DOI: 10.1002/asia.200600174

Anions and Polyanions of Oligoindenopyrenes: Modes of Electron Delocalization and Dimerization

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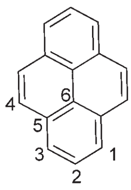
Abstract: A series of pyrene-based polycyclic aromatic compounds, indeno[*cd*]pyrene, diindeno[*cd,fg*]pyrene, diindeno[*cd,jk*]pyrene, tris-(*tert*-butylindeno[*cd,fg,jk*])pyrene, and tetrakis-(*tert*-butylindeno[*cd,fg,jk,mn*])pyrene, were reduced with alkali metals in [D_8]tetrahydrofuran, and the resulting anions were studied by NMR spectroscopy. It was found that the diatropic character of the dianions obtained depends on the number of annulated indeno groups. When one such group is present, a paratropic dianion is obtained, which is similar to the dianion of the parent pyrene; the effect, however, is weak. When more indeno groups are annulated, the dianions become diatropic owing to the greater number of five-membered rings that can acquire aromatic character as a result of reduction. The ^{1}H NMR chemical shifts of tetrakis-(*tert*-butylindeno[*cd,fg,jk,mn*])pyrene in the neutral state show an interesting dependence on concentration that reflects an association of the molecules in solution by π stacking. This phenomenon was not observed for the reduced species. The trianion radicals of tris-(*tert*-butylindeno[*cd,fg,jk*])pyrene and tetrakis-(*tert*-butylindeno[*cd,fg,jk,mn*])pyrene undergo reductive dimerization and form bilayered hexaanions.

Keywords: aromaticity · carbanions · polyanions · pyrene · reduction

Introduction

The correlation in monocyclic annulenes between aromatic character[1] and the total number of π electrons (the Hückel $4n+2$ rule)[2] does not necessarily hold for polycyclic π systems.[3] One of the best-known systems that shows this lack of compliance is pyrene (**1**), which contains $4n$ π electrons, but is nevertheless aromatic. The aromatic character of polycyclic π systems is most-simply explained by the "conjugated circuits model",[4] which weighs the contributions of all cycles of conjugation, including the peripheral π conjugation; the inner bond of pyrene is thus treated as a bridging perturbation to the annulene skeleton.



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The addition of two electrons to π-conjugated monocyclic systems that contain a Hückel $(4n+2)$ number of π electrons converts them into antiaromatic systems.[5] Likewise, the two-electron reduction of **1**[6] with alkali metals[7] affords an antiaromatic system ($\mathbf{1}^{2-}$).[8] However, the number of electrons is not the only parameter that determines the aromaticity of **1**. Recently, it was shown that the two-electron reduction of bent pyrenes does not necessarily yield antiaromatic compounds.[9]

Annulation of five-membered rings (5MRs)[10] to **1** can also alter its aromatic character. The aromaticity of **1** was found to decrease with an increase in the number of 5MRs.[10] When polycyclic aromatic hydrocarbons (PAHs) that contain 5MRs are reduced, however, the added charge concentrates mainly in the 5MRs, thus rendering them aromatic.[7] Fullerenes,[11] buckybowls,[12] and planar PAHs[13] all behave in this manner; the aromatic character and features

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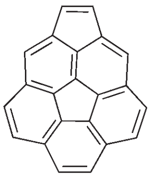
of their negatively charged species rely greatly on the number of 5MRs in the system.

The annulated groups can also affect the reactivity of the hydrocarbon. The *peri*-annulation on corannulene, the smallest curved subunit of C_{60}, with a 5MR as in **2** or an indeno group as in **3** leads to a drastic change in behavior and reduction outcome compared with the parent hydrocarbon.[12a] The presence of a dibenzofulvene subunit in **3** enables it to undergo a multistep reduction–dimerization process, which is not observed for **2**. On the other hand, the tetraanion of **2** yields a coordinative dimer with lithium cations, whereas **3** is not reduced to a tetraanion with lithium.[12c]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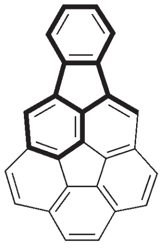
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Herein we report the NMR spectroscopic characterization of anions and polyanions that result from reduction with lithium and potassium metal of a series of pyrene-based compounds that are annulated with different numbers of indeno groups: indeno[*cd*]pyrene (**4**),[14] diindeno[*cd*,*fg*]pyrene (**5**),[15] diindeno[*cd*,*jk*]pyrene (**6**),[15] tris-(*tert*-butylindeno[*cd*,*fg*,*jk*])pyrene (**7**),[15] and tetrakis-(*tert*-butylindeno[*cd*,*fg*,*jk*,*mn*])pyrene (**8**).[15] This study concentrates on the effect the indeno subunits and their number have on the reactivity and aromatic character of the anions obtained.

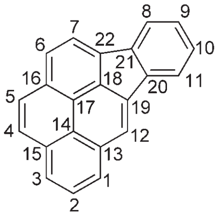
Abstract in Armenian:

Մի շարք պիրենային պոլիցիկլիկ առոմատիկ միածություններ ինդենո[*cd*]պիրեն, երկ[*cd,fg*]ինդենոպիրեն, երկ[*cd,jk*]ինդենոպիրեն, թրիս-(*tert*-բութիլինդենո[*cd,fg,jk*])պիրեն եւ թեթրաքիս-(*tert*-բութիլինդենո[*cd,fg,jk,mn*])պիրեն վերականգնվել են ալկալական մետաղներով [D_8]-թեթրահիդրոֆուրանում, իսկ առաջածած անիոնները ուսումնասիրվել են ՄՄՌ սպեկտրոսկոպիկ մեթոդով: Ցույց է տրվել, որ ստացված երկանիանիոնների առոմատիկ բնույթը կախված է անիլացված ինդենո խմբերի քանակից: Այդպիսի մեկ խմբի առկայությամբ առաջացող ոչառոմատիկ երկանիոնը նույնատիպ է արմատական պիրենի հետ, սակայն ավելի թույլ է: Մի քանի ինդենո խմբերի անիլացման դեպքում երկանիոնը դառնում է առոմատիկ, շնորհիվ վերականգման պրոցեսի, որը բերում է հինգ-անդամանի օղակների քանակի ավելացման: Թեթրակիս-(*tert*-բութիլինդենո[*cd,fg,jk*])պիրենում ^{1}H-ՄՄՌ քիմիական շեղումը դեպի չեզոք գոտի ցույց է տալիս հետաքրքիր կախվածություն կոնցենտրացիայից, որը պայմանավորված է π-կապակցմամբ: Այս երեւույթը չի դիտվել վերականգնված տեսակների դեպքում: Թրիս-(*tert*-բութիլինդենո[*cd,fg,jk*])պիրենի եւ թեթրակիս(*tert*-բութիլինդենո[*cd, fg, jk, mn*])պիրենի եռանիոն ռադիկալները ենթարկվում են վերականգնողական դիմերիզացման՝ առաջացնելով երկշերտանի հեքսանիոն:

Results and Discussion

Indeno[*cd*]pyrene (4)

The ^{1}H NMR spectrum of **4**[6] (22 π electrons in total) shows signals that are shifted to low field,[16] which is indicative of the aromaticity of the system.



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Reduction of **4** with lithium and potassium metals yields similar dianions (**4**$^{2-}$). The first reduction step affords a paramagnetic species (radical anion) that cannot be observed by ^{1}H NMR spectroscopy. The second charged species, **4**$^{2-}$, is diamagnetic, and therefore its ^{1}H and ^{13}C NMR chemical shifts could be measured. The proton chemical shifts of **4**$^{2-}$ range from 7.1 to 3.2 ppm, which shows that the system is strongly affected by anisotropy. The signals of the indeno subunit remain at relatively low field, whereas the signals of the pyrene subunit are shifted to very high field. The system has indeed acquired paratropic character as a result of reduction; however, its effect is more pronounced on the pyrene subunit. A comparison between the ^{1}H NMR chemical shifts of **1**$^{2-}$/2Li^{+} ($\delta = 0.02$, 2.20, and 0.93 ppm for 1-H, 2-H, and 4-H, respectively)[8] with those of **4**$^{2-}$ (Table 1) shows that annulation with an indeno subunit significantly reduced the overall paratropicity of the system. This is evident from the lower-field chemical shifts of the protons of the pyrene subunit of **4**$^{2-}$ relative to those of **1**$^{2-}$ (Table 1). The same effect is also observed for the chemical shifts of the internal carbon atoms C17 and C14. Although negative charge is added, the signals of these carbon atoms are actually shifted to lower field. Thus, these carbon atoms function as internal probes for the paratropic ring current found in the system. A comparison of the change in the chemical shifts of these carbon atoms from the neutral to the dianion state ($\Delta\delta = 18.22$ and 13.81 ppm for C17 and C14, respectively) shows that the difference is smaller than that encountered in **1**$^{2-}$ ($\Delta\delta =$ 33.70 ppm for C6).[8]

The K_C[17] values calculated for **4**$^{2-}$ (see Experimental Section, Equation (1)) show that the carbon atoms are also affected by anisotropy ($K_C = 108.4$ and 104.2 ppm per electron for **4**$^{2-}$/2Li^{+} and **4**$^{2-}$/2K^{+}, respectively).[18] This also means that an accurate estimate of the charge distribution from the ^{13}C NMR spectrum is not possible for **4**$^{2-}$. However, it is evident that C3 and C12 carry large charge densities as their signals are shifted to relatively high fields (i.e., $\delta = 93.45$ and 86.10 ppm for C3 and C12, respectively, in **4**$^{2-}$/2Li^{+}).

Further reduction of **4**$^{2-}$ with either lithium or potassium was not possible.

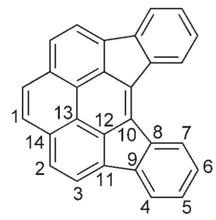
Diindeno[*cd*,*fg*]pyrene (5)

Diindeno[*cd*,*fg*]pyrene (**5**)[6] contains 28 π electrons in the neutral state; however, the proton chemical shifts of **5** clearly show that it is not antiaromatic but rather aromatic.

Table 1. A comparison between the ^{1}H NMR chemical shifts (in ppm) of the dianions of **1** and **4**.

	1-H	2-H	3-H	4-H	5-H	6-H	7-H	8-H	9-H	10-H	11-H	12-H
$\mathbf{1}^{2-}$/2Li$^+$	0.02[a]	2.20[a]	–	0.93[a]	–	–	–	–	–	–	–	–
$\mathbf{4}^{2-}$/2Li$^+$	3.60	4.56	3.28	4.41	4.98	4.57	5.77	7.04	6.17	6.12	6.92	4.09
$\mathbf{4}^{2-}$/2K$^+$	3.57	4.53	3.19	4.38	4.96	4.55	5.72	7.06	6.24	6.18	6.91	4.12

[a] Taken from reference [8].



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The reduction of **5** with lithium or potassium yields similar dianions ($\mathbf{5}^{2-}$). It is evident from the ^{1}H NMR chemical shifts ($\delta = 8.88$–6.52 ppm) that $\mathbf{5}^{2-}$ is aromatic. The K_C values calculated for $\mathbf{5}^{2-}$ ($K_C = 169.4$ and 168.1 ppm per electron for $\mathbf{5}^{2-}$/2Li$^+$ and $\mathbf{5}^{2-}$/2K$^+$, respectively) show that there is no significant anisotropy effect on the carbon atoms. The charge distribution of $\mathbf{5}^{2-}$ estimated from the ^{13}C NMR spectrum shows that most of the charge is concentrated in the 5MRs (Figure 1), as these rings function as electron-accepting groups.[13]

Further treatment with either lithium or potassium did not yield any other reduced species.

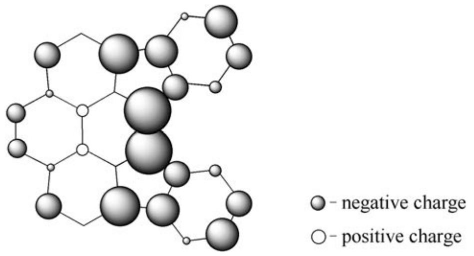
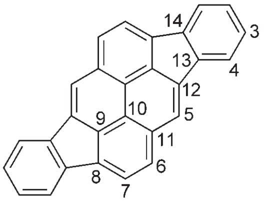


Figure 1. The charge distribution calculated for $\mathbf{5}^{2-}$/2K$^+$ according to the ^{13}C NMR spectrum (a similar charge distribution was obtained for $\mathbf{5}^{2-}$/2Li$^+$).

Diindeno[*cd,jk*]pyrene (6)

Diindeno[*cd,jk*]pyrene (**6**),[6] an isomer of **5**, is also aromatic. The reduction of **6** with lithium or potassium yields their respective dianions ($\mathbf{6}^{2-}$/2Li$^+$ and $\mathbf{6}^{2-}$/2K$^+$). The solubility of $\mathbf{6}^{2-}$ depends on the alkali-metal counterion; $\mathbf{6}^{2-}$/2Li$^+$ is hardly soluble in [D$_8$]THF, therefore only its ^{1}H NMR spectrum was measured,[19] whereas $\mathbf{6}^{2-}$/2K$^+$ is soluble, so both the ^{1}H and ^{13}C NMR spectra were recorded.



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The ^{1}H NMR spectra of $\mathbf{6}^{2-}$/2Li$^+$ and $\mathbf{6}^{2-}$/2K$^+$ are similar and show that the dianion is also aromatic. The only signal that is shifted to relatively high field ($\delta = 6.12$ and 6.14 ppm for $\mathbf{6}^{2-}$/2Li$^+$ and $\mathbf{6}^{2-}$/2K$^+$, respectively) is that of proton 6-H. This must be due to charge concentration on C6.

A K_C value of 140.8 ppm per electron was calculated for $\mathbf{6}^{2-}$/2K$^+$ from the ^{13}C NMR spectrum, which indicates that the carbon atoms are not significantly affected by anisotropy. The charge is mostly concentrated in the 5MRs and on the periphery of the molecule (Figure 2).

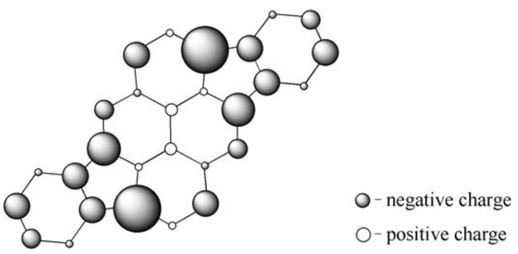
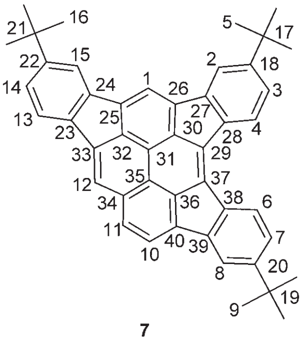


Figure 2. The charge distribution calculated for $\mathbf{6}^{2-}$/2K$^+$ according to the ^{13}C NMR spectrum.

Dianion $\mathbf{6}^{2-}$ could not be reduced further with either lithium or potassium.

Tris-(*tert*-butylindeno[*cd,fg,jk*])pyrene (7)

The ^{1}H NMR spectrum of **7**[6] shows that the compound is aromatic in its neutral state. When **7** is reduced with lithium



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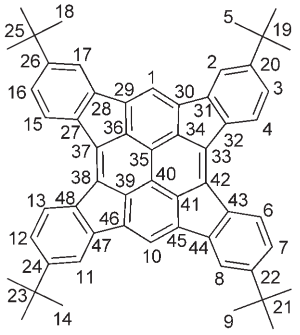
metal, only a radical anion is produced, and further reduction is not possible. The reduction with potassium, however, follows a totally different path, as a diamagnetic dianion ($\mathbf{7}^{2-}$/2K$^+$) is observed after the radical anion stage has been passed.

It is evident from the low-field shift of the signals of the protons of the pyrene moiety ($\delta_{avg}=7.79$ ppm) that $7^{2-}/2K^{+}$ is aromatic. The K_C value of $7^{2-}/2K^{+}$ (174.3 ppm per electron) shows that the carbon atoms are not affected by anisotropy effects; however, the charge distribution cannot be calculated, as a full assignment of the ^{13}C NMR spectrum of **7** was not possible owing to the low symmetry of the molecule and nonresolved peaks.

Further reduction of $7^{2-}/2K^{+}$ yields another diamagnetic species. This new species is the product of a coupling (see below) that takes place between two trianion radicals of **7** at C1 ($((7–7)^{6-}/6K^{+})$).[9b,c,20] The signal of this carbon atom is shifted to high field ($\delta=48.16$ ppm) and shows a $^{1}J_{C,H}$ coupling constant of 131.54 Hz, which is diagnostic for an sp^3-hybridized carbon atom. These results confirm that a reaction occurred at C1; however, the low symmetry of $(7–7)^{6-}/6K^{+}$ prevents full assignment of the ^1H and ^{13}C NMR spectra, and therefore its characterization as a dimer rests, in part, on the findings of the reduction of **8** (see below).

Tetrakis-(*tert*-butylindeno[*cd,fg,jk,mn*])pyrene (8)

According to calculations, **8**[6] deviates from planarity and is slightly bowl-shaped.[15] The ^1H NMR spectrum shows that the compound is aromatic in its neutral state.



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A special feature of the ^1H NMR spectrum of **8** is its dependence on concentration. ^1H NMR spectra of **8** in $[D_8]$THF were recorded over a range of concentrations, and it was found that the aromatic signals shift progressively downfield as the concentration decreases.[21,22] A decrease in concentration from 4.2×10^{-3} to 8.2×10^{-6} M at constant temperature (298 K) results in a downfield shift by 0.65 ppm of the signals of 1-H (Figure 3).[23,24] Such concentration dependence is commonly observed in the aggregation of disk-shaped aromatic systems (Figure 4).[25] In a face-to-face aggregate, the protons of one molecule are exposed to the ring currents of another, which results in shielding with a magnitude that depends on the number of molecules in the aggregate (Figure 4). The size of the aggregates in solution decreases at lower concentrations and results in a deshielding effect in the NMR spectra. Dilution of the solution to 4.1×10^{-6} M yields the lowest observable shift for 1-H ($\delta=8.17(5)$ ppm), as the spectroscopic characterization of more-dilute solutions is limited by the sensitivity of the NMR spectrometer. The difference in chemical shift on going from 8.2×10^{-6} to 4.1×10^{-6} M is very small ($\Delta\delta=0.001$ ppm), which means that the chemical shifts at the latter concentration are very close to those of the monomer.

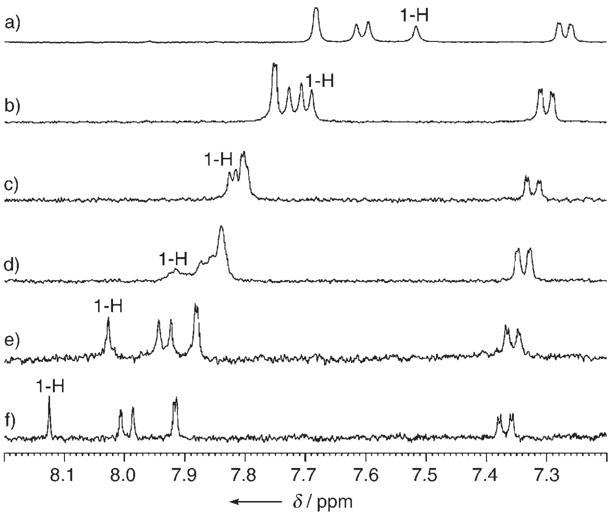

Figure 3. Concentration-dependent ^1H NMR spectra of **8** recorded at 298 K. a) 2.1×10^{-3} M; b) 1.0×10^{-3} M; c) 5.3×10^{-4} M; d) 2.6×10^{-4} M; e) 1.3×10^{-4} M; f) 3.3×10^{-5} M.

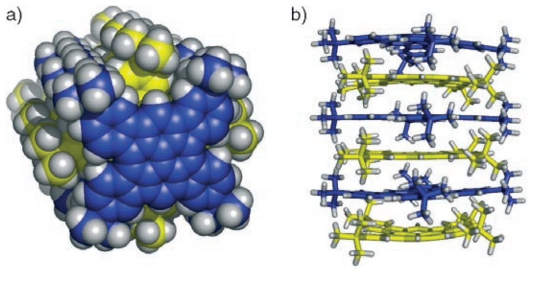

Figure 4. Graphical rendition of a possible stacking configuration of **8**. a) Top view and b) partial side view of the aggregate (the layers are drawn in different colors for clarity).

The growing general interest in π stacking of π conjugated systems as models for electron-conducting materials in organic electronic or optoelectronic devices[26] makes the electronic structure and reduction of **8** especially interesting. With lithium metal, the reduction of **8** affords a radical anion that could not be further reduced, even after prolonged contact with the metal.

The reduction with potassium takes a different path, and a diamagnetic dianion ($8^{2-}/2K^{+}$) is observed after the radical anion stage has been passed. The ^1H NMR chemical shifts of $8^{2-}/2K^{+}$ do not depend on temperature or concentration, which indicates that no π stacking occurs in this reduced state.

It is evident from the low-field shift of the signal of 1-H ($\delta=9.09$ ppm) that $8^{2-}/2K^{+}$ is aromatic in character.[27] The K_C value of $8^{2-}/2K^{+}$ (179.7 ppm per electron) shows that the carbon atoms are not affected by anisotropy effects, so their chemical shifts can be used to assess the charge distribution on the carbon skeleton (Figure 5). Such an analysis reveals that most of the charge is concentrated on the carbon atoms shared by the 5MRs and the pyrene core. Interestingly, the charge distribution around the pyrene subunit is very similar to that observed in $\mathbf{1}^{2-}$,[8a] that is, a node through the center and high charge concentration on C30 and C33 (and their symmetrical equivalents) in $\mathbf{8}^{2-}/2K^+$ and C1 and C4 in $\mathbf{1}^{2-}$. Unlike $\mathbf{1}^{2-}$, however, $\mathbf{8}^{2-}/2K^+$ is not paratropic, because the contribution of the pyrene 4*n* π-electron perimeter is drastically dampened by fusion to aromatic indenyl anions.

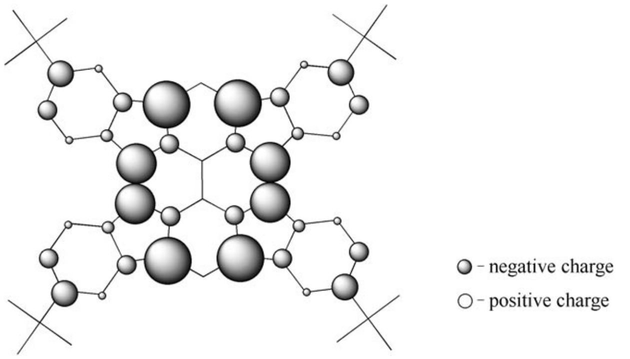

Figure 5. Charge distribution calculated for $\mathbf{8}^{2-}/2K^+$ according to the ^{13}C NMR spectrum.

Further reduction of $\mathbf{8}^{2-}/2K^+$ yields another diamagnetic species, the concentration of which grows as $\mathbf{8}^{2-}/2K^+$ disappears. This new species is the product of a coupling that takes place between two trianion radicals of **8** at C1 ($(\mathbf{8}\text{–}\mathbf{8})^{6-}/6K^+$; Figure 6).[20] Calculations (B3LYP/6-31G*) predict a high spin density at this carbon atom in the trianion radical, which explains why the reductive dimerization process occurs at this site.

The ^{13}C NMR chemical shift of C1 ($\delta = 49.60$ ppm) and its $^{1}J_{C1,1\text{-}H}$ coupling constant (127.24 Hz) provide strong evidence for its sp^3 hybridization. Incontrovertible proof for the formation of the new σ bond comes from heteronuclear multiple-bond correlation (HMBC) measurements, which show a $^{2}J_{C1,1\text{-}H}$ coupling. This coupling is possible only if C1 is connected to a symmetry-related *C1 atom through a σ bond.

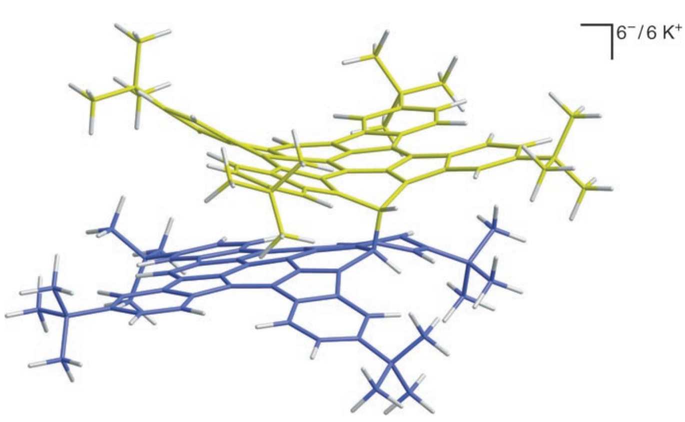

Figure 6. Schematic structure of the anionic dimer $(\mathbf{8}\text{–}\mathbf{8})^{6-}/6K^+$ (different colors are used for each part of the dimer for clarity).

The formation of such σ bonds is usually corroborated by the $^{3}J_{1\text{-H},*1\text{-H}}$ coupling that they yield in a proton-coupled heteronuclear single-quantum correlation with improved sensitivity (HSQCSI) experiment.[20] In this case, however, the coupling was not observed. The magnitude of this coupling depends on the dihedral angle between 1-H and *1-H. If this angle falls between 60 and 120 degrees, the coupling will be too be small to be observed in the NMR spectrum.[28] Therefore, the lack of $^{3}J_{1\text{-H},*1\text{-H}}$ coupling in this case gives an indication of the dihedral angle between 1-H and *1-H.

The ^{1}H NMR spectrum shows that the $(\mathbf{8}\text{–}\mathbf{8})^{6-}/6K^+$ dimer must have overall C_2 symmetry, as each tetraindenopyrene unit in the system yields a different signal for every proton, but the signals for one tetraindenopyrene unit are the same as those for the other unit. The signal of 1-H appears at $\delta =$ 7.07 ppm, which is very low field for a proton residing on an sp^3-hybridized carbon atom. This low-field shift may result from the position of the proton between two structural “bays” and an interaction with the second anionic layer.

Further evidence for the formation of the covalent dimer, $(\mathbf{8}\text{–}\mathbf{8})^{6-}/6K^+$, comes from NOESY studies. The NOESY spectrum shows unexpected interactions between the *tert*-butyl (5-H with 18-H and 9-H with 14-H) and aromatic signals (2-H with 17-H and 8-H with 11-H). These interactions are possible as $(\mathbf{8}\text{–}\mathbf{8})^{6-}/6K^+$ contains two closely packed anionic layers.

Further reduction of $(\mathbf{8}\text{–}\mathbf{8})^{6-}/6K^+$ leads to line-broadening, and eventually a new ^{1}H NMR spectrum emerges. The new spectrum contains multiple lines of weak intensity so that assignment could not be made. Therefore, this new species, which is most probably a tetraanion of **8**, could not be studied in more detail.

Overview of the Family

The ^{1}H NMR spectra of $\mathbf{4}^{2-}$, $\mathbf{5}^{2-}$, $\mathbf{6}^{2-}$, $\mathbf{7}^{2-}$, and $\mathbf{8}^{2-}$ clearly show that the aromatic character of the dianion is influenced by the number of annulated indeno groups. Annulation of a single indeno group, as in $\mathbf{4}^{2-}$, decreases the paratropicity of the system relative to $\mathbf{1}^{2-}$. This is evident in the ^{1}H NMR spectrum and the chemical shifts of the internal carbon atoms. The decreased paratropicity results from the extension of the π system and the concentration of charge in the 5MRs (see below). The annulation of two indeno groups on pyrene, as in **5** and **6**, changes the characteristics of the dianion totally. Instead of being paratropic, the dianions are diatropic.

The low-field shift of the signals of C13 in $\mathbf{5}^{2-}$ and C10 in $\mathbf{6}^{2-}$ results from their being external probes for the diatropic ring current of the 5MR. Atom C17 in $\mathbf{4}^{2-}$ is also an external probe for the 5MR, and therefore some of the low-field shift can result from the newly gained aromaticity of this ring. Such ring-current effects could explain why the signal of this internal carbon atom is shifted downfield with respect to that of its counterpart, C14.

Compounds **7** and **8** show high dependence on the alkali-metal counterion. Reduction with lithium gives only a radical anion; however, potassium reduces the compounds at least to a trianion radical. It is well-established that alkali-metal reduction of such large systems depends on the ability of the counterion to stabilize the anion formed.[7] Potassium, which forms a softer cation than lithium and also has a higher reduction potential, is able to reduce **7** and **8** even beyond the dianion stage, which is unusual for this series.

Experimental Section

1D and 2D NMR spectra were recorded on a Bruker DRX-400 pulsed FT spectrometer operating at 400.13, 100.62, and 155.51 MHz for ^{1}H, ^{13}C, and ^{7}Li, respectively. Experiments were conducted at the temperature which gave the best ^{1}H NMR spectrum. The temperature was calibrated with methanol.[29] ^{1}H and ^{13}C NMR chemical shifts were measured relative to the most-downfield peak of [D$_8$]THF (3.57 and 67.39 ppm, respectively, relative to SiMe$_4$). The ^{7}Li NMR spectrum was referenced to the frequency of the ^{1}H signal of dilute SiMe$_4$ in [D$_8$]THF (inferred from the ^{1}H solvent frequency) multiplied by the Ξ/100 value of 0.38863797 from IUPAC.[30] Calculations on tetraindenopyrene were performed at the B3LYP/6-31G* level of theory[31] with Spartan 02 (Linux version) from Wavefunction, Inc., Irvine (USA).

Reduction of the Samples

All the samples were reduced in 5-mm-diameter NMR glass tubes equipped with an upper reduction chamber. The pyrene derivatives (3 mg) were introduced into the lower chamber of the tube under an argon atmosphere. The alkali metal (kept in paraffin oil, cleansed from the oxidized layer, and rinsed in petroleum ether at 40–60 °C) was introduced under argon into the reduction chamber as lithium wire or a piece of potassium. The tube was then placed under high vacuum and dried by flame. In the case of potassium, the metal was sublimed several times, creating a potassium mirror within the reduction chamber. Anhydrous [D$_8$]THF ($\approx$1 mL, dried over a sodium/potassium alloy under high vacuum) was transferred under vacuum to the NMR tube and degassed several times. Finally, the tube was flame-sealed under high vacuum.

Controlled Reduction Process

The reduction took place when the solution of [D$_8$]THF was brought into contact with the metal by inverting the sample in solid dry ice. Reduction was stopped by returning the sample to the upright position, thus separating the metal from the solution. The formation of the anions was detected visually by changes in the color of the solutions and by ^{1}H NMR spectroscopy.

Charge-Distribution Calculations

The addition of negative charge to polycyclic π systems induces magnetic shielding on the nuclei; therefore, NMR spectroscopy can be used to analyze the charge distribution. The charge density on the carbon π framework was calculated by using the differences in chemical shift in the ^{13}C NMR spectra of the anion and neutral species [Eq. (1)]:[17]

$$\rho_\pi = \Delta\delta_C / K_C \qquad (1)$$

where ρ_π is the change in the π charge on the carbon atom, $\Delta\delta_C$ is the change in chemical shift for that carbon atom from the anionic to the neutral state, and K_C is a calculated proportionality constant (calculated as the sum of the differences in the chemical shifts divided by the total charge of the anion) with a value of about 160.0 ppm per electron. However, ring-current effects can induce large deviations from this value.[32]

NMR Data

4: ^{1}H NMR (400 MHz, [D$_8$]THF, 298 K): $\delta=8.70$ (s, 1H, 12-H), 8.46 (d, $J=7.64$ Hz, 1H, 1-H), 8.42 (d, $J=7.76$ Hz, 1H, 7-H), 8.29 (d, $J=7.69$ Hz, 1H, 3-H), 8.26 (d, $J=7.76$ Hz, 1H, 6-H), 8.17 (d, $J=6.64$ Hz, 1H, 11-H), 8.16 (d, $J=8.99$ Hz, 1H, 5-H), 8.10 (d, $J=9.03$ Hz, 1H, 4-H), 8.07 (d, $J=7.18$ Hz, 1H, 8-H), 8.06 (dd, $J=7.60$, 7.67 Hz, 1H, 2-H), 7.45 (dd, $J=7.48$, 7.04 Hz, 1H, 9-H), 7.40 ppm (dd, $J=7.56$, 7.41 Hz, 1H, 10-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 298 K): $\delta=142.9$ (C21), 140.0 (C20), 136.7 (C19), 134.1 (C22), 133.2 (C13), 131.7 (C16), 131.6 (C15), 131.5 (C18), 129.5 (C1), 129.1 (C9), 128.0 (C4), 127.7 (C3), 127.1 (C10), 127.5 (C5 and C2), 125.8 (C6), 124.1 (C15), 123.4 (C11), 122.6 (C17), 122.4 (C12), 122.4 (C8), 120.5 ppm (C7).

4^{2-}/2Li^{+}: ^{1}H NMR (400 MHz, [D$_8$]THF, 220 K): $\delta=7.04$ (d, $J=7.81$ Hz, 1H, 8-H), 6.92 (d, $J=7.79$ Hz, 1H, 11-H), 6.17 (dd, $J=7.24$, 6.47 Hz, 1H, 9-H), 6.12 (dd, $J=6.84$, 6.82 Hz, 1H, 10-H), 5.77 (d, $J=8.60$ Hz, 1H, 7-H), 4.98 (d, $J=7.95$ Hz, 1H, 5-H), 4.57 (d, $J=8.67$ Hz, 1H, 6-H), 4.56 (dd, $J=7.56$, 7.44 Hz, 1H, 2-H), 4.41 (d, $J=7.93$ Hz, 1H, 4-H), 4.09 (s, 1H, 12-H), 3.60 (d, $J=8.14$ Hz, 1H, 1-H), 3.28 ppm (d, $J=7.02$ Hz, 1H, 3-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 220 K): $\delta=146.4$ (C15), 145.5 (C13), 140.8 (C17), 138.9 (C14), 137.8 (C18), 135.5 (C2), 122.1 (C16), 120.9 (C5), 120.5 (C7), 113.3 (C21), 117.5 (C11), 116.8 (C8), 116.7 (C20), 113.9 (C6), 113.6 (C19), 110.2 (C22), 110.2 (C4), 109.2 (C9), 108.1 (C10), 102.8 (C1), 93.5 (C3), 86.1 ppm (C12); ^{7}Li NMR (155 MHz, [D$_8$]THF, 200 K): $\delta=-0.4$ ppm.

4^{2-}/2K^{+}: ^{1}H NMR (400 MHz, [D$_8$]THF, 220 K): $\delta=7.06$ (d, $J=7.95$ Hz, 1H, 8-H), 6.91 (d, $J=7.89$ Hz, 1H, 11-H), 6.24 (dd, $J=6.99$, 6.56 Hz, 1H, 9-H), 6.18 (dd, $J=6.92$, 6.58 Hz, 1H, 10-H), 5.72 (d, $J=6.70$ Hz, 1H, 7-H), 4.96 (d, $J=8.00$ Hz, 1H, 5-H), 4.55 (d, $J=8.85$ Hz, 1H, 6-H), 4.53 (dd, $J=9.55$, 7.56 Hz, 1H, 2-H), 4.38 (d, $J=8.00$ Hz, 1H, 4-H), 4.12 (s, 1H, 12-H), 3.57 (d, $J=8.07$ Hz, 1H, 1-H), 3.19 ppm (d, $J=7.05$ Hz, 1H, 3-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 220 K): $\delta=146.9$ (C15), 145.2 (C13), 140.9 (C17), 137.9 (C14), 136.8 (C18), 133.5 (C2), 122.0 (C5 and C16), 120.6 (C7), 118.2 (C11), 118.0 (C21), 117.3 (C8), 115.5 (C19), 115.5 (C20), 115.3 (C6), 111.2 (C4), 110.7 (C9), 109.5 (C22), 109.2 (C10), 103.1 (C1), 93.7 (C3), 88.6 ppm (C12).

5: ^{1}H NMR (400 MHz, [D$_8$]THF, 273 K): $\delta=8.44$ (m, 1H, 7-H), 8.28 (d, $J=7.72$ Hz, 1H, 3-H), 8.15 (d, $J=7.76$ Hz, 1H, 2-H), 7.99 (m, 1H, 4-H), 7.93 (s, 1H, 1-H), 7.45 (m, 1H, 6-H), 7.43 ppm (m, 1H, 5-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 273 K): $\delta=144.2$ (C9), 140.0 (C8), 137.4 (C11), 134.2 (C10), 134.1 (C12), 131.1 (C14), 130.0 (C5), 128.7 (C6), 127.7 (C2), 127.6 (C1), 127.6 (C7), 123.1 (C4), 122.1 (C13), 121.1 ppm (C3).

5^{2-}/2Li^{+}: ^{1}H NMR (400 MHz, [D$_8$]THF, 200 K): $\delta=8.85$ (d, $J=7.88$ Hz, 1H, 7-H), 8.04 (d, $J=7.69$ Hz, 1H, 4-H), 7.51 (d, $J=8.25$ Hz, 1H, 3-H), 6.95 (dd, $J=6.90$, 5.40 Hz, 1H, 6-H), 6.90 (s, 1H, 1-H), 6.73 (dd, $J=7.05$, 6.93 Hz, 1H, 5-H), 6.31 ppm (d, $J=8.25$ Hz, 1H, 2-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 200 K): $\delta=134.2$ (C12), 129.3 (C13), 127.1 (C14), 124.7 (C8), 122.4 (C9), 121.7 (C3), 120.9 (C7), 117.7 (C4), 114.8 (C1), 112.6 (C6), 112.0 (C11), 109.3 (C5), 108.9 (C2), 108.6 ppm (C10); ^{7}Li NMR (155 MHz, [D$_8$]THF, 200 K): $\delta=-1.5$ ppm.

5^{2-}/2K^{+}: ^{1}H NMR (400 MHz, [D$_8$]THF, 180 K): $\delta=8.88$ (d, $J=8.18$ Hz, 1H, 7-H), 8.14 (d, $J=7.65$ Hz, 1H, 4-H), 7.63 (d, $J=8.24$ Hz, 1H, 3-H), 7.09 (s and t, $J=6.80$ Hz, 2H, 1-H and 6-H), 6.85 (t, $J=6.84$ Hz, 1H, 5-H), 6.51 ppm (d, $J=8.24$ Hz, 1H, 2-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 200 K): $\delta=133.0$ (C12), 128.5 (C13), 127.2 (C14), 123.3 (C8), 122.1 (C9 and C3), 120.4 (C7), 118.7 (C4), 116.7 (C1), 114.5 (C6), 111.9 (C11), 110.9 (C2), 110.8 (C5), 105.6 ppm (C10).

6: ^{1}H NMR (400 MHz, [D$_5$]nitrobenzene, 420 K): $\delta=8.26$ (s, 1H, 5-H), 8.24 (d, $J=7.84$ Hz, 1H, 6-H), 8.14 (d, $J=7.84$ Hz, 1H, 7-H), 7.93 (m, 1H, 4-H), 7.84 (m, 1H, 1-H), 7.34 ppm (m, 2H, 2-H and 3-H); ^{13}C NMR (100 MHz, [D$_5$]nitrobenzene, 420 K): $\delta=141.6$ (C14), 140.2 (C13), 136.4 (C12), 135.1 (C8), 131.4 (C11), 131.2 (C9), 127.9 (C6), 127.7 (C2), 126.9 (C3), 121.8 (C4), 121.3 (C1), 120.9 (C10), 119.5 (C5), 119.2 ppm (C7).

6^{2-}/2Li^{+}: ^{1}H NMR (400 MHz, [D$_8$]THF, 220 K): $\delta=8.07$ (d, $J=7.70$ Hz, 1H, 4-H), 7.82 (d, $J=7.76$ Hz, 1H, 1-H), 7.22 (s, 1H, 5-H), 7.05 (d, $J=8.64$ Hz, 1H, 7-H), 6.91 (dd, $J=7.36$, 6.99 Hz, 1H, 2-H), 6.73 (dd, $J=7.14$, 6.77 Hz, 1H, 3-H), 6.12 ppm (d, $J=8.30$ Hz, 1H, 6-H); ^{13}C NMR (100 MHz [D$_8$]THF, 220 K): $\delta=132.5$ (C7), 126.1 (C4), 121.2 (C1), 117.8

(C2), 114.7 (C6), 108.6 (C3), 99.2 ppm (C5); ^{7}Li NMR (155 MHz, [D$_8$]THF, 220 K): $\delta=-1.3$ ppm. The ^{13}C NMR chemical shifts were obtained from the HSQCSI experiments.

6^{2-}/2K^{+}: ^{1}H NMR (400 MHz, [D$_8$]THF, 165 K): $\delta=8.11$ (d, $J=5.96$ Hz, 1H, 4-H), 7.85 (d, $J=6.67$ Hz, 1H, 1-H), 7.26 (s, 1H, 5-H), 7.10 (d, $J=7.76$ Hz, 1H, 7-H), 6.97 (m, 1H, 2-H), 6.81 (m, 1H, 3-H), 6.14 ppm (d, $J=7.93$ Hz, 1H, 6-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 165 K): $\delta=135.2$ (C9), 127.6 (C10), 127.2 (C11), 125.5 (C14), 123.3 (C13), 122.1 (C7), 118.9 (C4), 116.4 (C1) 115.6 (C2), 115.2 (C12), 112.5 (C6), 110.6 (C3), 105.6 (C5), 104.8 ppm (C8).

7: ^{1}H NMR (400 MHz, [D$_8$]THF, 298 K): $\delta=8.39$ (s, 1H, 1-H), 8.19 (d, $J=8.01$ Hz, 1H, 4-H), 8.11 (s, 1H, 2-H), 8.10 (d, $J=7.93$ Hz, 1H, 11-H), 8.08 (d, $J=7.95$ Hz, 1H, 6-H), 8.05 (s, 1H, 12-H), 8.04 (d, $J=8.23$ Hz, 1H, 10-H), 8.03 (d, $J=8.06$ Hz, 1H, 15-H), 7.91 (s, 1H, 8-H), 7.84 (d, $J=7.91$ Hz, 1H, 13-H), 7.49 (d, $J=8.02$ Hz, 1H, 3-H), 7.42 (d, $J=8.07$ Hz, 1H, 7-H), 7.39 (d, $J=7.94$ Hz, 1H, 14-H), 1.51 (s, 3H, 9-H), 1.47 (s, 3H, 5-H), 1.46 ppm (s, 3H, 16-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 300 K): $\delta=153.2$ (C29), 153.2, 152.6 (C33), 145.3, 144.4, 144.2, 139.4, 139.3, 139.2, 138.7, 137.9, 137.6 (C28), 137.5, 136.2, 135.4, 134.1, 133.5 (C32), 132.7, 132.5, 130.3, 127.0 (C4), 126.8 (C11), 125.9 (C7), 124.9 (C3), 124.9 (C14), 123.4 (C13), 121.3 (C35), 121.2 (C10), 120.6 (C8), 120.4 (C12), 120.2 (C15), 120.1 (C2), 118.7, 113.7 (C1), 35.7 (C19), 35.7 (C17), 35.6 (C21), 31.7 (C9), 31.6 (C16), 31.5 ppm (C5).

7^{2-}/2K^{+}: ^{1}H NMR (400 MHz, [D$_8$]THF, 240 K): $\delta=9.03$ (d, $J=9.10$ Hz, 1H, 6-H), 8.83 (d, $J=8.86$ Hz, 1H, 4-H), 8.69 (s, 1H, 1-H), 8.45 (s, 1H, 2-H), 8.34 (s, 1H, 8-H), 8.26 (s, 1H, 15-H), 8.08 (d, $J=8.14$ Hz, 1H, 13-H), 7.87 (s, 1H, 12-H), 7.77 (d, $J=8.40$ Hz, 1H, 10-H), 7.42 (d, $J=8.04$ Hz, 1H, 3-H), 7.39 (d, $J=8.57$ Hz, 1H, 7-H), 7.26 (d, $J=8.04$ Hz, 1H, 14-H), 6.84 (d, $J=9.08$ Hz, 1H, 11-H), 1.58 (s, 9H, 9-H), 1.57 (s, 9H, 5-H), 1.54 ppm (s, 9H, 20-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 240 K): $\delta=143.0$ (C3), 138.2 (C24), 137.3 (C18), 135.1 (C22), 134.6 (C20), 134.0 (C34 and C36), 131.9 (C27), 130.9 (C28), 129.2 (C30), 129.0 (C32), 128.6 (C34 and C36), 126.4 (C35), 123.3 (C39), 122.6 (C33), 122.4 (C10), 122.4 (C38), 121.3 (C31), 121.1 (C6), 121.0 (C4), 119.9 (C13), 117.2 (C26), 116.9 (C25), 116.8 (C14), 116.4 (C3), 116.0 (C1), 116.0 (C15), 115.6 (C2), 113.8 (C8), 112.7 (C7), 112.2 (C11), 110.4 (C4), 108.9 (C29), 106.3 (C40), 106.0 (C12) 35.6 (C19 and C21), 35.5 (C17), 33.2 (C5), 33.1 (C9), 32.8 ppm (C20).

(7–7)$^{6-}$/6K^{+}: ^{1}H NMR (400 MHz, [D$_8$]THF, 200 K): $\delta=8.77$–5.86 (aromatic protons), 6.57 (s, 1-H), 1.50–1.35 ppm (*t*Bu); ^{13}C NMR (100 MHz, [D$_8$]THF, 200 K) $\delta=134.4$–105.4 (C(sp^{2})), 48.2 (C1), 35.6–33.0 (C(sp^{3})).

8: ^{1}H NMR (400 MHz, [D$_8$]THF, 298 K): $\delta=7.61$ (s, $J=1.35$ Hz, 2H, 2-H), 7.49 (d, $J=7.96$ Hz, 2H, 4-H), 7.34 (s, 1H, 1-H), 7.24 (d, $J=8.1$ Hz, 2H, 3-H), 1.53 ppm (s, 9H, 5-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 298 K): $\delta=152.2$ (C20), 144.8 (C31), 140.0 (C30), 138.9 (C32), 137.3 (C34), 133.7 (C33), 127.0 (C4), 125.0 (C3) 120.0 (C2), 119.5 (C35), 113.9 (C1), 35.7 (C19), 31.9 ppm (C5).

8^{2-}/2K^{+}: ^{1}H NMR (400 MHz, [D$_8$]THF, 240 K): $\delta=9.09$ (s, 1H, 1-H), 8.98 (d, $J=8.35$ Hz, 2H, 4-H), 8.58 (s, 2H, 2-H), 7.53 (d, $J=8.23$ Hz, 2H, 3-H), 1.62 ppm (s, 18H, 5-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 240 K): $\delta=140.4$ (C20), 135.5 (C31), 134.0 (C32), 129.9 (C34), 122.8 (C4), 119.9 (C35), 117.3 (C30), 117.0 (C3) 116.3 (C1), 116.1 (C2), 114.8 (C33), 35.6 (C19), 33.0 ppm (C5).

(8–8)$^{6-}$/6K^{+}: ^{1}H NMR (400 MHz, [D$_8$]THF, 240 K): $\delta=8.95$ (s, 2H, 17-H), 8.90 (d, $J=8.56$ Hz, 2H, 15-H), 8.81 (d, $J=8.26$ Hz, 2H, 13-H), 8.54 (s, 2H, 10-H), 8.23–8.21 (m, 6H, 4-H, 11-H, and 6-H), 8.07 (s, 2H, 8-H), 7.29 (d, $J=8.11$ Hz, 2H, 12-H), 7.07 (s, 2H, 1-H), 7.01 (d, $J=8.36$ Hz, 2H, 16-H), 6.95 (d, $J=9.30$ Hz, 2H, 7-H), 6.58 (s, 2H, 2-H), 6.23 (d, $J=6.83$ Hz, 2H, 3-H), 1.78 (s, 18H, 18-H), 1.55 (s, 18H, 14-H), 1.07 (s, 18H, 9-H), 0.10 ppm (s, 18H, 5-H); ^{13}C NMR (100 MHz, [D$_8$]THF, 240 K) $\delta=138.6$ (C24), 137.5 (C22), 136.8 (C26), 136.2 (C47), 136.0 (C20 and CX), 135.0 (C48), 134.4 (C43), 133.4, 132.7 (2C), 132.1, 129.3 (CX), 126.7 (CX), 123.6 (C15 and C27), 123.59, 121.6 (C13), 121.3 (C4), 120.7 (C6), 120.2 (C32), 119.3, 117.6 (C45), 117.3 (C12), 116.1, 115.4 (C2 and C7), 115.4, 114.9 (C11), 114.8 (C8), 114.2 (C10), 113.8, 111.3 (C3), 108.3 (C29), 108.1, 107.8 (C16), 105.1 (C3), 104.4, 104.1 (C31), 49.6 ($^{1}J_{\mathrm{C,H}}=124.59$ Hz, C1), 35.7 (C25), 35.4 (C23), 35.2 (C21), 35.0 (C19), 33.4 (C18), 33.1 (C14), 32.8 (C9), 32.3 ppm (C5). CX = C39, C41, C44, or C47. The low symmetry of the system prevented a full assignment of the ^{13}C NMR spectrum. Two carbon signals could not be observed.

Acknowledgements

This work was supported by the United States–Israel Binational Science Foundation (BSF) and the US Department of Energy. I.A. is grateful for a Horowitz Foundation Scholarship.

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[23] Proton 1-H is located closest of all the protons to the core of the molecule, where the ring-current effects are felt strongly, hence this proton has the largest downfield shift.

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Received: June 1, 2006