Antiaromatic systems\textsuperscript{2} can be obtained by the addition of two electrons to π-conjugated cyclic systems, which contain a Hückel\textsuperscript{3} array of π-electrons. When dealing with polycyclic aromatic hydrocarbons (PAHs), one can refer to the “peripheral model”,\textsuperscript{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 4\(n\) \(+\) 2 conjugated π-electrons in its periphery. Accordingly, a two-electron reduction of 1 with alkali metals converts it into an antiaromatic system.\textsuperscript{5} Another aspect concerning the aromaticity of PAHs is their planarity, that is, the effect of curvature on the degree of aromaticity.\textsuperscript{6} Recently, it has been found that enforcing nonplanarity in pyrene, by tethering two remote positions,\textsuperscript{7} does not diminish the magnetic anisotropy effect of the bent system.\textsuperscript{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\text{metacyclo}[2\text{(2,7)pyrenophane} (2) and

\text{[7\text{(2,7)pyrenophane}(3),\textsuperscript{7c} were reduced with lithium metal.\textsuperscript{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).\textsuperscript{10} The reduction process, monitored by NMR, is accompanied by symmetry changes that are observable in both the \(^1\text{H} \text{NMR}\) and \(^{13}\text{C} \text{NMR}\) 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 \(^1\text{H} \text{NMR}\) spectrum of ion 2a (Table 1) that hydrogen atoms C3 and H4 (and their symmetrical equivalent atoms) are shifted to high field and that H1 is shifted to the aliphatic region.\textsuperscript{11} The \(^{13}\text{C} \text{NMR}\) 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 (\(\delta = 101\text{–}118\) ppm) is shifted to a higher field than the other (\(\delta = 125\text{–}147\) ppm). Further information concerning the reduction product was obtained from 2D NMR experiments. Proton coupled HSQCSI experiments\textsuperscript{12} made it possible to measure the one-bond CH-coupling constant of carbon atom C1, \(J_{\text{C1,H1}} = 162.3\) Hz. A three-bond coupling between H1 and its symmetrical equivalent H8, \(J_{\text{H1,H8}} = 8.7\) Hz, was measured using a carbon editing method.\textsuperscript{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 \(J_{\text{H1,H8}}\) 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.\textsuperscript{13} Further evidence for this new bond is the value of \(J_{\text{C1,H1}}\) (162.3 Hz for 2a, 163.2 Hz for 3a), which is consistent with a strained sp\(^3\)-hybridized carbon, as is the case in a cyclopropane ring.\textsuperscript{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 sp\(^3\)-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.\textsuperscript{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 \(^1\text{H} \text{NMR}\) and \(^{13}\text{C} \text{NMR}\) 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,\textsuperscript{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)\textsuperscript{17} clearly supports the above conclusion (Table 1).

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

---

\textsuperscript{1} The Hebrew University of Jerusalem.
\textsuperscript{2} Memorial University of Newfoundland.
is converted into a “cyclopropyl” anion fused to a “phenalenyl” 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 π-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 system, in such tethered systems can have a bend angle (θ) as high as 109.2° depending on the length of the tether: (a) Bodwell, G. J.; Bridson, J. N.; Houghton, T.; Kennedy, J. W. J.; Mannion, M. R. Angew. Chem., Int. Ed. Engl. 1992, 31, 1283. (b) Bodwell, G. J.; Bridson, J. N.; Houghton, T. J.; Kennedy, J. W. J.; Mannion, M. R. Chem.-Eur. J. 1999, 5, 1823. (c) Bodwell, G. J.; Fleming, J. J.; Mannion, M. R.; Miller, D. O. J. Org. Chem. 2000, 65, 5360. (8) The high field shift of the tethers proton shows that the nonplanar pyrene still exerts a strong magnetic anisotropy effect (see ref 7c).

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.106 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 diamons: both systems form a new π-bond as a means to “escape” from strained antiaromaticity.

Acknowledgment. We would like to thank Professors I. Agranat, K. Müllen, and L. T. Scott for fruitful discussions. We are grateful to the United States-Israel Binational Science Foundation (BSF) (M.R.) and the Natural Sciences and Engineering Research Council (NSERC) of Canada (G.J.B.) for financial support.

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.

References

(1) In partial fulfillment of the Ph.D. thesis of L.A.
(3) Hückel, E. Z. Phys. 1931, 70, 204.
(8) The high field shift of the tethers proton shows that the nonplanar pyrene still exerts a strong magnetic anisotropy effect (see ref 7c).
(11) The spectra were assigned using a combination of 2D NMR methods. The 13C NMR spectra of 2a and 3a exhibit an absorption at δ = 0 ppm.
(15) Such a localization of charge has been observed in similar systems. For example: ref 13a.
(18) The discrepancy between the chemical shift for carbon atoms C10 and C12 in 4, and those of 2a and 3a, is due to the absence of substituents in 4.
(20) Separate attempts at quenching the dianion, 2a, were made with iodine and dimethyl sulfate, and in both cases the product readily underwent polymerization.

JA0291991