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In-plane homoconjugation/homoaromaticity in preoriented 4N-anions—'scope and limitations'

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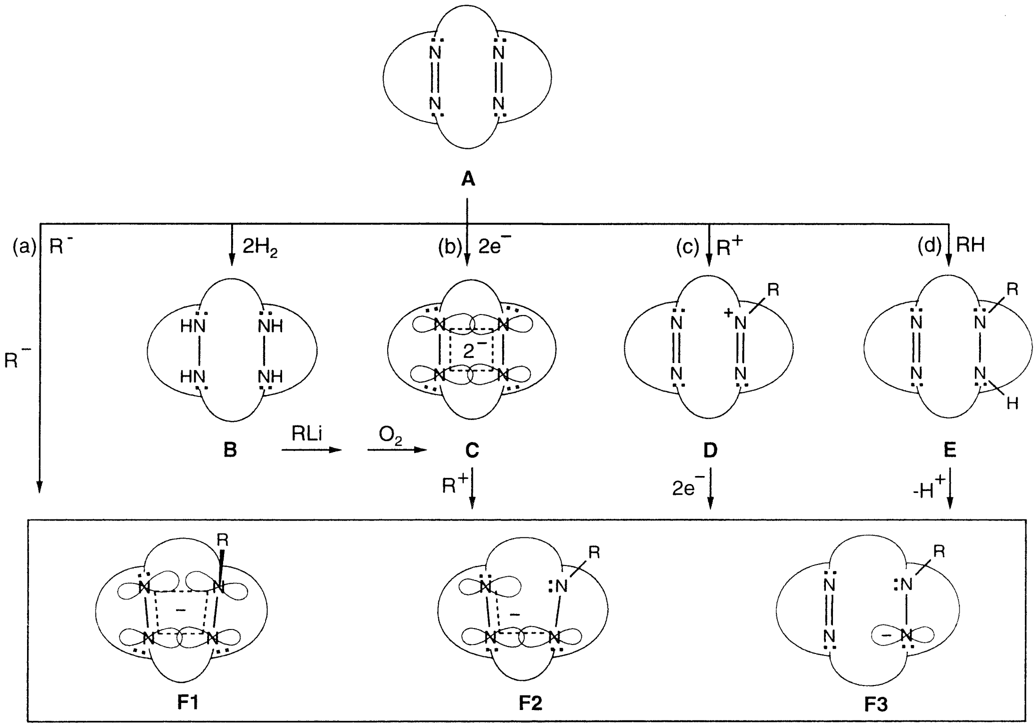
Abstract—By oxidation of (presumably) bislithiated, unusually proximate, *syn*-periplanar bishydrazines an alternative access to σ-bishomoaromatic 4N/6e dianions is realized. Formal *N*-alkylation/arylation of these 4N/6e dianions leads to novel, cyclically delocalized 4N/6e monoanions. Experimental realization is achieved by addition of metal organyls to proximate bisdiazenes as well as by deprotonation of the respective diazene/alkyl(aryl) hydrazines. The nature of the 4N/6e bonding motif is investigated by UV/Vis and NMR spectroscopy as well as by DFT calculations. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

For the understanding of 'supramolecular association' the study of non-bonding interactions under defined geometrical conditions is essential. With the rigid, preoriented bisdiazenes **A** being available, the operation of in-plane (σ) bishomoconjugative/bishomoaromatic bonding[1] in the derived radical anions (4N/5e) and dianions **C** (4N/6e) was demonstrated.[2–4] To gain an even more detailed understanding of these σ-homoconjugative interactions we (i) now



Keywords: σ-homoaromaticity; 4N/6e anions; preorientation.

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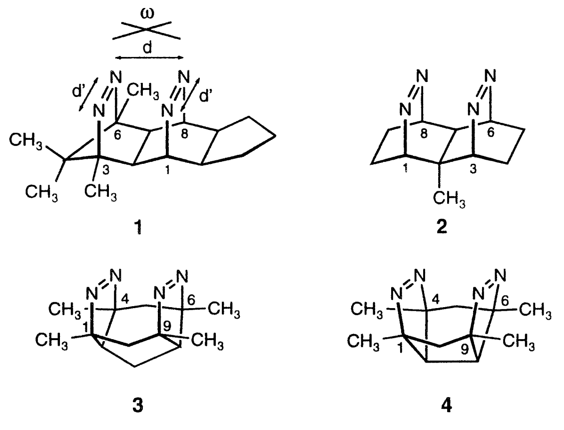


		1^1	2^1	3^8	4^8
d	DFT	2.837		3.088	3.288[7]
	Exp.	2.822	2.821/2.877	(2.989)*	
ω	DFT	174.8	168.6	160.6	145.9[7]
	Exp.	174.6	168.6	(164.0)*	

* for the 1,6-dichloro-4,9-dimethyl derivative[8]

Figure 1. Bisdiazenes **1**–**4**. Selected calculated (DFT) and experimental N···N distances *d* (Å) and interorbital angles *ω* (°).

generated the 4N/6e dianions **C** through air oxidation of (presumably) dilithiated bishydrazines and (ii) prepared 4N monoanions formally accessible by *N*-alkylation(arylation) of the dianions **C**. The bonding motif of these anions can be formulated as cyclic 4N/6e ion **F1**, homo-triazaallyl-type ion **F2**, and localized diazene/alkyl(aryl)hydrazide **F3** as extreme representations. Four synthetic routes interconnect the proximate bisdiazenes **A** and the monoions **F**: (a) addition of metal organyls (R^-), (b) two-electron transfer (dianions **C**) and subsequent alkylation (arylation), (c) *N*-alkylation(arylation) (diazene/diazenium combinations **D**) followed by reduction,[5] and (d) transformation of bisdiazenes **A** into the diazene/hydrazines **E** followed by deprotonation. Of these routes, (a) and (d) were explored (Scheme 1).

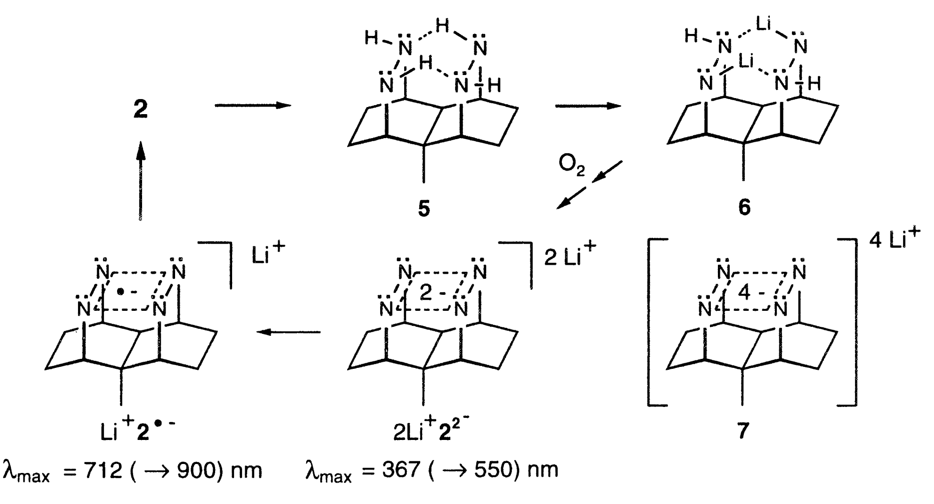
Substrates for this study are the bisdiazenes **1**–**4** (Fig. 1[2,8,9]). For the discovery of the dianions **C**, bisdiazenes **1**–**3**—with π,π-distances (*d*) of 2.8–3.1 Å and interorbital angles (*ω*) of 175–161° (B3LYP/6-31G*[6]) had been instrumental. Bisdiazene **4** is a limiting case as the more mobile skeleton can respond to charge/charge and through-space orbital interactions by adopting more or less distant (open) conformations.[7]

2. Results and discussion

2.1. Oxidation of lithiated bishydrazines to 4N/6e dianions

The oxidative route to dianions **C** (Scheme 2) was a 'spin-off' of our search for the as intriguing as speculative in-plane 4N/8e bishomo-*anti*aromatic bonding motif. After attempts to reduce the 4N/6e dianions to higher anions had failed, four-fold deprotonation of bishydrazine **5** (→**7**) was tested as an alternative. The extremely oxygen sensitive **5** had been quantitatively obtained by controlled catalytic hydrogenation of **2**.[9] In explorative experiments it had been shown that e.g. strained 2,3-diazabicyclo[2.2.2]octane, substructure of **5**, can be dilithiated.[9] In contrast, bismetallation of non-strained hydrazines had only been achieved with the help of charge-delocalizing substituents.[10] Upon addition of a large excess of MeLi to a solution of **5** in [D_8]THF a weakly colored solution was obtained from which a grass-green solid deposited (Fig. 2). Controlled addition of air rapidly homogenized the reaction medium: gradually the color changed to red ($2Li^+\mathbf{2}^{2-}$, λ_{max}=367 nm, tailing to 550 nm), then to deep green ($Li^+\mathbf{2}^{\bullet-}$, λ_{max}= 712 nm, tailing to 900 nm).

Ultimately, colorless bisdiazene **2** was quantitatively recovered. The structure of the grass-green solid could not be established yet. Rather than **6** or even **7** it is presumably a complex aggregate of bridged dilithiated **5** being soluble only in [D_{18}]HMPT.[11] Unfortunately, the ^1H NMR spectrum showed only a multitude of broadened signals between δ=4.0–0.5 and was further complicated by decomposition of the solvent.[9,11] No assignment was possible. Hydrolysis of the green solid under careful exclusion of oxygen led quantitatively back to bishydrazine **5**. For the oxidation



Scheme 2.

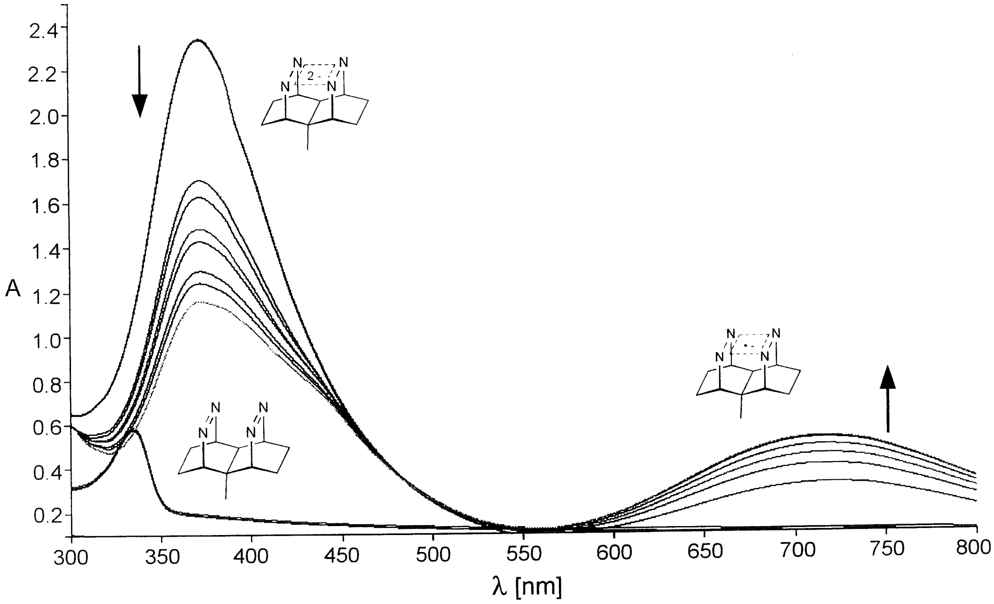
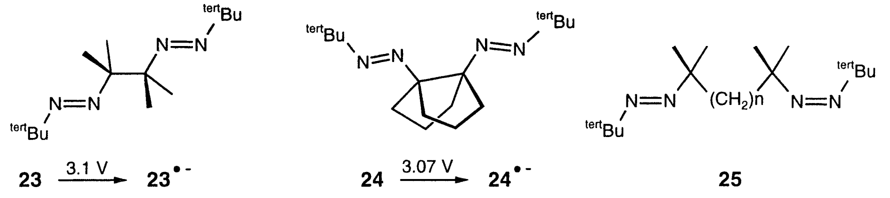


Figure 2. UV/Vis control of the oxidation $\mathbf{6}\rightarrow 2Li^+\mathbf{2}^{2-}\rightarrow Li^+\mathbf{2}^{\cdot -}\rightarrow\mathbf{2}$.



Scheme 3.

$\mathbf{6}$(?)$\rightarrow 2Li^+\mathbf{2}^{2-}$—formally loss of H_2—a sequence of one-electron oxidation steps is highly plausible. In addition to the UV/Vis absorption $2Li^+\mathbf{2}^{2-}$ was identified by ^{1}H NMR spectra.[2] Compared to an authentic sample significant line-shifts of 0.1–0.2 ppm (signals for the α-protons: [D_8]THF $\delta=3.12$ for 6-,8-H; 2.75 for 1-,3-H) and line broadening were noted. Control experiments confirmed that these effects were due to interaction between $2Li^+\mathbf{2}^{2-}$ and excessive MeLi. The formation of radical anion $Li^+\mathbf{2}^{\cdot -}$ from $2Li^+\mathbf{2}^{2-}$ was further confirmed by EPR measurements (THF/DME; no fine structure, *g*-factor 2.000–2.005); the well resolved spectra of the potassium salt are fully analyzed.[2b†]

2.2. 4N Monoions F derived from bisdiazene 2

2.2.1. Addition of MeLi to bisdiazene 2. The studies of the novel 4N monoanions **F** with the extreme bonding motives **F1**–**F3** began with the addition of metal organyls to bisdiazenes **A** (route a). Strained diazenes such as 2,3-diazabicyclo[2.2.2]octene and -heptene (DBO, DBH) are known to add metal organyls to their N=N double bond.[15] Exposure of **2** to excess MeLi in [D_8]THF (room temperature) led to the instantaneous formation of a ca. 9:1 mixture of deeply red 1:1 adducts, provisionally formulated as delocalized Li**8a** and Li**9a** (Scheme 4, the major isomer resulting from addition at the N-atoms (5,9) with larger distance *d*, Fig. 1). Even under much more forcing conditions no two-fold addition (e.g. **11a**) did occur. The UV/Vis absorption—a broad band with $\lambda_{max}=438$ nm tailing to 580 nm—kept its intensity for days, yet disappeared instantaneously upon contact with air. It is to be compared with $\lambda_{max}=366$ nm (tailing to 400 nm) for the yellowish adduct of MeLi to DBO as localized model[9] and attests to marked σ-homoconjugation. After hydrolysis the highly oxygen-sensitive, colorless diazene/methylhydrazines **12a** (**13a**) (ca. 9:1) were isolated quantitatively. There was no hint for homoconjugate protonation to give tetrazane **14a**.[16] Oxidation of **12a** with air led to tetrazolidine **10** as major oxidation product; no intermediate (diazene/azomethine imine?) was detectable.[2]

With **12a**(**13a**) first representatives of the very proximate, strictly *syn*-periplanar diazene/hydrazine substrates **E** were

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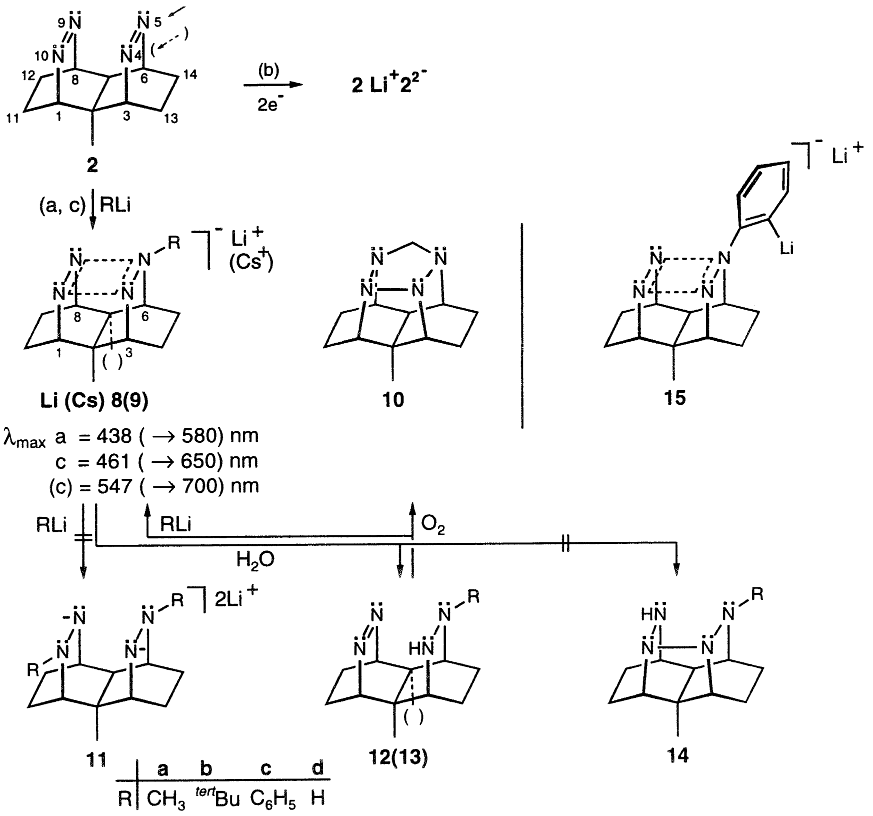
[†] In the context of 'scope and limitations' of the σ-bishomoaromatic 4N/6e bonding motif **C** the reductive behavior of more mobile bisdiazenes was of interest. The energy needed to bring about the appropriate geometrical changes in the respective dianions would give an estimate of the delocalization energy. These bisdiazenes would have to provide protection for their anions against tautomerization—a prerequisite which might considerably raise the energy needed to enforce the required orientation of the two N=N double bonds. Thus it was not too surprising that reduction experiments with the 1,5-bisdiazenes **23**[12] and **24**[13] gave no hint for the formation of 4N/6e dianions. By cyclovoltammetry with the proven, very carefully dried solvent/electrolyte system THF/TBAPF$_6$ (0.1N),[2b] only a first (irreversible) reduction potential in the high range for dialkyl diazenes (ca. −3.0 V, vs Ag/AgCl, 0.1–10 V s^{-1})[2b] was measured. Note, for **1**(**2**) a first reversible reduction wave at −2.38 (−2.36) V and a not fully reversible second one at −2.90 (−2.87) V had been related to the cyclic electron delocalization of the respective radical anions and dianions.[2b] Efforts to synthesize more promising bisdiazenes **25** (*n*=3, 10) by alkylation of the Li salt of acetone-^{tert}butylhydrazone with the corresponding diiodoalkanes[14] were unsuccessful (Scheme 3).[9]



Scheme 4.

at hand. Deprotonation of **12a**(**13a**) with MeLi (**E**→**F**) led neatly back to Li**8a**(Li**9a**) (route d). To allow for a detailed NMR analysis (Fig. 3)—particularly for comparison with the calculated counter-ion free structures—the cesium salts Cs**8a**(Cs**9a**) were analogously prepared ([D$_8$]THF, ^{tert}BuNHCs). With their less tight ion-pairing they were even more air-sensitive and more intense in color.[2b]

2.2.2. Addition of ^{tert}BuLi to bisdiazene 2. The response of **2** to ^{tert}BuLi ([D$_8$]THF, −90°C) turned into another demonstration of the remarkable stability of dianions **C** (Scheme 4).[17] Instead of addition (→Li**8b**(Li**9b**)) quantitative two-electron reduction to 2Li$^+$**2**$^{2-}$ did occur. Even under broadly varied conditions deep green radical anion (Li$^+$**2**$^{\cdot -}$) as a plausible intermediate was not observed. This behavior is in striking contrast to the reduction of bisdiazenes with Li metal.

2.2.3. Addition of PhLi to bisdiazene 2. Upon addition of PhLi to **2** (Scheme 4) the salts Li**8c**(Li**9c**) were formed. Their UV/Vis absorption (λ_{max}=461 nm, tailing to 650 nm) was distinctly redshifted compared to the Me-adducts Li**8a**(Li**9a**). Differently from the latter, any individual NMR assignment was prevented by exchange processes. Hydrolysis of Li**8c**(Li**9c**) followed by chromatographic separation, gave isomerically pure diazene/phenylhydrazine **12c** (**E**) which proved to be less oxygen sensitive than **12a**. By careful deprotonation of **12c** with MeLi, ^{tert}BuNHCs, or—preferably—benzylCs, a detailed NMR analysis became possible (Fig. 3). During the NMR experiments arene metallation of Li**8c** to **15** did occur but was too slow to interfere. The bright violet color of Cs**8c** (λ_{max}=547 nm, tailing to 700 nm) nicely demonstrates the looser aggregation compared to Li**8c**.[2b] Upon hydrolysis of Li**8c** (as well as of **15**) besides **12c** no tetrazane (**14c**) was detected.

2.3. 4N Monoions F derived from bisdiazene 1

The experiments with **1** as the most proximate of the bisdiazenes studied (Fig.1) were restricted to the reaction with MeLi (excess, Scheme 5). Aggregation phenomena did not impede the NMR analysis. The regiospecific formation of 1:1 adduct Li**16** as the only product (red solution, λ_{max}=456 nm, tailing to 620 nm, redshifted by 18 nm vis-à-vis that of Li**8a**(Li**9a**)) reflects the relative LUMO energies of the two N=N-units.[18] Once again more forcing conditions did not effect any second addition. Hydrolysis led to diazene/methylhydrazine **18** (**E**). If formed at all, tetrazane **17** is formed in less than 5% yield. Air oxidation of **18** led inter alia to known tetrazolidine **19**.[2]

2.4. 4N Monoions F derived from bisdiazenes 3 and 4?

Reactions of bisdiazenes **3** and **4** with MeLi were very slow. Steric hindrance by the bridgehead methyl groups, together with reduced reactivity of the less strained pyrazoline rings may be held responsible. Subsequently or parallel to the formation of MeLi adducts of not defined nature, olefinic (loss of N$_2$) and polymeric products (anionic polymerization) were generated.

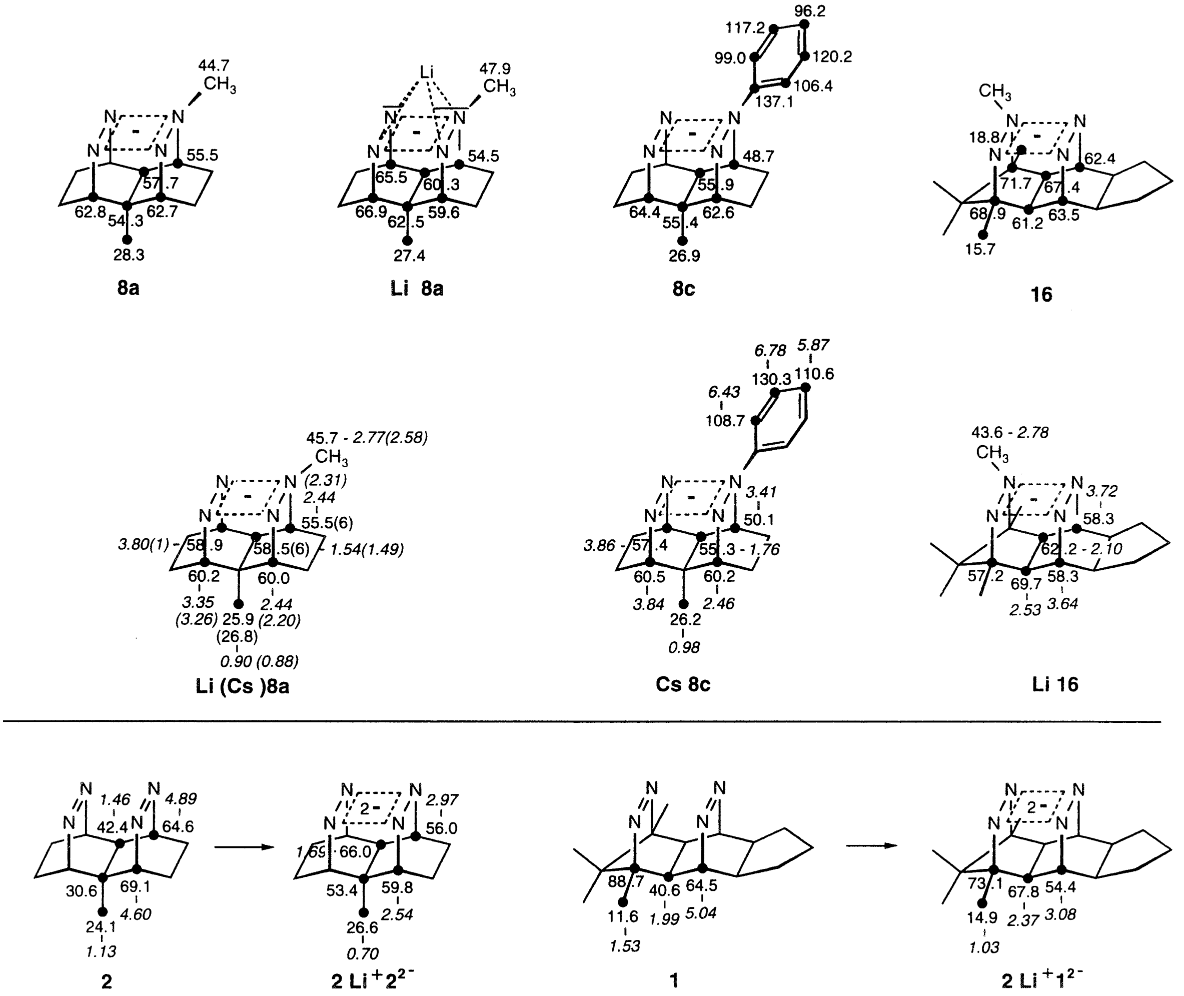
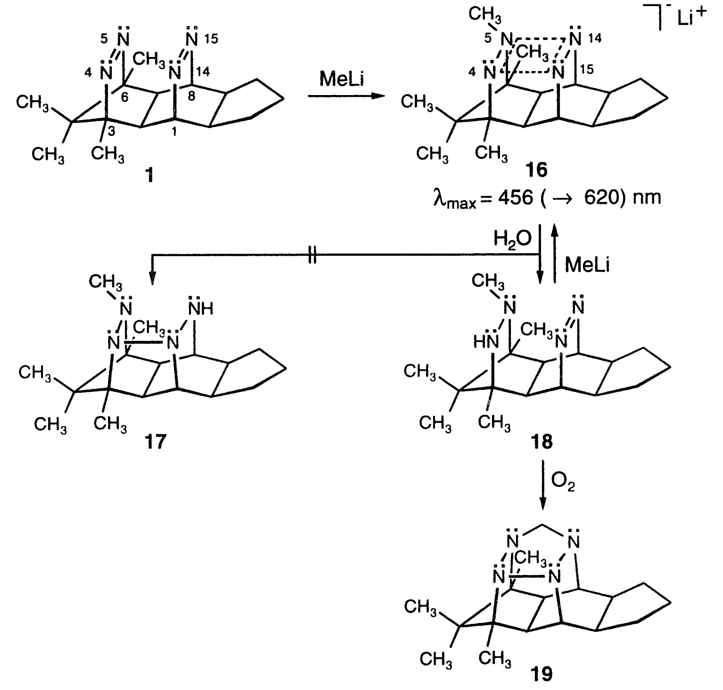


Figure 3. Experimental (Li(Cs)**8a**, Cs**8c**, Li**16**) and calculated (**8a**, Li**8a′**, **8c**, **16**) (B3LYP/6-31G*) ^{1}H and ^{13}C NMR shifts. For comparison the experimental data of **2**, 2Li$^+$**2**$^{2-}$, **1** and 2Li$^+$**1**$^{2-}$.



Scheme 5.

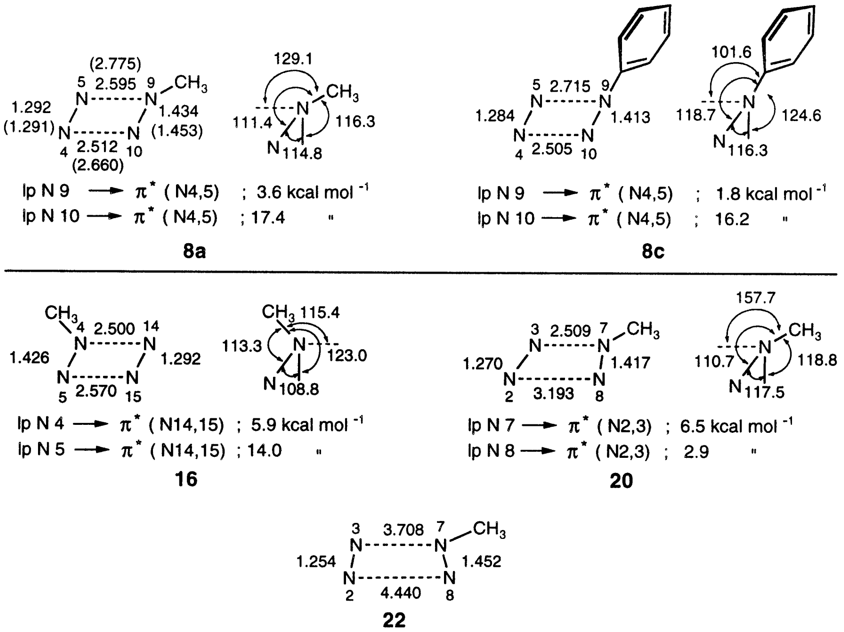


Figure 4. Calculated (B3LYP/6-31G*, counterion-free) transannnular N···N distances, N=N bond lengths (Å), valency angles for $NCH_3(C_6H_5)$ (°), interaction energies (NBO analyses).

2.5. Calculations

Essential criteria for cyclic in-plane electron delocalization in the dianions $2Li^+\mathbf{1}^{2-}$ and $2Li^+\mathbf{2}^{2-}$ were the substantial shifts of (a) the α-H (α-^{13}C) NMR signals to higher, (b) of the central β-H (β-^{13}C) NMR signals to lower field, and (c) the (calculated) geometrical changes associated with the reduction. The experimental (Li(Cs)**8a**, Cs**8c**, Li**16**) and calculated NMR data (**8a**, Li**8a′**, **8c**, **16**) ((B3LYP/6-31G*),[6] Fig. 3) exhibit similar trends. Specifically for Cs**8c** the effective conjugation with the phenyl substituent is demonstrated. The description as bishomoconjugated 4N/6e anions of type **F1**—rather than of σ-homoallylic anion type **F2** or of localized anion type **F3**—is supported by the geometrical changes (Fig. 4). In going from **2** to **8a**/**8c** and from **1** to **16** the transannular N···N distances are shortened and the N=N bonds lengthened to a degree somewhat smaller than for $\mathbf{2}\rightarrow\mathbf{2}^{2-}$ and $\mathbf{1}\rightarrow\mathbf{1}^{2-}$. As expected, the interaction energies (NBO analyses, transannular donation of electron density from N-lone pairs into N=N–π* orbitals) are significantly different for the two N=N bonds. For the more distant anions **20** and **22** (MeLi-addition to bisdiazenes **3** and **4**) the interaction energies are markedly reduced or practically zero.

3. Conclusion

Under appropriate structural circumstances (proximity, ‘anti-Bredt-protection’) the bisanionic 4N/6e σ-bishomoaromatic bonding motif **C** is stable enough to be generated by air oxidation of (presumably) dilithiated bishydrazines (**B**). The related 4N/6e monoanionic bonding motif **F1** featuring an almost perfect in-plane and a somewhat ‘out-of-plane’ (longer) homoconjugate N···N bond is proposed for a new class of highly persistent ions which result from the addition of metal organyls to the so far most proximate, efficiently anti-Bredt-protected bisdiazenes **A** (**1**, **2**) and from deprotonation of the derived *syn*-periplanar diazene/methyl(phenyl) hydrazines **E**. Even in competition with strong external electron delocalization (e.g. *N*-phenyl, **8c**) electron density is contributed to sustain the 4N cyclic electron delocalization. From NICS (nucleus independent chemical shift)[19] and ACID (anisotropy of the current-induced density)[20] calculations more information regarding the ‘aromaticity’ of these 4N/6e anions is expected.

4. Experimental

4.1. General

The experiments were generally performed in Schlenk-type apparatus under argon atmosphere. The glass ware was flame-dried in high vacuum, [D$_8$]THF with liquid Na/K alloy (sonification, vaccum-transferred into the reaction vessel), THF for preparative purposes with purple sodium naphtalide or sodium/benzophenoneketyl solution or solid ^{tert}BuLi, benzene with potassium. Melting points (mp) were determined on a Monoskop IV (Fa. Bock) and are uncorrected. IR spectra were recorded with Perkin–Elmer 457, UV spectra with Perkin–Elmer Lamda 15, MS spectra with Finnigan MAT 44S and MAT 8200. The UV/Vis cuvettes carried gas-tight joints. The NMR probes were prepared on a vacuum line, the tubes cooled with liquid nitrogen and sealed under high vacuum. Chemical shifts were mostly related to solvent signals (^{1}H (^{13}C): [D$_7$]THF=1.73 (25.3), [D$_5$]benzene=7.15 (128.0), TMS (δ=0.0)). The NMR assignments were corroborated by NOE measurements, NOESY, APT, H,H- and H,C-correlations. Assignments marked with *, ** can be interchanged.

MeLi (PhLi) solution in [D$_8$]THF: commercial 1.6 M MeLi solution in diethyl ether (1.6–1.8 M PhLi in cyclohexane/

diethyl ether 7:3) was evaporated to dryness under high vacuum, [D_8]THF was vacuum-transferred from Na/K suspension, the clear solution after 10 min again evaporated to dryness (high vacuum, last traces of diethyl ether are difficult to remove); [D_8]THF was added to give a ca. 0.2 M solution (MeLi: $\delta_H=-2.06$, $\delta_C=-15.5$; PhLi: $\delta_H=7.92$ (*m*), 6.86 (*o*), 6.77 (*p*)).

BnCs solution in [D_8]THF: Cs metal, covered by 2–3 cm toluene was molten by heating; for total dissolution it was sonificated (ca. 1 h for 100 mg). The brown–black solution was evaporated to dryness (high vacuum), to the very pyrophorous residue [D_8]THF was vaccum-transferred. The clear, dark solution was immediately used ($\delta_H=6.00$ (*m*), 5.40 (*o*), 4.73 (*p*), 2.29 (CH_2), additionally weak signals of side products).

^{tert}BuNHCs solution in ^{tert}butylamine: Cs metal was covered with ^{tert}butylamine (2–3 cm, degassed) and sonicated for several hours. Excess of metal, finely dispersed, was molten whereupon it precipitated together with CsOH. The clear, yellowish solution was used.

4.1.1. 2-Methyl-4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]-tetradecane (5). To a solution of **2** (150 mg, 0.73 mmol) in methanol (50 mL), carefully degassed by three freeze–pump–thaw-cycles, Pd/C (40 mg, 10%) was added. Under H_2 (1 bar) it was shaken for ca. 5 h. After filtration and removal of the solvent at room temperature (high vacuum) one isolated 150 mg (98%) of colorless, extremely oxygen-sensitive crystals, well soluble in DMSO, MeOH, moderately in $CHCl_3$, hardly in benzene, THF. ^{1}H NMR (500 MHz, $CDCl_3$): δ=4.6–3.9 (br, N–H), 2.89 (m, 6(8)-H), 2.62 (‘t’, 1(3)-H), 2.17 (m, 11a(13a)-H), 1.96 (m, 12s(14s)-H), 1.79 (m, 11s(13s)-H), 1.63 (m, 12a(14a)-H), 1.38 (t, 7-H), 1.02 (s, CH_3); $J_{1,11a}=2.7$ Hz, $J_{1,11s}=2.7$ Hz, $J_{6,14a}=1.3$ Hz, $J_{6,7}=2.1$ Hz, $J_{11a,11s}=12.8$ Hz, $J_{12a,12s}=11.8$ Hz, $J_{11a,12a}=12.8$ Hz, $J_{11s,12a}=6.8$ Hz. ^{13}C NMR ($CDCl_3$): δ=54.8 (C-1,-3), 50.6 (C-6,-8), 47.8 (C-7), 35.6 (C-2), 27.9 (C-12,-14), 26.9 (C-15), 25.9 (C-11,-13). MS (CI, NH_3, 70 eV): *m*/*z*=i.a. 208 (1) [M^+], 207 (6), 205 (100). Upon contact with air **5** was rapidly oxidized via **12d** back to **2**.

4.1.2. Lithiation of 5 and air oxidation. *UV/Vis control* (Fig. 1): *n*-BuLi (0.5 mL, 2.7 M in hexane) was added at room temperature to the suspension of **5** (10 mg) in THF (5 mL). Instantaneously a grass-green solid deposited from the weakly yellow-greenish solution. Short opening of the reaction vessel to air (ca. 1 s) caused rapid homogenation and a color change to deep red. A second short exposure to air generated at the solution/air interphase a green color, which changed back to the red upon shaking. After repeated exposure to air the solution became grass-green and finally colorless. Concentration provided ca. 10 mg of **2**. *^{1}H NMR control*: a solution of MeLi in diethyl ether (1.0 mmol, 0.63 mL of commercial 1.6 M solution) was concentrated to dryness (high vacuum). After addition of [D_8]THF (1 mL) the solution was added to **5** (20 mg, 0.1 mmol) whereupon a grass-green solid deposited from the weakly yellow-greenish solution. Injection of dry oxygen (1.10 mL, ca. 0.05 mmol) generated a clear, deeply red solution, which was transferred into the NMR tube. ^{1}H NMR (500 MHz, [D_8]THF): δ=i.a. 3.12 (br. s, 6-,8-H), 2.75 (br. s, 1-,3-H), 0.74 (s, CH_3), 4.00–2.50 (very br., MeLi complexes), 2.10–0.60 (very br., MeLi complexes, 7-,11a-,11s-,12a-,12s-,13a-,13s-,14a-,14s-H), −2.07 [($MeLi)_4$?]. The spectrum recorded after sonification of the NMR probe in the presence of a piece of K metal was practically unchanged.

4.1.3. Lithiation and cesiation of 2,3-diazabicyclo[2.2.2]-octane. To 2,3-diazabicyclo[2.2.2]octane (5 mg, 0.04 mmol) a solution of MeLi in diethyl ether (1.6 M, 0.30 mL, 0.48 mmol) was added. After concentration to dryness (high vacuum) the solid residue was dissolved in [D_6]THF (1 mL). An orange solid rapidly precipitated from the deeply red, clear solution. After filtration the solution was analyzed (Mono-Li salt). From this solution after 2 h again an orange solid had deposited which after addition of diazabicyclooctane was dissolved (clear red solution). ^{1}H NMR (250 MHz, [D_8]THF): δ=2.89 (br., 1,4-H), 2.08 (br. 5s-,6s-,7s-,8s-H), 1.83 (br.5a-,6a-,7a-,8a-H), −1.95 (br.s, [MeLi]$_4$?).

To the solution of 2,3-diazabicyclo[2.2.2]octane (10 mg, 0.09 mmol) in [D_6]benzene (1 mL) a drop of molden Cs metal was added. After warming to 40°C for 10 min a red solid precipitated (gas evolution). After separation the solid and excess of metal were washed with [D_6]benzene and dried in high vacuum. After addition of [D_8]THL (1 mL) and shaking the red-brown solution was decanted (Cs reacts with THF). ^{1}H NMR (500 MHz, [D_8]THF): δ=3.28 (br. s, N–H), 2.65 (br. s, 1-,4-H), 1.85 (br. s, 5s-,6s-,7s-,8s-H), 1.67 (br. s, 5a-,6a-,7a-,8a-H).

4.2. Reactions of 1–4 with MeLi (PhLi)

In an NMR tube linked to a vacuum line to diazene (0.02–0.03 mmol) MeLi (PhLi) solution in [D_8]THF (8 equiv.) was added, the tube was cooled with liquid nitrogen and sealed under high vacuum. In case of **1** and **2** the solutions became instantaneously brilliantly red (extremely oxygen-sensitive), in case of **3** within hours brownish-red (after days yellow-orange), in case of **4** within minutes brownish-red (persistent for days).

4.2.1. 2,9-Dimethyl-10-lithio-(Li8a) and 2,10-dimethyl-9-lithio-4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradec-4-enes (Li9a). To a solution of **2** (6 mg, 0.03 mmol) a solution of MeLi in diethyl ether (1.6 M, 0.15 mL, 0.24 mmol) was added. The instantaneously deeply red, extremely oxygen sensitive suspension was concentrated to dryness, the residue dissolved in [D_8]THF (l mL) to give a clear solution. ^{1}H NMR (400 MHz): δ=3.80 (br. s, 6-H)*, 3.35 [br. s, 3-H)*, 2.77 (br. s, N–CH_3), 2.44 (br. s, 1-,8-H), 2.10 (br. m, 12s-H), 1.81 (br. m, 11a-H), 1.54 (br. s, 7-H), 1.47–1.25 (br. m, 6-H), 0.90 (br. s, 2-CH_3). Li**9a**: δ=2.81 (br. s, N–CH_3), 0.92 (br. s, 2-CH_3). ^{13}C NMR (500 MHz, [D_8]THF): δ=60.2 (C-3)*, 60.0 (C-1)*, 58.9 (C-6), 58.5 (C-7), 55.5 (C-8), 45.7 (N–CH_3), 25.9 (2-CH_2), 23.9. 23.6, 21.7, 18.4 (C-11,-12,-13,-14). UV/Vis (THF): λ_{max}=438 nm, tailing beyond 550 nm.

4.2.2. 2-Methyl-,9-phenyl-10-lithio-4,5,9,10-tetraazatetracyclo [6.2.2.2^{3,6}.0^{2,7}]tetradec-4-ene (Li8c) cf. Li8a. ^{1}H NMR (500 MHz, [D_8]THF): δ=8.0–6.2 (several br. m), 4.1–3.3 (br. m), 2.2–0.9 (several br. m); UV/Vis (THF): λ_{max}=461 nm, tailing beyond 620 nm.

4.2.3. 3,4,6,16,16-Pentamethyl-5-lithio-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadec-4-ene (16) cf. Li8a. ^{1}H NMR (500 MHz, [D$_8$]THF): δ=3.72 (s, 1-H), 3.64 (s, 8-H), 2.78 (s, N–CH$_3$), 2.53 (d, $J_{2,7}$=12.5 Hz, 7-H), 2.10 (d, 2-H), 2.02 (m, 9-H), 1.97 (m, 13-H), 1.89 (m, 1-H), 1.67 (m, 3-H), 1.23 (m, 2-H), 1.09 (s, 3-CH$_3$), 1.05 (s, 6-CH$_3$), 1.00 (s, 16s-CH$_3$], 0.85 (s, 16a-CH$_3$). ^{13}C NMR (500 MHz, [D$_8$]THF): δ=70.5 (1-C), 69.7 (C-7), 62.6 (1-C), 62.2 (C-2), 58.3 (C-1)*, 57.2 (C-8)*, 44.6 (C-13), 43.6 (C-9, N-CH$_3$), 31.9 (CH$_2$), 31.3 (CH$_2$), 30.6 (C-10,-11,-12), 19.0 (16a-CH$_3$), 17.7 (16s-CH$_3$), 14.6 (6-CH$_3$), 12.5 (3-CH$_3$).

4.3. Reaction of 2 with ^{tert}BuLi

To **2** (5 mg, 0.02 mmol) at −90°C a solution of ^{tert}BuLi (pentane, 1.5 M, 0.13 mL, 0.2 mmol, 10 equiv.) was given (dark coloration). After evaporation to dryness (high vacuum) at −196°C [D$_8$]THF (1 mL) was added by vacuum-transfer. Upon warming up, the solution became deeply red, after exposure to air deeply green and ultimately colorless (according to ^{1}H NMR analysis **2** and compounds derived from the base and THF cleavage). 2Li$^+$**2**$^{2-}$ was identified (UV/Vis, ^{1}H, ^{13}C NMR) as single component of the red solution.

4.3.1. 2,9-(12a) and 2,10-Dimethyl-4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradec-4-enes (13a). To a solution of **2** (25 mg, 0.12 mmol) in THF (5 mL) MeLi (0.70 mL of 1.6 M solution in diethyl ether, 1.12 mmol, 9.3 equiv.) was added. After 30 min the brilliant red solution was quenched with degassed, distilled water (0.20 mL). After evaporation to dryness (high vacuum) with degassed benzene 26 mg of yellowish, highly oxygen-sensitive, on air rapidly darkening 9:1 mixture of **12a**/**13a** was extracted. ^{1}H NMR (500 MHz, [D$_8$]THF): δ=4.93 (‘d’, 6-H), 4.32 (‘t’, 3-H), 2.51 (‘t’, 8-H), 2.35 (s, N–CH$_3$), 2.27 (‘t’, 1-H), 2.18 (m, 1-H), 1.82 (m, 3-H), 1.69 (m, 7-H), 1.53 (m, 1-H), 1.30 (m, 2-H), 1.02 (s, 2-CH$_3$), 0.97 (m, 1-H). **13a**: δ=2.32 (s, N–CH3), 1.07 (s, 2-CH$_3$). ^{13}C NMR ([D$_8$]THF): δ=69.9 (C-3), 66.1 (C-6), 56.1 (C-7), 55.7 (C-1), 54.6 (C-8), 45.5 (N–CH$_3$), 25.9 (C-15), 23.3, 20.8, 19.3, 18.2. UV/Vis (MeOH): λ_{max} (log ε)=360 nm (3.02), 285 (3.17). MS (70 eV): *m*/*z*=i.a. 218 (15) [M$^+$−2H]: 135 (23), 41 (100). Protolysis of of an NMR probe of Li**8a**(Li**9a**) ([D$_8$]THF) with [D$_4$]methanol led to the same mixture of **12a**(**13a**) (NMR).

4.3.2. 2-Methyl-,9-phenyl-4,5,9,10-tetraazatetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradec-4-ene (12c) cf. 12(13)a. (25 mg, 0.12 mmol)/PhLi/cyclohexane–diethyl ether. After chromatographic workup a yellowish, uniform, and only moderately oxygen-sensitive solid was obtained, mp 173°C (dec.). ^{1}H NMR (500 MHz, CDCl$_3$): δ=7.10 (m, 2-H(*m*)), 6.98 (m, 2-H(*o*)), 6.68 (m, *J*=7.2 Hz, 8-H), 3.18 (br. s, N–H), 2.60 (‘t’, *J*=3.0 Hz, 1-H), 1.89 (m, 12s-, 13-H), 1.81 (m, 7-H), 1.79 (m, 11-H), 1.67 (m, 11-H), 1.56 (m, 14-H), 1.41 (m, 14-H), 1.34 (m, 12a-H), 1.10 (m, 13-H), 1.05 (s, CH$_3$). ^{13}C NMR (500 MHz, CDCl$_3$): δ= 151.4 (1-C), 128.6 (2-C(*m*)), 119.1 (1-C(*p*)), 115.8 (2-C(*o*)), 70.0, 66.0, 54.8, 54.4, 51.2 (C-1,-3,-6,-7,-8), 42.8 (C-2), 25.4, 22.1, 20.7, 20.2, 18.5 (C-11,-12,-13,-14,-15). ^{1}H NMR (500 MHz, [D$_8$]THF): δ=7.05 (m, 4-H(*m*,*o*), 6.62 (m, 1-H(*p*)), 5.14 (m, 6-H), 4.56 (‘t’. N–H), 2.63 (m, 1-H,), 1.93 (m, 13-H,), 1.87 (m, 7-H), 1.84 (m, 2-H), 1.64 (m, 2-H), 1.37 (m, 2H), 1.10 (s, CH$_3$), 1.02 (m, 13-H); 22.3, 21.6, 20.6 (C-11,-12,-14), 19.0 (C-13). UV/Vis (MeOH): λ_{max} (log ε)=252 nm (3.0), 316 (2.8), 369 (2.6). MS (70 eV): *m*/*z*(%): 282 (4) [M$^+$], 280 (5) [M$^+$−2H], 159 (8), 77 (100) [C$_6$H$_5$$^+$].

4.3.3. 3,4,6,16,16-Pentamethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadec-4-ene (18). Protolysis of an NMR probe of **16** ([D$_8$]THF) with [D$_4$]methanol neatly (TLC) led to NMR spectroscopically identified, oxygen-sensitive **18**. ^{1}H NMR (400 MHz, D$_8$]THF)/[D$_4$]methanol): δ=i.a. 5.08 (m, 1-H), 4.80 (m, 8-H), 2.30 (s, N–CH$_3$), 2.17 (d, 7-H, *J*=11.8 Hz), 2.O9 (d, 2-H, *J*=11.8 Hz). *Deprotonation of **12a** with MeLi*: NMR probe of **12a** (5 mg, 0.02 mmol)/MeLi (8 equiv.)/[D8]THF (1 mL). The ^{1}H NMR spectrum was identical with that recorded for the product of the MeLi addition to **2**. With Cs^{tert}BuNH: **12a** (5 mg, 0.02 mmol)/Cs^{tert}BuNH (8 equiv.)/[D$_8$]THF (1 mL). ^{1}H NMR (500 MHz, [D$_8$]THF): δ=3.81 (br. s, 6-H), 3.26 (br. s, 3-H), 2.58 (s, 9-CH$_3$), 2.31 (br. s, 8-H), 2.20 (br. s, 1-H), 2.14 (‘t’, *J*=11.6 Hz, 12*s*-H), 1.89 (br. m, 11*a*-H), 1.59 (br. m, 1-H), 1.49 (br. s, 7-H), 1.40 (br. s, 1-H), 1.30–1.23 (br. m, 4-H), 0.88 (s, 2-CH$_3$). ^{13}C NMR (500 MHz, [D$_8$]THF)): δ=58.6 (C-7), 55.6 (C-8), 26.8 (2-CH$_3$), 26.0 (C-11), 25.8, 18.7.

4.3.4. Air oxidation of 12a(13a)—9-methyl-1,2,4,15-tetraazahexacyclo[6.6.1.0^{2,11}.0^{4,15}.0^{5,10}.0^{9,14}]pentadecane (10). A solution of **12a**(**13a**) (4 mg) in non-degassed CDCl$_3$ (0.5 mL) was kept for 1 d at room temperature. According to TLC and ^{1}H NMR analysis there was ca. 50% conversion to mainly **10**[2] and some **2** (arising from **10**). **10**: ^{1}H NMR (250 MHz, CDCl$_3$): δ=i.a. 4.27 (d, 3$_{exo}$-H), 3.88 (dd, 3$_{endo}$-H), 2.75 (m, 5-,8-,11-,14-H), 1.07 (s, 9-CH3]; $J_{3exo,3endo}$= 10.7, $^5J_{3endo,10}$=1.2 Hz.

4.3.5. Deprotonation of 12c. (5 mg, 0.02 mmol)/MeLi (8 equiv.)/[D$_8$]THF (1 mL), cf. **12a**: the immediately deeply red, extremely oxygen-sensitive solution after 1–2 h at room temperature contained Li**8c** and **16**, after 24 h only the latter. Li**8c**: ^{1}H NMR (500 MHz, [D$_8$]THF): δ=7.04 (‘d’, *J*=8.2 Hz, 2-H(*m*)), 6.88 (‘t’, *J*=7.8 Hz, 2-H(*o*)), 6.36 (m, 1-H(*p*)), 3.87 (br. s, 6-H)*, 3.65 (br. s, 3-H)*, 3.34 (br. s, 8-H)], 2.58 (br. s, 1-H), 2.14 (br. s, 1-H], 1.75 (m, 3-H, i.a. 7-H), 1.47 (m, 5-H], 0.94 (s, 15-CH$_3$). **16**: ^{1}H NMR (400 MHz, [D$_8$]THF): δ=7.66 (‘d‘, *J*=6.0 Hz, 1-H), 6.73 (m, 1-H), 6.49 (‘d’, 1-H), 6.36 (‘t’, *J*=6.4 Hz, 1-H), 3.76 (br. s, 3-,6-H), 3.36 (br. s, 8-H), 2.51 (br. s, 1-H), 2.13 (br. s, 1-H), 1.76 (m, 3-H), 1.52 (m, 5-H), 0.97 (s, 15-CH$_3$). ^{13}C NMR (500 MHz, [D$_8$]THF)): δ=144.1 (1-C), 128.0 (1-C), 125.3 (1-C), 119.7 (1-C), 117.5 (1-C), 110.3 (1-C), 63.6, 60.6, 59.8, 58.8, 49.9 (C-1,-3,-6,-7,-8), 28.6, 24.7, 23.6, 21.6, 20.5. After addition of methanol and standard workup **12c** was isolated nearly quantitatively. *Deprotonation with BnCs (Cs^{tert}BuNH) in [D$_8$]THF*: Cs**8c**. ^{1}H NMR (500 MHz): δ=6.78 (br. m, 2-H(*m*)), 6.43 (br. m, 2-H(*o*)), 5.87 (‘t’, *J*=6.9 Hz, 1-H(*p*)), 3.86 (br. s, 6-H)*, 3.84 (br. s, 3-H)*, 3.41 (br. s, 8-H), 2.46 (br. s, 1-H), 1.97 (m, 1-H], 1.76 (br. s, 7-H), 1.68–1.53 (two m, 7-H), 0.98 (s,

CH_3); (benzene): δ=7.22–7.07 (m, 5-H), 2.31 (s, CH_3)]). ^{13}C NMR (500 MHz, [D_8]THF): δ=130.3 (2-C(*m*)), 110.6 (1-C(*p*)), 108.7 (2-C(*o*)), 60.5, 60.2, 57.4, 55.3, 50.1 (C-1,-3,-6,-7,-8). UV/Vis (THF): λ_{max}=547 nm. After addition of methanol and standard workup **12c** was isolated nearly quantitatively.

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