56-1; **29d**, 81025-57-2; **30a**, 80976-64-3; **30b**, 81025-58-3; **30c**, 81025-59-4; **30d**, 81025-60-7; bicyclo[3.1.0]hex-2-ene-6-*endo*-carbonyl chloride, 58846-09-6; *endo*-6-(diazomethyl)ketobicyclo[3.1.0]hex-2-ene, 80976-65-4; styrene, 100-42-5; *p*-methoxystyrene, 637-69-4; *p*-methylstyrene, 622-97-9; *p*-chlorostyrene, 1073-67-2; *m*-chlorostyrene, 2039-85-2; dimethyl fumarate, 624-49-7; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *exo*-3-chlorobicyclo[3.2.1]oct-2-en-2-ol, 80976-66-5; *exo*-bicyclo[3.2.1]oct-3-en-2-ol, 4802-43-1.

Super-Charged Polycyclic π Systems: Pyrene and Perylene Tetraanions

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Abstract: Fused benzenoid systems pyrene, perylene, and their alkyl and phenyl derivatives were reduced with sodium and potassium to the doubly and quadruply charged species. The dianions revealed paratropicity, while the tetraanions acquired diatropic, aromatic ring current. Some of the quadruply charged systems revealed a high degree of asymmetry which can be rationalized as a result of an asymmetrical location of the metal cations. This phenomenon, as well as ring current effects, is discussed in terms of ^{1}H, ^{13}C, and ^{23}Na NMR spectroscopies and theoretical calculations.

The problem of the contributions of various kinds of cyclic conjugations to the nature of polycyclic π-conjugated systems presents a subject of interest.[1] A comprehensive study of the species which are formed in the course of the reduction process of π-conjugated polycyclic hydrocarbons should give an insight into this challenging subject. The reasoning behind this allegation is that different stages in the reduction process are assumed to give rise to different, or even opposite, types of cyclic conjugation. The resulting carbanions can be classified by the number of negative charges taken up by the π system; this basic classification can be further subdivided by making reference to the diatropicity and paratropicity which are caused by the charging and are quite straightforwardly detected by NMR methods.

Singly charged polycyclic species such as indenyl[2] and fluorenyl[2,3] anions exhibit a considerably diatropic ring current, in line with their Hückeloid number of peripheral π electrons. In contrast, the cycloocta[*def*]fluorenyl anion[4] contains a periphery of 16 π electrons and was shown to be a paratropic, antiaromatic system. A large group of doubly charged carbanions is known, some of which are classified as aromatic, such as the *sym*-dibenzcyclooctatetraene,[5] dibenzpentalene derivatives,[6] heptalene,[7] etc. Other doubly charged species, examplified by phenanthrene,[8] anthracene,[8,9] and pyrene[10] dianions, reveal an enhanced paratropic character. Recently, the class of polycyclic anionic systems was extended to include triply charged species—the triindene trianion[11] and even quadruply charged molecules such as the octalene[12] and the acepleiadylene[13] tetraanions.

Table I. ^{1}H NMR Chemical Shifts (ppm)[a] of 1, 1^{2-}, 2S, and 2A

system	δ	assignment[b]
1	8.31 (d, $J = 7.6$ Hz)	1, 3; 8, 10
	8.11 (t, $J = 7.6$ Hz)	2; 9
	8.20 (s)	5, 6, 12, 13
1^{2-}[c]	0.01 (d)	1, 3; 8, 10
	2.22 (t)	2; 9
	2.94 (s)	5, 6, 12, 13
2S	5.20 (m,[d] $J = 7.8$ Hz)	1, 2; 9, 10
	5.99 (m,[d] $J = 7.8$ Hz)	3; 8
	4.17 (d,[e] $J = 1.9$ Hz)	12, 13
	5.64[f]	5, 6
2A	5.42 (m,[d] $J = 7.5$ Hz)	1, 2; 8, 9
	5.82 (m,[d] $J = 7.5$ Hz)	3; 10
	5.64 (AB, $J = 5.4$ Hz)	5, 6; 12, 13

[a] Chemical shifts are recorded with respect to the solvent signals and then referred to SiMe$_4$. [b] The numbering[18a] is as shown in Scheme I. [c] Reference 10. [d] Parts of an ABK pattern assigned to protons 1, 2, 3 (8, 9, 10). [e] The doublet is due to coupling with protons 1, 10. [f] This absorption is assumed to be hidden under the signals of protons 5, 6, 12, 13.

We have shown previously[14] that a four-electron reduction of benzenoid hydrocarbon such as pyrene (**1**) and perylene (**7a**) is feasible. The two neutral hydrocarbons **1** and **7a** exhibit low-field ^{1}H NMR absorptions (Tables I and VII) rationalized by the existence of an enhanced peripheral diatropic ring current. These systems afford a nice example of the two approaches which were suggested to account for the aromaticity of polyfused conjugated

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(1) (a) For reviews see: Agranat, I. *MTP Int. Rev. Sci.: Aromatic Compounds* **1973**, *3*, 139. (b) Platt, J. R. *J. Chem. Phys.* **1954**, *22*, 1448-1458. (c) Randic, M. *J. Am. Chem. Soc.* **1977**, *99*, 444-450. (d) Randic, M. *Pure Appl. Chem.* **1980**, *52*, 1587-1596. (e) Mallion, R. B. *Ibid.* **1980**, *52*, 1541-1548.

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(7) Oth, J. F. M., Müllen, K.; Konigshofen, H.; Wassen, J.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2387-2398.

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(11) Katz, T. J.; Slusarek, W. *J. Am. Chem. Soc.* **1980**, *102*, 1058-1063.

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(13) Becker, B. Ch.; Huber, W.; Müllen, K. *J. Am. Chem. Soc.* **1980**, *102*, 7803-7805.

(14) Minsky, A.; Klein, J.; Rabinovitz, M. *J. Am. Chem. Soc.* **1981**, *103*, 4586.

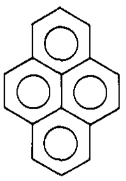
0002-7863/82/1504-2475$01.25/0

Table II. ^{13}C NMR Chemical Shifts (ppm)[a] and Charge Densities of 1, **2S**, and **2A**

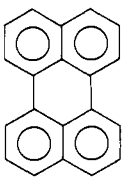
1	assignment[b]	1, 3, 8, 10	2, 9		4, 7, 11, 14		5, 6, 12, 13		15, 16
	δ	124.5	125.4		130.9		126.4		124.4
2S	assignment[b]	1, 10	2, 9	3, 8	4, 7	5, 6	12, 13	11, 14	15, 16
	δ	129.0	126.7	108.4	106.8	100.2	104.6	137.7	142.7
2A	assignment[b]	1, 8	2, 9	3, 10	4, 11	5, 12	6, 13	7, 14	15, 16
	δ	126.9	126.2	108.1	104.9	100.1	103.7	135.9	140.5
	ρ[c]	0.2939	0.3088		0.2376	0.2307			0.1666

[a] Recorded with respect to the solvent (THF) signals and referred to $SiMe_4$. [b] For numbering see Scheme I. [c] The charge densities for the quadruply charged species are deduced from $\omega\beta$ calculations.

ring systems. One approach, coined as the "peripheral model",[1b,15] emphasizes the contribution of the peripheral π conjugation to the aromatic character and considers the inner bonds as a bridging perturbation to the annulene skeleton. Pyrene (**1**) is best described in terms of this model—having a periphery of a Hückeloid number of conjugated π electrons. The second approach considers the local aromatic or antiaromatic contributions of the rings composing the polycycle.[1c,d,16] Adopting this model, perylene (**7a**) is depicted as two naphthalene moieties linked by single bonds. It is therefore of interest to confront spectroscopic and theoretical data of **1**, **7a**, and their derivatives with the data obtained from their carbanions, in order to better understand the nature of the ring current which characterizes the various species. The high symmetry (D_{2h}) of pyrene nad perylene obviously simplifies both the NMR spectra and the computational process.



1



7a

Results and Discussion

Pyrene Tetraanion (2). The dianion of pyrene (1^{2-}) has been previously prepared by reduction of the hydrocarbon with lithium metal in tetrahydrofuran at -40 °C.[10] The dianion was identified by ^1H NMR spectroscopy. The extreme high-field absorptions clearly indicate the existence of a pronounced paratropic antiaromatic effect which causes a shift of the center of gravity far beyond the value expected by the Schaefer and Schneider correlation.[2] This conclusion is supported by SCF calculations which predict a low degree of π-bond alternation in 1^{2-}, thus enabling an antiaromatic delocalization. As pointed out by Müllen, this type of delocalization is unfavorable in terms of Hückel's rule.

We have attempted the reduction of **1** with sodium and potassium metals at room temperature and monitored the process by ^1H NMR spectroscopy. After several hours of exposing **1** to the metal the signals of the neutral pyrene disappeared due to fast electron exchange between **1** and the radical species; no line broadening could be detected. After 4 days of exposure the deep purple solution exhibited a well-resolved but very complex ^1H NMR spectrum (Table I, Figure 1). The parameters of this spectrum are entirely different from those revealed by the paratropic species 1^{2-} (Table I) and remain unchanged for weeks. Bubbling of dry oxygen into the solution yields the starting material as a sole product. A similar experiment was also conducted in dimethoxyethane and afforded an identical spectrum. These results indicate that the ^1H NMR bands could not originate from a product of the reaction of the anion with itself or with the neutral pyrene, neither could it originate from a product of the reaction between the carbanion and the solvent. Quenching experiments with D_2O afforded tetradeuteriotetrahydropyrene (*m/e* 210, P + 1 = 211) as shown by electron capture and chemical ionization mass spectrometry. The quenching product is unstable and oxidizes in the air to yield a mixture of partially deuterated pyrene derivatives (*m/e* 202–209). We followed the progress of the reduction process by repeated sampling experiments. Samples were taken from the reaction mixture, quenched with water, and titrated potentiometrically to follow the formation of the base. The amount of sodium was monitored by atomic absorption. The concentration of base and sodium increased with time and after 4 days 3.3–4.0 equiv of base and 3.2–4.0 equiv of sodium atoms per molecule of **1** were detected. These results prove that the species responsible for the above-mentioned spectrum should be a quadruply charged anion **2**. The spectroscopic data (^1H, ^{13}C, and ^{23}Na NMR) of pyrene tetraanion and of quadruply charged pyrene derivatives (vide infra) point to the existence of a hitherto unknown phenomenon. We believe that the countercations (Na^+, K^+) are located at unsymmetrical positions around the carbanion (Scheme I). This assumption is supported by theoretical calculations[17] (SCF-MO and $\omega\beta$). The calculations assign the largest

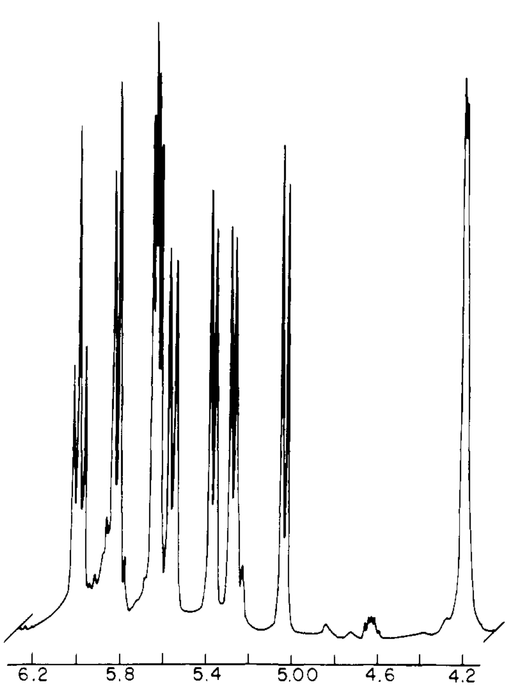
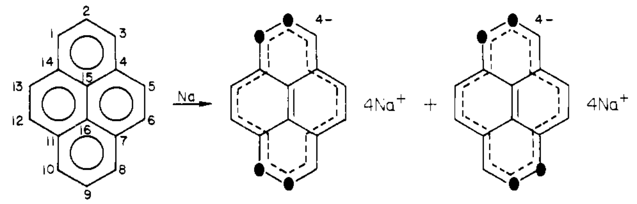


Figure 1. ^1H NMR spectrum (ppm, relative to $SiMe_4$) of pyrene tetraanion (**2**).

Scheme I [18a]



2S **2A**

the circles represent the metal ions

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(16) (a) Gutman, I.; Milun, M.; Trinajstic, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692–1704. (b) Gutman, I.; Milun, M.; Trinajstic, N. *Croat. Chem. Acta* **1976**, *48*, 87–95.

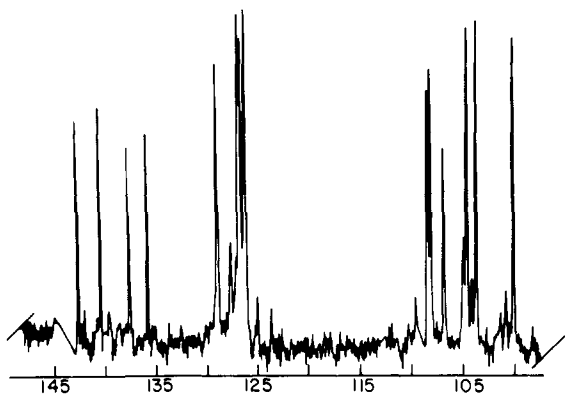


Figure 2. ^{13}C NMR spectrum (ppm, relative to $SiMe_4$) of pyrene tetraanion (**2**).

value of electron density in **2** to be located on carbons 2 and 9,[18a] while carbons 1, 3, 8, and 10 acquire the second highest charge density value (Table II). Hence, we deduce that two metal cations are located in the neighborhood of carbons 2 and 9 and the two remaining cations are situated in the vicinity of either of the carbon atoms pairs 1, 10 or 1, 8. This lack of symmetry is induced on the polycyclic π system and affords two distinct quadruply charged species which we have coined, according to the mutual locations of the metal cations, as syn (**2S**) and anti (**2A**) forms. The ^1H and ^{13}C NMR parameters[18a] (Tables I and II, respectively) are consistent with the above assumption.

The asymmetry gives rise to an ABK pattern for protons 1, 2, and 3 (8, 9, 10) of each of the quadruply charged forms **2S** and **2A**. The AB part belongs to protons 1, 2; 9, 10 and 1, 2; 8, 9 of the syn and anti forms, respectively. These protons are linked to those carbons which are assumed to bear a particularly high electron density. The K part is due to **2S** and **2A** protons 3; 8 and 3; 10 respectively. The lack of symmetry is also reflected on the protons 5, 6; 12, 13 of **2A** which reveal an AB pattern, while protons 5, 6; 12, 13 of **2S** are not influenced by the induced asymmetry, thus exhibiting two narrow doublets, probably due to coupling with remote protons (e.g., 1, 3 and 8, 10). The detailed assignment is based on splittings, integration, comparison with the spectra of multicharged pyrene derivatives (vide infra), and the intuitive assumption that the distortion of the π system of the syn form (**2S**) due to the more crowded distribution of the metal cations is to a slight degree higher than the distortion of the anti form (**2A**) π system. This distortion makes the centers 1, 2 and 9, 10 and especially the center 12, 13 more negative in **2S** than in **2A**, thus appearing in a higher field relative to the respective protons of **2A**. In contrast, the 3, 8 and 5, 6 protons of **2S** would be slightly deshielded in comparison to the respective protons of **2A**. The asymmetry is also manifested in the ^{13}C NMR spectrum. Instead of the expected five signals due to the five different types of carbons in the parent system **1** the spectrum of the tetraanion **2** is composed of 16 signals. This complexity is attributed to the presence of the two asymmetrical species, each of which gives rise to eight lines (Table II, Figure 2).

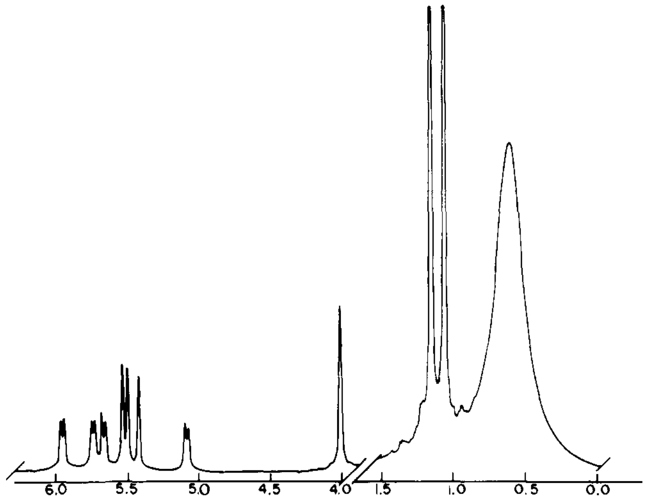
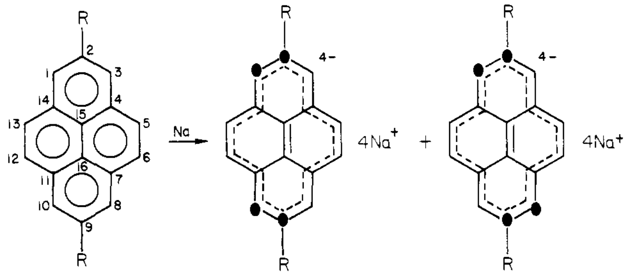


Figure 3. ^1H NMR spectrum (ppm, relative to $SiMe_4$) of 2,9-di-*tert*-butylpyrene tetraanion (**4**) as sodium salt.

Scheme II[18a]



3 **4S** **4A**

a, $R = CH_3$; b, $R = t\text{-}C_4H_9$

the circles represent the metal ions

This tentative assignment (Table II) is based on nondecoupled spectra and on the previously mentioned difference in the distortion of the π systems which we had attributed to the two charged forms. Hence, the ^{13}C NMR signals of the more distorted syn form should be shifted to low field relative to the respective ^{13}C NMR absorptions of the anti form, due to a slightly higher contribution of the paramagnetic terms to the shielding parameters.[18b] The ^1H NMR spectrum of the quadruply charged pyrene reveals along with the assymetry an enhanced diatropicity. As already mentioned,[10] the reduction of pyrene with lithium afforded a dianionic product; its high-field proton bands (with center of gravity at ca. 0.9 ppm) were rationalized in terms of the formation of an antiaromatic paratropic species. Our results indicate that when stronger reducing agents, e.g., sodium and potassium, are used, the reduction process does not afford the doubly charged species as the end product but proceeds to yield the quadruply charged system **2**. The relatively low-field proton NMR bands of the latter, centered at ~5.4 ppm, are meaningful considering the value of the ^1H NMR center of gravity as evaluated by the Schaefer and Schneider equation.[2] This equation, which correlates the ^1H NMR shifts only to changes in π-charge density, predicts a value of 4.9–5.0 ppm for the center of gravity of the proton spectrum of **2** (assigning a total shift of 10.7 ppm per unit of charge). Therefore, the existence of a peripheral diatropic ring current resulting from a 14C–18π periphery is pointed out. The peripheral approach, according to Hückel's rule and to Platt's suggestion,[1b] indicates an antiaromatic and aromatic character for the pyrene dianion (1^{2-}) and pyrene tetraanion, respectively. This conclusion is also supported by MO calculations[17] according to which the LUMO orbital of pyrene exhibits a nodal plane through the central carbon atoms. Consequently the molecular orbital which is occupied by the two additional electrons in 1^{2-} is of a pure peripheral

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(17) Modified ω calculations on Coulomb integrals: (a) Berson, J. A.; Evleth, E. M.; Hamlet, Z. *J. Am. Chem. Soc.* **1965**, *87*, 2901–2908. (b) Boyd, G. V.; Singer, N. *Tetrahedron* **1966**, *22*, 3383–3392. (c) Streitwieser, A. *J. Am. Chem. Soc.* **1960**, *82*, 4123–4135. For the π-electron SCF scheme see: Meyer, A. Y. *Theor. Chim. Acta* **1970**, *16*, 226–238. The evaluation of integrals is described in: Meyer, A. Y. *Theor. Chim. Acta* **1968**, *9*, 401–411. The structural parameters were based on crystallographic data (Trotter, J.; Camerman, A. *Acta Crystallogr.* **1965**, *18*, 636–646) but symmetry was restored in bond lengths.

(18) (a) We applied unconventional numbering of the π system (see schemes). The conventional numbering would have made the discussion and the tables very complicated due to the asymmetry which the charged species are endowed with. (b) It is well accepted that the main contributions to ^{13}C chemical shifts come from variations in the paramagnetic term of the Ramsey equation. This term strongly depends on the free valence and on the dimension and shape of the atomic orbitals. A strong distortion of the 2p orbitals would clearly give rise to an enhanced paramagnetic contribution. For references see: (a) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803–2807. (b) Alger, T. D.; Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1966**, *88*, 5997–5406. (c) Nelson, G. L.; Williams, E. A. In "Physical Organic Chemistry"; Wiley: New York, 1976; Vol. 12, pp 229–342.

Table III. ^1H NMR Chemical Shifts (ppm)[a] of 3a, 3b, 4a, and 4b

system	δ	assignment
3a	8.09 (s)	1, 3, 8, 10
	8.10 (s)	5, 6, 12, 13
	2.87 (s)	methyl protons
3b	8.16 (s)	1, 3, 8, 10
	8.37 (s)	5, 6, 12, 13
	1.70 (s)	*tert*-butyl protons
4a-S	5.09 (d, J = 5.0 Hz)	1; 10
	5.73 (d, J = 5.0 Hz)	3; 8
	5.47 (s)	5, 6
	4.03 (s)	12, 13
	1.47 (s)	methyl
4a-A	5.65 (d, J = 5.2 Hz)	1; 8
	5.96 (d, J = 5.2 Hz)	3; 10
	5.25 (d[b])	5, 6; 12, 13
	1.78 (s)	methyl
4b-S	5.10 (d, J = 4.7 Hz)	1; 10
	5.77 (d, J = 4.7 Hz)	3; 8
	5.63 (s)	5, 6
	4.01 (s)	12, 13
	1.02 (s)	*tert*-butyl
4b-A	5.78 (d, J = 5.0 Hz)	1; 8
	6.08 (d, J = 5.0 Hz)	3; 10
	5.55 (d[b])	5, 6; 12, 13
	1.12 (s)	*tert*-butyl

[a] Referred to $SiMe_4$; for numbering see Scheme II. [b] As it is emphasized in the text, the pattern revealed by protons 5, 6 and 12, 13 is an AB which is clearly shown only in the NMR spectrum of the reaction product of 3b and potassium.

nature. Although the MO calculations do not point to a similar nodal plane at the LUMO of the quadruply charged species, they assign a very low excess of electron density to these central carbons (see Table II). This finding (which was applied in the evaluation of the theoretical ^1H NMR center of gravity of **2**) indicates the large contribution of the 18-π-electron peripheral delocalization to the character of the quadruply charged pyrene.

2,9-Dimethylpyrene and 2,9-Di-*tert*-butylpyrene Tetraanions (4a and 4b). Properties which are similar to those encountered in the reduction process of the pyrene system are observed in the reaction of two pyrene derivatives, i.e., the 2,9-dimethylpyrene (**3a**) and 2,9-di-*tert*-butylpyrene (**3b**) systems with sodium (Scheme II).

The ^1H NMR parameters **3a**, **3b**, **4a**, and **4b** (Figure 3) are summarized in Table III. The existence of two isomeric syn and anti forms would result in a ^1H spectrum which consists of four doublets assigned to protons 1, 3 (and 8, 10)—two doublets in each form. An AB pattern would result from protons 5, 6 and 12, 13 of the anti form and two singlets for those protons in the syn form (Table III). Indeed, this is the observed NMR pattern especially in the spectrum of the product of the reaction between **3b** and potassium (Figure 4). Double resonance experiments indicate that the doublet at 6.08 ppm is coupled with the doublet at 5.78 ppm and the doublet at 5.86 ppm is coupled with the one at 5.19 ppm (J = 5.0 and 4.8 Hz, respectively). An AB pattern assigned to protons 5, 6; 12, 13 of the anti is observed at 5.57 ppm (center)—J = 8.8 Hz (further coupled to protons 1, 3, 8, 10, J = 0.9 Hz). Two singlets located at 5.63 and 4.06 ppm are assigned to protons 5, 6 and 12, 13, respectively, in the syn form.

Some important and instructive points should be noted. (i) Surprisingly enough, the influence of the induced asymmetry is extended to the methyl and even to the *tert*-butyl groups, thus doubling of alkyl bands is observed. (ii) The NMR signals of the *tert*-butyl protons of **4b** appear at higher field than those of the methyl protons of **4a**. The chemical shift difference between the two *tert*-butyl ^1H NMR absorptions ($\Delta\delta$ = 0.1 ppm) is less than the difference observed between the two methyl signals ($\Delta\delta$ = 0.3 ppm). These phenomena are rationalized by the larger distance of the *tert*-butyl protons relative to the methyl protons from the π backbone. Consequently the protons of the *tert*-butyl groups (**4b**) are less influenced by the diatropic ring current prevailing in the quadruply charged π moiety and are also less sensitive to the differences induced by the asymmetrically located cations.

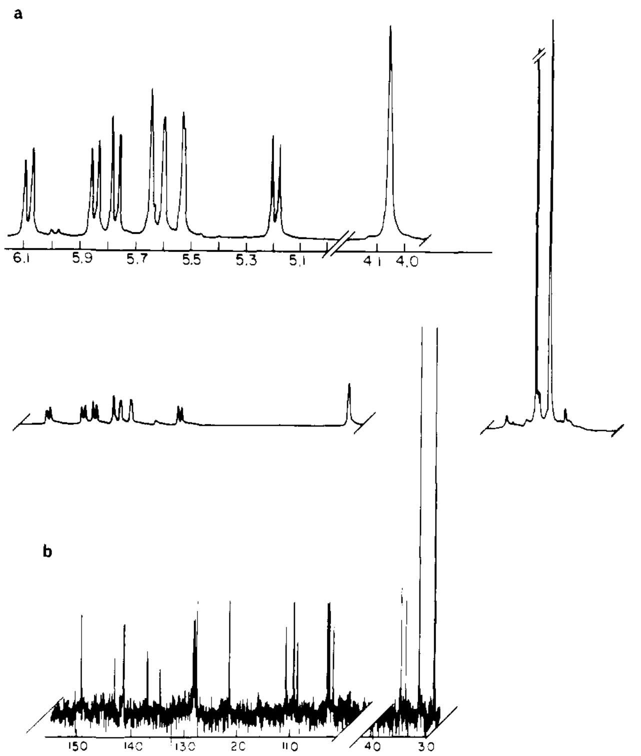

Figure 4. (a) ^1H NMR spectrum (ppm, relative to $SiMe_4$) of 2,9-di-*tert*-butylpyrene tetraanion (**4**) as potassium salt. (b) ^{13}C NMR spectrum (ppm, relative to $SiMe_4$) of 2,9-di-*tert*-butylpyrene tetraanion (**4**) as potassium salt.

(iii) Bubbling of dry oxygen into the solutions of **4a** and **4b** afforded the two starting materials **3a** and **3b**, respectively, as sole products. These observations lend strength to our assumption that **4a** and **4b** are indeed diatropic species endowed with an asymmetry which is due to the cations. The cations are located (as deduced from theoretical calculations) in positions similar to those found in **2**. When the reduction of **3b** with sodium was conducted at −5 °C, the disappearance of the NMR bands of the neutral compound was not followed by the formation of the previously described spectrum of **4b** (Table III). Instead, after 6 h, a very broad, unresolved absorption centered at 0.9 ppm was observed. The continuation of the reduction process for an additional 48 h at room temperature afforded a spectrum which exhibits the outset of absorptions at the range of 5.6 ppm and of two singlets at ~1.3 ppm, as well as the mentioned broad absorption at high field. The process ends after 6 days, giving rise to an NMR spectrum consisting of the well-resolved patterns assigned to the diatropic quadruply charged species **4b**, along with the broad band at 0.6 ppm (Figure 3). The reduction of **3b** was also performed with potassium metal. After 3 h at −78 °C the spectrum of the solution revealed only a large band at ~1.3 ppm. Twelve additional hours caused the development of well-resolved patterns at low field (5.6 ppm) as well as two singlets at ca. 1 ppm. This process was accompanied by a shift of the large band from ~1.3 to 0.05 ppm. After 6 days at 0 °C the absorption at 0.05 ppm totally disappeared and the anionic species exhibited well-resolved NMR patterns—almost identical with those obtained in the reaction of **3b** with sodium (Figure 4a). We attribute the large absorption at high field to the doubly charged species ($3b^{2-}$) being a paratropic, antiaromatic 16π–14C perimeter system. The combined data can be rationalized in terms of the influence of alkyl groups on neutral and charged π systems. As shown by theoretical considerations and by electrochemical studies, alkyl and especially *tert*-butyl groups destabilize the LUMO of neutral π systems (at ca. 0.1–0.2β units).[19a] The anionic charged species

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(19) (a) Streitwieser, A. "Molecular Orbitals Theory for Organic Chemists"; Wiley: New York, 1961; pp 182–184. (b) Reference 19a, pp 165–172.

Table IV. ^{13}C NMR Chemical Shifts (ppm)[a] and Charge Densities of 3b and 4b[d]

3b	assignment[b]	1, 3, 8, 10	2, 9		4, 7, 11, 14		5, 6, 12, 13		15, 16		
	δ	121.4	147.9		130.51		126.9		122.4		
4b-S	assignment[b]	1, 10	2, 9	3, 8	4, 7	5, 6	12, 13	11, 14	15, 16	quat	methyl
	δ	128.1	134.8	127.4	110.6	102.3	109.0	141.2	149.2	34.8	31.3
4b-A	assignment[b]	1, 8	2, 9	3, 10	4, 11	5, 12	6, 13	7, 14	15, 16	quat	methyl
	δ	127.9	134.7	121.3	108.4	101.5	102.6	136.7	142.9	33.9	28.5
	ρ[c]	0.2982	0.2787		0.2347	0.2303			0.1657	0.0340	

[a] Referred to SiMe$_4$. [b] Numbering is as shown in Scheme II. [c] The charge densities are deduced from $\omega\beta$ calculations. It is clearly shown that the combined densities of carbons 2(9) and the quaternary carbons is larger than the charge density on carbons 1, 3, 8, or 10. [d] As a potassium salt.

Table V. ^{1}H NMR Chemical Shifts (ppm)[a] of 5 and 6

system	2, 9	5, 6, 12, 13	ortho[b]	meta[b]	para[b]
5	8.13 (s)	8.30 (s)	7.79 (m[c])	7.66 (m[c])	7.59 (m[c])
6	4.66 (s)	4.62 (s)	6.86 (d, J = 7.58 Hz)	6.74 (dd, J = 7.58, 7.21 Hz)	6.43 (t, J = 7.18 Hz)

[a] Referred to SiMe$_4$; for numbering see Scheme III. [b] Phenyl-ring protons. [c] Center of a complex multiplet.

Table VI. ^{13}C NMR Chemical Shifts (ppm)[a] and Charge Densities of 5 and 6

system	1, 3, 8, 10	2, 9	4, 7, 11, 14	5, 6, 12, 13	15, 16	ipso[b]	ortho[b]	meta[b]	para[b]
5	140.3	128.6	127.4	124.4	125.2	136.5	129.8	127.5	126.4
6	137.0	141.0	144.2	107.0	149.5	111.6	122.1	128.1	119.1
ρ[c]	0.1822	0.2457	0.1013	0.1103	0.0633	0.0921	0.0796	0.0415	0.1174

[a] Referred to SiMe$_4$. For numbering see Scheme III. [b] Phenyl-ring carbons. [c] Charge densities of the quadruply charged species 6 deduced from $\omega\beta$ calculations.

are also destabilized due to inductive effects. Consequently, alkyl substituents decrease the tendency of a system to be reduced due to kinetic as well as thermodynamic factors, thus enabling the following of the stepwise development of the doubly and quadruply charged species. Potassium brings the reduction process to its end, while when using sodium, which is a milder reducing agent than potassium, a kind of equilibrium is reached. It can be deduced from the NMR integration parameter that at the end of the process the ratio of doubly charged to quadruply charged systems is four to one. The significant width of the high-field band attributed to the dianion points to the existence of considerably slow electron exchange processes between the dianion and the related mono- and trianion radicals. Furthermore, the observation that no line broadening is detected in the ^{1}H NMR bands of **4b** is rationalized by assuming that the electron exchange process between the trianion radical and the aromatic tetranion **4b** is faster. The link between the rate of electron exchange phenomena and the broadening of the NMR absorptions was shown to play an important role in the course of heptalene reduction[7,20] and will be further discussed later.

The ^{13}C NMR spectrum of **4a** and **4b** consists of 14 and 16 bands, respectively, at the low-field range and two and four bands, respectively, at the aliphatic, high-field range. This number of absorptions indicates once more the coexistence of the syn and anti forms of the quadruply charged systems **4a** and **4b**, assuming an incidental overlap in the spectrum of **4a**. The ^{13}C NMR spectrum of the anionic species which result in the reaction between **3b** and potassium reveals 15 bands at the low-field range and four lines at high field. The chemical shifts of this spectrum are very similar to those obtained in the reaction of **3b** and sodium, and are presented in Table IV (Figure 4b).

1,3,8,10-Tetraphenylpyrene Tetraanion (6). The reduction of 1,3,8,10-tetraphenylpyrene (**5**) afforded a dark blue solution which was shown to contain the quadruply charged species **6** by quenching experiments with D$_2$O. The NMR properties of **6** are of particular interest, especially as they reveal some conspicuous assimilarities when they are compared with the NMR spectra of the previously described tetraanions:

(a) When **1**, **3a**, and **3b** were subjected to metal reducing agents, the disappearance of the spectral lines was almost immediate and was not accompanied by any line-broadening phenomena. Neither was the appearance of the NMR absorptions of the quadruply charged species preceded by any line broadening. In contrast, when **5** is subjected to metal, a considerable line broadening is detected in the ^{1}H NMR absorptions of the neutral system until only one very broad absorption at ~7.8 ppm is observed. After 24 h at room temperature this broad band disappears and two large absorptions centered at ~6.8 and 4.7 ppm are detected. An additional 24 h were required to afford a highly resolved proton spectrum (Figure 5). An explanation of these observations is based on a geometry modification of the tetraphenylpyrene which occurs during the reduction process, i.e., change of the relative angle between the phenyl rings and pyrene skeleton. This process, which is unlikely to occur in the rigid pyrene and in its dialkylated derivatives, might lead to slowdown electron exchange processes between the neutral and the radical anion species **5**$^{-\cdot}$ and between the trianion radical **5**$^{3-\cdot}$ and the quadruply charged system **6**. As a consequence, ^{1}H NMR line-broadening phenomena are observable while they were not detected in the case of the reduction of **1**, **3a**, and **3b** in which the exchange processes are fast.

(b) The center of gravity of the phenyl protons NMR in **6** is diamagnetically shifted by ca. 1 ppm relative to the corresponding absorptions of the neutral compound **5**. Applying the Schaefer and Schneider correlation[2] as well as $\omega\beta$-MO calculations,[17] a number of ~2 units of negative charge is deduced to be distributed over the phenyl rings, leaving only ~2 negative charges for the pyrene skeleton. Hence the high-field shift of the center of gravity of the pyrene moiety of **6**, compared to that of charged pyrene and its dialkyl derivatives (4.63 ppm vs. 5.3–5.4 ppm), is unexpected. This "enigma" can be resolved by analyzing the different resonance contributions to the various charged species. In the quadruply charged pyrene and dialkylated derivatives, the dominant resonance contribution is the delocalization of 18-π electrons in the periphery which affords an enhanced aromatic diatropic ring current. In contrast, in the tetraphenylpyrene tetraanion (**6**) a pronounced contribution of an anti-Hückeloid number (i.e., 16) of π peripheral electrons prevails. This should result in a degree of a paratropic antiaromatic effect.

(c) The quadruply charged system **6** affords a simple, easily assigned ^{1}H and ^{13}C NMR spectra (Tables V and VI, Figure 5). Their simplicity is contrary to the very complex NMR patterns of **2**, **4a**, and **4b** and should be rationalized in terms of the existence

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Table VII. ^1H NMR Chemical Shifts (ppm)[a] of 7a, 7b, 8a, and 8b

system	1, 8, 10, 17	2, 7, 11, 16	3, 6, 12, 15	*tert*-butyl
7a	8.37 (d, $J = 7.4$ Hz)	7.56 (t, $J = 7.7$ Hz)	7.78 (d, $J = 7.8$ Hz)	
8a	4.91 (d, $J = 7.48$ Hz)	5.86 (dd, $J = 7.52, 7.80$ Hz)	5.02 (d, $J = 7.8$ Hz)	
7b	8.23 (d,[b] $J = 1.6$ Hz)		7.62 (d,[b] $J = 1.6$ Hz)	1.49 (s)
8b	5.15 (d,[b] $J = 1.98$ Hz)		5.21 (d,[b] $J = 2.02$ Hz)	1.22 (s)

[a] Referred to $SiMe_4$. The numbering is as shown in Scheme IV. [b] 1-4 coupling.

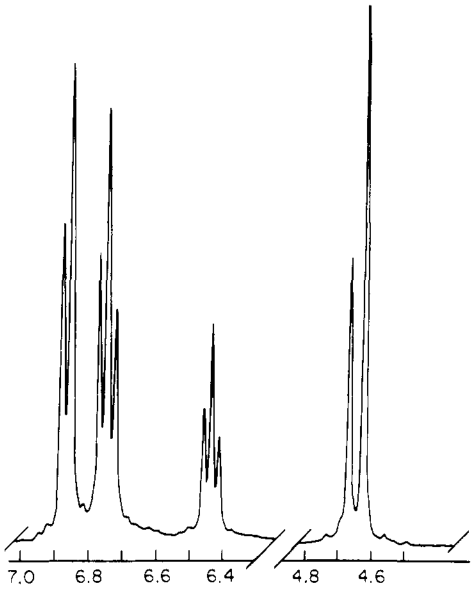
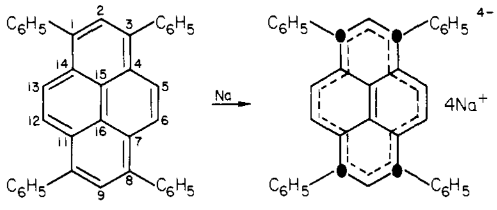


Figure 5. ^1H NMR spectrum (ppm, relative to $SiMe_4$) of 1,3,8,10-tetraphenylpyrene tetraanion (**6**).

Scheme III [18a]



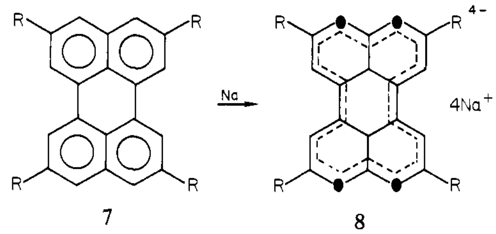
5 6

the circles represent the metal cations

of only one quadruply charged species which is endowed with high symmetry. Theoretical calculations performed on **6** show that when the charge density on the pyrene carbons linked to the phenyl rings (carbons 1, 3, 8, 10) is combined with the charge density on the phenyl ipso carbons, a higher value than the density on carbons 2 and 9 is obtained. This charge distribution is obviously different from the one encountered in the other multicharged anions. The charge distribution is in line with the spectroscopic results and gives rise to a symmetrical structure with respect to the metal cations as depicted in Scheme III.

Perylene Tetraanion (8a). The sodium reduction of the perylene system (**7a**) has already been performed[9] and the ^1H NMR absorptions of the resulting anionic species were assigned to the formation of the doubly charged system **7a**$^{2-}$. SCF-MO and $\omega\beta$ calculations which were carried on **7a**, **7a**$^{2-}$, and **8a** indicate that the nodal properties in the LUMO of the neutral perylene and in the HOMO of the doubly charged species **7a**$^{2-}$ are quite similar to those exhibited by the pyrene system. Therefore a pure 20π-18C peripheral picture of the perylene dianion is assumed. When the excess of charge is localized in the periphery, **7a**$^{2-}$ might be considered as a $4n\pi$ conjugated perimeter system, for which a substantial paramagnetic ring current would be expected. The relatively low-field ^1H NMR absorptions, with a center of gravity at 5.35 ppm, which were assigned to the dianion **7a**$^{2-}$ neither fit this expectation nor fit the high-field ^1H NMR of the pyrene dianion **1**$^{2-}$. This discrepancy tempted us to scrutinize the reduction process of the perylene species. The ^1H NMR spectrum of the purple solution formed by contact between **7a** and sodium (after one week) was identical with the spectrum reported by Lawler et al.[9] (Table VII). Quenching experiments with D_2O evinced the formation of a tetradeuteriotetrahydroperylene in high yield (m/e 260, P + 1 = 261, electron capture and chemical ionization mass spectroscopy), which is unstable and tends to oxidize in air to yield tetradeuterioperylene along with other dehydrogenated perylene derivatives (m/e 252–259).

Scheme IV [18a]



7 8

a, R = H; b, R = t-C_4H_9

the circles represent the metal cations

Summarizing the overall data the following points should be noted: (i) the relative low-field ^1H NMR of the anionic species, (ii) the perimeter contribution of $4n\pi$ electron perimeter to the doubly charged species predicted by theoretical considerations, and (iii) the quenching experiments which result in tetradeuterated species. These points lead us to conclude that the former assignment of the mentioned ^1H NMR spectrum (Table VII) to the dianion **7a**$^{2-}$ is erroneous and it should be ascribed to the quadruply charged species **8a**. The low-field absorptions of the latter are rationalized by the existence of a large contribution of a $(4n + 2)$-π electron conjugated perimeter which gives rise to an enhanced aromatic diatropic ring current. Calculations which were performed on **8a** clearly indicate that the highest electron density in this system is distributed on carbons 1, 8, 10, and 17 (Scheme IV). This distribution gives rise to a symmetrical species from the point of view of the mutual locations of the metal cations around the carbanion. This conclusion which points to a similar symmetry as revealed by the tetraphenylpyrene tetraanion (**6**) is supported by the simple ^1H and ^{13}C NMR spectra of **8a** (Tables VII and VIII). The assumed structure of **8a** is depicted in Scheme IV.

2,7,11,16-Tetra-*tert*-butylperylene Tetraanion (8b). The reduction process of 2,7,11,16-tetra-*tert*-butylperylene (**7b**) reveals similar characteristics as those observed in the reduction process of 2,9-di-*tert*-butylpyrene (**3b**). Contact with sodium metal at −15 °C for 24 h afforded a purple solution which exhibited a ^1H NMR spectrum consisting of one broad absorption centered at 1.49 ppm (Figure 6a). An additional 48 h of metal contact at room temperature were required to complete the reduction process and to afford a species with well-resolved ^1H NMR patterns (Figure 6b, Table VII). This spectrum consists of an absorption at 1.22 ppm assigned to the protons of the *tert*-butyl groups and two doublets at 5.11 and 5.22 ppm assigned to protons 1, 8, 10, 17 and 3, 6, 12, 15 (Scheme IV), respectively. The assignment is based on charge density considerations; the splitting is due to metacoupling, as shown by double resonance experiments. As in the 2,9-di-*tert*-butylpyrene (**3b**) reduction process, the high-field broad band is assigned to the doubly charged paratropic system **7b**$^{2-}$. The detection of this species becomes possible due to the influence of the *tert*-butyl groups which, as was previously dis-

Table VIII. ^{13}C NMR Chemical Shifts (ppm)[a] and Charge Densities of 7a, 7b, 8a, and 8b

system	1, 8, 10, 17	2, 7, 11, 16	3, 6, 12, 15	4, 5, 13, 14	9, 18	19, 20	quat.	methyl
7a	127.3	119.7	126.0	130.9	134.6	128.5		
8a	96.8	125.5	97.0	119.3	145.3	134.5		
7b	123.2	148.7	117.7	130.8	134.9	125.8	34.9	31.3
8b	93.4	146.8	95.9	119.4	145.8	132.1	34.1	31.5
ρ^b	0.3075	0.0898	0.2263	0.2172	0.1020	0.2165		

[a] Referred to $SiMe_4$; for numbering see Scheme IV. [b] Calculated by $\omega\beta$ for 8a.

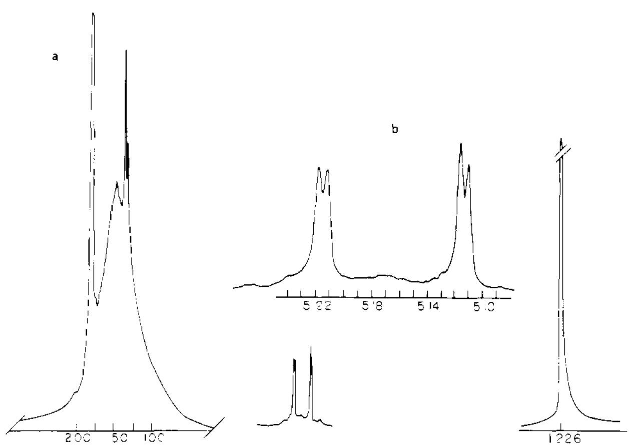


Figure 6. (a) ^1H NMR spectrum (ppm, relative to $SiMe_4$) of 2,7,11,16-tetra-*tert*-butylperylene dianion (**7b**$^{2-}$) (the band at 1.86 ppm is a solvent signal). (b) ^1H NMR spectrum (ppm, relative to $SiMe_4$) of 2,7,11,16-tetra-*tert*-butylperylene tetraanion (**8b**).

cussed, destabilize the anionic species and thus slow down their formation. The continuation of the process gives rise to the quadruply charged diatropic aromatic species. The simplicity of the ^1H (Figure 6b) and ^{13}C NMR (Table VIII) spectra indicates that the symmetry properties of **8b** (Scheme IV) are similar to those exhibited by **8a**.

The existence of the two different anionic species, the syn and anti forms of **2**, **4a**, and **4b**, is further supported by the following arguments: (i) The various factors which determine the solvation properties of alkali cation–π carbanion salts are well established.[21] These factors include the nature of the alkali cation, the temperature, the solvent, and the negative charge density in the organic moiety, which is a function of the size of the π system and the number of negative charges. Applying these factors on the quadruply charged pyrene, perylene, and their derivatives as sodium (or potassium) salts in THF at room temperature strongly indicates the dominance of an intimate contact-ion structure. This conclusion does not exclude the possibility of various types of equilibrium processes, which the solvated salts might undergo, e.g., an equilibrium between a neutral ion aggregate (tetraanion tightly paired to four cations) and charged ion pair (tetraanion paired to two cations).[22] Yet, the fact that the tetraphenylpyrene tetraanion (**6**) and the quadruply charged perylene (**8a**) do not reveal the syn and anti forms clearly shows that the observed asymmetry is not caused by such types of equilibrium processes. By the same argument we can exclude the existence of geometrical isomerism due to mututal locations of the metal cations—above or under the plane of the π system—as a source of asymmetry. Therefore we believe that the only reason for this phenomenon is the location of the cations which are tightly bound to asymmetrical positions in **2**, **4a**, and **4b** (or, in contrast, to symmetrical positions at **6**, **8a**, and **8b**). (ii) We have obtained the ^{23}Na NMR spectra of the quadruply charged systems. The ^{23}Na chemical shifts observed for all these systems are in low field relative to the chemical shift of aqueous sodium chloride, used as an external reference, indicating that the cations are located in the periphery of the carbanions and experience a deshielding effect from the induced diamagnetic ring current. However, the width of the ^{23}Na absorptions of the different species varies to a great extent. While the ^{23}Na bands of the symmetrical carbanions **6**, **8a**, and **8b** are relatively narrow (40–60 Hz width at half-height), the absorptions of the asymmetrical charged species **2**, **4a**, and **4b** are much broader (260–300 Hz). This remarkable difference is assumed to be caused mainly by the existence of two distinct "types" of cations in each of the syn and anti forms of the asymmetric systems. The different chemical shifts of the various types of cations superimpose to form the observed broad absorption. The mentioned geometrical isomerism (related to the mutual locations of the cations relative to the π plane) and the various types of equilibrium processes, which were shown to have no influence on the symmetry properties of the carbanions, might cause dissimilarities in the properties of the cations in all the charged species, thus broadening the ^{23}Na absorptions. Another important reason for the observed broad bands is the spherical symmetry distortion of the cations, caused by the organic anions (especially by those which were shown to be asymmetric). This distortion results in an enhanced quadrupole effect.[23]

Conclusions

Pyrene, perylene, and their derivatives are the first benzenoid hydrocarbons observed to undergo a four-electron reduction and yield quadruply charged systems. The conspicuous diatropic aromatic character of these tetraanions is derived from proton chemical shifts and emphasizes the significance of the peripheral electron delocalization vs. local skeletal contributions. This conclusion is of particular importance in the perylene case. Its representation as two naphthale moieties linked by long single bonds[19b] holds true for the neutral species; yet, this kind of representation is not valid for the description of the quadruply charged system due to two factors: (i) This depiction enforces a localization of two negative charges on each naphthalene moiety. Considering the fact that metal reduction of naphthalene affords only an anion radical, the local approach to the charged system seems to be most unlikely. (ii) Theoretical calculations point to a relatively low degree of bond alternation in the peripheral skeleton of quadruply charged perylene. The bonds which link the naphthalene moieties are much shorter than the respective bonds in the neutral species, thus enabling diatropic peripheral delocalization. Therefore, the generality of the peripheral model in predicting the aromaticity of polycyclic multicharged systems is clearly demonstrated.

The chemical shift parameters indicate a considerable influence of the metal cations on the π systems of those carbanions in which a tight contact ionpair situation prevails. This influence is observed in systems where the cations are asymmetrically located around the organic moiety, e.g., the pyrene and its dialkyl derived tetraanions. The lack of symmetry is induced on the anionic π systems, causing the salts to reveal a type of syn and anti isomerism, which is well observed in the ^1H, ^{13}C, and ^{23}Na NMR spectra.

Experimental Section

Materials. Pyrene (**1**) and perylene (**7a**) were purchased from BDH and Aldrich, respectively. 1,3,8,10-Tetraphenylpyrene (**5**) and 2,9-dimethylpyrene (**3a**) were kindly provided by Professor I. Agranat (Hebrew University of Jerusalem). 2,9-Di-*tert*-butylpyrene (**3b**) was prepared

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according to literature[24] procedure (mp 208 °C (lit. 206 °C). 2,7,11,16-Tetra-*tert*-butylperylene (**7b**) was prepared in the usual Friedel-Crafts alkylation procedure, using *tert*-butychloride, $AlCl_3$, and chlorobenzene as solvent (mp 312 °C from toluene). For NMR properties (^1H, ^{13}C spectra) see text and tables.

General Procedure for the Metal Reduction Process. A wire of sodium or potassium was introduced to the upper part of a prolonged NMR tube containing 10^{-3} M of the hydrocarbon dissolved in 0.8 mL of THF-d_8 (Aldrich reagent). The frozen solution of the hydrocarbon was degassed and then the tube was sealed under vacuum. By turning the tube the solution is brought into contact with the metal wire for controlled periods of time.

The NMR spectra were obtained (5-mm samples) on a Bruker WH-300 pulsed FT spectrometer operating at 300.133, 75.46, and 79.53 MHz for ^1H, ^{13}C, and ^{23}Na, respectively. The field/frequency regulations were maintained by locking to the solvent deuterium. The free induction decay signals were digitized and accumulated on an Aspect-2000 computer (32K).

Quenching Experiments. (a) A solution of the hydrocarbon **1** (1 g) in 100 mL of dry THF was cooled to −78 °C and stirred under nitrogen. A wire of sodium was introduced into the reaction flask. The resulting purple solution was cautiously allowed to warm to room temperature. Samples of 1 mL were taken from the reaction mixture after 6, 12, and 24 h and 2, 3, 4, 5, 6, and 14 days, quenched with water, and titrated potentiometrically to follow the formation of base (a Beckman zeromatic pH meter instrument). The amount of sodium was followed by atomic absorption (atomic-absorption spectrophotometer, Perkin-Elmer 403). (b) Two milliliters of dry THF were treated with sodium under nitrogen. After 2 weeks the mixtures were poured into D_2O. The compounds which resulted in the usual workup were analyzed with chemical ionization and electron capture mass spectroscopies.

Chemical ionization and electron capture mass spectroscopies were obtained with a DuPont 21-490 B single focusing instrument equipped with a commercial dual CI/EI source. Reagent gas was isobutane and the source temperature was 160 °C.

Acknowledgment. We thank Professor I. Agranat (Hebrew University of Jerusalem) for the generous gifts of 2,9-dimethylpyrene and 1,3,8,10-tetraphenylpyrene. We thank Dr. S. Zitrin, Mass Spectroscopy Unit, Criminal Identification Division, Police Headquarters (Jerusalem, Israel), for the mass spectroscopy measurements.

Registry No. 1, 129-00-0; **2A**, 80663-84-9; **2S**, 80663-85-0; **3a**, 15679-24-0; **3b**, 24300-91-2; **3b**$^{2-}$ K salt, 80664-63-7; **3b**$^{2-}$ Na salt, 80664-65-9; **4a-A** Na salt, 80663-86-1; **4a-S** Na salt, 80663-87-2; **4b-A** Na salt, 80663-88-3; **4b-S** Na salt, 80663-89-4; **4b-A** K salt, 80663-90-7; **4b-S** K salt, 80663-91-8; **5**, 13638-82-9; **6**, 80679-20-5; **7a**, 198-55-0; **7b**, 80663-92-9; **7b**$^{2-}$ Na salt, 80664-67-1; **8a**, 80663-93-0; **8b**, 80663-94-1.

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Reactions of Bi(cyclophosphazenes) with Sodium Alkoxides or Aryl Oxides[1,2]

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Abstract: Bi(cyclophosphazenes) (**2**) react with nucleophiles such as sodium trifluoroethoxide or sodium phenoxide by two alternative pathways—(a) with cleavage of the P–P ring linkage unit and cleavage of P–Cl bonds to yield organocyclotriphosphazenes (**3**) or (b) by cleavage of P–Cl bonds without rupture of P–P bonds to give organobi(cyclophosphazenes) (**6**). These latter species eventually undergo P–P bond scission with alkoxides or aryl oxides under more forcing reaction conditions. Cleavage of the bi(cyclophosphazenes) **2** or **6** also yields phosphazene anions (**4**), which react with alcohols to form hydridocyclotriphosphazenes (**5**). Treatment of these with chlorine brings about the conversion of the P–H to P–Cl units. The phosphazene anions (**4**) also react with allyl bromide with attachment of the allyl residue to the ring and with carbon tetrachloride to abstract Cl^+ and generate neutral chloroorganocyclotriphosphazene species (**9**). These interconnected processes were monitored by both product isolation and NMR spectroscopy. Appendices A and B (supplementary material) outline the interpretation of the more complex ^1H and ^{31}P NMR coupling patterns observed.

The synthesis of new, small-molecule organocyclophosphazenes underlies much of the current interest in the synthesis of new inorganic backbone high polymers. Organocyclophosphazenes are used both as models for the reactions of the analogous high polymers[3] and as "monomers" for polymer synthesis.[4] Prominent among the problems in this area is the need to find new synthesis routes for both cyclic and high polymeric phosphazenes that contain alkyl or aryl groups bonded to the inorganic skeleton through P–C bonds. One route to accomplish this end is via the reactions of halocyclophosphazenes or halophosphazene high polymers with organometallic reagents.[5–12]

We have recently described[5] how hexachlorocyclotriphosphazene reacts with a number of Grignard reagents to yield two types of organophosphazenes—one in which alkyl groups are attached as substituents to a cyclophosphazene ring and the second in which phosphazene ring coupling occurs to yield bi(cyclophosphazenes) linked by P–P bonds, with each phosphorus at the linkage site bearing an alkyl or aryl group. Such bi(cyclophosphazenes) may be models for the cross-linked high polymers that are often formed when Grignard reagents react with high polymeric $(NPCl_2)_n$. It is speculated that the crosslinks may involve P–P bonds.

Phosphorus–phosphorus bonds can be cleaved by a variety of reagents. Hence, it seemed possible that bi(cyclophosphazenes)

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