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Aromatic character of annelated dimethyldihydropyrenes

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ABSTRACT: Mitchell and co-workers recently estimated the order of aromaticity for dimethyldihydropyrene (DDP) nuclei in annelated derivatives using nucleus-independent chemical shifts (NICS). We found that two graph-theoretically defined energetic quantities, percentage topological resonance energy (% TRE) and bond resonance energy (BRE), can be used to predict readily the relative aromaticities of these hydrocarbons and their DDP nuclei, respectively. Since these quantities are not dependent on the areas of individual rings, they are better suited for estimating the degree of aromaticity. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: dimethyldihydropyrene; aromaticity; bond resonance energy; percentage topological resonance energy

INTRODUCTION

Aromaticity is one of the fascinating concepts in modern organic chemistry. It has been defined in structural, magnetic and energetic terms.[1] Historically, many chemists have discussed aromaticity most conveniently in terms of ^{1}H chemical shifts. Mitchell and co-workers noted that ^{1}H chemical shifts of the internal methyl groups in dimethyldihydropyrene (DDP, **1**) and its annelated derivatives (**2**–**7**) serve to assess the relative local aromaticities of the DDP nuclei.[2–4] As can be seen from Fig. 1, the internal methyl groups must be very sensitive NMR probes for aromaticity. The degree of bond localization that occurs along the periphery of the 14-membered ring was also used as a measure of local aromaticity for the DDP nuclei.[4,5]

In 1996, Schleyer *et al.* introduced a new quantity called the nucleus-independent chemical shift (NICS), the negative of the absolute magnetic shielding, usually computed at the ring centers, as an indicator of local aromaticity.[6] Negative and positive NICS values correspond to aromaticity and antiaromaticity, respectively. NICS values have been evaluated for many π-systems.[7] Mitchell and co-workers recently used the simple arithmetic average of the NICS values at the centers of four six-membered rings in a DDP nucleus (NICS Av) as a measure of the aromaticity of the nucleus.[4] The four six-membered rings in **1**–**7** are denoted **a**, **b**, **c** and **d** in Fig. 1. They found that the NICS Av values for **1**–**7** are in excellent agreement with the experimental order of local aromaticity for the DDP nuclei.[4]

We have developed graph theories of aromaticity and magnetotropicity for polycyclic π-systems within the framework of Hückel theory.[8–14] In this paper, we point out that the relative aromaticities of **1**–**7** and the DDP nuclei can be predicted readily using two graph-theoretically defined quantities, percentage topological resonance energy (% TRE) and bond resonance energy (BRE), respectively. This must be the simplest way for estimating relative local aromaticities for rather homologous polycyclic π-systems.

THEORY

First, some concepts and related graph theories are briefly surveyed. The TRE was defined graph-theoretically as an energetic criterion of aromaticity.[8–10] We use TRE as a standard measure of aromaticity. Percentage TRE (% TRE) is defined as 100 times the TRE divided by the total π-binding energy of the polyene reference.[10,13,14] This quantity is useful for estimating the relative aromaticities of different molecules. The BRE represents the contribution of a given π bond to the TRE.[13,14] If the smallest BRE in a π-system has a large negative value, the π-system will be kinetically unstable with chemically reactive sites.[13–16] In this sense, BRE is an index that represents both energetic and kinetic stabilities for local

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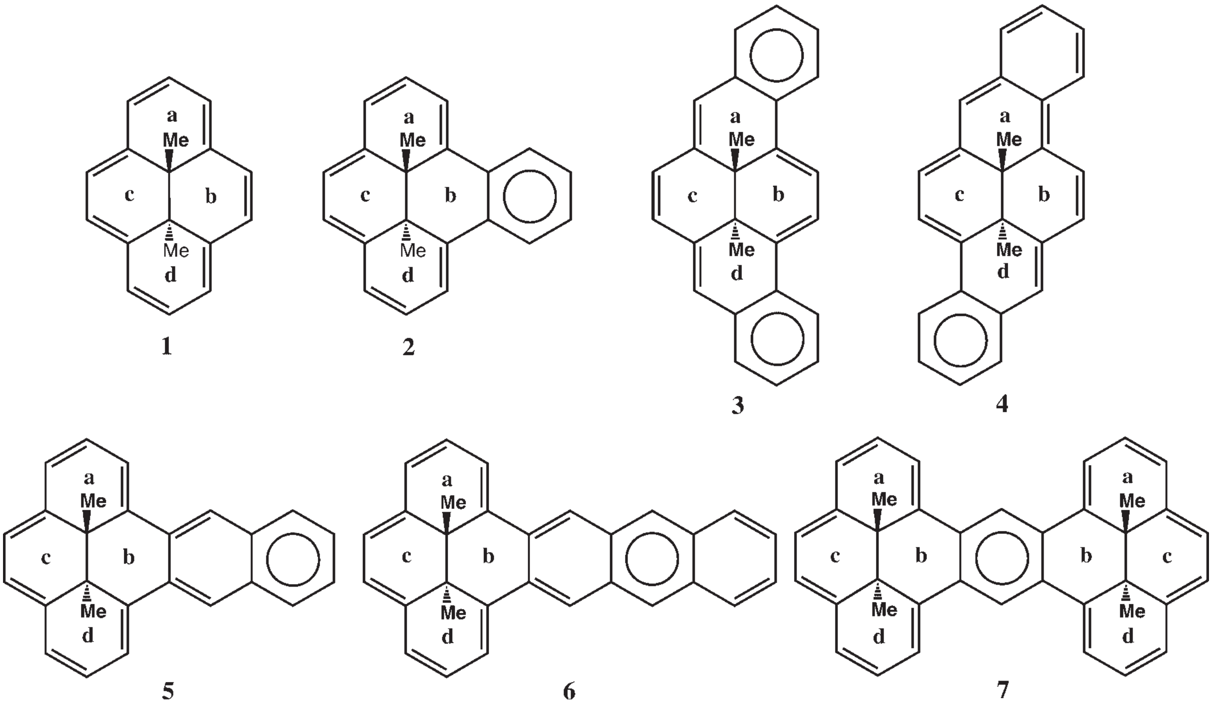


Figure 1. Dimethyldihydropyrene (**1**) and its annelated derivatives (**2**–**7**)

structures of a polycyclic π-system. Both TRE and BRE are given in units of $|\beta|$, where β is the standard resonance integral in Hückel theory.

π-Electron currents induced in polycyclic species were calculated using a graph-theoretical variant[10–12] of Hückel–London theory.[17] Let a π-system from which one or more circuits are chosen be denoted by G. Here circuits stand for all possible cyclic paths in G. Then a current intensity, I_i, induced independently in the ith circuit, r_i, can be expressed in the form[11,12]

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

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; G-r_i is the subsystem of G, obtained by deleting r_i from G; $P_{\mathrm{G}}(X)$ and $P_{\mathrm{G-r}_i}(X)$ are the characteristic polynomials for G and G-r_i, respectively; X_j is the jth largest zero of $P_{\mathrm{G}}(X)$; and j runs over all occupied π orbitals. If there are degenerate π orbitals or heteroatoms, this equation must be replaced by others.[11,12] Positive and negative values for I_i signify diatropicity and paratropicity, respectively. The current density map of a polycyclic π-system is obtained by superposing all such circuit currents.[11,12] It now is self-evident that π-electron currents obey Kirchhoff's law. Apparent bifurcation of a π-electron current at points where three π-bonds join can be rationalized straightforwardly in terms of circuit currents.[18]

Binsch and co-workers developed the theory of second-order double bond fixation.[19–22] First-order double bond fixation is such that the symmetry of the π-system is not lowered by the fixation. It is second-order bond fixation that lowers the symmetry of the π-system. They calculated the bond–bond polarizabilities $\pi_{\mu\nu,\kappa\lambda}$ for the fully symmetric model of the π-system and then diagonalized the matrix $\pi = (\pi_{\mu\nu,\kappa\lambda})$ of order $M \times M$, where M is the number of π-bonds. This equation will yield M eigenvalues. The largest eigenvalue $\lambda_{\max}$ is compared with the critical value λ_{crit}, which is usually taken to be $1.80\beta^{-1}$.[17–20] If $\lambda_{\max}$ is larger in magnitude than λ_{crit}, then the π-system is predicted to suffer a distortion as a consequence of second-order effects.

RESULTS AND DISCUSSION

NICS is the latest magnetic criterion of local aromaticity. NICS values at all ring centers of DDP (**1**) and its annelated derivatives (**2**–**7**) are summarized in Fig. 2. These values are those calculated by Mitchell and co-workers at the GIAO-HF/6–31G*//B3LYP/6–31G* level of theory.[4] Values presented at the centers of 14-membered rings are the NICS Av values for the DDP nuclei. All benzene rings in **2**–**7** are predicted to be highly aromatic with large negative NICS values. As shown in Table 1, the NICS Av values are in excellent agreement with the order of local aromaticity for the DDP nuclei estimated from the ^{1}H chemical shifts.[3,4] Among seven species, **1** and **4** exhibit the largest negative NICS Av values. On this basis Mitchell and co-workers classified the DDP nuclei of **1** and **4** as equally aromatic.[4] However, large negative NICS Av values for these two species

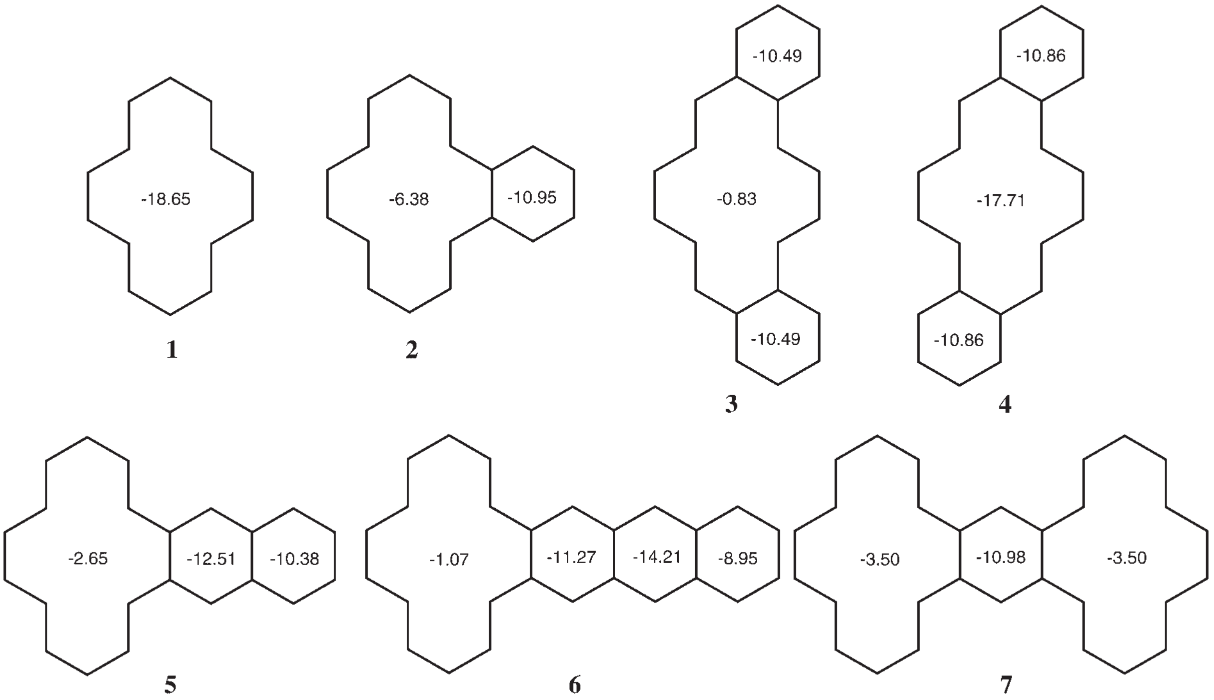


Figure 2. NICS values at the ring centers of **1**–**7**. Values in the DDP nuclei are the NICS Av values

Table 1. BREs, π-electron currents and NICS Av values for seven DDP nuclei

Species	BRE/$\vert\beta\vert$[a]	I_{DDP}/I_0[b]	NICS Av[b,c]
1	0.113 (1)	1.651 (1)	−18.65 (1)
2	0.089 (2)	1.499 (3)	−6.38 (3)
3	0.060 (6)	1.176 (7)	−0.83 (7)
4	0.086 (3)	1.565 (2)	−17.71 (2)
5	0.069 (4)	1.316 (5)	−2.65 (5)
6	0.058 (7)	1.199 (6)	−1.07 (6)
7	0.069 (5)	1.437 (4)	−3.50 (4)

[a] Values for the π-bonds that belong to the DDP nucleus but are not shared by other rings.
[b] The order of magnitude is given in parentheses.
[c] Values at the GIAO-HF/6–31G*//B3LYP/6–31G* level of theory.[4]

never indicate that the DDP nuclei are more aromatic than benzene rings because the areas of the 14-membered rings concerned are four times as large.

The current density maps of **1**–**7** are shown in Fig. 3. They were calculated assuming that each DDP nucleus is identical with an equilateral [14]annulene ring. The intensities of π-electron currents induced around the DDP nuclei (I_{DDP}) are included in Table 1. At the level of Hückel–London approximations,[11,12] the π-systems of **8**, **9** and **10** given in Fig. 4 are identical with those of **2**, **4** and **5**, respectively, because the relative positions of annelating rings are the same. The diatropicity order as evidenced by I_{DDP} is **1** > **4** > **2** > **7** > **5** > **6** > **3**. This order is exactly the same as that of local aromaticity for the DDP nuclei predicted by the NICS Av values.[4] Hence it is clear that the NICS Av values are closely associated with I_{DDP}, the former being caused by the latter.

According to Mitchell and co-workers,[4,5] the order of aromaticity in the DDP nucleus determined using the degree of bond localization is **1** = **4** > **2** > **3**, which is in accord with that of I_{DDP}. It seems very likely that a strong π-electron current is induced in a ring or a circuit that lacks marked bond localization. Except for **4**, the enhancement of bond localization by increasing benzannelation is observed.[23] Mitchell *et al.* stated that benzene rings have a powerful localizing power.[2] In this context, the λ_{max} values for **1**–**7** are presented in Table 2. It is not easy to interpret these values in terms of bond localization since the DDP derivatives are very diverse in geometry. However, it is clear that all λ_{max} values are smaller than $1.80\beta^{-1}$, suggesting that all the species are free from second-order bond localization. Note that first-order bond-length alternation is not allowed in **4**. This is why **4** suffers from the least degree of bond localization.

We evaluated BREs for all CC bonds in **1**–**7** assuming that all these bonds are equal in length. They are included in Fig. 3 and Table 1. By definition,[13,14] the BRE for any π-bond that belongs only to a given ring can also be interpreted as an indicator of local aromaticity for the ring. The BRE decreasing order of aromaticity of the DDP nuclei is then **1** > **2** > **4** > **5** > **7** > **3** > **6**. Interestingly, this order is slightly different from that predicted from the NICS Av values.[4] As suggested by Eqn (1), magnetic properties, such as ^{1}H chemical shifts, NICS and I_{DDP}, are strongly dependent on the areas of individual rings,[10–12] whereas energetic quantities, such as TRE and BRE, are dependent solely on molecular topology or connectivity of atoms.[8–10,13,14] This may possibly be the main origin of the small discrepancy found

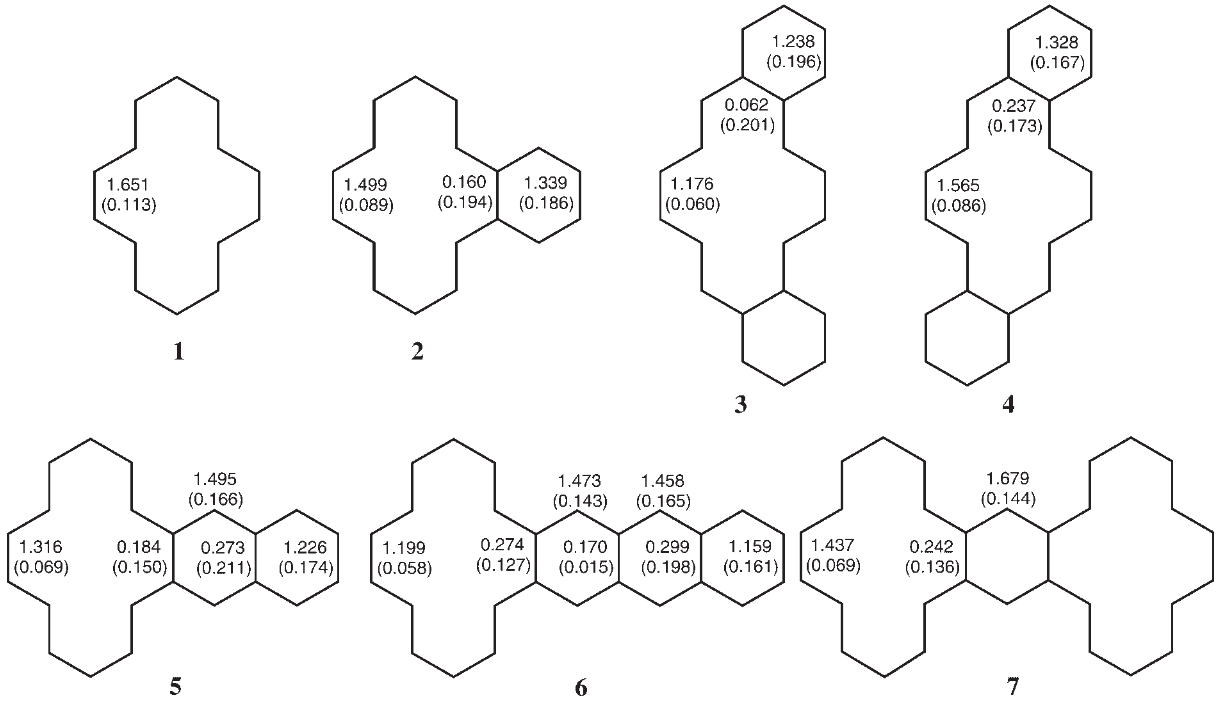


Figure 3. Current density maps for **1**–**7**, in which all current intensities are given in units of that for benzene. Values in parentheses are the BREs in units of $|\beta|$

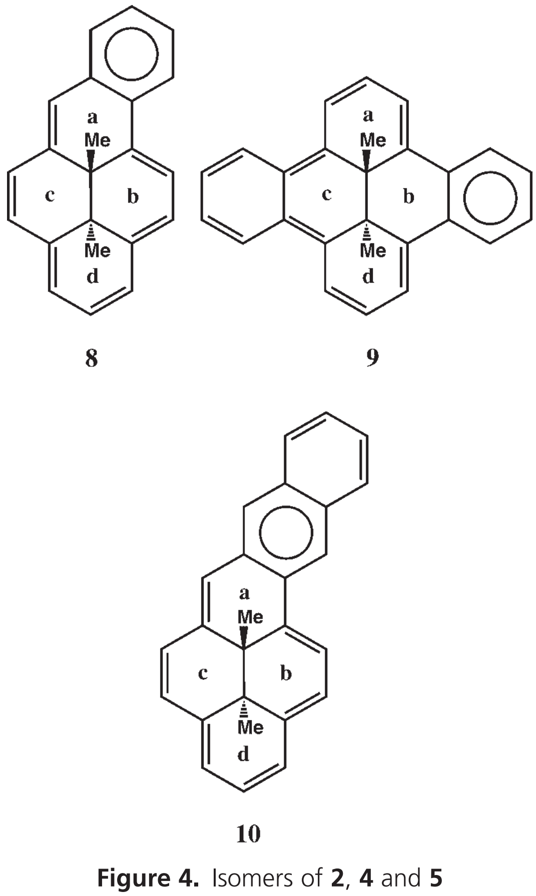


Figure 4. Isomers of **2**, **4** and **5**

between the orders of local aromaticity determined using I_{DDP} and BREs. Our BRE scale of local aromaticity is better suited as an index of aromaticity since it is dependent solely on molecular topology.

Examination of Table 1 reveals that the NICS Av values vary widely from molecule to molecule as compared with I_{DDP} and BREs. This must reflect the fact that I_{DDP} and BRE were calculated for π-systems in which all CC bonds are equal in length. In contrast, all NICS values employed in this study were calculated for realistic molecular geometries.[4] Wannere and Schleyer reported that for large annulenes, bond length alternation only reduces energetic stabilization somewhat but influences the magnetic properties, such as NICS, proton chemical shifts and ring-current magnetic susceptibilities, considerably.[24] This finding must apply to annelated DDPs.

NICS values at the centers of the benzene rings appear to illustrate the general trend of increasing aromaticity in the annelating rings on going from benz- (**2**) to naphth- (**5**) to anthrannelated (**6**) as the aromaticity of the corresponding DDP nuclei decreases.[4] However, this order of aromaticity in the annelating rings is not compatible with the order based on the current intensities and BREs for these rings, which is the benzene nucleus in **2** > the naphthalene nucleus in **5** > the anthracene nucleus in **6**. This order of local aromaticity is consistent with the % TREs for benzene (3.53 $|\beta|$), naphthalene (2.92 $|\beta|$) and anthracene (2.52 $|\beta|$).[10,14] The % TREs decrease in this order. We recently pointed out that relative NICS values do not always represent relative degrees of local aromaticity.[25,26]

Table 2. TREs, % TREs and λ_{max} values for seven DDP derivatives

Species	TRE/$\lvert\beta\rvert$	% TRE[a]	λ_{max}/β^{-1}
1	0.113	0.63 (6)	1.560
2	0.260	1.11 (5)	1.467
3	0.428	1.47 (1)	1.299
4	0.390	1.34 (2)	1.449
5	0.361	1.24 (4)	1.417
6	0.445	1.29 (3)	1.396
7	0.245	0.63 (7)	1.504

[a] The order of magnitude is given in parentheses.

The chemical formulae presented in Fig. 1 are the best Clar structures in which sextet rings are denoted by solid circles.[27,28] These sextet rings are the centers of high local aromaticity. We were then tempted to associate a strong current induced in the DDP nucleus of **4** with its Clar structure.[2] If all sextet rings are fixed somewhere in the π-system as in **2**, **3** and **7**, the DDP nucleus will sustain a relatively weak current. Strong π-electron currents are induced at these sextet rings and then marked bond length alternation is introduced into the DDP nucleus. On the other hand, if sextet rings can migrate into other benzene rings, marked bond length alternation will never be preferred.[27,28] This must be why **4** sustains a strong current along the DDP periphery.[2] In fact, the DDP nuclei of **2**, **3**, **5**, **6** and **7** undergo an appreciable degree of bond localization.[4,5,23] As for **5** and **6**, the migration of a sextet ring is confined to the naphthalene or anthracene nucleus.

As shown in the form of Eqn (1), a π-electron current induced in a polycyclic π-system can be partitioned among all possible circuits.[11,12] All circuits in **1**–**7** are diatropic since they all are $(4n+2)$-membered conjugated circuits.[10,29–31] For example, all non-identical circuits and circuit currents (i.e. currents induced in individual circuits) for two isomeric species, **3** and **4**, are presented in Fig. 5. Each has four non-identical circuits. It is noteworthy that **4** has a sextet ring that can migrate to another benzene ring and so sustains large induced currents in large 18- and 22-membered circuits. Since each circuit current is dependent straightforwardly on the area of the circuit, we might say that the NICS or current intensity change in the DDP nucleus does not always represent the order of aromaticity.[25,26]

An interesting comparison is that of the current density patterns of **4** and **3** in Fig. 3 with those of anthracene (**11**) and phenanthrene (**12**) in Fig. 6. The central benzene ring of **11** sustains a larger current than that of **12**. In the same manner, the central ring of **4** sustains a larger current than that of isomer **3**. Such a trend in π-electron currents obviously reflects the mobility of sextet rings. There is one mobile sextet ring in the π-systems of **4** and **11**, whereas those of **3** and **12** have two fixed sextet rings. BREs for edge benzene rings are larger for **4** and **11** than for **3** and **12**, respectively. Mitchell and co-workers predicted on the basis of the relative energies that **4** is

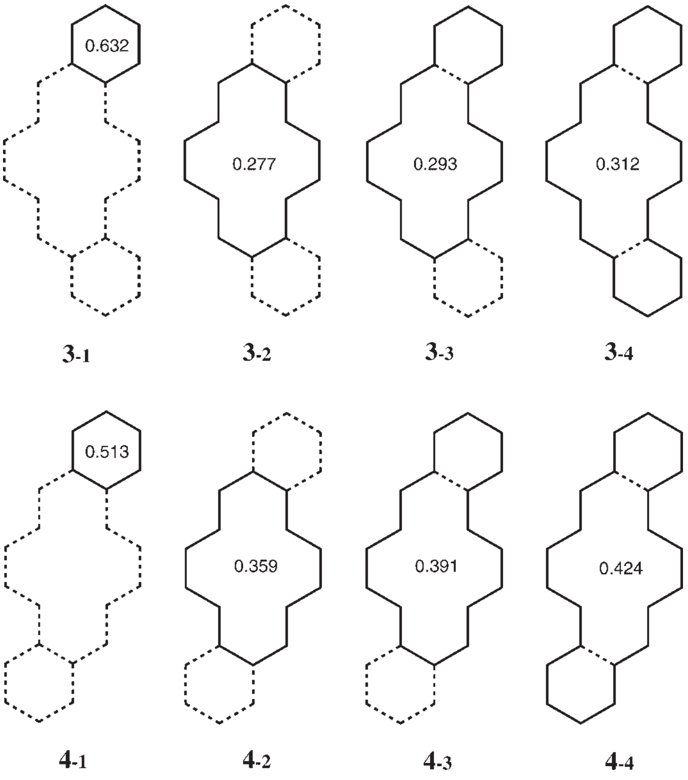
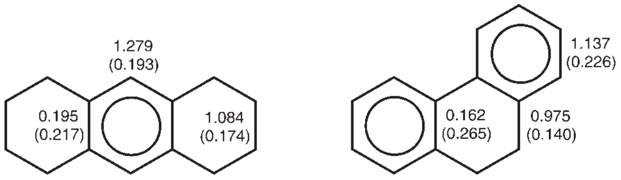


Figure 5. Non-identical circuits of **3** and **4**. Values given at the centers of individual circuits are the intentisities of circuit currents in units of that for benzene



11 **12**

Figure 6. Current density maps for anthracene (**11**) and phenanthrene (**12**), in which all current intensities are given in units of that for benzene. Values in parentheses are the BREs in units of $|\beta|$

more aromatic than **3**.[4,5] In fact, the % TRE is larger for **4** than that for **3**. In general, it is not easy to compare the degrees of global aromaticity for other DDP derivatives because they consist of highly aromatic benzenoid subsystems and a much less aromatic 14-membered ring.

CONCLUSION

NICS as a discriminator for aromaticity is qualitatively effective within related sets of compounds. We have shown that % TRE and BRE are very useful for readily ordering the relative aromaticities of annelated DDPs and their DDP nuclei. % TRE and BRE are independent of the areas of individual rings and are only dependent on the connectivity of conjugated atoms. Therefore, even though BRE may not be the best indicator of local aromaticity, it is free from errors of geometric origin. Note that aromaticity in principle is a state of energy. Various magnetic criteria of aromaticity must be more or less ambiguous owing to their geometry dependence. It is interesting that **4** sustains a large current along the 14-membered ring although it is less aromatic than isomer **3**. It is **3** that can be considered as a true dibenzannulene.[2]

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