π-Conjugated Benzoperylenes: Sequential C–S Bond Cleavage and Charge Distribution Patterns of the Anions

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Chemical reduction of polyaromatic hydrocarbons yielded solutions of long-lived polyanionic species. Reduction of a sulfur heterocycle afforded a stable sulfur-containing dianion. Sulfur extrusion from this dianion proceeded upon further contact with the reducing metal. NMR and UV studies indicate a sulfur extrusion mechanism different than that previously observed in THF. Electron transfer to the already reduced hydrocarbon skeleton results in the stepwise cleavage of the two C–S bonds and the extrusion of a sulfur atom. Dimers of aromatic hydrocarbons such as pyrene and phenanthrene have been reduced as well. The interplay between coulombic repulsions and resonance energies is described.

Introduction

Storage and transport of charges are of great importance in the fields of photo- or electrically conducting polymers.[1] In the study of a conductive polymer, smaller yet suitable fragments having similar conformational tendencies and exhibiting a minimum of interference and insulating effects are required. The rigidity of such systems helps in correctly mapping out the spin density along the conjugated segment and in determining the spin state of the system, both being of immense importance in the fields of chemiluminescence, magnetic materials and molecular electronics.[2] The effective conjugation present along a polymeric chain does not depend solely on the structure and topology of the fused entities. It also depends on the type of bonding which holds the subunits together and on the conformational variations that exist along the chain. Doping π-conjugated systems such as polycyclic aromatic hydrocarbons can reinforce the effects imposed on the system by charge delocalization patterns and thus be used to probe them. Polycyclic aromatic compounds linked together by various spacers, for which the degree of electronic interaction between the subunits increases with increasing π conjugation are classified as either redox or conducting polymers. The design and characterization of such stable redox entities having low π conjugation between the separate electron-storage units is a basic requirement in the design and synthesis of organic ferromagnets.[3] In polyaryl compounds the extent to which single-electron transport takes place, or the extent to which electron pairing is possible, depends intrinsically on the conformation of one entity relative to the other. While EPR studies showed that extended conjugation is present in anthrylenevinylene compounds, the interaction is missing when the vinyl spacer is omitted as in the bianthryl series.[4]

In attempting to bridge the gap between organic chemistry and material science we have been studying the electronic behavior of a series of polycyclic aromatic hydrocarbons among them a number of systems having heteroaromatic subunits.[5] The preparation of charged hydrocarbons containing sulfur atoms has been a challenge due to the relative weakness of the carbon−sulfur bond (65 kcal/mol). Very few examples of such reduced polycycles are known. Full or partial sulfur extrusion from heterocyclic compounds has been used extensively in organic synthesis as a method for ring cyclization and bond transformations.[6] The hydrodesulfurization or desulfurization processes have been of prime importance in the fuel and coal industries where extreme efforts have been made to learn and understand these processes on both the theoretical and practical levels.[7] Large amounts of data have been collected regarding the reactions of sulfur-containing hydrocarbons with metal complexes producing C−S bond scissions.[8] Alkali metal induced carbon−sulfur bond scission has been used with dialkyl and diaryl sulfides where sulfide-thiol transformations were required. These have been used primarily for the purpose of identifying sulfur-containing compounds in coal-tar, mineral oil and biological samples.[9] We have previously reported on the reductions of small annulated thiophene systems such as 1,3-diphenylbenzo[*c*]thiophene (**1**)[10] and benzo[*b*]thiophene (**2**)[11] and the stability of the carbon−sulfur bond. Unlike the stability observed with **1** and **2**, compound **3** was reported to suffer from a partial sulfur extrusion with cleavage of one of the two C−S bonds.[12] No mention was made of an initial reduction of the dibenzothiophene ring system.

Compounds **4**−**8** were used in this study as substrates for generating polyanion systems. The questions of charge delocalization and structural changes imposed by such electron transport processes are important in our continued study of reduced polyaromatic hydrocarbons and graphite-like surfaces. We now present the synthesis, characterization

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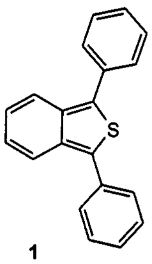

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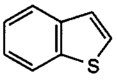

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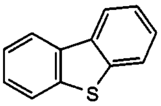

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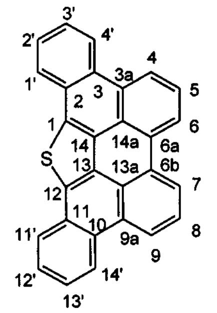

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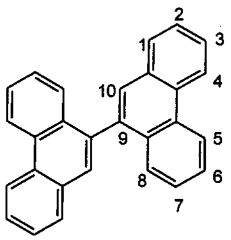

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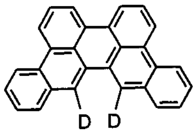

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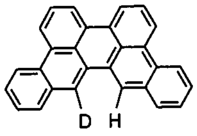

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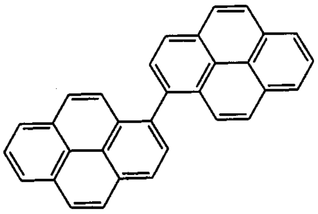

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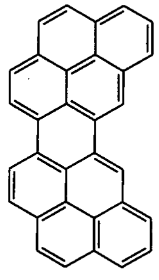

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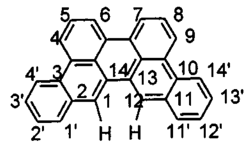


5HH

and electronic behavior of several related hydrocarbons along with Flavophen[13] (**4**) and its reduction profile.

Synthesis

Compound **4** was synthesized from tetraphenylthiophene by a milder procedure adapted from the original synthesis of Badger et al.[14] 2,3:10,11-Dibenzperylene (**5**; also labeled as **5HH**) was synthesized from **4** by sulfur extrusion or by utilizing a two-step approach leading to annelated perylenes.[14] Coupling of 9-bromophenanthrene by nickel-phosphane catalysed Grignard coupling,[15,16] afforded 9,9′-biphenanthryl (**6**) in 52% yield.[17] Nearly quantitative cyclization to **5** was achieved when treated with potassium in DME, followed by oxidation with cadmium chloride. Dimer **7** was similarly synthesized from 1-bromopyrene in a lower yield of 43%. Cyclization of **7** was achieved in the melt in the presence of sodium chloride and aluminum chloride[18] to afford 2,4:9,11-dinaphthoperylene (**8**)[19] in 60% yield.

Results and Discussion

Reduction of Flavophen (4)

Reduction of **4** to a dianion proceeded smoothly at −40 °C in the presence of potassium metal. Under identical conditions with lithium or with sodium the reduction did not proceed beyond the radical anion stage even after two weeks of contact. The first reduction step, accompanied by a deep blue color, resulted in the disappearance of the neutral species having UV/Vis bands at λ_{max} = 405, 381, 360, 316 and 295 nm, affording a paramagnetic species exhibiting a bathochromic (red) shift and no ^{1}H-NMR spectrum. Continued exposure to the metal yielded further changes in the electronic absorption spectrum, and the appearance of a sharp ^{1}H-NMR spectrum (Figure 1).

Quenching with oxygen afforded **4** as the sole product while quenching with D_2O yielded [D_2]-**4** having a base peak of *m/z* 386 in the GC-MS spectrum. We therefore, concluded that a two-electron reduction process had occurred with the formation of dianion **4**$^{2-}$. From the charge densities deduced for the dianion based on both NMR spectral data[20] and from the charge distribution profile calculated using semiemperical methods,[21] it is clear that only a small charge resides on the sulfur atom. While most of the carbon atoms carry small charge densities with δ^{13}C ranging from 104.6 to 139.5, C4 resonates at a higher field of δ = 97.2 with a measured second largest charge density of 0.20 e^-/carbon atom (Table 1).

The size and polarizability of the sulfur atom, which directs the added charge towards the α-carbon atom resonating downfield of C4 at δ = 104.6, also induces charge delocalization at C4 and C3′. The chemical shift of the α-carbon atom, C1, tells very little about the charge at that

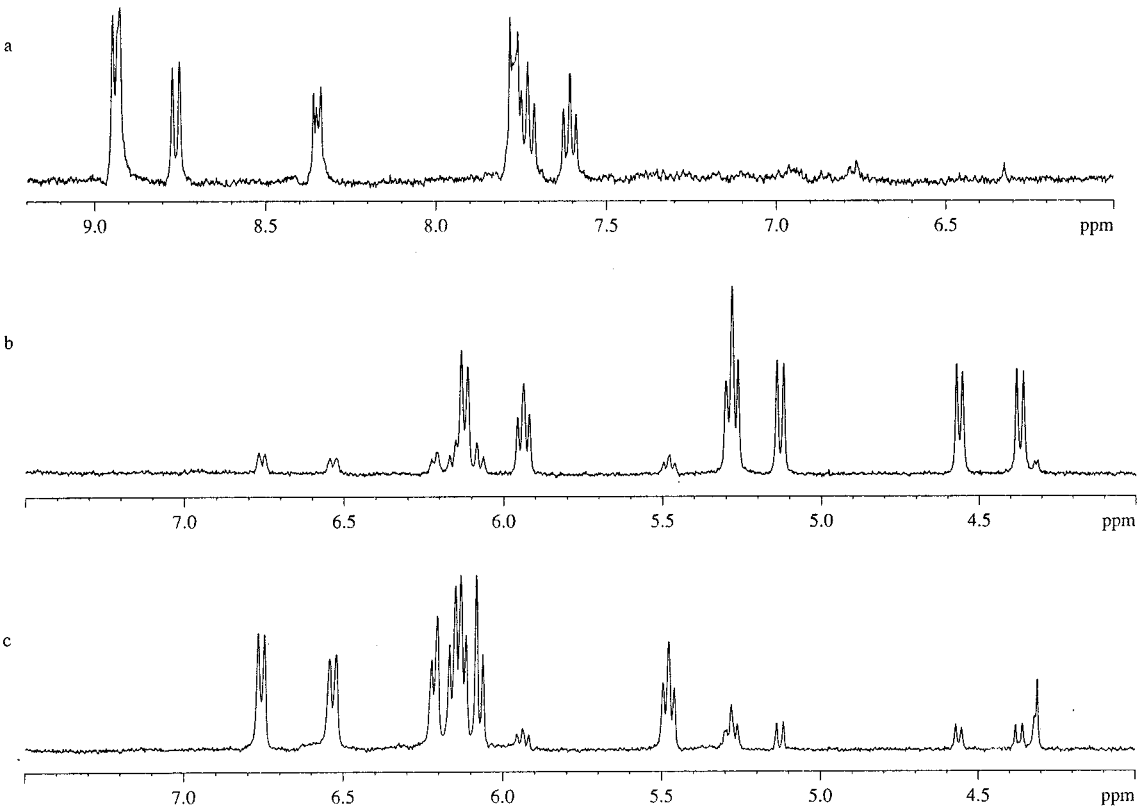


Figure 1. (a) ^1H NMR of sulfide **4**; (b) ^1H NMR of dianion **4**$^{2-}$/2K$^+$ at 240 K; (c) ^1H NMR of mixed dianions **4**$^{2-}$/2K$^+$ and **5**$^{2-}$/2K$^+$ at 240 K

Table 1. ^1H- and ^{13} C-NMR chemical shifts for neutral and reduced **4**

		1, 12	2, 11	3, 10	3a, 9a	4, 9	5, 8	6, 7	6a, 6b	13, 14	14a,13a	1′,11′	2′,12′	3′,13′	4′,14′
Neutral	^1H	–	–	–	–	8.87	7.71	8.31	–	–	–	8.87	7.68	7.56	8.76
4	^{13}C	137.4	131.7	129.2	129.7	123.8	127.0	124.6	128.1	126.7	130.0	126.8	126.0	125.3	123.4
4^{2-}/2K$^+$	^1H	–	–	–	–	4.60	5.31	4.37	–	–	–	5.13	5.97	5.31	6.13
(240 K)	^{13}C	104.6	123.0	119.7	118.3	97.2	128.8	108.2	139.5	106.3	133.8	120.7	124.9	109.8	125.4
Δδ	^1H	–	–	–	–	4.27	2.40	3.94	–	–	–	3.74	1.71	2.25	2.63
Δδ	^{13}C	32.8	8.7	9.5	11.4	26.6	−1.8	16.4	−11.4	21.3	−3.8	6.1	1.01	15.5	−2.0
Δq[a,b]	^{13}C	**−0.26**	−0.067	−0.073	−0.088	**−0.20**	+0.014	**−0.12**	+0.087	**−0.16**	+0.029	−0.047	−0.008	**−0.12**	+0.015
Δq[c]	^{13}C	−0.360	+0.078	−0.166	+0.069	−0.270	−0.130	−0.190	−0.046	−0.033	−0.003	−0.190	−0.110	−0.300	−0.048

[a] Calculated using $K_c = 130.31$. – [b] Values multiplied by −1 to reflect positive vs. negative charges. – [c] Calculated charges using AM1 methods.

position, because chemical shifts and charge densities of tertiary (C4) and quaternary (α-C1) carbon atoms should not be compared directly. One has to consider the effect of increasing electron density on going from the quaternary to the tertiary positions.[22] This implies that with the quaternary C1 exhibiting a charge density (−0.26) larger than that of C4 (−0.20) and C3′ (−0.12), a significant negative charge resides on C1, which agrees well with the calculated values. In fact, calculations suggest that most of the charge (69.8%) in **4**$^{2-}$ is delocalized in a 20π-phenanthro[*c*]thiophene-like segment of which C4, C1 and C14 are part, while the remainder is equally distributed between the remaining two phenyl-like moieties. Furthermore, calculations show that **4**$^{2-}$ does not behave as a substituted dibenzoperylene but rather as a diphenyl-substituted phenanthro[*c*]thiophene for which the bond orders are different. While C3−C3a appears as a full single bond, the C1−C2 bond is a double bond in character. This bond fixation which precedes charge localization on position C3′ rationalizes the rather large charge density residing on that carbon atom outside the phenanthro[*c*]thiophene-like segment (Figure 2).

Exposure of the THF solution containing dianion **4**$^{2-}$ to the metallic surface for an additional period resulted in the simultaneous appearance of a second set of bathochromic UV/Vis bands which intensified as the concentration of **4**$^{2-}$ decreased. The new anionic species exhibited a ^1H-NMR spectrum centered at about 1 ppm downfield to that obtained for **4**$^{2-}$ and had a new uneven set of two singlets at δ = 4.31 and 4.35, which indicates an increased total number of protons in the spectrum of about 14.6 protons.

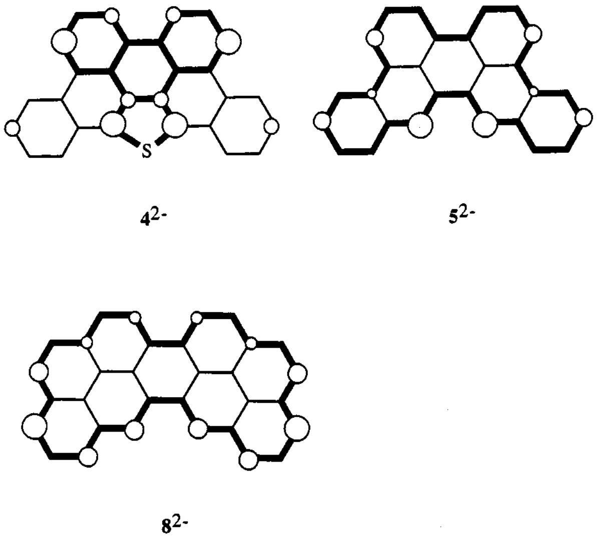


Figure 2. AM1 charge distribution in dianions $\mathbf{4}^{2-}$, $\mathbf{5}^{2-}$ and $\mathbf{8}^{2-}$

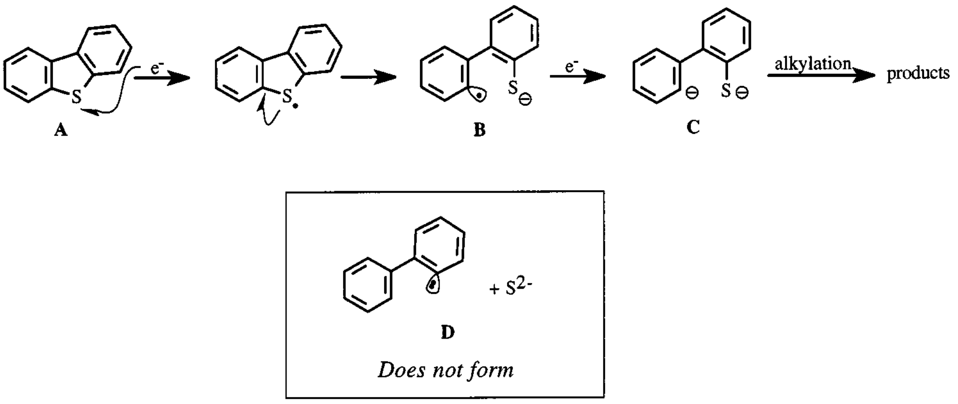
Quenching the sample with oxygen produced an orange-red solid whose GC-MS gave three molecular ion peaks at *m/z* 352,[23] 353 and 354. The ^{1}H-NMR spectrum of the same sample hinted at a structure similar to, yet different from that of the neutral sulfide **4**. The presence of the sulfur atom at the dianionic stage and the rather low molecular ions observed for the quenched sample of the later reduction species supported a sulfur extrusion from $\mathbf{4}^{2-}$ resulting from a prolonged contact with the reducing surface. The presence of MS molecular ions at *m/z* 353 and 354 along with the peculiar increase in the total number of protons indicated in the ^{1}H-NMR spectra of the quenched sample braces the idea that deuteron abstraction from the solvent occurred after an initial C−S bond cleavage and the formation of an aryl anion.

Sulfur Extrusion

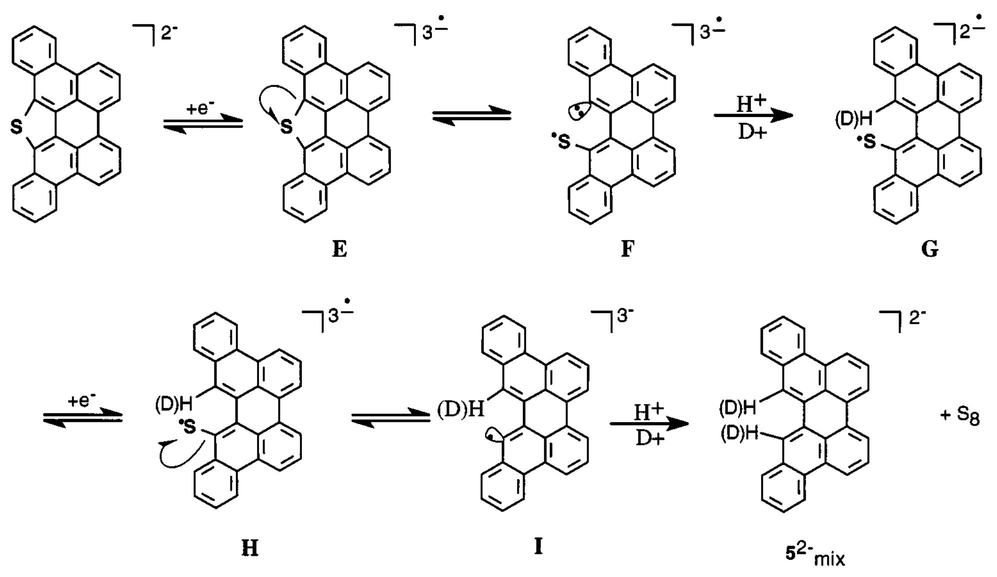
Carbon-sulfur bond scissions in sulfur-containing organic compounds[24] such as dibenzothiophene (**3**; structure **A**) in [D$_8$]THF in the presence of some electron source are known[12] to proceed by an initial electron transfer to the sulfur atom succeeded by homolytic cleavage to yield a sulfide anion and a carbon radical species **B** (Scheme 1).

Upon transfer of a second electron to the carbon radical a carbanion **C** is formed. Alkylation of both anions is possible. Further cleavage of the yet intact C−S$_{\text{anion}}$ bond of **C** to yield a sulfide salt and a vinyl anion species **D** has never been observed and is not otherwise possible. Francisco and Katritzky et al. demonstrated that compound **3** in ammonia in the presence of an alkali metal did not produce C−S bond cleavages but rather underwent Birch reduction and protonation.[25] They further showed that C−S bond scissions predominated only when conformational freedom allowed p-orbital overlap with the phenyl groups. In cases where the diaryl sulfides were capable of sustaining stable radical anions, extrusion of the sulfur atom proceeded via an episulfide intermediate similar to those produced in the thermal or catalytic processes. These episulfide intermediates break down with the evolution of monatomic sulfur species which catenate further to a stable S_8.[26] In no case has the evolution of a charged sulfide atom in the form of M_2S been either observed or considered. We believe that sulfur extrusion from a charged sulfur heterocycle, such as $\mathbf{4}^{2-}$, indeed requires a neutral atomic sulfur species to be evolved and base the mechanism for the unique sulfur extrusion from $\mathbf{4}^{2-}$ on the following points: (1) S_8 was isolated from the reaction tube along with hydrocarbon **5**; (2) dianion $\mathbf{4}^{2-}$ is a long-lived, stable species; (3) scission of a C−S bond should not result in the formation of a charged sulfur atom; (4) no hydrogenated products were observed, and (5) because of the rigidity of **4**, an episulfide intermediate is excluded. The extrusion begins with the introduction of a third electron into the *polycyclic ring system* $\mathbf{4}^{2-}$ to give a radical trianion (species **E**; Scheme 2), weakening one of the C−S bonds and ensuing the first homolytic cleavage of one of the organosulfide arms.

This scission affords a carbanion at one bay position and a sulfur radical (**F**). Proton (or deuteron) abstraction by the carbanion, with possible S−S radical dimerization[27] results in the radical dianion **G** prior to the introduction of another electron to the system. With the formation of the radical trianion **H**, the second C−S bond is cleaved and the carbanion formed is protonated to furnish an atomic sulfur



Scheme 1. Carbon-sulfur bond scission in the presence of electron source



Scheme 2. Sulfur extrusion from $\mathbf{4}^{2-}$

and a protonated dianion mixture labeled as $\mathbf{5}^{2-}{}_{mix}$. It is important to point out that on grounds of bond activation, the introduction of an electron to the radical-dianion species **G** is required for the weakening of the C−S$_{radical}$ bond and its ultimate cleavage.

Isotope Shift Effects

Protonation or deuteration of the carbanions formed as a result of the extrusion process affords three distinct isotopomers: doubly deuterated **5DD**, mono-deuterated monoprotonated **5HD** (same as **5DH**) and doubly protonated **5HH**.[28][29] The assignment of the two new closely resonating signals at $\delta = 4.31$ and 4.35 as H1 arising from species $\mathbf{5HD}^{2-}$ and $\mathbf{5HH}^{2-}$, respectively, is based on the expectation[30] that the proton signal H1 arising from species $\mathbf{5HD}^{2-}$ should appear upfield to that of $\mathbf{5HH}^{2-}$. This assignment was confirmed by the ^{1}H-NMR spectrum acquired for $\mathbf{5HH}^{2-}$, which was synthesized and reduced independently, and exhibited a singlet at $\delta = 4.35$ and a coupling constant of $^1J_{CH} = 152.0$ Hz in contrast to $^1J_{CD} = 24.1$ Hz measured for dianion $\mathbf{5HD}^{2-}$. A $^1J_{CD} = 23.8$ Hz was measured for the neutral sample. These values, in fact, agree nicely with the expected J_{CD} couplings derived from the gyromagnetic ratio calculated for γ_H/γ_D.[31] Since $J_{CH}/J_{CD} = \gamma_H/\gamma_D \approx 6.51$, $^2J_{CD}$ for $\mathbf{5HD}^{2-}$ is estimated at 23.3 Hz.

On the basis of a full ^{1}H assignment the percent composition of the mixture containing the three isotopomers was found to consist of 9% **5HH**, 17% **5HD** and 74% of **5DD**, as averaged over 3 runs.[32] The deviation from the statistical composition values expected for the four possible isotopomers is a consequence of the lack of reversibility and higher acidity of protiated impurities relative to that of [D$_8$]THF. The localized anions, formed as the C−S bonds break, abstract protons from the impurities prior to an attack on the deuterated solvent.

The charge perturbation imposed on the molecule by the deuteron(s) may be evaluated by examining the isotope effects on the nuclear shielding of the neighboring protons and carbon atoms.[30] The effect on the bay proton of $\mathbf{5HD}^{2-}$ was described above. The negative α, β and γ effects on the neighboring atoms are quite strong in the ^{13}C-NMR spectra of the dianion mixture of **5** (Figure 3).

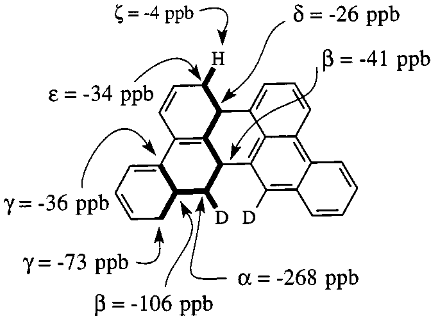


Figure 3. Negative isotope shifts in the 600-MHz ^{13}C- and ^{1}H-NMR spectra of $\mathbf{5DD}^{2-}/2K^+$

The carbon peak originally resonating as a strong signal at $\delta = 84.2$ for the dianion $\mathbf{5HH}^{2-}/2Li^+$ appears lower in intensity downfield of a resolved triplet of lines centered at $\delta = 83.9$ arising from the coupling of C1 (C12) by the deuteron in $\mathbf{5DD}^{2-}$. These α shifts of −268 and −316 ppb measured for the dianion and neutral **5DD**, respectively, are quite normal negative isotope effects for an α-carbon atom.[33] No other conclusive isotope shifts were determined from the neutral sample of $\mathbf{5}_{mix}$. For the dianion, the β effects on C2 and C14 are smaller than the α effect and are at −106 and −41 ppb, respectively. The large difference in size for these β effects in relation to each other results from the overlapping of a β and a γ effect on C14 (C13). Smaller γ effects are found for C1′ (−73 ppb) and C3 (−36 ppb). Surprisingly, there were two additional effects on the remote C6a and C6 carbon atoms, but none on C14a. The δ effect of −26 ppb on C6a and the ε effect on C6 amounting to −34 ppb arise from structural changes brought about by steric hindrance of the deuterons and not as a direct consequence of nuclear shielding. In the ^{1}H-NMR spectrum, a ζ effect is observed for H6 exhibiting a −4 ppb shift. This is also too distant to arise from bonding interactions and thus must arise from the imposed structural changes.

Redox Effects − Reduction and Cyclization of 6 and 7

In an effort to map-out the electronic differences between anions **4**$^{2-}$ and **5**$^{2-}$ clearly we synthesized hydrocarbon **5**, as described earlier. The ^{1}H-NMR spectrum of neutral **5** consists of a singlet, a doublet, two triplets and two overlapping multiplets, resonating as for **4** in the region δ = 7.6−8.7, and integrating to a total of 16 hydrogen atoms. Direct reduction of hydrocarbon **5** under identical conditions, yielded ^{1}H- and ^{13}C-NMR spectra identical to those obtained for **5HH**$^{2-}$/2K$^+$ (Table 2).

Treatment of dimer **6** with sodium in [D$_8$]THF in an evacuated NMR tube resulted in the formation of a brown solution exhibiting magnetic properties with no NMR spectra. After longer exposure to the metal, the ^{1}H-NMR spectrum consisted of seven signals having a center of gravity at δ = 5.65 and integrating to 18 protons. On the basis of the signal integration and splitting pattern, the species could be assigned as the two-electron or four-electron reduction product **6**$^{2-}$/2Na$^+$ or **6**$^{4-}$/4Na$^+$, respectively. Quenching experiments with water afforded the doubly protonated compound. A two-electron reduction should afford a triplet-state diradical anion species (**5b** in Scheme 3) which is thus NMR-inactive or a localized singlet dianion (structure **5c**) in which only one of the phenanthryl units is doubly charged and the other remain neutral.

It is important to note at this point that EPR studies indicated that while the radical anion of 1,1′-binaphthyl behaves as a π system with a homogeneous spin distribution, in 9,9′-bianthryl there is a complete localization of spin. Recently, the crystal structure of the triradical anion of 9,9′-bianthryl with sodium was determined.[34] Surprisingly and in support with the previous EPR studies, in the solvent-separated contact ion all three charges were located on only one of the two anthryl subunits. The coordination of all three sodium cations to only one anthryl segment clearly attests to the predominant localization of charge to only that half of the hydrocarbon. With **6** and **7** expected to be similar to binaphthyl, a certain degree of charge delocalization was expected.

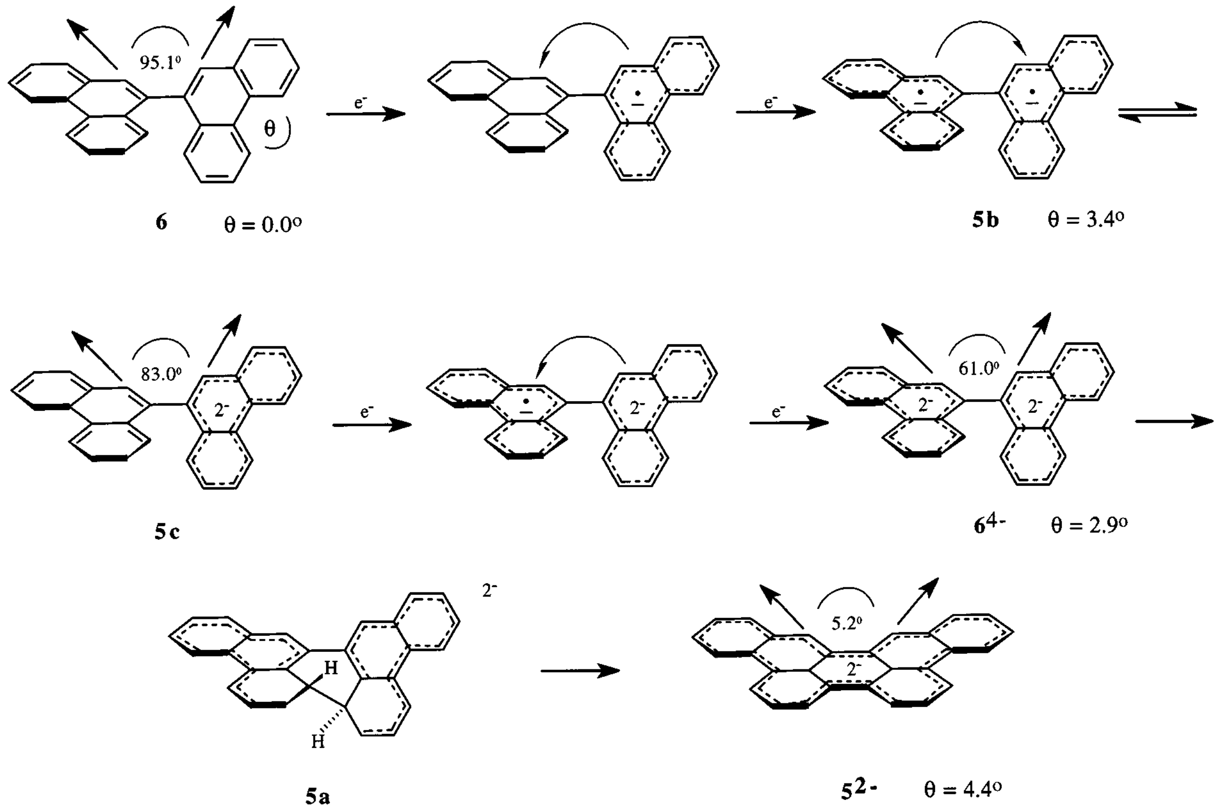
On the basis of the observed NMR spectra and of semi-empirical calculations which showed a reduction by 12.1% of the torsion angle between the two subunits upon reduction of **6** to the corresponding dianion, a delocalized species is suggested. The **6**$^{2-}$ species is in fact a hybrid of **5b** and **5c** in which the inter-ring bond allows conjugation through increased double bond character and with a certain degree of charge localization at the far ends of the two subunits. This affords a completely delocalized system in which steric and electronic repulsions seem to exist between the inner protons H8 and H8′ and possibly between excess charge residing around these carbon atoms. This repulsive interaction strengthens as the tetraanion is formed.

Anion **6**$^{4-}$/4Na$^+$ may be viewed as a dimer having two separate redox-active groups. A complete delocalization of the injected electrons over the entire dimer could result in a lowered redox state.[35] However, with the effective conju-

Table 2: ^{1}H and ^{13}C NMR chemical shifts for neutral and reduced **5** and **6**.

								9,9′-biphenanthryl (**6**)							
		10, 10′	10a, 10a′	4a, 4a′	4b, 4b′	5, 5′	6, 6′	7, 7′	8, 8′	9, 9′	8a, 8a′	1, 1′	2, 2′	3, 3′	4, 4′
Neutral	^{1}H	7.86	−	−	−	8.82	7.65	7.38	7.50	−	−	7.92	7.67	7.73	8.81
6	^{13}C	128.9	132.0	130.7	130.7	123.2	126.9	137.5	127.9	127.0	132.6	129.1	127.3	127.2	123.0
6^{4-}/4Na$^+$	^{1}H	3.45	−	−	−	6.50	6.07	6.07	7.04	−	−	5.22	5.59	4.78	6.13
(250 K)	^{13}C	**82.9**	148.2	124.0	138.4	120.8	122.2	124.5	123.0	105.5	141.6	118.5	129.3	106.5	122.1
								2,3:10,11-dibenzoperylene (**5**)							
		1, 12	2, 11	3, 10	3a, 9a	4, 9	5, 8	6, 7	6a, 6b	13, 14	14a, 13a	1′, 11′	2′, 12′	3′, 13′	4′, 14′
Neutral	^{1}H	8.67	−	−	−	8.64	7.75	8.42	−	−	−	7.64	8.01	7.65	8.64
5	^{1}C	121.8	132.7	132.6	135.7	123.0	127.5	121.9	127.6	131.6	130.5	127.2	129.4	127.4	123.2
5^{2-}/2K$^+$	^{1}H	4.35	−	−	−	6.21	6.15	6.52	−	−	−	6.08	6.12	5.48	6.75
(240 K)	^{13}C	**81.6**	139.4	121.7	142.2	104.8	121.3	113.6	128.6	121.8	131.9	120.1	126.6	109.1	123.0
5^{2-}/2Na$^+$	^{1}H	4.35	−	−	−	6.24	6.16	6.57	−	−	−	6.09	6.12	5.49	6.76
5^{2-}/2Li$^+$	^{1}H	4.64	−	−	−	6.03	5.99	6.25	−	−	−	5.95	5.99	5.35	6.64
(240 K)	^{13}C	**84.2**	140.7	120.7	140.2	103.8	121.5	113.4	122.0	117.9	133.3	122.4	126.4	108.7	123.6
$\Delta\delta$[a]	^{1}H	**+4.32**	−	−	−	+2.43	+1.6	+1.9	−	−	−	+1.56	+1.89	+2.17	+1.89
$\Delta\delta$[a]	^{13}C	**+37.6**	−6.7	+11.9	−4.5	+19.2	+6.0	+8.5	−5.6	+13.7	−2.8	+4.8	+3.0	+18.7	−0.4
Δq[b,c]	^{13}C	**−0.363**	+0.064	−0.115	+0.043	**−0.185**	−0.058	−0.082	+0.054	−0.132	+0.027	−0.046	−0.029	**−0.180**	+0.004
Δq[d]	^{13}C	−0.288	+0.044	−0.160	+0.058	−0.252	−0.135	−0.200	−0.035	+0.014	−0.015	−0.193	−0.104	−0.300	−0.058

[a] $\Delta\delta$ = neutral − (5^{2-}/2K$^+$). − [b] Calculated using K_c = 105.3. − [c] Values multiplied by −1 to reflect positive vs. negative charges. − [d] Calculated charges using AM1 methods.



Scheme 3. Reduction and cyclization of dimer **6**

gation being dependent on the topology and structure of the system, the present torsion about the inter-ring bond may inhibit to a significant extent of charge delocalization and thus promote charge localization to each of the two units.[36] Semiempirical calculations predict that the torsion angle decreases from 95.1% in the neutral species to 83.0% in the dianion in contrast to 61.0% in the charged tetraanion. This large and surprising decrease in the angle is due to increased conjugation between the two phenanthryl units despite the coulombic repulsions described above. In fact, localization of larger charge densities at C3 and C9 along with the distribution of smaller charge densities on ring positions C8a through C4b implies that the system minimizes coulombic repulsions between the charge centers and may also attempt to lower the energy associated with the formation of an antiaromatic system. This gain-loss pattern by which localization requires planarity but imposes repulsive interactions is at an overall favorable state with the gain in delocalization or resonance energy compensating the increase in coulombic repulsions. The increase in the double bond character at C9−C9′ is a direct consequence. The inharmonious distribution of charge results in the lowering of the anisotropic effects and is responsible for the lowfield shifts observed for $\mathbf{5}^{2-}$ as compared to $\mathbf{6}^{4-}$. The observed ^{1}H-NMR spectrum for $\mathbf{6}^{4-}/4Na^{+}$ is rather different from that obtained for the phenanthrene dianion[37] not only because it is lower in symmetry but more importantly because of electron delocalization through the inter-ring bond. Reduction of phenanthrene furnished a dianion having a ^{1}H-NMR spectrum with a center of gravity at $\delta = 1.34$, about 4.31 ppm to higher field of that of $\mathbf{6}^{4-}/4Na^{+}$ (Table 3).

Table 3. ^{1}H-NMR spectrum center of gravity of neutral and charged hydrocarbons

Compound		Center of gravity [ppm]
Phenanthrene	14π	7.68[44]
Phenanthrene dianion	16π	1.34[44]
6	14π (× 2)	7.93
$\mathbf{6}^{4-}/4Na^{+}$	16π (× 2)	5.65
5	26π	8.17
$\mathbf{5}^{2-}/2Na^{+}$	28π	5.95
pyrene	14π	8.15
Pyrene dianion	16π	0.97[45,46]
7	14π (× 2)	8.12
$\mathbf{7}^{4-}/4K^{+}$	16π (× 2)	5.12
8	26π	7.94
$\mathbf{8}^{2-}/2K^{+}$	28π	5.63

On reduction, small alternations in the C4−C4a−C4b−C5 dihedral angle of the bay region of the phenanthryl subunits are also evident. Even though these changes are much smaller than in the inter-ring dihedral angle, changes in the angle confirm and support the earlier observations that charged phenanthrenes are not planar.[38] The changes in the bay dihedral angle of $\mathbf{6}^{4-}$ stem from the relative localization of charge on one end of the bay region of the phenanthryl subunit and may be responsible for the diminished twist of each subunit in $\mathbf{6}^{4-}$, relative to the calculated dihedral angle of $\theta = 15.8°$ for the phenanthrene dianion.

The degree of electron delocalization over the whole dimer varies with changes in charge localizations at the interring positions. Lowering the charge densities at these positions by extension of the surface for potential delocalization results in a larger separation between the two subunits and a lowered conjugation. Since the interaction between the two phenanthryl units being largest due to the coulombic repulsions between H8 and H8′, a further decrease in the dihedral angle as a result of continued reduction, brings about the formation of a new C−C bond between these two positions.

Reduction of **6** with potassium yielded a deep blue solution exhibiting UV/Vis bands at λ_{max} = 837, 606, 566 and 520 nm and no high-resolution ^{1}H-NMR spectrum. Further exposure to the metal resulted in shifts of the UV/Vis bands to λ_{max} = 569 nm and the appearance of a sharp ^{1}H-NMR spectrum. This spectrum centered similarly to that of the lithium salt but slightly downfield to that of tetraanion $\mathbf{6}^{4-}/4Na^+$, consisted of a singlet, four doublets, a triplet and a multiplet: eight proton signals in total (Figure 4).

The presence of a singlet in the spectrum and the absence of a ninth proton hinted at a fast reductive cyclization that ensued in the formation of dianion $\mathbf{5}^{2-}$. The formation of intermediate species $\mathbf{6}^{4-}/4K^+$ or $\mathbf{6}^{4-}/4Li^+$ and species **5a** were not observed. Such cyclization intermediates have been previously observed in the syntheses of helicenes.[39] The absence of such spectra of intermediates attested to the instability of this intermediate and to the ease with which dianion $\mathbf{5}^{2-}$ is evolved.[40]

Prolonged contact of $\mathbf{6}^{4-}/4Na^+$ with the metal also resulted in $\mathbf{5}^{2-}$. However, in this case longer exposure periods were required as the cyclization of tetraanion $\mathbf{6}^{4-}/4Na^+$ proceeded at a rate of about 5% conversion per 24 hours.

Unlike the similar ^{1}H- and ^{13}C-NMR spectra of neutral **4** and **5**, their anions exhibit totally different electronic patterns as born out by their NMR spectra. Firstly, as was shown beforehand, the ^{1}H-NMR spectrum of $\mathbf{5}^{2-}$ is shifted downfield by about 1 ppm. Secondly, while the calculated charge densities for both $\mathbf{4}^{2-}$ and $\mathbf{5}^{2-}$ using AM1 methods are similar, the measured charge densities from the corresponding NMR spectra are different, as shown in Tables 1 and 2. The highest coefficient and charge density in $\mathbf{4}^{2-}$ lies on C1, C4, C14, C6 and on C3′, as discussed above. Other positions closer to the sulfur atom carry less charge. In $\mathbf{5}^{2-}$ C1 carries the largest charge density, as well, whereas C3′ and C4 take on only smaller charge densities. Reasons for these changes in the charge profiles of the two dianions are twofold: the removal of bond polarization and the return to an annelated perylene skeleton. Charge distribution comparison of $\mathbf{5}^{2-}$ with that of perylene dianion reveals great similarities in the distribution and magnitude of charge densities. The presence of two annelated benzene rings does not alter the charge profile of the perylene segment to a large extent. With the core of the perylene segment C14a−C6a−C6b−C13a−C13−C14 remains low in charge den-

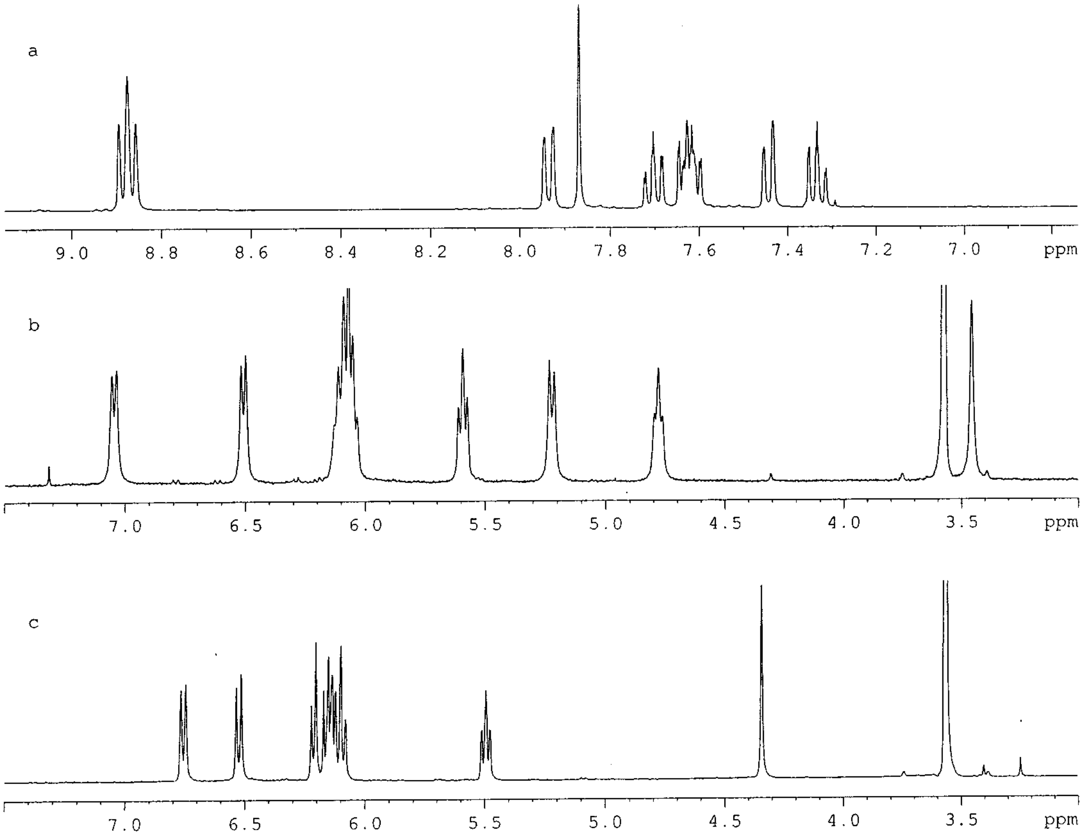


Figure 4. (a) ^{1}H NMR of dimer **6**; (b) ^{1}H NMR of tetraanion $\mathbf{6}^{4-}/4Na^+$ at 240 K; (c) ^{1}H NMR of dianion $\mathbf{5}^{2-}/2K^+$ at 240 K

sity, delocalization of charge is also maintained in the periphery.

Unlike **6** for which the isolation of the intermediate tetraanion **6**$^{4-}$ was observed upon reduction with sodium metal only, dimer **7** could be reduced to tetraanion **7**$^{4-}$ neither with sodium nor with potassium metal. In no case was the tetraanion lithium salt observed. The electronic picture displayed by tetraanion **7**$^{4-}$/4K$^+$ as elucidated from its ^{13}C-NMR spectrum, closely resembles that of the pyrene dianion. The highest charge densities are found on C8, C3, C6 and to a lesser extent on C4 due to coulombic repulsions similar to those described for **6**$^{4-}$. Because the phenanthrene dianion is expected to be more antiaromatic than the corresponding pyrene dianion, the conjugative stabilization is predicted to be better in **6**$^{4-}$. This, however, seems to contradict the greater reduction in dihedral angle (54.4°) for **7**$^{4-}$ (61.8° for **7**$^{2-}$ and 96.4° for neutral **7**) as compared with 61.0° in **6**$^{4-}$, and also to counter the empirical evaluation of conjugation as it arises from the charge densities at the bridgehead carbon atoms of **6**$^{4-}$ and **7**$^{4-}$. Higher charge densities are calculated at the bridgehead carbon atoms of **7**$^{4-}$. This should indicate a better conjugation in **7**$^{4-}$ than in **6**$^{4-}$, because the localization of charge on the subunits of **6**$^{4-}$ acts to lower the expected antiaromaticity of the phenanthryl dianion. Thus, conjugative stabilization in this case is less of a constraint.

Charge Localization at Bay Positions

Dianion **8**$^{2-}$ was produced on prolonged contact of tetraanion **7**$^{4-}$/4K$^+$with the metal (Figure 5).

The unavailability of a ^{13}C-NMR spectrum for the dianion over a range of temperatures limited the evaluation of the system to theoretical data only which indicate a peripheral delocalization pattern of an annelated perylene. A striking effect present as a direct outcome of the annelating benzene rings in both **5** and **8** is the chemical shift difference between the C6 and C1 carbon atoms and protons, situated in the two bay regions of **5**$^{2-}$ and the equivalent protons in **8**$^{2-}$. While the ^{13}C-NMR chemical shift difference between the two carbon atom signals amounts to only 0.1 ppm in the neutral species **5**, and 2.8 ppm in neutral **8**, this same shift difference is measured at 29.2 ppm in the corresponding dianion **5**$^{2-}$. Furthermore, these values are 10−20 ppm larger than those reported for the bay region carbon atoms of perylene[41] (**9**), benzo[*ghi*]perylene[42] (**10**) and their dianions.

AM1 calculations showed that upon reduction of **5** the bond length of C13−C14 reduces from 1.476 Å in the neutral species to 1.409 Å in the reduced species **5**$^{2-}$. This 0.067 Å decrease is larger than that of the equivalent bond C6a−C6b for which the bond length is shortened by 0.019 Å only. Hence, the severe repulsion expected between the bay protons should be minimized for protons H6a and H6b and be reinforced for H1 and H12. The polarization of the σ-bonds causes the upfield shifts of the ^{13}C-NMR bands for the bay-region carbon atoms[43] to $\delta = 84.2$ and 122.0 for C1 and C6a, respectively, relative to those of the corresponding carbon atoms in perylene dianion **9**$^{2-}$ ($\delta = 98.1$). The ^{1}H-NMR spectrum of **5**$^{2-}$ points to the fact that the opposite effect, expected for the proton shifts, is not manifested as the ^{1}H-NMR resonances of H1 and H12 are *shifted upfield*. While both H1 (H12) and H6 (H7) exhibit upfield shifts on reduction, the chemical shift difference of 4.32 ppm measured for H1 and H12 is clearly a direct consequence of excess charge residing at this bay region. An upfield shift of 1.9 ppm observed for bay protons H6 and H7 is more likely to result directly from the reduction process.

Conclusion

Compounds **4** and **5** are quite intriguing. Sulfur extrusion from the long-lived dianion **4**$^{2-}$ exhibits unique sequential C−S bond cleavages. The formation of a neutral sulfur atom and the intermediacy of two localized aryl anions at the bay region support the conclusion that this extrusion proceeds by a consecutive two-electron transport into the already reduced hydrocarbon. The resulting charged hydrocarbon exhibits a charge density profile consistent with an-

Table 4. ^{1}H- and ^{13} C-NMR chemical shifts for neutral and reduced **7** and **8**

		1,1′-Bipyryl															
		1	2	3	3a	4	5	5a	6	7	8	8a	9	10	10a	10b	10c
Neutral	^{1}H	–	8.36	8.17	–	7.90	7.68	–	8.19	8.07	8.26	–	8.19	8.22	–	–	–
7	^{13}C	136.7	124.9	128.0	131.9	128.0	126.2	131.4	129.2	126.3	125.6	131.3	125.4	127.9	130.5	126.5	125.2
7^{4-}/4K$^+$	^{1}H	–	4.67	5.77	–	6.06	4.85	–	4.85	5.53	4.72	–	4.72	4.99	–	–	–
(200 K)	^{13}C[a]	(124.2)	120.2	129.0	(142.0)	115.6	108.5	(126.4)	109.8	128.8	108.1	(128.2)	108.1	120.8	(141.6)	(140.9)	(139.2)
Δq[b,d]	^{13}C	−0.395	−0.148	+0.117	+0.319	−0.392	−0.560	−0.145	−0.614	+0.079	−0.554	−0.098	−0.547	−0.224	+0.351	+0.455	+0.443
Δq[c]	^{13}C	−0.167	−0.042	−0.424	+0.070	−0.347	−0.210	−0.023	−0.423	−0.027	−0.432	−0.005	−0.217	−0.212	+0.016	−0.035	−0.004

		2,4:9,11-Dinaphthoperylene															
		1, 12	2, 11	3, 10	3a, 9a	4, 9	5, 8	6, 7	6a, 6b	13, 14	13a, 14a	1′, 11′	2′, 12′	3′, 13′	3a′, 13a′	4′, 14′	5′, 15′
Neutral **8**	^{1}H	7.89	–	–	–	–	8.08	8.14	–	–	–	7.94	7.83	8.07	–	7.75	7.84
8^{2-}/2K$^+$	^{1}H	5.09	–	–	–	–	5.89	6.46	–	–	–	5.15	5.79	4.96	–	5.72	6.04
Δq[c]	^{13}C	**−0.266**	+0.044	−0.066	+0.045	**−0.167**	−0.125	**−0.154**	−0.056	+0.014	−0.048	**−0.272**	−0.069	**−0.322**	+0.059	**−0.252**	−0.078

[a] Chemical shifts in parentheses are tentative assignments only. − [b] Calculated using $K_c = 31.6$. − [c] Calculated charges using AM1 methods. − [d] Values multiplied by −1 to reflect positive vs. negative charges.

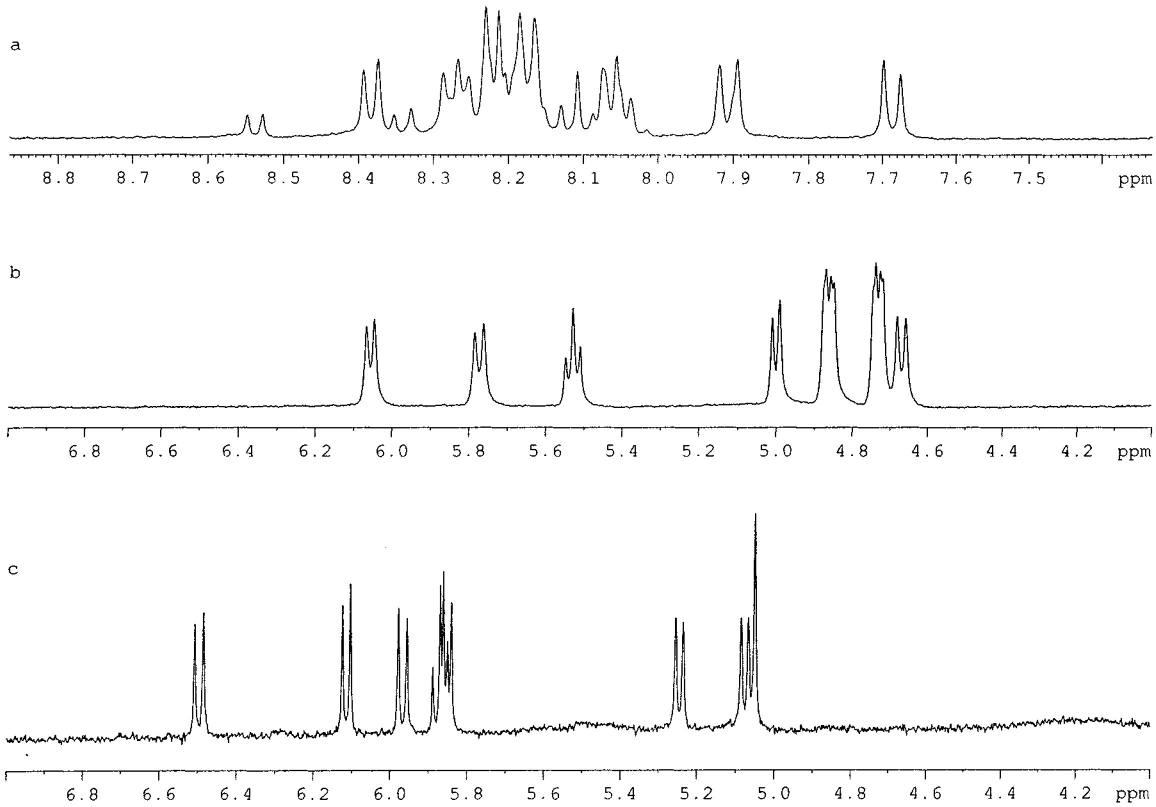
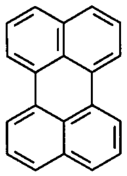


Figure 5. (a) ^{1}H NMR of dimer **7**; (b) ^{1}H NMR of tetraanion $\mathbf{7}^{4-}$/4K$^+$ at 200 K; (c) ^{1}H NMR of dianion $\mathbf{8}^{2-}$/4K$^+$ at 200 K



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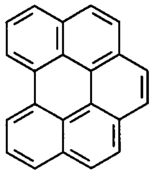

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nelated perylenes. The presence of isotopes in the bay region is a good tool in examining the changes imposed on the system. The existence of 5- and 6-bond isotope shifts are clearly unusual and point to the structural changes present mainly in the bay regions, as compared with the completely protonated system.

Charge distribution in dimer $\mathbf{6}^{4-}$ indicates that stabilization of the charged subunits is maintained through charge localization, by which the antiaromaticity of the phenanthryl dianion is reduced, and by a small degree of conjugation through the inter-ring bond. As the size of the subunits becomes larger as in dimer $\mathbf{7}^{4-}$, such inharmonious localization is no longer dominant and in the tetraanionic stage more conjugation is present.

Experimental Section

Chemical reductions of all compounds were carried out in specially constructed 5-mm NMR tubes equipped with a reduction chamber. The alkali metal, either lithium, sodium or potassium, was introduced into the reduction chamber as a thin lithium wire or as a mirror of metallic sodium or potassium produced by high vacuum distillation. Into the NMR tube containing 4−5 mg of the sample to be reduced and the metal, doubly distilled [D$_8$]THF was transferred under vacuum and the tube was then flame-sealed. Reduction proceeds when the solution is brought into contact with the metal by inversion of the NMR tube. All reductions were carried out at dry ice temperature. Differentiation between the various redox stages was achieved by utilization of UV/Vis and several NMR techniques. The appearance or disappearance of a paramagnetic radical stage was evident from the appearance or disappearance of the NMR spectrum and the loss of the relevant UV/Vis band. All low-temperature NMR spectra were recorded with a Bruker DRX-400 spectrometer at temperatures between 190 and 260 K. The study on the isotope shift effects in the anion of $\mathbf{5}^{2-}$ was performed with a Bruker DMX-600 MHz spectrometer. All spectral assignments were made using a multitude of correlation experiments such as COSY, NOESY, CH correlation and a LRCH correlation.

4: Copper(II) trifluoromethanesulfonate (6.52 g, 18 mmol, predried at 100°C under vacuum for 2 h) and aluminum(III) chloride (2.4 g, 18 mmol, 18 equiv.) were added to an argon-purged solution of tetraphenylthiophene (338 mg, 1 mmol) in 200 ml of CS_2. The entire mixture was allowed to stir at room temp. for 18 h. The mixture was allowed to stand for 2 h before the clear solvent was decanted off. Dichloromethane (25 ml) was added to the slurry and the solvents were evaporated under reduced pressure without heating. The resultant solid was taken up in conc. HCl (100 ml) and stirred overnight. The solution was filtered and the solid residue treated with a 10% solution of HCl, distilled water and a 10% ammonium hydroxide solution. The residue was then dried under vacuum and sublimed at 150−180°C at 10−2 Torr to yield **4** as a bright yellow solid. 310 mg, 81% yield, m.p. > 300°C. − MS (FD, 4 kV); *m/z* (%): 82.5 (100) [M$^+$].

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