

Clar's Aromatic Sextet Theory Revisited via Molecular Electrostatic Potential Topography

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Full characterization of the molecular electrostatic potential (MESP) topography of the π -regions of 12 polycyclic benzenoid hydrocarbons (PBHs) is carried out. Benzene is endowed with the most perfect circular distribution of π -delocalization, and the hexagonal rings of other systems possess varying degrees of lesser π -delocalization. The topographical features describe Clar's aromatic sextet theory very well and simplify the aromatic characterization of each ring of a PBH system. The concepts such as "aromatic dilution" observed for polyacene series and the "empty ring" in triphenylene, perylene, and coronene are clearly brought out from this study. The positions of (3, +3) critical points (CPs) are always observed very close to shorter bonds, providing valuable hints at how the π -electrons are shared among the carbons. Further, average values of the MESP at CPs calculated for each ring (\bar{V}_i^s) and for the whole molecule (\bar{V}_m^s) bear linear correlation with the local aromaticity values estimated by Li and Jiang and the hardness values reported by Zhou and Parr for the global aromaticity, respectively. Thus the mapping of the MESP topography provides an elaborate characterization of the π -regions of PBH systems and a description of the intimately connected aromaticity.

Introduction

The concept of aromaticity has existed in the chemical literature for a long time. There have been a number of studies, both experimental and theoretical, using different approaches and methods to arrive at a unified definition of it.^{1–27} These theoretical works can be classified into methods based on valence bond (VB) and molecular orbital (MO) approaches, as well as graph

theoretical studies. Such studies, though partially successful, have helped in the identification and creation of newer molecular systems and the unearthing of structure–activity relations. They have also enabled classification of molecular systems into various categories, such as aromatic, antiaromatic, pseudoaromatic, superaromatic, homoaromatic, heteroaromatic, etc. In all of these classifications, it is easier to describe the nature of aromaticity of a single-ring system compared to that of a many-ring system. The latter has an additional complication due to the local nature of the aromaticity. Here, any attempted method should be able to describe both the local (i.e., for each ring) and global characteristics of aromaticity. A classic example is provided by the phenanthrene molecule. The central ring of this molecule behaves like an olefin, but the other two rings resemble benzene to a large degree.⁷

One of the outstanding contributions to the study of polycyclic aromatic hydrocarbons was made by Clar.^{6,7} His group was instrumental in synthesizing a number of these systems and studying their reactivities, NMR properties, and UV spectra. Combining the experimental

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facts with his intuition, Clar proposed the sextet theory to explain the aromaticities (local and global) of this class of compounds.⁷ Clar's theory describes the aromaticity of a benzenoid hydrocarbon on the basis of the maximum number of sextets (a sextet is defined as six π -electrons represented by a circle) drawn for a system. The details provided by this theory will be unveiled in the later sections in conjunction with the present molecular electrostatic potential (MESP) topography-based study.

There have been many attempts to offer a theoretical justification for Clar's concepts in polycyclic benzenoid hydrocarbons (PBH).^{5,9,10,23,25} Aida and Hosoya¹⁰ have interpreted the aromatic sextet as the "higher order π -electronic correlation" due to the cooperative interaction of the units of closely correlated six π -electrons. Moyano and Panigua²² concluded from a study of polycyclic hydrocarbons, within the Hückel theoretical framework, that the preferred resonance structures are those that maximize the number of isolated aromatic sextets. Very recently, Li and Jiang²⁵ have used the Lanczos method for solving the VB model exactly for PBHs with up to 20 carbon atoms and discussed their local aromaticities based on the relative local hexagon energy (RLHE) as defined by Herndon and Ellzey.⁸ According to them, the benzene molecule is endowed with maximum aromaticity (RLHE = 1000) and other systems agree with Clar's intuitive ideas such as the "dilution of aromatic sextet" and "empty ring". Zhou and Parr²¹ have reported absolute and relative hardness as new measures of aromaticity for several cyclic conjugated systems including many PBHs and discussed generally the global value of it.

The present work mainly focuses on Clar's sextet concepts in PBH systems,⁷ as well as the local and global nature of aromaticity in terms of the MESP topographical characterization of the π -regions of these systems. This idea stems from the facts that the π -region of a molecule has an intimate connection with aromaticity and the MESP topography is one of the most suitable quantum chemical tools for examining the nature of it. Earlier topographical works on substituted benzenes strengthen this belief because the effect of a substituent over the aromatic π -region is clearly brought out from the position and values of the MESP critical points (CPs).^{28,29} The former even shows a linear correlation with the Hammett constants.²⁹ Also, the works of Politzer et al.^{30,31} mainly dealing with benzenoid systems have contributed largely toward establishing MESP as a key entity for the theoretical analysis of the properties of the π -regions of molecules. Further, the topographical characterization of MESP, $V(\mathbf{r})$, defined by

$$V(\mathbf{r}) = \sum_A^N (Z_A/|\mathbf{r} - \mathbf{R}_A|) - \int (\rho(\mathbf{r}')d^3\mathbf{r}'/|\mathbf{r} - \mathbf{r}'|) \quad (1)$$

(where Z_A is the nuclear charge and $\rho(\mathbf{r})$ is the electron

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density (ED)) has a major advantage over the popular electron density topography mapping as far as the π -regions are concerned. The latter turns out to be featureless at these regions, but because of the delicate balance between the nuclear and electronic terms in eq 1, negative-valued CPs do appear for the former. The nature, value, and distribution of these MESP CPs serve as a means for a detailed description of the π -regions.

In Bader's theory,³² which pioneered the studies of ED topography, different CPs of ED describe different types of atom-to-atom connectivity relations and thereby the atoms-in-a-molecule concept. For instance, the (3, -1), (3, +1), and (3, +3) points describe bonds, rings, and cages, respectively. In the same spirit, MESP topography also shows bond CPs, ring CPs,^{33a,b} pseudo (3, -3) CPs at the nuclear positions,³⁴ and cage CPs.^{33c,d} These types of CPs appear very close to the nuclear framework and thus possess positive MESP values (the first term in eq 1 will dominate over the second term). They have little use in describing the π -regions of a molecule and therefore are not calculated in the present work. Except for positively charged species, all the molecular systems will show negative-valued MESP CPs away from the molecular plane. For example, a (3, +3) MESP CP can be located above the midpoint of the C-C bond in ethylene. For the terminal C-C bonds of butadiene, (3, +3) CPs do appear which are connected by a (3, +1) CP above the mid C-C bond. H₂O shows two (3, +3) CPs for the oxygen lone pairs and are connected by a (3, +1) CP. In general, a (3, +1) MESP CP connects two (3, +3) CPs, and a (3, -1) CP can be located for a closed π -ring system above the ring plane.^{28,29} Recent works by Gadre et al. have shown that significant chemical meanings can be assigned for the position and values of the MESP CPs when considering the interactions between two oppositely charged species,^{35a} a charged species and a neutral molecule,^{35b} and two neutral molecules.^{35c,d} These and other related works^{35e-g} have illustrated that the negative-valued MESP CPs act as potential binding sites toward a positively charged species or the electron-deficient regions of a neutral molecule. The regions surrounding the most negative-valued CP, normally a (3,+3), emerge as the most likely binding site.

Methodology

All the molecular systems dealt with in the present work are optimized at the HF/6-31G level of theory using GAUSSIAN94.³⁶ At these geometries, MESP topological analyses are carried out employing the HF/6-31G(d,p) wave functions and

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using the UNIPROP³⁷ package. This method is followed because our earlier work on basis-set effects on the MESP topography^{28a} of substituted benzenes has brought out that this level of theory is quite adequate for a proper representation of their MESP topography. Because the present systems are all hydrocarbons, the topography is expected to be less complicated than that of an aromatic systems with different kinds of substituents attached to it. Further, the effect of correlation also does not change the overall topography of the MESP.³⁸ Topological analysis of $V(\mathbf{r})$ is based³⁹ on locating the points at which the first derivatives of it with respect to the x , y , and z coordinates vanish. The number of nonzero eigenvalues of the Hessian matrix characterizes those points as maxima, minima, and saddle points. An ordered pair (R, σ) is used as a notation for the CP where R and σ are called respectively as the rank and signature. For a nondegenerate CP of $V(\mathbf{r})$, $R = 3$, and hence σ assumes only four values,³² viz., -3 , $+3$, -1 , and $+1$.

Results and Discussion

Benzene: Signature of the Perfect Aromatic Sextet. Benzene is normally represented by drawing a circle inside a hexagon symbolizing the six π -electrons. This intuitive picture first proposed by Robinson¹ portrays benzene as the epitome of a perfect aromatic sextet. The quantum mechanical justification of this idea is already well-established, from the Hückel MO theory² to sophisticated modern theories.^{14,17,23} In general, the explanations are based on the delocalized nature of the occupied MOs. Though the above idea is very clear in every chemist's mind, the same is not reflected in the electron density ($\rho(\mathbf{r})$) topography. However, it is exhibited in a unique way by the topography of the corresponding MESP. This property shows a circular arrangement of six minima on either side of the ring with two adjacent minima connected via a saddle point of $(3, +1)$ signature. These MESP "rings" are observed approximately 1.73 Å from the ring plane. In addition to this, a $(3, -1)$ saddle point is observed on the C_6 axis 1.77 Å away from the ring plane. Figures 1a and 1b depict this unique situation (for all the molecules studied here, the $(3, +3)$, $(3, +1)$, and $(3, -1)$ MESP CPs are denoted as ai , bi , and ci , respectively, where i is an integer). It may appear that the high symmetry of this molecule is responsible for this unique situation. The most striking feature of the topography is the near constancy of the MESP values at the $(3, +3)$ and $(3, +1)$ CPs (-0.0326 and -0.0325 au, respectively). An earlier study^{33d} has also brought out the MESP topographical features in the benzene molecule in C_{6v} symmetry. This indeed brings out very smooth distribution of the π -electrons on either side of the hexagonal ring. Even moving toward the $(3, -1)$ saddle does not cause a significant increase in the

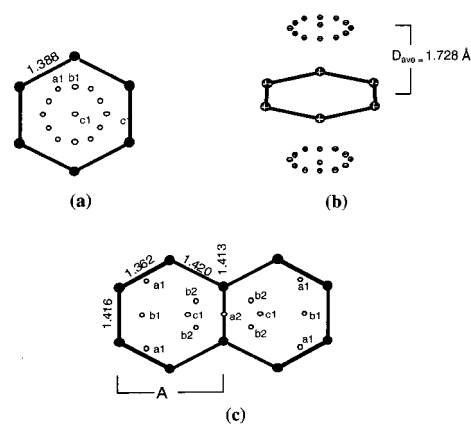


Figure 1. MESP topography of benzene: (a) top view, (b) tilted view, and (c) top view of naphthalene. See text for details of MESP CPs and values. Hydrogen atoms are not shown in this and other figures.

MESP value, which is -0.0316 au. The reason for this could be the absence of the dilution of the aromatic sextet.

We propose the use of these unique MESP topography features as a signature of the perfect aromatic sextet and the average value of the CPs observed over one side of the benzene ring (or the higher benzenoid hydrocarbon) as a measure of aromaticity. With this definition in mind, benzene is assigned a value -0.0325 au, which is scaled to 1000 to provide a direct comparison with the Li–Jiang scale.²⁵

We have also studied the MESP topography of five distorted benzenes^{13b,16,17} in C_{2v} symmetry. These geometries (1–5) are constructed by keeping the C–C bond alternation 0.2, 0.4, 0.6, 0.8, and 1.0 Å, respectively, from the equilibrium structure. All these distorted systems show only three $(3, +3)$ CPs on one side of the ring plane corresponding to the shorter C–C bonds, and two such CPs are connected via a $(3, +1)$ CP. All of them also show a $(3, -1)$ CP at the center region. The average value of the MESP CPs suggests that their aromaticity progressively decreases with increase in bond alternation, the values being 995, 990, 982, 971, and 952 for systems 1–5, respectively. The interesting point is that there is no sharp decrease in the aromaticity value with respect to the bond alternation, indicating the importance of the cyclic distribution of π -electrons.

Naphthalene. In the naphthalene molecule, two hexagonal C–C rings share a common C–C bond, and five π -electrons can be formally assigned for each ring. These features, as well as the reduction of symmetry compared to benzene, account for its similarities and differences with the latter. According to Clar,⁷ there can be only one sextet in this system. If we assume a sextet for one of the rings, the other ring contains two double bonds. The situation can be best represented by the resonance combination of two Clar structures (Figure 2a) or the four classical resonance structures (Figure 2b). However, the actual situation of π -delocalization is brought to light by the corresponding MESP topography as shown in Figure 1c. An overall view of the topography shows that the average value of the CPs has gone up (this is expected because 10 electrons are shared by two rings), and the most negative-valued CPs ($a1$'s) are observed at the end regions of the molecule. Also, larger differences between adjacent CPs can be seen as compared to those in benzene (for example, $a1$ and $b1$ differ by 0.0021 au).

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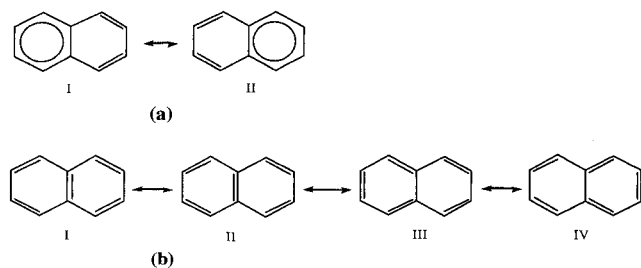


Figure 2. Naphthalene resonance structures: (a) Clar structures and (b) classical structures.

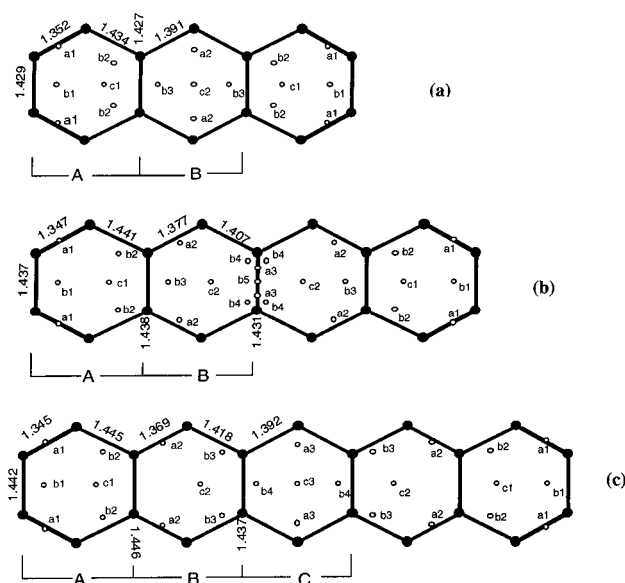


Figure 3. MESP topography of (a) anthracene, (b) tetracene, and (c) pentacene. See Table 1 for details of topography.

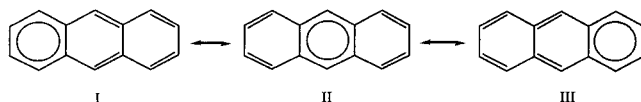


Figure 4. Clar formulas for anthracene.

Yet another observation is the smaller distance of the a1 CPs from the nearest C–C bond. In fact, the C–C bond nearest to the CP a1 is very susceptible to an addition reaction.⁴⁰ The bridging C–C bond over which a (3, +3) minimum (a2) is noticed can also lead to an addition product. Further, the C–C bonds closer to the (3, +3) minima (a1s and a2) are shorter than the other C–C bonds. Therefore, we conclude that the π -electrons of this molecule are more localized around the C–C bonds closer to the a1 and a2 type CPs compared to other bonds, thereby reducing the overall delocalization tendency. This picture of naphthalene suggests the formula depicted in Figure 7a, where a thick line represents a double bond that is equally shared by the two A rings. According to this formula, both rings are equivalent and closer to the “real” structure than any of the resonance structures. Resonance theory considers structures I or II (Figure 2b) as the most appropriate ones for representing naphthalene.⁴¹

Linear Polyacenes: Anthracene, Tetracene, and Pentacene. As compared to naphthalene, the above

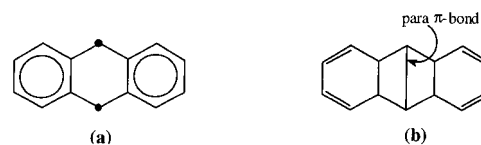


Figure 5. (a) Clar formula of anthracene with two aromatic sextets and two π -electrons localized on the para carbons. (b) Illustration of the para π -bond as portrayed by Clar.

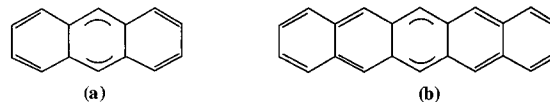


Figure 6. Formulas suggested for (a) anthracene and (b) pentacene from the MESP topography. See text for discussion.

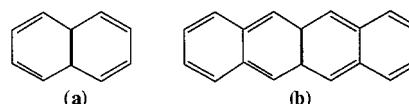


Figure 7. MESP topography-based formula for (a) naphthalene and (b) tetracene. See text for details.

Table 1. MESP Topography (CP, MESP value (V_c), and distance from the ring plane (D_c) of Anthracene, Tetracene, and Pentacene^a

molecule	CP, V_c , D_c	CP, V_c , D_c
naphthalene	a1, -0.0314, 1.70	b2, -0.0269, 1.90
	a2, -0.0274, 1.77	c1, -0.0267, 1.91
	b1, -0.0293, 1.77	
anthracene	a1, -0.0310, 1.68	b3, -0.0260, 1.92
	a2, -0.0274, 1.82	c1, -0.0241, 1.99
	b1, -0.0274, 1.79	c2, -0.0253, 1.95
	b2, -0.0244, 1.97	
tetracene	a1, -0.0306, 1.66	b3, -0.0250, 1.94
	a2, -0.0273, 1.79	b4, -0.0248, 1.96
	a3, -0.0248, 1.97	b5, -0.0248, 1.97
	b1, -0.0261, 1.81	c1, -0.0224, 2.05
	b2, -0.0229, 1.99	c2, -0.0240, 2.00
pentacene	a1, -0.0303, 1.66	b3, -0.0238, 1.96
	a2, -0.0271, 1.77	b4, -0.0242, 1.98
	a3, -0.0260, 1.84	c1, -0.0213, 2.08
	b1, -0.0252, 1.82	c2, -0.0228, 2.04
	b2, -0.0220, 2.00	c3, -0.0236, 2.01

^a V_c values are in au, and D_c is in Å. See text and Figures 1 and 3 for details.

molecules are characterized by the presence of one or more rings with opposite sides fused with two other rings. This results in the decrease in π -electron count per ring (e_r) as we go to higher members of this series (for example, e_r values for anthracene, tetracene, and pentacene are $14/3$, $18/4$, and $22/5$, respectively). This property is reflected in the increase in MESP value at CPs on going from anthracene to the higher acenes (Table 1). Further, the topography of MESP over each ring can clearly distinguish the differences in the π -electron distribution existing among them (Figure 3). Keeping this in view, we also report the average value of the MESP CPs over each ring of a PBH system. This quantity will be later related to the local aromaticity exhibited by each ring. Similarly to the naphthalene molecule, anthracene, tetracene, and pentacene also show the most negative MESP CPs (a1's) toward the end regions where the shortest C–C bonds are observed. The deviation of the

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MESP at the a1 CP from that observed at the center region of benzene, naphthalene, anthracene, tetracene, and pentacene is 0.0010, 0.0040, 0.0057, 0.0058, and 0.0067 au, respectively. This leads to the conclusion that π -electrons are more and more concentrated toward the end regions when we go to higher linear polyacenes. Also, the a1 type CPs appear progressively closer to the nearest C–C bond in this series of molecules (cf. Table 1). This feature can be correlated well with the reactivity of the acene series, which increases rapidly in the order benzene < naphthalene < anthracene < pentacene etc.^{6,7} Clar has explained this decrease in the benzenoid character in this series by invoking the sextet concept. According to him, one sextet is shared among several rings, which results in overall dilution of the benzenoid character of each ring (Figure 4), although this explanation is inadequate for quantifying the benzenoid character of each ring.

Other interesting observations are as follows. (i) In linear polyacenes, the pattern of MESP topography over the A ring (cf. Figures 1c and 3) is similar. (ii) The region over the mid C–C bond of naphthalene and tetracene (systems with even number of rings) show MESP minima. (iii) The MESP patterns for the central ring of anthracene and pentacene (systems with odd number of rings) are similar, with (3, +3) minima observed over the para carbons (i.e., a2 CPs of anthracene and a3 CPs of pentacene). The last observation (iii) is particularly noteworthy because the para carbons show reactions leading to saturation at these carbons.^{42,43} On the basis of the absorption spectra and NMR data of these molecules, Clar suggested localization of two π -electrons in the para region.⁷ He proposed a formula with two aromatic sextets for anthracene, as shown in Figure 5a, and argued that the second sextet, despite localization at the para carbons, may stabilize the system. Our results support his claim, and on the basis of the positions of MESP minima, we suggest the interesting alternate formulas (Figure 6a,b) for anthracene and pentacene, respectively. Clar went a step further and discussed the possibility of para π -bonds⁷ in anthracene (cf. Figure 5b). The MESP topography with two (3, +3) CPs near the para carbons connected by a (3, -1) saddle near the midpoint region of them, however, does not support this. Normally a (3, +1) connection with two (3, +3) saddles indicates conjugation, as in the case of benzene or polyenes.²⁹ Similarly to naphthalene, the MESP topography of tetracene proposed the most likely formula as the one shown in Figure 7b.

Triphenylene, Perylene, and Coronene: the Empty Ring Concept. In these systems, two different ring structures can be noticed, central (B) and peripheral (A's). All of these systems show higher benzenoid character as compared to most of the polycyclic benzenoid aromatics with the same number of rings.^{7,44–46} According to sextet theory, a structure with a higher number of sextets is close to the real structure and hence more stable. This suggests three sextets for triphenylene and coronene and two for perylene, as shown in Figure 8. In the case of perylene and coronene, more identical combinations are

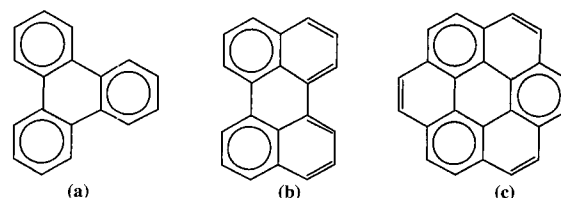


Figure 8. Sextet formulas of (a) triphenylene, (b) perylene, and (c) coronene.

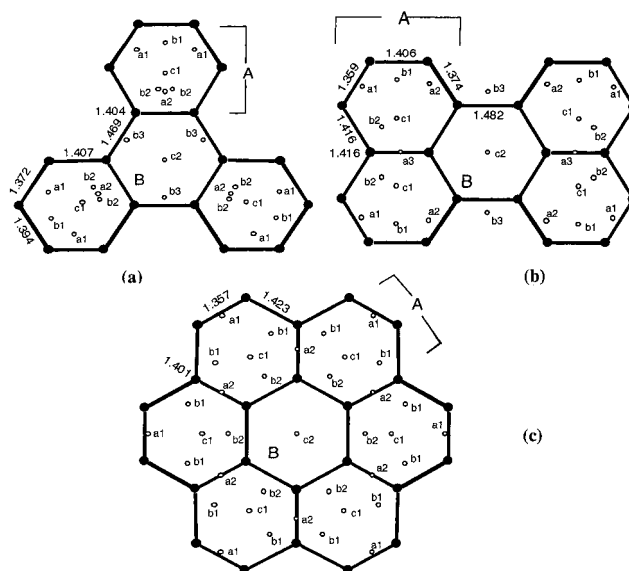


Figure 9. Top view of the MESP topography of (a) triphenylene, (b) perylene, and (c) coronene. Refer to Table 2 for the MESP values and their distance from the ring plane.

possible that also add to the stability of the system. However, drawing a sextet at the center leaves no space for a second sextet. Clar described this particular situation⁴⁷ by referring to the central ring as an empty ring. It implies that the center ring π -electrons are not in conjugation within that ring. MESP topography of these systems (Figure 9) strongly supports this concept. The most important observation is that (3, +3) CPs are conspicuous by their absence over the central ring. Further, the CPs over this ring show very small negative values and are maximally away from the ring plane (cf. Table 2). Similarly to the previous cases, the C–C bonds nearest to a (3, +3) minimum show more double bond character, thus suggesting the formulas shown in Figure 10a–c as the most likely representations of triphenylene, perylene, and coronene, respectively. A comparison of the MESP topography of naphthalene and perylene supports consideration of perylene as being made up of two naphthalene moieties connected via two C–C single bonds.⁷

Phenanthrene, Benzophenanthrene, Benzanthracene, and Chrysene. Compared to the linear polyacenes, one can draw a maximum of two sextets for these systems (cf. Figure 11), bringing out more localization of π -electrons toward the C–C bonds not involved in sextet formation. In other words, some regions of the molecule behave more like benzene and others more like olefins. This is indeed observed in many reactions of these molecules. For example, phenanthrene adds bromine

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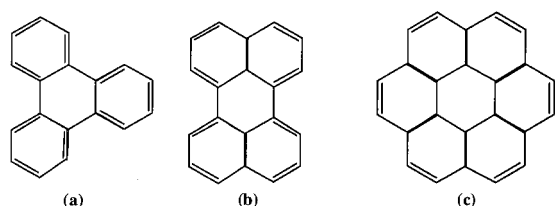
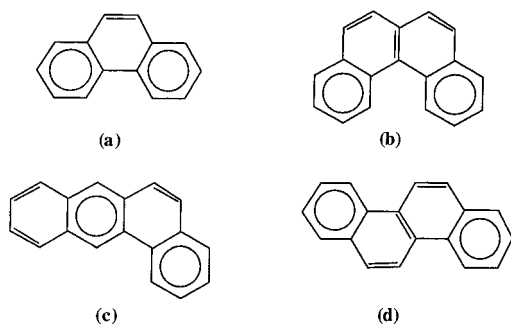
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Table 2. MESP Topography (CP, MESP value (V_c), and distance from the ring plane (D_c)) of Triphenylene, Perylene, and Coronene^a

molecule	CP, V_c , D_c	CP, V_c , D_c
triphenylene	a1, -0.0302, 1.74	b3, -0.0223, 2.09
	a2, -0.0282, 1.85	c1, -0.0281, 1.85
	b1, -0.0294, 1.77	c2, -0.0210, 2.24
	b2, -0.0282, 1.85	
perylene	a1, -0.0295, 1.72	b2, -0.0254, 1.93
	a2, -0.0288, 1.77	b3, -0.0214, 2.05
	a3, -0.0261, 1.93	c1, -0.0253, 1.95
	b1, -0.0278, 1.79	c2, -0.0191, 2.41
coronene	a1, -0.0284, 1.71	b2, -0.0233, 2.03
	a2, -0.0248, 1.93	c1, -0.0229, 2.04
	b1, -0.0239, 1.94	c2, -0.0199, 2.35

^a V_c values are in au, and D_c is in Å. See text and Figure 9 for details.

**Figure 10.** MESP topography-based formulas for (a) triphenylene, (b) perylene, and (c) coronene.**Figure 11.** Sextet formulas for (a) phenanthrene, (b) benzophenanthrene, (c) benzantracene, and (d) chrysene.

without a catalyst at the olefinic region (cf. Figure 11a) to form the relatively stable dibromide.⁷ Substitution and addition reactions are reported mainly on the B rings of benzophenanthrene (Figure 12b).⁴⁸ Various combinations of hydrogenated chrysenes are reported in the literature.⁴⁹ Benzantracene has been studied extensively as a carcinogen, and its epoxide formation reactions have been linked to carcinogenicity.⁵⁰ The MESP topographical studies of these systems (Figure 12 and Table 3) further elaborate the concept of Clar's sextet theory and identify the regions where the olefinic character is enhanced. The B ring of phenanthrene, with the nearest CP (a3) having a high negative value, is responsible for its high reactivity. For benzophenanthrene also, the (3, +3) CPs over the B rings (a2's) are very close to the C–C bonds and are endowed with high negative values. Similar features exist

Table 3. MESP Topography (CP, MESP value (V_c), and distance from the ring plane (D_c)) of Phenanthrene and Chrysene^a

molecule	CP, V_c , D_c	CP, V_c , D_c
phenanthrene	a1, -0.0307, 1.72	b3, -0.0242, 1.95
	a2, -0.0306, 1.72	b4, -0.0235, 2.03
	a3, -0.0305, 1.67	c1, -0.0276, 1.87
	b1, -0.0295, 1.76	c2, -0.0230, 2.06
	b2, -0.0276, 1.86	
chrysene	a1, -0.0303, 1.72	b3, -0.0267, 1.88
	a2, -0.0300, 1.72	b4, -0.0242, 2.00
	a3, -0.0270, 1.88	b5, -0.0246, 1.95
	a4, -0.0300, 1.69	b6, -0.0287, 1.77
	a5, -0.0256, 1.91	c1, -0.0266, 1.88
	b1, -0.0287, 1.77	c2, -0.0240, 2.02
b2, -0.0269, 1.88		

^a V_c values are in au, and D_c in Å. See text and Figure 12 for details.

in the other two systems also. For example, the very high reactivity of the C ring of benzantracene can be correlated to the observation of a (3, +3) CP (a6) just above the C–C bond whose carbon atoms do not belong to other rings. This CP is the closest of all of the other CPs to the molecular plane and has high negative value. Localized formulas can be drawn for these systems on the basis of the (3, +3) locations (Figure 13). Note that except for chrysene, the CP information is not sufficient to draw all the localized regions. But of course, there exists a natural choice to fill the valencies (the ring that shows a more negative nature of MESP is preferred for it). This is probably a result of the angular nature of these systems, which brings relatively strong nonbonded H...H interactions, or computational artifacts. The benzantracene formula is particularly interesting because it has a ring (C) that does not follow the alternate single and double bond pattern of a classical resonance structure.

A general observation for all of the 12 systems studied here is the presence of a (3, -1) CP for each ring (c1, c2, c3, and c4). This could be a unique feature of a π -ring system. In some cases (tetracene, triphenylene, phenanthrene, and chrysene) different CPs appear very close to each other, and in perylene, b3 CP is located above but outside the center ring. These may be due to the level of computation and may be artifacts of the basis set employed.

Average MESP of π -Region CPs: a Measure of Aromaticity. In Table 4, the average MESP values at the CPs observed over each ring of the PBH systems, \bar{V}_i are given separately along with the scaled up values, \bar{V}_i^s and the Li–Jiang (L–J) local aromaticity values.²⁵ Figure 14 shows the good linear correlation of \bar{V}_i^s against L–J values (correlation coefficient = 0.945). Also, average values of $V(r)$ at CPs observed for each face of a PBH system, \bar{V}_g is depicted in Table 5 along with the scaled up values, \bar{V}_g^s and the Zhou–Parr (Z–P) hardness values (η). Zhou and Parr have used η as a measure of the global aromaticity value.²¹ Correlation of \bar{V}_g^s against η also gives a near-linear correlation (Figure 15). Note that the coronene value, which deviates greatly from the Z–P scale, is not included in the correlation graph. Sometimes described as having superdelocalization of π -electrons, this molecule does not show a high aromaticity in terms of its MESP-derived value. The MESP-derived formula, however, shows six π -bonds equally shared by each two rings, reflecting its increased π -de-

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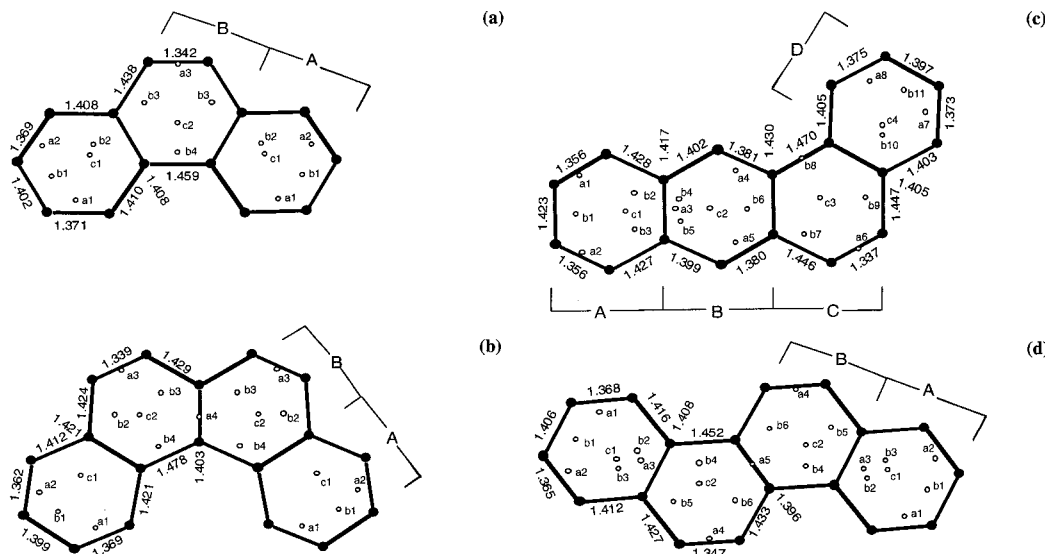


Figure 12. MESP topography of (a) phenanthrene, (b) benzophenanthrene, (c) benzantracene, and (d) chrysene. Tables 3 and 4 give the MESP values and distance of the CPs from the ring plane.

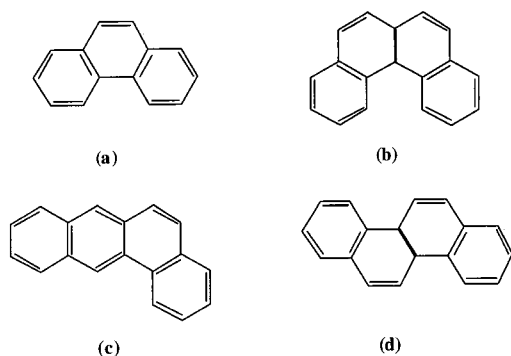


Figure 13. MESP topography-based formulas for (a) phenanthrene, (b) benzophenanthrene, (c) benzantracene, and (d) chrysene.

Table 4. MESP Topography (CP, MESP value (V_c), and distance from the ring plane (D_c)) of Benzophenanthrene and Benzantracene^a

molecule	CP, V_c , D_c	CP, V_c , D_c
benzophenanthrene	a1, -0.0311, 1.72	b2, -0.0245, 1.95
	a2, -0.0300, 1.73	b3, -0.0250, 1.92
	a3, -0.0291, 1.70	b4, -0.0254, 1.98
	a4, -0.0278, 1.86	c1, -0.0272, 1.89
	b1, -0.0291, 1.77	c2, -0.0242, 2.00
benzantracene	a1, -0.0304, 1.69	b5, -0.0257, 1.93
	a2, -0.0304, 1.69	b6, -0.0261, 1.90
	a3, -0.0257, 1.93	b7, -0.0221, 2.01
	a4, -0.0280, 1.80	b8, -0.0221, 2.07
	a5, -0.0276, 1.80	b9, -0.0227, 1.98
	a6, -0.0300, 1.66	b10, -0.0275, 1.85
	a7, -0.0299, 1.73	b11, -0.0293, 1.76
	a8, -0.0300, 1.73	c1, -0.0245, 1.96
	b1, -0.0275, 1.85	c2, -0.0253, 1.95
	b2, -0.0247, 1.95	c3, -0.0210, 2.15
	b3, -0.0246, 1.95	c4, -0.0275, 1.86
b4, -0.0257, 1.93		

^a V_c values are in au, and D_c is in Å. See text and Figure 12 for details.

localization compared to many other systems. The C–C bonds which are part of only one ring show more π -localization. Even the MESP-derived aromaticity value is not unexpected because it has the lowest π -electron count per ring (3.43). All of the other systems have a 4

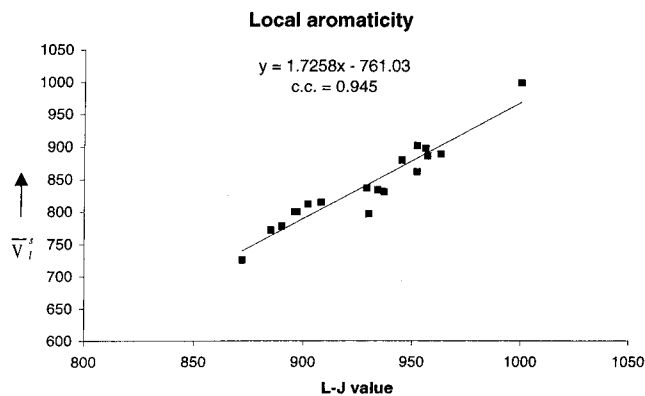


Figure 14. Correlation of MESP topography-derived local aromaticity of PBH systems against L–J values.

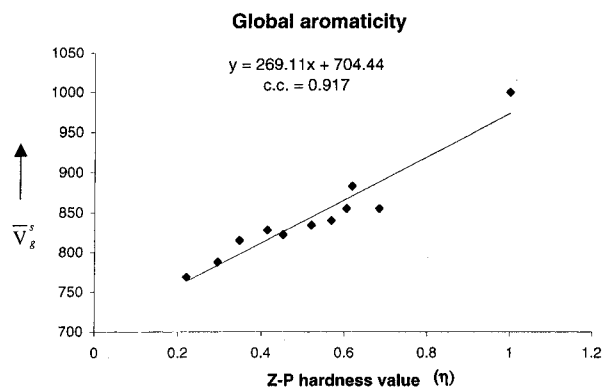


Figure 15. Correlation of MESP topography-derived global aromaticity of PBH systems against Z–P hardness values.

or greater π -electron count per ring. These two correlations thus strongly support that the MESP topographical characterization of the π -regions of the PBH systems is indeed useful for evaluating the local and global natures of aromaticity. It also complements the VB calculations of Li and Jiang and the hardness concept introduced by Zhou and Parr for aromaticity. We also note here that the procedure outlined here may or may not be applicable to heterocyclic aromatic systems because they might show entirely different MESP topographies due to factors

Table 5. MESP Topography-Derived (\bar{V}_l and \bar{V}_l^s) and Li–Jiang (L–J) Values of Local Aromaticities^a

molecule	\bar{V}_l^s , L–J value	molecule	\bar{V}_l , \bar{V}_l^s , L–J value
benzene	–0.0325, 1000, 1000	perylene	–0.0272 (A), 837, 929 –0.0206 (B), 634, 814
naphthalene	–0.0286, 880 (A), 945	coronene	–0.0246 (A), 757 –0.0199 (B), 612
anthracene	–0.0271 (A), 834, 934 –0.0264 (B), 812, 902	phenanthrene	–0.0292 (A), 898, 956 –0.0251 (B), 772, 885
tetracene	–0.0259 (A), 797, 930 –0.0253 (B), 778, 890	benzophenanthrene	–0.0293 (A), 902, 952 –0.0260 (B), 800, 897
pentacene	–0.0252 (A), 775 –0.0249 (B), 776 –0.0248 (C), 763	benzanthracene	–0.0270 (A), 831, 937 –0.0265 (B), 815, 908 –0.0236 (C), 726, 872
triphenylene	–0.0289 (A), 889, 963 –0.0220 (B), 677, 821	chrysene	–0.0288 (D), 886, 957 –0.0280 (A), 862, 952 –0.0260 (B), 800, 896

^a See text and MESP topography figures for details.

Table 6. MESP Topography-Derived (\bar{V}_g and \bar{V}_g^s) and Zhou–Parr (Z–P) Values of Global Aromaticities^a

molecule	\bar{V}_g , \bar{V}_g^s , Z–P value	molecule	\bar{V}_g , \bar{V}_g^s , Z–P value
benzene	–0.0325, 1000, 1.000	perylene	–0.0265, 815, 0.347
naphthalene	–0.0287, 883, 0.618	coronene	–0.0244, 750, 0.539
anthracene	–0.0269, 828, 0.414	phenanthrene	–0.0278, 855, 0.605
tetracene	–0.0256, 788, 0.295	benzophenanthrene	–0.0273, 840, 0.568
pentacene	–0.0250, 769, 0.220	benzanthracene	–0.0267, 822, 0.452
triphenylene	–0.0278, 855, 0.684	chrysene	–0.0271, 834, 0.520

^a See text for details.

such as electronegativity differences between atoms, presence of lone pairs, etc. Works in this direction are indeed necessary to clarify this point.

Conclusions

MESP topography is a powerful tool for the analysis of a variety of chemical phenomena, in particular when the local electron concentrations rise as a result of π -electrons, excess electrons (anions), lone pairs, bond-strain, etc. Several recent works on substituted benzenes, anions, base pairs, and strained systems support the above statement.^{28,29,31,33,35} The present work gives yet another illustration of the power of this tool by unearthing the characteristic features of the π -regions of PBH systems. Various aspects of Clar's aromatic sextet theory are seen to correlate very well with the MESP topographical features of these systems.

In comparison with benzene, which has six identical (3, +3) CPs for one face of the ring plane, each ring of all the annelated systems show three or less (3, +3) CPs with different values. This suggests that only benzene has a perfect six π -delocalization, which is intimately connected with its high symmetry, whereas the hexagonal rings of all the annelated systems show varying degrees of π -localizations. In light of this, the practice of drawing a

circle inside the ring for the PBH systems may be discouraged, and the formulas suggested in this work could be meaningfully used as alternatives. Further, the linear correlation of the MESP topography-based local and global aromaticity values with two independent theoretical results (viz., those by Li and Jiang²⁰ and Zhou and Parr²¹) brings out the intimate connection between aromaticity and the nature of π -electron distribution. The most encouraging aspect of the MESP topography mapping is its ability to directly distinguish each ring of a PBH system simply by looking at the CP distribution. This property could be further explored to study more complex problems such as the carcinogenic activity of PBH systems. Further, the MESP topography of the ring systems, exemplified in the present study by PBH systems, is expected to play a significant role in their stacking interactions. Works exploring these features are currently underway in our laboratory.

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