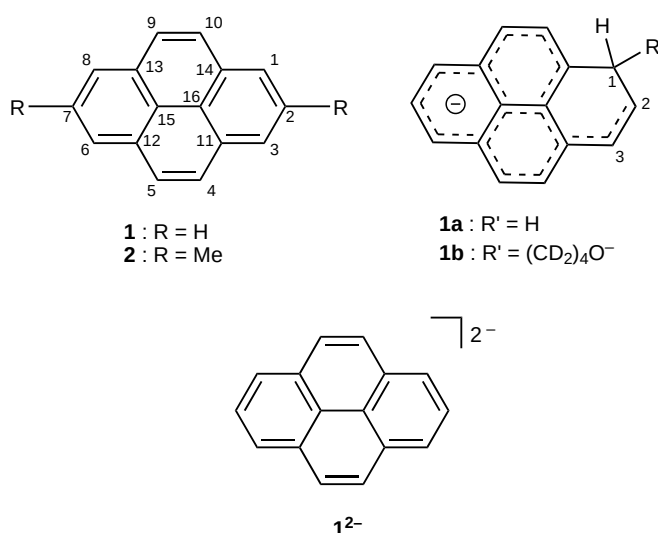


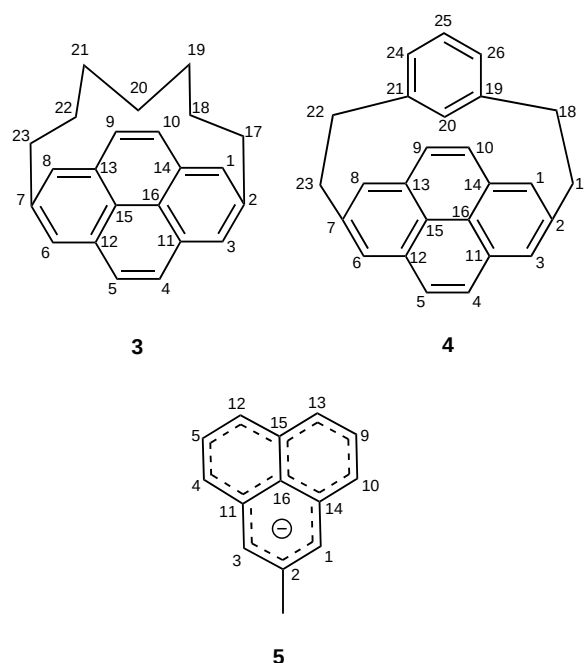
Reductive Dimerization of Tethered Pyrenes: Implications for the Reduction of Polycyclic Aromatic Hydrocarbons**

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The reduction of polycyclic aromatic hydrocarbons (PAHs) with alkali metals can, in some cases, afford a reductive dimerization process. This process takes place in systems that have the capability of forming a stable anionic subunit and concentrating a high electron density on a specific carbon atom, which will eventually form a new σ bond.^[1] Such behavior has been recently reported in the reduction of indenocorannulene, which undergoes a four-step reductive dimerization/bond-cleavage process.^[1d] The reduction of pyrene (**1**) and 2,7-dimethylpyrene (**2**) with alkali metals has been thoroughly studied.^[2] The reduction affords different products depending on solvent, counterion, and temperature. Three primary diamagnetic species can be detected when **1** (Scheme 1) is reduced with lithium metal in $[D_8]THF$: a protonated pyrene monoanion (**1a**), a dianion (**1²⁻**), and a solvent-molecule-incorporated monoanion (solvent cleavage; **1b**).^[2c] The same results are obtained when **2** is reduced with lithium metal. Protonation of the monoanion radicals of **1** and **2**, and the solvent cleavage by their respective dianions at room temperature, illustrate that these species are very reactive. Another aspect of interest in the chemistry of pyrene is its aromatic character. Recent reports suggest that imparting nonplanarity in pyrene, by tethering two remote positions, does not significantly decrease the magnetic anisotropy effect of its nucleus in the neutral state.^[3] To evaluate the effect of strain on the reduction of pyrene, two curved systems, [7](2,7)pyrenophane (**3**; Scheme 2)^[3a] and [2]metacyclo[2](2,7)pyrenophane (**4**)^[4] were reduced with lithium metal in $[D_8]THF$, and the reduction process was followed by NMR spectroscopy. The two-electron reduction of strained pyrene moieties affords totally unexpected results. A new σ bond is formed, to avoid strained antiaromaticity.^[5] A careful and detailed follow up of the reduction process of **3**



Scheme 1. Structures of pyrene molecules (**1** and **2**), the protonated and solvent-incorporated pyrene monoanions (**1a** and **b**), and the dianion (**1²⁻**).



Scheme 2. Structures of [7](2,7)pyrenophane (**3**), [2]metacyclo[2](2,7)pyrenophane (**4**), and the 2-methylphenalenyl anion (**5**).

and **4** led to the observation of unexpected and hitherto unknown intermediary one-electron reduction products.^[6] A reductive dimerization process is observed for the radical anions of **3** and **4** instead of protonation, as is the case in **1** and **2**. Thus, the strain-relieving process in the dianions of **3** and **4** is preceded by an intermolecular σ -bond formation, which results from electron coupling. Each pyrene moiety in the dimerization, protonation, and solvent-cleavage products has the same local symmetry because the reactions all occur at the same carbon atom. This makes it very difficult to distinguish between these products using standard 1H and ^{13}C NMR

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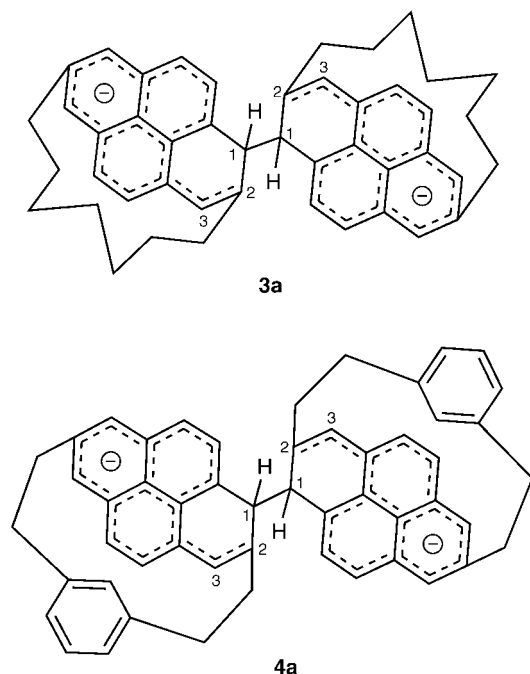
Table 1: The NMR data of hydrogen and carbon atoms H6 and C6 of the different reduction products of **1**, **2**, **3**, and **4**.

	δ H6 [ppm]	δ C6 [ppm]	$^1J_{\text{C,H}}$ [Hz]	$^3J_{\text{H},^* \text{H}}$ [Hz]	Integration
Dimerization	3.2–3.4	48.3–48.7	128–130	~10	1 H atom
Protonation	4.0–4.2 ^[a]	34.0–35.0 ^[a]	124–125 ^[b]	not observed	2 H atoms
Solvent Cleavage	3.7–3.8 ^[a]	43.0–48.0 ^[a]	124–125 ^[b]	not observed	1 H atom

[a] Taken from ref. [2]. [b] See ref. [8]

experiments. However, based on our recent findings,^[1d,5] it is now possible to suggest some basic rules of thumb that can help distinguish the products by way of standard 2D NMR experiments and simple integration (Table 1).

The reduction of **3** (colorless) and **4** (pale yellow) with lithium metal, which is accompanied by color change, gives the diamagnetic species **3a** (claret; Scheme 3) and **4a** (brown), which both give complex ^1H and ^{13}C NMR spectra (Table 2). The ^1H NMR spectrum of **3a** exhibited no dynamic



Scheme 3. Structures of the dimeric species **3a** and **4a**.

processes over a wide range of temperatures (165–273 K). In addition, it is noteworthy that the signal of hydrogen atom H6 is shifted to high field. The ^{13}C NMR spectrum exhibits a signal at an extremely high field ($\delta = 48.3$ ppm; assigned to C6, see Table 2) with a one-bond coupling constant ($^1J_{\text{C6,H6}}$) of 128.3 Hz. The rest of the carbon atoms are divided into two groups, of which one

($\delta = 99$ –119 ppm) is at a higher field than the other ($\delta = 129$ –143 ppm). The ^7Li NMR spectrum showed an absorption at $\delta = 0$ ppm, which implies the presence of solvent-separated ion pairs. Long-range CH-correlation experiments (heteronuclear multiple-bond correlation (HMBC)) conducted on species **3a** afforded three-bond interactions that helped to fully assign the carbon spectra. In addition, a long-range correlation between carbon atom C6 and hydrogen atom H6, which resides on C6, was observed.^[7] In the short-range CH-correlation (proton-coupled heteronuclear single quantum coherence signal-improved (HSQCSI)) experiment, a coupling between hydrogen atom H6 and its symmetrical equivalent was observed from the ^{13}C satellites ($^3J_{\text{H6},^* \text{H6}'} = 10.3$ Hz).^[8] Similar results were obtained for ion **4a** (Table 2).^[9]

The high-field absorption of carbon atom C6 in species **3a** and **4a**, and the magnitude of its $^1J_{\text{C,H}}$ coupling constant are compatible with an sp^3 -hybridized carbon atom. This means that the high-field shift of both carbon atom C6 and hydrogen atom H6 is a result of rehybridization. The HMBC experiments and the $^3J_{\text{H6},^* \text{H6}'}$ coupling constant indicate that a reaction has taken place between two identical C6 carbon atoms of separate molecules, thus forming the sp^3 -hybridized carbons, which in turn lowers the symmetry of the system. These arguments can also be applied to differentiate between the products of protonation, dimerization, and solvent cleavage (Table 1).

The dimerization of two units of **2** and **3** can be explained by means of a radical coupling at carbon atom C6. It has been previously shown for pyrene that position C6 (and its symmetrical counterparts) has the highest spin density for the odd electron in the monoanion radical,^[10] which rationalizes the high reactivity of this site and the likelihood of it undergoing radical coupling. Such radical coupling will leave a negative charge on carbon atom C7 that can be delocalized

Table 2: ^{13}C NMR and ^1H NMR (in parenthesis) chemical shifts, in ppm, of the pyrene moiety of **3**, **3a**, **4**, and **4a** in $[\text{D}_8]\text{THF}$.^[a]

	C1 (H1)	C2	C3 (H3)	C4 (H4)	C5 (H5)	C6 (H6)	C7	C8 (H8)	C9 (H9)	C10 (H10)	C11	C12	C13	C14	C15	C16
3	130.8 (7.50)	131.0	130.8 (7.50)	127.2 (7.80)	127.2 (7.80)	130.8 (7.50)	131.0	130.8 (7.50)	127.2 (7.80)	127.2 (7.80)	132.9	132.9	132.9	132.9	131.5	131.5
3a	119.3 (5.62)	135.5	114.8 (5.71)	110.0 (5.95)	129.7 (5.98)	48.3 ^[b] (3.22)	99.4	129.6 (5.78)	131.9 (6.63)	102.7 (5.71)	142.7	105.2	110.6	142.2	140.6	135.8
4	130.5 (7.10)	134.7	128.6 (7.50)	126.6 (7.60)	126.6 (7.60)	128.6 (7.50)	134.7	130.5 (7.10)	126.9 (6.50)	126.9 (6.50)	133.8	133.8	132.2	132.2	131.2	131.2
4a	118.3 (5.24)	131.4	114.1 (5.82)	109.3 (6.02)	129.1 (5.91)	48.7 ^[c] (3.41)	95.7	129.0 (5.87)	129.8 (6.26)	102.6 (5.26)	143.0	103.5	113.1	142.5	140.5	135.8
5^[d]	104.3	135.2	104.3	103.1	128.1	–	–	–	128.1	103.1	144.7	103.1	103.1	144.5	144.7	137.6

[a] The ^{13}C NMR of **5** is also added for comparison. [b] $^1J_{\text{C6,H6}} = 128.2$ Hz, $^3J_{\text{H},^* \text{H}} = 10.3$ Hz. [c] $^1J_{\text{C6,H6}} = 130.0$ Hz, $^3J_{\text{H},^* \text{H}} = 10.6$ Hz. [d] Taken from ref. [11].

over the remainder of the pyrene moiety. The ^{13}C NMR spectra show that this is indeed the case, as carbon atom C7 is shifted to high field. In addition it can be seen that the negative charge is distributed over alternating carbon atoms on the periphery of a phenylene unit, which explains why two sets of carbon atoms are observed in the ^{13}C NMR spectra. The good agreement between the carbon chemical shifts of the phenylene moiety of **3a** and **4a** and those of the 2-methylphenalenyl anion (**5**; Scheme 2)^[11] supports this conclusion.

The nonplanarity of the pyrene unit in **3** and **4**, which is induced by the tether, imparts an element of asymmetry to each half of the respective dimers. This leads to the possibility of different diastereomeric reduced species, depending on the position of the connection. Even if one assumes that the new σ bond forms on the less hindered *exo* faces of the pyrene moieties, two possible products still remain: a *meso* or a D/L pair. From the data available, it appears as though only one diastereoisomer dominates. Unfortunately, it is not possible to fully assign the relative stereochemistry of the dimers, although it is apparent from the above-mentioned $^3J_{\text{H},\text{H}}$ coupling constants ($^3J_{\text{H}_6,\text{H}_6} = 10.3\text{ Hz}$ for **3a** and $^3J_{\text{H}_6,\text{H}_6} = 10.6\text{ Hz}$ for **4a**) that they adopt an *anti* conformation about the new σ bond.

The fact that the same behavior is observed in both **3** and **4** implies that the isolated benzene ring in **4** has little or no effect on the overall reduction process. This also indicates that electron transfer through the "cyclophane hub" is minimal.^[12] Moreover, under very similar reduction conditions, the nonplanar systems **3** and **4** afford a reductive dimerization process (major product) whereas the planar systems, **1** and **2**, undergo protonation (minor product). It is noteworthy that both processes are accompanied by the production of an aromatic phenalenyl anion entity,^[13] which stabilizes the negative charge in the system.

The difference between the two sets of systems is the alkane tether. This has the dual function of enforcing nonplanarity on the polycyclic aromatic portion of the systems and increasing their solubility; this is evident from the comparatively high solubility of **3** and **4**. It seems that nonplanarity does not significantly alter the spin distribution in the radical anion of all the systems as protonation and dimerization take place at the same carbon atom. However the full effect of nonplanarity in such systems is not yet understood.^[14]

With respect to solubility, the effect of the tether on the systems is better understood. In our experiments, some precipitate was seen along with the protonation products of **1** and **2**. The solubility of the precipitate increased with temperature, but no diamagnetic species, other than the protonation product was observed in the NMR spectra. Müllen et al. previously reported that at low temperatures, the radical anion of **1** might be in equilibrium with a diamagnetic dimer, which undergoes cleavage at higher temperatures.^[2c] Taking the above-mentioned facts into consideration, it is possible to postulate that a dimeric product is also afforded from **1** and **2** but cannot be observed by NMR spectroscopy because of its low solubility.^[15] Edlund et al. have encountered such a case with the reduction of azulene,

where a dimeric precipitate was formed, which upon further reduction was cleaved to afford the azulene dianion.^[1b]

Compounds **3** and **4** afford a reductive dimerization process upon a single-electron reduction, prior to the formation of an intramolecular σ bond. This process was not observed in the planar systems **1** and **2**. It is possible to see that differentiating between dimerization, protonation, and solvent cleavage can be achieved by the use of simple NMR experiments (Table 1). The $^2J_{\text{C,H}}$ and $^3J_{\text{H},\text{H}}$ couplings obtained from the HMBC and proton-coupled HSQCSI experiments, respectively, can be used as a means of detecting the formation of novel and unexpected dimeric compounds.

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- [7] This is, in fact, a $^2J_{\text{C,H}}$ (not a $^3J_{\text{C,H}}$) correlation.
- [8] Compounds **1** and **2** were reduced for comparison: Although the specified interaction in the HMBC is possible in both **1a**, **1b**, and their equivalents in **2**, neither it nor the specific HSQCSI coupling were observed for them in our experiments.
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