Among the fundamental concepts upon which chemistry is based, the notion of aromaticity seems to play a particular and, in a sense, a rather disturbing role. A variety of chemical and physical phenomena are interpreted as caused by, or directly related to, the aromatic nature of substances. The predisposition to electrophilic substitutions vs. low proclivity toward additions, the unusual tendency of species to release a positive or negative group (e.g., cyclopentadiene, cycloheptatriene), and the existence of significant dipole moments due to uneven electron distribution over different moieties of the molecule are some known examples of how significantly aromatic character and the tendency of species to acquire such a character influence chemical behavior.

Important physical properties such as enhanced magnetic susceptibilities and characteristic electronic transitions, as expressed by NMR and UV patterns, are also interpreted as originating from the aromatic nature prevailing in the system under observation. Aromativity and antiaromaticity (vide infra) play a crucial role in determining properties of species not only in their ground but also in their excited states. Consideration of the relative extent of aromatic or antiaromatic contributions to the transition states was shown to be fully equivalent to consideration of orbital symmetry in predicting allowed chemical reactions. Thus, the importance of aromaticity in determining reaction paths is made clear.

In view of the fundamental significance of aromatic character, the general interest in it, and the fact that the first quantum mechanical explanation to this phenomenon was provided as early as 1931, it is surprising that the concept is still far from being defined and understood. The confusion associated with this subject is mainly due to the fact that neither aromaticity nor ring current phenomena, which are taken as directly related to aromatic nature, is a physically observable phenomenon. Thus, the question whether all the previously mentioned chemical and spectroscopic phenomena are really due to aromaticity is by no means a trivial one, and should be seriously considered.

The numerous definitions suggested to characterize aromaticity point to the heart of the problem. The most comprehensive definition is based on the energy content of systems. Aromatic molecules are defined as systems that sustain cyclic π-electron delocalization. 

(1) The term super-charged systems was introduced by us in order to describe quadruply charged hydrocarbon systems (see ref 26).


(6) E. Hückel, Z. Phys., 70, 204 (1931); ibid., 72, 310 (1931).

that reduces the energy content of the systems relative to corresponding model compounds without such cyclic delocalization. Similarly, a cyclic \( \pi \)-electron delocalization that leads to an enhanced destabilization and therefore to a high energy content characterizes antiaromatic systems.\(^8\) This energetically based definition is clearly of importance because of its concern with the very basic sense of aromaticity, i.e., the stabilization, or destabilization, caused by cyclic electron delocalizations. Yet, this definition can hardly serve as a useful criterion due to theoretical and experimental difficulties involved with the notion of energy content.

More practical definitions can be classified into two general groups: criteria based on purely theoretical concepts and those that refer to experimentally observable phenomena. Hückel’s rule\(^6\) exemplifies the first group by assigning aromatic character to planar, monocyclic, conjugated systems with \((4n + 2)\) \( \pi \) electrons in their periphery.

The perimeter model, suggested by Platt,\(^9\) is an extension of Hückel’s rule (valid rigorously only for monocyclic conjugated polyes) to polycyclic structures. This model, based on the free-electron theory, emphasizes the relationship between \((4n + 2)\) \( \pi \) electrons and aromatic character. Systems with \(4n\) \( \pi \) electrons in the peripheral path of conjugation would be inclined to reveal antiaromatic properties, while those with \((4n + 1)\) or \((4n + 3)\) \( \pi \) electrons would be estimated as nonaromatic. Cross-links and inner sp\(^2\) carbons are treated as small perturbations to the peripheral skeleton. The most useful definition among those related to experimentally observable phenomena is based on magnetic anisotropy.\(^4\) According to this criterion aromatic compounds are defined as cyclic or polycyclic systems that sustain a diamagnetic ring current and consequently exhibit a total diatropic (downfield) chemical shift relative to vinyl protons. Paramagnetic ring current is expected to be induced in antiaromatic species resulting in a paratropic (upfield) band displacement in the NMR spectrum.\(^5\)

The described definitions have been widely used to characterize aromaticity. However, the correlation between these criteria and aromatic nature is by no means simple. There is no straightforward explanation why the number of \( \pi \) electrons in the periphery of polycyclic systems correlate with aromaticity and why inner cross-links serve only as small perturbations. In other words, Platt’s model is used without a full, proper theoretical justification. Similarly, the relationship between magnetic susceptibility of a polycycle and its energy content, as a function of electronic conjugation, is highly complex.\(^10\) One can therefore conclude that the deficiencies connected with various definitions reflect the difficulties associated with the elusive nature of aromaticity in conjugated polycyclic systems.

In this Account we summarize our research on polycyclic ionic species. The study of charged polycycles permits the monitoring of magnetic properties as a function of the total number of \( \pi \) electrons and of the number of electrons in the conjugated periphery, i.e., in terms of Platt’s model. Such a treatment enables a cross-examination and a critical discussion of different criteria of aromatic and antiaromatic nature. It is our belief that a better and deeper understanding of these definitions is of crucial importance for a more general view of the aromatic concept to be established. The systems studied include doubly and quadruply charged polycyclic ions, totally benzenoid or ions with nonbenzenoid components.

**Ring Currents in Systems with a Planar Cyclooctatetraene (COT) Moiety**

The theoretically based Hückel\(^6\) and Platt concepts\(^9\) ascribe antiaromatic character to those mono- and polycyclic systems that contain a conjugated array of \(4n\) \( \pi \) electrons in their periphery. Pople and Untch\(^11\) as well as Longuet-Higgins\(^12\) have used the theory of magnetic susceptibility to show that such \(4n\) \( \pi \) conjugated systems should show paramagnetic ring current. This would result in a total, paratropic high-field \(^1\)H NMR chemical shift relative to vinyl protons, in a similar sense to the diatropic low-field \(^1\)H NMR absorptions revealed by \((4n + 2)\) \( \pi \) aromatic species. In contrast to the abundant examples of aromatic species, only a few examples of “real” antiaromatic systems are known.\(^8\) The difference between the two groups is obviously due to the inherent instability of \(4n\) \( \pi \) species, which results in high reactivity, nonplanarity, and pronounced bond-length alternation. The nonplanarity of the \(8-\pi\) cyclooctatetraene (COT) challenged us to design a polycyclic system in which the COT moiety is forced to planarity. Cycloocta[def]fluorene (1)\(^13\) seems to fulfill this requirement on the basis of geometrical considerations, i.e., the planarity of the rigid fluorene component is expected to form a nearly octagonal angle in the COT moiety and thus to result in its planarity.

With reference to Platt’s concept,\(^9\) the 16-\( \pi \) system 1 is expected to have antiaromatic character that, according to the magnetic criterion, would result in a paramagnetic ring current. Indeed, we find that the vinyl protons in 1 are significantly high-field shifted as compared to closely related polycycles with a nonplanar COT moiety, e.g., 3 and 4.\(^13\) Clearly, the paratropic character is extended over the benzene components—their protons NMR absorptions appear at 6.8–7.7 ppm, a relatively high-field shift.

Deprotonation of 1 using BuLi resulted in the formation of cycloocta[def]fluorenly anion (2).\(^13\) During this process the hybridization of C-11 is altered from sp\(^3\) to sp\(^2\). Thus the anionic system possesses a fully conjugated periphery. The anion can therefore be represented as a perturbed antiaromatic peripheral \(15\)C-16\( \pi \) annulene anionic system. The changes in the \(^1\)H NMR chemical shifts of 2 vs. those of the neutral compound 1 are expected to be the result of two different contributions: (a) a high-field shift due to negative charge shielding and (b) a further paratropic shift originating from the enhanced paramagnetic, antiaromatic character of the perturbed 16-\( \pi \) system. Indeed, a total high-field shift of ca. 6 ppm is observed after deprotonation.

To assess the contribution of the charge shielding effect on the \(^1\)H NMR chemical shifts, the deprotona-

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tion of cyclopenta[def]phenanthrene (5) to 6 was examined. Here, a [13C-14π] peripheral system per-

turbed by an inner double bond is obtained. The aromatic character expected to be sustained in such a system is found to cancel efficiently the shielding effects of the negative charge and, even more so, a total low-field 1H NMR shift of ca. 2 ppm is observed.

Consequently, the enhanced high-field shift observed in 2 compared with that revealed by 6 should be attributed mainly to a substantial contribution of an antiaromatic character that in turn is related to the 16-π peripheral conjugation. In the same sense, a diamagnetic aromatic character is to be attributed to the [13C-14π] system 6. The comparison of the chemical shifts of 2 and 6 emphasizes the importance of the number of π electrons in the system’s periphery. Trinajstic calculated a negative resonance energy per electron (REPE = −0.011) for 215 confirming its antiaromaticity, while a positive resonance energy was estimated for 6.

The planarity of the COT component in 1 drew our attention to the possibility of pursuing the oxidation of the conjugated periphery to the corresponding dication. Oxidation of 1 did not afford an identified species. Therefore, we decided to look into the behavior of the carbonyl derivative 7. This oxidation process studied in a superacid medium (SbF$_5$FSO$_3$H).16 In this environment protonation of the carbonyl (i.e., 7 → 8) and oxidation of the conjugated periphery are anticipated. The resulting protonate would be a triply charged system that might, in principle, reveal two different modes of electron distribution: (a) Three positive charges localized over the peripheral carbon atoms. In this case a [15C-12π] system 9a is obtained, which should exhibit antiaromatic character, according to Platt’s model. (b) One positive charge might be localized at the protonation site, while the two other charges are delocalized over the dibenzo-cyclooctatetraene dicaticonic component perturbed to a rather small extent by a protonated carbonyl group. The other delocalization mode, depicted as 9b, would result in an antiaromatic trication [15C-12π] peripheral system.

In order to establish these conclusions and to differentiate between the charge-deshielding and the aromatic diatropic effects on the chemical shift, we examined the oxidation process using as reference system cyclopenta[def]phenanthrene ketone (10). Reaction of 10 with SbF$_5$FSO$_3$H at low temperature resulted in the protonate 11, which, at room temperature, underwent a two-electron oxidation to the corresponding cyclopenta[def]phenanthrene dication protonate (12).18 The dication 12 is formally derived from 9 by the elimination of a vinylic group and is expected, according to Platt’s concept, to be a nonaromatic (or even antiaromatic) [14C-12π] system. Therefore, the deshielding that accompanies the oxidation process 11 → 12 acts as an indicator of charge-deshielding effect only. The total down field shift observed in 12 is ca. 16 ppm. This value, which is smaller than the value suggested by the charge-density—chemical shift correlation (21.7 ppm),18 is rationalized in terms of an ac-

companying paratropic, antiaromatic contribution. The large contribution of diamagnetic, aromatic nature of the character of 9 is emphasized.

Dual Aromaticity in Doubly Charged Polycyclic Pentalene Derivatives

The dibenzo[bc]pentalene system (13) and its derived dianion and dication afford nice examples of the various problems that inherently beset any assessment of aromatic character based upon theoretical grounds. Platt's model deals with the number of π electrons in the molecular periphery and pays little attention to inner carbons and bonds in the pericondensed systems. Moreover, this peripheral approach does not consider the possibility of different or opposing contributions to aromaticity afforded by different parts of the molecule, a possibility that even the relatively "simple" catacondensed systems may present. As was pointed out by Randić, Platt's approach improperly assigns a decisive role to the largest path of conjugation and neglects the contributions of smaller electronic arrays. A second structural approach proposed to account for aromatic (or antiaromatic) character in polynuclear systems considers therefore the local, relative contributions of the rings composing the polycycle.

According to Platt's model, the planar, fully conjugated [16C-18π] dibenzo[bc]pentalene system should reveal a clear antiaromatic nature due to a cyclic conjugation of a 4n π electrons. The aromatic contribution of the two six-membered rings is completely overlooked, which intuitively seems unjustified. The local model suggested by Randić and applied on 13 estimates an intermediate status, assigning the system 63.6% aromatic character. The opposing conclusions as estimated by the two different theoretical approaches emphasize the special importance of the experimental, magnetic criterion of aromaticity.

The 1H NMR chemical shifts exhibited by 13 are composed of a multiplet centered at 6.90 ppm and a singlet at 6.40 ppm assigned to the benzene ring protons and to the vinylic protons, respectively. A comparison of these chemical shifts to those obtained from a dihydro derivative of 13, i.e., 14, and from 1,4-diphenylbutadiene (15) is revealing. The benzene protons of 14 appear at 7.25 ppm, those of 15 at 7.35 ppm, and the vinylic 1H NMR chemical shifts of the latter at 6.8 ppm. A general high-field trend is obviously exhibited by 13, which we believe can be rationalized only by assuming a paramagnetic, antiaromatic contribution. Yet, the extent of the paratropic shift is by far smaller than the high-field shift observed in "truly" antiaromatic species, such as pyrene dianion (vide infra) or the dinitrogen ions derived from anthracene and phenanthrene.

magnetic criterion seems therefore to support the local concept by assigning only a partial antiaromatic character to 13. Failure of the peripheral model is attributed in this case to improper consideration of the contribution of the benzene rings to the overall character of the system.

The conjugated hydrocarbon 13 undergoes twofold reduction and oxidation processes to afford the corresponding dianion and dication, respectively. Dianion 16 is predicted to possess an aromatic character by both the peripheral model, being a [16C-18π] system, and the local model, being composed of four 6-π-electron rings. It is closely related, peripherally and locally, to the tetracene system. Thus, this dianion constitutes a rather inadequate example in the quest for a general, structural criterion of aromaticity. Yet, its 1H NMR properties are of interest. In contrast with the case of cycloocta[def]fluorenyl anion (2), the two main factors that contribute to the observed chemical shift, i.e., charge densities and ring currents, operate in 16 in opposing directions. There is shielding due to the two negative charges and deshielding due to the formation of the expected induced diamagnetic ring current as a result of the 18-π-electron delocalization. The mentioned charge density-chemical shift correlation predicts a total shielding of 21.4 ppm (10.7 × 2) of the protons, in 16, relative to the neutral 13, or an average shielding of 1.34 ppm for each proton (21.4/16). As can be seen from Table I, the average chemical shift as a result of the formation of 16 remains almost unchanged. The effect of the diamagnetic ring current that nullifies the influence of the negative charges is therefore clearly established. It should be noted that despite the two negative charges, the benzene ring protons are deshielded, thus emphasizing the peripheral operation of the diamagnetic ring current.

When 13 is treated with SbF₅ in SO₂ClF, a dark-purple solution attributed to the formation of the dication 17 appears. The dicaticonic nature of 17 is deduced from its 13C NMR parameters. A total downfield shift of 342 ppm is observed, a value that is in good agreement with the Spiesecke and Schneider correlation. In principle, this dication can be depicted as a system composed of two 8-π-electron antiaromatic indenyl cation moieties or as a [16C-14π] peripheral

<table>
<thead>
<tr>
<th>Table I</th>
<th>1H NMR Data of Dibenzo[bc]pentalene (13) and the Derived Dianion 16 and Dication 17</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
<td>H-3, H-6, H-11, H-14, H-4, H-5, H-12, H-1, H-9</td>
</tr>
<tr>
<td>13</td>
<td>6.90b</td>
</tr>
<tr>
<td>16</td>
<td>7.65 (d, J = 8 Hz)</td>
</tr>
<tr>
<td></td>
<td>7.24 (d, J = 8 Hz)</td>
</tr>
<tr>
<td>δH</td>
<td>0.75, 0.34</td>
</tr>
<tr>
<td>17</td>
<td>9.90 (d, J = 7.4 Hz)</td>
</tr>
<tr>
<td></td>
<td>9.52 (d, J = 7.4 Hz)</td>
</tr>
<tr>
<td>δH</td>
<td>3.0, 2.62</td>
</tr>
</tbody>
</table>

a Chemical shifts reported relative to SiMe₃ (ppm). b Center of multiplet. c δH was deduced from its 13C NMR parameters. d δH was estimated as the difference in the chemical shift of the respective protons in 13 and 16.
Aromatic Character in Pericondensed Polycycles

Diindenocyclo[cd,m]perylene (18) is a pericondensed system in contrast with the previously described catacondensed species. The neutral system is composed of fully aromatic components. Yet, 18 possesses a conjugated periphery of 28 π electrons, which constitutes an antiaromatic system.

The 1H NMR spectrum of 18 consists of an AA′BB′ centered at 7.65 ppm, attributed to the benzene ring protons, and an AB pattern at 8.32 ppm that belongs to the naphthalene components. This is a planar, fully conjugated system with, by definition, an antiaromatic periphery. Yet, its low-field 1H NMR spectrum, centered at 8.00 ppm, points toward the existence of diamagnetic ring currents that are “localized” in the different components (naphthalene and benzene rings) of the molecule. We have to assume that those components are coupled only to a weak extent. Theoretical calculations performed on 18 strengthen this conclusion by estimating relatively large bond lengths to those bonds that connect the aromatic moieties.

Upon treatment of 18 with sodium metal in THF, the two-electron reduction product 19 is obtained. The 1H NMR spectrum of the deep-blue solution consists of an AA′BB′ pattern at 7.75 ppm, assigned to the benzene ring protons, along with an AB spectrum at 8.04 ppm. Despite the shielding caused by the two negative charges, the overall center of gravity is high-field shifted during the reduction process by only 0.08 ppm. This clearly suggests the operation and dominance of a diamagnetic ring current. Dianion 19 has in principle an aromatic periphery of 30 π electrons, while its various charged components can no longer be described as aromatic moieties.

In view of these results the operation of two clearly different mechanisms leading to aromatization is to be assumed. The neutral species 18 is best visualized as being composed of weakly coupled aromatic moieties with localized conjugated circuits and localized diamagnetic ring currents. In contrast, the dianion should be depicted as a peripheral (4n + 1) π aromatic system, weakly perturbed by inner bonds.

The manifestation of aromatic character in neutral systems as well as in their doubly charged derivatives (as exhibited in the described systems and observed in other species, such as biphenylene and its dication derivatives) emphasizes the fundamental difference between mono- and polycyclic systems. In monocyclic conjugated species only one “peripheral” array of π electrons is possible and their aromatic character can be straightforwardly predicted by means of Hückel’s model, unless geometrical distortions occur. In contrast, polycyclic systems can accommodate, in principle, more than one mode of electron delocalization over the π framework, each mode with a different contribution to the overall character of the system. Two such general modes have been mentioned, a dominant peripheral delocalization or dominant contributions of local arrays that are weakly coupled.

At this stage it seems that we are facing “circular” argumentation: an experimental method such as determination of magnetic properties should be applied to the studied system prior to the decision as to which theoretical criterion should be adopted to predict aromaticity.

The problem of choosing the proper theoretical criterion is equivalent to the assignment of the proper relative contributions to the different modes of conjugation. An attractive possibility to overcome this obstacle derives from consideration of one of the basic characteristics related to the aromatic phenomenon. The already mentioned tendency of conjugated systems to acquire aromaticity, or to remain aromatic, suggests that the mode of π-electron distribution that prevails in a system and determines its character 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. Thus, the neutral dibenzopentalene (13) and diindenoperylene


(18) are predicted by the peripheral criterion to exhibit antiaromatic nature. The local model, on the other hand, assigns a partially aromatic and fully aromatic character to 13 and 18, respectively, an assignment clearly mirrored by the experimental, magnetic criterion. The dibenzopentalene dication (17) is predicted to reveal nonaromatic or even antiaromatic patterns by the local contributions model yet is expected to be aromatic by the peripheral criterion. The chemical shifts of the resulting species clearly support the second possibility.

**Quadruply Charged Benzenoid Polycycles: Super-Charged Hydrocarbons**

Further insight into the various modes of π delocalization is gained by scrutiny of the charging processes that occur in the reduction of pyrene (20) and perylene (21). The pyrene and the perylene systems are purely benzenoid polycycles of 14 and 18 π electrons, respectively, in their conjugated peripheries. Both the peripheral model, which emphasizes the contribution of the largest conjugated circuit, and the local approach, emphasizing, in this case, the benzenoid contributions, assign fully aromatic character to 20 and 21. The low-field, diatropic 1H NMR spectra revealed by the two systems (20 and 21) exhibit 1H NMR centers of gravity at 8.22 and 7.90 ppm, respectively, fully justifying this assignment.

Pyrene (20) forms a doubly charged system 22 upon reduction with lithium metal at low temperatures.20

Theoretical calculations estimate a nodal plane through the central carbon atoms in the LUMO of the pyrene systems. Thus, the molecular orbital that accommodates the two additional electrons in the dianion 22 can therefore be depicted as a \([14\pi-16\pi]\) peripheral system and is predicted by means of the peripheral, as well as the local, model (each of the four benzenoid moieties suffers a deviation from the "Hückeloid" number of six \(\pi\) electrons) to reveal antiaromatic character. Indeed, the extreme high-field 1H NMR absorptions of 22 (with a center of gravity at ca. 0.8 ppm) indicate the existence of a pronounced paramagnetic, antiaromatic effect.

We have shown that a stable quadruply charged species, e.g., 23, is obtained by applying sodium or potassium metal to the solution (in tetrahydrofuran or 1,2-dimethoxyethane) of the neutral hydrocarbon 20 or its alkyl or phenyl derivatives.26,27 The evidence for the formation of the tetraanions is based on quantitative analysis and quenching experiments.26

The quadruply charged pyrene 23 offers an interesting case. While the two-electron-reduction process is assumed to quench the diatropicity of the neutral compound in terms of both the peripheral and local models, the tetraanion presents an example of opposing results. The local approach assigns a nonaromatic or even an antiaromatic character to 23. In contrast, aromaticity is predicted by the peripheral model, as due to a \([14\pi-18\pi]\) system. In view of our previous discussion the second, peripheral approach should prevail.

This assumption is nicely supported by theoretical considerations as well as by 1H NMR spectroscopy. Calculations26 performed on the charged species assign a very low excess of negative charge to the central carbon atoms in the quadruply charged species pointing to the peripheral nature of 23. The 1H NMR of the tetraanion is shifted to low field (4.0–6.0) relative to that of the dianion 22 and even to the value predicted by the solely charge-dependent correlation.18 This observed diatropic phenomenon is rationalized by means of the formation and dominance of an aromatic diamagnetic ring current in 23.

Alkyl and phenyl derivatives of pyrene, as well as the perylene system, undergo a similar reduction process to form the respective quadruply charged species, all of which reveal low-field, diatropic 1H NMR chemical shifts, analogous to those revealed by the pyrene tetraanion.26 The generality of the four-electron-reduction process in benzenoid polycyclic systems and the validity of the peripheral \(\pi\)-delocalization model are therefore demonstrated.

The 1H and 13C NMR patterns of the quadruply charged systems reveal some interesting and unexpected phenomena. While the pyrene, 2,7-dimethylpyrene, and 2,7-di-tert-butylpyrene tetraanions (23, 23a, and 23b, respectively) exhibited very complex 1H and 13C NMR spectra, quite startling in view of the high degree of symmetry of the respective neutral systems, the 1,5,6,8-tetraphenylpyrene tetraanion 24 and perylene tetraanion 25 showed the expected, simple NMR patterns. Several spectral properties are particularly surprising. Two, instead of one, methyl and tert-butyl signals appear in the 1H NMR spectra of 23a and 23b. Two methyl and four tert-butyl signals are exhibited in the 13C NMR spectra of 23a and 23b, instead of the expected one and two signals, respectively. Symmetry considerations call for five 13C NMR signals in the aromatic, low-field range of the neutral pyrene, 2,7-dimethylpyrene, and 2,7-di-tert-butylpyrene systems, and the same number of signals is expected in the corresponding tetraanions. Yet, instead of these five absorptions, the pyrene and 2,7-di-tert-butylpyrene tetraanions (23 and 23b, respectively) reveal 16 13C NMR low-field bands and the quadruply charged 2,7-dimethylpyrene system (23a) exhibits 15 absorptions.

In a clear contrast, the spectral patterns (1H and 13C) of the neutral hydrocarbon 20 or its alkyl or phenyl derivatives 24, 25a, and 25b are predicted by the peripheral model and are confirmed by the theoretical calculations. The evidence for the formation of the tetraanions is based on quantitative analysis and quenching experiments.26,27
NMR of 1,3,6,8-tetraphenylpyrene and perylene tetra- 
ra-ions (24 and 25, respectively) reveal the expected, 
simple NMR patterns.

Theoretical calculations (ωB and SCF-MO) performed 
on the multicharged species suggest a rationale for these 
unexpected spectral phenomena.28 The calculations 
assign the largest value of electron density in 23, 23a, 
and 23b to be located on carbons 2 and 7, while the 
second highest negative charge density is assigned to 
carbons 1, 3, 6, and 8. In view of these results we as- 
sume that two of the counterions (Na⁺ or K⁺) are 
situated near carbons 2 and 7, while the two remain- 
ing counterions are in the vicinity of either carbon atoms 1 
and 6 or 1 and 8. The lack of symmetry imposed by the 
positions of the counterions is induced on the polycyclic 
π system to afford two distinct, highly unsymmetric, 
quadruply charged species, which were dubbed the syn 
(S) and anti (A) isomers, viz., 23S and 23A,28 according 
to the locations of the counterions. The existence of these 
two different unsymmetric isomers is revealed by their 
complex NMR patterns. In contrast, the calculations 
estimate a symmetrical distribution of the negative 
charges in the tetraphenylpyrene and perylene tetra- 
raions (24 and 25).29 Therefore no dissymmetry is 
expected. 22Na NMR line-shape studies of these poly- 
ions imply the existence of two species with a very low 
degree of sodium mobility.

Concluding Remarks

Studies of charged polycyclic species provide us with 
new insights into challenging problems of aromatic 
chemistry. The charging process leads to an extension 
of aromatic and antiaromatic series into new homo- 
and isoelectronic species. Consequently, a better and deeper 
understanding of the basic relationship between the 
number of π electrons and their modes of conjugation 
and aromaticity is obtained. The modes of charge 
distribution over the π framework (easily deduced from 
1H and 13C NMR patterns) and the ways by which these 
modes are dominated by the aromatic driving force are 
highlighted through the charging processes. Our studies 
that demonstrate that highly charged aromatic systems 
are easily obtained (a fact believed to be linked to the 
enhanced aromatic stabilization) point to the not yet 
fully appreciated role of the aromatic nature.

Research on polycyclic systems is almost as old as 
organic chemistry, and it seems to be far from being 
exhausted.

(29) The dots on the drawings represent the locations of the counterions.

The Role of Local Stress in Solid-State Radical Reactions

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Received November 22, 1982

Although synthetic and mechanistic organic chemists 
have traditionally concentrated on reactions in fluid 
media, it is not difficult to argue that organic reactions 
in nonfluid media are at least equally important. 
Certainly it would be a mistake to regard biochemical 
reactions, or other reactions that involve rigid or 
structured phases, as occurring in simple fluids. This 
is true for a wide variety of processes, including such 
useful reactions as those of photoresists and heteroge- 
eous catalysts and such deleterious reactions as those 
involving in the weathering and aging of synthetic or 
natural materials, including humans. In order to control 
and exploit organic reactions in nonfluid media, chem- 
ists must develop the same sort of intuition about these 
processes that they have developed for fluid-phase re- 
actions.

Organic reactions in amorphous solids may have 
broader practical significance than those in crystals, but 
a number of research groups have concentrated their 
efforts on crystals, because highly ordered media offer 
more opportunities for detailed mechanistic investiga- 
tion and for sophisticated reaction control. Recent 
reviews of this work demonstrate an elegant and 
informative blending of the structural and dynamic 
techniques of physical chemistry (particularly X-ray 
diffraction, electron microscopy, solid-state spectro- 
copy, and computer simulation) with the synthetic 
and analytical techniques of organic chemistry.1

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