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Aromaticity of Closed-Shell Charged Polybenzenoid Hydrocarbons

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S Supporting Information

ABSTRACT: The aromatic stabilization of closed-shell charged polybenzenoid hydrocarbons (PBHs) has been scrutinized by means of energetic and magnetic aromaticity criteria and by direct measures of electron delocalization. Thus, topological resonance energies and their circuit contributions, ring current maps, and multicenter delocalization indices have been calculated for a series of 18 polybenzenoid cations containing from 3 to 10 benzene rings. All calculations indicate that the closed-shell cations have a similar degree of aromaticity compared to that of the corresponding closed-shell neutral PBHs. All cations investigated display a large degree of electronic delocalization in the ring, accompanied by significant aromatic stabilization and a strong diatropic peripheral electron current. Graph theoretical models describe perfectly the aromatic features of these hydrocarbon fragments, showing how they can be understood as a superposition of specific neutral PBHs. The large aromatic character of these systems suggests they may be relatively stable upon formation at combustion conditions, like those given in the interstellar medium. It has been postulated that closed-shell fragments of PBHs may play an important role in the photoluminescent phenomenon known as extended red emission.
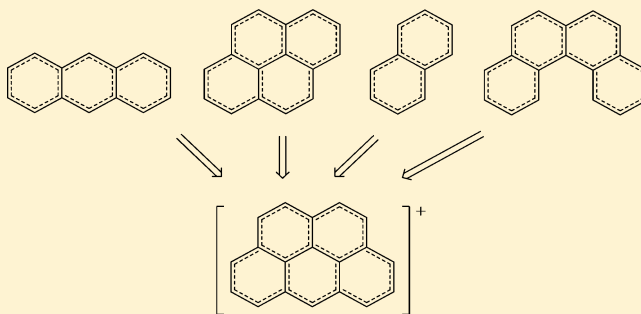
INTRODUCTION

The physicochemical properties of large polycyclic aromatic hydrocarbons (PAHs), in particular those formed exclusively by benzene units, called polybenzenoid hydrocarbons (PBHs), have been the object of much interest over the last years because of the huge number of technological applications of these materials. Besides graphene,[1−4] the cornerstone of the PBH family, smaller polybenzenoids can also be employed as active materials in optoelectronics and molecular electronics.[5] The recent synthesis of relatively large PBHs[6,7] has turned the field of molecular electronics into a very active branch of physics. For example, it has been shown that single molecules of large PAHs adsorbed on graphite can have diode-like properties[8−10] and fullerene-like structures can act as molecular electronic amplifiers.[11]

On the other hand, PBHs are thought to be responsible for some of the diffuse interstellar bands and unidentified emission bands in the mid-IR range[12] (also known as extended red emission (ERE)).[13] Nowadays, the presence of these large molecules in the interstellar medium is accepted,[14] but the role played by different kinds of PBH fragments, namely, neutral, cationic, and anionic closed-shell or radical systems in the ERE, is still an open question.[15] Particularly attractive among these are the closed-shell charged PBHs, both isolated[16] and cluster-forming.[17] The lack of experimental data for these highly reactive species (there is no gas phase spectroscopic data available) makes them good topics for computational chemistry

studies. An additional drawback for experimental studies is the fact that the precursors of these closed-shell cations are neutral open-shell radicals, which are very reactive and unable to be isolated. Unlike the open-shell PBH cations, which can undergo nonradiative relaxation from electronic excited states because of their open-shell electron configuration[18] (they have been rejected as possible contributors to ERE[19]), the closed-shell cations may be good candidates for exhibiting strong luminescence.

Recently, some computational studies have pointed out that the closed-shell PBH cations and their clusters could be the determinant in the explanation of the ERE.[16,17,20,21] These studies have focused on ab initio determinations of the electronic[17,20,21] and infrared[16] spectroscopic properties. It must be remarked that the analysis of the PAH fragments formed by combustion processes[22] indicates that cations with an odd number of carbon atoms are predominant in the fragments containing up to 50 carbons, and above 50 atoms, fragments with even and odd numbers of carbon atoms are in equal proportions. As pointed out in ref 16, due to the fact that interstellar PBHs are probably produced under combustion-like conditions, the closed-shell cations may well represent an
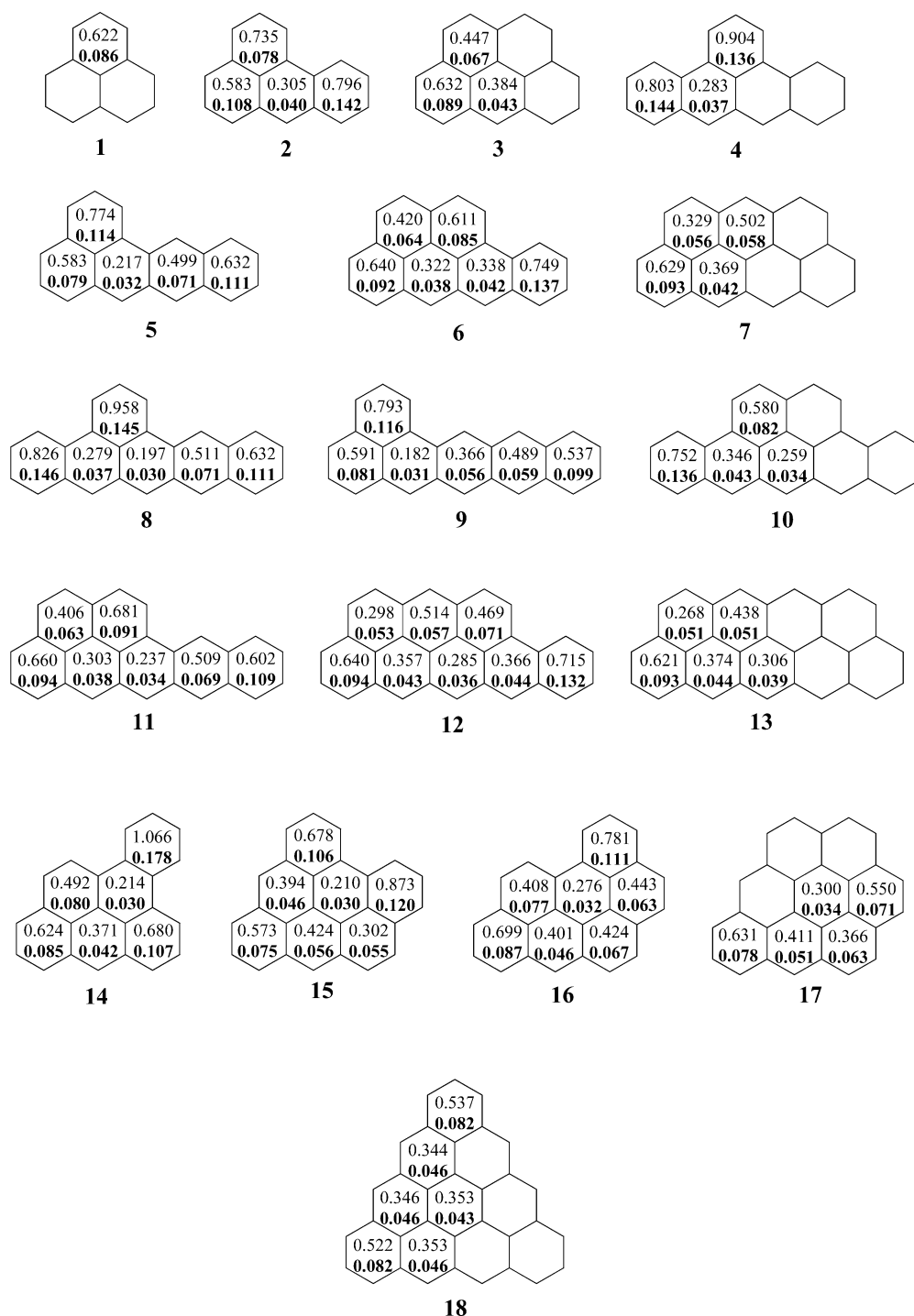
Figure 1. 6-DIs calculated with the *pp* approach and CCEs (numbers in bold) for the benzenoid rings in the series of csc-PBHs.

important fraction of the small and medium size PBHs in these regions.

In this work, we analyze the aromatic character of several small and medium size fragments of closed-shell PBH cations because, as pointed out in ref 20, aromaticity can be an important source of thermodynamic stability in these species. We employ the three main criteria of aromaticity, namely, energetic stabilization, magnetic response, and electron delocalization. Additionally, we show, comparing graph theoretical models with ab initio results, how the aromatic properties of these systems result simply from the superposition of specific neutral PBHs. Previous studies were performed on the ring current and the aromatic stabilization energy of phenalenyl cation[23,24] and also on benzoanthracenyl and benzopyrenyl cations using the conjugated circuits model.[25] However, an exhaustive analysis of the aromatic behavior of a large series of these compounds and a further investigation of the relation with the most widely studied family of neutral PBHs have not been carried out yet. The results presented in this work point toward significant stabilization of closed-shell PBH cation fragments.

COMPUTATIONAL METHODS

The series of molecules considered here consists of 18 small and medium size polybenzenoid cations containing an odd number of carbon atoms (Figure 1). All the molecules adopt a closed-shell ground state electron configuration. For simplicity, from now on we denote the set of closed-shell cations as "csc-PBHs", and the set of closed-shell neutral systems as "csn-PBHs". For the ab initio calculations, we employed the density functional theory functional B3LYP in combination with the 6-31G(d,p) basis set. All structures were confirmed to be energy minima through the analysis of the corresponding harmonic frequencies. For the calculation of the geometries and wave functions, we employed the Gaussian 09 program.[26] For the calculation of multicenter indices,[27,28] Mulliken atomic domains have been employed.[29] At a monodeterminantal level and using the Mulliken atomic domains, the six-center index (SCI) or six-center delocalization index (6-DI),[27] which is the index calculated in this work for the benzene rings of the csc-PBHs, is calculated from the bond order matrix terms and reflects the degree of electron delocalization over the atoms in the ring.

Calculations of ring currents and multicenter indices were performed using the pseudo-π (pp) approach,[30,31] where use is made of the long-known fact that the σ framework of a hexagonal arrangement of hydrogen atoms is isomorphic to the π system of a benzene ring. Pseudo-π calculations exploit this similarity by removing all hydrogen atoms from a true PBH, replacing all carbon atoms with hydrogen atoms, and using the STO-3G basis set.[30,32] The currents were obtained with the ipsocentric approach,[33−36] which has been implemented in our own Fortran routines requiring formatted checkpoint files from Gaussian 09 as the only input. The reason for the use of the pp method in these calculations is merely computational. It has been shown for the calculation of ring currents[30] and multicenter indices[37] in csn-PBHs that this approach provides essentially the same information. Also, it was shown in ref 34 that the pp method produces a ring current map of the phenalenyl cation that is nearly indistinguishable from the one obtained using the full calculation. This is because the main important factors here are the symmetry and the shape of the molecular orbitals. Symmetry does not depend on the basis set, and the shape of the orbitals is not significantly altered by the number of basis functions employed. Furthermore, despite the dependence of magnetic response in the ipsocentric approach on energy differences between the occupied and virtual orbitals, there is quite good quantitative agreement. We always consider a magnetic field in the z-direction (perpendicular to the plane formed by the carbon skeleton) and compute the perturbed orbitals using the first-order coupled Hartree−Fock approach (FO−CHF). Ring currents are plotted on a grid in the xy plane with a diatropic current represented by a counterclockwise circulation. Because, to the best of our knowledge, this is the first time that multicenter indices are calculated for csc-PBHs, we have recalculated the multicenter indices for the "real" systems using the 6-31G(d,p) basis set in order to confirm that the pp results are reliable.

The total aromatic stabilization energy has been estimated by means of the topological resonance energy (TRE)[38,39] and the local contribution of each benzene ring by the cyclic conjugation energy (CCE).[40−43] CCE provides a local picture of the aromatic stabilization energy as it can be calculated for any ring circuit in a PAH. CCE is defined at the Hückel molecular orbital (HMO) level as the difference between the total energy of the π-electron system and the energy of a reference system where the contribution coming from the given circuit is neglected but any other structural features are taken into account. On the other hand, the TRE is the difference between the total energy of the π-electron system and the energy of a reference system where the contributions coming from all the circuits are neglected.

RESULTS AND DISCUSSION

Electron Delocalization. The extent of the cyclic electron delocalization within the benzene rings of csc-PBHs has been quantified by means of the 6-DI. In Figure 1, the 6-DIs obtained with the pp approach are shown for each symmetry unique ring.

In general, all 6-DIs calculated for csc-PBHs are in the range of the values obtained previously for the series of csn-PBHs.[44] For the csn-PBHs enumerated in Table 1, the largest 6-DI is

Table 1. Topological Resonance Energies per Electron (TREPE) Calculated for the Series of csc-PBHs and for Some Representative Examples of csn-PBHs

molecule	TREPE[a]	molecule	TREPE[a]
1	0.034	benzene	0.046
2	0.034	naphthalene	0.039
3	0.035	anthracene	0.034
4	0.035	triphenylene	0.041
5	0.033	tetracene	0.031
6	0.035	chrysene	0.038
7	0.034	phenanthrene	0.039
8	0.033	pyrene	0.037
9	0.031	perylene	0.037
10	0.035	coronene	0.039
11	0.033		
12	0.034		
13	0.033		
14	0.036		
15	0.035		
16	0.036		
17	0.036		
18	0.031		

[a]In β units.

found for benzene (1.581) and the lowest for the inner ring of perylene (0.131) (these numbers are not collected in the table but have been extracted from ref 44). This suggests that the degree of cyclic electron delocalization within a benzenoid ring in a closed-shell PBH is not heavily perturbed by the presence of a positive charge.

In general, one can observe from the values shown in Figure 1 that the larger the ring condensation, the lower the local ring electron delocalization. As the ring condensation increases, the electrons belonging to a particular ring are more delocalized along the neighboring rings, so the local ring electron delocalization decreases.

In order to check the reliability of the pp approach in cations, we also calculated the 6-DI for the complete molecular systems using the 6-31G(d,p) basis set. Figure 2 represents the correlation with the pp results. As one can see, there is a very good linear correlation, reflecting the fact that the pp approach preserves the electron delocalization of the real molecule as was previously found in csn-PBHs.[37] As it has been shown that in

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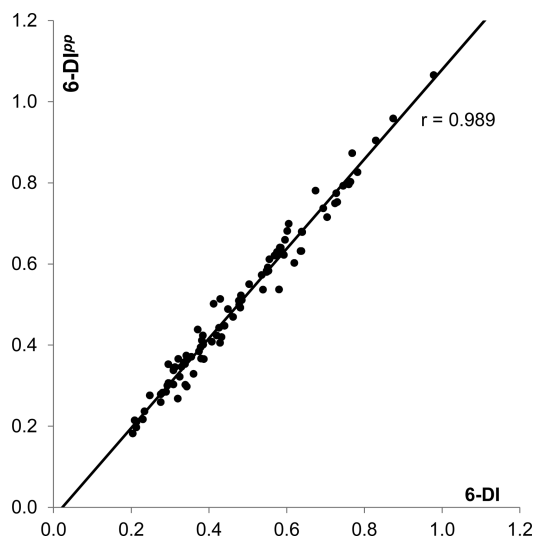
Figure 2. Comparison of the six-center delocalization indices calculated with the *pp* approach (6-DI^{pp}) and those calculated with the 6-31G(d,p) basis set (6-DI) for the benzenoid rings in the series of csc-PBHs.

csn-PBHs, the *pp* approach, demonstrated to work for multicenter indices, also performed very well for ring current maps, and because we have shown that it also works well for csc-PHB's, one can rightfully assume it to perform well for csc-PBH ring current maps. Note that this is supported by the observation of the agreement between the presently computed pseudo-π currents for the phenalenyl cation and the ab initio ones reported by Cyrański et al.[24]

Magnetic Response. Another important feature of aromatic PBHs is that they support strong diatropic ring electron currents when an external magnetic field is applied perpendicular to the ring plane. Remarkable is the presence of strong peripheral diatropic currents in these systems. Sometimes, due to only partial cancellation of diatropic currents running over common bonds between neighboring rings, some paratropic circulation may appear. This does not refute global aromatic circulation, as such partial cancellation-based current is usually of quite small magnitude (for instance, see the ring current map of coronene in ref 45).

To the best of our knowledge, the magnetic response of csc-PBHs has not been investigated, except for the specific case of phenalenyl cation.[23,24] Three main magnetic indicators of large electron delocalization are usually considered: magnetic susceptibility exaltations, large negative nuclear independent chemical shifts,[46] and, as mentioned above, strong diatropic ring currents. Among them, the latter is free of contributions from localized electrons. The ring current maps obtained with the *pp* approach for some molecules of the series of csc-PBHs are shown in Figure 3. The ring current maps of the whole series are included as Supporting Information, together with those obtained with the minimal basis set using the real system. As one can see, all molecules present a significant diatropic circulation around the peripheral carbons, reflecting strong delocalization of the π electrons. Sethson et al.,[23] using the London-Hückel approximation, and Cyrański et al.,[24] using the ipsocentric method, have already shown the strong diatropic current supported by the phenalenyl cation. The ring currents presented in this work demonstrate their results can be extended to the whole series of PBHs. The diatropic currents

are qualitatively similar to the currents displayed by csn-PBHs like phenanthrene, pyrene, perylene, coronene, etc. (For example, see the *pp* ring currents reported in refs 30 and 47.) On the other hand, most of the internal electron currents cancel, resulting in weak paratropic circulations in some cases.

Aromatic Stabilization. An often convincing argument to establish the aromatic character of a molecule is a large aromatic stabilization energy (ASE). Different ways of quantifying the ASE have been proposed by means of homodesmic or isodesmic reaction schemes,[48] but the TRE is free of arbitrary reference reactions and very successful in the study of PBHs. Additionally, the TRE per electron (TREPE) allows for comparison between molecules of different sizes. The values of the TREPE obtained for the series of csc-PBHs and some representative examples of csn-PBHs are collected in Table 1. The magnitude of the TREPEs in csc-PBHs is comparable to that of the TREPEs in csn-PBHs. In fact, quite small differences are found along the series, whose values (given in units of the resonance integral β) are comprised between 0.031 and 0.036 in csc-PBHs and 0.031 and 0.041 in csn-PBHs (after leaving out the particular case of benzene). Our results are close to those published previously for molecule **1**. Resonance energies of 27.2 and 21.1 kcal/mol for this molecule were previously calculated by Randić[25] and Sethson et al.[23] using the conjugated circuits model and the HMO approach, respectively (the latter calculated considering $\beta \approx 70$ kcal/mol), and an ASE of 34.5 kcal/mol was more recently reported by Cyrański et al.[24] from ab initio calculations. The TRE obtained in this work for molecule **1** is 28.6 kcal/mol (considering the same value for β). On the other hand, the TREs of molecules **2** and **3** are 38.1 and 44.1 kcal/mol, respectively, in good agreement with those reported by Randić[25] (34.4 and 43.1 kcal/mol, respectively).

Topological resonance energies are in turn the collective reflection of the conjugation energies in every individual circuit of the molecule. Of special interest are the conjugation energies of benzene-like circuits and their comparison with other local aromaticity descriptors such as the 6-DIs. Ponec et al.[49] compared the CCEs and 6-DIs for a series of csn-PBHs, finding a good correlation between both. In Figure 1, we have collected the CCEs for the series of csc-PBHs. The values obtained are comparable to those obtained for csn-PBHs,[49] reflecting again a similar degree of aromaticity among cations and neutral species. In Figure 4, these values are represented against the 6-DIs. The correlation, although not excellent, indicates a good correspondence between ring electron delocalization and aromatic stabilization in csc-PBHs. This correlation is supported by the analytical relation between multicenter indices and TREPEs derived for annulenes by Cioslowski et al. at the HMO level.[50] This relation was later employed to estimate the values of the CCEs in PBHs from multicenter indices.[51]

Conjugated Circuits Approach. A valence bond graph theoretical approach based on equally weighted charged Kekulé structures[52] can be introduced for csc-PBHs. In this simple graph theoretical model, the electron conjugation can be represented by superposition of different charged Kekulé structures. It was recently shown[53] that the conjugated circuits model (CCM) of Randić[54] can be formally deduced starting from the Herndon–Simpson valence bond model[52,55] and introducing proper bond creation and annihilation operators. Properties like the resonance energy or the magnetic susceptibility exaltation can be estimated by simple enumeration of conjugated circuits. For the first time, we have applied
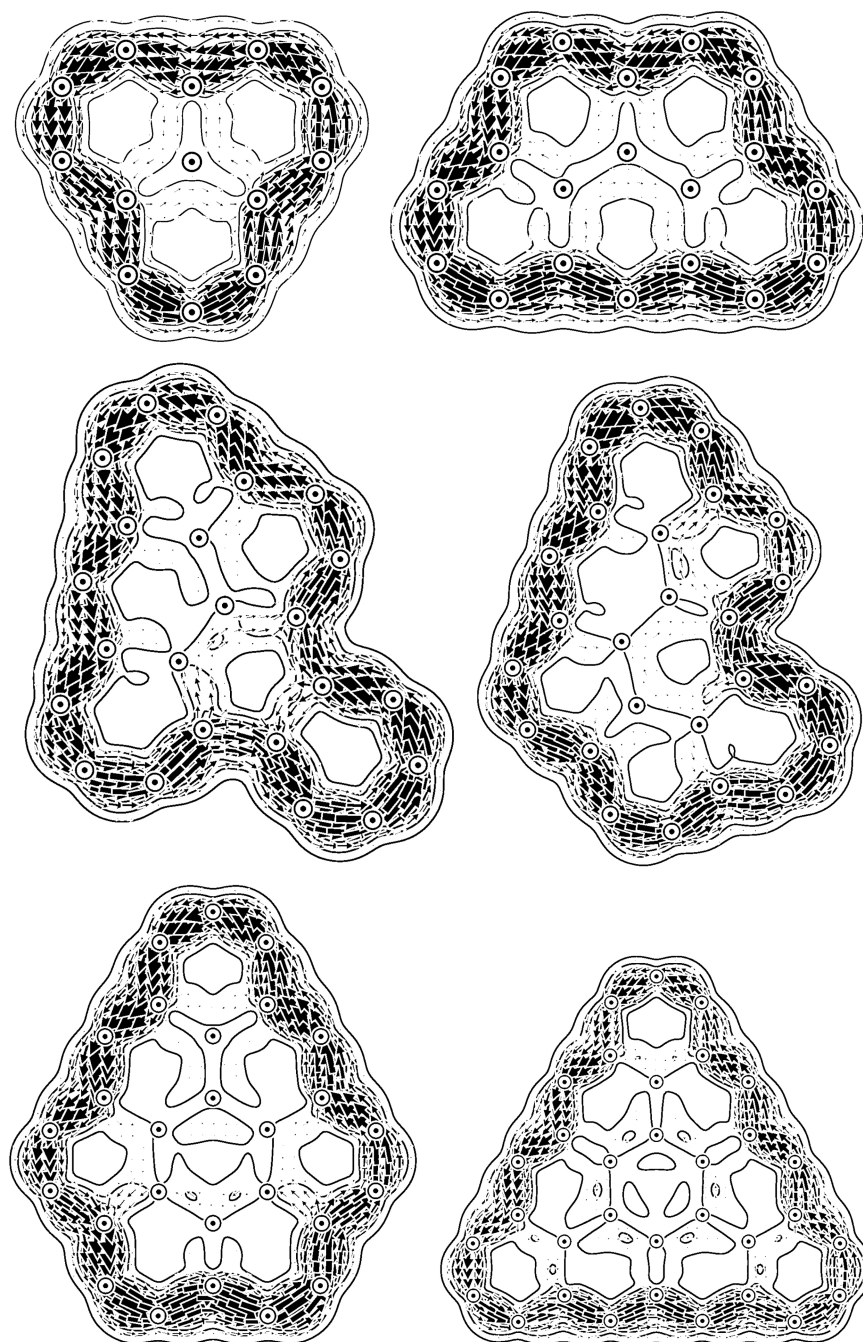
Figure 3. Ring current maps obtained with the *pp* approach for the series of csc-PBHs.

here the CCM model to estimate the multicenter electron delocalization of the benzene rings of PBHs in a manner similar to the way in which the contributions of these rings to the resonance energy are calculated. Thus, we have taken the first five molecules of the series, enumerated the benzene-like conjugated circuits, and calculated the 6-DIs (6-DI^{CC}) using the following expression

$$6\text{-DI}^{CC} = \frac{n_{CC}}{n_K} 6\text{-DI}^{benz} \tag{1}$$

where n_{CC} and n_K represent the number of conjugated circuits for the corresponding benzene ring and the number of Kekulé structures, respectively. 6-DI^{benz} is the six-center delocalization index for the isolated benzene molecule.

The good linear correlation found with the *pp* 6-DIs is presented in Figure 5. This good correlation suggests that the CCM model may be a good tool for the estimation of multicenter indices. This finding should be explored somewhere else for a larger set of PBHs, including neutral, cationic, and anionic. Here, we will focus on the similarities between the representation of the electron conjugation in csc-PBHs and csn-PBHs using Kekulé structures. In order to explore this, we have gathered the Kekulé structures in groups, where each group is formed by a localized fragment (involving the charged carbon atom) and a delocalized fragment (neutral). Given that each Kekulé structure has the same weight, the weight of each group in the total electronic structure is equal to the ratio between the number of Kekulé structures involved in the group, which are in
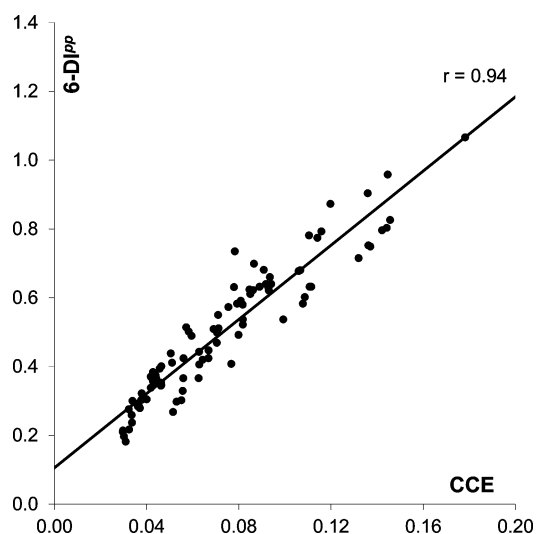
Figure 4. Six-center delocalization indices calculated with the *pp* approach (6-DI^{pp}) versus the CCEs for the benzenoid rings in the series of csc-PBHs.
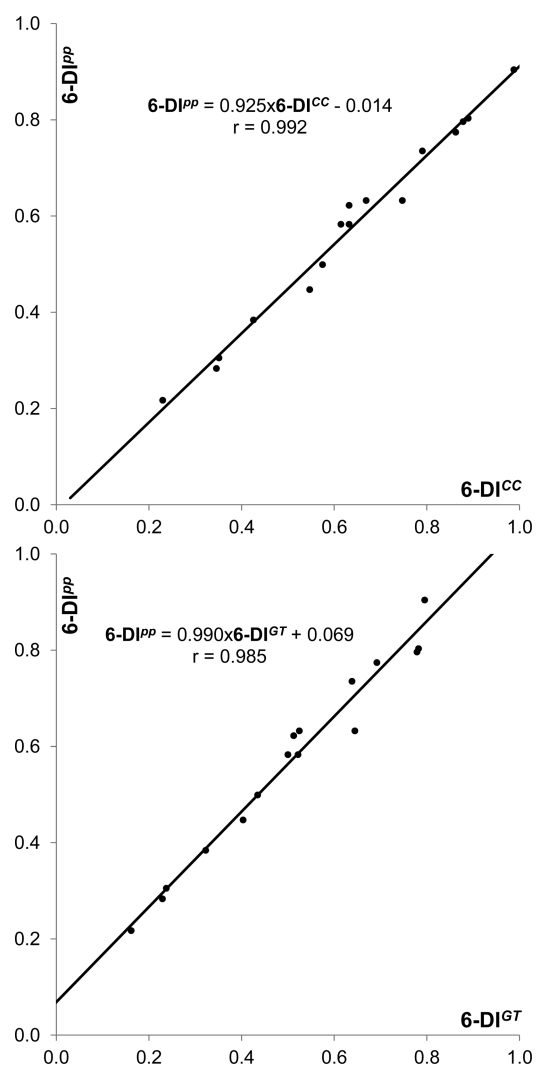
Figure 5. Comparison of six-center delocalization indices calculated with the *pp* approach (6-DI^{pp}) and those obtained with the conjugated circuits model (6-DI^{CC}) and superposition of isolated neutral PBHs (6-DI^{GT}) for the rings of molecules **1**−**5**.

turn generated by bond alternation within the neutral fragment, and the total number of Kekulé structures.

This is illustrated in Figure 6 for molecule **3**, where the neutral fragments correspond to anthracene, pyrene, benzo-
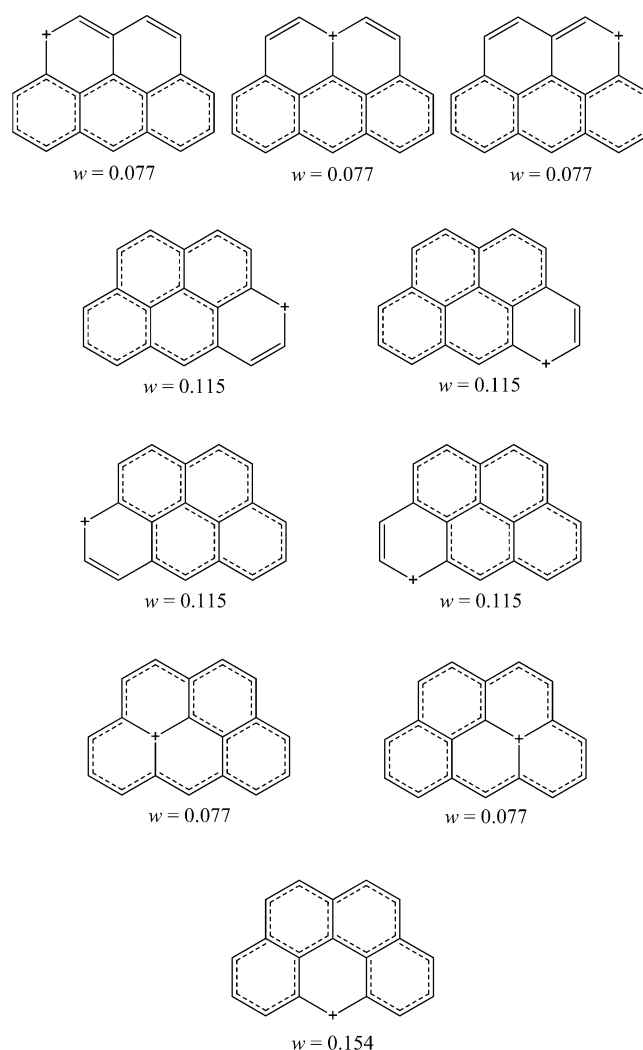

Figure 6. Groups of Kekulé structures and their relative weights (w) in molecule **3**.

phenanthrene, and a fragment containing the peripheral carbons and naphthalene. The electron conjugation in csc-PBHs and its associated properties are then given by the electron conjugation in the neutral delocalized fragments, which are constructed with csn-PBHs. In order to check if this interpretation holds at the ab initio level, we have calculated the 6-DIs (6-DI^{GT}) in the first five molecules of the series from those of the isolated neutral fragments (6-DI^{I}), multiplying each value by the corresponding weight (w_I) according to eq 2, where N_G represents the number of groups or isolated neutral fragments.

$$6\text{-DI}^{GT} = \sum_{I=1}^{N_G} w_I 6\text{-DI}^{I}$$

(2)

Correlation of the values obtained with the *pp* 6-DIs is shown in Figure 5. As one can see, the linear correlation found is quite good, which means the electron delocalization in csc-PBHs can be understood as a superposition of the electron

delocalization in selected csn-PBHs. In addition, we have calculated the bond currents using the conjugated circuits approach introduced in ref 51. For csc-PBHs, the bond currents can be calculated by superposition of the bond currents of the isolated neutral fragments, multiplied by the corresponding weight, w_I. As in csn-PBHs,[53] the current maps of closed-shell cations match pretty well with those obtained ab initio. In order to show this concordance, we have depicted in Figure 7 the
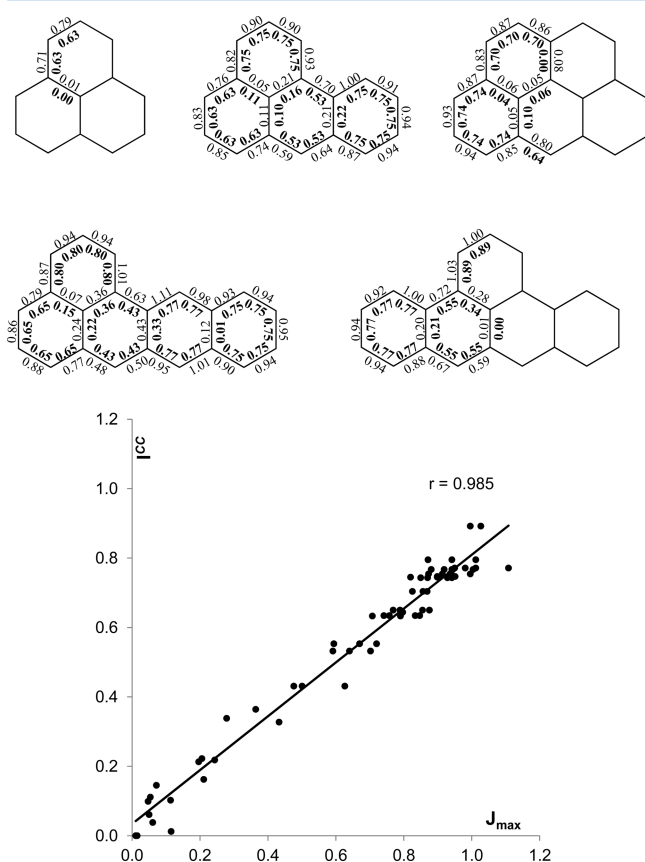
Figure 7. Comparison of the bond currents obtained from conjugated circuits, I^{CC} (boldface type), and the maximum of the current density at the CC bonds, J_{max} (lightface type), obtained with the *pp* model for the rings of molecules **1−5**.

bond currents calculated from conjugated circuits and the maximum of the *pp* current density, J_{max}, along the bond line. Figure 7 also shows the good linear correlation found between both magnitudes.

SUMMARY

In this work, we have investigated the aromatic character of the series of closed-shell cationic polybenzenoids (csc-PBHs). According to energetic-, magnetic-, and electron density-based criteria, csc-PBH fragments are aromatic systems. They display large ring electron delocalization, high aromatic stabilization energies, and strong diatropic peripheral electron currents. Comparison with aromatic properties of typical closed-shell neutral polybenzenoids (csn-PBHs) reflects rather few and modest differences. Similarities have been explained by a simple graph theoretical model based on conjugated circuits. Thus, the electron conjugation in a csc-PBH can be understood as superposition of the electron conjugation in some selected csn-PBHs, which can be deduced from the charged Kekulé

structures of the former. Summarizing, we can state that, despite the reactivity associated with their positive charge, the large aromatic character of the csc-PBHs could make them relatively stable upon formation in required conditions, for instance in the interstellar medium, as has been postulated on the basis of experimental data.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Pseudo-π and STO-3G ring current maps of the whole set of molecules studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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