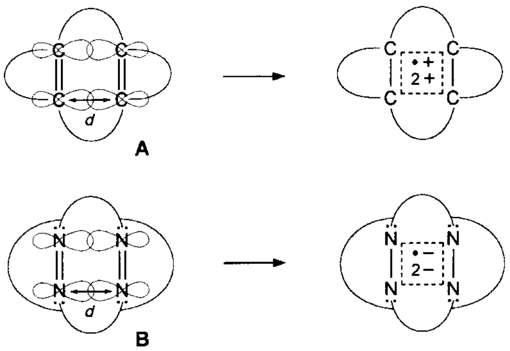
Do Nonclassical, Cyclically Delocalized 4N/5e Radical Anions and 4N/6e Dianions Exist?—One- and Two-Electron Reduction of Proximate, Synperiplanar Bis-Diazenes**

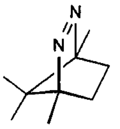
Kai Exner, Dieter Hunkler, Georg Gescheidt,* and Horst Prinzbach*

Dedicated to Professor Hans Fritz
on the occasion of his 70th birthday

Rigid, proximate, synperiplanar and "*anti*-Bredt" protected caged dienes **A** (Scheme 1; $d = 2.8-3.0$ Å) fulfill the prerequisites for one- and two-electron oxidation to nonclassical, theoretically intriguing, and surprisingly stable 4C/3e radical cations and 4C/2e dications ("σ-bis-homoaromaticity").[1] Reduction to the corresponding 4C/5e radical anions and 4C/6e dianions was not possible so far.[2] Upon oxidation of the comparably proximate bis-diazenes **B** (Scheme 1; $d = 2.8-3.0$ Å),[3–6] electrons are removed from n_- orbitals, with through-space interaction between the n_- orbitals being not significant (photoelectron spectroscopic analysis).[3] Here we show that one- and two-electron reductions of such bis-diazenes provides access to previously unknown, nonclassical, cyclically delocalized 4N/5e radical anions $\mathbf{B}^{\bullet-}$ and 4N/6e dianions $\mathbf{B}^{2-}$ of unusual persistence.[2] Systematic ESR studies of the relatively facile one-electron reduction of cycloaliphatic monodiazenes have been published.[7, 8] For the ions of type $\mathbf{C}^{\bullet-}$, $\mathbf{D}^{\bullet-}$, and $\mathbf{E}^{\bullet-}$, which are of interest here as references, ^{14}N hyperfine coupling constants between +0.8 and +1.0 mT have been measured; in $\mathbf{E}^{\bullet-}$ the unpaired electron is localized in one of the two pyrazoline rings. No mention was made of a significant deepening of the color or of a subsequent reduction step.[7, 9]



Scheme 1. One- and two-electron oxidation of the caged dienes **A** to 4C/3e radical cations and 4C/2e dications as well as one- and two-electron reductions of similarly proximate bis-diazenes to 4N/5e radical anions $\mathbf{B}^{\bullet-}$ and 4N/6e dianions $\mathbf{B}^{2-}$.



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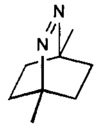

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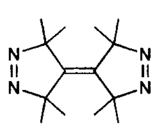

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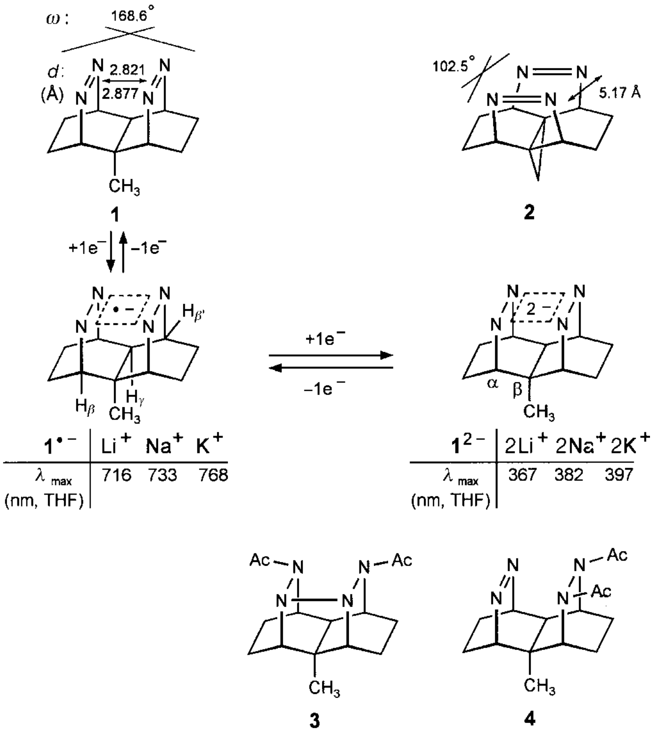
In spite of their favorable d/ω parameters, photoexcitation of the bis-diazenes **1** (Scheme 2) and **5** (Scheme 3), did not lead to $[N_2 + N_2]$ cycloaddition (only N_2 eliminination occurred). However, transannular N–N bond formation was observed in the case of their *N*-oxides.[3, 5] When degassed, dry solutions of **1** and **5** in THF (ca. 4×10^{-2} M) were exposed at room temperature to freshly cut thin lithium sheets,[7] immediate reduction to the deep green radical anions $\mathrm{Li}^+\mathbf{1}^{\bullet-}$ and $\mathrm{Li}^+\mathbf{5}^{\bullet-}$ ($\lambda_{max} = 716$ and 712 nm, respectively) took place. Within minutes the color changed to the red (golden yellow at high dilution) of the dianions $(\mathrm{Li}^+)_2\mathbf{1}^{2-}$ and $(\mathrm{Li}^+)_2\mathbf{5}^{2-}$ ($\lambda_{max} =$ 367 and 396 nm, respectively). When exposed to air, the red samples immediately became green and then colorless; neutral **1** and **5** were identified as the residues. After addition of acetic anhydride to $(\mathrm{Li}^+)_2\mathbf{1}^{2-}$ a mixture of **1** (11 %), **3** (37 %), and **4** (52 %) was isolated; reaction of $(\mathrm{Li}^+)_2\mathbf{5}^{2-}$ gave mainly **7** (95 %).[10] Radical anions and dianions with Na^+, K^+, and Cs^+ as counterions were generated with the corresponding metal mirrors. The longest wavelength UV/Vis absorption of the radical anions and dianions (with the exception of



$\mathbf{1}^{\bullet-}$	Li^+	Na^+	K^+
λ_{max} (nm, THF)	716	733	768

$\mathbf{1}^{2-}$	$2Li^+$	$2Na^+$	$2K^+$
λ_{max} (nm, THF)	367	382	397

Scheme 2. Reduction of **1** to give the deep green radical anion $\mathbf{1}^{\bullet-}$ and further reduction to the dianion $\mathbf{1}^{2-}$. Addition of acetic anhydride to $(\mathrm{Li}^+)_2\mathbf{1}^{2-}$ gives a mixture of **1** (11 %), **3** (37 %), and **4** (52 %). The longest wavelength UV/Vis absorptions of the radical anion and dianion are significantly dependendent on the counterion.

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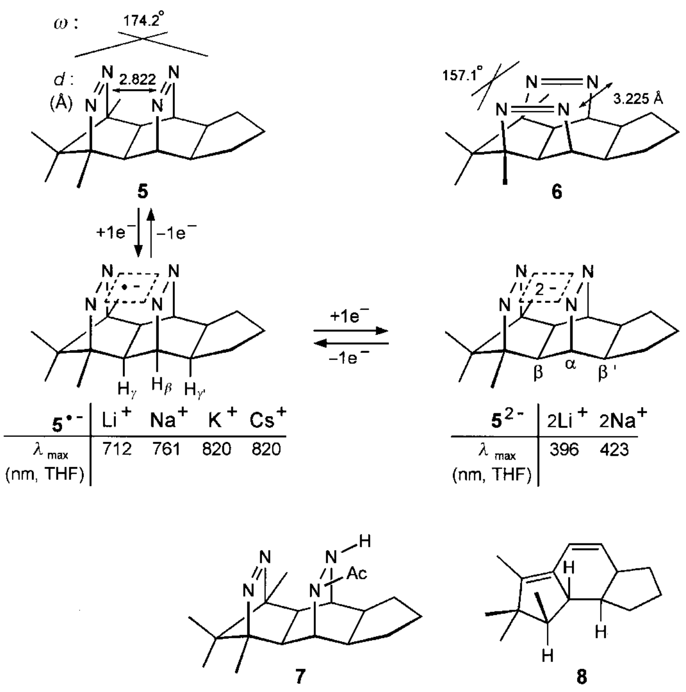

Scheme 3. Reduction of **5** to give the deep green radical anion in $\mathbf{5}^{\bullet-}$ and further reduction to the dianion in $\mathbf{5}^{2-}$. Addition of acetic anhydride to $(Li^+)_2\mathbf{5}^{2-}$ gives **7** (95 %). The longest wavelength UV/Vis absorptions of the radical anion and dianion are significantly dependendent on the counterion. At 25 °C $(K^+)_2\mathbf{5}^{2-}$ decomposes rapidly to **8**, which was isolated in almost quantitative yield.

Table 1. Hyperfine coupling constants [mT] und *g* factors of $K^+\mathbf{1}^{\bullet-}$ and $K^+\mathbf{5}^{\bullet-}$.

$K^+\mathbf{1}^{\bullet-}$	$K^+\mathbf{5}^{\bullet-}$
+0.625 (1 H_γ)	+0.842 (2 H_γ)
+0.420 (2N)	+0.430 (2N)
+0.396 (2N)	+0.340 (2N)
+0.189 (2H)	+0.098
+0.168 (2H)	+0.066
−0.016	−0.021
$g = 2.0042$	$g = 2.0039$

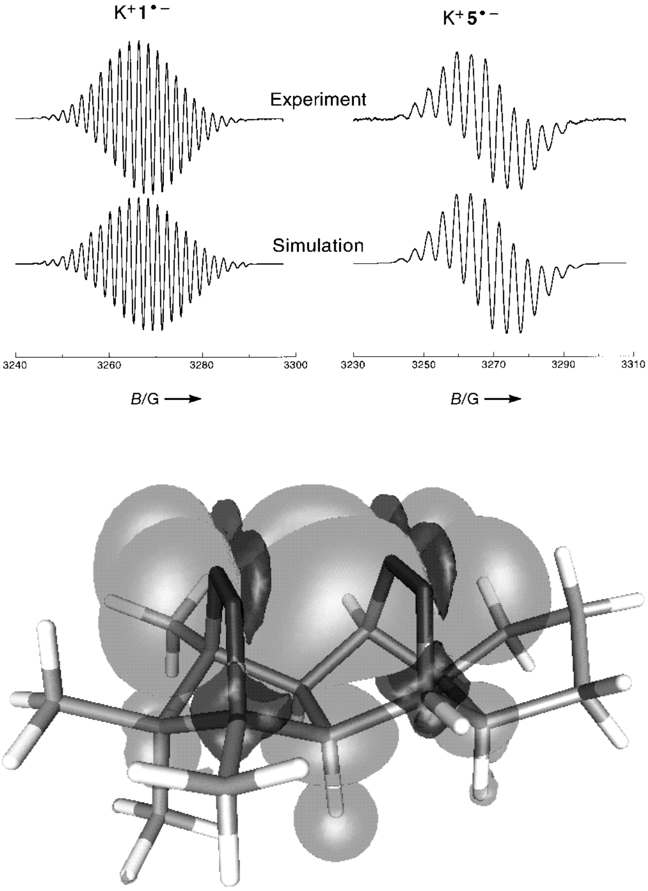

Figure 1. ESR spectra (1,2-dimethoxyethane, −40 °C) of $K^+\mathbf{1}^{\bullet-}$ and $K^+\mathbf{5}^{\bullet-}$ (top), and the calculated spin-density distribution for $\mathbf{5}^{\bullet-}$ (bottom).

$Na^+\mathbf{5}^{\bullet-}$; the spectra are temperature-invariant between −60 and +25 °C) depends significantly on the counterions. A bathochromic shift of 108 nm is observed on going from $Li^+\mathbf{5}^{\bullet-}$ to $K^+\mathbf{5}^{\bullet-}$, and of 30 nm from $(Li^+)_2\mathbf{1}^{2-}$ to $(K^+)_2\mathbf{1}^{2-}$, in agreement with the decreasing ion association. Solutions of the radical anions in THF at room temperature remain unchanged for days, and those of the dianions even survive prolonged heating at 100 °C; only $(K^+)_2\mathbf{5}^{2-}$ decomposed rapidly at 25 °C to give **8** in almost quantitative yield[10] and (presumably) N_2 and N_2^{2-}. In solution **1** and $(Li^+)_2\mathbf{1}^{2-}$ synproportionate to $Li^+\mathbf{1}^{\bullet-}$.

For the formulation of the green radical anions as $\mathbf{1}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$, in which five electrons are cyclically delocalized in the plane of the four N atoms (4N/5e), besides the deep colors, the ESR analyses are decisive. Degassed solutions of **1** and **5** at −70 to +25 °C were reduced for a short time (Li, Na, K, Cs) and, still free of dianions, used for ESR experiments. The ^1H hyperfine coupling constants were determined by ENDOR and TRIPLE measurements,[11] and are presented in Table 1 for the well-resolved spectra of $K^+\mathbf{1}^{\bullet-}$ and $K^+\mathbf{5}^{\bullet-}$ (Figure 1, top). The central criteria for the distinction from localized structures are: the symmetry of the neutral precursors is retained on the time scale of the hyperfine coupling measurements, the ^{14}N hyperfine coupling constants, which were determined by simulation, are pairwise comparable, and with 0.420/0.396 mT for $K^+\mathbf{1}^{\bullet-}$ and 0.430/0.340 mT for $K^+\mathbf{5}^{\bullet-}$ only roughly half the size of the ones typical for the reference ions $\mathbf{C}^{\bullet-}-\mathbf{E}^{\bullet-}$;[7] the delocalization of charge and spin is rather uniform over both diazene units. There is excellent agreement with calculations at the B3LYP/6-31G* level,[12, 13] which give ^{14}N hyperfine coupling constants of 0.434/0.384 mT for $\mathbf{1}^{\bullet-}$ and 0.453/0.346 mT for $\mathbf{5}^{\bullet-}$.[14] The unusually large hyperfine coupling constants of the γ-protons (0.625 and 0.842 mT) are explained by the calculated spin-density distributions (shown for $\mathbf{5}^{\bullet-}$ in Figure 1, bottom), and can be taken as an indication of a relatively large spin density between the diazene units.[7d, 9]

Compounds **1** and **5** were exhaustively reduced over Li in $[D_8]$THF (ca. 4×10^{-2} M), and the resulting red solutions were used to record high-resolution ^1H and ^{13}C NMR spectra at room temperature. The assignments (Figure 2) were confirmed by NOE and selective $^1H/^{13}C$ decoupling experiments. In agreement with the delocalized, C_s-symmetrical electron configurations in $(Li^+)_2\mathbf{1}^{2-}$ and $(Li^+)_2\mathbf{5}^{2-}$, the high-field shifts

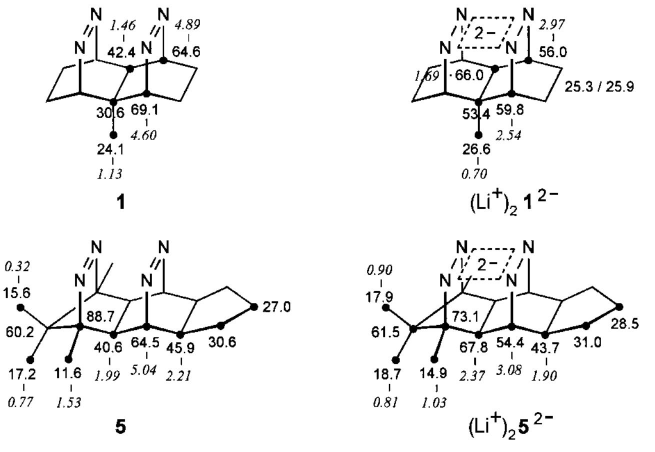

Figure 2. Assignments of ^1H and ^{13}C NMR signals for **1**, **5**, $(Li^+)_2$**1**$^{2-}$, and $(Li^+)_2$**5**$^{2-}$ in [D$_8$]THF.

of the α-H (α-^{13}C) signals are similar [$\Delta\delta = -1.92/-2.06$ ($-8.6/-9.3$) for $(Li^+)_2$**1**$^{2-}$; $\Delta\delta = -1.96$ ($-10.1/-15.6$) for **6**$^{2-}(Li^+{}_2)$]; the large low-field shifts of the ^1H and ^{13}C signals of the β-protons (β-C atoms) that are flanked by the two N_2 bridges are also similar [$\Delta\delta = +0.23$ ($+23.6/+22.8$) for $(Li^+)_2$**1**$^{2-}$; $\Delta\delta = +0.38$ ($+27.2$) for $(Li^+)_2$**5**$^{2-}$].

The B3LYP/6-31G* calculations on the bis-diazene **5**[12, 13] reproduce the X-ray data well[5] and confirm for **5**$^{\bullet-}$ and **5**$^{2-}$ (free of counterions) the energetic advantage of the cyclic conjugation with plausible lengthening ($+0.063$ ($+0.051$); $+0.132$ ($+0.120$) Å) of the vicinal and shortening (-0.141; -0.228 Å) of the transannular N–N distances relative to **5** (Figure 3).

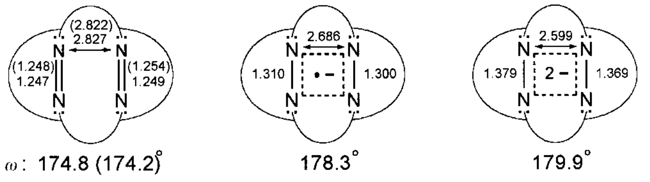

Figure 3. Structural data calculated at the B3LYP/6-31G* level for **5** (X-ray data in parentheses), **5**$^{\bullet-}$, and **5**$^{2-}$.

The thermodynamic properties of this novel class of σ-bis homoaromatic dianions **B**$^{2-}$,[15] the relationship between cyclic conjugation and structural parameters (d, ω), the structural details in the solid state as a function of the counterions, and the formation of counterion-free ions in the gas phase are central aspects of forthcoming investigations, which will include cyclovoltammetric studies. Initial results[16] show that reduction of **2**, which is more mobile and far less proximate than **1**, and of **6**, which is the N_2/N_2 metathesis isomer of **5** (from which it differs only slightly), did not lead to formation of deeply colored ions.

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[16] In an ene/diazene[17] with a structure very similar to that of the bisdiazene **5** (one N–N double bond is replaced by a C–C double bond), after one-electron reduction the spin density remains more strongly localized in the diazene unit (according to calculations:[12] ρ(N=N) = 0.765; ρ(C=C) = 0.168; ^{14}N hyperfine coupling constant: 0.71/0.77 mT).[2]

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Self-Assembling Supramolecular Daisy Chains**

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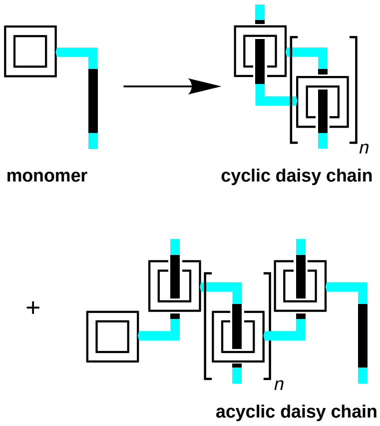

Figure 1. Cyclic and acyclic daisy chains which can be formed by a self-complementary monomer unit.

The design and synthesis of supramolecular polymers[1] is one of the major goals of contemporary supramolecular chemistry.[2] Hydrophobic bonding, hydrogen bonding, and metal coordination have all been used[1] successfully to self-assemble[3] supramolecular polymers in solution and in the solid state. We have devised a self-assembling approach to supramolecular polymer formation (Figure 1) which relies upon the self-complementarity of monomers incorporating a π electron rich macrocyclic "head" and a π electron deficient acyclic "tail" that are unable to interact intramolecularly.[4] Cyclic and/or linear oligomers, self-assemble spontaneously in solution by the insertion of the tail of one monomer through the cavity within the head of another. The driving forces responsible for this recognition event are [C-H···O] hydrogen bonds augmented by π–π stacking interactions between the complementary π electron deficient and π electron rich recognition sites. Here, we report a) the syntheses of four different self-complementary monomers, b) the spectroscopic evidence for their self-assembly to afford supramolecular oligomers in solution, and c) the X-ray crystal structure of a homodimeric cyclic supermolecule formed when one of the monomers crystallizes from solution.

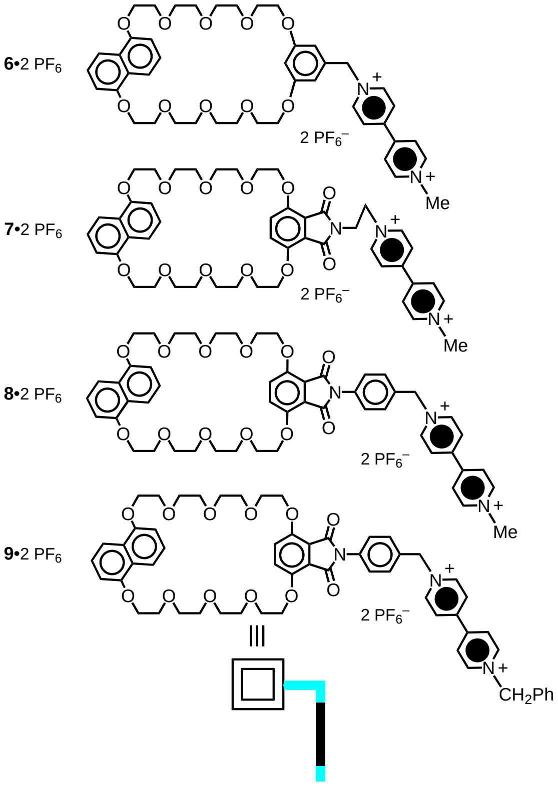

Figure 2. The self-complementary monomers $\mathbf{6}\cdot 2\,PF_6$–$\mathbf{9}\cdot 2\,PF_6$.

The four monomers $\mathbf{6}\cdot 2\,PF_6$–$\mathbf{9}\cdot 2\,PF_6$ (Figure 2) were synthesized[5] as illustrated in Scheme 1. Reaction of *N*-methyl-4,4′-pyridylpyridinium hexafluorophosphate with the macrocyclic polyether **1** gave $\mathbf{6}\cdot 2\,PF_6$ in a yield of 14% after counterion exchange. Reaction of 4,4′-bipyridine with the macrocyclic polyethers **2** and **3**, followed by the alkylation of the resulting hexafluorophosphate salts $\mathbf{4}\cdot PF_6$ and $\mathbf{5}\cdot PF_6$ with methyl iodide or benzyl chloride, gave the self-complemen-

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