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Local Aromaticities in Large Polyacene Molecules

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There has been controversy on the relative aromaticities of individual rings in a large polyacene molecule. Nucleus-independent chemical shift (NICS) values suggest that the highly reactive inner rings might be more aromatic than the outer ones and even more aromatic than benzene. We evaluated the bond resonance energies (BREs) and hypothetical geometry-independent π-electron currents for a series of linear polyacenes and noticed that for large polyacene molecules the inner rings are never more aromatic than the outer ones. Global HOMA (harmonic oscillator model of aromaticity) values are highly correlative with percentage topological resonance energies (% TREs) but not with average NICS values. Magnetic properties, such as NICS and ring-current intensity, are highly dependent on molecular geometry and so must be carefully related to aromaticity.

Introduction

Linear polyacenes become more reactive with an increase in the number of rings, so that the higher members cannot be characterized experimentally.[1,2] Major chemical reactions occur preferentially at the inner rings. The successive reduction in the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is another example of monotonic behavior in the polyacene series.[3,4] Such progressions in acene properties coincide with the sequential loss of aromaticity.[3,5,6] The percentage topological resonance energy (% TRE) decreases on going to higher polyacene members.[7] Since there is only one sextet ring in all polyacene molecules, the number of nonsextet rings increases along the polyacene series.[1,2] Even if so, it is very impressive that higher polyacenes are extremely reactive.[1,2]

There has been controversy about which rings in a large polyacene molecule are more aromatic than the others.[8,9] Schleyer et al. stressed that the inner rings are more aromatic than the outer ones because the inner rings exhibit larger negative nucleus independent chemical shift (NICS) values at the ring centers.[9] In fact, NICS has been introduced as a measure of local aromaticity.[10] According to this magnetic measure, the highly reactive inner rings appear to be more aromatic than the less reactive outer rings and even more aromatic than benzene itself.[9] We, however, found that NICS is not always reliable as a measure of local aromaticity when it is applied to polycyclic π-systems.[11−13] In this study, we attempt to critically evaluate the local aromaticities in linear polyacene molecules using our graph theories of aromaticity[14,15] and magnetotropicity.[16−18] We use the term "magnetotropicity" when diatropicity and paratropicity are referred to collectively.

Theory

Topological resonance energy (TRE) and bond resonance energy (BRE) are typical energy quantities defined by our graph theory of aromaticity.[14,15,19,20] TRE represents a stabilization energy due solely to cyclic π-conjugation, which is given relative to the π-binding energy of the graph-theoretically defined polyene reference.[14,15] We believe that aromaticity is an energy quantity in nature[21,22] and therefore use TRE as a standard measure of aromaticity. Note that Schleyer et al. justified NICS as an index of local aromaticity by correlating it with the aromatic stabilization energy for monocyclic (five-membered) π-systems.[10] The % TRE is defined as 100 times the TRE, divided by the total π-binding energy of the polyene reference.[19,20] This quantity is useful when one wants to compare the aromaticities of different molecules. BRE represents the contribution of a given π bond to the TRE.[19,20] If the smallest BRE in a π-system has a large negative value, the π-system will be kinetically very unstable with chemically reactive sites. Both TRE and BRE are given in units of $|\beta|$, where β is the standard resonance integral in Hückel theory. We assume that all benzene rings are regular hexagons in shape.

A graph-theoretical variant[17,18] of Hückel−London theory[23] is utilized to calculate the intensities of π-electron currents magnetically induced in polycyclic π-systems. According to this theory, a π-electron current induced in a polycyclic π system can be partitioned formally among all possible circuits in it. Here, all possible circuits stand for all possible cyclic paths that can be chosen from a π-system.[24] This does not imply that all circuit currents flow independently because their intensities are interdependent.[25] Our graph theories totally rely on the acknowledgment of all possible circuits in a π-system.[14−18] Let a π-system from which one or more circuits can be chosen be denoted by G. Then a current intensity assignable to the ith circuit, I_i, is expressed in the form:[17,18]

$$I_i = 18 I_0 \frac{S_i}{S_0} \sum_{j}^{\mathrm{occ}} \frac{P_{\mathrm{G}-\mathrm{r}_i}(X_j)}{P'_{\mathrm{G}}(X_j)} \qquad (1)$$

where I_0 is the intensity of a current induced in the benzene ring; S_i and S_0 are the areas of r_i and the benzene ring, respectively; $\mathrm{G}-\mathrm{r}_i$ is the subsystem of G, obtained by deleting r_i from G; $P_{\mathrm{G}}(X)$ and $P_{\mathrm{G}-\mathrm{r}_i}(X)$ are the characteristic polynomials for G and $\mathrm{G}-\mathrm{r}_i$, respectively; X_j is the jth largest root of the equation $P_{\mathrm{G}}(X) = 0$; and j runs over all occupied π orbitals. If there are degenerate π orbitals, this formula must be replaced by others.[17] Positive and negative values for I_i signify diatropicity and paratropicity, respectively.

In fact, circuit currents thus defined are consistent with the extended Hückel rule proposed by Hosoya et al.,[25] in the sense

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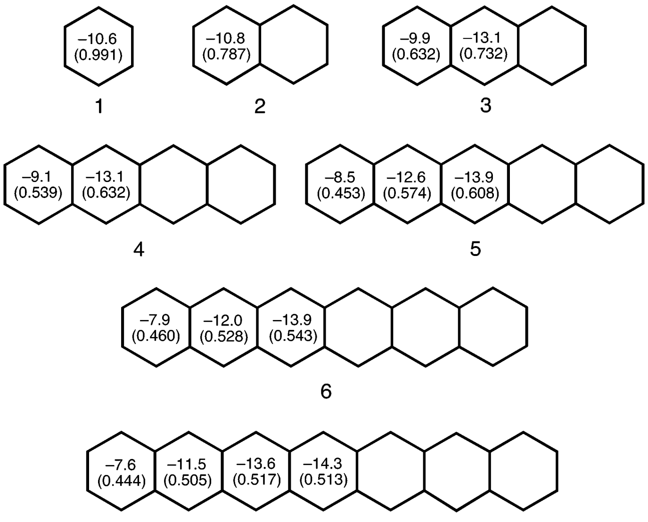

Figure 1. NICS(1) values for all nonidentical rings in benzene and six polyacenes. The HOMA values for individual rings are given in parentheses. NICS(1) and HOMA values were taken from refs 9 and 8, respectively.

TABLE 1: Global HOMA and % TRE Values for Benzene and Polyacenes

species	HOMA[a]	% TRE
benzene (**1**)	0.991	3.53
naphthalene (**2**)	0.811	2.92
anthracene (**3**)	0.718	2.52
naphthacene (**4**)	0.668	2.27
pentacene (**5**)	0.628	2.11
hexacene (**6**)	0.629	1.99
heptacene (**7**)	0.624	1.91

[a] Taken from ref 8.

TABLE 2: TREs and MREs for Benzene and Polyacenes

species	TRE/$|\beta|$	MRE/$|\beta|$
benzene (**1**)	0.273	0.222
naphthalene (**2**)	0.389	0.289
anthracene (**3**)	0.475	0.341
naphthacene (**4**)	0.553	0.393
pentacene (**5**)	0.630	0.448
hexacene (**6**)	0.706	0.504
heptacene (**7**)	0.783	0.551

that for neutral π-systems, I_i values are positive and negative in sign for $(4n + 2)$- and $4n$-membered circuits, respectively.[16−18,26,27] This indicates that $(4n + 2)$- and $4n$-membered circuits are diatropic and paratropic, respectively. This aspect of magnetotropicity fully justifies the partition of a total π-electron current in the form of eq 1. The Hückel-like rule of superaromaticity for charged paracyclophanes and the counter-rotating rim and hub currents in coronene can be rationalized successfully in terms of circuit currents.[28,29] These facts also support the utility of eq 1.

As can be seen from eq 1, the intensity of the circuit current is proportional to the following quantity:

$$A_i = 4\sum_j^{\text{occ}} \frac{P_{\mathrm{G}-\mathrm{r}_i}(X_j)}{P'_{\mathrm{G}}(X_j)} \qquad (2)$$

We reported in 1981 that A_i can be interpreted as an approximate contribution of the ith circuit to the TRE.[26] In other words, the intensity of each circuit current reflects the contribution of the circuit to aromatic stabilization energy. It follows that the sum of A_i values over all circuits must represent the approximate TRE. For the reasons given previously,[27] we call the sum a magnetic resonance energy (MRE), which means a TRE-like quantity derived from the magnetic response of the π-system. Like TRE, MRE is a function of molecular topology only. MRE is highly correlative with TRE.[27] Such interpretation of MRE as a kind of aromatic stablization energy (ASE) is advantageous, in that no hypothetical polyene reference is required to evaluate ASE.

Results and Discussion

NICS is defined as the negative of the magnetic shielding calculated at a ring center.[9,10] Positive and negative NICS values at ring centers are associated primarily with paramagnetic and diamagnetic π-electron currents, respectively. Schleyer and others have referred to NICS as a convenient indicator of local magnetotropicity or local aromaticity for polycyclic π-systems.[9,10,30] NICS(1) values at the ring centers of benzene and six polyacenes are graphically summarized in Figure 1, which are the ones calculated by Schleyer et al. at the IGLO/TZ2P//B3LYP/6-311+G** level of theory.[9,31] NICS(1) represent the value calculated at the ring center and 1 Å above the molecular plane.

When such a magnetic criterion of aromaticity is applied to polyacenes, the inner rings are predicted to be more aromatic than the less reactive outer ones because they exhibit large negative NICS(1) values at the centers of the rings.[9] It follows that the reactive inner rings are more aromatic than benzene itself. As can be seen from Figure 1, the NICS(1) values at the centers of the central rings increase as the size of the polyacene molecule increases. Schleyer et al. say that the central rings in larger polyacene molecules are more aromatic even if they are much more reactive.[9] The NICS(1) values at the centers of the edge rings necessarily decrease on going to larger polyacene members.

The HOMA (harmonic oscillator model of aromaticity) value is a geometric indicator of aromaticity defined using the degree of bond-length alternation.[8,9] The HOMA values reported for individual rings of **1**−**7**[8] are given in parentheses in Figure 1. These were calculated on the basis of B3LYP/6-311G** geometries. At a glance, it appears that the NICS(1) value correlate well with the corresponding HOMA value.[9] Both HOMA and NICS indicate that for each polyacene molecule the central rings might be more aromatic than outer ones. Like the negative of the NICS(1) value, the HOMA value is larger at the inner rings.[8] However, the HOMA values for the central rings gradually decrease on going to the larger polyacenes. This trend in the HOMA values is in marked contrast to that in the NICS(1) values. In addition, the global HOMA value, i.e., the HOMA value for an entire π-system, also decreases on going to larger polyacenes.[8] The global HOMA values for **1**−**7**[8] are listed in Table 1. For example, the global HOMA value for **7** is about a half that for benzene. In line with this, the % TRE for **7** is about a half that of benzene. Thus, the global HOMA value is highly correlative with the % TRE but not with the average NICS values obtained by averaging the NICS values at all ring centers.

As properly pointed out by Schleyer et al.,[9] the NICS(1) values are due to the contribution of the ring concerned as well as that of the remote rings. The latter contribution, however, is small (10% or less).[9] The current density maps we calculated for **1**−**7** are shown in Figure 2, where all current intensities are given in units of that induced in the benzene ring. The magnetic

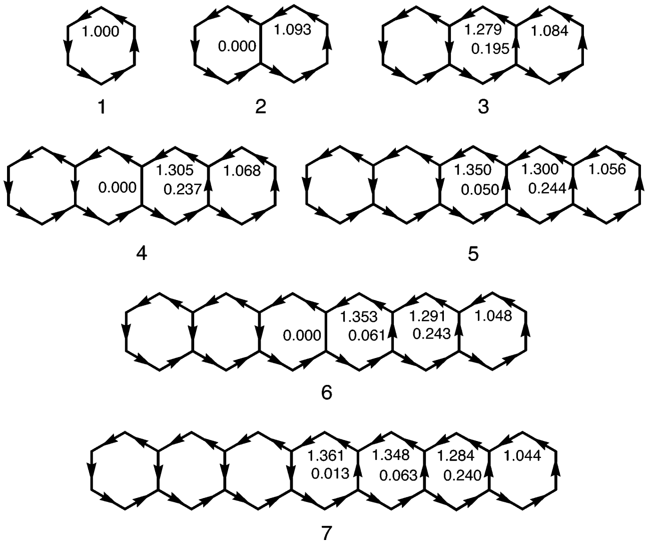

Figure 2. Current density maps of benzene and six polyacenes. Currents are given in units of that for benzene.

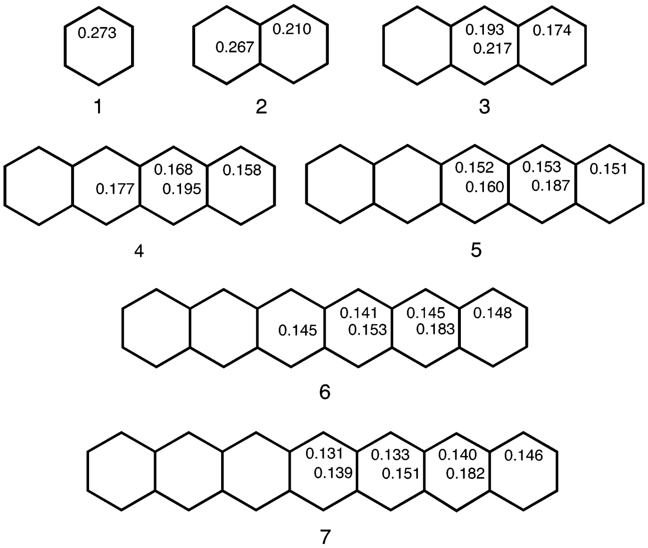

Figure 3. BREs in units of $|\beta|$ for benzene and six polyacenes.

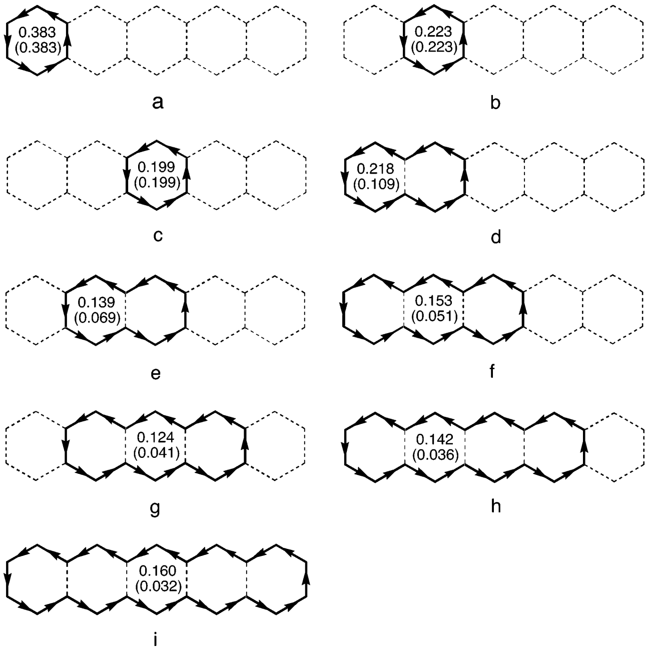

Figure 4. Intensities of the circuit currents induced in pentacene (**5**). All circuit currents are given in units of that for benzene. The current intensities induced in the geometry-independent reference (**5′**) are given in parentheses.

field is assumed to be perpendicular to the plane of this figure; counterclockwise and clockwise arrows denote diamagnetic and paramagnetic π-electron currents, respectively. The NICS values actually reflect quite well the ring currents and their intensities calculated not only by us (Figure 1) but also by others.[32,33] Current intensities induced in **1**−**7** are identical with those calculated without reference to circuits by Haigh and Mallion,[34] indicating that eq 1 is an exact formula for circuit currents.

All rings in all polyacenes are diatropic in harmony with large negative NICS(1) values at their ring centers. In general, the central rings in higher polyacene molecules sustain larger diatropic currents. The edge rings necessarily sustain smaller currents. There is no doubt that each NICS(1) value straightforwardly reflects the magnetotropicity of the ring concerned; rings that sustain large diatropic currents exhibit large negative NICS(1) values without exceptions. This in turn proves that our Hückel molecular orbital (HMO) model is numerically reasonable and acceptable.

The % TRE for **1**−**7** are added in Table 1. The order of aromaticity can readily be derived from the relative magnitudes of the % TREs. The order of aromaticity of polyacenes thus determined is simply opposite to the order of the molecular size. Schleyer et al. predicted from the NICS(1) values that, despite the increasing reactivity from benzene to heptacene, the degrees of aromaticity are nearly constant.[9] The average NICS(1) values for **1**−**7** indeed lie in the very narrow range between −10.6 and −11.4. It is evident that these average NICS(1) values do not reflect the order of aromaticity derived from the % TREs. Furthermore, neither Dewar resonance energies per π-electron[22] nor Hess−Schaad resonance energies per π-electron[3] are correlative with these average NICS values.

BRE is useful for estimating the contribution of individual π bonds to aromaticity.[19,20] The BREs for all species are presented in Figure 3. All π bonds in polyacenes have positive BREs, which is consistent with the view that all these molecules are aromatic with positive TREs. As for **3**−**7**, the bonds shared by two inner rings exhibit smaller BREs than those shared by two outer rings, which indicates that the inner rings concerned are less aromatic than the edge rings. However, the bonds shared by two inner rings in higher polyacenes exhibit smaller BREs than those in smaller polyacenes. Likewise, the bonds shared by two outer rings in higher polyacenes exhibit smaller BREs than those in smaller polyacenes. These aspects of BREs also support the lower aromaticity of higher polyacenes. Thus, our prediction of the aromaticity order based on TRE and BRE is quite different from that of Schleyer based on NICS(1) values.[9]

Why does the % TRE order of aromaticity differ from the NICS order? A clue to this problem is obtained by partitioning the total π-electron current among the circuits.[17,18] All circuits in polyacenes were found to sustain diamagnetic currents because all of them are $(4n + 2)$-membered conjugated circuits.[25,35,36] As shown in Figure 4, the π-system of pentacene (**5**) has nine nonidentical circuits and fifteen circuits in all. By superposing the currents induced in these circuits, we can reproduce the current density map of this hydrocarbon in Figure 1. As far as polyacenes are concerned, all circuits make comparable contributions to the global π-electron current. For example, circuits **e**−**i** in **5** indeed sustain comparable circuit currents. Steiner and Fowler noted that the conventional interpretation of diatropic/paratropic (aromatic/antiaromatic) behavior in terms of NICS values may give a misleading picture

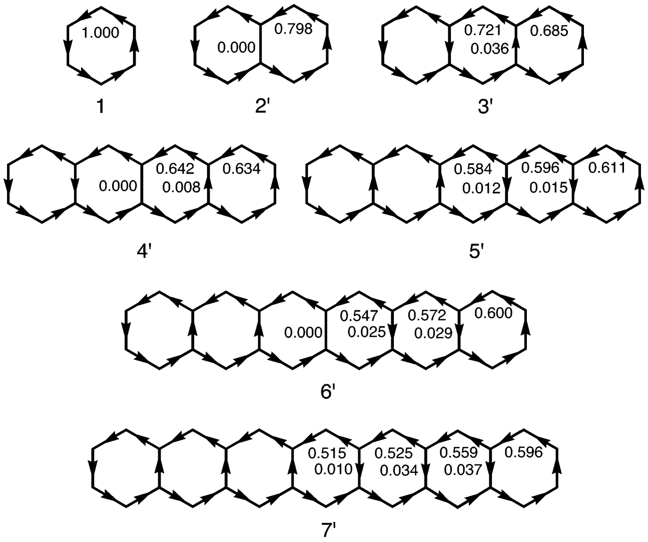

Figure 5. Hypothetical current density maps of the hypothetical references for benzene (**1′**) and six polyacenes (**2′**−**7′**) obtained by assuming that all circuits have the same area as benzene. All currents are given in units of that for benzene.

of the local flow of currents in a polycyclic π-system.[37] This problem can be solved exactly by partitioning the total current among the circuits.

As can be seen from eq 1, the intensity of the *i*th circuit current is proportional not only to the A_i value but also to the circuit area S_i.[17,18] If a molecule is artificially deformed to reduce the areas of all rings or all circuits, the entire π-electron current will be more or less decreased. To visualize such a geometric feature of π-electron currents, hypothetical π-electron currents were evaluated by assuming that all circuit areas in **1**−**7** are equal to that of the benzene ring (i.e., $S_i = S_0$ for all circuits). Of course it is impossible to deform a polycyclic π-system in this manner because all circuit areas are interdependent. The hypothetical current density maps thus obtained for polyacenes are shown in Figure 5, where the hypothetical reference systems that sustain such hypothetical π-electron currents are denoted by **2′**−**7′**. Actual benzene (**1**) is identical with the corresponding reference system (**1′**). We see from this figure that the peripheral diatropic currents in **2**−**7** are reduced to a large extent in **2′**−**7′**. These hypothetical current density maps clearly show that large circuits with large areas contribute much to the peripheral currents in actual π-systems although their contribution to MRE is fairly small.[27]

The current intensities induced in all nonidentical circuits of **5′** are given in parentheses in Figure 4. They represent the contribution of individual circuits to the global ring current. The intensity of the *i*th hypothetical circuit current is proportional solely to the A_i value or the contribution of the circuit to MRE. Therefore, the current density pattern in the hypothetical reference must reflect the TRE and/or the BREs. It should be noted that, as in the case of annulenes, larger circuits contribute less to aromaticity with smaller A_i values. Therefore, it is obvious that large contributions of large circuits to the global current induced in actual π-systems are due primarily to their large areas. Thus, the current density map of an actual polycyclic π-system does not reflect aromaticity accurately. This way of reasoning applies to the interpretation of NICS(1) values for a polycyclic π-system because they reflect the current density in an actual π-system.

It is very interesting to note that each bond current in hypothetical reference systems is highly correlative with the corresponding BRE in Figure 3. Here, a bond current stands for the intensity of a π-electron current that flows though a given bond. All peripheral CC bonds in **2′**−**7′** sustain smaller bond currents than those in **1**. Likewise, all BREs for **2′**−**7′** are smaller than those for **1**. For example, the BREs for the peripheral bonds of the central ring in **7′** are about a half those for CC bonds in benzene. Likewise, the peripheral π-electron currents in the central ring of **7′** is about a half those for benzene. The edge rings carry a bit larger peripheral currents and exhibit a bit larger BREs for the peripheral π bonds. In this context, close examination of A_i values revealed that outer six-, ten-, and fourteen-membered circuits have somewhat larger A_i values than their respective inner ones. Thus, the current density distribution in a hypothetical reference system bears a close resemblance to the BRE distribution of the real π-system. We are now convinced that the central rings in higher polyacenes **5**−**7** have fairly small aromatic character as compared to the edge rings.

Concluding Remarks

We have seen that NICS values calculated at the ring centers of polycyclic π systems do not always reflect local aromaticities of the rings. Higher polyacenes have large negative NICS values at all ring centers although they are less aromatic with smaller % TREs. We have repeatedly pointed out that NICS is not always a good indicator of aromaticity for polycyclic π-systems.[11−13] Like other magnetic indices, NICS suffers from geometry-dependency.[38] In general, large conjugated circuits contribute much to magnetic properties but much less to aromaticity.[25,36,37] This is the main reason NICS values are large at the centers of the inner rings in polyacenes. We showed that central rings of polyacenes exhibit less local aromaticity than the edge rings. Note that all of the TREs, BREs, and circuit currents, all employed in this study, are defined exactly within a simple Hückel framework so that these quantities are theoretically consistent with each other.[14−21,26−29] The caveat emerging from this paper would apply to all methods relying on π-electron currents, for instance to our own current intensities in Figure 2, and to other current density plots, e.g., from the Fowler/Steiner groups.[32,33]

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