π-Conjugated Anions: From Carbon-Rich Anions to Charged Carbon Allotropes

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Stable π-conjugated anions are formed in the reaction of π-conjugated systems with alkali metals. Reactivity, aromatic properties and aggregation of the anions are described. Bowl-shaped and fullerene anions, as well as helicene and planar polycyclic anions, are discussed vis-à-vis their aromaticity and charge delocalization pattern.

Introduction

Anions derived from the reactions of neutral, fully π-conjugated hydrocarbons with alkali metals such as Li, Na, K, Rb, and Cs were first studied some 85 years ago.[1,2] The study of charged π-conjugated systems represents a bridge between physical organic and theoretical chemistry. With the recent discovery of novel π-conjugated molecules such as fullerenes and nanotubes, a renewed insight into the charge distribution, magnetic properties, and electronic structures of these materials revived interest in the field.

The chemical preparation of the carbanions of conjugated π-systems is being carried out in two principal ways.

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

The main method involves the preparation via an electron transfer process by alkali metals. The second involves an electron shuttle which is by itself a reduced hydrocarbon that acts to transport electrons to insoluble systems. In both cases, the reduction leads to various degrees of charging, ranging from monoanions to hexaanions and even to higher charged species. In an alternating fashion some of these species have paired electrons and are diamagnetic, some have odd number of electrons and are thus paramagnetic. The various species can be studied by magnetic resonance spectroscopy, optical spectroscopy, X-ray diffraction and via photoinduced ET reaction in which solvated electrons are involved. Experimental criteria for charge distribution and aromaticity are derived from the NMR parameters, and the local chemical shifts differences allow the determination of the charge distribution pattern. The number of π-electrons involved in a conjugated system influences the HOMO/LUMO gap; this may lead to electronic states that are close to one another.[3] The magnetic properties of aromatic species serve as an experimental criterion for aromaticity-antiaromaticity.[4] Thus in annulenes with $(4n+2)$π-electrons in their perimeter the signals of the outer protons will be shifted in their NMR spectrum to a low field and the signals of the inner protons to a high field.[5] Systems with $(4n)$π-electrons show the opposite behavior. Simple annulenes, cyclophanes and annulenes within annulenes e.g. corannulene and Kekulene,[5] show such a behavior.

The formation, the mode of charge distribution, the storage and transport of charge, the thermodynamic behavior, and the reactivity of a wide range of novel π-conjugated polyanions are described herein. It has been suggested that the ability of a system to maintain a peripheral ring current is quenched as the perimeter of the system increases beyond a certain size. Marked changes in ring currents are observed with symmetry variations in the topology of the charged annulenes (e.g. **1–4**, vide infra). While the simple annulenes are not strictly defined as polycyclic systems, inner-cavity bond formation can afford such systems in which both annulenic and polycyclic behaviors are maintained. One such system is the corannulene **5**. However it should be noted that for polycyclic π-systems, a correlation between aromatic character and the total number of π-electrons does not always exist. In principle, destruction of the central core by bond breaking would ultimately afford a classical polycyclic helicene, to which no annulenic behavior could be attributed. Proceeding from simple annulenes to helicenes and to planar polycyclic hydrocarbons, unlike in the case of corannulene itself, the ability of the system to accept electrons in a stepwise reduction process depends, inter alia, on the ability of the individual building blocks to transport the imposed charge among themselves. Stilbene, and its higher styrylbenzene homologues, make up the first group of small, fully conjugated hydrocarbons, reduction of which affords insight into the interchain charge transport operative through olefinic bonds, as in the case of polyenic annulenes. The oligoarylenes, on the other hand, act as reductive precursors for the synthesis of small helicenes and planar polycyclic hydrocarbons. The topological relationship that

exists between the subunits in the arylenes or in the olefin-bridged systems can either quench or favor electron transfer. Electron transfer to multi-charged arylene systems often results in reductive cyclizations and the formation of small helicenes. Extreme charge localization may be best exhibited in larger helicenes, which make up the third part of this review. As in the helicenes and arylenes, through-space interactions and electron hopping can provide greater control over the electron-transfer process in the case of annulenes and cyclophanes. Increasing the carbon-to-hydrogen ratio by going from annulenes to corannulene **5** results in drastic alterations in the electronic behavior of the system. Further expansion of the carbon framework to the ultimate carbon allotropes C_{60} and C_{70} and to graphite provides a fascinating insight into potential systems exhibiting unique optical and electrical properties. In each case ion-solvation equilibria should not be overlooked.

The Effect of the Counterion and of π-Delocalization Patterns in Charged Cyclophanes: Cyclophanes as Annulenes

As a direct consequence of the simple topology of annulenes, their orbital energies can form a closed shell with an orbital sequence exhibiting characteristic regularities.[3] In even-membered rings, the orbitals occur in degenerate pairs (except for the energetically lowest and highest levels, which are both nondegenerate); thus, a $(4n+2)$π-system is characterized by a stable closed shell. Bond length alternation associated with Jahn-Teller distortion also leads to closed shells in $(4n)$annulenes.[4] The reduction of annulenes allows a straightforward alternating interconversion of $(4n)$ and $(4n+2)$π-systems, and thus can be used as a good model for theory and spectroscopy.[5] The increased number of π-electrons involved in a conjugated monocycle influences the HOMO/LUMO gap, thereby leading to distorted ground state configurations.

Annulenes with aromatic rings built into the perimeter have become readily available by means of multiple Wittig reactions.[6] [2.2.0.2.2.0]Paracyclophane[7] **1** has a rigid backbone with a well-defined ring configuration. The neutral cyclophanes, which formally have 32 π-electrons $(4n)$ around the periphery, can be regarded as normal aromatic compounds with no significant contributions from the large conjugated perimeter. Hückel calculations predict a set of nondegenerate LUMO and NLUMO (0.288β and 0.480β, respectively), in accordance with the lower symmetry of **1** relative to a simple π-conjugated polyenes. Annulene **1** can therefore be expected to yield stable di- and tetraanions upon reduction.

Semiempirical calculations predict that **1** and **2**[8] should maintain fairly planar π-structures in the charged forms. This suggests that the reduction is accompanied by a considerable geometrical change, as well as by an increased barrier to rotation of the benzene rings about the adjacent single bonds. Such large, stable, cyclic anions, with fairly planar conjugated π-system, can be expected to exhibit unusual magnetic properties.

1   2   3

4   5   6

7   8   9

C_{60} C_{70}
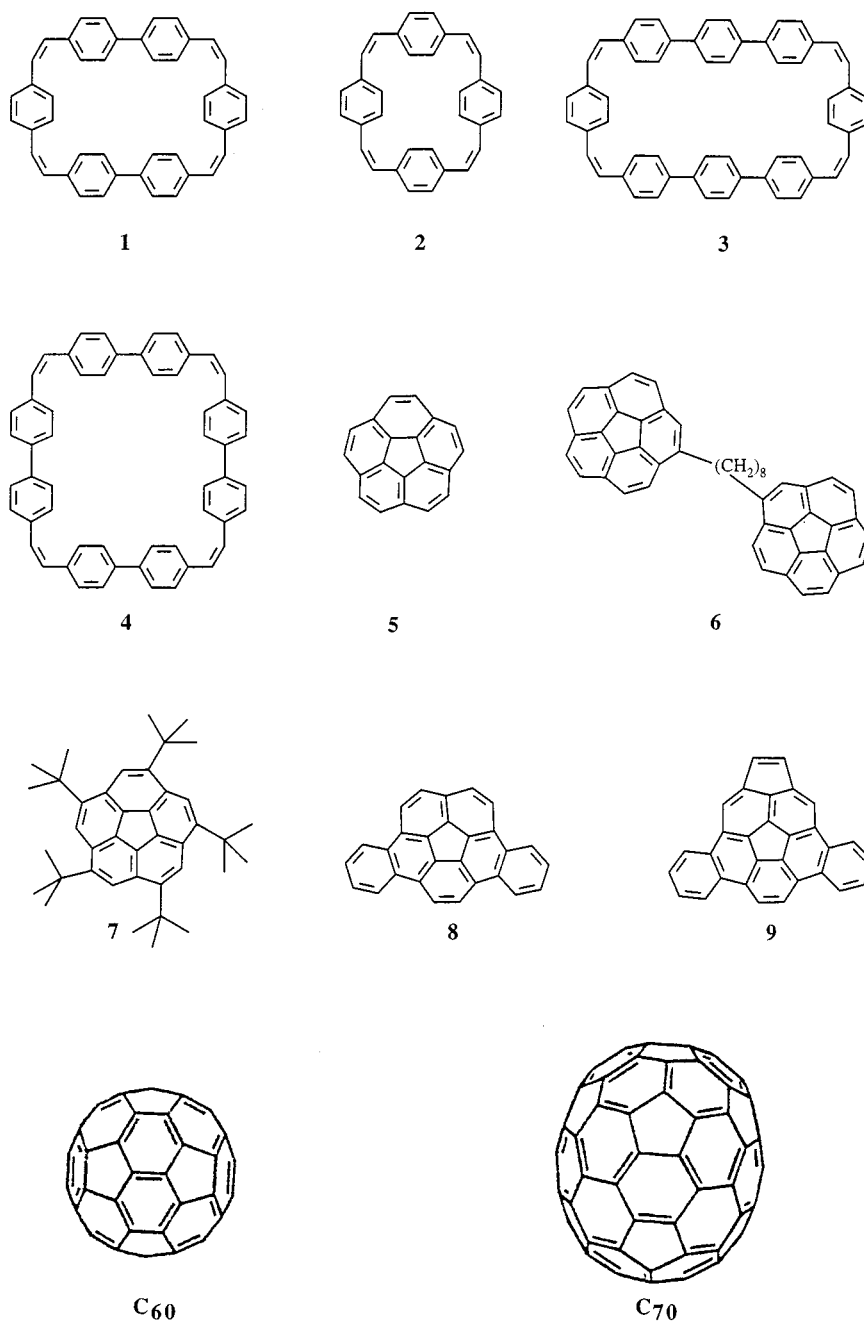
Cyclophane **1** was first synthesized and reduced with lithium[6] and potassium.[9] Careful contact with lithium metal at low temperature (195 K) led to a temperature-dependent ¹H-NMR spectrum, which was assigned to the dianion of **1**. As a result of the strong diatropic ring current, the signals of the inner protons are shifted to higher field, while an opposite effect is exerted on the peripheral protons.

Further contact of **1**²⁻ with the metal did not yield the expected tetraanion. The stable dianion was the only species detectable in solution. Quenching the dianion with oxygen yielded the starting material as the sole recovered product.

The reduction of **1** with potassium, however, proceeded differently. The peripheral ring current effect of the dianion

of **1** with potassium, as reflected in the change in proton chemical shifts, was dramatically enhanced relative to that in the dianion with lithium.[9] It is to be expected from the polarizing power of the counterions that they may influence the mode of the π-charge distribution within the anion. Any perturbations in the cyclic π-conjugation are predicted to partly quench the observed ring current effects. The small lithium cation is more effective in attracting the π-charge and thus in decreasing the ring current effect of the perimeter. Hence, the most extreme shift differences for the inner and outer protons are achieved by potassium reduction. However, the influence of the reducing metal on the charged cyclophane is found to be weaker when we move to systems with smaller perimeters. Cyclophane **2**, which

was first synthesized and reduced using lithium,[6a] yielded stable di- and tetraanions.[10] The dianion of **2** with the better reducing metal (potassium) appears immediately after a brief contact with the metal, but, in contrast to **1**, both lithium and potassium salts exhibit very similar ^{1}H- and ^{13}C-NMR spectra.[9]

Further reduction of **1**[2−] with potassium produces a new ^{1}H-NMR spectrum, attributable to the tetraanion.[9] Addition of four electrons to the periphery of the neutral system renders the system anti-aromatic (36 π-electrons). Due to improved conjugation, the tetraanion is characterized by a stronger than expected paramagnetic behavior, and a greater change in chemical shift is observed for the inner protons. In the case of **2**, reduction with potassium led to the formation of the tetraanion only after an extended reaction time. This unstable tetraanion gives rise to a very weak, broad ^{1}H-NMR spectrum, while no ^{13}C-NMR spectrum could be detected. Besides differences in their stabilities, the tetraanions of **2** with both lithium and potassium as counterions behave similarly with only minor differences in their chemical shifts.

Further reduction of **1**[4−] with potassium led to the disappearance of the spectrum, presumably as a result of the formation of a new paramagnetic species. Quenching of all anions of **1** (**1**[2−], **1**[4−], **1**[.5−]) with oxygen quantitatively afforded the starting material and thus supports the assumption that the final stage of charging was indeed a more highly reduced species (radical-penta anion).

The subtle competition between electronic stabilization and coulomb effects is influenced not only by the distribution of the π-charge within the substrate, but also by its interaction with the counterions and the solvent. While the reduction of **2** with lithium led to stable di- and tetraanions,[10] the reduction with potassium yielded a stable dianion, and only after a long contact with the metal did further reduction to the unstable tetraanion occur. The opposite behavior was found in cyclophane **1**. While the reduction with lithium stopped at the dianion, cyclophane **1** could be reduced with potassium to its tetraanion and even further. Such a situation, where small polycyclic compounds yield stable anions with lithium while larger systems prefer a heavier alkali metal like potassium has been previously observed.[11] The explanation is based mainly on the differences in ion pairing equilibria and the capability of the lithium cations to aggregate and to stabilize the anions.

Polycyclic anions exist in solution as rapidly equilibrating mixtures of solvent-separated and contact ion pairs, the ratio of which is very sensitive to the experimental conditions.[12] In anions with efficient π-charge delocalization, such as annulenes, it is accepted that solvent separated ion pairs are favored.[13] The efficiency of reduction of small systems with lithium is influenced by the relatively high charge density, and hence the tendency of lithium cations to form stable anions. As we move to larger polycyclic systems, it is not the reduction potential of lithium but the stability of the lithium salt that is formed in the early reduction state that impedes further reduction. However, with potassium metal, where a stable structure cannot be formed

in the initial stage of reduction, the reductive ability depends on whether the system is large enough to accommodate the extra charge and on whether it can be surrounded by the larger potassium cations. This ability usually leads to stable, highly reduced hydrocarbons.

The [7]Li chemical shifts of the lithium counterions have been shown to be sensitive to the mode of ion pairing. Cations located directly above the plane of the carbanion would lie in the shielding region of a diatropic system; consequently, the [7]Li chemical shift can give us an indication of the degree to which the lithium cation resides in the internal cavity of the compounds. In dianions **1**[2−] and **2**[2−], we find [7]Li chemical shifts of $\delta = 4.7$ and $\delta = 2.0$, respectively. It seems that while the internal cavity becomes more spacious, the preferred location of the lithium cations is still above the cavity, but closer to the molecular plane. Larger rigid cyclophanes, such as **3** and **4**, can accommodate the cation closer to the center of their cavity and are thus expected to show extreme chemical shifts to low or high field depending on the magnetic properties of the π-system.

Corannulene: A Representative of Curved π-Systems

The carbon framework of corannulene **5** represents the polar cap of buckminsterfullerene. It is not until C_{20} is reached that the C_{60} fragments acquire the most interesting feature of buckminsterfullerene, i.e. its curvature.[14,15] As model compounds for fullerene anions, curved-surface corannulene derivatives are of great interest. The progression from smaller to larger charged fragments on the fullerene surface allows a better understanding of fullerene-like anions. As these highly strained curved molecules represent a compromise between strain and conjugation, the nature of the aromaticity in these systems is of great interest.

Although the synthesis of **5** was achieved by Barth and Lawton in 1966,[16] this interesting bowl-shaped hydrocarbon remained relatively inaccessible prior to the studies of Scott et al.[17] and two alternative synthetic routes reported by Siegel[18] and Zimmermann[19] due to the difficulty of the original method. The ^{1}H-NMR spectrum of **5** consists of one line ($\delta = 7.93$, THF, 298 K), indicating a diamagnetic ring current about the perimeter. It was first found[20] that reduction of **5** with excess lithium metal in [D$_8$]THF leads to a series of three color changes, to green, purple, and finally brownish-red. The ^{13}C-NMR spectrum corresponding to the final stage shows three bands ($\delta = 86.8$, 95.1, and 112.4) at very high field compared to those of the neutral hydrocarbon ($\delta = 127.9$, 132.3, and 136.9). The total change in chemical shift of $\Sigma\Delta\delta = 722$ ppm, as well as quenching experiments that resulted in tetrahydrocorannulene as a major product, provide convincing evidence for the quadruply-charged system, **5**[4−]. The ^{1}H-NMR spectrum of **5**[4−], however, consists of a single line at $\delta = 6.95$. In view of the high electron density in the tetraanion, such a low field chemical shift points to a significant induced diamagnetic ring current effect. The "annulene-within-an-annulene" model first suggested for **5** by Barth and Lawton[16,21] nicely describes the tetraanion as a system that has particu-

lar stability as an aromatic cyclopentadienyl anion (6e/5C) surrounded by an aromatic (18e/15C) annulenyl trianion. This charge distribution was supported by MNDO calculations on the lithium salt of **5**,[22] and thus demonstrates the domination of aromatic stabilization over the Coulomb repulsion induced by four negative charges. However, molecular orbital calculations,[21] carried out at both the semiempirical AM1 and ab initio levels, suggest that the tetraanion structure may be more complicated than the highly symmetrical "anion-within-a-trianion" model. The ab initio calculation suggests somewhat less than the 1.0 excess electron density within the central ring that would be required for this model.[21,23]

Analysis of the quenching product, tetrahydrocorannulene,[24] by NMR spectroscopy shows clearly that, as expected, one proton is attached to the hub while the other three are attached to the perimeter, and hence supports the annulene model.[24]

At the time of these earlier studies on **5**, there was no evidence to suggest that the corannulene tetraanion, with its four lithium cations, might exist as a dimer. Although the structure of **5** seems ideal to allow close packing and attractive π-π interactions, the crystal structure of the neutral compound does not show any degree of bowl-stacking.[15] However, an interaction between **5** and its radical cation **5•+** in the gas phase had been observed.[25] MNDO calculations,[8] including the lithium cations of what, at that stage, was believed to be a monomeric tetraanion, yielded a global minimum where all four lithium cations reside on the convex face of a bowl-shaped tetraanion.

The first evidence for the formation of dimers of the corannulene tetraanion was provided by studies on derivatives of **5**.[26] Owing to their lower symmetry, dimers of monosubstituted corannulene tetraanions are expected to exhibit supramolecular stereochemistry, existing in *meso* and *d,l* dimeric forms. Reduction of *tert*-butyl-**5** with excess lithium metal in [D8]THF leads to two sets of alkyl groups in almost equal abundance, thus pointing to the presence of tightly bound dimers. Compelling evidence for dimerization comes from the successful detection of a "mixed dimer" between **5**⁴⁻/4Li⁺ and *tert*-butyl-**5**⁴⁻/4Li⁺.[26] Diffusion measurements[27] on **5** show a significant decrease in the self-diffusion coefficient of the tetraanion, indicating an increased solvation of the anion, association of the cations, and self-aggregation.

The ⁷Li-NMR spectrum of **5**⁴⁻ recorded at a low temperature (210 K)[26] features two signals of equal intensity (δ = –4.5 and –11.7). These chemical shifts represent two different types of lithium cations: one sandwiched between the two tetraanion decks (CIP) and one on the outside (SSIP). The addition of lithium bromide causes an averaging with the broad (SSIP) ⁷Li signal at low temperature, but not with the sharp ⁷Li signal (CIP).[26] This phenomenon provided further support for the dimeric nature of **5**⁴⁻. At higher temperatures (e.g. 260 K), the Li cations all exchange, resulting in a single line at δ = –8.1.

Although the geometries of the corannulene components in these dimers could not be gleaned from NMR experiments, semiempirical MNDO molecular orbital calculations[28] clearly favored a "stacked-bowl" geometry (convex face to concave face). The equivalence of the four external lithium cations was accounted for in terms of rapid intermolecular exchange. However, to explain the equivalence of the two corannulene units, it was necessary to propose a rapid bowl-to-bowl inversion of both corannulene decks. The validity of this proposal was supported both theoretically[26] and experimentally.[29]

Due to its doubly-degenerate, low-lying LUMO, the corannulene dianion **5**²⁻ was thought to be paramagnetic.[8] However, a Jahn–Teller distortion led to the eventual detection of ¹H- and ¹³C-NMR spectra of the dianion.[30] The extreme high-field shifts of the protons (δ = –5.6) are typical of molecules with a paratropic ring current[31] and can be explained by the "annulene model", where a cyclopentadienyl anion (6e/5C) is placed in the center of an antiaromatic (16e/15C) annulene perimeter.

The temperature-dependent behavior of the proton spectrum, which is no longer seen at high temperature ($T >$ 230 K), was attributed to mixing of a low-lying triplet state into the electronic structure of the corannulene dianion with increased temperature.[30] Such temperature-dependent ¹H-NMR behavior has been reported previously for polycyclic anions.[32]

Despite the two extra electrons in its backbone, the ¹³C-NMR spectrum of **5**²⁻ shows three single peaks (δ = 120, 154, and 204) at low field relative to those of the neutral compound. The extremely low field signal of the quaternary hub carbon (δ = 204) can be explained by the strong deshielding effect of the outer antiaromatic ring current.

Quenching of the dianion with water affords dihydrocorannulene as the major product, as well as some tetrahydrocorannulene and corannulene due to an electron transfer process. Assignment of the dihydrocorannulene signals shows that the two protons reside on the perimeter.[33] The ⁷Li-NMR spectrum of **5**²⁻ features only one broad absorption around δ = 3.3–3.7 (T = 173–220 K), showing only a small temperature effect, which is typical for loose ion-pair structures (SSIP).[34] Based on its magnetic behavior (¹H-, ¹³C-, and ⁷Li NMR), it was concluded that **5**²⁻ exists as a monomer with two associated lithium cations.

The radical anion and the tri-radical anion of **5** are both paramagnetic species and so can be followed by EPR. The EPR spectrum of the corannulene mono-radical anion **5•⁻** shows an 11-line hyperfine pattern (αH = 0.157 mT) for the ten equivalent protons.[35,36] Differences seen with potassium and lithium as counterions are negligibly small.[30] Counterion couplings were observed in the triradical anion lithium species.[36]

The trianion radical of **5** with lithium (**5•³⁻**) shows a highly resolved EPR spectrum where additional ⁷Li (and ⁶Li[36]) couplings are evident [g = 2.0025, αH = 1.62 mT, α⁷Li (I = 3/2) = 0.04–0.10 mT].[30] As no change in the characteristic hyperfine pattern could be observed in the EPR spectra of the trianion radical over the entire reduction process from the di- to the tetraanion, a dimerization process for the trianion can be ruled out.

The detection and characterization of all four reduction stages with lithium metal allows the delineation of a full reduction path for corannulene, which indicates that the formation of the dimer takes place only at the tetraanionic stage.[30] Following the early studies on the corannulene anions, it was accepted that lithium is the only alkali metal that can produce the highly charged tetraanion due to its tendency to aggregate. Recently,[30] however, we have succeeded in detecting the ^{1}H- and ^{13}C-NMR spectra of di- and tetraanions of corannulene with all alkali metals other than sodium (sodium was the only metal with which the reduction terminated at the dianion stage).

In view of the formation of the octalithium dimer of corannulene 5, the two corannulene units bridged by an alkane chain in 1,8-dicorannulenyl octane 6[24] can be expected to provide a pre-organized sandwich in the charged form. Such an organized system reduced with alkali metals could thus be expected to form either *intra*- or *inter*molecular sandwiches. Similar to the reduction of 5, the reduction of 6 with lithium, potassium, and cesium led to the paramagnetic tetraanion (bis-dianion) followed by the appearance of a diamagnetic octaanion, while reduction with sodium stopped at the tetraanion.[24]

The ^{7}Li-NMR spectra of 6[8-] show similar behavior as seen for 5[4-]. The two signals seen at low temperature (δ = −4.5 and −11.5) coalesce at 275 K to give one sharp line (δ = −8.3). The calculated barrier for the exchange process in 6[8-] ($\Delta G^{\#}_{275}$ = 13.7 kcal/mol) is somewhat higher than that in the case of 5[4-] ($\Delta G^{\#}_{265}$ = 13.2 kcal/mol) and may point to further stabilization of the charged species.

The question of *inter*- vs. *intra*molecular interaction in 6[8-] was investigated by diffusion measurements and by competition studies, i.e. aggregation with free 5. Both experiments pointed to an *intra*molecular sandwich formation.[24]

Despite its considerable curvature, 5 is surprisingly flexible. The bowl-to-bowl inversion barrier has been determined by NMR methods to be $\Delta G^{\#}_{230}$ = 10.2 ± 0.2 kcal/mol.[29] In 6, each methylene unit of the bridge can, in principle, serve as a diastereotopic probe for the bowl-to-bowl inversion process of the corannulene units. The barrier for the bowl-to-bowl inversion in 6 is found to be $\Delta G^{\#}_{230}$ = 10.9 ± 0.3 kcal/mol. Using a remote methylene group in 6, which is sufficiently distant from the effect of the induced magnetic field of charged moieties yet still sensitive to the bowl-to-bowl inversion process, enabled us to determine the bowl-to-bowl inversion barriers in 6[4-]/4K[+] and 6[4-]/4Cs[+] ($\Delta G^{\#}_{230}$ = 8.8 ± 0.3 kcal/mol and $\Delta G^{\#}_{230}$ = 9.2 ± 0.3 kcal/mol, respectively).[37] These low barriers can be rationalized by taking into account the better conjugation and thus the closeness to planarity of the highly charged systems. For all octaanions of 6, the dynamic behavior points to low barriers, as was suggested in the initial study of the corannulene tetraanion.[26]

In the reduction of 1,3,5,7,9-penta-*tert*-butyl-corannulene 7 with lithium, four reduction stages are observed.[38] The paratropic dianion and the diatropic tetraanion resemble the behavior seen with 5. In the final stage of the reduction, however, three distinct tetraanionic species could be detected; the two sandwich-type diastereomers, as in 5, and another species assigned as a tetraanionic monomer (which slowly disappears).

Dibenzo[*a,g*]corannulene 8[39] and dibenzo[*a,g*]cyclopenta[*kl*]corannulene 9[40] are extended corannulenes with extra conjugated five- and six-membered rings. These compounds are extended subunits of C_{60} with 28 and 30 carbon atoms, respectively, in which the bowl-type structure is maintained. The additional five-membered ring in 9 leads to a significant increase in curvature relative to 5.[41] The potential energies[11] for the LUMOs of 8 and 9 (semiempirical AM1 calculations) are calculated to be −1.180 eV and −1.558 eV, respectively, even lower than in the case of 5 (−1.028 eV). In 8 and 9, as in 5, the LUMO is nondegenerate, but there is only a small energy gap between the LUMO and the NLUMO (0.22 eV and 0.62 eV, respectively), which thus allows the formation of highly reduced species.[42] The reduction products of 8 and 9 show a dependence on the reducing metals as well as on the π-array of electrons. With lithium, 8 and 9 could not be reduced to a tetraanion as disappearance of the spectra occurs. The total change in the carbon chemical shifts in 8[2-] and 9[2-] with lithium were $\Sigma\Delta\delta$ = +50 ppm and $\Sigma\Delta\delta$ = −178 ppm, respectively ($Kc_{(exp)}$ = +25 and −89 ppm per unit of charge, respectively). These values are markedly different from those obtained for 5[2-] ($\Sigma\Delta\delta$ = +366 ppm and $Kc_{(exp)}$ = +183 ppm). It thus seems that the strong paratropic effect that operates in 5[2-] and leads to very low-field shifts in its carbon spectrum is absent in 8[2-] and 9[2-]. Such behavior is reasonable, since the magnitude of a paramagnetic ring current is known to be inversely related to the size of the HOMO–LUMO gap,[43] and the gap for these dianions increases in the order 5[2-] < 8[2-] < 9[2-]. The $Kc_{(exp)}$ values of 8[2-] and 9[2-] are a characteristic feature of polycyclic systems.[43c] The external fused rings, mainly the five-membered ring in 9[2-], exert a strong charge-withdrawing effect. In 8[2-] and 9[2-] there is a distortion of the "annulene behavior", although some annulenic effect of the internal five-membered ring, especially in 8[2-], is still present. Reduction of 8 and 9 with potassium leads first to the dianions, and then new spectra are seen due to the corresponding tetraanions. Both 8 and 9 behave similarly upon reduction, although their different π-topologies give rise to opposite characteristics in the magnetic field (NMR). The center of gravity of the chemical shifts in the ^{1}H-NMR spectrum of 8[4-] is shifted to lower field (center of gravity at δ = 6.32) relative to 8[2-] (center of gravity at δ = 3.51), reflecting the diatropic (4n+2)π character of this new species. The center of gravity of the ^{1}H chemical shifts of 9[4-] appears at higher field (center of gravity at δ = 5.58) than that of 9[2-] (center of gravity at δ = 6.93), as can be expected for a (4n)π system (antiaromatic).

There is an obvious difference between the behavior of 5 and that of the extended corannulenes 8 and 9 in the reduction reaction. While the reduction with lithium led to the most stable tetraanion of 5, the tetraanions of 8 and 9 were only produced with potassium. This behavior can be ex-

plained by the tendency of 5^{4-} to dimerize, unlike the monomeric forms of 8^{4-} and 9^{4-}.[11]

Benzannelation of corannulene modifies the π-topology and the charge delocalization pattern so that the anions no longer behave as annulenes within annulenes. Compounds **8** and **9** have the characteristics of large polycyclic systems with some annulenic character rather than the highly pronounced annulene character of corannulene **5**.

Helical π-Conjugated Anions

As a result of severe steric interactions between the terminal benzene rings, the helicenes[44] adopt a spiral configuration with C_2 symmetry.[45,46] The smallest of the helicene series is phenanthrene **10**. Computational studies of the degree of helicity in phenanthrene point to the fact that upon reduction to the dianion (10^{2-}), planarity is disrupted, with the bay dihedral angle increasing from complete planarity to 15.8°.[47] Phenanthrenes substituted at the bay region, i.e. at C^4 and C^5, such as in **11** and **12**, afford the smallest neutral helicenes.[48] The effect of nonplanarity on the properties of the charged systems in these helicenes was studied by comparing neutral and charged **13**. The racemization of **13** having a diastereoscopic isopropyl marker at the bay region position C^4 yielded a free-energy barrier ($\Delta G^{\ddagger}$) for the racemization process of 22.2 kcal mol^{-1}. For 13^{2-}, the calculated barrier was 15.4 kcal mol^{-1}. The most important
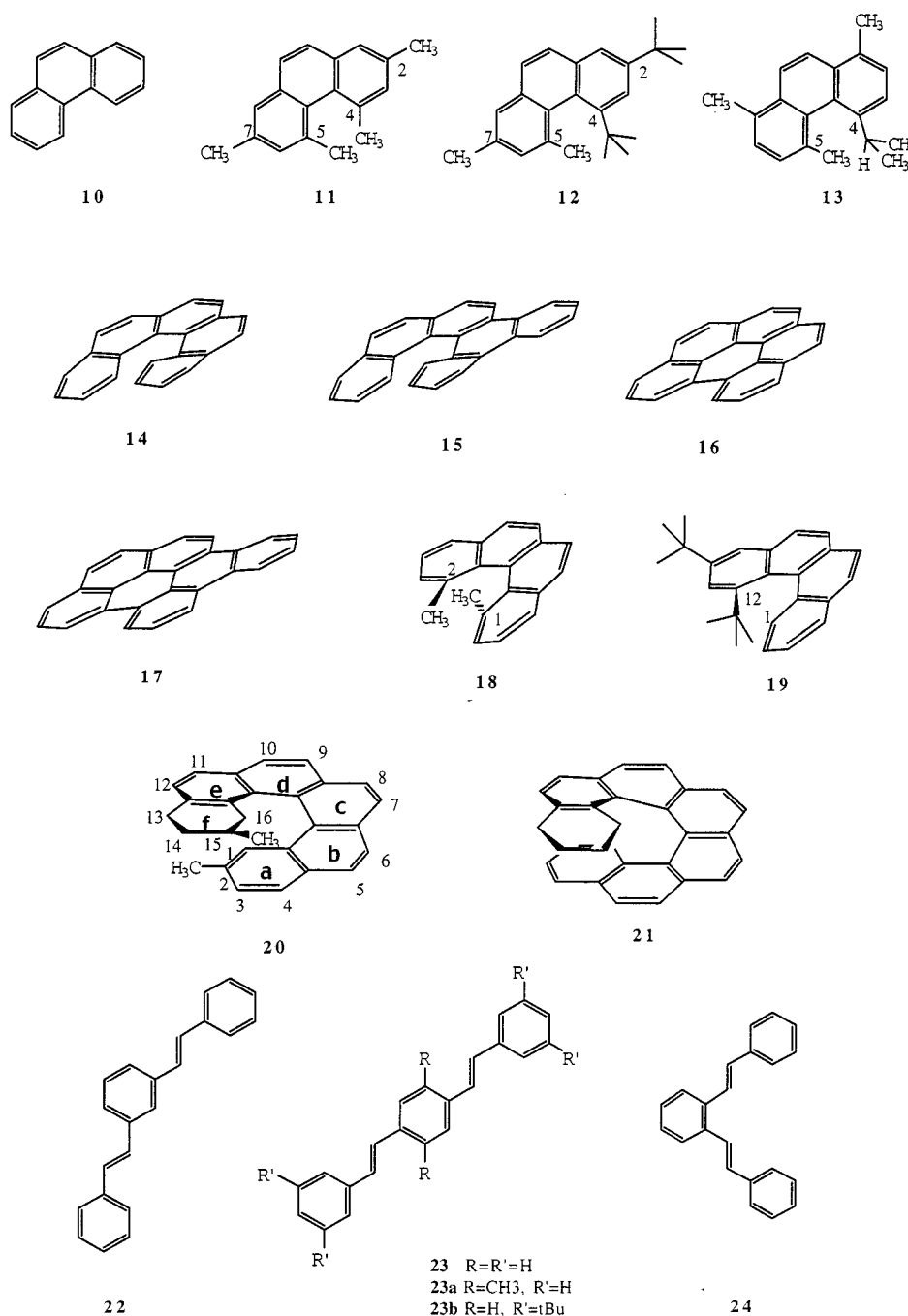
structural parameter obtained from the theoretical study of the racemization of **13** was the twist angle of 38.34° for the bay region carbons. The coplanar configuration of the bay region of **13** does not permit the methyl group at C^5 and the isopropyl group at C^4 to exchange positions. Such a coplanar transition state for racemization requires a calculated free energy of ca. 36 kcal mol^{-1}. It was therefore concluded that the transition state involves complex movements. The dianion may adopt a planar structure, thus allowing better delocalization, or it may induce localization resulting in a twisted configuration. The decreased barrier for the racemization observed in the dianion is a direct consequence of the C^9–C^{10} bond elongation.[49] Similar bond elongations are observed in all other helicene anions.

The paratropic shifts and the line shapes of the signals in the ^{1}H-NMR spectra of the substituted phenanthrene dianions can be used as probes for determining the antiaromaticity of the systems. On going from **10**$^{2-}$ to **11**$^{2-}$ or **12**$^{2-}$, the ^{1}H-NMR lines become much narrower and a highly resolved spectrum can be recorded. Dianion **10**$^{2-}$/2Na$^+$ shows no spectrum, even at –70 °C, while with lithium a well-resolved spectrum is observed. A significant narrowing of the lines is observed for **11**$^{2-}$. When sodium is used, the spectrum of **11**$^{2-}$ at –70 °C consists of narrow lines with no apparent spin-spin couplings. The lithium salt of **11**$^{2-}$ gives a well-resolved spectrum, even at room temperature. Dianion **12**$^{2-}$, however, shows spectra at higher temperatures with both sodium and lithium. The diatropicity of the system is said to be independent of the helicity, as observed from the changes brought about by different substituents at the bay positions C^4 and C^5. However, in the $(4n)\pi$ charged systems, a relationship between the paratropicity and the helicity has been established. Since antiaromaticity requires an efficient delocalization, as does aromaticity, the twisting of the system quenches its antiaromatic properties.[32,50]

Higher homologues of **10**, such as pentahelicene **14** and benzo[a]pentahelicene **15**, are reduced to stable dianions, further electron transfer afforded the cyclization products **16** and **17**, respectively, as shown in Figure 1.[51] Alkyl substitution at positions C^1 and C^{14} of **14** or further arene annelation at the terminal positions of the pentahelicene prevent such cyclizations and allow the isolation of reduced states. The inability of helicenes **14**, **15**, **18**, **19**, **20**, and **21** to bear a large excess of charge is evident from their reduction only to dianions.[52,53] Comparison with systems of similar size, which are capable of producing highly charged anions, as is the case in corannulene **5**, requires an explanation. Due to the helicity of the system and the close proximity of the terminal benzene rings, charge distribution is incapable of depositing electron density at the far ends of the molecule. As a consequence, coulombic repulsions between the charged layers result in the relocation of charge at the central rings of the helicene units, which in turn prevents the storage of further imposed charge. This explanation is borne out by the localization patterns observed in the ^{1}H-NMR spectra of **18**$^{2-}$, **20**$^{2-}$, and **21**$^{2-}$ as compared with their neutral analogues. For a similar reduction step of helicenes,

the average change in proton chemical shifts seems to depend both on the size of the helicene (charge per carbon), and the degree of helicity (intensity of paratropicity effect). In 1,12-dimethyl[4]helicene **18**, there are only four benzene rings in the framework and a relatively low helicity. Thus, **18**$^{2-}$ is expected to be paratropic [$\Delta\delta_H$(average) = –4.63 ppm]. In charged 2,15-dimethyl[6]helicene **20**$^{2-}$, although the framework is larger, the degree of paratropicity increases [$\Delta\delta_H$(average) = –6.36 ppm]. Three significant chemical shifts are worth pointing out in the ^{1}H-NMR spectrum of **20**$^{2-}$. The chemical shifts of H^1/H^{16}, H^8/H^9, and H^7/H^{10} exhibit total shifts of –7.81, –9.35, and –7.77 ppm, respectively. Such significant paratropic effects, especially for H^8/H^9 and H^7/H^{10}, point to charge densities residing on the corresponding carbon atoms, besides the strong ring current present in the planar portion of the molecule. The high-field shift observed for H^1/H^{16} does not stem from the increased paratropicity of the system, but rather from the relative positioning of the two protons with respect to the terminal rings **A** and **F**.
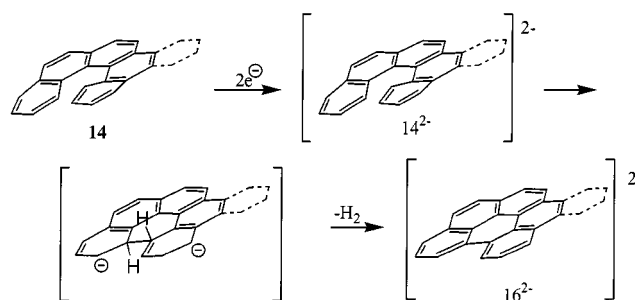

Figure 1. Reductive cyclization of [5]helicene **14**

[7]Helicene **21**, having the largest skeleton, exhibits the smallest paratropic effect among the three dianions. Only one strong paratropic shift of –8.16 ppm is observed in the system due to H^1/H^{18} residing at the ends of the helicene. This shift stems from the relative positioning of the protons in the ring system, as is the case for H^1 and H^{16} in **20**$^{2-}$.

Cross-Conjugated Aromatics: Extended Stilbenes

Much interest has been focused on the design of organic systems that are capable of storing and transporting charge. Effective conjugation through the molecule should result in a single extended system with a significantly altered HOMO–LUMO gap. Such a system may be described by a single potential minimum. Interruption of the resonance mobility by introducing conjugative insulators or saturated bridges results in a certain degree of uncoupling of the bonded subunits, with the degree of conjugation between them being dependent on the inter-ring bond.[54]

Localization of charge in a hydrocarbon with extended conjugation can be achieved by restricting the topology.[55] Furthermore, excess charge residing on a polymer can be confined to a segment made up of only a small number of building units. The behavior exhibited by the oligomeric segment should be closely related to that of the polymer.[56] Such is the case with *meta*-distyrylbenzene **22**$^{2-}$, in which the excess charge is localized on just one of the stilbene

units.[57] While the reduction of **22** to a tetraanion can be attributed to the absence of resonance conjugation through the *meta* topology, the reduction of *para*-distyrylbenzene **23** to a tetraanion is based on the ability of **23** to fold through an *s-trans/s-cis* mechanism.[58] Such a mechanism causes an interruption in the charge delocalization of **23**[2–] and facilitates the introduction of a second pair of electrons, as shown in Figure 2. The electronic distribution in **23**[4–] exhibits fully quinoidal characteristics as compared with that in dianion **23**[2–], where some charge localization remains. Substitution of the alkyl groups as in **23a** or **23b** quenches the folding mechanism, and thus both compounds afford only dianions.[58,59] The rather puzzling finding that the *ortho*-distyrylbenzene **24** is capable of accepting four electrons with reduction to the tetraanion has been explained in terms of the cation solvation effect.[60] With the close proximity of the two olefinic bonds, the two charge centers of **24**[4–] are better solvated by the cationic shell, thus **24** is a better electron acceptor than **23**.
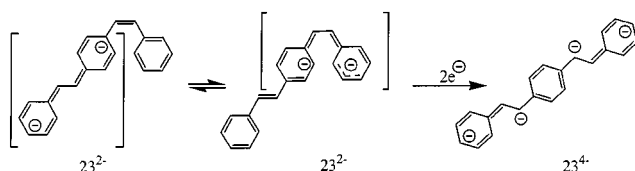

Figure 2. Reduction of a *p*-distyrylbenzene polaron to a tetraanion

EPR and electron absorption studies of higher homologues such as **25** seem to support the evidence gathered in the study of the disubstituted systems **22–24**. No spectral dependence on chain length was found in the absorption spectra of the *meta* series. In all cases, the absorptions at lower wavelengths resembled those of the stilbene radical anion. Whether the conjugation present in the system is restricted by substitution, as in **22**, or by spontaneous folding, such as in **23**, the basic polaron segment that is charged is the stilbene unit.

Anions derived from cyclophanes such as **26**, **27**, and **28** are unique in the sense that possible through-space interactions can strengthen their charge storage properties.[61,62] The forced proximity of the charged cyclophane decks results in a migration of the charge to the molecular periphery. Reduction of **27** and **28** leads to tetraanions with all alkali metals utilized.[59] Although there are slight differences in the chemical shifts, the charge distribution with Na, Li, or K is practically the same. The total ^{13}C-NMR chemical shift order of Na > K > Li points to a different behavior of the system under SSIP (lithium salt) and CIP (potassium and sodium) conditions, which is supported by UV/Vis studies. Slow rotation of the phenyl groups is apparent. Charge density distribution along the *p*-distyrylbenzene segment in **27**[4–] is identical to that observed in **23a**[2–]. Stepwise reduction of the cyclophanes studied by electrochemistry begins with the introduction of the first electron into one of the decks, followed by introduction of a second electron into either the already charged deck or the neutral segment. Fast and efficient electron hopping facilitates the formation of a triplet-state paramagnetic diradical species.

As the two other electrons are introduced, a doubly-charged two-deck cyclophane tetraanion is obtained. The ^{7}Li-NMR spectrum exhibits only a single peak for the lithium cation at $\delta_{Li} = -1.1$. The appearance of only one signal does not necessarily indicate a fully symmetric positioning of the four lithium atoms, but may more correctly attest to a fast exchange on the NMR time scale.[63,64] Semiempirical calculations, however, indicate that the lithium cations are situated near the olefinic bonds. The structure in which the cations are closer to the cyclophane center is higher in energy.[8]

The derivatives *trans*-**29** and *cis*-1,2-bis(9-anthryl)ethylene **30**, synthesized utilizing McMurry[65] and Wittig reactions, respectively, were reduced to the corresponding di- and tetraanions and characterized at low temperatures.[66] The NMR spectral data clearly showed the two dianions **29**[2–] and **30**[2–] to be identical. Likewise, the tetraanions were found to be identical. This points to the fact that the two compounds undergo significant conformational changes, with one common intermediate conformation, at each of the reduction stages. With the NMR spectra of the dianions **29**[2–] and **30**[2–] exhibiting extra signals compared to those observed for the neutral species, the existence of an averaged planar conformation is evident. At the tetraanionic stage, further conformational changes take place in the system. The ^{1}H-NMR spectra of **29**[4–] and **30**[4–], as compared with those of the corresponding dianions, point to the increased symmetry of the tetraanion. Under quenching conditions, the tetraanion originating from both **29** and **30** produces only the *trans* isomer **29** with no trace of **30**.[66] The fact that the reduction process produces planarity in the dianion and nonplanarity upon further reduction to the tetraanion suggests that there are significant changes in the charge distribution patterns in the two species, as shown in Figure 3. Electrochemical reduction[67] of **29** revealed no interaction between the anthryl subunits ($E_2 - E_1 = 0$). In **33**, however, a potential difference of $E_2 - E_1 = -0.21$ V was measured, indicating a greater interaction between the anthryl units. Similar results were obtained when the Stokes' shifts were considered for both compounds, indicating that **33** possesses a more planar conformation.[68] Despite **33** maintaining a less favorable electronic topology, the release of strain as compared with the 9,9′-substitution of **29** minimizes the energy difference between the aromatic and quinoid forms, thus allowing for better conjugation through the inter-ring bond.

Reduction of compound **32** affords the highly charged hexaanion.[66] The preceeding dianion and tetraanion stages are triplet anions, which are paramagnetic in character and hence NMR inactive. The highly charged hexaanion **32**[6–] was found to exist in the all-*trans* configuration, with most of the imposed charges residing on the external anthryl subunits. The charge distribution pattern exhibited by **32**[6–] is similar to those observed in the tetraanions **29**[4–] and **30**[4–].

The isolation of long-lived polyanions such as **32**[6–] is of great interest, not only due to its electron-storage capabilities, but also in view of the selectivity of the process. While many carbon-rich systems are incapable of storing more
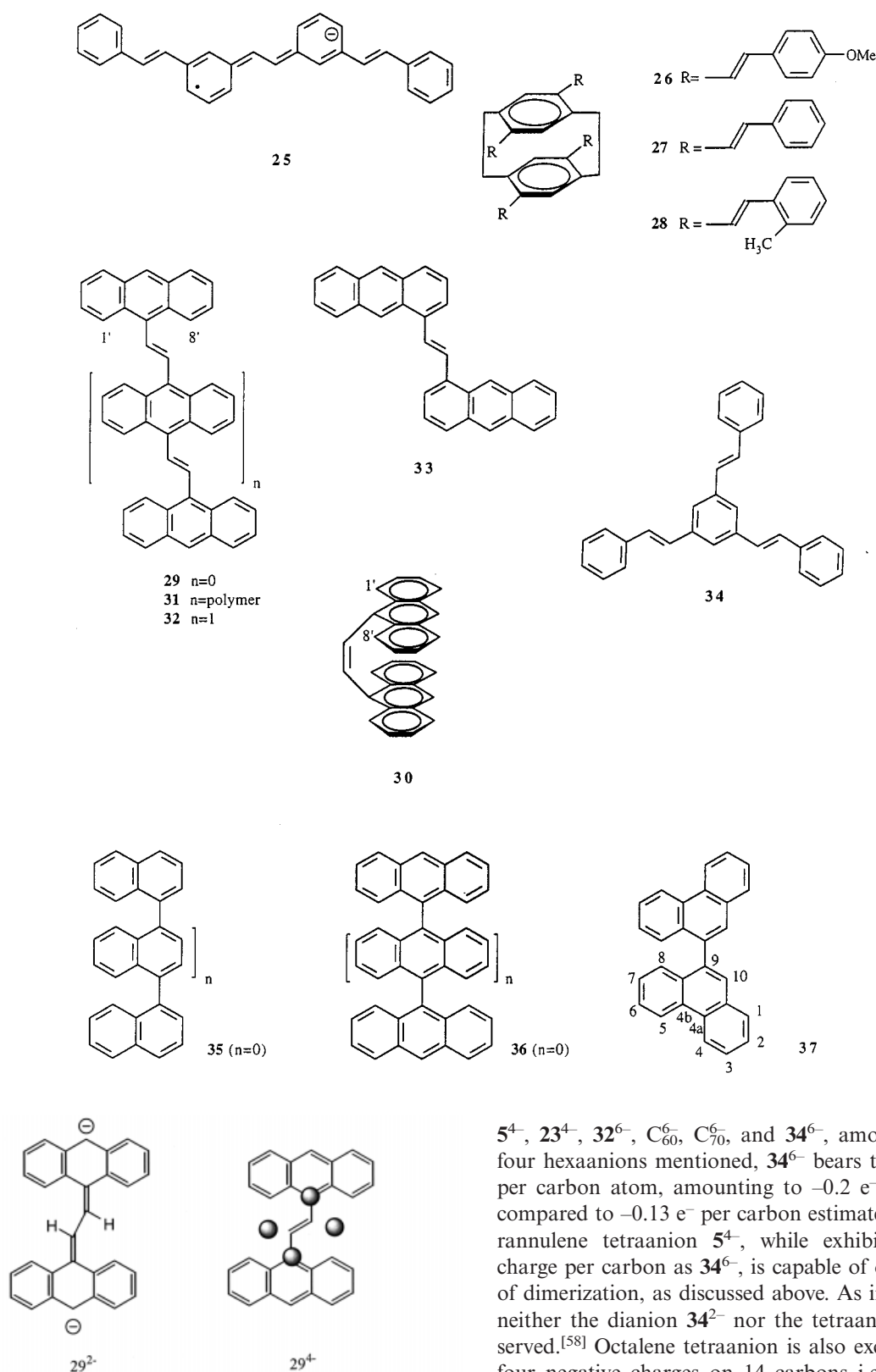
25

26 R=

27 R=

28 R=

29 n=0
31 n=polymer
32 n=1

33

30

34

35 (n=0)

36 (n=0)

37

29^{2-} 29^{4-}

Figure 3. Charged density distributions in dianion 29^{2-} and tetra-anion 29^{4-} (the spheres indicate the location of the lithium cations)

than two electrons upon reduction, other smaller hydrocarbons are transformed into polyanions with great ease. In the polyanion family, one considers systems such as 1^{4-}, 2^{4-},

5^{4-}, 23^{4-}, 32^{6-}, C_{60}^{6-}, C_{70}^{6-}, and 34^{6-}, among others. Of the four hexaanions mentioned, 34^{6-} bears the greatest charge per carbon atom, amounting to -0.2 e^- per carbon[58] as compared to -0.13 e^- per carbon estimated for 32^{6-}.[66] Corannulene tetraanion 5^{4-}, while exhibiting an identical charge per carbon as 34^{6-}, is capable of doing so by virtue of dimerization, as discussed above. As in the case of 32^{6-}, neither the dianion 34^{2-} nor the tetraanion 34^{4-} were observed.[58] Octalene tetraanion is also exceptional as it has four negative charges on 14 carbons i.e. 0.28 e^- per carbon.[66b] Semiempirical calculations point to a reduction mechanism involving a single stilbene polaron, as was observed in the case of 22^{4-} and 23^{4-}. A two-electron transfer to the neutral molecule **34** reduces one of the stilbene units, creating a dianionic polaron segment attached to two almost neutral phenylene arms. With the dianion triplet state

lying only 0.035 eV above the singlet state, the system exists in a triplet–singlet equilibrium with overall paramagnetic character. Introduction of two electrons into the dianion also results in triplet-state species, having a stilbene dianion and two phenylene arms each charged with a single electron. There is no spin pairing at this stage, and the tetraanion remains paramagnetic. Like the charge profile observed for **23**[4−], the charge distribution in **34**[6−] is homogeneous and is concentrated at the internal ends of the olefinic bonds.[58]

Planar π-Conjugated Anions

In the arylene series **35–38**, the ability of the system to transport and store charge depends not only on the size of the acene electrophore but also on the magnitude of the steric hindrance present between the electrophores. The magnitude of the steric interaction may be used as a criterion for the evaluation of the existence or absence of π-conjugation in the system.[5] One immediate outcome is the creation of multi-charged anions. Several studies of the geometries and conformations of a series of diarylenes yielded potential curves for the various systems. For 1,1′-binaphthyl **35**, the rotational movement about the inter-ring bond showed minima at 50° and at 130°.[69,70] For 9,9′-bianthryl **36**, the rotational barrier increases, and the system adopts

a ground state conformation with an inter-ring angle of nearly 90°.[71,72] This conformational change leads to only a small interaction between the two subunits in **36** as compared with that in **35**. Only a small potential difference is observed between the first and second electron transfers in **36**. In fact, when a higher oligomer is examined ($n > 0$), no significant alteration is observed in the first reduction potential.[73,74] Reduction of **36** yields a triplet dianion[75,76] and a tetraanion composed of two noninteracting subunits.[77] Recently, a crystal structure of the radical trianion of **36** showed that 81% of the total charge resides on just one of the two anthryl subunits.[78] The remaining charge resides on the second anthryl group and arises from the *intra*molecular interaction of this almost neutral anthryl segment with a second charged molecule in the solid phase. System **35**, however, acts as a single π-system.

In the case of 9,9′-biphenanthryl **37**[79] and 1,1′-bipyryl **38**,[80] the behavior of the redox system depends on the reduction conditions and on the ion pairing. Although the topology of both **37** and **38** is expected to be similar to that of **35**, the redox behavior would appear to be different. An explanation is provided by the size of the orbital coefficients of the SOMO calculated for the bridgehead carbons.[81] A stable diamagnetic dianion is obtained upon contact of **37** with the reducing metal.[79] Semiempirical calculations

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47[2−]

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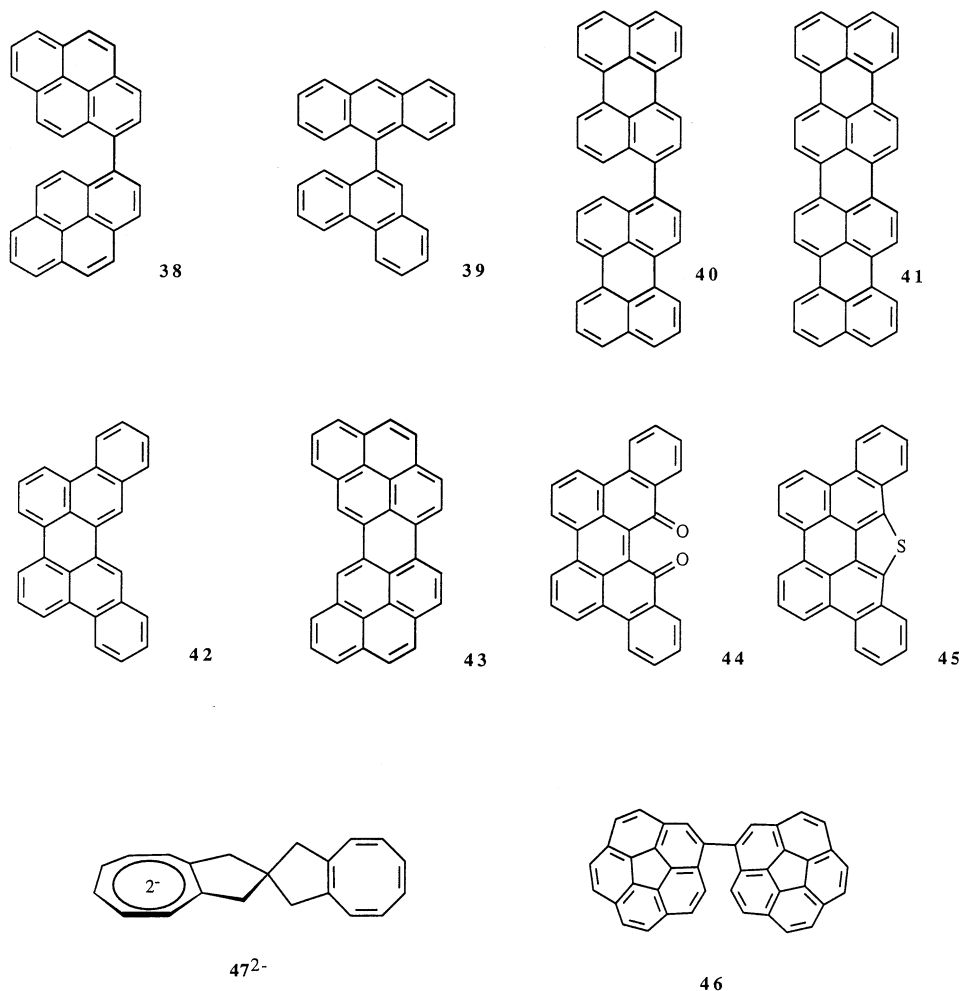
showed a decrease of 12.1° in the torsion angle and an increase in the double bond character at the inter-ring bond as a direct result of the reduction. This leads to a completely delocalized system in which steric electronic repulsions exist between the inner protons H[8] and H[8′] and possibly between the excess charge residing around these atoms. The repulsive interaction is enhanced as the tetraanion 37^{4-} is formed. With increased interaction between the subunits, further reduction of the torsional angle to 61.0° in the charged tetraanion, as compared to 95.1° in neutral **37** and 83.0° in 37^{2-}, is observed. Localization of greater charge densities at C[3] and C[9] of the anions, along with the distribution of lesser charge densities at the ring positions C[8a] through to C[4b], implies that the system minimizes coulombic repulsions between the charge centers and so attempts 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.[79] The degree of electron delocalization over the whole dimer varies with changes in charge localizations at the inter-ring positions. Lowering of the charge densities at these positions by extension of the surface for potential delocalization (as in going from phenanthrene subunits to pyrene units) results in a greater separation between the two subunits and hence a lower conjugation. A further decrease in the dihedral angle as a result of continued reduction leads to the formation of a new C–C bond, thereby yielding dianion 42^{2-}.[83]

Both dianions 42^{2-} and 43^{2-} exhibit charge distribution profiles consistent with oligoperinaphthalene systems (of which perylene is a member).[82] The charge densities are greatest at the peri positions, equivalent to the C[1] and C[8] positions in naphthalene. Further charge resides at the four bay positions of 42^{2-} and 43^{2-}. While the charge residing at the bay regions of 43^{2-} is comparable with that in the perylene dianion, the charge density at one of the bay regions of 42^{2-} is quite large.[83] Of the total charge, 36% resides on the two bay region carbons C[1] and C[12]. The degree to which this high charge density affects the system as a whole is evident from long-range isotope effects observed in the C[1]–C[12] deuterated system and from the polarization of the C–C bonds as predicted by semiempirical calculations. However, the most compelling evidence comes from the reaction of the dianion with molecular oxygen to yield diketone **44** in high yield.[83]

The effects that take place in a neutral system upon substitution of a heteroatom are highly important in the understanding of the influence of the heteroatom on the charge distribution patterns and the ability of the atom to quench paratropicity in charged states. Several heteroaromatic systems have been investigated in the neutral and charged states.[84] One such case is the sulfur derivative of hydrocarbon **42**, i.e. **45**. Reduction of **45** results in a dianion which is considerably different from 42^{2-}. While 42^{2-} exhibits a charge distribution pattern in which charge densities are concentrated at the periphery of the system, sulfide dianion

45^{2-} behaves as a disubstituted phenanthro[*c*]thiophene.[79] In such a charge distribution, the involvement of the thiophene ring in carrying some charge is reflected in the small charge that resides on the sulfur atom itself. On further reduction, dianion 45^{2-} undergoes loss of sulfur atom through an extrusion sequence initiated by charge transfer to the carbon segment of the molecule and not to the sulfur atom as is traditionally observed in C–S bond cleavages. Successive bond cleavages and protonations lead to anion 42^{2-}.[79]

Similar cyclization products were obtained when anions 38^{4-} and 40^{4-} were exposed to the metallic surface to yield 43^{2-} and 41^{2-}, respectively.[79] However, no such cyclization was observed in the case of 39^{4-}.[85] In contrast to the nonplanar geometries of the tetraanions derived from the diacenes, their cyclized products are planar and behave as single redox units. This results in a lowered reduction power and anions with a smaller charge.[86,87]

In bicorannulenyl **46**, such reductive cyclization is not expected. Reduction of **46** with lithium resulted in a species identical in color to the dianion of **5**, yet no ^{1}H-NMR spectrum could be observed. The formation of a paramagnetic diradical system existing in a fast equilibrium as in the case of 37^{2-} clearly occurs. No further reduction products were observed.[24]

One unique and extreme situation where the effect of electron hopping may be investigated is the dianion of the spirodicyclooctatetraenyl system 47^{2-}.[88] Prolonged contact with the reducing metal affords a tetraanion, in which there is no interaction between the two octatetraenyl subunits. However, the less highly charged systems $47^{1\bullet-}$ and 47^{2-} are of greater interest. The monoanion is fully localized. Even at high temperatures, there is no indication of any charge hopping from one subunit to the other. For the dianion, the ^{1}H- and ^{13}C-NMR spectra indicate beautifully the presence of one charged planar cyclooctatetraenyl dianion and one neutral tub-shaped cyclooctatetraene subunit.[89] The unique charge localization observed here stems from the characteristics of the subunit. Upon introduction of an electron to the cyclooctatetraene system, a flattening of the system is observed. Furthermore, the stabilization of the dianion compensates for the electronic repulsion involved in introducing a second electron to an already charged system.[90]

A Highly Reactive Graphite Electron Donor

In 1954, Rüdorff and Schulze[91] used X-ray diffraction analysis to describe the structure of the first-stage intercalation product of potassium and graphite. The graphite layers in C_8K, the color of the solid,[92] and its reactions with organic and inorganic materials[93,94] helped in explaining the unique nature of this material. The graphite intercalate C_8K is a useful and efficient reducing agent. Its highly ordered structural characteristics along with its high reactivity makes it a reagent of choice over such classical reduction reagents such as alkali metals in liquid ammonia. The ease of preparing the reagent, the inexpensive materials required, and the possibility of performing the reactions at relatively

high or low temperatures affords a reagent capable of executing organic reactions under room temperature conditions in short periods of time. Moreover, the inability of large polyaromatic hydrocarbons to mimic the reactivity of the reagent as a metal intercalate adds to the unique nature of C_8K.[95] The properties of C_8K as a catalyst and reactant in organic synthesis have been exploited in a wide range of organic reactions. Among the many reactions are stereospecific debrominations,[96] reductions of double bonds in α,β-unsaturated ketones, carboxylic acids, and Schiff bases,[97] alkylation of carbon acid derivatives such as nitriles, esters,[98] and imines,[99] reductive cleavage of C–S bonds in vinylic[100] and allylic[101] sulfones, and reductive coupling of alkyl and aryl halides.[102]

(a) Reductive Coupling of Aromatic Acid Esters and Ketones: The reaction of C_8K with carbonyl compounds served as a model in understanding its mode of action. Benzophenone undergoes reductive coupling in the presence of C_8K to give the corresponding pinacols.[103] The reaction of methyl benzoate, on the other hand, yielded phenanthroquinone in a one-pot reaction, as did that with benzil. When dimethyl diphenate was treated with C_8K, three major products were isolated: fluorene, fluorenol, and phenanthroquinone, as shown in Figure 4. Traces of fluorenone were also isolated. On the basis of kinetic studies, the "layer-edge" mechanism was suggested to explain these reactions of α-ketones.[104,105] A diketone such as benzil interacts with two adjacent potassium atoms of the intercalate to afford a benzil dianion linked to the graphite layer-edge. At this stage, the two phenyl rings are in a *syn* conformation, allowing ring-closure to occur with the formation of a dihydro compound. Aromatization and aerial oxidation results in the phenanthroquinone. However, a similar reaction with potassium metal does not yield the desired quinones.[106]
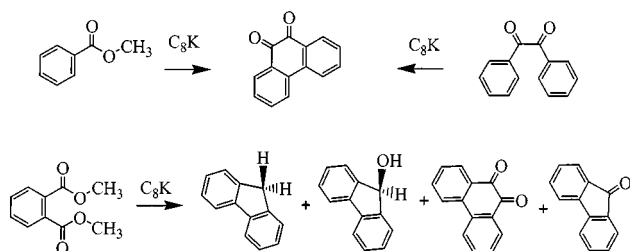

Figure 4. Reactions of C_8K with esters and ketones

(b) Reductive Cyclizations in Aromatic Hydrocarbons Containing Nitrogen Atoms: Cyclizations of substituted aromatic heterocycles such as **48** and **50** yield heterocycles **49** and **51**, respectively, as the sole products in high yields (Figure 5).[107] The layer-edge mechanism described above was also found to be operative in the cyclizations of compounds **48** and **50**.[104,105]

(c) Birch-Type Reduction of Aromatic Compounds: A unique application of the C_8K reagent is the Birch-type reduction of aromatic hydrocarbons, performed in ethereal solutions. Treatment of dialkylnaphthalenes with C_8K affords fair to good yields of 1,4-dihydronaphthalenes. The
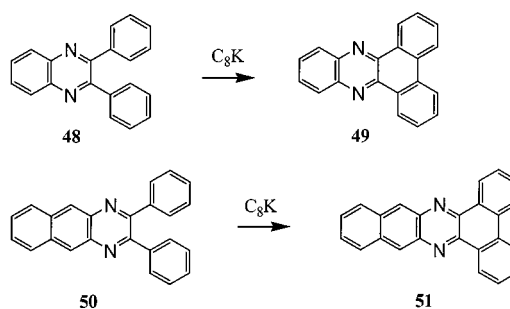

Figure 5. Reductive cyclization of nitrogen containing hydrocarbons

effect of electron-donating groups on the Birch reduction of naphthalene derivatives is known. Under C_8K conditions, the reduction of **52** occurs only on the unsubstituted ring and yields **53**, while substitution at the 2,3-positions promotes the reduction of both rings and the isolation of both **55** and **56**. In contrast to the temperature dependency of the Birch reduction in ammonia, in the presence of a large excess of C_8K and at elevated temperatures, the product composition does not change. Only one of the two benzene rings is reduced.[108] The amount of C_8K used has an influence on the overall conversion of naphthalene derivatives to the corresponding 1,4-dihydronaphthalenes. The optimal conditions for this conversion were found to be 1:12.5 starting material to C_8K. Smaller ratios were found to lower the yields.

(d) Reduction of Aromatic Hydrocarbons: Potassium metal reduces polycyclic aromatic hydrocarbons and forms π-conjugated anions, nearly all $(4n)π$ in character. The reduction with the potassium intercalate, although less reactive and hence more selective than the metal itself, produces identical results.

Fullerenes: Charging via an Electron Shuttle and Their Electron Delocalization

In 1985, it was discovered that vaporization of graphite by laser irradiation produces stable C_{60} and C_{70} [109] The calculated and experimentally detected[110] structures of these fullerenes point to the existence of highly symmetrical cavities. Kroto, Heath, O'Brien, Curl, and Smalley made the remarkable discovery that buckminsterfullerene, C_{60}, is a stable molecule due to geodesic and electronic properties inherent in the truncated icosahedral cage structure.[111]

For polycyclic π-systems, there is not always a correlation between aromatic character and the total number of π-electrons. In fullerenes, which are not only polycyclic, but also three-dimensional, such a correlation is even less obvious. Since they have no hydrogen to replace and the orbitals that make up their π-system have significant s-character, fullerenes undergo a variety of addition reactions rather than substitution, which is typical for polycyclic aromatic hydrocarbons. The resonance energy of fullerenes, however, is only slightly less than that of graphite. The question of π-delocalization and the degree to which the π-electrons are

free to move about the surface of the molecule may be partially answered by the use of magnetic techniques.

The ^{13}C-NMR spectrum of C_{60} in benzene consists of a single line at $\delta = 142.7$, confirming the icosahedral structure.[112] The ^{13}C-NMR spectrum of C_{70} in benzene consists of five lines ($\delta = 150.7$, 148.1, 147.4, 145.4, and 130.9), confirming the highly symmetrical football-shaped structure (C_{5h} symmetry).[113]

The triply-degenerate LUMO in C_{60}[114] and the doubly-degenerate LUMO+1, close in energy to a nondegenerate LUMO, in C_{70}[115] confirm that the hexaanions of these two molecules are accessible. Cyclic voltammetric data[116] show six reversible electron reductions of these two fullerenes [$E_{1/2}(C_{60}) = -0.98$, -1.37, -1.87, -2.35, -2.85, and -3.26 V and $E_{1/2}(C_{70}) = -0.97$, -1.34, -1.78, -2.21, -2.70, and -3.07 V], thus providing evidence for the electrochemical production of these hexaanions.

Reduction of a mixture of C_{60} and C_{70} using lithium metal in [D_8]THF with the aid of an ultrasonic bath generated a red-brown solution.[117] The ^{13}C-NMR spectrum at room temperature showed a single line at $\delta = 156.7$ for the reduction of C_{60} and five resonances for the reduced C_{70} ($\delta = 158.3$, 152.3, 149.6, 137.9, and 133.7). Despite the imposed charges, both anions are deshielded. However, in contrast to the remarkable deshielding effect exhibited by the anion of C_{60} (14 ppm/carbon atom), only a slight deshielding is shown by the anion of C_{70} (0.9 ppm/carbon atom). The ^{7}Li-NMR spectrum of a mixture of reduced C_{60} and C_{70} at room temperature shows a broad signal at $\delta = 1.6$, indicating a solvent-separated ion pair/contact ion pair equilibrium.[118]

The internal cavities of C_{60} and C_{70} were found to be sufficiently large to encapsulate a helium atom and thus form stable helium compounds.[119] The ^{3}He atom used as an internal probe for the magnetic shielding environment inside the fullerene allowed studies of the aromaticity of the fullerenes. The ^{3}He-NMR chemical shifts of ^{3}He atoms encapsulated in C_{60} and C_{70} are found to be $\delta = -6.3$ and -28.8, respectively.[120] These results indicate a significant diamagnetic ring current in C_{60} and an even larger one in C_{70}.

The hexaanions of C_{60} and C_{70} were calculated to show diamagnetic behavior; however, C_{60} was expected to show the largest magnetic effects. London calculations of the ring current chemical shift for an atom at the center of C_{60}^{6-} predicted a value of $\delta = -40.5$.[121,122] More recently, ab initio calculations of a central ^{3}He atom (^{3}He@C_{60}) indicated an even larger shielding for the hexaanion of C_{60} ($\delta = -58.3$[122] and -56.1[123]). While the He atom in He@C_{60} is predicted to be strongly shielded on reduction to the hexaanion, theory predicts the opposite for He@C_{70}. Both London and ab initio calculations predict values corresponding to a considerable deshielding relative to that in the neutral system ($\delta = -12.0$[124] and -10.6,[125] respectively).

Preliminary attempts to prepare the hexaanions of ^{3}He@C_{60} and ^{3}He@C_{70} under strongly reductive conditions (excess lithium metal with sonication) failed to give any ^{3}He-NMR signals. Addition of corannulene, which served

as an efficient electron carrier between the lithium metal and the solid C_{60}, facilitated reduction of the fullerenes under gentle conditions so as to afford their hexaanions.

Reduction of ^{3}He@C_{60} and ^{3}He@C_{70} with excess lithium metal and corannulene as mediator showed ^{3}He-NMR spectra of both endohedral fullerene hexaanions.[126] As predicted, the ^{3}He inside the C_{60} hexaanion was more strongly shielded ($\delta = -48.7$), while that inside the C_{70} hexaanion was more strongly deshielded ($\delta = +8.3$) relative to those in the neutral fullerenes. Figure 6 summarizes graphically the changes in ^{3}He chemical shifts upon reduction of ^{3}He@C_{60} and ^{3}He@C_{70} to their hexaanions.

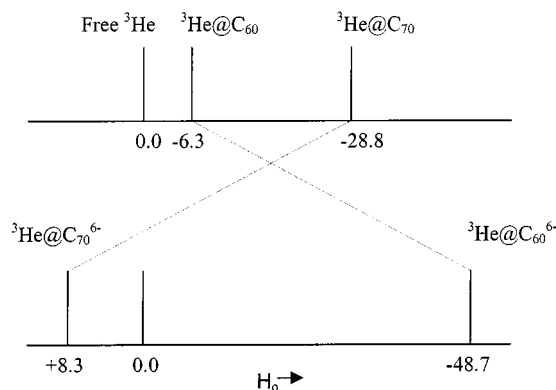Figure 6. ^{3}He NMR chemical shifts of ^{3}He@C_{60} and ^{3}He@C_{70} and their respective hexaanions

Reduction of C_{60} and C_{70} with all other alkali metals leads to colored solutions that probably contain the anion radicals. Further reduction leads to products that are too insoluble for analysis by solution NMR spectroscopy.

The strong shielding/deshielding effect on the ^{3}He atoms inside these fullerenes provides compelling evidence for the ability of electrons to move freely about the surfaces of such spheroidal π-systems.

Acknowledgments

[1] [1a] W. Schlenk, J. Appenrodt, A. Michael, A. Thal, *Chem. Ber.* **1914**, *47*, 473–490. – [1b] W. Schlenk, E. Bergmann, *Liebigs Ann. Chem.* **1928**, *463*, 1–322. – [1c] W. Schlenk, E. Bergmann, *Liebigs Ann. Chem.* **1928**, *464*, 1–42.

[2] N. D. Scott, J. F. Walker, V. L. Hansley, *J. Am. Chem. Soc.* **1936**, *58*, 2442–2444.

[3] [3a] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, **1961**. – [3b] M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, **1969**.

[4] [4a] G. Binsch, I. Tamir, R. D. Hill, *J. Am. Chem. Soc.* **1969**, *91*, 2446. – [4b] G. Binsch, I. Tamir, *J. Am. Chem. Soc.* **1969**, *91*, 2450. – [4c] T. Nakajima, *Pure Appl. Chem.* **1971**, *2*, 219. – [4d] T. Nakajima, A. Toyota, S. Fujii, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1022.

[5] K. Müllen, *Chem. Rev.* **1984**, *84*, 603–646.

[6] [6a] B. Thulin, O. Wennerström, H. E. Högberg, *Acta Chem. Scand. (B)* **1975**, *29(1)*, 138–139. – [6b] K. Müllen, H. Unterberg, W. Huber, O. Wennerström, U. Norinder, D. Tanner, B. Thulin, *J. Am. Chem. Soc.* **1984**, *106*, 7514–7522.

[7] B. Thulin, O. Wennerström, I. Somfai, B. Chmielarz, *Acta Chem. Scand. (B)* **1977**, *31*, 135–140.

[8] MNDO-MOPAC Version 6, J. J. P. Stewart, *QCPE Bull.* **1983**, *3*, 455.

[9] E. Shabtai, O. Segev, M. Rabinovitz, to be published.

[10] W. Huber, K. Müllen, O. Wennerström, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 624–625.

[11] A. Weitz, E. Shabtai, M. Rabinovitz, M. S. Bratcher, C. C. McComas, M. D. Best, L. T. Scott, *Chem. Eur. J.* **1998**, *4*, 234–239.

[12] T. E. Hogen-Esch, J. Smid, *J. Am. Chem. Soc.* **1966**, *8*, 307.

[13] M. Szwarc, *Carbanion Living Polymers and Electron Transfer Processes*, Wiley, New York, **1968**.

[14] P. W. Rabideau, A. Sygula, *Acc. Chem. Res.* **1996**, *29*, 235–242.

[15] J. C. Hanson, C. E. Nordman, *Acta Crystallogr. (B)*, **1976**, *32*, 1147–1153.

[16] [16a] W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1966**, *88*, 380–381. – [16b] W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1971**, *93*, 1730–1745.

[17] [17a] L. T. Scott, M. M. Hashemi, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1991**, *113*, 7082–7084. – [17b] L. T. Scott, P.-C. Cheng, M. M. Hashemi, M. S. Bratcher, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1997**, *119*, 10963–10968.

[18] A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1992**, *114*, 1921–1923.

[19] G. Zimmermann, U. Nuechter, S. Hagen, M. Nuechter, *Tetrahedron Lett.* **1994**, *35*, 4747–4750.

[20] A. Ayalon, M. Rabinovitz, P.-C. Cheng, L. T. Scott, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1636–1637.

[21] This view has been a matter of some controversy: [21a] P. W. Rabideau, Z. Marcinow, R. Sygula, A. Sygula, *Tetrahedron Lett.* **1993**, *34*, 6351–6354. – [21b] Z. Zhou, *J. Phys. Org. Chem.* **1995**, *8*, 103–107.

[22] A. Ayalon, M. Rabinovitz, *Pure Appl. Chem.* **1993**, *65*, 111–118.

[23] A. Sygula, P. W. Rabideau, *J. Mol. Struct.* (THEOCHEM) **1995**, *333*, 215–226.

[24] E. Shabtai, R. E. Hoffmann, P.-C. Cheng, E. Bayrd, D. V. Preda, L. T. Scott, M. Rabinovitz, *J. Chem. Soc., Perkin Trans. 2* **2000**, 129–133.

[25] H. Becker, G. Javahery, S. Petrie, P.-C. Cheng, H. Schwarz, L. T. Scott, D. K. Bohme, *J. Am. Chem. Soc.* **1993**, *115*, 11636–11637.

[26] A. Ayalon, A. Sygula, P.-C. Cheng, M. Rabinovitz, P. W. Rabideau, L. T. Scott, *Science* **1994**, *265*, 1065–1067.

[27] Y. Cohen, A. Ayalon, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 816–818.

[28] M. J. S. Dewar, W. Thiel, *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907.

[29] The barrier for bowl-to-bowl inversion of the neutral corannulene derivative was determined to be 10.2 kcal/mol (L. T. Scott, M. M. Hashemi, M. S. Bratcher, *J. Am. Chem. Soc.* **1992**, *114*, 1920–1921). The barriers for bowl-to-bowl inversion of the dianion with Cs and K were determined to be 8.8 kcal/mol and 9.2 kcal/mol, respectively (E. Shabtai, M. Rabinovitz, L. T. Scott, manuscript in preparation).

[30] M. Baumgarten, L. Gherghel, M. Wagner, A. Weitz, M. Rabinovitz, P.-C. Cheng, L. T. Scott, *J. Am. Chem. Soc.* **1995**, *117*, 6254–6257.

[31] K. Müllen, T. Meul, P. Schade, H. Schmickler, E. Vogel, *J. Am. Chem. Soc.* **1987**, *109*, 4992–5003.

[32] [32a] R. Frim, A. Mannschreck, M. Rabinovitz, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 919–921. – [32b] A. Minsky, A. Y. Meyer, M. Rabinovitz, *Tetrahedron* **1985**, *41*, 785–791.

[33] As yet unpublished results from our laboratory.

[34] [34a] R. H. Cox, H. W. Terry Jr., L. W. Harrison, *J. Am. Chem. Soc.* **1971**, *93*, 3297–3298. – [34b] H. Günther, D. Moskau, P. Best, D. Schmalz, *Angew. Chem. Int. Ed. Engl.* **1987**, *25*, 1212–1220.

[35] J. Janata, J. Gendell, C.-Y. Ling, W. Barth, L. Backes, H. B. Mark, Jr., R. G. Lawton, *J. Am. Chem. Soc.* **1967**, *89*, 3056–3058.

[36] G. Zilber, V. Rozenshtein, P.-C. Cheng, L. T. Scott, M. Rabinovitz, H. Levanon, *J. Am. Chem. Soc.* **1995**, *117*, 10720–17025.

[37] Results presented at the Hong Kong ISNA-9 conference; *Proceedings*, pp. 117, 1998, to be published.

[38] A. Weitz, M. Rabinovitz, P.-C. Cheng, L. T. Scott, *Synth. Met.* **1997**, *86*, 2159–2160.

[39] [39a] M. S. Bratcher, L. T. Scott, National Meeting of the American Chemical Society, San Diego, CA, March **1994**, Abstr. no. ORGN 420. – [39b] L. T. Scott, unpublished results presented at the Symposium on Synthetic Hydrocarbon Chemistry, Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, December **1994**. – [39c] L. T. Scott, M. S. Bratcher, Eighth International Symposium of Novel Aromatic Compounds, Braunschweig, Germany, July 30 – August 4, **1995**, Abstr. no. 7. – [39d] M. S. Bratcher, Ph.D. Dissertation, Boston College, **1996**.

[40] Synthesis to be published elsewhere: [40a] C. C. McComas, B.Sc. Thesis, Boston College, **1996**. – [40b] M. D. Best, B.Sc Thesis, Boston College, **1997**.

[41] A. Sygula, H. E. Folsom, R. Sygula, A. H. Abdourazak, Z. Marcinow, F. R. Fronczek, P. W. Rabideau, *J. Chem. Soc., Chem. Commun.* **1994**, 2571–2572.

[42] F. Gerson, W. Huber, *Acc. Chem. Res.* **1987**, *20*, 85–90.

[43] [43a] A. Minsky, A. Y. Meyer, M. Rabinovitz, *Tetrahedron Lett.* **1982**, *23*, 5351–5354. – [43b] A. Minsky, A. Y. Meyer, R. Poupko, M. Rabinovitz, *J. Am. Chem. Soc.* **1983**, *105*, 2164–2172. [43c] B. Eliasson, U. Edlund, K. Müllen, *J. Chem. Soc., Perkin Trans. 1I* **1986**, 937.

[44] K. P. Meurer, F. Vögtle, *Top. Curr. Chem.* **1985**, *127*, 1–76.

[45] [45a] R. H. Martin, *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 649–660. – [45b] F. B. Mallory, C. W. Mallory, *Org. React.* **1983**, *30*, 1–8. – [45c] W. H. Laarhoven, W. J. C. Prinsen, *Top. Curr. Chem.* **1984**, *125*, 63–130.

[46] C. Rosini, L. Franzini, A. Raffaelli, P. Salvadori, *Synthesis* **1992**, *6*, 503–517.

[47] A. Ioffe, A. Ayalon, M. Rabinovitz, *J. Chem. Soc., Perkin Trans. 2* **1994**, 1115–1116.

[48] H. Scherübel, U. Fritzsche, A. Mannschreck, *Chem. Ber.* **1984**, *117*, 336–343.

[49] R. Frim, G. Zilber, M. Rabinovitz, *J. Chem. Soc., Chem Commun.* **1991**, 1202–1203.

[50] R. Frim, A. Goldblum, M. Rabinovitz, *J. Chem. Soc., Perkin Trans. 2* **1992**, 267–274.

[51] A. Ayalon, M. Rabinovitz, *Tetrahedron Lett.* **1992**, *33*, 2395–2398.

[52] A. Weitz, Ph.D. Dissertation, Hebrew University of Jerusalem, **1997**.

[53] A. Weitz, M. Rabinovitz, *Synth. Met.* **1995**, *74*, 201–205.

[54] [54a] M. Baumgarten, W. Huber, K. Müllen, *Adv. Phys. Org. Chem.* **1993**, *28*, 1–44. – [54b] A. Bohnen, H. J. Räder, K. Müllen, *Synth. Met.* **1992**, *47*, 37–63.

[55] M. Rabinovitz, *Top. Curr. Chem.* **1988**, *146*, 99–169.

[56] J. L. Brédas, A. J. Heeger, *Macromolecules* **1990**, *23*, 1150–1156.

[57] H. Gregorius, M. Baumgarten, R. Reuter, N. Tyutyulkov, K. Müllen, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1653–1655.

[58] R. Benshafrut, M. Rabinovitz, Z. Dee-Noor-Barzilay, A. de Meijere, *J. Phys. Org. Chem.* **1999**, *12*, 1–7.

[59] E. Shabtai, M. Rabinovitz, B. König, B. Knieriem, A. de Meijere, *J. Chem. Soc., Perkin Trans. 2* **1996**, 2589–2595.

[60] A. Böhm, M. Adam, H. Mauermann, S. Stein, K. Müllen, *Tetrahedron Lett.,* **1992**, *33*, 2795–2798.

[61] K. Müllen, H. Unterberg, W. Huber, O. Wennerström, U. Norinder, D. Tanner, B. Thulin, *J. Am. Chem. Soc.* **1984**, *106*, 7514–7522.

[62] [62a] R. Frim, F. W. Raulfs, H. Hopf, M. Rabinovitz, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 174–175. – [62b] R. Frim, M. Rabinovitz, H. Hopf, J. Hucker, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 232–233.

[63] R. H. Cox, H. W. Terry, Jr., L. W. Harrison, *Tetrahedron Lett.* **1971**, *50*, 4815–4818.

[64] R. H. Cox, H. W. Terry, Jr., *J. Magn. Reson.* **1974**, *14*, 317–322.

[65] M. J. Carvey, D. J. Doss, *J. Org. Chem.* **1988**, *53*, 5963–5964.

[66] [66a] A. Weitz, M. Rabinovitz, K. Müllen, B. Becker, to be published. – [66b] K. Müllen, J. F. M. Oth, H. W. Engles, E. Vogel, *Angew. Chem. Int. Ed. Engl.* **1979**, *27*, 1922–1927.

[67] R. O. Garay, H. Naarmann, K. Müllen, *Macromolecules* **1994**, *27*, 1922–1927.

[68] H. D. Becker, *Pure Appl. Chem.* **1982**, *54*, 1589–1604.

[69] [69a] A. Gamba, E. Rusconi, M. Simonetta, *Tetrahedron* **1970**,

26, 871–877. – [69b] K. R. Wilson, R. E. Pincock, *Can. J. Chem.* **1977**, *55*, 889–894. – [69c] M. Dietrich, J. Heinze, *J. Am. Chem. Soc.* **1990**, *112*, 5142–5145.

[70] U. Anton, K. Müllen, *Macromolecules* **1993**, *26*, 1248–1253.

[71] [71a] M. Baumgarten, U. Müller, *Synth. Met.* **1993**, *57*, 4755–4761. – [71b] A. Subaric-Leitis, Ch. Monte, A. Roggan, W. Rettig, P. Zimmerman, J. Heinze, *J. Chem. Phys.* **1990**, *93*, 4543–4556.

[72] U. Müller, M. Adam, K. Müllen, *Chem. Ber.* **1994**, *127*, 437–444.

[73] M. Baumgarten, U. Müller, A. Bohnen, K. Müllen, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 448–451.

[74] U. Müller, M. Baumgarten, *J. Am. Chem. Soc.* **1995**, *117*, 5840–5850.

[75] K. Müllen, M. Baumgarten, N. Tyutyulkov, S. Karabunarliev, *Synth. Met.* **1991**, *40*, 127–136.

[76] H. Hoshino, K. Kimura, M. Imamura, *Chem. Phys. Lett.* **1973**, *20*, 193–196.

[77] [77a] W. Huber, K. Müllen, *J. Chem. Soc., Chem Commun.* **1980**, 698–700. – [77b] A. Minsky, M. Rabinovitz, *J. Am. Chem. Soc.* **1984**, *106*, 6755–6759.

[78] H. Bock, Z. Havlas, D. Hess, C. Näther, *Angew. Chem. Int. Ed.* **1998**, *37*, 502–504.

[79] R. Benshafrut, M. Rabinovitz, R. E. Hoffman, N. Ben-Mergui, K. Müllen, V. S. Iyer, *Eur. J. Org. Chem.* **1999**, 37–48.

[80] M. Baumgarten, U. Anton, L. Gherghel, K. Müllen, *Synth. Met.* **1993**, *57*, 4807–4812.

[81] M. Baumgarten, K. Müllen, *Top. Curr. Chem.* **1994**, *169*, 1–103.

[82] M. Baumgarten, K.-H. Koch, K. Müllen, *J. Am. Chem. Soc.* **1994**, *116*, 7341–7348.

[83] R. Benshafrut, M. Rabinovitz, R. E. Hoffman, K. Müllen, *J. Org. Chem.* **1999**, *64*, 644–647.

[84] [84a] Y. Cohen, J. Klein, M. Rabinovitz, *J. Am. Chem. Soc.* **1988**, *110*, 4634–4640. – [84b] Y. Cohen, A. Y. Meyer, M. Rabinovitz, *J. Am. Chem. Soc.* **1986**, *108*, 7039–7044.

[85] A. Minsky, M. Rabinovitz, *J. Am. Chem. Soc.* **1984**, *106*, 6755–6759.

[86] [86a] K. Müllen, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 204–217. – [86b] J. Fiedler, W. Huber, K. Müllen, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 443–444.

[87] A. Subaric-Leitis, Ch. Monte, A. Roggan, W. Rettig, P. Zimmermann, J. Heinze, *J. Chem. Phys.* **1990**, *93*, 4543–4555.

[88] [88a] G. Krummel, K. Müllen, *Tetrahedron Lett.* **1988**, *29*, 2809–2812. – [88b] P. Auchter-Krummel, K. Müllen, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1003–1006.

[89] [89a] S. W. Staley, C. K. Dustman, K. L. Facchine, G. E. Linkowski, *J. Am. Chem. Soc.* **1985**, *107*, 4003–4007. – [89b] G. Krummel, W. Huber, K. Müllen, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1290–1291.

[90] [90a] F. A. L. Anet, A. J. R. Bourn, Y. S. Lin, *J. Am. Chem. Soc.* **1964**, *86*, 3576–3577. – [90b] T. J. Katz, *J. Am. Chem. Soc.* **1960**, *82*, 3784–3785.

[91] W. Rüdorff, E. Z. Schulze, *Anorg. Chem.* **1954**, *277*, 156.

[92] G. R. Hennig, *J. Chem. Phys.* **1965**, *43*, 1201–1206.

[93] L. B. Ebert, D. R. Mills, A. R. Garcia, J. L. Scanlon, *Mater. Res. Bull.* **1985**, *20*, 1453–1460.

[94] L. B. Ebert, *Carbon* **1985**, *23*, 585–587.

[95] R. Benshafrut, M. Rabinovitz, unpublished results.

[96] M. Rabinovitz, D. Tamarkin, *Synth. Commun.* **1984**, *14*, 377–379.

[97] M. Contento, D. Savoia, C. Trombini, A. Umani Ronchi, *Synthesis* **1979**, 30–32.

[98] D. Savoia, C. Trombini, A. Umani Ronchi, *Tetrahedron Lett.* **1977**, *7*, 653–656.

[99] D. Savoia, C. Trombini, A. Umani Ronchi, *J. Org. Chem.* **1978**, *43*, 2907–2910.

[100] P. O. Ellingsen, K. Undheim, *Acta Chem. Scand. (B)*, **1979**, *33*, 528–530.

[101] D. Savoia, C. Trombini, A. Umani Ronchi, *J. Chem. Soc., Perkin Trans. 1* **1977**, 123–125.

[102] [102a] F. Glocking, D. Kingston, *Chem. Ind.* **1961**, *8*, 1037. – [102b] D. E. Bergbreiter, J. M. Killough, *J. Am. Chem. Soc.* **1978**, *100*, 2126–2134.

[103] D. Tamarkin, M. Rabinovitz, *Synth. Met.* **1984**, *9*, 125–128.

[104] D. Tamarkin, D. Benny, M. Rabinovitz, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 642–643.

[105] D. Tamarkin, M. Rabinovitz, *J. Org. Chem.* **1987**, *52*, 3472–3474.

[106] D. Tamarkin, Ph.D. Dissertation, Hebrew University of Jerusalem, **1987**.

[107] [107a] D. Tamarkin, Y. Cohen, M. Rabinovitz, *Synthesis* **1987**, 196–197. – [107b] D. Tamarkin, M. Rabinovitz, *Synth. Met.* **1988**, *23*, 487–491.

[108] I. S. Weitz, M. Rabinovitz, *J. Chem. Soc., Perkin Trans. 1* **1993**, 117–120.

[109] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162–163.

[110] [110a] W. Kratschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 354–358. – [110b] D. R. McKenzie, C. A. David, D. J. H. Cockayne, D. A. Muller, A. M. Vassallo, *Nature* **1992**, *355*, 622–624.

[111] [111a] R. E. Curl, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1566–1576. – [111b] H. Kroto, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1578–1593. – [111c] R. E. Smally, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1594–1601.

[112] R. Taylor, J. P. Hare, A. K. Abdul-Sada, H. W. Kroto, *J. Chem. Soc., Chem. Commun.* **1990**, 1423–1425.

[113] H. W. Kroto, *Nature* **1987**, *329*, 529–531.

[114] [114a] D. A. Bochvar, E. G. Galpern, *Dokl. Akad. Nauk. SSSR* **1973**, *209*, 610–612; *Proc. Acad. Sci. SSSR* **1973**, *209*, 239–241 (English translation). – [114b] I. V. Stankevich, M. V. Nikerov, D. A. Bochvar, *Russ. Chem. Rev.* **1984**, *53*, 640–655. – [114c] R. A. Davidson, *Theor. Chim. Acta* **1981**, *58*, 193–195. – [114d] A. D. Haymet, *Chem. Phys. Lett.* **1985**, *122*, 421–424.

[115] P. W. Fowler, J. Woolrich, *Chem. Phys. Lett.* **1986**, *127*, 78–83.

[116] [116a] Q. Xie, E. Pérez-Cordero, L. Echegoyen, *J. Am. Chem. Soc.* **1992**, *114*, 3978–3980. – [116b] K. Merholz, P. Tschuncky, J. Heinze, *J. Electroanal. Chem.* **1993**, *347*, 425. – [116c] D. Dubois, G. Moinot, W. Kutner, M. T. Jones, K. M. Kadish, *J. Phys. Chem.* **1992**, *96*, 7137–7145. – [116d] Y. Ohsawa, T. Saji, *J. Chem. Soc., Chem. Commun.* **1992**, 781–782.

[117] W. Joseph, G. K. Surya Prakash, G. A. Olah, D. S. Tse, D. C. Lorents, Y. K. Bae, R. Malhotra, *J. Am. Chem. Soc.* **1991**, *113*, 3205–3206.

[118] T. E. Hogen-Esch, J. Smid, *J. Am. Chem. Soc.* **1967**, *89*, 2764–2765.

[119] M. Saunders, H. A. Jimenez-Vazquez, R. J. Cross, R. J. Poreda, *Science* **1993**, *259*, 1428–1430.

[120] M. Saunders, H. A. Jimenez-Vazquez, R. J. Cross, S. Mroczkowski, D. I. Freedberg, F. A. L. Anet, *Nature* **1994**, *367*, 256–258.

[121] R. C. Haddon, *Nature* **1995**, *378*, 249–255.

[122] M. Bühl, W. Thiel, H. Jiao, P. v. R. Schleyer, M. Saunders, F. A. L. Anet, *J. Am. Chem. Soc.* **1994**, *116*, 6005–6006.

[123] J. Cioslowski, *Chem. Phys. Lett.* **1994**, *227*, 361–364.

[124] R. C. Haddon, A. Pasquarello, *Phys. Rev. B* **1994**, *50*, 16459–16463.

[125] M. Bühl, *Chem. Eur. J.* **1998**, in press.

[126] E. Shabtai, A. Weitz, R. C. Haddon, R. E. Hoffman, M. Rabinovitz, A. Khong, R. J. Cross, M. Saunders, P.-C. Cheng, L. T. Scott, *J. Am. Chem. Soc.* **1998**, *120*, 6389–6393.