Applications of Hückel-Su-Schrieffer-Heeger method

I. Carbon-carbon bond lengths in polycyclic aromatic hydrocarbons

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Abstract

The equilibrium carbon-carbon (C-C) bond lengths in π -electron hydrocarbons are very sensitive to the electronic ground-state characteristic. In the recent two papers by Stolarczyk and Krygowski (J Phys Org Chem, 34:e4154,e4153, 2021) a simple quantum approach, the Augmented Hückel Molecular Orbital (AugHMO) model, is proposed for the qualitative, as well as quantitative, study of this phenomenon. The simplest realization of the AugHMO model is the Hückel-Su-Schrieffer-Heeger (HSSH) method, in which the resonance integral β of the HMO model is a linear function the bond length. In the present paper, the HSSH method is applied in a study of C-C bond lengths in a set of 34 selected polycyclic aromatic hydrocarbons (PAHs). This is exactly the set of molecules analyzed by Riegel and Müllen (J Phys Org Chem, 23:315, 2010) in the context of their electronic-excitation spectra. These PAHs have been obtained by chemical synthesis, but in most cases no diffraction data (by X-rays or neutrons) of sufficient quality is available to provide us with their geometry. On the other hand, these PAHs are rather big (up to 96 carbon atoms), and ab initio methods of quantum chemistry are too expensive for a reliable geometry optimization. That makes the HSSH method a very attractive alternative. Our HSSH calculations uncover a modular architecture of certain classes of PAHs. For the studied molecules (and their fragments – modules), we calculate the values of the aromaticity index HOMA.

Keywords Polycyclic aromatic hydrocarbons (PAHs) · Bond lengths · AugHMO model · HSSH method

Introduction

The world of hydrocarbon chemistry [1] is now open to materials science, where carbon-based materials offer new perspectives for electronics [2]. The π -electron hydrocarbons and all-carbon molecules (fullerenes, nanotubes, and graphene) are at the center of interest in this respect. There is a vast landscape of π -electron hydrocarbons, extending from benzene to graphene, which belongs to the polycyclic

aromatic hydrocarbons (PAHs). This is an area for scientific prospectors equipped with proper experimental and/or theoretical tools.

Klaus Müllen and his coworkers have made seminal contributions to the chemistry, physics, and theory of PAHs; see the review article by Riegel and Müllen [3] and the references therein. Ref. [3] contains a summary of spectroscopic properties of 34 molecules belonging to various families of PAHs. These molecules have been obtained by chemical synthesis (many of them by Müllen et al.), but in most cases their equilibrium geometries are not known. The present article, based on the theory set forth in two recent papers by Stolarczyk and Krygowski [4, 5], is intended as a supplement to the Riegel and Müllen paper [3] by providing the most relevant geometry data—the carbon-carbon (C-C) bond lengths.

The equilibrium C-C bond lengths, derived from the diffraction studies of PAHs (in the crystalline phase), vary as much as 0.15 Å [6]. This variability of bond lengths is a consequence of the coupling between the nuclear framework and the system of *mobile* electrons that occupy the molecular orbitals of the π -symmetry (the π MOs) [4,

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5]. However, the quest for sufficiently accurate equilibrium C-C bond lengths poses a challenge to both experiment and theory.

On the experimental side, one faces difficulties in obtaining good-quality monocrystals. Moreover, the usual diffraction techniques (by X-rays or neutrons) suffer from the limitations of the basic theoretical model which translates the diffraction data into the molecular geometry. This model, in which spherical atoms are subject to uncorrelated thermal motions, neglects (i) the changes of the electronic density due to chemical bonding (contributing to the X-ray diffraction), as well as (ii) the rigid-body motions of the whole molecule. The latter effects, affecting both the X-ray and neutron studies, are especially important in the case of flat and rigid structures of PAHs. The influence of factors (i) and (ii) on the equilibrium C-C bond lengths is well documented in the X-ray studies of naphthalene and anthracene by Brock et al. [7]. Nevertheless, ample raw X-ray and neutron structural data provide a basis for meaningful chemometric studies of bond lengths in PAHs; see papers of Kiralj and Ferreira [6], Kiralj et al. [8], and references therein. Such studies allow a glimpse into another factor affecting the molecular C-C bond lengths derived from crystal structural data: (iii) the influence of crystal-packing forces [6].

On the theory side, there are convergence problems of quantum-mechanical calculations with respect to (i) orbital basis sets and (ii) electronic-correlation contributions. Moreover, full geometry optimization becomes quite costly for big molecules. One finds these problems especially acute in calculations for π -electron systems, PAHs in particular. The density functional theory (DFT) seems to be the *ab initio* method of choice for the geometry optimization of such molecules as PAHs. In the study of acenes (from naphthalene $C_{10}H_8$ to hexacene $C_{26}H_{16}$) by Kadantsev et al. [9], the geometries of these molecules were optimized by using three popular variants of approximate DFT functionals (SVWN5, PBE, and B3LYP), and a big Gaussian basis set (6-311++G(d,p)). The comparison of the equilibrium C-C bond lengths calculated by means of the SVWN5, PBE, and B3LYP functionals reveals differences which often exceed 0.01 Å. One has to concede that “benchmark” geometries of even relatively small PAHs (up to 26 carbon atoms) have not been yet established.

As it has been already in the past, a carefully crafted semi-empirical quantum approach may come to a rescue. In Refs. [4, 5], a very simple Augmented Hückel Molecular Orbital (AugHMO) model has been designed for this purpose. It allows for a qualitative, as well as quantitative, study of the bond-length variation in general π -electron molecules (i.e., those which are planar or locally planar). The simplest realization of the AugHMO model, the Hückel-Su-Schrieffer-Heeger (HSSH) method,

was parametrized [5] for the π -electron hydrocarbons and all-carbon molecules. A comparison with available experimental data demonstrated [5] that the HSSH method is capable of a good description of the C-C bond lengths in a variety of π -electron hydrocarbons and carbon systems, including fullerene C_{60} , polyacetylene, and graphene. It was also found [5] that the HSSH results use to be quite similar to those calculated by means of the B3LYP functional with a modest Gaussian basis set (6-31G(d)). Interestingly, for acenes, the C-C bond lengths calculated by means of the B3LYP/6-31G(d) approach by Firouzi and Zahedi [10] are in almost perfect agreement with those calculated by Kadantsev et al. [9] by means of the B3LYP/6-311++G(d,p) approach. It should be also stressed that, in contrast to *ab initio* methods, the HSSH method of Ref. [5] can be applied to PAHs containing thousands of carbon atoms.

In the present paper, we apply the HSSH method to calculate the equilibrium C-C bond lengths for the set of 34 polycyclic aromatic PAHs presented in the Riegel and Müllen paper [3]. In our study, we keep the classification of PAHs, as well as the numbering of the molecules, employed in Ref. [3]:

- Clarenes (i.e., fully benzenoid hydrocarbons [11, 12]): molecules **1–14**, see “Clarenes,” Figs. 2 and 3.
- K-region PAHs: molecules **15–20** (plus ovalene), see “K-Region PAHs,” Figs. 4 and 5.
- Phenacenes: molecules **21–25**, see “Phenacenes,” Fig. 6.
- Rylenes: molecules **26–29**, see “Rylenes,” Fig. 7.
- Acenes: molecules **30–34** (plus naphthalene), see “Acenes,” Fig. 8.

HSSH calculations

The HSSH bond-length optimization procedure is a (simplified) analog of the molecular-geometry optimization techniques that employ the analytical gradients and Hessians of the total molecular energy [13]. In the HSSH method, the hydrocarbon under study is fully characterized by its topology of C-C bonds (which is coded in the form of the topological matrix [4, 5]).

At the start of the calculations, all the C-C bonds are put equal to the value for benzene, $R_{\text{ben}}^e = 1.397$ Å. Then, the usual Hückel calculations follow, yielding the π molecular orbitals (π MOs) and the π -electron bond orders p_{bond} . This is the 0th interaction, fully equivalent to the standard Hückel approach. In each subsequent step (iteration), the condition of the vanishing gradient of the total HSSH energy is enforced: this amounts to iterating the *linear* bond-order bond-length (BO-BL) relationship:

$$R_{\text{bond}}^e = R^0 - x p_{\text{bond}}^e, \quad (1)$$

where R_{bond}^e and p_{bond}^e , respectively, are the equilibrium bond length and the π -electron bond order for a given C-C bond. $R^0 = 1.523 \text{ \AA}$ and $x = 0.189 \text{ \AA}$ are two geometrical parameters of the AugHMO model of π -electron hydrocarbons [4, 5]. In the HSSH method for hydrocarbons [5], there is also a third geometrical parameter $y = 0.2756 \text{ \AA}$ which determines the slope of a linear function $\beta(R)$ describing the dependence of the “resonance integral” β (< 0) on the C-C bond length R . In order to improve the rate of convergence of the iterative procedure, the Hessian of the HSSH total energy is calculated and applied [4]. In our calculations for PAHs, we assumed that the iterations stopped when the subsequent values of bond-length differences dropped below $5 \cdot 10^{-6} \text{ \AA}$. To this end, five “direct iterations” using Eq. 1 followed by two to three iterations involving the Hessian were always sufficient.

Some clarifications concerning the application of the HSSH method [4, 5] to PAHs are in order:

- (I) This method optimizes *only* the bond lengths, and it is assumed that the optimal valence angles (the C-C-C ones in the case of PAHs) are consistent with the optimized C-C bond lengths, and are as close to 120° as possible. Reducing the molecular geometry solely to the C-C bond lengths seems justified for such molecules as PAHs, and contribute to the computational effectiveness of the HSSH method.
- (II) While Eq. 1 looks like a relationship of *local character*, it should be remembered that the π -electron bond orders p_{bond} are derived from the set of completely delocalized occupied π molecular orbitals [4]. And in the HMO model (as well as in the AugHMO one), these bond orders appear to be sensitive probes of molecular topology. When this is of interest, one may use Eq. 1 to recover the values of the *equilibrium* π -electron bond orders p_{bond}^e from the corresponding calculated equilibrium C-C bond lengths R_{bond}^e . BO-BL relationships of the linear (and also of the quadratic) form were extensively used by Kiralj et al. [8] in order to relate the *experimental* C-C bond lengths, obtained from crystal diffraction studies, to the *theoretical* bond orders calculated by using various theoretical methods. That methodology is different from the one employed in the present paper, but in some cases (a linear BO-BL relationship of the form of Eq. 1, bond orders corresponding to the SCF and VSCF methods [8]), their *linear regression coefficients* were quite close to our values of R^0 and x .
- (III) PAHs belong to the *class of alternant π -electron hydrocarbons* [5], and within the HMO (AugHMO) model the Coulson-Rushbrooke theorem [14] holds:
 - (i) The π -electron orbital energies for the occupied and unoccupied states are placed symmetrically with

respect to the value of the “Coulomb integral” α ,
 (ii) the net π -electron charges [4] at the C atoms are equal to 0.

- (IV) Every PAH contains an even number of π electrons ($N^\pi = 2n$), equal to the number of carbon atoms ($M = 2n$). The ground state of the PAH molecule involves n doubly occupied π MOs of lowest orbital energies, and thus corresponds to the closed shell (the spin singlet). In our calculations, we monitor the HOMO-LUMO gap (nonzero), and the smallest eigenvalue (positive) of the Hessian of the total HSSH energy.
- (V) In the HSSH calculations for hydrocarbons, we employ the Hückel energy units:

$$\alpha = 0, \quad |\beta| \equiv |\beta(R_{\text{ben}}^e)| = 1, \quad (2)$$

where $R_{\text{ben}}^e = 1.397 \text{ \AA}$ serves as the reference C-C bond length [5]. Thus, the only empirical parameters of the HSSH model are the abovementioned three geometrical parameters: R^0 , x , and y , plus R_{ben}^e .

HOMA index

We used our HSSH-optimized C-C bond lengths to calculate the values of the aromaticity index HOMA of Krygowski and coworkers [15–18]. HOMA (Harmonic-Oscillator Measure of Aromaticity) is currently considered the most important indicator of the aromatic character of π -electron molecules (or their fragments), based solely on the values of bond lengths. For a π -electron hydrocarbon, the definition of HOMA reads as [15, 16]

$$\text{HOMA} = 1 - \frac{\kappa}{N} \sum_{\text{bond}} (R_{\text{bond}}^e - R_{\text{opt}})^2, \quad (3)$$

where the summation runs over all N carbon-carbon bonds in the π -electron hydrocarbon (or its fragment), $\kappa = 257.7 \text{ \AA}^{-2}$ is a normalization constant, while $R_{\text{opt}} = 1.388 \text{ \AA}$ represents the optimal value of the C-C bond length in the HOMA model. Although of energetic provenience [15], HOMA of Eq. 3 is dimensionless and fulfils condition $0 \leq \text{HOMA} \leq 1$ (smaller HOMA indicates lower aromatic character). It was found [17, 18] that definition (3) can be rewritten in a more revealing form:

$$\text{HOMA} = 1 - \text{EN} - \text{GEO} = 1 - \kappa (R_{\text{av}} - R_{\text{opt}})^2 - \frac{\kappa}{N} \sum_{\text{bond}} (R_{\text{bond}}^e - R_{\text{av}})^2, \quad (4)$$

where

$$R_{\text{av}} = \frac{1}{N} \sum_{\text{bond}} R_{\text{bond}}^e \quad (5)$$

is the average C-C bond length in the π -electron hydrocarbon (or its fragment). The components EN and GEO

may be interpreted as some “dearomatization” contributions originating from the bond-length elongation and bond alternation, respectively [18]. Let us note that the EN component is simply a quadratic function of R_{av} , and that the EN and GEO components (and thus HOMA) are sensitive to the rounding errors in the values of R_{bond}^e .

Modular architecture of PAHs

The carbon skeletons of PAHs are finite jigsaw cuts from the honeycomb lattice of graphene. At the perimeter of a PAH, there is a number of methine groups ($>CH$), corresponding to the C atoms with two C neighbors; of all the remaining C atoms, each has three C neighbors. The varied shapes of PAHs determine the corresponding topologies of the C-C bonds, which may be represented by the so-called Hückel graphs (see Ref. [19], p. 28). We shall use such graphs in the figures throughout the paper: the C atoms are graph vertices, and the C-C σ bonds are graph edges (the H atoms and the C-H bonds are absent). In the AugHMO model [4, 5], the topologies of the C-C bonds translate into the bond-length patterns. A practical realization of that model, the HSSH method described in “HSSH calculations,” is used here exactly in the same manner as ab initio methods with full geometry optimization [13]: with no constraints, scaling factors, external corrections, etc. Therefore, the final results (the equilibrium C-C bond lengths) and their analysis are not subject to some preconceived notions.

Our HSSH calculations for PAHs reveal a considerable spread (of ca. 0.1 Å) of their equilibrium C-C bond lengths: from 1.363 Å (bond a in pyrene (15), see Fig. 4) to 1.461 Å (bond m' in perylene (26), see Fig. 7). These values are to be compared with the HSSH result for the C-C bond in graphene [5], equal to 1.424 Å.

A careful and unbiased analysis of all the calculated C-C bond lengths has led us to the following observation: some classes of PAHs (clarenes, rylenees, and a subclass of the K-region PAHs) are well represented by *modular architecture*. In particular, the equilibrium ground-state geometry of a PAH belonging to one of these classes can be assembled from certain standard molecular fragments (modules) of fixed geometries, connected by C-C bonds (linkers) of fixed lengths. The set of modules employed in the present study is depicted, in the form of Hückel graphs, in Fig. 1. These modules are assumed to have “natural” symmetries, independent of the particular molecular environment. More details will be provided in sections devoted to clarenes (“Clarenes”), K-region PAHs (2) (“K-Region PAHs (2): “superbenzene” derivatives”), and rylenees (“Rylenees”).

How are the bond lengths corresponding to the modules and linkers computed? Take the example of bond a in

module **A3**: the length $\overline{R_a^e}$ was calculated by averaging over all the 28 symmetry-unrelated occurrences of this type of bond in the molecules containing the **A3**-module (see Figs. 2, 3, and 5). As a measure of the spread of the actual values of this bond length, we used the absolute value of a maximal difference:

$$\Delta_a = \max |R_a^e - \overline{R_a^e}|, \quad (6)$$

corresponding to the abovementioned set of 28 values of R_a^e .

Clarenes

Eric Clar proposed [11, 12] that the fully benzenoid hydrocarbons are special because of being ideal superpositions of six-electron units—the “Clar sextets.” Thus, it seems quite proper to call this class of PAHs “clarenes.” The family of clarenes taken from Ref. [3] consists of 14 molecules, for convenience split into two subsets shown in Figs. 2 and 3.

Every molecule of clarene contains $6N$ carbon atoms and can be partitioned into N six-carbon-atom benzene-like fragments, hereafter called the A-modules. Each A-module carries six π electrons—this is the abovementioned Clar sextet. Within a given molecule, the A-modules (depicted in Fig. 1) are connected by C-C bonds, hereafter called the AA-linkers. The **An**-module ($n = 2, 3, 4, 5, 6$) uses n linkers to connect with other modules; benzene may be considered a “honorary” **A0**-module, while the phenyl group (usually not appearing in PAHs) is the **A1**-module. Modules **A4** and **A4'** correspond to two different arrangements of four linkers. Moreover, linkers connecting the same pair of modules (e.g., **A3-A5**) may correspond to different linking topologies: see, e.g., linker u in molecule 12, and linkers u' and u'' in molecule 6.

Within a clarene molecule, the A-modules correspond to the so-called “full” (hexagonal) carbon rings, while those hexagonal rings which contain (three) linkers are called “empty” rings [11]. Our HSSH calculations demonstrate that, with sufficient accuracy, each clarene can be additively assembled from standard A-modules, connected *via* some standard AA-linkers. The results in Tables 1 and 2 are quite convincing: the **An**-modules ($n = 2 - 5$) have well-defined geometries (with characteristic bond lengths), and the AA-linkers of a given type have nearly constant lengths. It is seen that within the A-modules the bond lengths are distinctly shorter than those corresponding to the AA-linkers. Clearly, this is an indication that the Clar sextets are, to some degree, *localized* within the A-modules (i.e., the “full” rings).

The **An**-modules ($n = 2 - 5$) necessarily have to be located at the perimeter of a given clarene. The interior

Fig. 1 A-, B-, and C-modules. Hückel graphs, with symbols of symmetry nonequivalent bonds; directions of linkers (with no endpoint C-atoms) are indicated

of the molecule, if sufficiently big, is filled with the **A6**-modules. Quite surprisingly, **A6** cannot be considered a rigid building block: in a less symmetric surrounding, its perfect $6mm$ (C_{6v}) symmetry¹ becomes visibly perturbed. The most important cases of **A6** deformations are presented in Table 3. In molecules **11** and **20** (see Fig. 5), the molecular symmetry group $3m$ (C_{3v}) induces some *bond alternation* in the central **A6**-module; however, this effect is absent in molecule **14** due to a different orientation of the molecular-symmetry elements with respect to the central **A6** hexagon. A similar pattern of deformation is found in molecule **19**, despite its lower symmetry corresponding to the m (C_s) group. It is apparent that bond alternation is the softest mode of deformation of the **A6**-module.

It should be noted that in a PAH molecule all the carbon atoms having three C neighbors are completely inert [20], and thus the **A6**-modules do not contribute to chemical

reactivity—all the chemistry takes place at the perimeter of the molecule, involving the methine groups of the **An**-modules with $n = 2 - 5$.

The inspection of the HOMA values and its components in Table 4 indicates that the **An**-modules retain, to some degree, the aromaticity of the benzene molecule. It is seen that it is EN (and thus R_{av}) which is mostly responsible for diminishing of HOMA with the increase of n (the number of linkers).

On the path from clarenes to graphene

In a series of papers, Tyutyulkov, Müllen, and their collaborators [21–24] posed a question: “is graphene an ultimate large hydrocarbon?” In order to find the answer, they analyzed various aspects: structural (topology), energetic (the energy spectra), and the influence of defects (including these with unpaired spins) and different edge structures. Their findings suggest [21] that the electronic-correlation effects should lead to a nonzero gap in the energy spectrum

¹We use here the symbols corresponding to the planar point groups [5]

Fig. 2 Clarenes (1). Hückel graphs, with symbols of symmetry nonequivalent A-modules and AA-linkers

of PAHs, even in the limit of an infinite molecule (thus, strictly speaking, the metallic limit is not reached).

We are going to use our HSSH results for clarenes to approach the above question from the perspective of molecular geometries: the C-C bond lengths, and also the HOMA values derived from them.

The molecular values of HOMA and its components collected in Table 5 show that the aromatic character of clarenes is lowering with their size. Both the EN and GEO components contribute to this effect. As clarenes grow larger, one finds that (i) the value of R_{av} increases and thus departs from the HOMA value of R_{opt} , and (ii) the HOMO-LUMO gap (as calculated within the HSSH model) diminishes. Even if big clarenes are still far from the graphene limit, one may speculate that the metallic character and aromaticity are in conflict. The HOMA result for graphene suggests its low aromaticity, despite the fact that graphene is the most stable of all π -electron hydrocarbon and carbon molecules (as the molecular enthalpies of formation attest).

The modular architecture of clarenes, uncovered in the course of our HSSH calculations, provides further insights. It is seen that the *perimeter* of a clarene assumes a definite geometric structure corresponding to some arrangement of the **A_n**-modules ($n = 2 - 5$). On the other hand, for very big clarenes, their *interior* is expected to approach the geometric structure of (infinite) graphene. To this end, the equilibrium bond lengths corresponding to bonds *a* and *a'* in the **A6**-module (see Fig. 1), and the equilibrium bond length corresponding to the **A6-A6** linker (*z'*, see molecule **14** in Fig. 3) should approach the HSSH value for graphene (1.424 Å).

For the largest PAH in this study, molecule **14** (96 C atoms), we found $R_a^c = R_a^e = 1.419$ Å, $R_{z'}^c = 1.435$ Å, quite far from the graphene limit. However, when one averages over three bond lengths adjacent to any C atom in any **A6**-module, the result is very close to 1.424 Å. Our tentative conclusion from the above observation is as follows: even in relatively small clarenes, their interiors “prepare” for becoming graphene-like.

Fig. 3 Clarenes (2). Hückel graphs, with symbols of symmetry nonequivalent A-modules and AA-linkers

Table 1 A-modules (up to A5). HSSH equilibrium C-C bond lengths (in Å)

	Module										
	Benz.	A2		A3		A4		A4'		A5	
Bond	R^e	$\overline{R^e}$	Δ	$\overline{R^e}$	Δ	$\overline{R^e}$	Δ	$\overline{R^e}$	Δ	$\overline{R^e}$	Δ
a	1.397	1.406	0.002	1.397	0.003	1.388	0.002	1.402	0.000	1.403	0.000
b	—	1.389	0.002	1.404	0.004	1.412	0.003	1.416	0.000	1.417	0.001
c	—	1.409	0.002	1.415	0.002	1.410	0.001	—	—	1.416	0.002
d	—	1.409	0.001	—	—	1.420	0.002	—	—	—	—

Table 2 AA-linkers. HSSH equilibrium C-C bond lengths (in Å)

Linker	$\overline{R^c}$	Δ	Linker	$\overline{R^c}$	Δ
m (A2-A2)	1.456	0.001	w (A4-A4)	1.447	—
n (A2-A3)	1.455	0.001	w' (A4-A4)	1.442	0.001
o (A2-A4)	1.452	0.002	x (A4-A6)	1.439	—
p (A2-A4')	1.456	0.000			
q (A2-A5)	1.454	0.001			
r (A3-A3)	1.455	0.001	y (A5-A5)	1.438	—
r' (A3-A3)	1.444	0.000	y' (A5-A5)	1.447	—
s (A3-A4)	1.452	0.001	z (A5-A6)	1.437	0.001
s' (A3-A4)	1.443	0.001	z' (A5-A6)	1.436	0.000
t (A3-A4')	1.456	—			
u (A3-A5)	1.453	0.000			
u' (A3-A5)	1.442	—			
u'' (A3-A5)	1.443	—			
v (A3-A6)	1.440	0.003	z'' (A6-A6)	1.436	0.002

We thus propose, with some exaggeration, that a big clarene molecule has a “hard shell” made of some **An**-modules ($n = 2 - 5$), protecting an interior consisting of “softer” **A6**-modules, which, with the growing size of the molecule, lose their identities and, finally, melt into a homogenous honeycomb lattice of graphene. In the language of the Clar sextet concept [11], one may say that, on the path to the graphene limit, the “full” and “empty” rings in the clarene interior become indistinguishable. There is a consonant observation coming from the theoretical studies of (topological) ring currents in clarenes by Dickens and Mallion [25, 26]. In Ref. [26], the authors stated that “...as the number of rings in the structure increases, the ... sharp distinction between ‘full’ and ‘empty’ rings begins to break down, as far as ring currents are concerned.”

While experimental and theoretical studies of graphene focus on its interior, it should be remembered that every real graphene specimen has a *boundary*, involving dangling bonds or some substituted atoms (hydrogens, for example). In particular, such a boundary may have a form of some regular perimeter consisting of the methine groups, as in the case of clarenes or K-region PAHs of “**K-Region PAHs**.”

Table 3 A6-modules, HSSH equilibrium C-C bond lengths (in Å)

Molecule	R_a^c (Å)	R_a^c (Å)	$\frac{1}{2} (R_a^c + R_a^c)$	$R_a^c - R_a^c$
11	1.420	1.414	1.417	0.006
19	1.421	1.414	1.417	0.007
20	1.424	1.413	1.419	0.010

In molecules **11**, **19**, and **20**, a pattern of *alternating* bonds (a' a_3) is seen. Full averaging over the remaining molecules containing **A6**-modules gives $R_a^c = R_a^c = 1.417$, $\Delta = 0.003$

Table 4 A-Modules. R_{av} , EN, GEO, and HOMA values

Module	R_{av} (Å)	EN	GEO	HOMA
Benzene	1.397	0.021	0.000	0.979
A2	1.402	0.051	0.021	0.928
A3	1.405	0.076	0.013	0.911
A4	1.409	0.110	0.043	0.847
A4'	1.406	0.086	0.012	0.902
A5	1.412	0.150	0.011	0.839
A6	1.417	0.217	0.000	0.783

Therefore, studies of giant PAHs are of utmost relevance to the science of graphene.

K-Region PAHs

Riegel and Müllen [3] coined the name “K-region PAH” to denote the PAH which can be derived from a clarene having one or more “bays” within its perimeter. The “bay” consists of four C atoms arranged as in the s-cis butadiene molecule (at the “mouth” of the bay there are two methine groups, causing some steric tension). Examples of such bays are seen in clarenes **1** - **14**. The K-region emerges when the mouth of the bay is closed with a two-carbon insertion of the formula $-\text{CH}-\text{CH}-$; we shall call this insertion the “f-handle,” alluding to the bond f in phenanthrene (**21**); see Fig. 6. Obviously, the new molecule does not fit the clarene paradigm, and the K-region (corresponding to the f-handle) introduces some olefinic character to the molecule (for a

Table 5 Clarenes. Molecular values of R_{av} (in Å), EN, GEO, and HOMA

Molecule	R_{av} (Å)	EN	GEO	HOMA
1	1.409	0.119	0.106	0.775
2	1.412	0.147	0.105	0.748
3	1.412	0.143	0.115	0.742
4	1.413	0.164	0.103	0.733
5	1.414	0.175	0.099	0.727
6	1.414	0.176	0.102	0.722
7	1.414	0.175	0.100	0.725
8	1.413	0.158	0.112	0.730
9	1.416	0.199	0.090	0.711
10	1.417	0.219	0.080	0.701
11	1.416	0.208	0.086	0.706
12	1.417	0.222	0.082	0.696
13	1.417	0.214	0.086	0.700
14	1.418	0.238	0.073	0.689
Graphene	1.424	0.334	0.000	0.666

Fig. 4 K-region PAHs (1): pyrene, coronene, and ovalene. Hückel graphs, with symbols of symmetry nonequivalent bonds

detailed discussion on the chemical and spectral properties of the K-region PAHs, see Ref. [3]).

The K-region PAHs of Ref. [3] may be conveniently divided into two groups: one containing pyrene and coronene (and ovalene, added here), and second composed of molecules which may be derived from “superbenzene” (9), see Fig. 3.

K-Region PAHs (1): pyrene, coronene, and ovalene

Pyrene, coronene, and ovalene, depicted in Fig. 4, are well-known PAHs. Their C-C bond lengths are listed in Table 6: a closer inspection of these data indicates that no obvious transferable fragments (modules) can be identified. This is a striking contrast with the clarenes of the previous section. One can identify the “olefinic” f-handles as the a-bonds in all three molecules, and the f-bond in ovalene.

The molecular values of HOMA and its components are collected in Table 7. The general trends are similar to those for clarenes (see Table 5), with the GEO contributions being slightly larger. Let us note that HOMA for coronene is much lower than that for benzene, and not very different from that of graphene (see Table 4).

Table 6 Pyrene, coronene, and ovalene. HSSH equilibrium C-C bond lengths (in Å)

Bond	Pyrene	Coronene	Ovalene
a	1.363	1.374	1.382
b	1.444	1.429	1.419
c	1.418	1.411	1.412
d	1.432	1.430	1.425
e	1.406	—	1.438
f	1.397	—	1.367
g	—	—	1.440
h	—	—	1.405
i	—	—	1.422
j	—	—	1.432
k	—	—	1.417
l	—	—	1.438

K-Region PAHs (2): “superbenzene” derivatives

The second group of the K-region PAHs of Ref. [3] can be derived by inserting the f-handles into the bay regions of clarene 9, called [27] “superbenzene” (according to that nomenclature, clarene 12 is “supernaphthalene,” and clarene 14 is “superphenalene”). One insertion gives molecule 17, two (different) insertions—molecules 18 and 19, and three insertions—molecule 20 (see Fig. 5).

In molecules 17 - 20 one may identify the A3- and A6-modules corresponding to clarene 9, with practically “frozen” structures (see Table 2) (also linkers r and v are unchanged). But a new module can be identified: this is the C4-module (see Fig. 1), involving fourteen C atoms (and fourteen π electrons), which resembles the phenanthrene molecule (21), a “honorary” C0-module. As seen in Table 8, the (averaged) equilibrium C-C bond lengths of the C4-module are pretty well transferable, and so are the corresponding linkers (linker k being here a bit of exception).

The values of HOMA and its components for phenanthrene and the C4-module are collected in Table 9. The molecular values of HOMA and its components presented in Table 10 show that each insertion of the f-handle into clarene lowers its HOMA, and thus diminishes its aromatic character.

Phenacenes

The first five members of the family of phenacenes are shown in Fig. 6. With the growing size, they approach

Table 7 Pyrene, coronene, and ovalene. Molecular values of R_{av} , EN, GEO, and HOMA

Molecule	R_{av} (Å)	EN	GEO	HOMA
Pyrene	1.411	0.141	0.142	0.717
Coronene	1.414	0.179	0.118	0.703
Ovalene	1.416	0.203	0.118	0.679

Fig. 5 K-Region PAHs (2). Hückel graphs, with symbols of symmetry nonequivalent A- and C-modules, and linkers

a limit of a π -electron polymer (not the 2D structure of graphene). The bond lengths of phenacenes are presented in Table 11; here also we see no clue to identify transferable modules, although some regularities in bond lengths are clearly visible.

Our HSSH equilibrium C-C bond lengths in phenacenes may be compared with those calculated by Firouzi and

Zahedi [10] by means of the ab initio B3LYP/6-31G(d) approach. The agreement is satisfactory, with the exception of the “bridge bonds” (of the symbols d, h, and j), for which the HSSH values are smaller by ca. 0.02 Å (similar trends are found also in acenes, see “Acenes”).

The molecular values of HOMA and its components for phenacenes are presented in Table 12. It seems that these quantities converge to some limiting values in the case of the polyphenacene polymer.

Table 8 C-Modules and AC- and CC-linkers. HSSH equilibrium C-C bond lengths (in Å)

Bond	Phenanth.	C4		Linker		
	R^e	$\overline{R^e}$	Δ		$\overline{R^e}$	Δ
a	1.411	1.419	0.003	j (A3-C4)	1.449	0.001
b	1.385	1.381	0.002	k (A6-C4)	1.436	0.005
b'	1.385	1.408	0.001	l (C4-C4)	1.442	0.001
c	1.416	1.421	0.003			
c'	1.414	1.425	0.001			
d	1.410	1.412	0.001			
e	1.442	1.434	0.001			
e'	1.446	1.432	0.001			
f	1.365	1.370	0.001			

Rylenes

In Fig. 7, we present the first four members of the family of rylenes. As in the case of the family of phenacenes,

Table 9 C-modules. R_{av} , EN, GEO, and HOMA values

Module	R_{av} (Å)	EN	GEO	HOMA
Phenanth.	1.408	0.107	0.129	0.764
C4	1.413	0.158	0.093	0.749

Table 10 “Superbenzene” (**9**) and K-region PAHs (**2**). Molecular values of R_{av} , EN, GEO, and HOMA

Molecule	R_{av} (Å)	EN	GEO	HOMA
9	1.416	0.199	0.090	0.711
17	1.416	0.206	0.091	0.703
18	1.417	0.213	0.091	0.696
19	1.417	0.213	0.092	0.695
20	1.418	0.225	0.113	0.662

Table 11 Phenacenes. HSSH equilibrium C-C bond lengths (in Å)

Bond	Molecule				
	21	22	23	24	25
a	1.411	1.415	1.413	1.414	1.414
b	1.385	1.382	1.383	1.382	1.383
b'	1.385	1.382	1.383	1.383	1.383
c	1.416	1.419	1.418	1.418	1.418
c'	1.414	1.418	1.416	1.417	1.417
d	1.410	1.411	1.411	1.411	1.411
e	1.442	1.435	1.438	1.437	1.437
e'	1.446	1.439	1.442	1.441	1.441
f	1.365	1.370	1.368	1.369	1.368
f'	—	—	1.376	1.374	1.375
g	—	1.433	1.436	1.435	1.435
g'	—	—	1.426	1.428	1.427
h	—	1.400	1.404	1.403	1.403
i	—	—	1.431	1.434	1.433
i'	—	—	—	1.429	1.428
j	—	—	—	1.407	1.406
k	—	—	—	—	1.431
k'	—	—	—	—	1.437
l	—	—	—	—	1.372

Fig. 6 Phenacenes. Hückel graphs, with symbols of symmetry nonequivalent bonds **Table 12** Phenacenes. Molecular values of R_{av} , EN, GEO, and HOMA

Molecule	R_{av} (Å)	EN	GEO	HOMA
21	1.408	0.107	0.129	0.764
22	1.410	0.124	0.133	0.743
23	1.411	0.135	0.136	0.729
24	1.411	0.142	0.136	0.722
25	1.412	0.147	0.137	0.716

with the growing size rylenes approach a limit of a π -electron polymer. However, in difference to phenacenes, rylenes display modular architecture, based on the ten C atom, ten π -electron **B2**- and **B4**-modules (see Fig. 1). They may be considered as analogs of naphthalene (see Fig. 8), a “honorary” **B0**-module. The bond lengths for the **B2**- and **B4**-modules, together with the lengths of the corresponding BB-linkers, are presented in Table 13.

The values of HOMA and its components for the B-modules are presented in Table 14, and the molecular values of these parameters calculated for rylenes appear in Table 15.

Acenes

The first six members of the family of acenes are shown in Fig. 8. Acenes are similar to phenacenes of “Phenacenes.” They also, with the growing size, approach a limit of a π -electron polymer. The bond lengths of acenes are presented in Table 16; here also we see no clue to identify transferable modules despite some regularities in bond lengths.

We compared our HSSH equilibrium C-C bond lengths in acenes with those calculated by Firouzi and Zahedi [10] by means of the ab initio B3LYP/6-31G(d) approach. As in the

Fig. 7 Rylenes. Hückel graphs, with symbols of symmetry nonequivalent B-modules and BB-linkers

Fig. 8 Acenes. Hückel graphs, with symbols of symmetry nonequivalent bonds

Table 13 B-modules and BB-linkers. HSSH equilibrium C-C bond lengths (in Å)

Naphth.		B2		B4		Linker	$\overline{R^c}$	Δ
Bond	R^c	$\overline{R^c}$	Δ	$\overline{R^c}$	Δ			
a	1.421	1.414	0.001	1.405	0.002	m' (B2-B2)	1.461	—
b	1.377	1.381	0.001	—	—	m (B2-B4)	1.458	0.001
b'	—	1.390	0.002	1.395	0.002	n (B4-B4)	1.454	0.001
c	1.425	1.424	0.000	—	—			
c'	—	1.427	0.000	1.426	0.000			
d	1.414	1.415	0.000	1.417	0.001			

Table 14 B-modules. R_{av} , EN, GEO, and HOMA values

Module	R_{av} (Å)	EN	GEO	HOMA
Naphth.	1.406	0.081	0.125	0.794
B2	1.408	0.102	0.081	0.817
B4	1.410	0.126	0.045	0.829

Table 15 Rylenes. Molecular values of R_{av} , EN, GEO, and HOMA

Molecule	R_{av} (Å)	EN	GEO	HOMA
26	1.408	0.107	0.129	0.764
27	1.410	0.124	0.133	0.743
28	1.411	0.135	0.136	0.729
29	1.411	0.142	0.136	0.722

Table 16 Acenes. HSSH equilibrium C-C bond lengths (in Å). For benzene $R_a^c = 1.397$ Å

Bond	Molecule					
	Naphth.	30	31	32	33	34
a	1.421	1.431	1.435	1.438	1.439	1.440
b	1.377	1.370	1.367	1.366	1.365	1.364
c	1.425	1.435	1.440	1.442	1.443	1.444
d	1.414	1.426	1.433	1.437	1.439	1.441
e	—	1.404	1.395	1.390	1.388	1.387
f	—	—	1.416	1.422	1.425	1.427
g	—	—	1.432	1.437	1.439	1.441
h	—	—	—	1.406	1.401	1.398
i	—	—	—	—	1.413	1.416
j	—	—	—	—	1.439	1.441
k	—	—	—	—	—	1.408

Table 17 Acenes. Molecular values of R_{av} , EN, GEO, and HOMA

Molecule	R_{av} (Å)	EN	GEO	HOMA
Benzene	1.397	0.021	0.000	0.979
Naphth.	1.406	0.081	0.125	0.794
30	1.409	0.118	0.168	0.714
31	1.411	0.141	0.181	0.678
32	1.413	0.156	0.183	0.661
33	1.413	0.166	0.179	0.655
34	1.414	0.174	0.173	0.653

case of the phenacenes, see “[Phenacenes](#),” the agreement is satisfactory, with the exception of the “bridge bonds” (of the symbols d, g, and j), for which the HSSH values are smaller by ca. 0.02 Å.

The molecular values of HOMA and its components for acenes are presented in Table 17. As seen, for long acenes the HOMA values drop below the value for graphene, equal to 0.666 (a high chemical reactivity of long acenes is to be noted).

Concluding remarks

Our HSSH study of the equilibrium C-C bond lengths corresponding to the PAHs considered in the review paper by Riegel and Müllen [3] reveals that some classes of PAHs (clarenes of “[Clarenes](#),” K-region PAHs of “[K-Region PAHs](#),” and rylenes of “[Rylenes](#)”) can be described by employing the modular architecture concept. The classes of clarenes and K-region PAHs may be expanded to accommodate PAHs of arbitrary sizes, thus, in a sense, approaching a limit of the graphene lattice contained within a boundary. That boundary, or a perimeter, is built of some **An**-modules ($n = 2, 3, 4, 5$), eventually plus the **C4**-modules in the case of the K-region PAHs. The interior, corresponding to the “bulk” graphene, is made solely of the **A6**-modules.

Our present HSSH study of PAHs geometries (see our analysis in “[On the path from clarenes to graphene](#)”) provides a suggestive indication that the interiors of PAHs, with their growing sizes, converge to the infinite model of graphene, with indistinguishable “full” and “empty” hexagonal rings. In a future paper, we are going to pursue this problem by performing HSSH calculations for very big clarenes and K-region PAHs (with hundreds to thousands carbon atoms).

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Availability of data and materials No additional data is of relevance.

Declarations

Consent for publication The co-author (J. H. Kwapisz) is aware and approve of the submission.

Conflict of interest The authors declare no competing interests.

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