

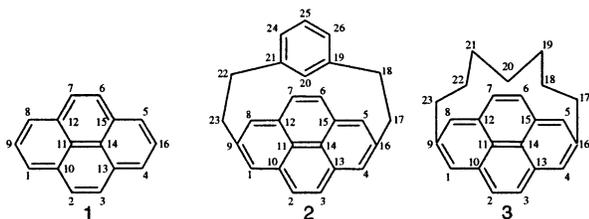
“The Great Escape” from Antiaromaticity: Reduction of Strained Pyrenes

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Antiaromatic systems² can be obtained by the addition of two electrons to π -conjugated cyclic systems, which contain a Hückel³ array of π -electrons. When dealing with polycyclic aromatic hydrocarbons (PAHs), one can refer to the “peripheral model”,⁴ which emphasizes the contribution of the peripheral π -conjugation to the aromatic character of the system and considers the inner bonds as a bridging perturbation to the annulene skeleton. One of the most known systems which behave according to this model is pyrene (**1**), which has $4n + 2$ conjugated π -electrons in its periphery. Accordingly, a two-electron reduction of **1** with alkali metals converts it into an antiaromatic system.⁵ Another aspect concerning the aromaticity of PAHs is their planarity, that is, the effect of curvature on the degree of aromaticity.⁶ Recently, it has been found that enforcing nonplanarity in pyrene, by tethering two remote positions,⁷ does not diminish the magnetic anisotropy effect of the bent system.⁸ This means that the magnetic criterion for aromaticity is still valid in such systems. To assess the effect that nonplanarity might exert on the two-electron reduction of pyrene, two strained pyrene based molecules, the cyclophane [2]metacyclo[2](2,7)pyrenophane (**2**) and [7](2,7)pyrenophane (**3**),^{7c} were reduced with lithium metal.⁹ The reduction process was followed by NMR spectroscopy.



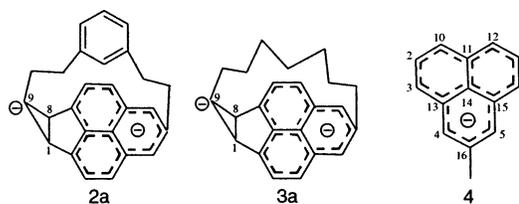
The two-electron reduction of **2** (colorless solution) and **3** (pale yellow) with lithium metal affords ions **2a** (brown) and **3a** (wine-red).¹⁰ The reduction process, monitored by NMR, is accompanied by symmetry changes that are observable in both the ¹H NMR and the ¹³C NMR spectra (Table 1). A closer look into the NMR spectra can give insight on as to what causes the symmetry change. It is evident from the ¹H NMR spectrum of ion **2a** (Table 1) that hydrogen atoms **H3** and **H4** (and their symmetrical equivalent atoms) are shifted to high field and that **H1** is shifted to the aliphatic region.¹¹ The ¹³C NMR spectrum (Table 1) of **2a** exhibits two signals at high field pertaining to the pyrene moiety: $\delta = 33.7$ and 30.1 ppm assigned to **C1** and **C9**, respectively. In addition, it can be seen that the remaining carbons of the pyrene moiety are divided into two sets in which one ($\delta = 101$ –118 ppm) is shifted to a higher field than the other ($\delta = 125$ –147 ppm). Further information concerning the reduction product was obtained from 2D NMR experiments. Proton coupled HSQCSI experiments¹² made it possible to measure the one-bond CH-coupling constant of carbon

atom **C1**, $^1J_{C1,H1} = 162.3$ Hz. A three-bond coupling between **H1** and its symmetrical equivalent **H8**, $^3J_{H1,H8} = 8.7$ Hz, was measured using a carbon editing method.¹² HMBC experiments showed an unexpected long-range coupling between hydrogen atom **H1** and carbon atom **C9**. Similar results were obtained for ion **3a** (Table 1).

There are two possible explanations why carbon atoms **C1** and **C9**, in both **2a** and **3a**, are shifted to a very high field: one is a chemical reaction, which is accompanied by a carbon rehybridization, and the second is the concentration of high charge on these atoms. The $^3J_{H1,H8}$ coupling constant (8.7 Hz for **2a**, 9.1 Hz for **3a**) shows what is happening in the reduction of both **2** and **3**: this coupling is possible only when there is a σ covalent bond, between carbon atom **C1** and its symmetrical equivalent carbon atom **C8**. Such a bond will transform the benzene ring into a “cyclopropano”–“cyclopentano” ring system.¹³ Further evidence for this new bond is the value of $^1J_{C1,H1}$ (162.3 Hz for **2a**, 163.2 Hz for **3a**), which is consistent with a strained sp³-hybridized carbon, as is the case in a cyclopropane ring.¹⁴ In addition, such a bond converts the unexpected correlation seen in the HMBC experiments, between hydrogen atom **H1** and carbon atom **C9**, into a regular three-bond CH-correlation. The new σ -bond can also explain the high field absorption of carbon atom **C1**, which becomes sp³-hybridized, as well as the “aliphatic” hydrogen atom **H1**. Under this scenario, the high field shift of carbon atom **C9** results from the localization of charge on it.¹⁵ This presumption is supported by the fact that no unresolved CH-correlations (neither short-range nor long-range) were found for this carbon atom.

The ¹H NMR and ¹³C NMR spectra also give insight on as to what is happening with the rest of what was the pyrene moiety. It can be seen that in both anions, **2a** and **3a**, carbon atoms **C3**, **C4**, and **C10** (and their symmetrical equivalent atoms, Table 1) are at a higher field than the rest of the carbon atoms, and the same applies for hydrogen atoms **H4** and **H3**. These carbon and hydrogen atoms constitute a section of the periphery of phenalene,¹⁶ and the reason for their high field shift is the delocalization of the extra charge on the periphery of the phenalene moiety. The good agreement between the carbon chemical shifts of the phenalene moiety of **2a** and **3a** and those of the 2-methylphenalenyl anion (**4**)¹⁷ clearly supports the above conclusion (Table 1).¹⁸

It can be seen that the two-electron reduction of the nonplanar systems, **2** and **3**, produces an extraordinary result: a pyrene moiety



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Table 1. ^{13}C NMR and ^1H NMR (in Parentheses) Chemical Shifts, in ppm, of the Pyrene Moiety of **2**, **2a**, **3**, and **3a** in $\text{THF}-d_6^a$

	C1 (H1)	C2 (H2)	C3 (H3)	C4 (H3)	C5 (H5)	C6 (H6)	C7 (H7)	C8 (H8)	C9	C10	C11	C12	C13	C14	C15	C16
2	128.6 (7.5)	126.6 (7.6)	126.6 (7.6)	128.6 (7.5)	130.5 (7.1)	126.9 (6.5)	126.9 (6.5)	130.5 (7.1)	134.7	133.8	131.2	132.2	133.8	131.2	132.2	134.7
2a	33.7 ^b (2.4)	125.6 (6.2)	101.6 (5.1)	108.1 (4.8)	108.1 (4.8)	101.6 (5.1)	125.6 (6.2)	33.7 (2.4)	30.1	118.1	146.9	118.1	145.1	136.5	145.1	140.5
3	130.8 (7.5)	127.2 (7.8)	127.2 (7.8)	130.8 (7.5)	130.8 (7.5)	127.2 (7.8)	127.2 (7.8)	130.8 (7.5)	131.0	132.9	131.5	132.9	132.9	131.5	132.9	131.0
3a	33.9 ^c (2.3)	125.7 (6.2)	101.6 (5.2)	107.9 (5.1)	107.9 (5.1)	101.6 (5.2)	125.7 (6.2)	33.9 (2.3)	29.2	118.5	147.6	118.5	145.8	136.9	145.8	141.6
4^d		128.1	103.1	104.3	104.3	103.1	128.1			103.1	144.7	103.1	144.7	137.6	144.5	135.2

^a The ^{13}C NMR of **4** is also added for comparison. ^b $^1J_{\text{C1,H1}} = 162.3$ Hz, $^3J_{\text{H1,H8}} = 8.7$ Hz. ^c $^1J_{\text{C1,H1}} = 163.2$ Hz, $^3J_{\text{H1,H8}} = 9.1$ Hz. ^d Taken from ref 17.

is converted into a “cyclopropyl” anion fused to a “cyclopenta” ring that is fused to a “phenalenyl” anion.

What is the driving force of this process? The two-electron reduction of **1** with alkali metals produces an antiaromatic species. It seems that in the two-electron reduction of **2** and **3**, which contain a nonplanar pyrene moiety, the system deftly dodges getting into a very unfavorable strained antiaromatic state by undergoing an intramolecular chemical reaction. The new σ -bond formed between carbon atoms **C1** and **C8** has a dual function: on one hand, it releases some of the strain in the pyrene moiety by producing a “cyclopropyl” anion, which because of its geometrical requirements introduces a pronounced fold into what was the pyrene moiety, leaving behind a relatively flat aromatic “phenalenyl” anion.¹⁹ On the other hand, it provides a means for separating the two charges, thus allowing the system to avoid acquiring antiaromatic character. This process can be viewed as the “sacrifice” of a part of the molecule – a benzene ring is converted into a strained “cyclopropyl” anion, for the benefit of the rest of the anion – a flatter system that contains a new aromatic entity – the “phenalenyl” anion.²⁰

The isolated benzene ring in **2** has little or no effect on the overall reduction process; therefore, it can be deduced that the driving force for the whole process might be stemming mainly from the strain in the pyrene system, which is dictated by the length of bridge.^{10b}

While nonplanarity has no drastic effect on the aromatic character of the pyrene moiety in **2** and **3**,⁸ it plays a crucial part in their reduction to dianions: both systems form a new σ -bond as a means to “escape” from strained antiaromaticity.

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Supporting Information Available: 1D and 2D NMR spectra of **2**, **2a**, **3**, and **3a** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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