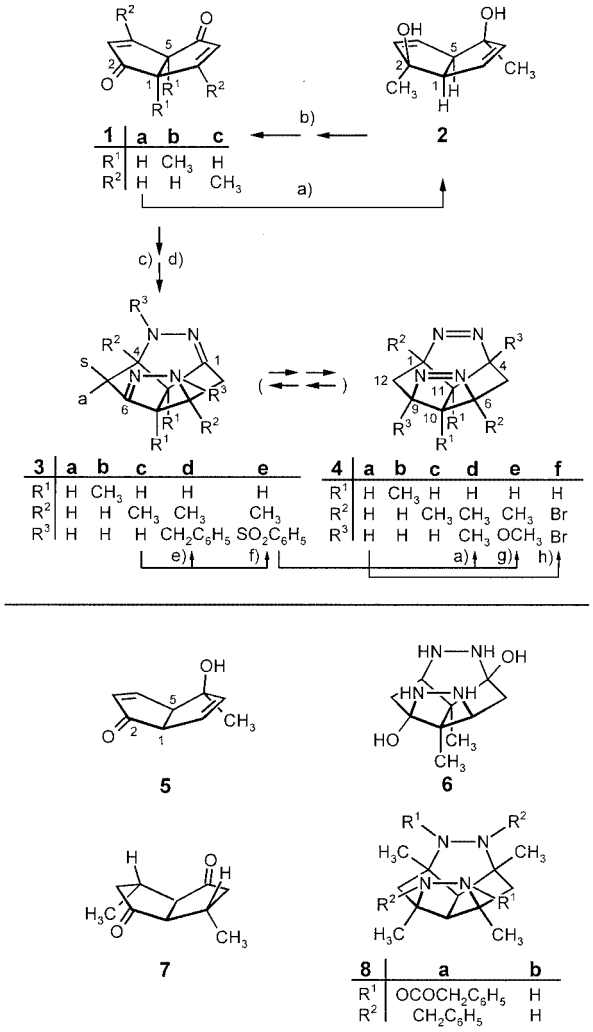
The bis(diazenes) **A**−**D** experienced a much acclaimed comeback with the discovery − initiated by the one-/two-electron oxidation of similarly preoriented C=C/C=C substrates ("pagodadienes") to highly persistent, in-plane delocalized σ-bis(homoconjugated) cations [4C/3(2)e][16] − that one-/two-electron reduction provides access to in-plane σ-bis(homoconjugated) radical anions (4N/5e) and σ-bis(homoaromatic) dianions (4N/6e) with theoretically novel bonding.[17−19] Tetra *N*-Oxides were subsequently shown to undergo one-/two-electron oxidation to equally intriguing cations [4N/3(2?)e, cubic 4O4N/11(10)e?].[20]

In this paper we present an updated, full account of our activities directed towards the synthesis of **B**-, **C**-, and **D**-type bis(diazenes), which in the greater part have already been employed in photochemical and electron-transfer studies. In addition, recent electron-transfer experiments with two **B**-type bis(diazenes) featuring N=N/N=N distances close to the van der Waals limit and performed in the hope of gaining more insight into the structure/persistence relationship of the 4N/5(6)e bonding motifs are also reported.

In this last context, bridging α to the N=N double bonds as in, for example, the hexacyclic skeleton **E**, has been pursued as a means through which to prohibit diazene → hydrazone tautomerization and to enforce closer "proximity". From calculations,[21] **E**-type bis(diazenes), optimally "preoriented" with appreciable exothermicity for their metathetical isomerization, had emerged as first choice targets for the demonstration of photo[2+2] cycloadditions.[2b,2e] Most regrettably, though, numerous attempts to construct such **E**-type skeletons had met with failure.[2c−2e]



Scheme 1. a) $CH_3Li/CeCl_3$, THF, room temp., 2 h; 85 (50−70)%; b) PCC, K_2CO_3, room temp., 10 h, 77%; c) $N_2H_4{\cdot}H_2O$, ethanol, room temp., 10 h, 100%; d) $N_2H_4{\cdot}H_2O$, ethanol, room temp. → 80 °C, 4 d; ca. 75(50); e) $C_6H_5CH_2Br$, DMSO, K_2CO_3, room temp. → 40 °C, 10 h, 41%; f) $C_6H_5SO_2Cl$, pyridine, 12 h, 90%; g) CH_3OH, room. temp. → 40 °C, 85%; h) Br_2, CH_2Cl_2, room. temp., 2.5 h, 75%

Results and Discussion

1. Syntheses

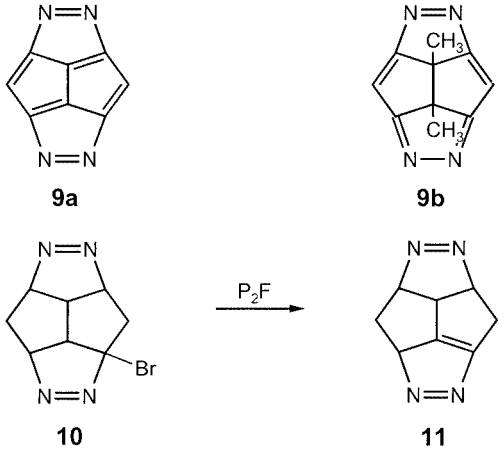
B-Type Bis(diazenes) 4b−f (Scheme 1):[22] The synthesis of bis(diazene) **4a**, the parent **B** structure, from bicyclic dienedione **1a** and hydrazine hydrate has been described in detail in the context of our attempts to use N=N/N=N complexation as a way to enforce closer proximity.[23] To recap, after a smooth double Michael addition of hydrazine to **1a**, cyclization [cf. bis(pyrazolidine) **6**], and dehydration, vigorous "one-pot" conditions (80 °C, sealed ampoule, 10 d[2i]) were necessary to effect the isomerization of the, thermodynamically less stable bis(pyrazoline) [bis(hydrazone)] **3a** to **4a**. The poor yield (40−50% of **4a**, together with polymers) had been attributed to the lack of stereocontrol in the Michael addition steps and to the loss of highly strained **3a** through polymerization. The 10,11-and 1,6-dimethyl-bis(diazenes) **4b** and **4c** were approached analogously from the 1,5-dimethyl- and 4,6-diene-2,6-diones **1b** and **1c**. For the reaction between **1b** (from butane-2,3-dione and dimethyl 2-oxomalonate)[24] and hydrazine, steric protection of the convex side (α) by the methyl groups promised higher selectivity in the Michael addition steps. In fact, when **1b** was added very slowly to an excess of $N_2H_4{\cdot}H_2O$ (ethanol) at room temperature, a complex reaction mixture had after 10 h changed into a single product (TLC). After evaporation, the air-sensitive **3b** was isolated nearly quantitatively and, being highly air-sensitive, was used without further purification. Obviously, the Michael additions had occurred in an α-specific manner and the subsequent condensations only in intercyclic fashion, bridging C4/C2 and C8/C6 (rather than C4C/6 and C8/C2). On standing, **3b** slowly equilibrated to a ca. 9:1 mixture with **4b,** CH_3/CH_3 steric strain in the more rigid **4b** being the probable cause for this thermodynamic situation.[25] Under forcing "one-pot" conditions, the 9:1 equilibrium mixture of **3b** and **4b** was produced in ca. 75% yield with bis(pyrazolidine) **6** as a ^1H NMR spectroscopically identifiable intermediate. Still, selective solubility − extraction with water (**3b**) or CH_2Cl_2 (**4b**) − provided a convenient means of separation and, by repeated equilibration, the tedious acquisition of **4b**.

Access to dienedione **1c** as precursor of **4c** was first attempted through a double Michael addition of a methyl cuprate to **1a** and dehydrogenation.[26] The α,α-dimethyl diketone **7** was formed highly selectively by addition of Me_2-CuLi to **1a**, but no means to effect the dehydrogenation could be found. "Alkylative 1,3-carbonyl transposition"[27] (**1a** → **2** →**1c**) provided the solution. Whilst **1a** instantaneously polymerized upon contact with CH_3Li or CH_3MgBr, it selectively added the reagent $CH_3Li/CeCl_3$ [28] from the convex (α) side to give the C_2-symmetrical 2β,6β-bis(carbinol) **2** (85%) via the spectroscopically identified intermediate **5**. For the subsequent double rearrangement/oxidation sequence to provide the air- and acid-sensitive **1c**, a serviceable result (77%) was achieved with pyridinium chlorochromate/K_2CO_3. Bis(diazene) **4c** was produced in ca. 50% yield from the reaction between **1c** and $N_2H_4 \times H_2O$ under "one-pot" conditions, together with polymers (cf. **4a**). As also demonstrated with **1b,** in the reaction performed at room temperature, after 12 h intermediate **3c** had been formed in nearly quantitative yield and being, like **3b**, air-sensitive, was directly used. With **3c** now readily to hand, a convenient route to the 1,4,6,9-tetramethylbis(diazene) **4d** was attainable. A two-step sequence of double *N*-sulfonylation (**3e**) and double S_N2' substitutive alkylation of **3e** with $CH_3Li/CeCl_3$ provided **4d** in an overall yield of 50−70%. For comparison, the total yield of the first elaborated sequence − *N*-benzylation (**3d**), CH_3-addition ($CH_3Li/CeCl_3$)/hydrazide interception (**8a**), hydrogenolytic deprotection (**8b**), oxidation − was never better than ca. 10%.

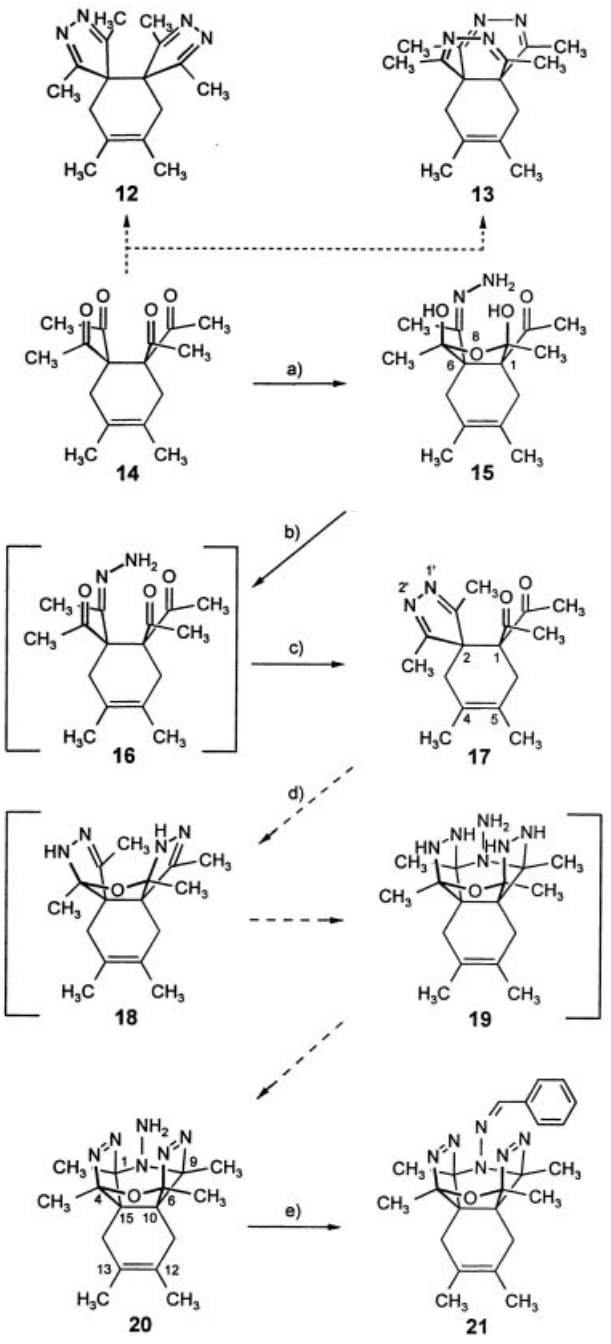
As part of our efforts directed towards the **E**-type skeletons (Figure 1), activated bis(pyrazolines) such as **3e** and bridgehead-halogenated bis(diazenes) such as the tetrabromo compound **4f** had figured as key intermediates. In explorative experiments, **3e** added methanol to give **4e**, formally a S_N2' substitutive methoxylation, and treatment of **4a** with bromine afforded **4f** (75%), presumably through nucleophilic addition to the corresponding hydrazones.

Like parent bis(diazene) **4a**, compound **4b** and the allylically substituted derivatives **4c**−**f** proved thermally stable enough to be sublimed under reduced pressure (60−100 °C, 10^{-3} Torr), but decomposed near their melting points. They could be stored at room temperature with exclusion of light and air. Their preference for rather "closed" conformations in solution (**B**, Figure 1) was manifested in, inter alia, the degree of deshielding exerted by the N=N double bonds on the *syn*-methylene protons [e.g. $\Delta(\delta_{5(12)\text{-}H_s} - \delta_{5(12)\text{-}H_a}) =$ 0.98 ppm for **4c**, 1.44 ppm for **4d**; cf. 1.04 ppm for **4a**[3a]]. The n → π* transitions in **4b** (CH_3CN, 343 nm), **4c** (339 nm), and **4d** (343 nm) hardly differed from that in **4a** (339 nm), but that in **4f** (CH_3OH, 330 nm) was significantly blue-shifted.

In the context of our longstanding interest in fulvalene-type hydrocarbons,[29] more recently revitalized by the polyunsaturated dodecahedranes (C_{20} fullerene),[30] allylically brominated **4a** and **4b** (e.g., **4f**) became of interest as potential precursors of **9a** and **9b**, the tetraaza analogues of the "classical"[31] $C_{12}H_6$ tetraquinene and tetracyclic $C_{12}H_8$ [10]annulene.[32] In exploratory experiments with monobromide **10** and Schwesinger's P_2F base,[33] β-elimination proved straightforward, the strongly bent[34] ene/bis(diazene) **11** being, as might be expected,[35] very prone to polymerization.



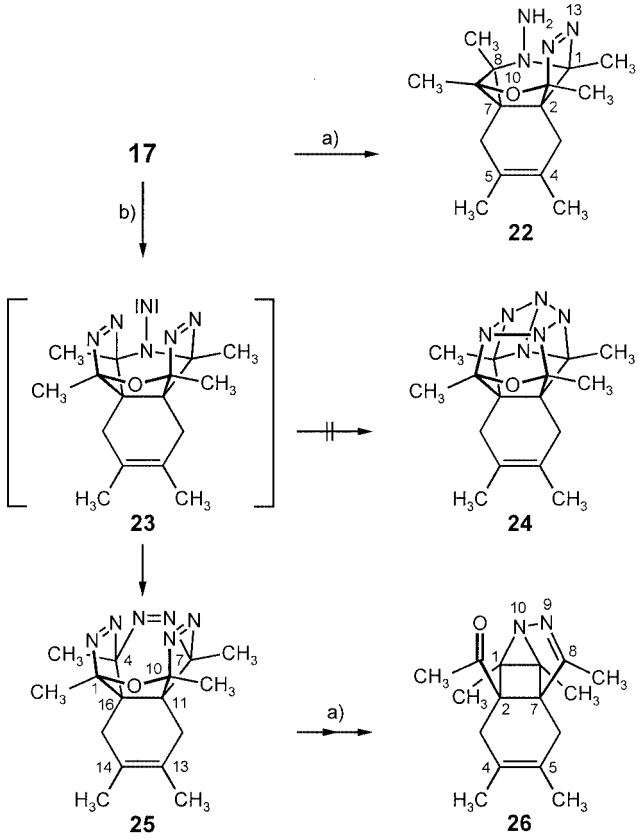
The complex looking **B**-type bis(diazene) **20** (Scheme 2), featuring an unusual oxapentaaza-cyclodecadiene subunit, was discovered fortuitously.[36] Treatment of tetraacetylcyclohexene **14**[37] with hydrazine had been part of a project[9] to construct allylically peralkylated *syn*-periplanar bis(diazenes) (kinetically stabilized tetrazetidines) via bis(isopyrazoles) such as **12** or bis(dihydropyrazines) such as **13**.[38] In practice, treatment of **14** with hydrazine under highly varied conditions had generally produced multi-component reaction mixtures. To avoid some of the complications involved, anhydrous hydrazine and aprotic solvents were used. In experiments performed with an excess of reagent at 0 °C (CH_3CN), the air-sensitive hydrazone/acetal **15** was formed quantitatively, presumably only formally through readdition of the evolving water. Upon warming to room temperature, **15** slowly lost water, while upon being heated (60 °C) in high vacuum, dehydration, presumably to **16**, as a highly unstable solid material, was total. When freshly prepared **16** was treated at 0 °C with $LiClO_4$ as a weak Lewis acid with careful exclusion of moisture, the thermally labile spiro(isopyrazole) **17** became the major product (60%). With **17** seemingly half way to the targeted dispiro(isopyrazole) **12**, the conditions of the condensation **14** → **15** were applied, first with one equivalent of hydrazine. In a very complex mixture including some oxygen-sensitive components, no individual product could be identified. The picture was simplified by use of an increased excess of reagent. When a solution of **17** and ca. four equivalents of hydrazine in CH_3CN was stirred at 0 °C under O_2 and with exclusion of light, three (at least, by TLC) new components were slowly replaced by one, C_s (or C_2) symmetrical (^1H, ^{13}C NMR), species. This $C_{16}H_{24}N_6O$ compound (MS) was isolated in good yield (80%) in the form of pale yellowish, light-sensitive crystals, and was spectroscopically identified as allylically permethylated bis(diazene) **20**. Sublimation at 160 °C/10^{-6} Torr was unproblematic, and decomposition started only well above the melting



Scheme 2. a) anhydr. N_2H_4, CH_3CN, O °C, 12 (5)h, 100(80)%, b) 10^{-3} Torr, room temp. → 60 °C; c) $LiClO_4$, CH_2Cl_2, 0 °C, 30 h, 60%; d) anhydr. N_2H_4, CH_3CN, O_2, O °C, 5 h, 80%; e) C_6H_5CHO, *p*-toluenesulfonic acid, benzene, room temp., 2.5 h, 73%

point of 210 °C. The *O*-bridged bis(pyrazoline) **18** and the oxygen-sensitive tris(hydrazine) **19** are plausible intermediates en route to **20**. Particularly for comparison of the photochemical behavior, the Schiff base **21** was prepared. It was possible to perform an X-ray crystal structure analysis on crystals of **20** obtained from CH_3CN (Figure 2).[39] With d_{av} = 2.97 Å and ω = 154.3°, the proximity parameters are significantly better than those given in Figure 1 for the parent tetramethyl-**B** structure.[36] The C_s symmetry manifested in the NMR spectra of **20** (likewise **17**) attested to the flexibility of the cyclohexene ring.

In relation to the n → π* absorption of **4a**(**b**) [339 (343) nm], the longest-wavelength UV/Vis absorption of **20** [$\lambda_{max}(CH_3CN)$ = 394 nm, ε = 245] was remarkably red-shifted, raising speculations that the *n*-electron pairs of the two "bridge" heteroatoms might extend the N=N/N=N chromophore through homoconjugation. Irradiation with monochromatic light (254 nm) only produced polymers, but use of a sensitizer (acetone) and n → π*-excitation selectively gave the "reluctant" monodiazene **22** (Scheme 3). As pointed out previously,[1a] a geometrically very similar model diene (d = 3.10 Å, ω = 153.3°) efficiently underwent C=C/C=C photocycloaddition.[11] The relatively rigid, nearly in-plane orientation of the NH_2 group and the proximate N=N double bonds (distances of ca. 2.9 Å) suggested a route to the all-*cis*-persubstituted pentazolidine **24** through bis(homoconjugate) [2+2+2] cycloaddition in the corresponding aminonitrene **23**.[40] Like tetrazetidines, pentazolidines are a still elusive family of all-nitrogen heterocycles.[41] Oxidation of **20** with $[Pb(OAc)_4]$ furnished a yellow, crystalline compound of the correct composition in high yield [$C_{16}H_{22}N_6O$, 80−90%, $\lambda_{max}(CH_3CN)$ = 394 nm, ε = 245]: the tris(diazene) **25**, a persubstituted oxa-hexaaza-cycloundecatriene with three homoconjugated N=N bonds, resulting from β-migration in **23**. Upon n → π* excitation, **25** lost two N_2 units to give **26** (39%) together with polymers.



Scheme 3. a) 800-W daylight lamp, Solidex filter, CH_3CN, −40 °C, 74(39)%; b) $[Pb(OAc)_4]$, K_2CO_3, CH_2Cl_2, room temp., 1 h, 80%

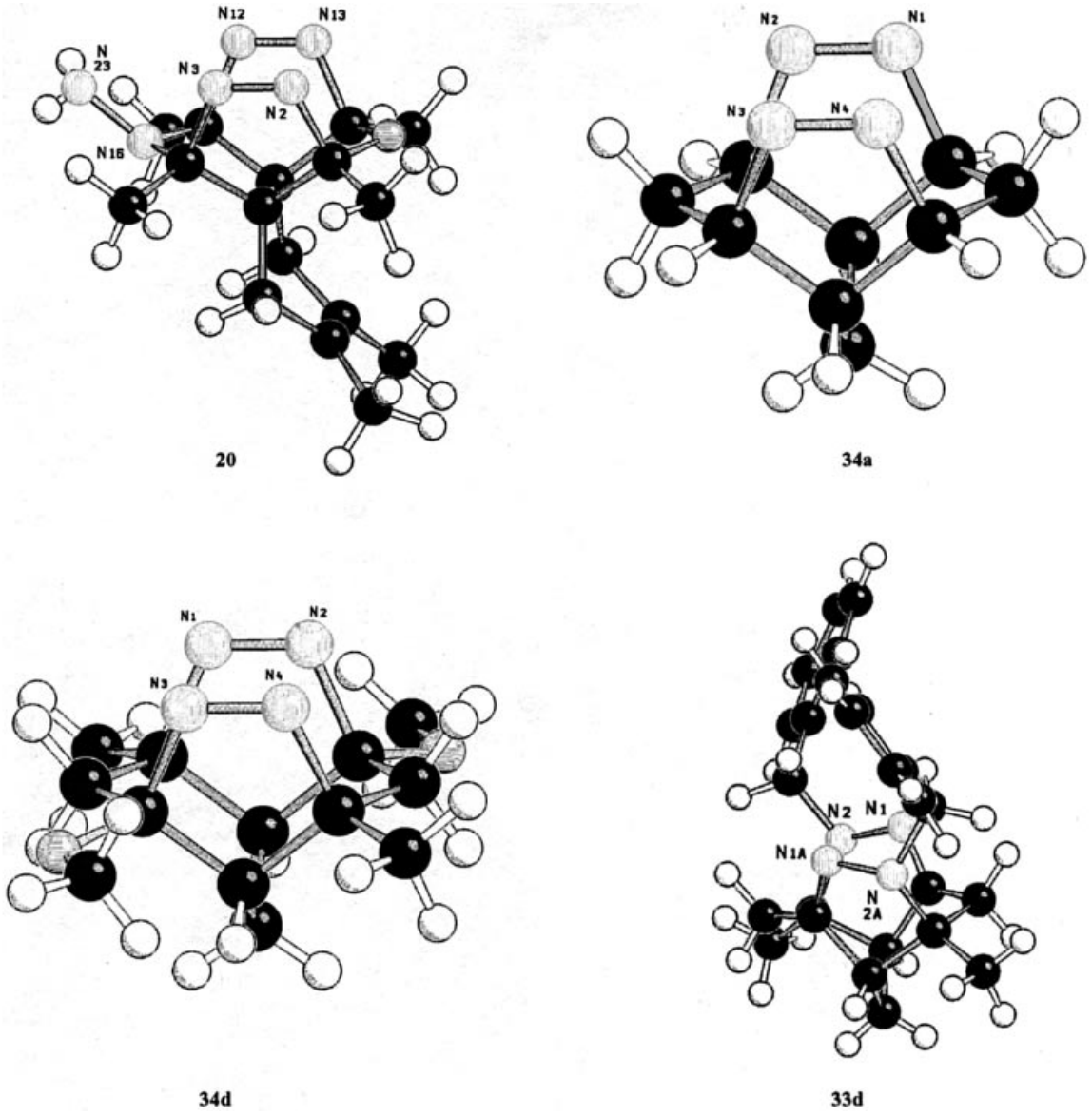
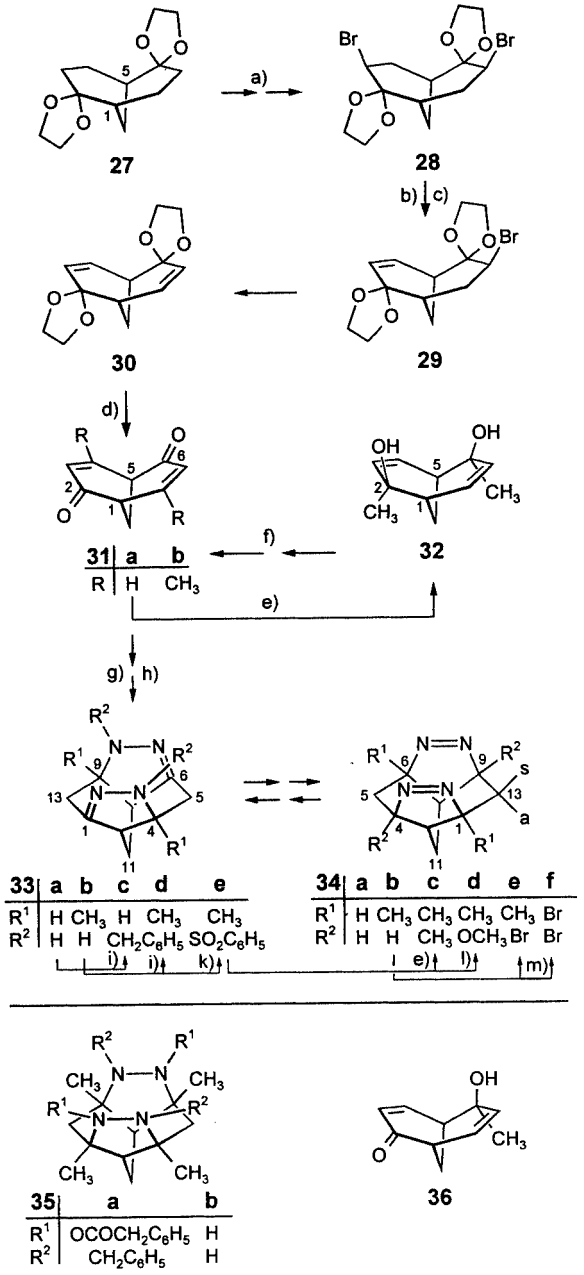


Figure 2. X-ray crystal structures of bis(diazenes) **20**, **34a, 34d** and bispyrazoline **33d;** N=N/N=N distances (d, Å) and interorbital angles (ω,°)

Table 1. Selected distances and angles for **20**, **34a** and **34d**

	20	**34a**	**34d**
	N2··N13/N3··N12	N1··N4/N2··N3	N1··N3/N2··N4
d	2.939 2.999	3.048 3.027	2.980
ω	154.3	159.6	163.1

C-Type Bis(diazenes) 34a−f (Scheme 4): The bis(diazenes) **34a,** 1,6-dimethyl-substituted **34b** and 1,4,6,9-tetramethyl-substituted **34c** were constructed in analogy to the **B**-type analogues **4a−c** (Scheme 1) and in line with the pioneering study of Mellor et al.[14,42a−42c] For **34a** and **34b**, the dienediones **31a** and **31b** served as starting materials. For the preparation of **31a**, the sequence from bicyclo[3.3.1]-nonane-2,6-dione (from paraformaldehyde and dimethyl malonate, "Meerwein ester")[43] → **27** → **28** → **30** → **31a** was developed. In the case of **31b** a proven, but somewhat modified, three-step procedure starting with formaldehyde and acetylacetone[42d] was followed. Still, with **31a** expeditiously available, the two-step sequence worked out for **1c** became an alternative. In practice, the highly side-selective (α) addition of MeLi/$CeCl_3$ to **31a** and oxidative transposition of bis(carbinol) **32** furnished **31b** in up to 60%



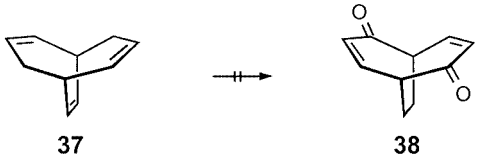
Scheme 4. a) $C_5H_5NBr_3$, THF, −78 °C → room temp., 2 h, 87%; b) CH_3ONa, DMSO, 80 °C, 2 h, 81%; c) CH_3ONa, DMSO, 90 °→ 120 °C, 4 h, 68%; d) acetone, sulfosalicylic acid, 40 °C, 6 h, 90%; e) $CH_3Li/CeCl_3$, THF, diethyl ether, room temp.2(10)h; 82(71)%; f) PCC, K_2CO_3, room temp., 10 h, 77%; g) $N_2H_4{\cdot}H_2O$, ethanol, room temp. 15 h; 100%. h) $N_2H_4{\cdot}H_2O$, ethanol, K_2CO_3, reflux, 7 h, 60%; i) $C_6H_5CH_2Br$, DMF, K_2CO_3, 80 °C, 16 h, 60(70)%; k) $C_6H_5SO_2Cl$, pyridine, room temp.,12 h, 72%; l) CH_3OH, room. temp. → 40 °C, 80%; m) Br_2, CH_2Cl_2, −78 °C → room. temp., 82(84)%; n) NCS, $CHCl_3$, room temp., 4 h, 92%

yield. From the controlled reactions of **31a** and **31b** with $N_2H_4{\cdot}H_2O$ the bis(pyrazolines) **33a** and **33b** were produced nearly quantitatively and, being less torsionally strained but still air-sensitive, were used directly after evaporation of the reaction solutions. Under conditions somewhat less forcing than the "one-pot" operations with **1a** or **1c**, the yields achieved for **34a** and **34b** were higher (60 and 80%). For the synthesis of the tetramethyl compound **34c**, as for **4d**, the two-step procedure **33b** → **33e** → **34c** (overall ca. 50%) replaced the preparatively unserviceable five-step route **31b** → **33b** → **33d** (X-ray structure, Figure 2)[39] → **35a** → (**35b**) → **34c** (ca. 10% overall[3c,3d]).

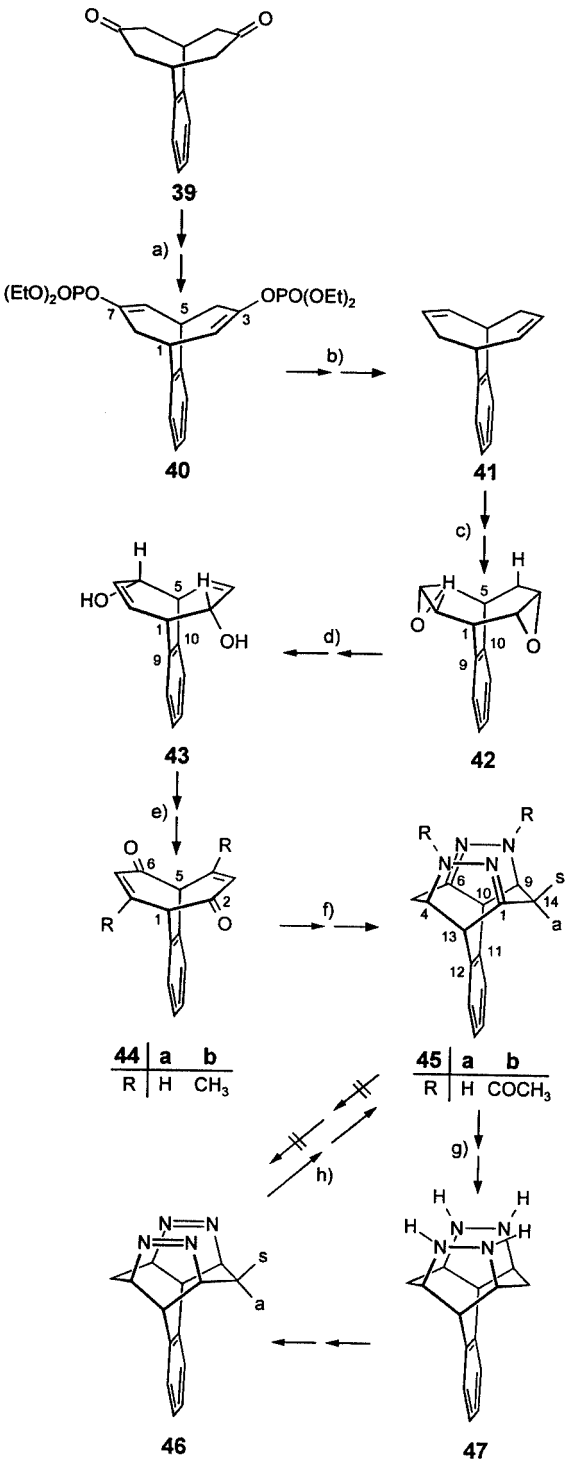
As noted for the skeletons **4,** all efforts to bridge the allylic positions in **34a** (C1/C4;C6/C9, cf. **E**, Figure 1) remained without success. In this context, inter alia, the dimethyl-dimethoxy compound **34d** (see: Figure 2)[39] and the bridgehead-halogenated **34e** and **34f** were prepared.

The bis(diazenes) **34a**−**f** are, in common with the series **4a**−**f**, thermally persistent up to their melting points and storable at room temperature in the absence of light and oxygen. The spectral trends cited for **4a**−**f** as characteristics of "proximate", closed conformations influenced by the buttressing bridgehead substituents are similarly notable. Thus, the shift differences $\Delta[\delta_{5(13)H_s} - \delta_{5(13)H_a}]$ increase from **34a** (δ = 1.19 ppm), to **34b** (δ = 1.33 ppm), to **34c** (δ = 1.44 ppm) and the n → π* transitions are, if only very slightly, bathochromically shifted (333 nm for **34a**, 334 nm for **34b**, 335 nm for **34c**). The X-ray structural analyses[39] for **34a** [*d*(av.) = 3.04 Å, calculated 3.15 Å, ω = 156.3°, Figure 1] and **34d** underline these trends (Table 1).

D-Type Bis(diazenes) 46: (Scheme 5)[15] At the planning stage, bicyclo[3.3.2]decadienedione **38**[44] had been targeted as a precursor for the parent bis(diazene) **D** (Figure 1). This approach, however, came to an early end when no way to transform bicyclo[3.3.2]decatriene **37**[45] into **38** could be found. Recourse was therefore made to the 9,10-benzoanellated derivative **46**, for which the calculated *d*/ω parameters (MMX) hardly differed from those of parent **D** and for which the starting material was readily accessible in the form of benzocyclooctene-3,7-dione **39**.[46] However, the seemingly trivial transformation **39** → **41** proved tricky. Ultimately, the Fetizon procedure[47] was once more[48] found to be of practical use, superior to various procedures that had been severely hampered by side reactions (primarily bridging in the eight-membered ring[49]).



The intermediate bis(enolate) provided effective charge separation and thus a moderately selective formation of the C_2-symmetrical bis(enol) ester **40** (66%). Hydrogenolysis of this to give the diene **41,** though, turned out to be somewhat erratic (60−90%), primarily due to the difficulty in controlling overreduction. In exceptional cases, the yield could drop to ca. 30%. The reagent of choice for the twofold epoxidation of waxy solid **41** was dimethyldioxirane (DMDO) α,α-diepoxide **42** accounted for ca. 80% of the quantitatively produced mixture with the α,β isomer. After this mixture had been exposed to standard conditions for epoxide → allylic alcohol rearrangement (LDA/THF), only the major 2α,6α-diol **43** was isolated after chromatographic



Scheme 5. a) $(CH_3)_2CHLi$, THF, −78 °C → room temp., TMEDA, diethyl chlorophosphate, room temp., 66%; b) Li, NH_3, −78 °C, *t*BuOH, 96%; c) DMDO, acetone, room temp., 10 h, 100%, d) $(CH_3)_2CHLi$, THF, −78 °C → room temp., 72%; e) pyridinium dichromate, CH_2Cl_2, 2 h, 45−60%; f) $N_2H_4\times H_2O$, methanol, room temp. 10 h; 100%. g) $NaCNBH_3$, methanol, room temp., 48 h, $CuCl_2$, NH_3,, 60−75%. h) CH_3CO_2H, ethanol

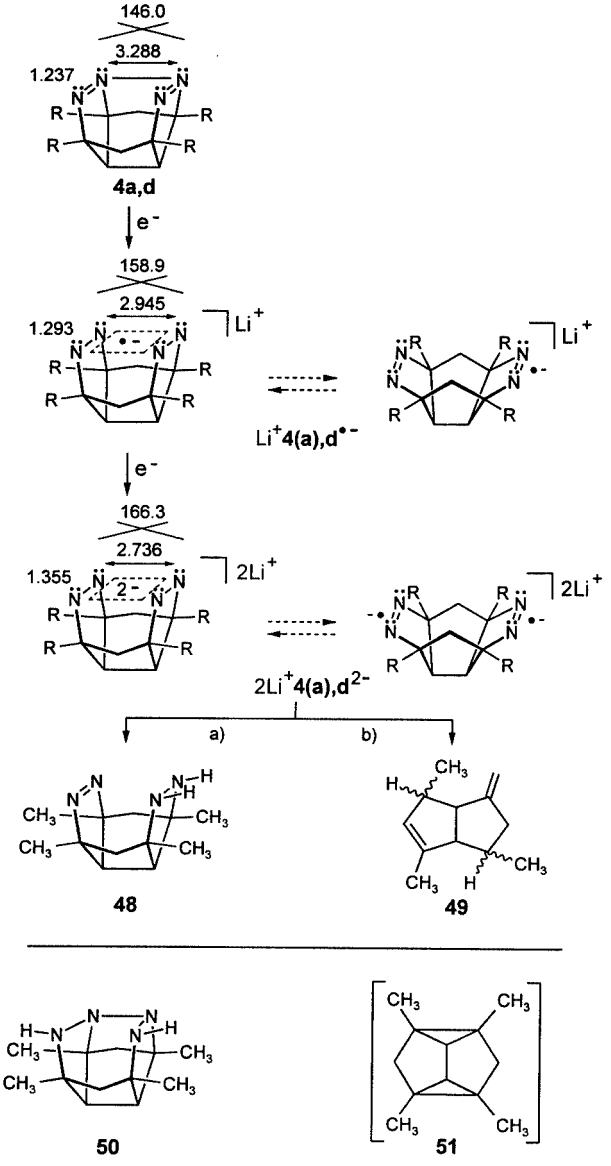
workup (72%), and this was oxidized to give the crystalline diene-2,6-dione **44a**, if only in modest yield (45−60%, λ_{max} (MeOH) = 363, 236 nm; cf. λ_{max} (EtOH) = 314, 230 nm for cycloocten-2-one[50]). It should be added that the stereochemistry formulated in **42** and **43** was not unequivocally corroborated by the ^1H NMR spectroscopic data but was highly plausible in view of the established α-additions to the carbonyl groups of **39**. When **44a** was added slowly to a vast excess of $N_2H_4\cdot H_2O$ at room temperature, C_2-symmetrical bis(pyrazoline) **45a** was the rapidly and quantitatively generated product, which was derivatized as the bis(acetamide) **45b**. Bis(diazene) **46** was expected to be thermodynamically less stable than **45a**; and indeed, under "one-pot" conditions, not even traces of **46** were produced. A detour through reduction of **45a** to the bis(hydrazine) **47** (with $NaBH_3CN$[51] rather than $LiAlH_4/AlCl_3$ [52]) and immediate oxidation ($CuCl_2$) was straightforward. During chromatography of the crude material on base-treated silica gel, however, **46** (60−75% isolated) was partly isomerized back to **45a**. The isomerization was rapid and total upon addition of acetic acid to a solution of **46** in ethanol. H,H Coupling constants [$J_{1,13(4,13)(6,10)(9,10)}$ = 11.0, $J_{1,14s(4,5s)(5s,6)(9,14s)}$ = 5.4, $J_{1,14a(4,5a)(5a,6)(9,14a)}$ = 3.0 Hz] and n → π* absorption (CH_3OH, 336 nm) fitted with expectations based on the rather "closed" structure calculated for parent **D**-bis(diazene).

2. Electron Transfer to the Bis(diazenes) 4a and 4d

For the reported $M^+4N/5e\cdot^-$ and $2M^+4N/6e^{2-}$ ion pairs,[17−19] the calculated differences in N=N/N=N preorientation (counter-ion-free *d*: 2.7−3.0 Å, ω: 179−163°; $^-$*d*: 2.6−2.7 Å, ω: 180−175°) in ion pairing and kinetic protection were manifested in their greatly differing lifetimes. Thus, the green radical anions (λ_{max} = 700−900 nm) generated through short contact of the **A**- (**A_{12}**, **A_{22}**), **C**- (**34a, 34c**), and **D**-type (**46**) bis(diazenes) to Li, K, or Cs either persisted at room temperature for days or even months (**A_{12}**, **A_{22}**, **34c**), or decayed within minutes if not seconds (**34a**, **46**). Nevertheless, all five radical anions could be analyzed spectroscopically by ESR, and the three most persistent ones (Li^+**A_{12}**$\cdot^-$, Li^+**A_{22}**$\cdot^-$, Li^+**34c**$\cdot^-$) allowed smooth reduction to the golden yellow (red at NMR concentrations) $2Li^+$**A_{12}**$^{2-}$, $2Li^+$**A_{22}**$^{2-}$, and $2Li^+$**34c**$^{2-}$ dianions (λ_{max} = 360−430 nm), the absorbance remaining constant for weeks. Thermodynamically meaningful information became available when the first and second reduction potentials ($E_{1/2}$ ca. −2.4; −2.9 V) were recorded by cyclic voltammetry for the most proximate **A_{12}** and **A_{22}** bis(diazenes), together with the first reduction potential ($E_{1/2}$ = −2.72 V) for the more "distant" **34c**.

In Figure 1, the **B_{11}**-bis(diazenes) (**4a**, **4d**) possess the largest N=N distances, close to the limiting van der Waals distance, and the smallest interorbital angles. These skeletons also display the highest mobility and so adjust more easily to the geometrical changes necessitated by the respective, "tighter" 4N/5(6) anions, but could also avoid the imposed concentration of charge by changing into more "extended" conformations. From the B3LYP/6−31G* calculations,[7] the counter-ion-free anions derived from **4a** and **4d** emerged as cyclically in-plane delocalized $4N/5(6)e\cdot^-$

species (Scheme 6). Extended localized conformations (e.g., N=N·⁻/N=N·⁻; N=N/N=N^{2-}) were significantly higher in energy.[53] The changes in N=N/N=N distances (d), N=N bond lengths (d'), and interorbital angles (ω) on going from neutral **4d** to radical anion **4d**·⁻ [$\Delta d(d')$ = −0.34(+0.056) Å, Δω = +12.9°] to dianion **4d**$^{2-}$ [$\Delta d(d')$ = −0.21(+0.062) Å, Δω = +7.4°] − as consequences of homoconjugational/homoaromatic interaction − are even larger than seen for the structurally closest reductions **34c** → **34c**·⁻ (Δd = −0.26 Å, Δω = +8.7°) → **34c**$^{2-}$ (Δd = −0.17 Å, Δω = +5.6°). Still, with d = 2.95 Å (ω = 158.9°) for **4d**·⁻ and d = 2.74 Å (ω = 166.3°) for **4d**$^{2-}$, the homoconjugate distances are longer, the interorbital angles smaller.



Scheme 6. Calculated (B3LYP/6−31G*) N=N/N=distances (d, Å), N=N bond lengths (d', Å) and interorbital angles (ω,°) for the counter-ion-free, in-plane delocalized ("closed") **4d**, **4d**·⁻ and **4d**$^{2-}$. a) **4d,** Li, [D$_8$]THF, room temp., 1 h, H_2O; b) **4d,** Li, [D$_8$]THF, room temp., 50−70 h, H_2O

In UV-monitored reduction experiments with **4a** (Li, carefully degassed and dried THF) under various conditions (−60 up to +20 °C), rapid decomposition without evolution of color was noted. In the case of **4d**, the color of the THF solutions changed to green, then to golden yellow (15−20 min, λ_{max} = 400 nm, tailing to ca. 580 nm); this color, though, was clearly less brilliant than that seen in the reduction of **34c**. When such a sample was exposed to air after one hour, instantaneous decoloration occurred, without the green color of the intermediate radical anion being discernible,[18a,18b] and **4d** was recovered nearly quantitatively. The ^{1}H NMR spectra (500 MHz) of homogeneous, more concentrated (ca. 4 × 10^{-2} M, brownish-red) [D$_8$]THF solutions, recorded ca. 1 hour after exposure to Li (room temperature), proved surprisingly complex. In addition to broad absorptions with sharp singlet signals between δ = 2.1 and 1.1 ppm, presumably due to higher aggregated dianions, very weak signals (5−8% of total integrated intensity) were recorded for, in all probability, 2Li$^+$**4d**$^{2-}$, doublet signals with δ = 3.05 and 2.25 ppm (J = 14.9 Hz) for 5(12)-H$_s$ and 5(12)-H$_a$, dia- and paramagnetically, respectively, displaced versus δ = 3.28/2.02 ppm for neutral **4d**. The shift differences of Δδ = +0.23/−0.23 ppm, to be compared with Δδ = +0.14/−0.35 for **34c** → 2Li$^+$**34c**$^{2-}$ (2.55 → 2.41; 1.52[54] → 1.87 δ), reflect a good in-plane alignment with the N$_4$-ring for the *syn*-hydrogen atoms. After ca. 2 h, additional signals appeared at δ = 4.8 and 5.4 ppm and increased slowly at the expense of the doublet signals of 2Li$^+$**4d**$^{2-}$, disclosing the latter's decomposition to olefinic products. Practically total twofold reduction of a sample after ca. 1 hour exposure to Li was confirmed when addition of deoxygenated H_2O to the brownish-red THF solution furnished the extremely oxygen-sensitive diazene/dihydrodiazene **48** nearly quantitatively (traces of **4d**). As in the protonation of 2Li$^+$**34c**$^{2-}$, but differently from that of the **A**-type dianions, homoconjugate addition (here to give tetrazane **50**) did not occur. When water was added to samples kept much longer in contact with the metal (50−70 h), besides mainly **4d** (50−60%, oxidation of **48**), a small amount (5−10%, roughly corresponding with the NMR proportion for 2Li$^+$**4d**$^{2-}$) of a mixture of highly volatile $C_{12}H_{18}$ hydrocarbons (inter alia, isomers **49**) was separated chromatographically, but was found to be too complex for individual assignments (specifically, triasterane **51**, known as a product of the direct irradiation (λ > 280 nm) of **4d**,[2g,55] was not a major component). As before,[18a] it can only be speculated about the sequence of events implying the formal extrusion of two Li$^+$N$_2$·⁻ (N$_2$/2Li$^+$N$_2^{2-}$?) units. Because of the very complex product composition, neither ^{13}C NMR spectroscopic data for 2Li$^+$**4d**$^{2-}$ nor ESR data for the radical anion (Li$^+$**4d**·⁻) could be secured.

Conclusions

The discovery of novel bonding motifs has developed into a major reward for the enormous investment that had gone into the synthesis of the **A**−**D**-type bis(diazenes). It

needs no further comment that these bis(diazenes), thanks to the fixed *cis* arrangement of four nitrogen substituents on more or less rigid carbon skeletons, are also valuable building blocks in synthesis. A forthcoming paper will be devoted to their use for the construction of cage structures as potential hosts for the so far unknown bonding motifs with seven and six electrons cyclically delocalized in the plane made up of two parallel hydrazine units [4N/7(6)e cations].[56] Sound calculated and experimentally obtained evidence is provided that Li-mediated one-/two-electron transfer even to the comparably "distant" bis(diazene) **4d** enforces the formation of bis(homoconjugated) Li^+**4d**$^{\cdot -}$ and $2Li^+$**4d**$^{2-}$ ion pairs, if only as minor, comparably short-lived components of very complex ion clusters. It is reasonable to relate the decrease in stability (persistence) of these ion pairs, at least in part, to their geometries, with the so far longest documented homoconjugate N=N/N=N distances (*d*) and poorest orbital alignments (ω). As stated previously,[18a] a more quantitative assessment of the degree of thermodynamic stabilization ["σ-bis(homoaromaticity)", ring current] in the 4N/6e dianions has to await the outcome of ongoing calculations.

Experimental Section

General Remarks: Melting points were determined with a Monoskop IV (Fa. Bock) instrument and are uncorrected. Elemental analyses were performed by the Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. IR spectra were measured with a Perkin−Elmer 457 or a Phillips PU 9706 machine, ^{1}H NMR spectra with a Bruker AC 250 or AM 400 instrument, and ^{13}C NMR spectra with a Bruker AM 400. When necessary, assignments were confirmed by homo- and heteronuclear decoupling and by H,H and H,X correlation experiments. Chemical shifts are given relative to TMS (δ = 0 ppm), coupling constants in Hz; if not specified otherwise, the 250 MHz (^{1}H) and 100.6 MHz (^{13}C) spectra recorded in $CDCl_3$ are given; values marked with an asterisk are interchangeable. Mass spectra were run with a Finnigan MAT 44S spectrometer (EI, 70 eV, if not specified differently). All reactions with metallorganic reagents were performed with careful exclusion of air, the condensation reactions with hydrazine hydrate generally in deoxygenated solutions (p.a. grade solvents). For TLC, silica gel plates 60 F_{254} (Merck, Darmstadt) were used. The silica gel used for column chromatography was purchased from Merck (0.040−0.063 mm) or ICN, Biomedicals GmbH (0.032−0.063 mm). The conditions for the reduction experiments were generally those of the preceding study.[18a]

4,8-Dimethylbicyclo[3.3.0]octa-3,7-diene-2,6-dione (1c): K_2CO_3 (708 mg, 5.12 mmol) was dried at 110 °C for 4 h. After addition of pyridinium chlorochromate (3.32 g, 15.4 mmol) and CH_2Cl_2 (35 mL) and stirring for 30 minutes, a solution of **2** (850 mg, 5.1 mmol) in CH_2Cl_2 (50 mL) was added dropwise (2 h). After the mixture had been stirred for 10 h, filtered, and concentrated in vacuo, the solid residue was chromatographed [silica gel, cyclohexane/ethyl acetate, 1:1, R_f(**1c**) = 0.28] to provide colorless crystals (635 mg, 77%); m.p. 107 °C (cyclohexane). IR (KBr): $\tilde{\nu}$ = 1678 cm^{-1} (C=O), 1604 (C=C). ^{1}H NMR: δ = 5.70 (s, 3-,7-H), 3.50 (s, l-,5-H), 2.25 (s, 2 CH_3) ppm. ^{13}C NMR: δ = 202.5 (C-2,-6), 174.6 (C-4,-8), 127.9 (C-3,-7), 57.8 (C-1,-5), 18.1 (CH_3) ppm. $C_{10}H_{10}O_2$ (162.2): calcd. C 74.04, H 6.23; found C 73.67, H 6.07.

2α,6α-Dimethylbicyclo[3.3.0]octa-3,7-diene-2β,6β-diol (2): $CeCl_3 \cdot H_2O$ was dehydrated at 160 °C/0.1 Torr for 8 h, and was then flame-dried until the pink powder became grayish. Dry THF (Na/benzophenone, 110 mL), then followed at −78 °C by MeLi (28.0 mL, 1.6 M solution in diethyl ether, 44.8 mmol), were added dropwise to anhydrous $CeCl_3$ (11.1 g, 44.8 mmol). After this system had been stirred for 60 minutes, the solution of **1a** (2.00 g, 14.9 mmol) in anhydrous THF (50 mL) was slowly added at room temperature. After total conversion (3 h), the mixture was hydrolyzed (satd. aqueous NH_4Cl) and concentrated in vacuo. The residue was extracted with diethyl ether (5 × 50 mL) and the dried organic phase ($MgSO_4$) was concentrated in vacuo. The solid residue was flash chromatographed (silica gel, cyclohexane/ethyl acetate, 1:1), the main fraction R_f(**2**) = 0.30 was concentrated, and colorless crystals (2.10 g, 85%) were isolated; m.p. 108 °C (cyclohexane). IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} (OH), 1620 (C=C). ^{1}H NMR: δ = 5.85 (d, 4-,8-H), 5.61 (d, 3-,7-H), 3.08 (s, 1-,5-H), 2.17 (s, 2 OH), 1.38 (s, 2 CH_3) ppm; $J_{3,4}$ = 6.0 Hz. ^{13}C NMR: δ = 139.0 (C-4,-8), 130.7 (C-3,-7), 82.9 (C-2,-6), 58.8 (C-1,-5), 28.2 (CH_3) ppm. $C_{10}H_{14}O_2$ (166.2): calcd. C 72.26, H 8.51; found C 72.60, H 8.91. Occasionally a small amount (up to 5%) of **6β-Hydroxy-6α-methylbicyclo[3.3.0]octa-3,7-diene-2-one (5)** (R_f = 0.14) was separated. Colorless crystals, m.p. 64 °C (cyclohexane). IR (KBr): $\tilde{\nu}$ = 3444 cm^{-1} (OH), 1684 (C=O). ^{1}H NMR: δ = 7.68 (d, 4-H), 5.99 (d, 3-H), 5.74 (d, 6-H)*, 5.56 (7-H)*, 3.32 (s, 1-,5-H), 2.21 (s, OH), 1.46 (s, CH_3) ppm; $J_{3,4}$ = 6.0 Hz. ^{13}C NMR: δ = 210.3 (C-2), 164.1 (C-4), 138.9 (C-6), 131.9 (C-3)*, 129.1 (C-7)*, 82.2 (C-8), 56.9 (C-1)**, 54.5 (C-5)**, 29.6 (CH_3). $C_{10}H_{14}O_2$ (150.2) ppm.

10,11-Dimethyl-2,3,7,8-tetraazatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodeca-1,6-diene (3b): A solution of **1b** (325 mg, 2.0 mmol) in ethanol (25 mL) was slowly added (30 min) at room temperature to a solution of hydrazine hydrate (250 mg, 5.0 mmol) in ethanol (5 mL). After stirring until total conversion (TLC, ca. 10 h) and concentration in vacuo, the yellowish, water-soluble solid residue consisted of practically pure, highly air-sensitive **3b** (380 mg, ca. 100%), m.p. 155 °C (dec.) and was used as such. IR (KBr): $\tilde{\nu}$ = 1656 cm^{-1} (C=N). ^{1}H NMR (D_2O): δ = 3.28 (d, 4-,29-H_s), 2.81 (dd, 5-,12-H_s), 2.45 (d, 5-,12-H_a), 0.92 (s, 2 CH_3) ppm; $J_{4,5a(9,12a)}$ = 6.0, $J_{5a,5s(12a,12s)}$ = 18.5 Hz. ^{13}C NMR (D_2O): δ = 164.5 (C-1,-6), 63.8 (C-4,-9), 58.4 (C-10,-11), 32.2 (C-5,-12), 14.8 (CH_3) ppm. HRMS: calcd. for $C_{10}H_{14}N_4$ 190.1219; found 190.1210. A sample of **3b** equilibrated after 7 days at room temp. to a ca. 9:1 mixture with **4b**.

4,9-Dimethyl-2,3,7,8-tetraazatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodeca-1,6-diene (3c): See **3b**. Hydrazine hydrate (400 mg, 8.0 mmol)/ethanol (5 mL)/**1c** (325 mg, 2.0 mmol)/ethanol (25 mL)/30 min. After stirring for ca. 12 h and concentration in vacuo, the yellowish solid residue (380 mg) consisted of nearly pure, air-sensitive **3c**, m.p. 97 °C (dec.), and was used as such. IR (film): $\tilde{\nu}$ = 1592 cm^{-1} (C=N). ^{1}H NMR (500 MHz, CD_3OD): δ = 3.27 (d, 5-,12-H_s), 2.46 (s, 10-,11-H), 2.39 (d, 5-,12-H_a), 1.38 (s, 2 CH_3) ppm; $J_{5a,5s(12a,12s)}$ = 15.0 Hz. ^{13}C NMR (CD_3OD): δ = 125.9 (C-1,-6), 57.3 (C-10,-11), 45.4 (C-5,-12), 23.9 (CH_3) ppm. $C_{10}H_{14}N_4$ (190.3): calcd. C 63.13, H 7.42, N 29.45; found C 63.47, H 7.48, N 28.97.

3,8-Dibenzyl-4,9-dimethyl-2,3,7,8-tetraazatetracyclo-[7.2.1.0^{4,11}.0^{6,10}]dodeca-1,6-diene (3d): K_2CO_3 (5.46 g, 40.0 mmol) and benzyl bromide (1.71 g, 10.0 mmol) were added to a solution of **3c**, prepared from hydrazine hydrate (800 mg, 16.0 mmol) and **1c** (650 mg, 4.0 mmol) in anhydrous DMF (65 mL). After the mixture had been stirred for ca. 10 h, warmed to 40 °C for 4 h (total conversion, TLC), and evaporated in vacuo, the solid residue was dissolved in CH_2Cl_2 (50 mL) and washed with phosphate buffer (pH 7). After concentration of the dried ($MgSO_4$) organic phase,

the solid residue (ca. 900 mg) was flash chromatographed (silica gel, cyclohexane/ethyl acetate, 2:1), to afford oily, air-sensitive **3d** (608 mg, 41%). This, sensitive even to base-treated silica gel, was partly lost during its separation. IR (KBr): $\tilde{\nu}$ = 1662 cm^{-1}, 1489 (C=C). ^1H NMR: δ = 7.30 (m, 10-H), 4.25 (1-H) 3.81 (d, 2-H) 3.70 (s, 10-,11-H), 3.05 (d, 5-,12-H_s), 2.01 (d, 5-,12-H_a), 1.59 (s, 2 CH_3) ppm; J_{C,H_2} = 14.0, $J_{5a,5s(12a,12s)}$ = 9 Hz. ^{13}C NMR: δ = 164.3 (C-1,-6), 139.7, 128.4, 128.3, 126.9 (10 C), 81.5 (C-4,-9), 62.4 (C-10,-11), 53.8 (C-1′), 33.2 (C-5,-12), 25.2 (CH_3) ppm. MS: *m*/*z* (%) = 370 (17) [M^+], 279 (28) [M −$CH_2C_6H_5^+$], 185 (50), 91 (100) [$CH_2C_6H_5$].

4,9-Dimethyl-3,8-di(phenylsulfonyl)-2,3,7,8-tetraazatetracyclo-[7.2.1.0^{4,11}.0^{6,10}]dodeca-1,6-diene (3e): See **3c**. Benzenesulfonyl chloride (915 mg, 5.2 mmol) was added to a solution of **3c**, prepared from hydrazine hydrate (400 mg, 8.0 mmol) and **1c** (325 mg, 2.0 mmol) in anhydrous pyridine (7 mL). After the deep red solution had been stirred for ca. 12 h and concentrated in vacuo, the brownish-red, rapidly decomposing solid material (ca. 90% **3e**) was used as such. For analytical purposes, a small amount of material was separated, with substantial loss, by flash chromatography (silica gel, $CHCl_3$/MeOH, 10:1). ^1H NMR: δ = 8.78 (m, 2 H), 8.01 (m, 4 H), 7.55−7.45 (m, 4 H), 3.51 (d, 5-,12-H_s), 2.63 (s, 10-,11-H), 2.51 (s, 5-,12-H_a), 1.50 (s, 2 CH_3) ppm; $J_{5a,5s(12a,12s)}$ = 14.7 Hz. $C_{22}H_{22}N_4O_4S_2$ (470.7).

2,3,7,8-Tetraazatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodeca-2,7-diene (4a): This compound was prepared on gram-scale as described,[23a] except for the more simple use of a sealed round-bottomed flask and a shorter reaction time (3 d).

10,11-Dimethyl-2,3,7,8-tetraazatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodeca-2,7-diene (4b): See **4a** ("one-pot" reaction conditions).[23] A solution of **1b** (330 mg, 2.0 mmol) in ethanol (30 mL) was slowly added (2 h) at room temperature to a stirred solution of hydrazine hydrate (400 mg, 8.0 mmol) in anhydrous ethanol (30 mL). After the mixture had been kept at 80 °C for 3 days and concentrated in vacuo, the brownish, oily residue contained a ca. 9:1 mixture of **3b** and **4b** (270−290 mg, 77−79%, ^1H NMR). Dissolved in CH_2Cl_2/acetone (20:1), the mixture was filtered through silica gel [R_f(acetone/CH_2Cl_2/ethyl acetate, 1:1:1) = 0.40]. Only **4b** (30 mg, 8%) was eluted; colorless crystals; m.p. 140 °C (toluene, dec., N_2 elimination). UV (CH_3CN): λ_{max} (ε) = 343 nm (770). IR (KBr): $\tilde{\nu}$ = 1540 cm^{-1} (N=N). ^1H NMR: δ = 4.58 (d, 1-,4-,6-,9-H), 3.48 (d, 5-,12-H_s), 2.50 (dt, 5-,12-H_a), 1.18 (s, 2 CH_3) ppm; $J_{1,12a(4,5a)(6,5a)(9,12a)}$ = 8.0, $J_{5a,5s(12a,12s)}$ = 15.0 Hz. ^1H NMR (D_2O): δ = 4.71 (d, 1-,4-,6-,9-H), 3.22 (d, 5-,12-H_s), 2.67 (dt, 5-,12-H_a), 1.18 (s, 2 CH_3) ppm. $J_{1,12a(4,5a)(6,5a)(9,12a)}$ = 8.5, $J_{5a,5s(12a,12s)}$ = 16.0 Hz. MS (CI, NH_3): *m*/*z* (%) = 208 (10) [M + NH_4]$^+$, 191 (3) [M + H]$^+$. HRMS: calcd. for $C_{10}H_{14}N_4$ 190.1219; found 190.1201. For convenient separation, the 9:1 mixture was extracted either with water (**3b**) or CH_2Cl_2 (**4b**). Pure **4b** after 7 days at room temp. had equilibrated with **3b,** ratio ca. 1:9.

1,6-Dimethyl-2,3,7,8-tetraazatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodeca-2,7-diene (4c): See **4a**. Hydrazine hydrate (400 mg, 8.0 mmol)/ethanol (2.5 mL)/**1c** (300 mg, 1.85 mmol)/ethanol (30 mL)/4 h. After the mixture had been heated at 80 °C for 10 days and concentrated in vacuo, the solid residue (ca. 50% **4c** and polymers) was flash chromatographed on silica gel. The residue of the fraction with R_f (acetone/$CHCl_3$, 5:1) = 0.41 was crystallized from THF, providing colorless crystals (90 mg, 51%); m.p. 147 °C (dec., N_2 elimination). The crystals survived sublimation (60 °C, 10^{-3} Torr) unchanged. IR (KBr): $\tilde{\nu}$ = 1538 (C=N). UV (CH_3CN): λ_{max} (ε) = 339 nm (501), 198 (906). ^1H NMR: δ = 4.94 (ddd, 4-,9-H), 3.48 (d, 5-,12-H_s), 2.53 (dd, 10-,11-H), 2.29 (dd, 5-,12-H_a), 1.32 (s, 2 CH_3) ppm; $J_{4,5a}$ = 8.3, $J_{4,5s}$ < 1, $J_{5a,5s}$ = 15.1, $J_{4,10}$ = 2.9, $J_{4,11}$ = 4.7 Hz. ^{13}C NMR: δ = 102.6 (C-1,-6), 95.9 (C-4,-9), 53.7 (C-10,-11), 39.0 (C-5,-12), 22.7 (CH_3) ppm. MS (CI, isobutane): *m*/*z* (%) = 191 (100) [M + H]$^+$. $C_{10}H_{14}N_4$ (190.3): calcd. C 63.11, H 7.43, N 29.45; found C 62.65, H 7.03 N 29.14.

1,4,6,9-Tetramethyl-2,3,7,8-tetraazatetracyclo[7.2.1.0^{4,11}.0^{6,10}]-dodeca-2,7-diene (4d): See **2**. **From 3e:** A solution of freshly prepared, crude **3e** (900 mg, ca. 800 mg **3e**, ca. 1.8 mmol) in anhydrous THF (80 mL) was slowly added (60 min) to a suspension of the MeLi/$CeCl_3$ reagent (dry $CeCl_3$, 1.05 g, 4.3 mmol, THF, 75 mL; MeLi, 3.6 mL, 1.6 M in diethyl ether, 5.8 mmol). The brownish suspension was stirred for 12 h, and then hydrolyzed (satd. aqueous NH_4Cl, 50 mL). After extraction with *tert*-butyl methyl ether (5 × 60 mL), the dried ($MgSO_4$) organic phase was concentrated in vacuo and the solid residue was filtered through silica gel ($CHCl_3$/MeOH, 1:1). After standard workup and crystallization (diethyl ether), colorless crystals (195−270 mg, 50−70%) were isolated; they remained unchanged during sublimation at 70 °C/10^{-3} Torr. M.p. 167 °C (dec., N_2 elimination). UV (CH_3CN): λ_{max} (ε) = 343 nm (470). IR (KBr): $\tilde{\nu}$ = 1547 cm^{-1} (N=N). ^1H NMR: δ = 3.48 (d, 5-,12-H_s), 2.19 (s, 10-,11-H), 2.04 (d, 5-,12-H_a), 1.35 (s, 4 CH_3) ppm; , $J_{5s,5a(12s,12a)}$ = 15.1 Hz. ^1H NMR ([D_8]THF): δ = 3.28 (d, 5-,12-H_s), 2.18 (s, 10-,11-H), 2.02 (d, 5-,12-H_a), 1.26 (s, 4 CH_3) ppm; $J_{5s,5a(12s,12a)}$ = 14.9 Hz. ^{13}C NMR: δ = 102.6 (C-1,-4,-6,-9), 59.5 (C-10,-11), 46.2 (C-5,-12), 24.1 (CH_3) ppm. MS (CI, isobutane, 200 eV), *m*/*z* (%) = 219 (100) [M + H]$^+$. $C_{12}H_{18}N_4$ (218.3): calcd. C 66.02, H 8.31, N 25.67; found C 65.87, H 8.43, N 25.76. **From 8a:** A solution of crude **8a** (ca. 500 mg, 0.75 mmol) in ethanol/ethyl acetate (100 mL, 1:2) was vigorously stirred over Pd/C (10%, 300 mg) under H_2 (1 bar). After total conversion (5 h, **8b**), a saturated aqueous $CuCl_2$ solution (3 mL) was added and stirring was continued for 1 h. Aqueous NH_3 was added until the blue color persisted. After standard workup (diethyl ether), concentration in vacuo, and chromatography (silica gel, cyclohexane/ethyl acetate, 1:5), **4d** (65 mg, 40%) was isolated.

1,6-Dimethoxy-4,9-dimethyl-2,3,7,8-tetraazatetracyclo-[7.2.1.0^{4,11}.0^{6,10}]dodeca-2,7-diene (4e): After a solution of crude **3e** (80 mg, ca. 70 mg **3e**, 0.15 mmol) had been stirred in anhydrous methanol (5 mL) for 2 days, two products were identified (ca. 1:2 mixture of monoadduct and **4e**, TLC, ^1H NMR,); after this had been kept at 40 °C for 6 h, only **4e** was present. After concentration in vacuo and filtration through silica gel ($CHCl_3$/MeOH, 10:1) oily **4e** (32 mg, 85%) was isolated. IR (KBr): $\tilde{\nu}$ = 1557 cm^{-1} (N=N). ^1H NMR (400 MHz): δ = 3.56 (d, 5-,12-H_s), 3.46 (s, 2 OCH_3), 2.42 (s, 10-,11-H), 2.39 (d, 5-,12-H_a), 1.42 (s, 2 CH_3) ppm; $J_{5a,5s(12a,12s)}$ = 14.8 Hz. ^{13}C NMR: δ = 129.4 (C-1,-6), 100.8 (C-4,-9), 54.7 (2 OCH_3), 53.9 (C-10,-11), 42.3 (C-5,-12), 23.7 (CH_3) ppm. MS (CI, isobutane), *m*/*z* (%) = 252 (15), 251 (100) [M + H]$^+$, 223 (3), 220 (2) [M + H − OCH_3]$^{\cdot+}$, 194 (4), 179 (4), 137 (2). $C_{12}H_{18}N_4O_2$ (250.3).

1,4,6,9-Tetrabromo-2,3,7,8-tetraazatetracyclo[7.2.1.0^{4,11}.0^{6,10}]-dodeca-2,7-diene (4f): A solution of Br_2 (2.70 mL, 15.0 mmol) in CH_2Cl_2 (50 mL) was slowly added (2 h) at −78 °C to a solution of **4a** (160 mg, 1.0 mmol) in CH_2Cl_2 (5 mL). After the mixture had been stirred at room temp. for 2.5 h, concentrated in vacuo, and filtered through silica gel (CH_2Cl_2), the solid residue was crystallized from CH_2Cl_2. Colorless crystals (358 mg, 75%) were isolated, and these started to eliminate N_2 at ca. 190 °C. UV (CH_3OH): λ_{max} (ε) = 330 nm (20). IR (KBr): $\tilde{\nu}$ = 1517 cm^{-1} (N=N). ^1H NMR: δ = 4.12 (d, 5-,12-H_s)*, 3.57 (s, 10-,11-H), 3.39 (d, 5-,12-H_a)* ppm; $J_{5s,5a(12s,12a)}$ = 15.8 Hz. ^{13}C NMR: δ = 96.9

(C-1,-4,-6,-9), 63.4 (C-10,-11), 51.4 (C-5,-12) ppm. MS (CI, NH_3): *m/z* (%) = 496 (6) [M + NH_4^+], 291 (25), 264 (27), 262 (56), 198 (18), 181 (40), 170 (100). HRMS: calcd. for $C_8H_6{}^{79}Br_4N_4$ 473.7326; found 473.7305.

3,8-Dibenzyl-2,7-bis(benzyloxycarbonyl)-1,4,6,9-tetramethyl-2,3,7,8-tetraazatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodecane (8a): See **2**. A solution of **3d** (200 mg, 0.54 mmol) in THF (9 mL) was added dropwise (45 min) to a suspension of the MeLi/$CeCl_3$ reagent prepared at −78 °C in THF (10 mL) (MeLi, 1.35 mL, 1.6 M in diethyl ether, 2.16 mmol; anhydr. $CeCl_3$, 534 mg, 2.16 mmol). After the mixture had been warmed slowly (3 h) to −5 °C, benzyloxycarbonyl chloride (740 mg, 4.3 mmol) was added. After the mixture had been stirred for 6 h it was hydrolyzed (15 mL H_2O). After standard workup, the oily residue, consisting of at least three components, was chromatographed (silica gel, cyclohexane/ethyl acetate, 3:1) and the major fraction (R_f = 0.20) was concentrated in vacuo. The ca. 90% pure, waxy **8a** (180−190 mg, ca. 50%) was used as such. ^{1}H NMR: δ = 7.4−7.2 (m, 20 H), 5.04 (d, CH_2), 4.96 (d, CH_2), 4.12 (d, CH_2), 3.88 (d, CH_2), 2.91 (d, 10-,11-H), 2.43 (d, 5-,12-H′), 2.12 (d, 5-,12-H), 1.68 (s, 2 CH_3), 1.16 (s, 2 CH_3) ppm; J_{C,H_2} = 12.5, J_{C,H_2} = 14.0, $J_{5a,s(13a,3s)}$ = 15.3 Hz.

1-Acetyl-6-(1′-hydrazonoethyl)-7,9-dihydroxy-3,4,7,9-tetramethyl-8-oxabicyclo[4.3.0]non-3-ene (15): Anhydrous hydrazine (0.15 mL, 4.96 mmol) was added to a solution of **14** (150 mg, 0.54 mmol) in CH_3CN (3 mL). After the mixture had been stirred at 0 °C for 12 h, conversion was total (TLC). Concentration in vacuo at 0 °C afforded a crystalline solid, which was thoroughly washed with diethyl ether; 157 mg (100%) were recovered and used as such; m.p. 128−130 °C (dec.). UV (CH_3CN): λ_{max} (ε) = 272 nm (sh, 85), 226 (2180). IR (KBr): $\tilde{\nu}$ = 3296 cm^{-1} (N-H), 1699 (C=O), 1622 (C=C). ^{1}H NMR (400 MHz): δ = 2.55 (d, 2-H)*, 2.34 (s, CH_3CO), 2.21 (d, 5-H)*, 1.90 (d, 5-H′)*, 1.81 (s, CH_3CN), 1.79 (d, 2′-H)*, 1.68 (s, 4-CH_3)**, 1.64 (s, 7-CH_3)***, 1.62 (s, 3-CH_3)**, 1.30 (s, 9-CH_3)*** ppm; $J_{2,2'(5,5')} \approx$ 17.0 Hz. ^{13}C NMR: δ = 206.2 (C=O), 159.7 (C=N), 124.3, 120.3 (C-3,-4), 103.6, 101.9 (C-7,-9), 62.3, 61.6 (C-1,-6), 34.8, 31.6 (C-2,-5), 27.7 (CH_3CO), 23.7, 21.6 (3-,4-CH_3), 18.8, 18.4 (7-,9-CH_3), 15.9 (CH_3CN) ppm. MS: *m/z* (%) = 311 (32) [M + H]$^+$, 293 (30) [M + H − H_2O]$^+$, 275 (12) [M + H − 2H_2O]$^+$, 234 (18), 233 (100) [M − OH − NH_3 − CH_3CO]·$^+$, 189 (78)[M − H_2O − NH_3 − 2$COCH_3$]·$^+$. Upon warming to room temp., **15** slowly lost water; after 2 h at 60 °C in high vacuum (10^{-4} Torr), dehydration to a rapidly decomposing solid (presumably **16**) was total. $C_{16}H_{24}N_2O_3$ (292.4): calcd. C 65.73, H 8.27 N 9.58; found 66.01, H 8.36, N 10.12.

Spiro Compound 17: A suspension of a freshly prepared sample obtained by dehydration of **15** (**16**, 160 mg, 0.55 mmol) and $LiClO_4$ (10 mg) in CH_2Cl_2 (5 mL) was stirred for 30 h. After filtration and concentration in vacuo, the solid residue was chromatographed (silica gel, acetone). Concentration of the major fraction (R_f = 0.29) provided a yellowish, air-and heat-sensitive, highly viscous oil (90 mg, 60%, decomposition above 60 °C), which was used as such. UV (CH_3CN): λ_{max} (ε) = 227 nm (3470). IR (KBr): $\tilde{\nu}$ = 1719 cm^{-1} (C=N), 1688 (C=O). ^{1}H NMR: δ = 2.63 (3-H)*, 2.24 (s, 6-H)*, 2.19 (s, $COCH_3$), 2.07 (s, 3′-,5′-CH_3), 1.77 (s, 5-CH_3)**, 1.69 (s, 4-CH_3)** ppm. ^{13}C NMR: δ = 202.6 (C=O), 178.0 (C-3′,-5′), 122.8 (C-4)*, 121.8 (C-5)*, 66.6 (C-1)**, 65.9 (C-2)**, 35.8 (C-6)***, 33.4 (C-3)***, 28.1 ($COCH_3$), 18.9 (5-CH_3)****, 18.5 (4-CH_3)****, 16.2 (3′-,5′-CH_3) ppm. $C_{16}H_{22}N_2O_2$ (274.4): calcd. C 70.04, H 7.66, N 10.33; found C 69.46, H 8.08, N 10.21.

16-Amino-1,4,6,9,12,13-hexamethyl-5-oxa-2,3,7,8,16-pentaazapentacyclo[7.6.1.0^{4,15}.0^{6,10}.0^{10,15}]hexadeca-2,7,12-triene (20): A solution of **17** (126 mg, 0.46 mmol) and anhydrous hydrazine (0.06 mL, 1.82 mmol) in CH_3CN (6 mL) was stirred at 0 °C under exclusion of light under O_2 until only one product was observed (5 h, TLC). After removal of the volatiles in vacuo (10^{-3} Torr), the solid residue was chromatographed on silica gel (CH_2Cl_2/ethyl acetate, 5:1). Only the yellowish **20** was eluted (115 mg, 80%), and this remained unchanged upon sublimation at 160 °C/10^{-3} Torr. Just before melting at 210 °C, elimination of N_2 occurred. Crystals obtained from CH_3CN proved suitable for X-ray structural analysis. UV (CH_3CN): λ_{max} (ε) = 394 nm (245), 364 (300), 251 (sh, 1155), 221 (2015). IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (N−H), 1735, 1570 (N=N). ^{1}H NMR (400 MHz): δ = 1.87 (d, 11-,14-H), 1.82 (d, 11′-,14′-H), 1.78 (s, 12-,13-CH_3), 1.42 (s, 1-,9-CH_3)*, 1.38 (s, 4-,6-CH_3)* ppm; $J_{11,11'(14,14')}$ = 14.0 Hz. ^{13}C NMR: δ = 126.6 (C-12,-13), 123.6 (C-4,-6), 112.45 (C-1,-9), 58.4 (C-10,-15), 31.1 (C-11,-14), 19.2 (12-,13-CH_3), 19.0 (1-,9-CH_3)*, 17.7 (4-,6-CH_3)* ppm. MS: *m/z* (%) = 288 (6) [M − N_2]·$^+$, 245 (12) [(M − $COCH_3$]$^+$, 217 (18) [M − N_2 − $COCH_3$]$^+$, 43 (100) [$COCH_3$]. $C_{16}H_{24}N_6O$ (316.4): calcd. C 60.74, H 7.65, N 26.56; found C 60.82, H 7.52, N 26.89.

16-Benzylidenamino-1,4,6,9,12,13-hexamethyl-5-oxa-2,3,7,8,16-pentaazapentacyclo[7.6.1.0^{4,15}.0^{6,10}.0^{10,15}]hexadeca-2,7,12-triene (21): A solution of **20** (60 mg, 0.21 mmol), benzaldehyde (53 mg, 0.50 mmol), and *p*-toluenesulfonic acid (1 mg) in benzene (2 mL) was stirred at room temperature until total conversion (2.5 h, TLC). After concentration in vacuo, chromatographic separation (silica gel, CH_2Cl_2/ethyl acetate, 20:1), and crystallization (diethyl ether), yellowish crystals (60 mg, 73%) were isolated. m.p. 173 °C. UV (CH_3CN): λ_{max} (ε) = 410 nm (165), 310 (1055), 225 (665). IR (KBr): $\tilde{\nu}$ = 1564 cm^{-1} (N=N). ^{1}H NMR (400 MHz): δ = 8.88 (s, N=C−H), 7.73 (m, 2-H), 7.38 (m-, 2-H), 7.34 (m, 1-H), 2.02 (d, 11-,14-H), 1.92 (d, 11-,14-H′), 1.82 (s, 12-,13-CH_3), 1.66 (s, 1-,9-CH_3)*, 1.45 (s, 4-,6-CH_3)* ppm; $J_{11,11(14,14')}$ = 14.0 Hz. ^{13}C NMR: δ = 145.4 (C=N), 135.6 (1 C), 129.2 (1 C), 128.5 (2 C), 126.9 (2 C), 126.8 (C-12,-13), 123.5 (C-4,-6), 112.2 (C-1,-9), 59.4 (C-10,-15), 31.3 (C-11,-14), 19.3 (4-,6-CH_3), 19.2 (12-,13-CH_3), 17.6 (1-,9-CH_3) ppm. HRMS: calcd. for $C_{23}H_{28}N_6O$ 404.2325; found 404.2314.

14-Amino-1,4,5,8,9,11-hexamethyl-10-oxa-12,13,14-triazapentacyclo[6.5.1.0^{2,7}.0^{2,11}.0^{7,9}]tetradeca-4,12-diene (22): A degassed solution of **20** (32 mg, 0.10 mmol) in CH_3CN (20 mL), kept at −40 °C in a Solidex vessel, was irradiated with a 800-W daylight lamp until total conversion (TLC monitoring). After concentration in vacuo, the brownish, solid residue, consisting of one monomeric component and polymers (TLC), was filtered through silica gel (ethyl acetate). The eluted solid crystallized from diethyl ether to provide colorless crystals (21 mg, 74%); m.p. 130 °C (dec.; loss of N_2). UV (CH_3CN): λ_{max} (ε) = 360 nm (120), 307 (sh, 250), 222 (1900). IR (KBr): $\tilde{\nu}$ = 1540 cm^{-1} (N=N). ^{1}H NMR (400 MHz): δ = 1.92 (d, 3-H)*, 1.78 (d, 6-H)**, 1.73 (d, 6-H′)**, 1.70 (s, CH_3), 1.68 (s, CH_3), 1.66 (s, CH_3), 1.59 (s, CH_3), 1.53 (d, 3-H′)*, 1.30 (s, CH_3), 1.12 (s, CH_3) ppm; $J_{3,3'}$ = 16.0, $J_{6,6'}$ = 15.0 Hz. ^{13}C NMR: δ = 127.0 (C-4)*, 127.6 (C-5)*, 125.3 (C-11), 111.9 (C-1), 80.6 (C-9), 65.6 (C-8), 64.1 (C-2), 38.4 (C-7), 30.4 (C-3), 25.8 (C-6), 20.8 (CH_3), 19.4 (2 CH_3), 18.3 (CH_3), 14.7 (CH_3), 13.3 (CH_3) ppm. MS: *m/z* (%) = 288 (20) [M·$^+$], 245 (21) [(M − $COCH_3$]$^+$, 217 (100) [M − N_2 − $COCH_3$]$^+$, 200(36), 189 (48), 43 (99) [$COCH_3$]. HRMS: calcd. for $C_{16}H_{24}N_4O$ 288.1959; found 288.1901.

1,4,7,10,13,14-Hexamethyl-2,3,5,6,8,9-hexaaza-17-oxapentacyclo-[8.6.1.0^{4,16}.0^{7,11}.0^{11,16}]heptadeca-2,5,8,13-tetraene (25): K_2CO_3 (150 mg), followed by [$Pb(OAc)_4$] (78 mg, 0.20 mmol), were added to a solution of **20** (64 mg, 0.20 mmol) in CH_2Cl_2 (10 mL). After the mixture had been stirred at room temp. until total conversion (TLC, 1 h), filtered, and evaporated in vacuo, the solid residue was

chromatographed (silica gel, ethyl acetate). From the main fraction (R_f = 0.59), yellowish crystals (50−57 mg, 80−90%) were obtained, m.p. 125 °C (dec.). UV (CH_3CN): λ_{max} (ε) = 365 nm (305), 345 (sh, 235), 225 (2030). IR (KBr): $\tilde{\nu}$ = 1542 cm^{-1} (N=N). ^1H NMR (400 MHz): δ = 1.92 (d, 12-,15-H), 1.76 (s, 13-, 14-CH_3), 1.68 (s, 1-,l0-CH_3), 1.58 (d, 12-,15-H′), 1.47 (s, 4-,7-CH_3) ppm; $J_{12,12'(15,15')}$ = 15.5 Hz. ^{13}C NMR: δ = 125.9 (C-13,-14), 124.1 (C-1,-10), 100.4 (C-4,-7), 50.5 (C-11,-16), 27.5 (C-12,-15), 19.8 (13-,14-CH_3), 19.2 (1-,10-CH_3), 11.1 (4-,7-CH_3) ppm. MS (CI, NH_3): *m/z* (%) = 305 (20), 304 (100) $[M + NH_4 - N_2]^+$, 288 (18) $[M + 2H - N_2]^+$, 287 (18) $[M + H - N_2]^+$. HRMS: calcd. for $C_{16}H_{22}N_6O$ 314.1855; found 314.1848.

2-Acetyl-1,4,5,8,11-pentamethy1−9,10-diazatetracyclo-[5.3.1.0^{2,7}.0^{1,11}]undeca-4,8-diene (26): A degassed solution of **25** (35 mg, 0.11 mmol) in CH_3CN (20 mL), kept at −40 °C, was irradiated with a daylight lamp (800 W, solidex vessel) until total conversion (TLC, only one product besides polymers). After concentration in vacuo, the brownish oily residue was filtered through silica gel (ethyl acetate); a highly viscous oil (11 mg, 39%) was isolated. UV (CH_3CN): λ_{max} (ε) = 297 nm (sh, 190), 225 (2000). ^1H NMR (400 MHz): δ = 2.52 (m, 3-H)*, 2.42 (m, 6-H)*, 2.35 (m, 3-H′)**, 2.01 (s, CH_3CO), 1.92 (m, 6-H′)**, 1.89 (s, 1-CH_3)***, 1.74 (s, 4-CH_3)***, 1.70 (s, 5-CH_3)***, 1.55 (s, 11-CH_3)***, 1.09 (s, 8-CH_3) ppm; $J_{3,3'}$ = 16.5, $J_{6,6'}$ = 17.0 Hz. ^{13}C NMR: δ = 213.5 (C=0), 179.0 (C-8), 124.9 (C-4)*, 122.8 (C-5)*, 68.3 (C-1)**, 65.3 (C-11)**, 58.9 (C-2)**, 55.1 (C-7)**, 34.0 (C-6)***, 30.1 ($COCH_3$), 27.8 (C-3)***, 20.0 (4-CH_3)****, 19.6 (5-CH_3)****, 14.7 (1-CH_3)****, 11.2 (11-CH_3)****, 8.61 (8-CH_3) ppm. MS (70 eV, CI, NH_3): *m/z* (%) = 259 (8) $[M + 1]^+$, 219 (6), 213 (16), 191 (10), 187 (7), 88 (14), 78 (22). HRMS: calcd. for $C_{16}H_{22}N_2O$ 258.1732; found 258.1726.

Bicyclo[3.3.1]nonane-2,6-dione Diethylene Acetal (27): A solution of bicyclo[3.3.1]nonane-2,6-dione[46] (19.2 g, 126.0 mmol), ethane-1,2-diol (17 mL, 332 mmol), and *p*-toluenesulfonic acid × H_2O (0.3 g) in benzene (150 mL) was heated at reflux for 24 h with azeotropic removal of water. After standard workup (diethyl ether) and sublimation of the solid residue, colorless needles (22.6 g, 75%) were isolated; m.p. 68−73 °C. ^1H NMR: δ = 4.0−3.8 (m, 8 H, OCH_2), 2.0−1.85 (m, 4 H, 1-,5-H, 9-H), 1.8−1.6 (m, 8 H, 3-,4-,7-8-H). −^{13}C NMR: δ = 110.7 (C-2,-6), 64.4 (OCH_2), 64.2 (OCH_2), 36.0 (C-4,-8), 31.6 (C-3,-7), 29.4 (C-1,-5), 23.7 (C-9). MS: *m/z* (%) = 240(24)[$M^{\cdot+}$], 99(100).

(3β,7β)-Dibromobicyclo[3.3.1]nonane-2,6-dione Diethylene Acetal (28): Pyridinium tribromide (65.8 g, 206 mmol) was added to a solution of **27** (22.6 g, 94 mmol) in THF (200 mL), kept at −78 °C. The red suspension was stirred for 1 hour and then warmed to room temperature over 2 h. The suspension was poured into vigorously stirred ice-water (700 mL), and the uniform (TLC) precipitate was filtered off and crystallized from methanol (100 mL) to provide the compound (32.5 g, 87%); m.p. 202 °C. ^1H NMR: δ = 4.44 (dd, 3-,7-H), 4.21 (m, 2 OCH_2), 3.97 (m, 2 OCH_2), 2.45−2.55 (m, 4 H, 4-,8-H, 9-H), 2.12 (m, 4-,8-H′), 2.02 (m, 1-,5-H) ppm; $J_{1,9(5,9)}$ = 3.0 Hz. ^{13}C NMR: δ = 108.7 (C-2,-6), 66.5 (OCH_2), 65.8 (OCH_2), 54.3 (C-3,-7), 41.6 (C-1,-5), 33.8 (C-4,-8), 27.9 (C-9) ppm. $C_{13}H_{18}Br_2O_4$ (398.1): calcd. C 39.22, H 4.57; found C 39.10, H 4.60.

7β-Bromobicyclo[3.3.1]non-3-ene-2,6-dione Diethylene Acetal (29): Compound **28** (7.0 g, 18.0 mmol) was added to a suspension of freshly prepared $NaOCH_3$ (1.35 g, 25.0 mmol) in dry DMSO (40 mL). After having been heated at 80 °C for 2 h, the brownish mixture was cooled to room temperature and poured onto ice-water (200 mL). The aqueous phase was saturated with NaCl and extracted with diethyl ether (5 × 50 mL). The combined organic phases were washed with brine (20 mL) and dried (Na_2SO_4). After concentration in vacuo and crystallization (cyclohexane), colorless needles (4.6 g, 81%) were obtained, m.p. 157 °C, R_f (CH_2Cl_2) = 0.18. IR (KBr): $\tilde{\nu}$ = 1644 cm^{-1} (C=C). ^1H NMR: δ = 6.08 (dd, 4-H), 5.72 (d, 3-H), 4.71 (dd, 7-H), 4.3−3.8 (m, 4 OCH_2), 2.56 (ddt, 9-H), 2.44 (m, 5-H), 2.2−2.0 (m, 1-,8-H, 8-,9-H′) ppm; $J_{3,4}$ = 10.5, $J_{4,5}$ = 6.3, $J_{7,8}$ = 12.3, $J_{7',8,}$ = 5.3, $J_{9,9'}$ = 12.9 Hz. ^{13}C NMR: δ = 133.5 (C-4), 131.4 (C-3), 108.5 (C-6)*, 105.6 (C-2)*, 66.4 (OCH_2), 65.7 (OCH_2), 65.0 (OCH_2),64.3 (OCH_2), 53.7 (C-7), 40.3 (C-5)**, 39.4 (C-1)**, 36.0 (C-8), 29.3 (C-9) ppm. MS: *m/z* (%) = 318 (25), 316 (25) [$M^{\cdot+}$], 237 (100) $[M - Br]^+$, 99 (83), 55 (92). HRMS: calcd. for $C_{13}H_{17}{}^{79}BrO_4$ 316.0310; found 316.0300.

Bicyclo[3.3.1]nona-3,7-diene-2,6-dione Diethylene Acetal (30): See **29**. Compound **28** (32.5 g, 82.0 mmol)/$NaOCH_3$ (26.4 g, 490 mmol)/DMSO (150 mL). The mixture was stirred at 90 °C for 2 h, then for 2 h at 120 °C (TLC monitoring). After workup and crystallization (cyclohexane), colorless crystals (13.3 g, 68%) were isolated; m.p. 76−78 °C, R_f (CH_2Cl_2) = 0.10. IR (KBr): $\tilde{\nu}$ = 1639 cm^{-1} (C=C). ^1H NMR: δ = 5.79 (dd, 4-,8-H), 5.28 (d, 3-,7-H), 3.95−3.60 (m, 4 OCH_2), 2.21 (m, 1-,5-H), 1.98 (t, 9-H) ppm; $J_{3,4(7,8)}$ = 10.2, $J_{4,5(8\cdot9)}$ = 5.9, $J_{5,9}$ = 2.9 Hz. ^{13}C NMR: δ = 132.6 (C-4,-8), 126.9 (C-3,-7), 107.4(C-2,-6), 65.0 (2 OCH_2), 64.4 (2 OCH_2), 38.1 (C-1,-5), 28.5 (C-9) ppm. MS: *m/z* (%) = 236 (6) [$M^{\cdot\cdot+}$], 170 (100), 91 (98). $C_{13}H_{16}O_4$ (236.3): calcd. C 66.07, H 6.84; found C 66.47, H 6.54.

Bicyclo[3.3.1]nona-3,7-diene-2,6-dione (31a): A solution of **30** (13.3 g, 56.0 mmol) and sulfosalicylic acid·$2H_2O$ (0.50 g, 2.0 mmol) in acetone (150 mL) was stirred at 40 °C until total conversion (TLC, 6 h). After standard workup and crystallization (cyclohexane), colorless needles (7.5 g, 90%) were obtained; m.p. 78−80 °C. IR (KBr): $\tilde{\nu}$ = 1673 cm^{-1} (C=O), 1601 (C=C). ^1H NMR: δ = 7.00 (dd, 4-,8-H), 5.87 (d, 3-,7-H), 3.33 (dt, 1-,5-H), 2.77 (t, 9-H) ppm; $J_{1,8(4,5)}$ = 6.8, $J_{1,9}$ = 3.0, $J_{3,4(7,8)}$ = 10.5 Hz. ^{13}C NMR: δ = 193.5 (C-2,-6), 146.4 (C-4,-8), 126.1 (C-3,-7), 45.8 (C-1,-5), 34.4 (C-9) ppm. MS: *m/z* (%) = 148 (32) [$M^{\cdot+}$], 120 (45) $[M - CO]^{\cdot+}$, 91 (100). $C_9H_8O_2$ (148.2): calcd. C 72.94, H 5.45; found C 73.01, H 5.67.

4,8-Dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (31b). (a) Modified Original Procedure:[42d] A suspension of paraformaldehyde (1.5 g, 17 mmol) in acetylacetone (10.0 g, 100.0 mmol) and triethylamine (0.5 mL) was homogenized by heating to 60 °C. The solution was stirred at room temperature for 5 days, triethylamine (0.5 mL) being added daily. After concentration in vacuo, the yellowish, oily residue was dissolved in benzene (30 mL) and, together with *p*-toluenesulfonic acid monohydrate (600 mg, 3.0 mmol), was heated at reflux in a Dean−Stark apparatus; after 3 days ca. 2 mL of water had been collected. After standard workup ($CHCl_3$, 80 mL), the solid residue was purified by flash chromatography (silica gel, cyclohexane/ethyl acetate 3:1) and crystallized from cyclohexane to afford yellow needles (3.6 g, 41%). M.p. 125 °C (cyclohexane), R_f(cyclohexane/ethyl acetate, 1:1) = 0.30. **(b) From 32:** See **2** → **1c**: Dry K_2CO_3 (350 mg, 2.5 mmol), pyridinium chlorochromate (1.60 g, 7.5 mmol), CH_2Cl_2 (20 mL), **32** (450 mg, 2.5 mmol), CH_2Cl_2 (30 mL). After stirring at room temperature for 8 h , filtration, workup, chromatography (silica gel, cyclohexane/ethyl acetate, 1:1) and crystallization (cyclohexane), 310 mg (70%) were obtained.

4β,8β-Dimethylbicyclo[3.3.1]nona-2,6-diene-4α,8α-diol (32): MeLi (9.4 mL, 1.6 M solution in diethyl ether, 15.0 mmol) was added

dropwise at −40 °C, over 60 minutes, to a solution of **31a** (1.00 g, 6.8 mmol) in anhydrous THF (25 mL). After having been slowly warmed up (12 h) and then heated at reflux (2 h), the mixture was hydrolyzed (satd. aqueous NH_4Cl, pH 7). After the bulk of the THF had been distilled, the residue was extracted with CH_2Cl_2 (5 × 30 mL). After standard workup, the colorless solid was purified by flash chromatography (silica gel, CH_2Cl_2/cyclohexane, 1:1, R_f (**32**) = 0.11) and crystallized (CH_2Cl_2/cyclohexane, 1:1). 1.00 g (82%) of colorless crystals were isolated; m.p. 151 °C. IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} (OH), 1640 (C=C). ^1H NMR: δ = 5.82 (dd, 2-,6-H), 5.60 (d, 3-,7-H), 2.31 (dt, l-,5-H), 1.91 (t, 2 H, 9-H), 1.64 (s, OH), 1.36 (s, 2 CH_3) ppm; $J_{1,2(5,6)}$ = 6.0, $J_{1,9}$ = 3.1, $J_{2,3(6,7)}$ = 9.8 Hz. ^{13}C NMR: δ = 135.8 (C-2,-6), 128.3 (C-3,-7), 74.3 (C-4,-8), 40.4 (C-1,-5), 29.5 (C-9), 27.7 (CH_3) ppm. CI MS (isobutane): *m/z (%)* = 163 (10) $[M + H - H_2O]^+$, 145 (100) $[M + H - 2H_2O]^+$. $C_{11}H_{16}O_2$ (180.3): calcd. C 73.27, H 8.96; found C 73.89, H 9.01. An occasional by-product was identified as separately prepared **36**.

2,3,7,8-Tetraazatetracyclo[7.3.1.0^{4,12}.0^{6,10}]trideca-1,6-diene (33a): See **3b**. A solution of **31a** (148 mg, 1.0 mmol) in ethanol (30 mL) was added dropwise over 3 h to a solution of hydrazine hydrate (100 mg, 2.0 mmol) in ethanol (2 mL). This system was stirred for 12 h and heated at reflux until total conversion (3 h, TLC). After concentration in vacuo the solid residue was practically pure, air-sensitive **33a** [175 mg, 100%, R_f($CHCl_3$/CH_3OH, 12:1) = 0.11] which was used as such. ^1H NMR (CD_3OD): δ = 4.14 (t, 4-,9-H), 3.25 (m, 10-,12-H), 2.61 (ddd, 5-,13-H_s), 2.34 (d, 5-,13-H_a),2.21 (t, 11-H) ppm; $J_{4,5(9,13)}$ = 5.7, $J_{4,12(9,10)}$ = 6.0, $J_{5,5'}$ = 13.5, $J_{5,12(10,13)}$ = 1.5, $J_{10,11(11,12)}$ = 3.0 Hz. ^{13}C NMR(CD_3OD): δ = 163.6 (C-1,-6), 69.1 (C-4, −9), 46.1 (C-10,-12), 32.7 (C-5,-13), 17.9 (C-11) ppm. HRMS: calcd. for $C_9H_{12}N_4$ 176.1062; found 176.1054.

4,9-Dimethyl-2,3,7,8-tetraazatetracyclo[7.3.1.0^{4,12}.0^{6,10}]trideca-1,6-diene (33b): See **33a.** Hydrazine hydrate (355 mg, 7.1 mmol)/ethanol (10 mL)/**31b** (500 mg, 2.84 mmol)/ethanol (150 mL)/3(12) h. After concentration in vacuo, the solid residue was practically pure, air-sensitive **33b** (590 mg, 100%) and was used as such. ^1H NMR: δ = 5.35 (br., 2 NH), 2.89 (t, 10-,12-H), 2.45 (d, 5-,13-H_s), 2.33 (d, 5-,13-H_a), 1.92 (t, 11-H), 1.48 (s, 2 CH_3) ppm; $J_{10,11(11,12)}$ = 3.1, $J_{5,5'(12,12')}$ = 13.4 Hz.

3,8-Dibenzyl-2,3,7,8-tetraazatetracyclo[7.3.1.0^{4,12}.0^{6,10}]trideca-1,6-diene (33c): A solution of freshly prepared **33a** (600 mg, 3.4 mmol) and benzyl bromide (1.71 g, 10 mmol) was heated at 80 °C for 16 h in the presence of K_2CO_3 (500 mg). After standard workup and flash chromatography (silica gel, ethyl acetate/cyclohexane, 2:1), the major fraction (R_f = 0.34) was concentrated in vacuo and the yellowish residue was crystallized (diethyl ether) to afford colorless crystals (850 mg, 70%); m.p.125 °C. IR (KBr): $\tilde{\nu}$ = 1609 cm^{-1} (C=N), 1488 (C=C). ^1H NMR: δ = 7.50−7.11 (m, 10 H), 4.68 (d, CH_2), 4.24 (d, CH_2), 4.07 (t, 4-,9-H), 3.28 (m, 10-,12-H), 3.0 (d, 5-, 13-H_s), 2.02 (ddd, 5-,13-H_a), 2.00 (t, 11-H) ppm; $J_{4,5(9,13)}$ = $J_{4,12(9,10)}$ = 6.0, $J_{5,5'(13,13')}$ = 14.2, $J_{5,12(10,13)}$ = 1.4, $J_{10,11(11,12)}$ = 3.0 Hz. ^{13}C NMR (400 MHz): δ = 160.2 (C-1,-6), 138.7, 128.7, 128.5, 127.1 (12 C), 71.9 (C-4,-9), 53.8 (2 CH_2), 45.7 (C-10,-12), 24.2 (C-5,-13), 18.1 (C-11) ppm. MS: *m/z* (%) = 356 (18) $[M^+]$, 91 (100). HRMS: calcd. for $C_{23}H_{24}N_4$ 356.2000; found 356.2010.

3,8-Dibenzyl-4,9-dimethyl-2,3,7,8-tetraazatetracyclo[7.3.1.0^{4,12}.0^{6,10}]trideca-1,6-diene (33d): See **33c**. Freshly prepared **33b** (ca. 600 mg, 2.8 mmol), benzyl bromide (1.7 g, 10 mmol)/K_2CO_3 (500 mg)/80 °C/16 h. After standard workup, flash chromatography (silica gel, ethyl acetate/cyclohexane, 2:1, R_f = 0.15), and crystallization (THF), colorless crystals (650 mg, ca. 60%) were isolated; m.p.176−177 °C. IR (KBr): $\tilde{\nu}$ = 1621 cm^{-1}, 1489 (C=C). ^1H NMR: δ = 7.45−7.2 (m, 10 H), 4.55 (d, CH_2), 3.95 (d, CH_2), 3.02 (10-,12-H), 3.00 (d, 5-,13-H_s), 2.01 (ddd, 5-,13-H_a), 1.90 (t, 11-H), 1.48 (s, 2 CH_3) ppm; $J_{5,5'(13,13')}$ = 14.0, $J_{10,11(11,12)}$ = 3.1 Hz. ^{13}C NMR (400 MHz): δ = 159.4 (C-1,-6), 140.2, 128.4, 128.3, 126.8, 80.7 (C-4,-9), 52.3 (2 CH_2), 51.6 (C-10,-12), 30.7 (C-5,-13), 24.1 (CH_3), 17.6 (C-11) ppm. MS: *m/z* (%) = 384 (15) $[M^{\cdot+}]$, 293 $[M - C_6H_5CH_2]^+$, 199 (88), 91 (100). $C_{25}H_{28}N_4$ (384.5): calcd. C 78.09, H 7.34, N 14.57, found C 77.61, H 7.15, N 14.13.

4,9-Dimethyl-3,8-bis(phenylsulfonyl)-2,3,7,8-tetraazatetracyclo[7.3.1.0^{4,12}.0^{6,10}]trideca-1,6-diene (33e): See **3e**. A solution of freshly prepared **33b** (590 mg, 3.0 mmol) and benzenesulfonyl chloride (1.5 mL, 11.8 mmol) in pyridine (5 mL) was stirred, under exclusion of air, at room temp. for 12 h. After standard workup and crystallization (methanol), colorless crystals (1.05 g, 72%) were obtained; m.p. 222 °C R_f($CHCl_3$/MeOH, 10:1) = 0.38. IR (KBr): $\tilde{\nu}$ = 1622 cm^{-1}, 1471, 1446, 1339. ^1H NMR: δ = 8.02−7.98 (m, 4 H), 7.59−7.49 (m, 6 H), 3.05 (d, 5-,13-H_s), 2.92 (t, 10-,12-H), 2.21 (d, 5-,13-H_a), 1.89 (t, 11-H), 1.88 (s, 2 CH_3) ppm; $J_{5,5'(13,13')}$ = 14.3, $J_{10,11(11,12)}$ = 2.7 Hz. ^{13}C NMR(400 MHz): δ = 163.9 (C-1,-6), 140.7 (C-15,-13), 24.2 (2 CH_3), 15.2 (C-11) ppm. FAB-MS: *m/z* (%) = 485 (66) $[M^{\cdot+}]$, 343 (40 $[M - PH_sO_2]^+$, 307 (40), 154 (100), 136 (80). $C_{23}H_{24}N_4O_4S_2$ (484.6).

2,3,7,8-Tetraazatetracyclo[7.3.1.0^{4,12}.0^{6,10}]trideca-2,7-diene (34a): See **4b**. Hydrazine hydrate (850 mg, 17.0 mmol)/ethanol (5 mL)/**31a** (1.00 g, 6.8 mmol)/ethanol (100 mL), room temperature. After complete formation of **33a** (TLC) and addition of K_2CO_3 (2.35 g, 17.0 mmol), the mixture was heated at reflux until total conversion (TLC, 5−7 h). After standard workup (CH_2Cl_2), chromatography (silica gel, CH_2Cl_2/acetone, 10:1), and concentration of the major fraction, the residue was crystallized from CH_3CN to afford colorless prisms (720 mg, 60%) ; m.p. 175 °C (dec., N_2 elimination). UV (CH_3CN): λ_{max} (ε) = 333 nm (790), 201 (845). IR (KBr): $\tilde{\nu}$ = 1550 cm^{-1} (N=N). ^1H NMR: δ = 4.92 (ddd,1-,4-,6-,9-H), 3.07 (dt, 5-,13-H_s), 2.35 (tt, 10-,12-H), 1.88 (dt, 5-,13-H_a), 1.57 (t, 11-H) ppm; $J_{1(4),12:6(9),10)}$ = 10.5, $J_{1,13'(13',9;6,5';5',4)}$ = 1.5, $J_{1,13(13,9;6,5;5,4)}$ = 6.9,, $J_{5,5'(13,13')}$ = 16.2, $J_{10,11}$ = 3.0 Hz. ^{13}C NMR: δ = 85.2 (C-1,-4,-6,-9), 23.7 (C-10,-12), 18.5 (C-5,-13), 15.6 (C-11) ppm. MS: *m/z* = 176 (14) $[M^{\cdot+}]$, 79 (100). $C_9H_{12}N_4$ (176.3): calcd. C 61.31, H 6.87, N 31.79; found C 60.98, H 6.71, N 31.91.

1,6-Dimethyl-2,3,7,8-tetraazatetracyclo[7.3.1.0^{4,12}.0^{6,10}]trideca-2,7-diene (34b): See **34a**. Hydrazine hydrate (794 mg, 14.2 mmol/ethanol (5 mL)/**31b** (1.00 g, 5.7 mmol)/ethanol (100 mL)/K_2CO_3 (1.97 g, 14.2 mmol)/reflux, 5−7 h. Colorless needles (930 mg, 80%) were recovered; m.p. 158 °C (CH_3CN) (dec., N_2 elimination), R_f(CH_2Cl_2/ethyl acetate, 1:1) = 0.27. IR (KBr): $\tilde{\nu}$ = 1563 cm^{-1} (N=N). UV (CH_3CN): λ_{max} (ε) = 334 nm (408), 196 (970). ^1H NMR: δ = 4.97 (ddd, 4-,9-H), 2.89 (dd, 5-,13-H_s), 1.70 (dt, 10-,12-H), 1.56 (dd, 5-,13-H_a), 1.50 (t, 11-H), 1.36 (s, 2 CH_3) ppm; $J_{4,12(9,10)}$ = 10.5, $J_{4,5'(9,13')}$ = 1.5, $J_{4,5(9,13)}$ = 7.4, $J_{10,11(11,12)}$ = 3.1, $J_{5,5'(13,13')}$ = 15.8 Hz. ^{13}C NMR: δ = 89.8 (C-1,-6), 87.0 (C-4,-9), 31.1 (C-10,-12), 28.0 (CH_3), 26.1 (C-5,-13), 16.9 (C-11) ppm. $C_{11}H_{16}N_4$ (204.3): calcd. 64.68 H 7.89 N 27.43; found C 64.49, H 7.99, N 27.12.

1,4,6,9-Tetramethyl-2,3,7,8-tetraazatetracyclo[7.3.1.0^{4,12}.0^{6,10}]-trideca-2,7-diene (34c): See **4d**. A solution of **33e** (1.82 g, 3.8 mmol) in THF (150 mL) was slowly added (2 h) at room temperature to a stirred suspension of the MeLi/$CeCl_3$ reagent prepared at −78 °C in THF ($CeCl_3$, 2.60 g, 10.6 mmol, THF, 150 mL, MeLi, 6.4 mL, 1.6 M diethyl ether, 10.3 mmol). Stirring was continued for 10 h. After hydrolysis (aqueous NH_4Cl), standard workup (diethyl

ether) and filtration through silica gel [R_f(ethyl acetate) = 0.27], colorless crystals (620 mg, 71%) were isolated; m.p. 109−110 °C ($CHCl_3$). UV(CH_3CN): λ_{max} (ε) = 212 nm (1010), 335 (500). IR (KBr): $\tilde{\nu}$ = 1556 cm^{-1} (N=N). ^1H NMR: δ = 2.73 (d, 5-,13-H_s), 1.50 (t, 10-,12-H), 1.37 (s, 4 CH_3), 1.29 (d, 5-,13-H_a), 1.26 (t, 11-H) ppm; $J_{5,5'\ (13,13')}$ = 15.3, $J_{10,11\ (11,12)}$ = 3.3 Hz. ^{13}C NMR(400 MHz): δ = 91.6 (C-1,-4,-6,-9), 38.5 (C-10,-12), 33.9 (C-5,-13), 28.8 (CH_3), 18.0 (C-11) ppm. MS (CI, NH_3): *m*/*z* (%) = 250 (15) $[M + NH_4]^+$, 233 (30) $[M + H]^+$, 176 (12) $[M - 2N_2]^{\cdot +}$, 161 (22) $[M - 2N_2 - CH_3]^+$. $C_{13}H_{20}N_4$ (220.3): calcd. C 67.21, H 8.68, N 24.12; found C 67.52, H 8.72, N 23.98. From **35a:** See **8a**. **35a** (84 mg, 0.12 mmol)/ethanol/ethyl acetate (25 mL, 1:1)/Pd/C (10%, 80 mg)/H_2 (1 bar). 26 mg (92%).

1,6-Dimethoxy-4,9-dimethyl-2,3,7,8-tetraazatetracyclo-[7.3.1.0^{4,12}.0^{6,10}]trideca-2,7-diene (34d): See **4e**. After a solution of **33b** (100 mg, 0.50 mmol) in anhydrous methanol (5 mL) had been warmed at 40 °C until total conversion (6 h), three products were detected (TLC). Concentration in vacuo afforded a solid residue, which was chromatographed (silica gel, ethyl acetate) to afford colorless, crystalline **34d** (50 mg, 40%); [R_f(ethyl acetate) = 0.46], m.p. 194 °C, besides two oily components (mono-CH_3OH-addition/substitution). IR (KBr): $\tilde{\nu}$ = 1657 cm^{-1}, 1619 (N=N). ^1H NMR: δ = 3.30 (s, 2 OCH_3), 3.00 (d, 5-,13-H_s), 1.70 (t, 10-,12-H), 1.65 (d, 5-,13-H_a), 1.51 (t, 11-H) ppm; $J_{5,5'(13,13')}$ = 15.3, $J_{10,11(11,12)}$ = 3.2 Hz. ^{13}C NMR: δ = 119.5 (C-1,-6), 99.9 (C-4,-9), 50.7 (OCH_3), 35.2 (C-10,-12), 32.7 (C-5,-13), 27.3 (CH_3), 17.7 (C-11) ppm. HRMS: calcd. for $C_{13}H_{20}N_4O_2$ 264.1586; found 264.1572.

4,9-Dibromo-1,6-dimethyl-2,3,7,8-tetraazatetracyclo-[7.3.1.0^{4,12}.0^{6,10}]trideca-2,7-diene (34e): See **4f**. A solution of dry bromine (1.00 g, 5.0 mmol) in CH_2Cl_2 (10 mL) was slowly added (2 h) at −78 °C to a solution of **34b** (50 mg, 0.25 mmol) in CH_2Cl_2. After the mixture had been stirred at room temperature (5 h), TLC monitoring confirmed the exclusive formation of **34e** [R_f(cyclohexane/ethyl acetate, 1:1) = 0.50]. Standard workup, filtration of the crude solid (silica gel), and crystallization (CH_2Cl_2/cyclohexane, 1:1) provided colorless prisms (73 mg, 82%); m.p. 165 °C (dec., N_2 elimination). UV (CH_3CN): λ_{max} (ε) = 338 nm (300). IR (KBr): $\tilde{\nu}$ = 1538 cm^{-1} (N=N). ^1H NMR: δ = 3.36 (d, 5-,13-H_s), 2.25 (t, 10-,12-H), 2.11 (d, 5-,13-H_a), 1.93(t, 11-H), 1.51 (s, 2 CH_3) ppm; $J_{5,5(13,13')}$ = 14.7, $J_{10,11(11,12)}$ = 3.0 Hz. ^{13}C NMR: δ = 98.2(C-1,-6), 93.2 (C-4,-9), 42.1(C-10,-12), 38.0 (C-5,-13), 27.7 (CH_3), 17.3 (C-11) ppm. $C_{11}H_{14}Br_2N_4$ (362.1): calcd. C 36.48, H 3.91, N 15.48; found C 36.87, H 4.00, N 15.12.

1,4,6,9-Tetrabromo-2,3,7,8-tetraazatetracyclo[7.3.1.0^{4,12}.0^{6,10}]-trideca-2,7-diene (34f): See **34e**. Compound **34a** (176 mg, 1.0 mmol)/CH_2Cl_2(70 mL)/bromine (6.50 g, (41.0 mmol)/CH_2Cl_2 (70 mL). The crude product was purified by filtration [silica gel, R_f(CH_2Cl_2) = 0.60] and crystallization (cyclohexane/ethyl acetate, 1:1) to afford colorless prisms (414 mg, 84%); m.p. 181 °C (dec., N_2 elimination). UV(CH_3CN): λ_{max} (ε) = 339 nm (300). IR (KBr): $\tilde{\nu}$ = 1530 cm^{-1} (N=N). ^1H NMR ($CDCl_3$/[D_6]DMSO): δ = 3.50 (d, 5-,13-H_s), 2.97 (d, 5-,13-H_a), 2.95 (t, 10-,12-H), 2.34 (t, 11-H) ppm; $J_{5,5'(13,13')}$ = 15.8, $J_{10,11(11,12)}$ = 3.4 Hz. ^{13}C NMR ($CDCl_3$/[D_6]DMSO): δ = 93.6 (C-1,-4, −6,-9), 44.8 (C-10,-12), 39.6 (C-5,-13), 15.3 (C-11) ppm. $C_9H_8Br_4N_4$ (491.8): calcd. C 21.98, H 1.68, N 11.39; found C 22.50, H 2.01, N 11.78.

3,8-Dibenzyl-2,7-di(benzyloxycarbonyl)-1,4,6,9-tetramethyl-2,3,7,8-tetraazatetracyclo[7.3.1.0^{4,12}.0^{6,10}]tridecane (35a): See **8a**. $CeCl_3$ (257 mg, 1.04 mmol)/THF (5 mL), −78 °C, MeLi (0.65 mL, 1.04 mmol)/diethyl ether, **33c** (100 mg (0.26 mmol)/THF (3 mL)/3 h. After warming to −5 °C, addition of benzyloxycarbonyl chloride (363 mg, 2.1 mmol) and workup, the oily mixture (379 mg) of at least three components was chromatographically separated (silica gel, cyclohexane/ethyl acetate, 4:1). From the fraction with R_f = 0.15, colorless, crystalline **35a** (58 mg, 35%) was isolated; m.p. 97 °C. IR (KBr): $\tilde{\nu}$ = 1685 cm^{-1} (C=O). ^1H NMR: δ = 7.4−7.2 (m, 20 H), 5.15 (d, 2 CH_2), 5.05 (d, 2 CH_2), 4.06 (d, 2 CH_2), 3.89 (2 CH_2), 2.16 (d, 5-,13-H_s)*, 2.04(t, 10-,12-H), 1.94 (d, 5-,13-H_a)*, 1.86 (t, 11-H), 1.57 (s, 2 CH_3), 0.93 (2 CH_3) ppm; $J_{C,H2}$ = 12.5, $J_{C,H2'}$ = 14.7, $J_{5,5'(13,13')}$ = 16.5, $J_{10,11(11,12)}$ = 3.1 Hz. ^{13}C NMR: δ = 153.7, 140.0, 136.9, 128.3, 128.0 127.7, 126.6 (20 C), 66.7 (CH_2), 63.7 (C-5,-13), 62.9 (CH_2), 58.2 (C-1,-6), 48.3(C-4,-9), 46.3(C-10,-12), 30.1 (CH_3), 22.7 (CH_3), 16.9 (C-11) ppm. MS: *m*/*z* (%) = 684 (19) $[M^{\cdot +}]$, 549 (48) $[M - OCOCH_2C_6H_5]^+$, 458 (7) $[(M - OCOCH_2C_6H_5 - CH_2C_6H_5]^{\cdot +}$, 323 (25) $[M - 2OCOCH_2C_6H_5 - CH_2C_6H_5]^+$, 91 (100) $[CH_2C_6H_5]$. $C_{43}H_{48}N_4O_2$ (684.9): calcd. C 79.10, H 7.16, N 8.61; found C 78.93, H 7.41, N 8.58.

6β-Hydroxy-6-methyl-bicyclo[3.3.1]nona-3,7-dien-2-one (36): See **32**. Compound **31a** (300 mg, 2.0 mmol)/THF (8 mL))/MeLi (1.25 mL, 1.6 M in diethyl ether, 2.0 mmol). Colorless crystals (230 mg, 70%), m.p. 61 °C (cyclohexane), were isolated by flash chromatography (silica gel, cyclohexane/ethyl acetate, 1:1) (**36**, R_f = 0.25), besides residual **31a** and **32** (10−15%). IR (KBr): $\tilde{\nu}$ = 3344 cm^{-1} (OH), 1658 (C=O). ^1H NMR: δ = 7.02 (ddd, 4-H), 5.91 (d, 3-H), 5.77 (ddd, 8-H), 5.58 (d, 7-H), 2.90 (m. 1-H)*, 2.79 (m, 5-H)*, 2.32 (m, 9-H), 2.15 (m, 9-H′), 1.71 (s, OH), 1.52 (s, CH_3) ppm; $J_{1,8}$ = 6.2, $J_{3,4}$ = 10.5, $J_{4,5}$ = 6.6, $_{4,9'}$ = 2.3, $J_{7,8}$ = 9.8, $J_{8,9}$ = 1.5, $J_{9,9'}$ = 13.5 Hz. ^{13}C NMR ($CDCl_3$): δ = 199.8 (C-2), 150.9 (C-4), 135.3 (C-8), 126.8 (C-3)*, 126.1 (C-7)*, 71.1 (C-6), 44.7 (C-1)**, 41.6 (C-5)**, 31.6 (C-9), 29.4 (CH_3) ppm. MS: *m*/*z* (%) = 164 (20) $[M^{\cdot +}]$, 149 (50), 131 (95) $[(M - CH_3 - H_2O]^+$, 43 (100). $C_{10}H_{12}O_2$ (164.2).

3,7-Bis(diethoxyphosphoryloxy)-9,10-benzobicyclo[3.3.2]deca-2,6,9-triene (40): *n*BuLi (6.8 mL of 2.7 M solution in *n*-heptane, 18.4 mmol) was added at −78 °C to a solution of diisopropylamine (2.05 g, 20.2 mmol) in anhydrous THF (15 mL). After the mixture had been stirred for 15 minutes a solution of **39** (2.00 g, 9.35 mmol) in anhydrous THF (70 mL) was added dropwise. After 30 minutes, TMEDA (8 mL) and diethyl chlorophosphate (3.58 g, 20.8 mmol) were added to the orange reaction solution. Upon warming to room temperature and stirring for 10 h, it was hydrolyzed (satd. aqueous NH_4Cl, 10 mL). Standard workup (diethyl ether) and filtration of the crude, oily product (4.7 g) through silica gel ($CHCl_3$/MeOH, 10:1) delivered a yellowish oil (3.03 g, 66%). IR (KBr): $\tilde{\nu}$ = 1272 cm^{-1} (P=O). ^1H NMR: δ = 6.95−7.20 (4 H), 5.92 (ddd, 2-,6-H), 4.10 (q, 4 OCH_2), 3.53 (ddd, 1-,5-H), 2.66 (m, 4-,8-H), 1.27 (t, 4 CH_3) ppm; $J_{1,2(5,6)}$ = 9.2 Hz. ^{13}C NMR: δ = 148.9, 148.8 (C-3,-7), 142.1, 127.7, 127.2, 114.2, 114.1 (6 C), 64.4, 64.3 (4 OCH_2), 38.8, 38.7 (C-4,-8), 22.6 (C-1,-5), 16.3, 16.2, 16.1 (4 CH_3) ppm. MS: *m*/*z* (%) = 486 (2) $[M^+]$, 332 (15), 178 (100). $C_{22}H_{32}O_8P_2$ (486.4).

9,10-Benzobicyclo[3.3.2]deca-2,6,9-triene (41): NH_3 (ca. 50 mL) was condensed into diethyl ether (10 mL) at −78 °C. After addition of thinly cut Li (1.05 g, 152 mmol), stirring for 30 minutes, and addition of *t*BuOH (5.7 mL, 59.7 mmol), a solution of **40** (3.02 g, 6.35 mmol) in THF (20 mL) was added dropwise. Stirring was continued for 3 h, and NH_4Cl was then added until total decolorization. After concentration and standard workup, the crude, colorless oil (1.7 g) was filtered through silica gel (cyclohexane). Colorless, crystalline **41** (up to 1.11 g, 96%) was isolated, occasionally containing some higher hydrogenated material, which did not, however, interfere with the subsequent oxidation. IR (KBr): $\tilde{\nu}$ = 1657 cm^{-1}, 1569 (C=C). ^1H NMR: δ = 7.15 (m, 4 H), 5.89 (dd, 2-,6-H), 5.65 (dddd, 3-,7-H), 3.44 (m, 1-,5-H), 2.46 (m, 4-,8-H)

ppm; $J_{1,2(5,6)}$ = 1.8, $J_{2,3(6,7)}$ = 11.6, $J_{1,3(5,7)}$ = 0.6, $J_{2,4(6,8)}$ = 2.4 Hz. ^{13}C NMR: δ = 144.4, 129.2 (4 C), 128.3 (C-2,-6), 127.5 (C-3,-7), 126.5 (2 C), 44.4 (C-1,-5), 34.0 (C-4,-8) ppm. MS: *m*/*z* (%) = 182 (40) [M·$^+$], 167 (50), 141 (75), 128 (100). HRMS: calcd. for $C_{14}H_{14}$ 182.1095; found 182.1080.

9,10-Benzobicyclo[3.3.2]deca-2,6,9-triene 2,3(α);6,7(α)-Dioxide (42): A freshly prepared solution of DMDO in acetone (170 mL ca. 0.06 M, 10.2 mmol) was added dropwise at room temperature to a solution of **41** (475 mg, 2.61 mmol) in CH_2Cl_2 (20 mL). After the mixture had been stirred for 10 h and concentrated in vacuo, the solid residue (560 mg, 100%) consisted of a mixture of **47** (80%, m.p. 183 °C) and its *exo*/*endo* isomer. Since chromatographic separation (silica gel) was not possible without significant decomposition, this mixture was used as such. ^{1}H NMR: δ = 6.95−7.20 (m, 4 H), 3.50 (ddd, 1-,5-H), 3.40−3.10 (m, 2-,3-,6-,7-H), 2.52 (dd, 2 H), 2.35 (ddd, 2 H) ppm; $J_{4,4'(8,8')}$ = 16.2 Hz. ^{13}C NMR: δ = 136.7 (C-9,-10), 129.8 (C-11,-14), 127.5 (C-12,-13), 56.7, 54.3 (C-2,-3,-6,-7), 42.9 (C-1,-5), 27.4 (C-4,-8) ppm. MS: *m*/*z* (%) = i.a. 214 (42) [M·$^+$], 171 (7), 141 (26), 131 (52), 128 (100). $C_{14}H_{14}O_2$ (214.3).

9,10-Benzobicyclo[3.3.2]deca-3,7,9-triene-2α,6α-diol (43): *n*BuLi (10.4 mL of 2.5 M solution in *n*-hexane, 26.0 mmol) was added at −78 °C to a solution of diisopropylamine (3.32 g, 32.8 mmol) in anhydrous THF (130 mL). After the mixture had been stirred for 15 minutes, a solution of **42** (560 mg, 2.61 mmol) in anhydrous THF (30 mL) was added dropwise. After stirring for 10 h at room temperature, it was hydrolyzed (phosphate buffer, pH ca.7). Standard workup (CH_2Cl_2) provided a crude solid material (540 mg), which was chromatographed (silica gel, cyclohexane/ethyl acetate, 1:1) to afford colorless crystals (402 mg, 72%); m.p. 188 °C. IR (KBr): $\tilde{\nu}$ = 1458 cm^{-1}, 1415 (C=C). ^{1}H NMR: δ = 6.95−7.20 (m, 4 H), 6.10 (ddd, 4-,8-H), 5.68 (ddd, 3-,7-H), 4.25 (m, 2-,6-H), 3.35 (ddd, 1-,5-H) ppm; $J_{1,2(5,6)}$ = 4.0, $J_{1,8(4,5)}$ = 8.8, $J_{2,3(6,7)}$ = 5.4, $J_{3,4(7,8)}$ = 11.8 Hz. ^{13}C NMR: δ = 140.4 (C-9,-10), 131.2 (C-4,-8)*, 130.7 (C-3,-7)*, 129.4 (C-11,-14), 127.2 (C-12,13), 67.9 (C-2,-6), 51.7 (C-1,-5) ppm. MS: *m*/*z* (%) = 214 (4) [M$^+$], 196 (100) [M − H_2O]·$^+$. HRMS: calcd. for $C_{14}H_{14}O_2$ 214.0993; found 214.0984.

9,10-Benzobicyclo[3.3.2]deca-3,7,9-triene-2,6-dione (44a): Pyridinium dichromate (423 mg, 1.12 mmol) was added in small portions to a solution of **43** (151 mg, 0.70 mmol) in anhydrous CH_2Cl_2. After total conversion (ca. 2 h), the mixture was filtered (celite) and chromatographed (silica gel, $CHCl_3$). Colorless crystals (96−120 mg, 45−60%) were isolated, m.p. 148 °C. UV (MeOH): λ_{max} = 363, 236 nm. IR (KBr): $\tilde{\nu}$ = 1654 cm^{-1} (C=O), 1561 C=C). ^{1}H NMR: δ = 7.25−7.30 (m, 4 H), 7.02 (dd, 4-,8-H), 5.93 (dd, 3-,7-H), 4.61 (dd, 1-,5-H) ppm; $J_{1,8(4,5)}$ = 9.8, $J_{1,7(3,5)}$ = 1.5, $J_{3,4(7,8)}$ = 11.6 Hz. ^{13}C NMR: δ = 189.6 (C-2,-6), 143.2 (C-4,-8), 135.2 (C-9,-10), 129.8 (C-11,-14), 128.7 (C-4,-8)*, 128.5 (C-3,-7)*, 64.4 (C-1,-5) ppm. MS: *m*/*z* (%) = 10 (71) [M·$^+$], 181 (100) [M − CHO]$^+$, 153 (98) [M − CH_2=CHCH=OH]$^+$. $C_{14}H_{10}O_2$ (210.2): calcd. C 79.88, H 4.79; found C 79.91, H 4.72.

11,12-Benzo-2,3,7,8-tetraazatetracyclo[7.4.1.0^{4,13}.0^{6,10}]tetradeca-1,6,11-triene (45a): A solution of **44a** (105 mg, 0.50 mmol) in methanol (30 mL) was slowly added at room temperature to a stirred solution of hydrazine hydrate (500 mg, 10.0 mmol) in methanol (5 mL). After 2 h only one product was present (TLC). After concentration in vacuo the oily, uniform, air-sensitive residue (119 mg, 100%) slowly solidified [R_f (MeOH,$CuCl_2$) = 0.30] and was used as such. ^{1}H NMR (CD_3OD): δ = 7.3−7.4 (m, 4 H), 4.18 (m, 4-,9-H), 4.11 (d, 10-,13-H), 2.41 (d, 5-,14-H′), 2.32 (dd, 5-,14-H) ppm; $J_{4,5(9,14)}$ = 3.7, $J_{4,13(9,10)}$ = 7.2, $J_{5,5'(14,14')}$ = 13.7 Hz. ^{13}C NMR (CD_3OD): δ = 160.7 (C-1,-6), 135.6 (C-11,-12), 131.6 (C-13,-16)*, 129.7 (C-14,-15)*, 75.1 (C-4,-9), 56.5 (C-10,-13), 32.8 (C-5,-14) ppm. MS: *m*/*z* (%) = 238 (51) [M·$^+$], 223 (36), 183 (56), 169 (100). HRMS: calcd. for $C_{14}H_{14}N_4$ 238.1218; found 238.1206.

3,8-Diacetyl-11,12-benzo-2,3,7,8-tetraazatetracyclo[7.4.1.0^{4,13}.0^{6,10}]-tetradeca-1,6,11-triene (45b): A solution of **45a** (24 mg, 0.10 mmol) and acetic anhydride (108 mg, 15.1 mmol) in anhydrous pyridine (2 mL) was stirred for 10 h. After concentration in vacuo and filtration through silica gel (cyclohexane/ethyl acetate, 1:1), crystals (23 mg, 71%) were isolated; m.p. > 250 °C; R_f($CHCl_3$/MeOH, 10:1) = 0.51. IR (KBr): $\tilde{\nu}$ = 1658 cm^{-1} (C=O), 1594 (C=C). ^{1}H NMR: δ = 7.4−7.25 (m, 4 H), 5.12 (ddd, 4-,9-H), 4.14 (m, 10-,13-H), 2.93 (ddd, 5-,14-H′), 2.35 (ddd, 5-,14-H), 2.43 (s, CH_3), 2.35 (s, CH_3) ppm; $J_{4,5(9,14)}$ = 3.4, $J_{4,5'(9,14')}$ = 1.8, $J_{4,13(9,10)}$ = 7.9,, $J_{5',13(10,14')}$ = 0.9, $J_{5,13(10,14)}$ = 0.6, $J_{5,5'(14,14')}$ = 13.1 Hz. ^{13}C NMR: δ = 170.8 (C-1,-6), 159.7(CO), 132.9 (C-11,-12), 130.7 (C-15,-18), 129.3 (C-16,-17), 68.0 (C-4,-9), 54.8 (C-10,-13), 29.1 (C-5,-14), 21.9 (CH_3) ppm. MS: *m*/*z* (%) = 322 (84) [M$^+$], 280 (77) [(M − C_2H_2O]$^+$, 238 (100) [M − $2C_2H_2O$]·$^+$. $C_{18}H_{18}N_4O_2$ (322.4): calcd. C 67.07, H 5.63, N 17.38; found C 67.19, H 5.12, N 17.11.

11,12-Benzo-2,3,7,8-tetraazatetracyclo[7.4.1.0^{4,13}.0^{6,10}]tetradeca-2,7,11-triene (46): $NaCNBH_3$ (120 mg, 2.0 mmol) was added (trace of methyl red) under exclusion of air to a solution of **45a** (120 mg, 0.50 mmol) in anhydrous MeOH (20 mL). HCl (2 N) was added until the color of the indicator changed from yellow to red (pH 4). After the mixture had been stirred for 48 h at room temperature., conc. HCl (1 mL) was added. The solution was stirred (10 min) and hydrolyzed (aqueous $NaHCO_3$). After filtration and concentration in vacuo, the residue [highly oxygen-sensitive bis(pyrazolidine) **47**] was dissolved in ethanol (10 mL). An ethanolic $CuCl_2$ solution, and after 10 min a conc. NH_3 solution, were added until a deep blue color persisted. After standard workup ($CHCl_3$), the crude solid (118 mg, 98%) was filtered through deactivated silica gel (triethylamine, $CHCl_3$/MeOH, 30:1). Colorless crystals (75 mg, 63%) were isolated; m.p. 153 °C (dec., elimination of N_2). UV (MeOH): λ_{max} (ε) = 336 nm (810), 200 (12880). IR (KBr): $\tilde{\nu}$ = 1552 cm^{-1} (N=N), 1492(C=C). ^{1}H NMR: δ = 7.23 (m, 15-,18-H)*, 7.15 (m, 16-,17-H)*, 5.03 (ddd, 1-,4-,6-,9-H), 3.16 (t, 10-,13-H), 3.12 (dt, 5-,14-H_s), 1.51 (dt, 5-,14-H_a) ppm; $J_{1,13(4,13)(6,10)(9,10)}$ = 11.0, $J_{1,14a(4,5a)(5a,6)(9,14a)}$ = 5.4, $J_{1,14s(4,5s)(5s,6)(9,14s)}$ = 3.0, $J_{5a,5s(14a,14s)}$ = 16.1 Hz. ^{13}C MR: δ = 135.3 (C-11,-12), 131.8 (C-15,-18), 127.8 (C-16,-17), 85.2 (C-1,-4,-6,-9), 41.3 (C-10,-13), 21.1 (C-5,-14) ppm. MS: *m*/*z* (%) = 238 (3) [M·$^+$], 182 (4) [M − $2N_2$]·$^+$, 167 (96), 128 (100). $C_{14}H_{14}N_4$ (238.3): calcd. C 70.57, H 5.92; found C 70.84, H 6.05.

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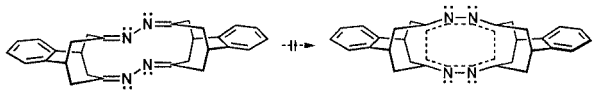

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