π-Electron Currents Induced in Polycyclic Benzenoid Hydrocarbons and Their Relationship to Clar Structures

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When an external magnetic field is applied to polycyclic benzenoid hydrocarbon molecules, a π-electron current is induced in the π system. This current can be partitioned formally among the constituent benzene rings. Part of the π-electron current assigned to each benzene ring is called the ring current. The distribution of large diatropic ring currents in a polycyclic benzenoid π system was found to be in excellent agreement with that of sextet rings in the Clar structure. This supports the view that six-membered circuits are the main origin of aromatic stabilization. However, formal ring currents in nonbenzenoid hydrocarbons are not always related to their aromaticity.

Introduction

Clar structures, which were intuitively devised by Clar,[1,2] are often written for polycyclic benzenoid hydrocarbons (PBHs) to do without detailed discussion of their stability and reactivity. He assigned π-electron sextets to discrete benzene rings in PBHs and the remaining π electrons to double bonds.[1,2] Such sextet rings are usually indicated by solid circles in the rings concerned. Sextet rings and formal double bonds must be separated by one formal single bond from each other. Sextet rings are considered to be main aromatic centers. Formal double bonds indicate that these CC bonds have polyene-like character. The best Clar structure is the closed-shell one with a maximum number of sextet rings. Clar structures for benzene (**1**) and nineteen closed-shell PBHs (**2**−**20**) are presented in Figure 1.

Clar structures have been rationalized in several theoretical ways. They are consistent with the simplest conjugated circuit theory based on sextet-type resonance interactions only.[3−5] Sextet rings are associated with a large number of sextet-type resonance interactions. For a PBH with a single Clar structure, the number of sextet rings is close to the number of sextet-type resonance interactions per Kekulé structure.[5] Hosoya et al. noted that π-bond orders due to three high-lying occupied molecular orbitals are large around the sextet rings.[6] So-called benzene character is large at sextet rings.[6,7] We previously noted that the bond resonance energy (BRE) distribution in a PBH is fully consistent with its Clar structure.[8] In general, CC bonds that form sextet rings have large positive BREs.

An external magnetic field induces π-electron currents in mono- and polycyclic π systems.[9] Individual ring centers are then either shielded or deshielded by the induced π current. Schleyer et al. introduced the nucleus-independent chemical shift (NICS) as a criterion for local aromaticity,[10−14] which is defined as the negative of the magnetic shielding at some selected point in space, e.g., at a ring center. Recently, Moran et al. found that sextet rings in PBHs always have large negative NICS values.[14] Thus, aromaticity proved to be closely related to magnetotropicity (i.e., diatropicity or paratropicity). In this paper, we show that the Clar structures of PBHs can easily be derived from the ring-current distributions calculated with simple Hückel molecular orbital (HMO) theory. The finding made by Moran et al.[14] motivated us to do this work.

Theory

π-Electron currents induced in **1**−**20** were calculated using our variant of Hückel−London theory.[15−19] All π bonds in PBHs were assumed to have equal resonance integrals. All possible cyclic paths in a polycyclic π system are called circuits. A π-electron current is given as a superposition of the currents induced in all circuits.[18,19] That is, a π-electron current is induced separately in individual rings at the limit of zero magnetic field. Our variant of Hückel−London theory is the only one that can demonstrate this aspect of π-electron currents explicitly. As far as PBHs are concerned, π-electron currents calculated in this manner reproduce well those obtained by ab initio molecular orbital calculations.[20,21] Each bond current, i.e., a current flowing through a given π bond, is then a sum of currents induced in all circuits that share the bond. Bond currents thus obtained were checked by examining if they can be reproduced by standard procedures for π-electron current calculation.[22−24]

π-Electron currents induced in a PBH molecule have often been partitioned not among the circuits but among the constituent benzene rings.[25−28] In this paper, we define the term "ring current" as part of a π-electron current assigned to each of the benzene rings. It is an apparent ring contribution to the π-electron current.[25−28] In Figure 2 is illustrated how to partition the coronene π-electron current into seven ring currents. Because a π-electron current is not induced separately in the individual benzene rings, the ring current thus defined is not a physically sound concept. For example, the ring current assigned to each benzene ring in naphthalene (**2**) consists of the currents induced in the six- and ten-membered circuits.[18,29] The current induced in the six-membered circuit is only 46% of the overall ring current. However, as will be seen below, ring currents can be utilized as a very practical tool for justifying the Clar structures of PBHs.

Topological resonance energy (TRE) is a kind of energetic criterion defined graph-theoretically for aromaticity.[8,16,30−32] Positive and negative TREs are associated with aromaticity and antiaromaticity, respectively. The percentage TRE (% TRE) is useful for comparing the degrees of aromaticity in different molecules.[8,16] It is defined as 100 times the TRE, divided by the total π-binding energy of the polyene reference. TREs and % TREs for **1**−**20** are listed in Table 1. BRE is defined as a

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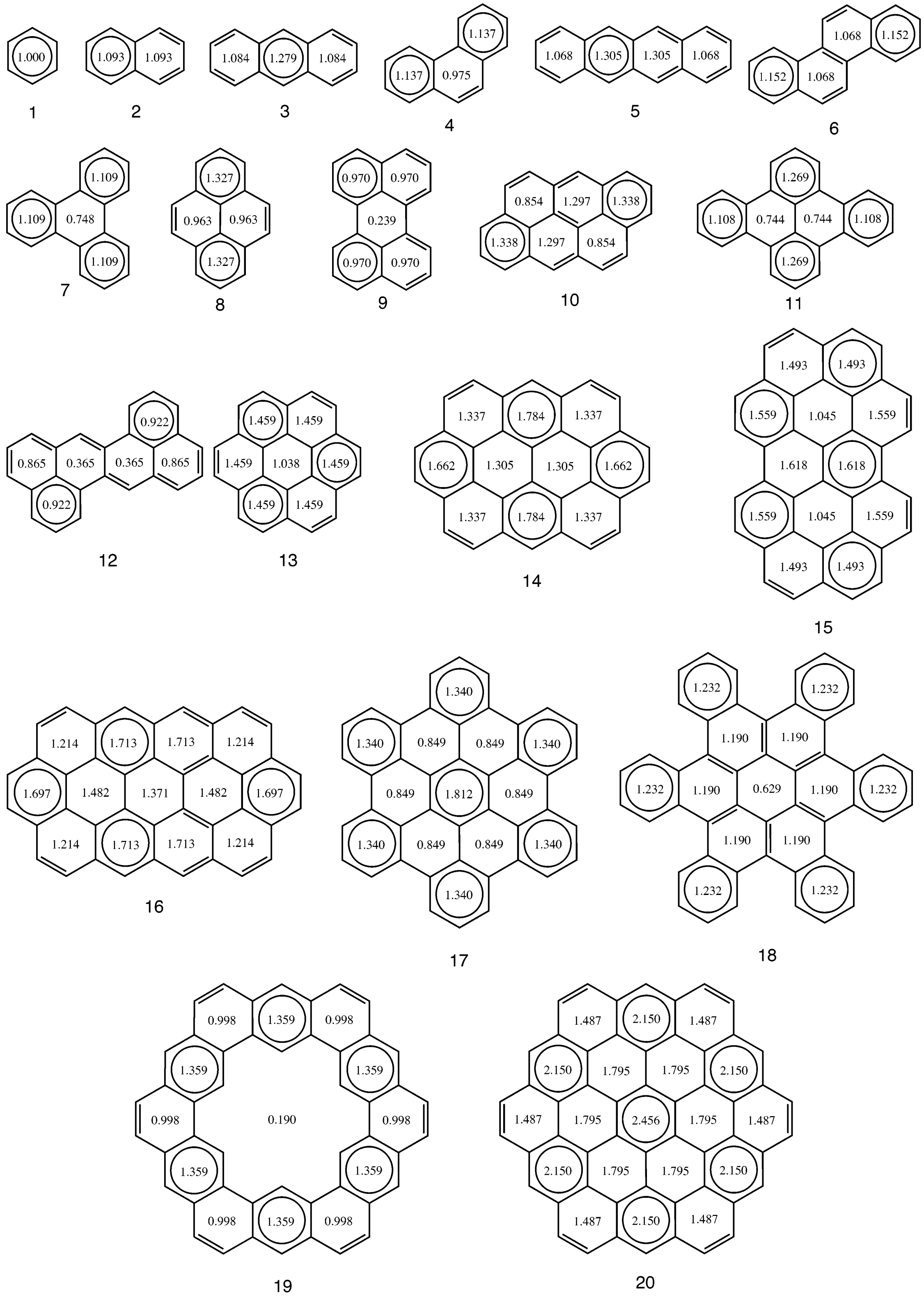


Figure 1. Clar structures for benzene (**1**) and nineteen polycyclic benzenoid hydrocarbons (**2**−**20**). Ring currents assigned to individual rings are given in units of the value for benzene.

contribution of a given π bond to the TRE.[8,33,34] It has been used successfully as an index of kinetic stability for a variety of polycyclic π systems. Both TREs and BREs are calculated within the framework of HMO theory. If all π bonds located around a given ring in a polycyclic π system have positive BREs, the ring can be considered one of the aromatic centers or a ring of local aromaticity.[8]

Results and Discussion

Ring currents in **1**−**20** are graphically summarized in Figure 1. They are given in units of the value for benzene. In general, small even-membered conjugated circuits, such as most hexagonal circuits in PBHs, contribute much to aromaticity and diatropicity.[15,16,35−37] Because **1**−**20** consist of hexagonal

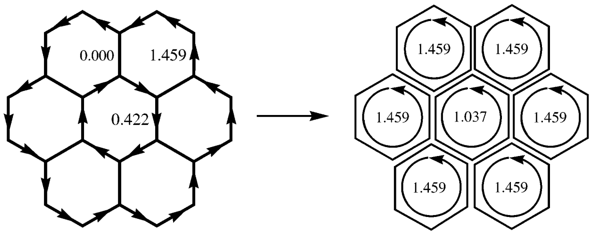


Figure 2. π-Electron current and the formal ring currents in coronene (**13**).

TABLE 1: TREs and %TREs for Benzene and Polycyclic Benzenoid Hydrocarbons

species	TRE/$\lvert\beta\rvert$	% TRE
benzene (**1**)	0.273	3.53
naphthalene (**2**)	0.389	2.92
anthracene (**3**)	0.475	2.52
phenanthrene (**4**)	0.546	2.89
naphthacene (**5**)	0.553	2.27
chrysene (**6**)	0.688	2.81
triphenylene (**7**)	0.739	3.01
pyrene (**8**)	0.598	2.73
perylene (**9**)	0.740	2.69
dibenzo[*def*,*mno*]chrysene (**10**)	0.766	2.51
dibenzo[*fg*,*op*]naphthacene (**11**)	0.983	2.96
dibenzo[*hi*,*qr*]naphthacene (**12**)	0.780	2.36
coronene (**13**)	0.947	2.82
ovalene (**14**)	1.224	2.70
circumbiphenyl (**15**)	1.521	2.82
circumanthracene (**16**)	1.476	2.59
hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (**17**)	1.739	2.92
hexabenzo[*a*,*d*,*g*,*j*,*m*,*p*]coronene (**18**)	1.912	2.84
kekulene (**19**)	1.569	2.34
dodecabenzocoronene (**20**)	2.096	2.70

benzene rings only, they are aromatic with large positive % TREs. All ring currents flow counterclockwise because they are diatropic. Intensities of benzene ring currents lie in the wide range from 0.239 to 2.456. It is noteworthy that benzene rings with relatively large diatropic currents in PBHs correspond to sextet rings in the Clar structures. This approach to a Clar structure is consistent with the one based on the distribution of NICS values in the π system.[8]

PBHs can be classified into two groups according to the number of Clar structures that can be written for the π system. Only one Clar structure can be written for such PBHs as **1**, **4**, **7**, **8**, **11**, **14**, **17**, **19**, and **20**. In these PBH molecules, fixed sextet rings sustain large diatropic currents. Therefore, their Clar structures are in perfect agreement with the ring current distributions. Formal double bonds in a Clar structure, if any, have more or less polyene-like character.[1,2] For the other PBHs, more than one Clar structure can be written because π-electron sextets cannot be assigned to all of the benzene rings that sustain large diatropic currents. Such a situation is illustrated by three PBHs in Figure 3. Polyacenes **2**, **3**, and **5** are prototypical PBHs of this group. More than one Clar structure can likewise be written for **6**, **9**, **10**, **12**, **13**, **15**, **16**, and **18**.

PBHs in which all carbon atoms belong to sextet rings are so-called fully benzenoid hydrocarbons.[1,2] Among them are benzene (**1**), triphenylene (**7**), dibenzo[*fg*,*op*]naphthacene (**11**), and hexabenzo[*bc*,*ef*,*hi*,*kl*,*no*,*qr*]coronene (**16**). They have no formal double bonds in the Clar structures. Their Clar structures necessarily contain the largest number of sextet rings per carbon atom. Fully benzenoid hydrocarbons are PBHs with the largest % TREs[8] and large energy separations between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)[38] and hence are chemically least reactive.[1,2]

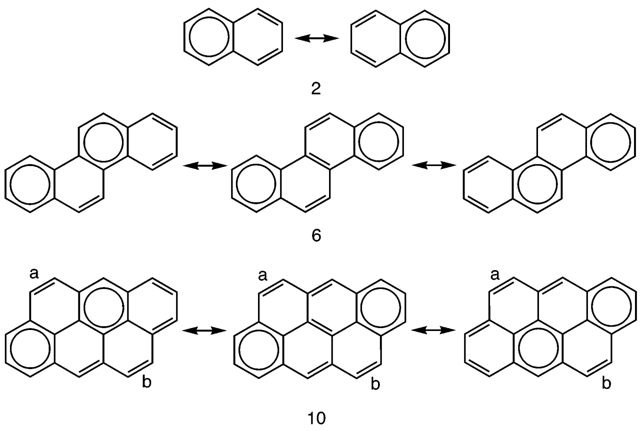


Figure 3. All Clar structures conceivable for naphthalene (**2**), chrysene (**6**), and dibenzo[*def*,*mno*]chrysene (**10**).

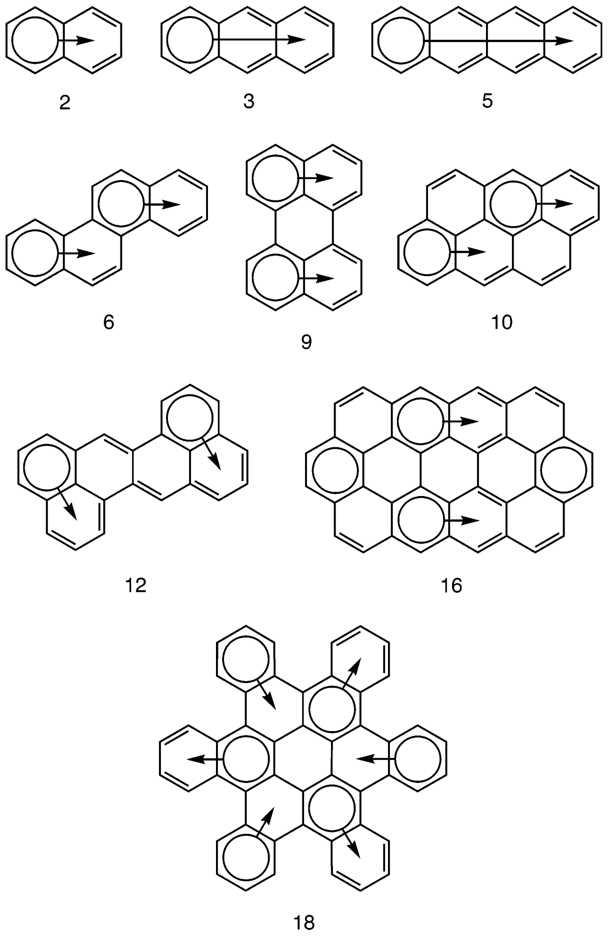


Figure 4. Clar structures with arrows for nine polycyclic benzenoid hydrocarbons.

All polyacenes have only one sextet ring irrespective of the number of constituent benzene rings.[1,2] Figure 3 indicates explicitly that the only sextet in anthracene (**3**) is shared by all benzene rings. To describe such mobility of a sextet, one assumes that two π electrons of the sextet can migrate from one ring to the other.[1,2] This is symbolized by an arrow as shown in Figure 4. Double bonds located in the pathway of each arrow do not indicate more than that there are two π electrons in these bonds. In fact, polyacenes do not contain true double bonds just as benzene does not contain three double bonds.[1,2] However, higher polyacenes are highly reactive because the only sextet of π electrons is diluted in higher members, so that they become much less aromatic with smaller % TREs.[1,2,39]

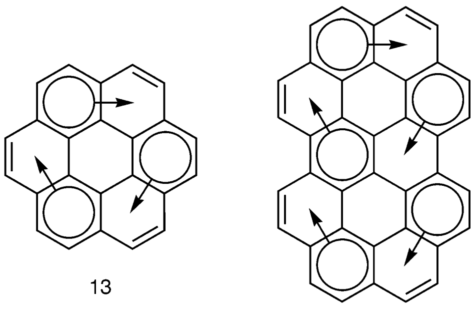


Figure 5. Superaromatic hydrocarbons, coronene (**13**) and circumbiphenyl (**15**).

As to polyacenes, all of the rings sustain large diatropic currents. One may note that inner rings in anthracene (**3**) and naphthacene (**5**) sustain somewhat larger ring currents. Therefore, we are somewhat reluctant to choose one of the edge rings as a sextet ring. The NICS values reported by Schleyer et al. are fully consistent with these current intensities.[10,12] For example, NICS values for **5** are -9.1 and -13.1 ppm at the edge and inner rings, respectively.[14] It seems that this is the only flaw in the present appraoch to Clar structures. Higher diatropicity of the inner rings itself can be explained by taking into account sextet- and decet-type resonance interactions.[36,37] Inner rings are shared by one six- and two ten-membered conjugated circuits, whereas edge rings are shared by one six- and one ten-membered conjugated circuit. Ring currents assigned to these rings are sums of the currents induced in these circuits.

Perylene (**9**) and dibenzo[*hi*,*qr*]naphthacene (zethrene, **12**) have two naphthalene-like substructures. As in the case of naphthalene (**2**), each substructure has one π-electron sextet, which can migrate within the substructure. One central ring in **9** and two central rings in **12** are called empty ones because they never become sextet rings.[1,2] These rings do not participate in the formation of conjugated circuits. Such empty rings sustain very small diatropic ring currents. Two fixed double bonds in the center of **12** must have polyene-like character.

As may be seen from Figure 4, two naphthalene-like substructures can also be chosen from the Clar structures of chrysene (**6**), dibenzo[*def,mno*]chrysene (anthanthrene, **10**), and circumanthracene (**16**). Each substructure consists of two adjacent benzene rings with relatively large ring currents. Figure 3 shows that three Clar structures can be written for **6** and **10**. All CC bonds in **6** can in principle take part in the formation of sextet rings. However, bonds **a** and **b** in **10** are double bonds of polyene-like character because they do not participate in the formation of sextet rings in any Clar structure. Two naphthalene-like substructures can be chosen from the Clar structure of circumanthracene (**16**). There are six naphthalene-like substructures in hexabenzo[*a,d,g,j,m,p*]coronene (**18**). Therefore, all of the rings but the central one can achieve sextets and so sustain large diatropic currents.

Two degenerate Clar structures can be written for coronene (**13**). This hydrocarbon is not fully benzenoid because it always has three formal double bonds in the Clar structure. However, Clar proposed that, if three sextets in **13** migrate into the neighboring rings, a further π-electron current, originating from the rotating sextets, must be generated as indicated in Figure 5.[1,2] The extra stability produced by the molecular sextet migration current may be called "superaromaticity".[1,2] Not only **13** but also circumbiphenyl (**15**) is superaromatic in this sense.[1,2] All of the five sextets in **15** can migrate synchronously into the neighboring rings. As can be seen from Table 1, these superaromatic species have large % TREs and are similar in chemical behavior to fully benzenoid hydrocarbons.[1,2]

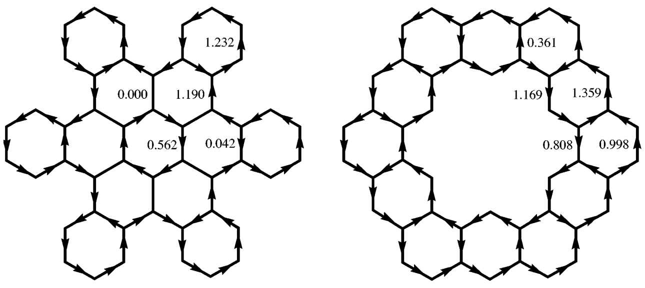


Figure 6. π-Electron currents induced in hexabenzo[*a,d,g,j,m,p*]-coronene (**18**) and kekulene (**19**).

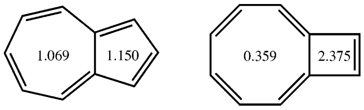
The central ring of hexabenzo[*a,d,g,j,m,p*]coronene (**18**) is apparently paratropic with a small positive NICS value ($+0.1$ ppm).[14,21] This molecule is not planar because of the bumping between perimeter hydrogens.[14,21] Figure 6 shows that clockwise bond currents are induced along the central benzene ring of **18**. These paratropic bond currents simply indicate that the diatropic ring current in the central ring is more or less smaller than those in the surrounding rings. The net magnetotropicity of the central ring can be revealed by partitioning the π-electron current into the ring currents. As shown in Figure 1, the central ring really sustains a diatropic current even though it is weak in intensity. This hydrocarbon is not superaromatic. Even if the sextets move between neighboring rings, no circular movement is created.[1,2]

Kekulene (**19**) is not an authentic PBH because it can be viewed as dodecabenzo[18]annulene.[40] As in the case of other PBHs, however, all of the rings are associated with aromatic conjugated circuits. In fact, a small diatropic current is assignable to the central eighteen-membered ring.[40] The central eighteen-membered circuit is presumably the main origin of diatropicity in this large $(4n + 2)$-membered ring. The fact that there are six sextets in the Clar structure witnesses that **19** is not an annulenoid but a benzenoid hydrocarbon.[11,20,41,42] A very small current is induced along the macrocyclic structure.[41]

In this context, one should note that the NICS value at the center of **19** is positive in sign ($+5.0$ ppm).[11] As shown in Figure 6, clockwise bond currents are induced along the central eighteen-membered ring.[41] These bond currents arise from the partial cancellation of currents induced in the central and outer rings. According to the original interpretation of NICS values, the central eighteen-membered ring is antiaromatic although we do not like to accept this view. This type of difficulty can be avoided by utilizing a ring current as an indicator of local aromaticity. We have shown in Figure 1 that the central ring in **19** is aromatic with a diatropic ring current.

Dodecabenzocoronene (**20**) has not been synthesized yet, probably because it is very large in molecular size. This hydrocarbon is predicted to be not only highly aromatic with a large % TRE but also highly diamagnetic with seven sextet rings.[14,21]

Finally, we must note that the present approach to Clar structures cannot be applied to nonbenzenoid hydrocarbons. For example, π-electron currents induced in azulene (**21**)[18,29] and bicyclo[6.2.0]decapentaene (**22**)[43] can be formally partitioned among the two rings. As shown in Figure 7, it appears that two nonbenzenoid rings in **21** and **22** sustain diatripic currents as in the case of naphthalene (**2**). However, it is an artifact because such diatropicity arises not from individual rings but from the peripheral ten-membered circuits.[18,29,43] Note that **21** is aromatic



21 22

Figure 7. Ring currents assigned to individual rings in azulene (**21**) and bicyclo[6.2.0]decapentaene (**22**).

with a % TRE of +1.14 but that **22** is antiaromatic with a % TRE of −3.46.[16,30,31] As already pointed out,[35−37] small even-membered conjugated circuits contribute much to aromaticity. Five- and seven-membered rings in **21** must be essentially nonaromatic, whereas four- and eight-membered ones in **22** must be antiaromatic in nature. Large diatropic currents induced in the peripheral ten-membered circuits of **21** and **22** overwhelm the currents induced in smaller circuits. Therefore, π-electron currents in these hydrocarbons cannot be partitioned meaningfully among the rings. For this reason, local aromaticities in these nonbenzenoid hydrocarbons cannot be predicted from the ring current intensities.

Concluding Remarks

For a variety of closed-shell PBHs, ring currents as defined in this paper can be used as a practical indicator of local aromaticity. This is a rather surprising thing because not individual rings but individual circuits are the real origin of aromaticity and magnetotropicity. Clar structures for PBHs proved to reflect straightforwardly the distribution of large diatropic ring currents in the π system. Thus, the locations of aromatic centers in **1−20** are in excellent agreement with those of sextet rings in the Clar structures. Clar sextet rings not only sustain large diatropic currents but also have large negative NICS values at the ring centers. This must be closely associated with a large weight of sextet-type resonance interactions in the PBH π systems.[3−7] Ring currents presented in the paper can easily be calculated with HMO theory. To obtain reliable NICS values, however, much more sophisticated molecular orbital calculations must be performed. Ring currents are better suited for estimating the degrees of local aromaticity in individual benzene rings.

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