π-Conjugated polycyclic anions; interplay between topology, electronic structure and patterns of charge distribution

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Abstract: Magnetic properties of polycyclic anions serve as a probe for their mode of delocalization. These anions gain stability either by minimizing paratropicity or by gaining diatropicity. In the case of the paratropic $4n\pi$ anions, minimizing paratropicity is achieved by modification of the system's geometry or by partitioning of the charge. The anions can gain diatropicity by reorganization of their path of π-delocalization. The latter can be achieved by obeying the Randić conjugated $(4n+2)\pi$ circuits model or by delocalization of $(4n+2)\pi$ electrons along the molecular perimeter. Diindeno[cd:lm]perylene (8) and aceheptylene (7) dianions exemplify the strive to aromaticity. Dibenzo[b,g]chrysene dianion (3^{2-}) and substituted phenanthrene dianions ($4^{2-}-6^{2-}$) exemplify the minimization of paratropicity. Corannulene (19) accepts electrons to an extent where diatropicity of the anion is achieved. This leads to the formation of an aromatic tetra-anion, which represents an anion within an anion, both having $(4n+2)\pi$ perimeters.

INTRODUCTION

The thermodynamic characteristics of conjugated molecules and their magnetic properties are the basis of the experimental criteria of aromaticity and antiaromaticity [1]. While aromaticity involves enhanced stabilization of ground state cyclic π-conjugated molecules relative to their acyclic analogs, antiaromaticity refers to the unique destabilization of the cyclic system relative to its acyclic analog. Although the Hückel rule [2] was originally restricted to monocyclic systems, as was Breslow's notion of antiaromaticity [3], much interest had been stimulated on the theoretical and experimental aspects of polycyclic systems [4]. The variability of structure and topology of these systems affords an insight into the experimental criteria for aromaticity and antiaromaticity [5].

The prevalence of induced ring currents in conjugated molecules led to the establishment of magnetic criteria for aromaticity and antiaromaticity, *i.e.* diatropicity and paratropicity, respectively [6]. While diatropicity (low-field shift) serves as an efficient probe for the characterization of aromatic systems endowed with $(4n+2)\pi$ electrons (*vide infra*), there was no such efficient tool to sense antiaromaticity. The relationship between paratropicity and antiaromaticity was by no means a simple one.

Charging of π-conjugated systems, especially polycyclic hydrocarbons, can magnify the effects linked to charge delocalization patterns and therefore focus on the mechanisms by which such molecules stabilize themselves [7]. This can happen either by gaining aromaticity or by minimizing antiaromaticity. As a result of the charging process, a molecule can contain $(4n+2)\pi$ or $4n\pi$–electrons, depending on the reduction process. An aromatic ion can be formed in a process of successive one-electron reductions or oxidations up to a point where an array of $(4n+2)\pi$–electrons is achieved. Molecular rearrangements can also lead, *via* chemical transformations, to the formation of aromatic diatropic systems. If the reduction or oxidation process will result in the formation of charged paratropic $4n\pi$ "antiaromatic" species the system can gain stabilization by modification of the system's topology or by reorganization of the electron delocalization pattern. We wish to demonstrate that charged polycyclic systems strive to achieve diatropicity or to avoid/minimize paratropicity whenever possible. Phenomena such as reorganization of π-electrons or bonds, segregation of charges or excessive charging of neutral molecules can be rationalized in terms of decreasing the energy content of charged polycyclic systems.

DISCUSSION

1. Minimizing paratropicity

Dianions of annulenoannulenes have recently been prepared and used to discriminate between different modes of π-delocalization [8]. Polycyclic π-conjugated dianions were prepared and their spectroscopic behaviour in the ^{1}H- and ^{13}C-NMR spectrum has been studied in recent years [7]. It has also been shown that dianions derived from monocyclic and polybenzenoid hydrocarbons exhibit the expected π-charge distribution over the entire carbon framework within the limits set

by the charge alternation concept [9]. The extent of paratropic character exhibited by a π-conjugated anion with cyclic conjugation is said to reflect the degree of its antiaromaticity [6]. Paratropicity is evidenced by the additional high-field shifts in the proton NMR spectrum. These shifts appear in addition to the high-field shift due to shielding by the negative charge of the ions. Neutral aromatic systems endowed with a low degree of symmetry and a wide HOMO-LUMO gap (ΔE) will become paratropic as a result of a two-electron reduction process that yields dianions. This process will result in the formation of a narrow ΔE gap in the dianion. It was suggested that the extent of ΔE as obtained from Hückel MO and MNDO calculations affects the line shape and paratropicity of these dianions. A good correlation between the paratropicity and ΔE suggests a link between paratropicity and antiaromaticity [7]. When ΔE is taken into account, the spectroscopic observable paratropicity affords a good probe for the theoretical notion of antiaromaticity. Moreover, there is a relationship between ΔE of the neutral system and the dianion. The larger HOMO-LUMO gap of the neutral system results in a smaller gap of the anion. This phenomenon is reflected by the system's paratropicity and can be observed in phenanthrene, which has a larger ΔE than anthracene in the neutral $(4n+2)\pi$ hydrocarbon and is calculated to show a smaller ΔE and a higher degree of paratropicity in the dianion [6].

In view of all the above, one should expect high-field shifts in paratropic anions to be much more significant than the shift expected from the charge effect alone as calculated by using charge-chemical shift correlations [10].

Dibenzo[a,c]naphthacene (1) was reduced by alkali metals to give the respective radical ion 1⁻· and dianion 1²⁻ [11]. NMR and ESR studies showed that the dianion 1²⁻ and the radical anion 1⁻· behave as if they were composed of two separate substructures, thus indicating a segregation within the pertinent antibonding orbital. In the radical anion, the unpaired electron occupies in principle the same orbital (LUMO) as the two paired electrons of 1²⁻. The ¹H-NMR spectrum of 1²⁻ (Table 1) can clearly be divided into two parts. The high-field signals (2.7-4.7 ppm) belong to the linear "anthracene" moiety (H-C(1) to H-C(6) and H-C(15) to H-C(16)) while the low-field signals (6.6-7.6 ppm) are attributed to the angular "phenanthrene" moiety (H-C(7) through H-C(14)). The ¹³C-NMR spectrum of 1²⁻ also revealed partitioning of charge [11b]. As ¹³C-NMR chemical shifts are less prone to anisotropy effects and are very sensitive to the charge density at the carbons, they clearly show the charge partitioning in 1²⁻. Most of the charge in 1²⁻ is located in the linear part of the molecule, i.e. the "anthracene" part, while the "phenanthrene" moiety of 1²⁻ is almost neutral. As the quaternary carbon atoms are known to bear very little negative charge, or even positive charge, it is not surprising that the chemical shifts of C(4a), C(5a), C(15a) and C(16a) appear in the low-field region of the ¹³C-NMR spectrum of 1²⁻. The NMR observations also emphasize the role of charge alternation [9] in the highly charged linear section of the dianion. These results are supported by ωβ-Hückel type calculations. From these calculations the total π-charge population on the linear part of 1²⁻ is found to be -1.45 while only -0.55 units of charge are located on the "phenanthrene" component. ESR studies on the radical anion 1⁻· revealed the same proportionality of partitioning of charge, i.e. -0.74 and -0.26 units of charge residing on the linear and angular moieties, respectively [11b]. These observations are in accordance with the LUMO of 1, which is largely localized on the linear part, being populated.
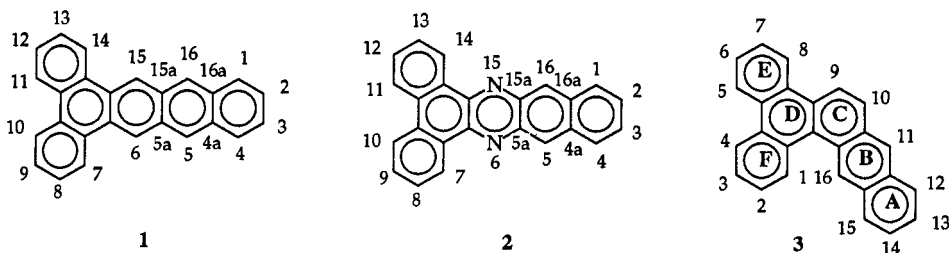

Table 1: ¹H-NMR chemical shifts [ppm][a] of 1²⁻ and 2²⁻

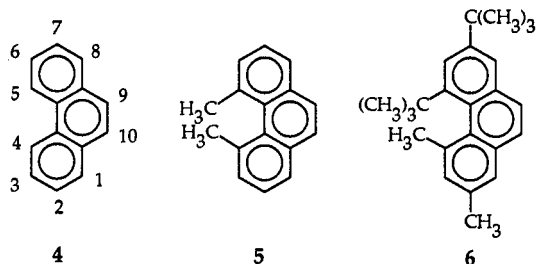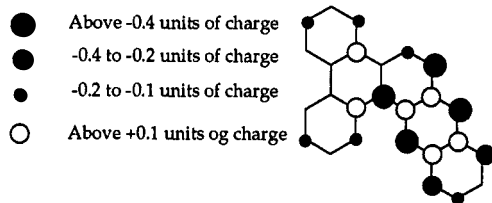| Compound	H1,4[b]	H2,3	H5,16	H6,15	H7,14	H8,13	H9,12	H10,11
1²⁻/2Na⁺	4.12	4.68	2.70	3.45	6.57	6.66	6.45	7.64
2²⁻/2Na⁺	5.71	5.71	4.49	-	7.76	7.01	6.75	8.04

[a] ppm downfield from TMS, in THF-d₈. [b] For numbering of protons see structure.

The dianion derived from tribenzo[a,c,i]phenazine (2²⁻) shows a similar charge partitioning as 1²⁻. There is some quench of paratropicity due to the heteroatoms. The ¹H-NMR signals at 8.04-6.75 ppm are attributed to the "phenanthrene" moiety H-C(7) through H-C(14), while H-C(1) through H-C(4), H-C(5) and H-C(16) appear at 5.71 and 4.49 ppm, respectively (Table 1) [12].
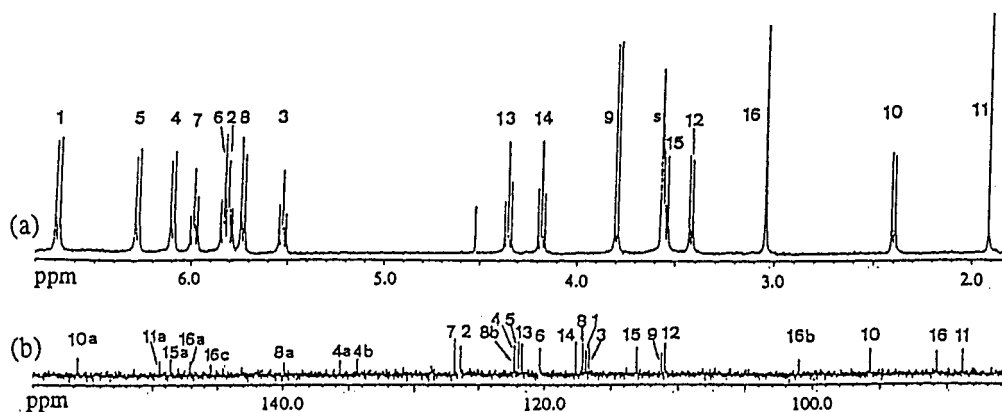
Figure 1: Proton (a) and Carbon (b) NMR spectra of 3^{2-}

In order to substantiate the suggestion that a combination of a linear and an angular component of a polycyclic dianion will show partitioning of charge and segregation of MO's, we studied the NMR spectra of dibenzo[b,g]chrysene dianion (3^{2-}) (Figure 1). This is an isomeric structure of 1^{2-} in which the relative orientation and link between the linear and angular moieties had been modified [13]. The neutral hydrocarbon was charged by reaction with lithium or sodium metal and the dianion showed the same tendency of charge segregation as was shown by anions 1^{2-} and 2^{2-}. Dianion 3^{2-} can also be divided into two moieties according to its NMR spectrum. Here too, the linear part shows a significant high-field shift (1.9-4.4 ppm, H-C(9) through H-C(16)) as compared with the NMR signals of the angular moiety (5.5-6.7 ppm, H-C(1) through H-C(8)). From the ^{13}C-NMR spectrum of 3^{2-} it can be seen that the charge distribution is not homogeneous and that most of the charge is located on the linear part in an alternate fashion. The hydrogen bearing carbons, i.e., C(9) through C(16), are negatively charged to a large extent, while the quaternary carbons C(10a), C(11a), C(15a), and C(16a) bear a very small negative or even positive charge (Scheme 1).

Scheme 1 Calculated charge densities of 3^{2-}
● Above -0.4 units of charge
● -0.4 to -0.2 units of charge
● -0.2 to -0.1 units of charge
○ Above +0.1 units og charge

4   5   6

The angular "phenanthrene" or "biphenyl" moiety remains nearly neutral. MNDO calculations [26], taking into account two lithium atoms as counter-cations, show that the most stable structure is the one where the lithium atoms are above and below two adjacent rings B and C and that the dianion is not planar. The lithium atom above ring C may have a small interaction with carbon atom C(1) and thus inducing some negative charge on carbon C(1).

This unusual charge distribution in these three 4nπ conjugated dianions can be interpreted in terms of minimization of paratropicity-antiaromaticity and seems to be a general property of such anions. When one compares the calculated HOMO-LUMO energy gap of each of the system's components, i.e. the anthracene and phenanthrene dianions, it arises that the phenanthrene dianion has a smaller ΔE than the anthracene dianion (0.231 and 0.310 β units, respectively). The Hückel ΔE value for phenanthrene is 1.20β but only 0.82β for anthracene. By forcing the electrons into the linear system, i.e., the "anthracene" moiety of 1^{2-} and 3^{2-}, the charged system is then combined of an anthracene dianion and a neutral phenanthrene moiety, thus the total paratropicity is reduced and destabilization due to antiaromaticity is minimized. In other words, the more stable (4n+2)π system (phenanthrene) will afford a less stabilized 4nπ system (phenanthrene dianion) and vice versa. In the case of 1^{2-} and 3^{2-}, this charge distribution also enables an efficient charge alternation in the dianion [9,13], that helps to stabilize the linear component of 1^{2-} and 3^{2-}.

Paratropicity can be minimized also by geometrical deformation within the molecular skeleton. In a way, this is the opposite phenomenon to the well-known planarization which occurs in cyclooctatetraene when it accepts two electrons in order to gain aromaticity [14]. In this route of minimizing antiaromaticity the molecule is not divided into two subsystems, each fully conjugated, but the entire π-conjugation all over the molecule is minimized by reducing the π-orbital overlap, achieved by out-of-plane deformations of the molecular skeleton. This phenomenon can be clearly observed when charging small helicenes, e.g. 4,5-substituted phenanthrenes. Phenanthrene (4) itself is planar in its neutral state and shows aromatic

nature. By reducing it with lithium or sodium, a dianion which possesses a very high paratropicity, is obtained [7]. Theoretical calculations (MNDO) predict that phenanthrene dilithium salt is not planar and has a twist angle C(4)-C(4a)-C(4b)-C(5) of *ca.* 19 degrees [15]. The predicted helicity has not yet been confirmed experimentally. However, by enforcing helicity on the neutral skeleton, one should be able to trace the role that helicity plays in the paratropic nature of the backbone of the phenanthrene dianion.

Substituents at positions 4 and 5 sustain a high steric hindrance and thus enforce deformation of the phenanthrene system to form a helicene [15]. The bulkiness of the substituents at positions 4 and 5 determines the degree of distortion from planarity (Table 2).

Table 2. The influence of the spatial structure of $4n\pi$ polycyclic helicene dianions on their ^{1}H-NMR spectra and calculated twist angle.

Compound	δ 9-H.10-H[a]		Calcd twist angle $\theta°$ (MNDO)		NMR parameters[a,b]
	Hydrocarbon	Dianion	Hydrocarbon	Anion	
4	7.83	-1.14	2	19.87	0.62 (d, 2H, 1- and 8-H, J=6.5)
					0.80 (d, 2H, 4- and 5-H, J=5.7)
					2.75 (t, 2H, 2- and 7-H, J=6.5)
5	7.57	1.23	36.86	58.82	2.40 (d, 2H, 1- and 8-H, J=6.3)
					3.62 (d, 2H, 3- and 6-H, J=6.3)
					4.32 (t, 2H, 2- and 7-H, J=6.3)
6	7.59	2.49d	42.21	74.04	2.87, 3.07 (s, 1H, 1H, 1- and 8-H)
	7.87d	2.28d			4.15, 4.54 (s, 1H, 1H, 3- and 6-H)
	(J=2 Hz)	(J=2 Hz)			1.23, 0.73 (s, 9H, 9H, t-Bu)
					1.42, 0.84 (s, 3H, 3H, Me)

[a] NMR spectroscopic data for Li salts given in ppm relative to TMS; THF-d_8 line at δ 3.67 taken as standard.

[b]δ Values and coupling constants (J values in Hz) for the anions (9- and 10-H data not included in this column).

4,5-Dimethylphenanthrene (5) has a twist angle of θ=36.8°, while its dilithium salt has a twist angle of θ=58.8° (both as calculated by MNDO). The chemical shift of the protons at the 9-10 positions is much less shifted to high-field than the observed shift for phenanthrene dianion itself ($\Delta\delta_H$=6.34 vs. 8.97 ppm). The carbon atoms to which these protons are attached, *i.e.* carbon atoms at the 9,10 positions still bear a very similar charge density as in 4^{2-}. 2,4-Di-tert-butyl-5,7-dimethylphenanthrene (6) has a twist angle of θ=42° in its neutral state. The calculated angle for the dilithium salt is 74°. Here, the 9,10 protons appear at 2.49 and 2.28 ppm and the $\Delta\delta_H$ is 5.1 and 5.59 ppm, respectively, as compared to the neutral hydrocarbon. The charges on the 9,10 carbons of 6^{2-} are very close to the charges on the carbons of 5^{2-}, and phenanthrene dianion (4^{2-}). This deviation from planarity of even the parent dianion 4^{2-} may reflect the tendency of minimizing paratropicity by reducing the degree of overlap of orbitals in the $4n\pi$ system.

From all the above it can be concluded that the less planar the molecule, the lesser is the extent of its paratropicity. This can be accounted for by the poorer π-orbital overlap.

2. Gaining aromaticity

Since antiaromaticity is unfavorable, whenever aromaticity can be achieved, the charged system may find routes leading towards aromaticity. These routes can either be electronic reconfiguration of the system, or bond rearrangement or both. In some systems the route by which aromaticity may be gained is simply addition of electrons to the system by excessive charging. As already mentioned, the most comprehensive definition of the numerous definitions and criteria suggested to define aromaticity is the one based on the energy content of aromatic systems. Dewar [17] has defined aromatic molecules as cyclic species with a large resonance energy in which all the atoms in the ring take part in a single conjugated array. In other words, aromatic systems sustain a cyclic π-electron delocalization which reduces the energy content of the systems relative to that of corresponding model compounds without cyclic delocalization. Similarly, antiaromatic systems reveal a cyclic π-electron delocalization which leads to a strong destabilization and therefore to a high energy content in respect to analogous acyclic compounds [2]. As a criterion of aromaticity or antiaromaticity, it is difficult to apply this energetically based definition in practice. The more practical definitions can be classified into two general groups: criteria based on purely theoretical concepts and those which refer to experimentally observable phenomena. The peripheral criterion suggested by Platt [18] exemplifies the first group of definitions by assigning aromatic character to a cyclic or polycyclic system with $(4n+2)\pi$-electrons in its periphery. Systems with $4n\pi$-electrons in the path of conjugation would be inclined to reveal antiaromatic properties, while those with $(4n+1)$ or $(4n+3)$ peripheral conjugated π-electrons would be estimated as nonaromatic. This structural. concept is based on the free electron theory and treats crosslinks and inner sp^2 carbons as small

perturbations. The most useful definition among those which relate to experimentally observable phenomena is based on magnetic anisotropy [7].

By electronic reconfiguration we mean that the path of π-conjugation is changed as a consequence of the reduction process to achieve aromaticity, and not just to minimize antiaromaticity. A good example for this tendency of charged systems to arrange themselves in an aromatic array can be found in the dianion derived from Hafner's aceheptylene (7) [16].

Aceheptylene (7) itself is a cyclic polyolefinic system that hardly shows an aromatic character as can be monitored by its ^{1}H-NMR spectrum (Table 3); most protons of 7 absorb at relatively high-field (5-6 ppm) which is very characteristic of vinylic protons. However, the ^{1}H-NMR spectrum of 7[2-] shows a total low-field shift of the proton's center of gravity as compared to 7, despite the addition of two negative charges. This diamagnetic shift could only be accounted for by the formation of an aromatic species. From ωβ-Hückel type calculations it can be predicted that electrons which accommodate the LUMO will be located to a large extent on the central carbon atom (C(13)). This prediction can clearly be verified by the ^{13}C-NMR spectrum of 7[2-] (Table 4). As a consequence of the proximity of the negative charges, elongation of the bond distances should occur and thus decrease the π-conjugation through these bonds. The peripheral 14π-electron system exhibits an aromatic character, as is clearly reflected in the ^{1}H-NMR spectrum of 7[2-].
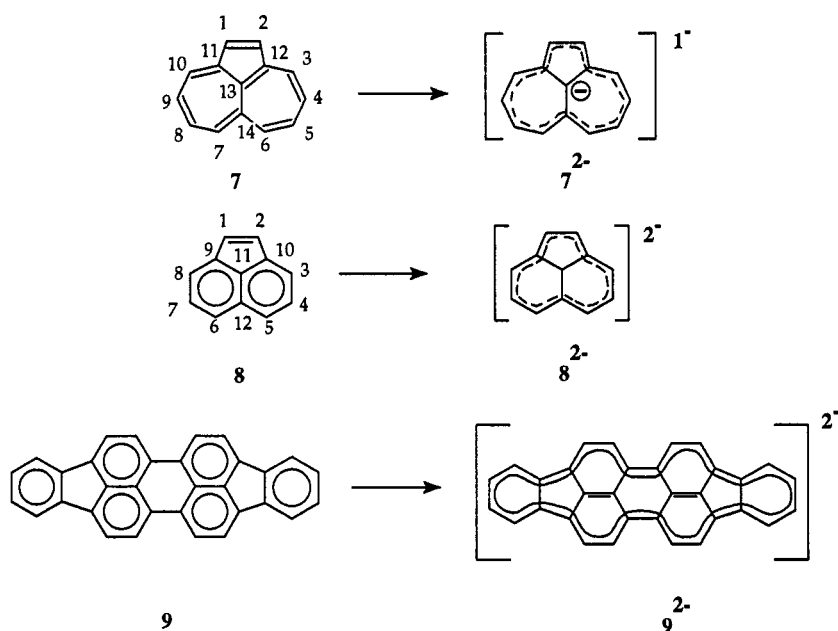
A somewhat different situation may be found in the dianion of acenaphthylene (8[2-]) [16]. Here the two extra electrons resulting from the reduction will be delocalized over the perimeter and the central carbon atom (C(11)) will remain uncharged. This pattern of delocalization is in contrast to the neutral compound in which the aromaticity is gained by delocalization only over the naphthalene moiety; ωβ-Hückel calculations, however, predict very small LUMO coefficients for the central carbon atom. Thus electrons occupying this MO would be delocalized only over the perimeter. Therefore, the NMR spectrum of 8 is interpreted in terms of 11 carbons 13π-electron system, affording a nonaromatic dianion.

The pericondensed system diindeno[cd:lm]perylene (9) [19] illustrates the validity of two approaches of π-delocalization patterns which can be applied to the same carbon skeleton. The neutral molecule appears to comply with the Randić conjugated circuits model [20], as it is a diatropic system despite having 28π-electrons in the periphery. The ^{1}H-NMR spectrum is centered at 8.00 ppm and points towards its diatropicity. Calculations (ωβ) also predict a bond lengthening of the bonds which connect the fluoranthene moieties [19]. Treatment of 9 with sodium metal in THF-d$_8$ yields a two-electron reduction product. The formed dianion is also diatropic (7.75 ppm, center of gravity of the spectrum) despite the addition of only two electrons to a diatropic molecule [10]. In this case the dominance of a peripheral (4n+2)π-system of 26π-electrons in the perimeter may account for the diatropicity of the dianion. Calculations (ωβ) show that 9[2-] has a HOMO exhibiting a nodal plane through the central carbon atoms. Both 9 and 9[2-] demonstrate that the π-electron distribution mode will be the one that results in diatropic aromatic nature, as was pointed out in detail also in the case of 7[2-]. It seems that the aforementioned tendency of conjugated systems to acquire aromaticity, or to remain aromatic is a general one. It suggests that the mode of π-electron distribution that prevails in a system and determines its charcter is the one that results in aromatic nature and reduces antiaromatic contributions. Thus, when the two theoretical criteria predict different results, the one that should be adopted is the criterion that assigns a prevailing aromatic contribution, or a reduced antiaromatic character.

Table 3: ^{1}H-NMR Patterns[a] of **7** and **7**[2-]

	H1,2	H3,10	H4,9	H5,8	H6,7	[1]H center of gravity of the heptalene moiety	Overall ^{1}H center of gravity
7	6.98 (s)	6.71 (d,*J*= 9.1 Hz)	5.19 (dd,*J*= 10.6,8.9 Hz)	5.79 (dd,*J*= 11.8,8.6 Hz)	5.36 (d,*J*= 12.0 Hz)	5.77	6.00
7[2-]	7.08 (s)	6.54 (d,*J*= 9.3 Hz)	6.75 (t,*J*= 9.0 Hz)	5.76 (t,*J*= 9.1 Hz)	7.61 (d,*J*= 9.1 Hz)	6.66	6.75

[a]ppm, referenced to Me4Si; for numbering, see the schemes.

Table 4: ^{13}C-NMR Patterns[a], Charge Densities, and Relevant Orbital Coefficients in **7** and **7**[2-].

	C1,2	C3,10	C4,9	C5,8	C6,7	C11,12	C13	C14
7 δ (^{13}C)	123.3	142.6	120.9	140.4	132.5	135.1	153.1	158.9
charge density[b]	-0.0867	0.0450	-0.0136	0.0539	0.0013	-0.0674	0.0422	0.0930
LUMO coefficients[b,c]	0.1160	0.3356	0.0005	0.3897	0.1406	0.1387	0.4415	0.4137
HOMO coefficients[b,d]	0.2829	0.1578	0.3626	0.0758	0.3235	0.3913	0.0	0.0
7[2-] δ (^{13}C)	112.4	97.1	121.1	91.4	119.7	123.9	85.6	114.7
charge density[b]	-0.1422	-0.1432	-0.0865	-0.1870	-0.1021	-0.1525	-0.2178	-0.1555

[a] ppm, referenced to Me4Si; for numbering, see the schemes.

[b]As obtained from ωβ calculations.

[c]The ortbial into which two electrons are added in the reduction process.

[d]The orbital out of which two electrons are subtracted in the oxidation process.

Aromaticity can sometimes be gained by an unexpected bond rearrangement of an unstable anion. Such a rearrangement takes place when deprotonation of tribenzocyclooctane (**10**) occurs (Scheme 2) [21]:

Scheme 2
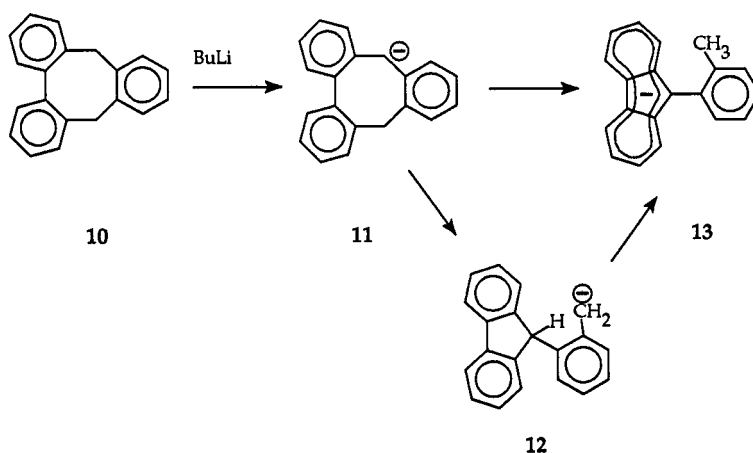
After the mono anion **11** is formed from **10**, the base does not abstract another proton to give the fully conjugated dianion that could have been derived from **10**, but instead, an intramolecular aromatic substitution reaction takes place. Probably, this reaction takes place via the formation of the benzylic anion **12** as an intermediate, leading to the much more stable aromatic fluorenyl anion **13**.

The same rearrangement occurs when tetrabenzo[a,de,h,kl]bicyclo[6.6.0]tetradecane (14) reacts with excess of butyllithium in HMPT (150°C, 1h, N_2)(Scheme 3). The dianion 15 exhibits very similar ^1H and ^{13}C-NMR spectra to those known for the dianion of dibenzo[cd,gh]pentalenide (16^{2-}). In 16^{2-} all the extra charge is located on the peripheral carbons and not on the two central carbons. This array gives a 14π-electrons aromatic charged system [21].

Scheme 3

14   15   16
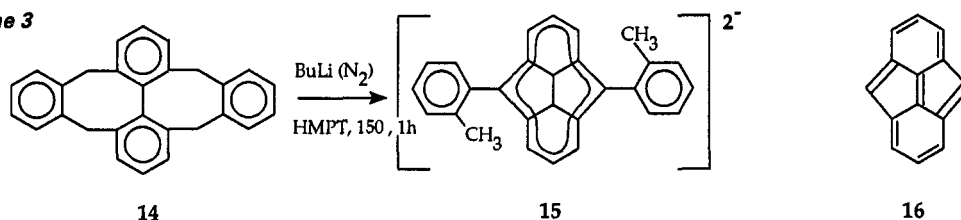
Finally, aromaticity can be gained (or regained) by successive charging, *i.e.* formation of highly charged systems with an aromatic electronic array. The formation of aromatic-diatropic tetraanions is not uncommon. Octalene (17) was shown by Vogel and Müllen [22] to form the tetraanion 17^{4-} *via* a successive four electron reduction by an alkali metal. This dianion has a D_{2h} symmetry. The tetracyclic acepliadylene (18) first synthesized by Boekelheide [23] also gave a tetraanion upon lithium reduction. This tetraanion prepared by Müllen [24], fulfils Platt's approach [18] concerning polycyclic π-conjugated systems as it has 14π-electrons in its perimeter.
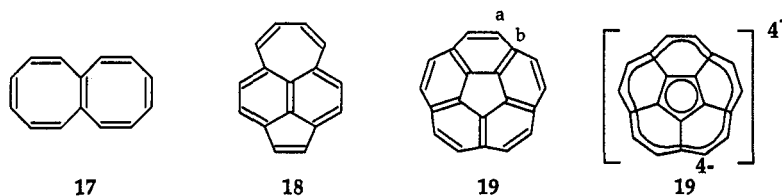

17   18   19   19

Figure 2

Table 5: ^1H and ^{13}C-NMR parameters[a] of 19 and 19^{4-}

Nucleus	19	19^{4-}/4Li$^+$
^1H	7.95	6.95
^{13}C (hub)	136.9	112.4
^{13}C (rim (a))	128.1	89.8
(rim (b))	132.3	95.1

[a] ppm, relative to TMS, in THF-d_8

Corannulene (19) is an aromatic bowl-shaped hydrocarbon [25a]. Its ^1H-NMR spectrum consists of one line at 7.95 ppm, indicating a diamagnetic ring current on the perimeter. This evidence may suggest that the corannulene can be visualized as a negatively charged five-membered ring within a [15]-annulene cation rim [25b], and having a total of 20π-electrons. One can expect that by the reduction of 19 to its corresponding dianion, aromaticity can be achieved by a full delocalization of all 22π-electrons over the entire molecule, *i.e.*, modifying the mode of π-delocalization. Since corannulene is not planar this route may result in some planarization of the bowl. Planarization should be involved with an increase of steric hindrance. However, MNDO [26] as well as Hückel calculations show a two-fold degeneracy for the LUMO's. This arrangement of MO's may suggest easy four successive electron transfer processes to form a tetraanion. Indeed, the reduction of corannulene (19) by lithium in THF affords an anion that shows a very high shift of its ^{13}C resonances (Table 5, Figure 2) with $\Sigma\Delta\delta_{C_i}$ value of -720 ppm. Using a K_C value of 180 ppm/e [10] it suggests that the corannulene system bears four extra electrons, thus being a tetraanion (19^{4-}). The degree of charging is supported also by the quench reaction with water, that leads to the tetra-hydro derivative as the main product. The ^1H-NMR spectrum of this lithium salt (19^{4-}) shows a very moderate shift to high-field. This is accounted for by the new aromatic annulene that is formed that consists of an inner pentadienyl anion within a 15-carbons, 18π-electrons annulene rim. This charge distribution is supported also by MNDO calculations of the lithium salt of 19 where all lithium atoms are located on top of four outer rings from the outside of the bowl. The average charge on the hub's carbons is -0.22 units of charge. The average charge on the rim's hydrogen bearing carbon atoms is also -0.22 units of charge for each, while on the remaining five quarternary carbon atoms at the rim the average calculated charge is -0.14 for each atom [27].

CONCLUSIONS

Magnetic properties of polycyclic anions served as a tool for the study of their modes of charge delocalization and molecular geometry. Reorganization of the paths of electron delocalization occurs whenever a $(4n+2)\pi$ array can be achieved. On the other hand, when only $4n\pi$ systems can be obtained, minimization of paratropicity takes place. Such a minimization can be achieved either by structural deformation or by segregation of charge and MO's. A remarkable molecular rearrangement affords a highly strained dibenzopentalenide dianion derivative (15), thus exhibiting the strive towards aromaticity. The formation of corannulene tetraanion (19^{4-}) demonstrates the domination of aromatic stabilization over the Coulomb repulsion induced by four negative charges.

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