MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **82** (2019) 139-162

ISSN 0340 - 6253

Coding Canonical Clar Structures of Polycyclic Benzenoid Hydrocarbons

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(Received July 1, 2018)

Abstract

For polycyclic benzenoid hydrocarbons, on the basis of their ring bond orders, it was possible to devise a method for evaluate quantitatively the Clar formulas, arriving at a "canonical Clar structure". For encoding such structures one must address each ring in the benzenoid. Earlier, such aa code had been devised for benzenoids, but it was limited to cata-condensed benzenoids. Now a new code is proposed, which works for both catafusenes and perifusenes, and it is illustrated by 42 polycyclic benzenoid hydrocarbons having between 2 and 13 rings. A set of six rules (or priority requirements) determines the orientation of the Car structure that is then scanned, one ring at a time, from the uppermost left to the lowermost right ring. Jumping from one acenic row to the next is denoted by the operator j/. Scanning is performed from along acenic rows from left to right, but if for a new row one has to move in the inverse direction, the operator i: serves for this purpose; A Clar sextet ring is denoted by letter o, and any other ring by letter x. A void one-ring space is denoted by letter v. Letters i and v are have to be repeated for each ring position in a row. Codes are enclosed in square brackets. For instance, benz[a]anthracene has a canonical Clar structure that is encoded as [oj/xox].

1 Introduction

In a recent effort to characterize local aromaticity in benzenoid hydrocarbons on purely structural basis, [1] we revisited Clar's Aromatic Sextet Theory [2] and we were interested to see how can one arrive at *unique* Clar structures for *all* benzenoid hydrocarbons. Clar's "fully *benzenoid hydrocarbons*" have either "aromatic sextet rings or "empty" rings, and have a single Clar structure. Such benzenoids have also been called "claromatics" [3].

The smallest illustration of a fully benzenoid hydrocarbon with more than one benzenoid ring is triphenylene, in which to three nonadjacent CC bonds of the central “empty ring” are attached three aromatic sextet rings. However, there are additional polycyclic benzenoid hydrocarbons having only a single Clar structure, which in addition to aromatic sextet rings may have rings with a single C=C bond. (The reader is reminded that a Clar formula has the maximum number of sextet circles, and that no sextet rings may be adjacent). The smallest illustration is provided by phenanthrene, in which two aromatic sextet rings are attached to the central ring having a single C=C bond. For more general benzenoid hydrocarbons however, one can write *several* Clar formulas as is illustrated in Figs. 1 and 2 on naphthalene, anthracene, tetracene, benzanthracene, and chrysene.

Clar was interested to have a single structural formula for all benzenoids and he came to an ingenious idea to replace the set of individual Clar structures by a single structure to which an arrow was added to indicate all the adjacent rings, which can be a site of aromatic sextets. The single Clar structures for such systems are illustrated at the bottom of Fig. 1 for the five mentioned benzenoids having “migrating” rings, as Clar referred to the adjacent sextet rings. In this article, the authors consider an alternative to the same problem: can one choose a single Clar structures among several possible alternatives to be selected as the canonical structure? With the recent introduction of numerical Clar structures [4, 5] a new quantitative tool became available, and this problem appears to be less formidable than it looked when considering qualitative Clar structures.

2 Ring bond orders (RBO)

The new tool is the notion of RBO [6], which is related to an old tool, the Pauling CC bond orders [7], which keep the count for each CC bond in all Kekulé valence structures of a conjugated hydrocarbon the occurrence of that bond as C=C bond. The novelty was that instead of considering individual CC bonds, this time one considers *all six CC bonds* forming individual benzenoid rings and one calculates their average. Clearly, in the case of benzene, for the two Kekulé valence structures, each CC bond appears alternatively q as C=C, thus the total is six C=C bonds, giving RBO = 6/2 = 3.000.

In Table 1 we have listed all RBO values for 42 benzenoid hydrocarbons considered in this article. As one can see from Table 1 all RBO values are less than 3.000. Rings with the highest RBO are, locally speaking, more aromatic that the remaining rings in the same molecule and more similar to benzene rings. An equally important result of the outlined structural approach to characterization of aromaticity was to see that all adjacent acenic migrating sextets have equal amounts of C=C double bond character. When trying to partition the results of molecular orbital calculations to individual rings in polycyclic conjugated benzenoids, this particular result disagreed with simple MO calculations based on Hückel molecular orbitals HMO [8] and with results of of Polansky and Derflinger [9], or later more advance MO calculations [10]. In such calculations terminal migrating rings have been found to be more aromatic that the centrally located migrating sextets. This is in contrast to more recent calculation of Schleyer and collaborators using the approach based on NICS (Nucleus Independent Chemical Shifs) [11]. For more on use of RBO to characterization of the degree of aromaticity see the recent review of one of the present authors [12].

The concept of RBO has shown that the numerical Clar structures offer good quantitative characterization of Clar structures and illustrate the fact at the set of Kekulé valence structures has the necessary structural information for construction of Clar formulas for any benzenoid hydrocarbon. In a way it is amazing to learn that Clar had so deep an insight into the nature of benzenoid hydrocarbons that he was able to propose novel structural formulas for benzenoids, and that after 45 years [13] were found to be “hidden” in the set of Kekulé valence structures of benzenoid hydrocarbons, from which Clar’s formulas can be fully reconstructed [6].

3 Average variation of ring bond orders

In a recent extension of application of RBO to characterization of local aromaticity of benzenoid hydrocarbons the present authors realized, in view that all migrating sextets have the same RBO, that an additional structural feature ought to be considered that will differentiate among adjacent migrating sextets. So attention was given to the fact that rings in most benzenoid hydrocarbons, including migrating rings, show minor variations in their CC bonds lengths, while in benzene all CC bonds are equal. For example, if one looks at a terminal ring of anthracene in its four Kekulé valence structures (Fig. 2, last row of structures), one can find that in two of them, CC bonds appear as C=C three times, and in the other two only twice.

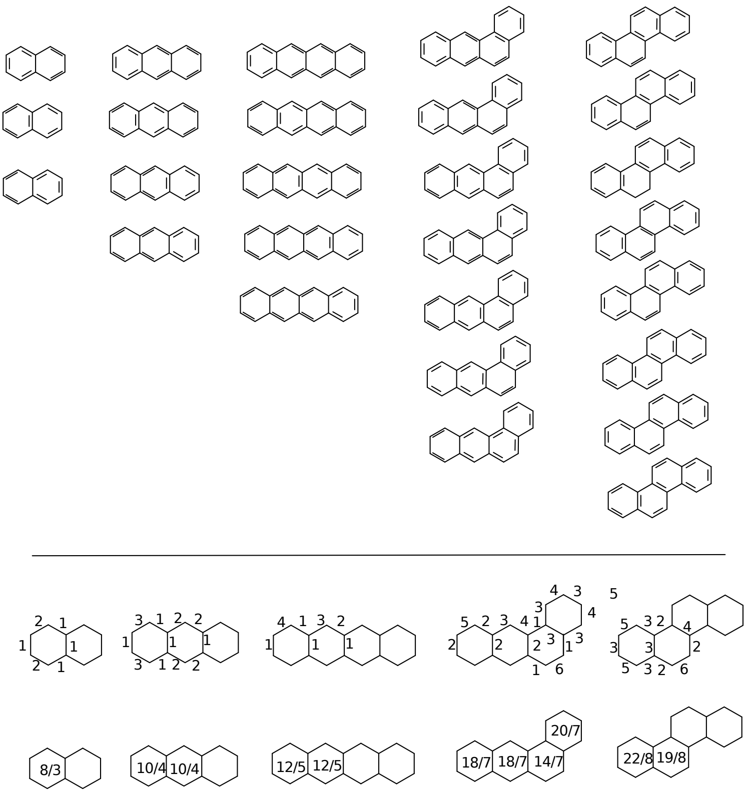


Figure 1. Upper rows, Kekulé valence structures for five smaller benzenoid hydrocarbons medium row, the count for each CC bond how often it appears as a C=C bond in all Kekulé structures; lowest row, ring bond orders.

This give the total count of 10 C=C bonds in the four Kekulé valence structures of anthracene, or on average 10/4 = 2.500. The same is the case for the central ring, giving again for total 10/4 = 2.500. In contrast (Fig. 2, row of structures under the horizontal line), the variations of CC bond orders are lower in the central ring. To evaluate this variation, one adds for each ring the differences in RBO (absolute integers) between each pair of adjacent bonds in a ring, and one normalizes it by dividing it by 6K, number of ring bonds (6) times number of Kekulé valence structures (K). Thus, for the central ring of anthracene the variations in bond ordered amounts to 4, while variations in the terminal ring are twice as big, totaling to 8, which after normalized gives the values shown in Table 1 (rings lower script letters), which are 0.167 and 0.333, for the central and the terminal rings, clearly, suggesting that he central ring is more similar to the benzene. So of the four Clar's structures of anthracene in Fig. 1 we selected the second Clar structure as canonical (which is from this point of view equal to the third structure, which is symmetry related. This is analogous to naphthalene, where as canonical structure one can take the first or the second structures, which are also symmetry related).

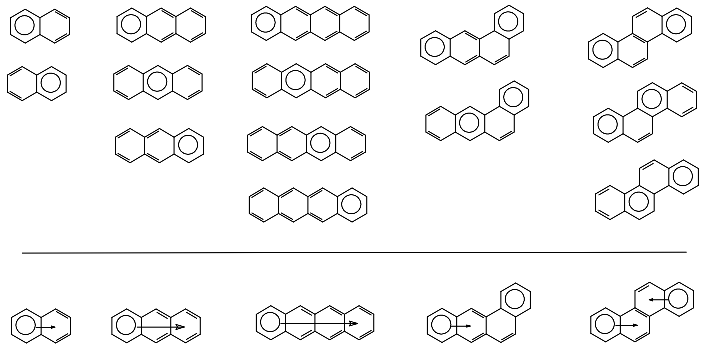


Figure 2. The five benzenoids from Fig. 1 with Clar structures, and their representation as single Clar formulas with arrows indicating migrating sextets.

We decided in this article to use the outlined characterization of local aromaticity, based on two parameters (x, y), *x* being the local RBO and *y* being the average deviations in CC bond orders for the neighboring CC bonds in each benzenoid ring, to characterize individual benzenoid rings in aromatics benzenoid hydrocarbons. We should add here that according to the Generalized Hückel 4*n*+2 Rule of Aromaticity [12] polycyclic benzenoid hydrocarbons having only conjugated circuits of size 4n+2 are aromatic. Gutman and Cyvin [14] provided the proof that benzenoid hydrocarbons can have only conjugated circuits of size 4*n*+2, hence are all aromatic. This result of the Generalized Hückel 4*n*+2 Rule of Aromaticity, which applies to hundreds of existing benzenoid hydrocarbons can be contrasted to the famous Hückel 4n+2 Rule of Aromaticity [15], which applies to less that dozen compounds, though including also non benzenoid monocyclic systems, like [18]annulene, and several heterocyclic systems.

Going back to our characterization of benzenoid rings with (x, y) coordinates, which allowed the construction of a two-dimensional local aromaticity map [1], one can state that this approach by discriminating among the migrating rings, goes beyond the Clar model. It allows one to choose one of the migrating sextet formulas (like those of Fig. 2) to be selected as Clar canonical structure, giving priority to the Clar formula with the sextet ring of the greatest similarity to the benzene ring.

In Figs. 3–6 we show the so selected canonical Clar structures for the 42 benzenoid considered in this article. In Fig. 3 are the canonical Clar structures for 9 benzenoids **1**–**9** having less that five benzenoid rings. In Fig. 4 are the canonical Clar structures for 14 benzenoids **10**–**23** having five benzenoid rings. In Fig. 4 are the canonical Clar structures for 8 benzenoids **24**–**31** having six benzenoid rings. Finally, in Fig. 6 are the canonical Clar structures for 11 benzenoids **32**–**42** having more than six benzenoid rings.

In the accompanying Tables 1–4 one can compare the average RBO values for all rings (highest values in row ABC…). The value of abc… give the average CC bond deviations in rings, which determines for canonical Clar structure where the Clar sextet circle is placed, thus unjustifying the selection of Clar sextet rings in the canonical formulas.

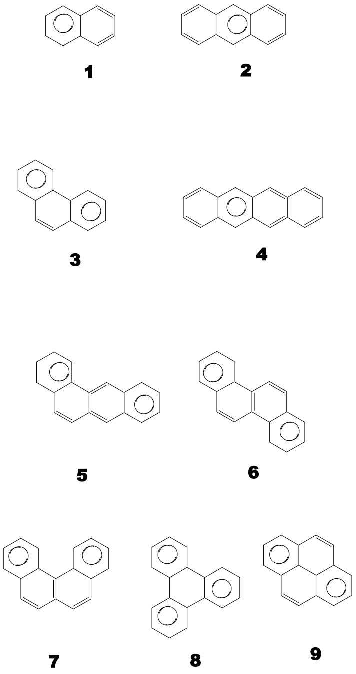
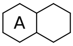
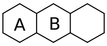
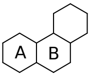
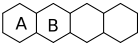
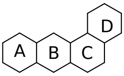
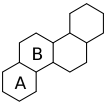
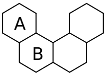
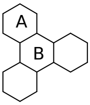
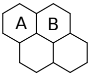
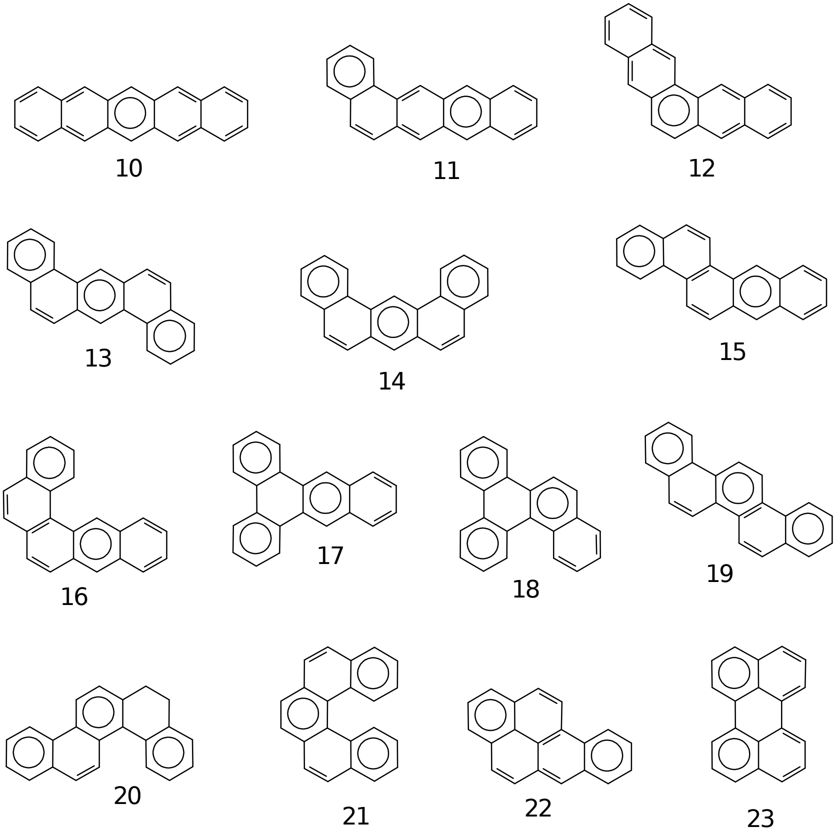


Figure 3. Canonical Clar structures of polycyclic benzenoid hydrocarbons with 2, 3, and 4 benzenoid rings.

Table 1. Benzenoids 1–9.

1		A =2.667 a =0.222
2		A =2.500 B =2.500 a =0.333 b =0.167
3		A =2.800 B =2.200 a =0.133 b =0.333
4		A =2.400 B =2.400 a =0.400 b =0.333
5		A =2.571 B =2.571 C =2.000 D =2.857 a =0.286 b =0.238 C =0.381 D =0.095
6		A =2.750 B =2.375 a =0.167 b =0.333
7		A =2.750 B =2.375 a =0.167 b =0.333
8		A =2.750 B =2.375 a =0.167 b =0.333
9		A =2.889 B =2.167 a =0.074 b =0.333



10 11 12

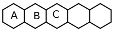
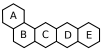
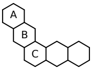
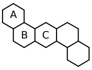
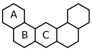
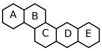
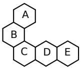
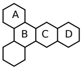
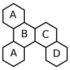
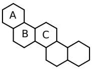
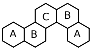
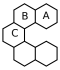
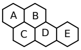
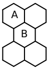
13 14 15

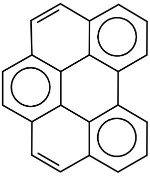
16 17 18 19

20 21 22 23

Figure 4. Canonical structures of PBHs **10–23** having five benzenoid rings.

Table 2. part 1 Benzenoids 10–23.

10		A =2.333 B =2.333 C =2.333 a =0.444 b =0.333 c =0.222
11		A =2.889 B =1.889 C =2.444 D =2.444 E =2.444 a = 0.074 b =0.407 c = 0.296 d =0.222 E =0.370
12		A =2.600 B =2.600 C =1.800 a =0.433 b =0.433 c =0.300
13		A =2.833 B =2.308 C =2.538 a =0.111 b =0.361 c =0.111
14		A =2.833 B =2.308 C =2.538 a =0.111 b =0.361 c =0.111
15		A =2.727 B =2.455 C =2.182 D =2.545 E =2.545 a =0.182 b =0.273 c =0.364 d =0.182 e =0.303
16		A =2.727 B =2.455 C =2.182 D =2.545 E =2.545 a =0.182 b =0.273 c =0.364 d =0.182 e =0.303
17		A =2.923 B =1.486 C =2.615 D =2.615 a =0.051 b =0.205 c =0.205 d =0.256
18		A =2.857 B =1.571 C =2.500 D =2.714 a = 0.095 b =0.333 c = 0.262 d =0.190
19		A =2.769 B =1.750 C =2.667 a =0.154 b =0.308 c =0.231
20		A =2.769 B =2.308 C =2.538 a =0.154 b =0.308 c =0.231
21		A =2.833 B =2.308 C =2.538 a =0.154 b =0.361 c =0.111
22		A =2.667 B =2.333 C =2.000 D =2.333 E =2.667 a =0.111 b =0.259 c =0.333 d =0.185 e =0.222
23		A =2.667 B =1.333 a =0.222 b =0.222



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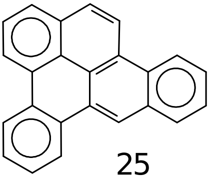

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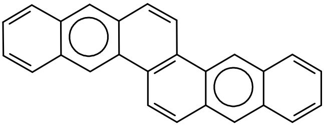

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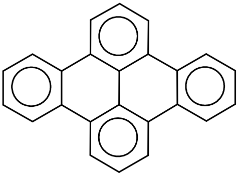

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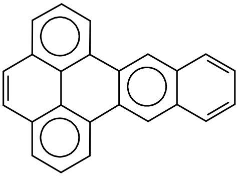

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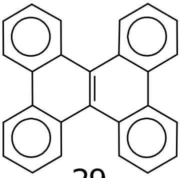

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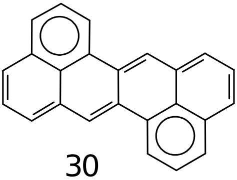

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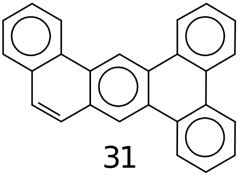
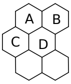
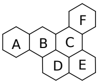
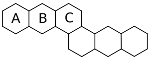
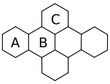
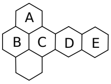
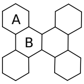
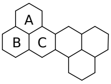
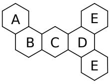


31

Figure 5. Canonical structures of PBHs **24–31** having six benzenoid rings.

Table 3. Benzenoids 24–31.

24		A =2.286 B =2.714 C =2.500 D =1.643 a =0.286 b =0.119 c =0.167 d =0.119
25		A =2.706 B =2.353 C =1.471 D =2.353 E =2.706 F =2.941 a =0.196 b =0.235 c =0.235 d =0.275 e =0.137 f =0.039
26		A =2.286 B =2.714 C =2.500 D =1.643 a =0.286 b =0.119 c =0.167 d =0.119
27		A =2.900 B =1.650 C =2.800 a =0.067 b =0.283 c =0.033
28		A =2.750 B =2.188 C =2.438 D =6.625 E =2.625 a =0.104 b =0.313 c =0.229 d =0.208 e =0.250
29		A =2.286 B =2.714 a =0.286 b =0.119
30		A =2.900 B =1.650 C =2.800 a =0.067 b =0.283 c =0.033
31		A =2.818 B =2.136 C =2.727 D =1.545 E =2.909 a =0.121 b =0.348 c =0.121 d =0.333 e =0.061

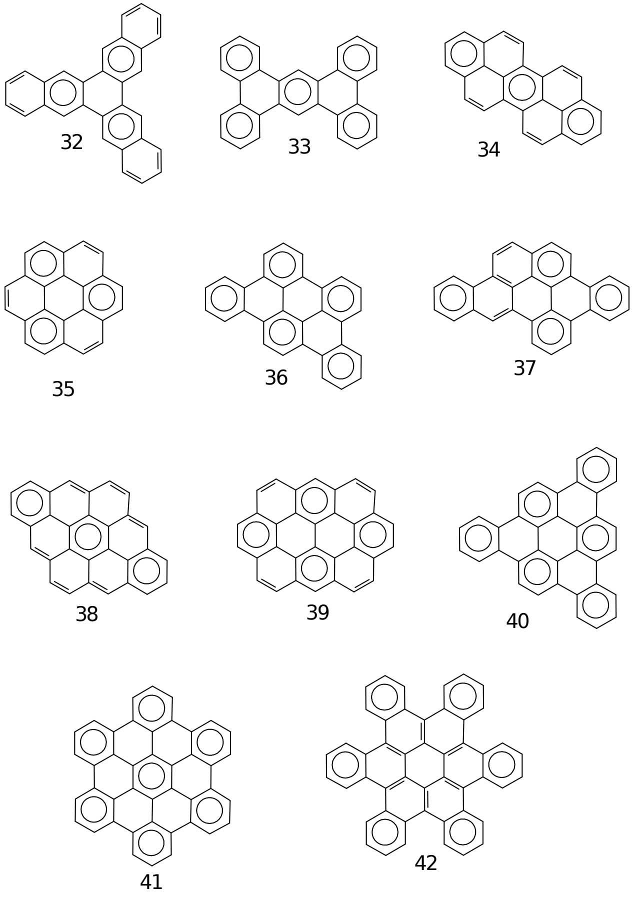
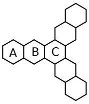
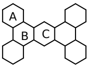
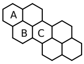
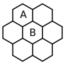
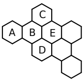
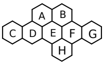
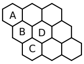
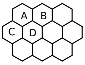
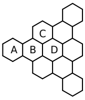
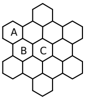
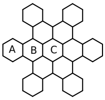


Figure 6. Canonical structures of PBHs **32**–**42** having six benzenoid rings.

Table 4 Benzenoids 32–42.

32		A = 2.643 B = 2.643 C = 1.071 a = 0.238 b = 0.214 c = 0.286
33		A = 2.900 B = 1.600 C = 2.800 a = 0.067 b = 0.333 c = 0.067
34		A = 2.667 B = 2.167 C = 2.333 a = 0.057 b = 0.278 c = 0.111
35		A = 2.400 B = 1.800 a = 0.020 b = 0.000
36		A = 2.889 B = 2.800 C = 1.711 D = 1.644 E = 2.689 a = 0.074 b = 0.044 c = 0.289 d = 0.170 e = 0.067
37		A = 2.410 B = 2.692 C = 2.718 D = 2.667 a = 0.513 b = 0.412 c = 0.188 d = 0.291 E = 1.359 F = 1.795 G = 2.872 H = 2.821 e = 0.179 f = 0.308 g = 0.085 h = 0.068
38		A = 2.600 B = 2.150 C = 1.900 D = 2.000 a = 0.067 b = 0.283 c = 0.467 d = 0.217
39		A = 2.200 B = 2.400 C = 2.500 D = 1.900 a = 0.267 b = 0.100 c = 0.100 d = 0.100
40		A = 2.865 B = 1.788 C = 2.663 D = 2.654 a = 0.090 b = 0.287 c = 0.086 d = 0.154
41		A = 2.800 B = 1.300 C = 2.400 a = 0.033 b = 0.200 c = 0.000
42		A = 2.825 B = 2.238 C = 1.050 a = 0.278 b = 0.098 c = 0.000

4 Coding canonical Clar structures of polycyclic benzenoid hydrocarbons

We continue now with discussion of the coding for the proposed canonical Clar structures. In a paper on local aromaticity [1], we have shown that Clar structures of polycyclic benzenoid hydrocarbons (PBHs) can be evaluated quantitatively for the partial aromaticity of each ring, and that a canonical Clar structure can be devised for each PBH. In the present communication, we describe a general code for canonical Clar structures. For the first time, each ring is individually mentioned in the code for a large variety of PBHs..

Dualist of PBHs are a special type of graphs consisting of vertices corresponding to centers of each ring, and of edges connecting the vertices in adjacent rings; thus the hexagonal (honeycomb) net has a dualist which is triangular net. Unlike normal graphs, dualists have angles that do matter. Cata-condensed PBHs (catafusenes) have dualists devoid of circuits, whereas perifusenes have dualists with triangles, and corona-fusenes that have larger rings that are not peripheries of triangle aggregates.

Although structures of PBHs are uniquely determined by their outer contours for which various codes have been devised, no general coding system is known that allows one for to identify and localize individual rings in a PBH.

The dualist of a catafusene consists of vertices that are the centers of benzenoid rings, and of straight edges linking vertices corresponding to adjacent rings. As a side remark, by adding the specification that a terminal ring should always be indicated by a dot in the code, the Balaban-Harary 3-digit code [16,17] does allow individual rings to be identified, but it is limited to catafusenes and cannot be applied to perifusenes. This code is based upon digits 0, 1, and 2 specifying angles along the longest path in the dualist. If the angle between two adjacent vertices of the dualist is 180º, then the corresponding ring is denoted by digit 0; if the angle is 120º or 240º, the digits 1 and 2, respectively, are used in that code. Benzenoids whose codes differ only in interchange of digits 1 and 2 have a different geometry but otherwise have a one-to-one correspondence between their rings, and are called isoarithmic [18]. From the various possible digit sequences the selected one corresponds to the smallest number formed by the digit sequence.

In all structures, we assume that two CC bonds in each benzenoid rings are vertical. We also assume that an “acenic line” is a horizontal sequence of adjacent benzenoid rings (the usual way of representing naphthalene or anthracene).

We ignore polycyclic benzenoid hydrocarbons that are not kekulean, or are not superimposable on the graphene net, such as helicenes (e.g. hexahelicene) or cyclacenes (acne bracelets), as well as coronafusenes.

We use for kekulean benzenoids either mathematical-chemical terms (portions of graphene of adjacent hexagons on the honeycomb lattice), or graph-theoretical terms (portions of the triangular lattice); they have dualists such that numbers of tip-up and tip-down triangles are equal.

5 Coding of canonical Clar structures for PBHs (catafusenes and perifusenes)

In this paper, we propose to modify he code that was valid only for catafusenes [16, 17] to encode canonical Clar structures of perifusenes and catafusenes based on the following rules:

(1) Branches from the min path are enclosed in round brackets (parentheses).

(2) Terminal vertices at the two main path extremities, as well as one-ring branches are indicated by a dot.

(3) A Clar sextet ring is indicated by underlining the corresponding digit or dot.

(4) The code is enclosed in braces (curly brackets), e, g, for pentacene {.000.}.

As consequences for these rules, the first and last symbols within the braces are dots, and two not-vicinal symbols are both underlined. Fully benzenoid polycyclic hydrocarbons (also called claromatics) consist of Clar sextet rings and empty rings (with no rings having only one or two double bonds). The number of benzenoid rings is the sum of numbers of dots and digits.

6 Code for canonical Clar structures for PBHs (catafusenes and perifusenes)

In the following glossary, each benzenoid ring is assumed to be mentioned individually following an “acenic line”. Directions are indicated either by “clock” or “map” usual conve-ntions. Jumping from one line to the next one follows “direction 4 o’clock (i. e. from North-East to South-West)” and continues from left to right on acenic lines. Thus, the code indicate that the number of acenic lines equals the number of semicolons plus one.

After establishing a procedure for obtaining canonical Clar formulas for polycyclic benzenoids in a previous publication [1], we now present Canonical Clar Codes (CCCs) for these structures. We have devised this code using lower-case letters (allowing digits only exceptionally) as follows.

Glossary

o = Clar ring (no o rings are allowed to be adjacent);

x = non-Clar ring, i.e. empty ring or a ring one or two double bonds, therefore the total number of benzenoid rings is the sum of a x-type and o-type rings;

v = void space for one hexagon; vv void for two hexagon spaces; vvv void for three spaces, etc.

j/ = jump to next lower horizontal level (j stands for "jump"); there number of acenic is equal to one plus the number of times j appears in the statements;

i: = (i :s stands for "inverse direction"): move to one ring in inverse direction (9 o'clock, or from East to West), ii: for moving to 2nd ring in inverse direction, iii: for moving to 3rd ring,

The code in enclosed in square brackets.

When operators i or v have to be repeated than three times, one can use digits, e. g i4 for iiii, or v5 for vvvvv.

In the following, we show Canonical Clar Codes for all possible kekulean benzenoids with 2 to 5 rings. Several benzenoids with 6 and more rings are also discussed. The basic idea is to assign a letter to each position on succeeding "acenic line", taking into account that a position can contain a Clar ring, a non-Clar ring, or a void space. On each acenic line, one starts from the left-most ring of type-o or type-x, to the right-most type-o or type-x ring, including letters o, x, or v for each position. Operators j (jump) and i (inverse-move) must be followed by punctuation marks / and : , respectively.

The polycyclic benzenoid names are followed by page numbers (in round brackets) for vol. 1 of J. R. Dias, *Handbook of Polycyclic Hydrocarbons*, Elsevier, Amsterdam, 1987, which provides additional information for each PBH[19].

On a Cartesian system with angles 120 °, a polycyclic benzenoid hydrocarbon with no symmetry can be represented in 12 different versions. Clearly, we need to devise a unique version based on the following hierarchical requirements (this means that orientations that do not comply with an upper requirement should be abandoned without considering further requirements):

(i) *minimal j val*; this means that for benzenoids with an ovoid structure, a horizontal orientation is favored; for benz[a]anthracene devoid of symmetry; this requirement reduces to four the possible versions, and for the symmetrical pyrene it reduces them to two;

(ii) *minimal v and i values*; for benz[a]anthracene this requirement reduces the possible versions to two;

(iii) *minimal v and i values in the final statement(s);* this requirement reduces the possible code versions of triphenylene to one;

(iv) *maximal numbers of o and x rings in the final statement(s*); for benz[a]anthracene this requirement reduces the possible code versions to one.

(v) *late appearance of o, v, and i in final statement(s);* on other words, one favors concentration if information as close to the end as possible; for benzo[c]phenanthrene this requirement reduces the possible code versions to one.

(vi) *minimal occurrence of i and v in the final statement(s);* for tribenzo-coronene this requirements reduced the possible cods from two to one.

Thus, benz[a]anthrcene will be coded as [oj/xox], excluding all other possible 11 codes, and perylene as [xj/i:oxxxj/i:o]. The codes of the smallest claromatics with 4 and 6 rings, respectively are [oj/xoj/ii:o[o] for triphenylene and [oj/ii:oxxoj/ii:o] for dibenzo[e,l]pyrene. In the following, we present the code for all catafusenes and perifusenes with 2 to 5 benzenoid rings, and in addition we also present the slightly modified Balaban-Harary code for canonical Car structures of the corresponding catafusenes .

2 rings

1, Naphthalene $C_{10}H_8$ 35) [ox]; {.̲.}}

3 rings

2, Antrtaene $C_{14}H_{10}$ (p. 135) [xox]; {.0’}

3, Phenanthrene $C_{14}H_{10}$ (p. 136) [oj/xo; {.1.}

4 rings

4, Tetracene (napthacene) $C_{18}H_{12}$ (p. 136) [xoxx]; {.00.}

5, Benz[a]anthrcene $C_{18}H_{12}$ (p. 137)) [oj/xox]; {.10.}

6, Chryssne $C_{18}H_{12}$ (p.138) [oxj/xo]; {.12.}

and isoarithmic benzo[c]phenanthrene **7** $C_{18}H_{10}$ (p. 137) [oxj/iii:ovj/o]; {{.11.}

8, Triphenylene $C_{18}H_{12}$ (p. 138) [oj/ii:oxj/o]; {.1(.).}

9, Pyrene $C_{16}H_{10}$ (p. 205) [oxj/i:xo]

5 rings

10, Pentacene $C_{22}H_{14}$ (p. 139([xxoxx]; {.000.}

11, Benzo[a]-tetracen*e* [$C_{22}H_{14}$ (p. 139) [oj/xxo]; {.001.}

12, Pentaphene $C_{22}H_{14}$ [(p. 140) xj/xj/oxx]; {.010.}

13, Dibenz[a,j]j]anthracene $C_{22}H_{14}$ (p. 141) [oj/xoxj/o]; {.102.}

and isoarithmic dibenz[a,j]anthracene $C_{22}H_{14}$ (p. 141) **14**, [ovvoj/iii:xox];{.101.}

15, Benzo[b]chrysene $C_{22}H_{14}$ (p. 141) [xoxj/xo]; {.120.}

and the isoarithmic dibenzo[b,g]phenanthrene $C_{22}H_{14}$ (p. 140) **16**, [xi:oj/xox]; {.110.}

17, Dibenz[a,c]anthracene $C_{22}H_{14}$ (p. 144) [oj/xoxj/iii:o]; {.{1(.)0.}

18, Benzo[g]chrysene $C_{22}H_{14}$ (p. 144) [oxj/xoj/i:o]; {.1(.)2.}

19, Picene $C_{22}H_{14}$ (p. 143) [oj/xoj/xo]; {.121.}

with isoaritthmic **20,** benzo[c]chrysene $C_{22}H_{14}$ (p. 143), [oxj/iii:oxvo]; {.112.} and **21**, so aldibenzo[b,g]phenanthrene (pentahelicene) $C_{22}H_{14}$ (p. 142) [[xoj/ii:oj/xo]; {.111.}

22. Benzo[a]pyrene $C_{20}H_{12}$ [(p. 206) [xoxj/oi:x]

23. Perylene $C_{20}H_{12}$ (p. 206) [xj/i:oxxxj/i:o]

6 rings

24. Benzo[ghi]perylere $C_{22}H_{12}$ (p. 271), [xoj/ii:oxj/i:xo]

25, Dibenzo[a,e]pyrene $C_{24}H_{14}$ ((p, 207) [oj/iiii:oxxj/ii:xo]

26. Benzo[b,k]chrysene $C_{26}H_{16}$ (p. 148), [xoxj/xox], {.0120.}

27, Dibenzo[fg,op]tetracene $C_{24}H_{14}$ p. 207, [oj/ii:oxxoj/ii:o]

28, Dibanzo[de,qr]tetracene $C_{24}H_{14}$ (p. 209), [[oj/i:xxxj/iiiio]

29. Benzo[g,p]chrysene, dibnzo[a,c[triphenylene $C_{26}H_{16}$ (p. 163), [ovoj/ii:xxj/iovo]; {.1(.)1(.).}

30, Zethrene, dibenzo [de,mn]tetracene $C_{24}H_{14}$ (p/ 213) oj/i:xxxxj/i:o]

31, Tribenzo[a,c,h]anthracene $C_{26}H_{16}$ (p. 161), [ovvoj/iii:xoxj/o]; {.101(.)2.}

7 rings

32. Naphtho[2,3-h]pentaphene, [2.2.2]hepta-starphene $C_{30}H_{18}$ (p. 174), [oj/iii:xoxj/oj/x], {.01(0)0.}

33. Tetrabenzo[a,c,h,j]anthracene $C_{30}H_{18}$ (p. 178), [ovvoj/iii:xoxj/iii:ovvo]; {.1(.)01(.).}

34. Dibenzo[cd,lm]perylene, peropyrene $C_{26}H_{14}$ ([. `74) [oxj/i:xoxj/i:xo]

35. Coronene $C_{24}H_{12}$ (p. 326) [oxj/ii:xxoj/ii:ox]

8 rings

36. Tribenzo[fg,ij,rs]petaphene $C_{30}H_{16}$ (p. 277) [oj/ii:oxxoj/ii:oxj/o]

37. Benzo[st]nahtho[2,1,8,7-defg]pentacene $C_{24}H_{12}$ (p. 282) [xoj/oxxxoj/o]

9 rings

38. Dibenzopbc,kl]coronene, dibenzo[ijk,tuv]erpyrene] $C_{30}H_{14}$ (p. 364) [oxxj/ii:xoxj/ii:xxo]

10 rings

39.Ovalene $C_{32}H_{14}$ (p. 370) [xoj/ii:oxxoj/iii:xox]

40.Tribenzo[a,g,m]coronene $C_{36}H_{18}$ (p. 354) [oj/ii:oxj/iii:oxxoj/ii:ocj/o]

13 rings

41. Hexabenzo[bc,ef,kl,no,qr]coronene $C_{42}H_{18}$ (p. 388) [[oj/ii:oxxoj/iii:xoxj/iii:oxxoj/ii:o]

42. Hexabenzo[a,d,g,j,m,p]coronene $C_{48}H_{24}$ (p. 359) [oj/ii:ox/iii:oxxoxj/xvo]

The competition for the optimal orientation of PBHs takes into account all six requirements (i) to (vi). As examples, the three isoarithmic PBHs **19**, **20**, and **21** will be discussed.

For picene (**19**), the are four orientations with two jumps that outdo all other orientations according to requirement (1). Two of them, descending from Northwest to Southeast (or from 10 to 4 o'clock directions) win according to requirement (ii) as they involve no i or v operators. Finally, the orientation displayed in Fig, 3 is preferred according to requirement (iv) because it has two rings in the last line, unlike the other candidate with only one ring.

For benzochrysene (**20**), according to criterion (i) here are four candidates with only one jump, and two of them fail according to requirement (iv) because they have less rings in the bottom line. The winning orientation, according to requirement (iv) and displayed in Fig. 3 for benzochrysene has more rings at the end of the line than the other competitor.

There are six possible orientations for pentahelicene (**21**) with two jumps, and the winner displayed in Fig. 3 according to criterion (iv) has more rings at the end of the line than all other competitors.

Clar and coworkers [20] argued that the fully benzenoid **36** is more stable than its isomer with one less Clar sextet **37** (which adds maleic anhydride in an electrocyclic Diels-Alder reaction). It was shown that this kind of reactivity can be correlated with the topology of PAB dualists [21].

We are aware of the complete equivalence of the six outer rings in coronene, yet had to make an arbitrary decision for having one canonical structure for this PBH. Observe that coronene is the only benzenoid having all migrating rings in nonlinear (i.e. cyclic) positions. Coronene transmits further to its benzo-derivatives this need for arbitrariness. We will start with an analogy involving adding benzenoid rings: from naphthalene we can add one new ring by replacing two hydrogen atoms from a convex CH=CH group by a C_4H_4 chain, obtaining anthracene or phenanthrene; or we can replace two hydrogen atoms from a concave CH–C–CH group by a C_3H_3 chain, obtaining a free radical, triangulene; however, if we perform twice this operation we obtain pyrene, a normal PBH. Similarly, we can obtain from coronene two different stable hexabenzocoronenes by "convex" and "concave" replacements performed six times, $C_{48}H_{24}$ (**42**) and $C_{42}H_{18}$(**41**), respectively. For the former PBH, six-fold symmetry leads to the same arbitrary decision for a canonical structure despite the symmetry. The latter PBH is "claromatic" (fully benzenoid), preserving its symmetry; it appears on the cover of Clar's 's book "The Aromatic Sextet" [2]. The symmetric tribenzocoronene (**40**) obtained by "convex" replacement is also claromatic and stable, but the tribenzocoronene obtained by "concave" replacement is non kekulean, an unstable diradical.

Among the three types of benzenoid rings in Clar formulas (sextet rings, empty rings, and rings with one or two double bonds), the third group causes the most trouble. This is the group that is traversed by an arrow, in Clar's formulation. Various authors have published contradictory aspects if such rings, e. g. the central ring of anthracene had been viewed as being either the least aromatic (as attested by its reactivity as a *para*-diradical) or the most aromatic (by virtue of its paramagnetic ring current). Gutman [22], Schleyer [11,23], Polanski[9], and other authors [24] have argued that the higher thermodynamic stability of phenanthrene than that of anthracene justifies considering anthracene to be less aromatic than phenanthrene. In general, [*n*]-acenes become less stable and more reactive towards oxidation or hydrogenation as the number *n* of rings increases, whereas their isomeric fibonacenic counterparts remain stable even for larger *n* values.

Many chemists consider that aromaticity is a multidimensional concept [25-31], and that thermodynamic stability is orthogonal to kinetic activation energies for electrocyclic Diels-Alder reactions. Several authors [32-40] have stressed the importance of quantitative evaluation of aromaticity, and of the aromatic paramagnetism. Our results agree with Schleyer's findings and indicate that an inner ring in an acene should have a Clar sextet circle. If one looks at a Clar picture of graphene, one sees only Clar sextet rings and empty rings; two Clar sextet circles are separated by two empty rigs in each acenic direction.

In conclusion, the present set of six hierarchical requirements for encoding the canonical Clar structures of benzenoids may serve for other purposes when one needs to address individual rings of catafusenes or perifusenes. Various proposed boundary codes [41,42 may also serve for characterizing such large PBHs: the six orientation requirements listed in the present paper should also be taken into consideration in order to characterize uniquely the PBS, taking into account the fact that there exist up to 12 possible orientations when no symmetry elements exist.

The new code may become a useful tool for the electronic industry, which needs large perifusenes (benzenoid hydrocarbons whose carbon skeleton is a fragment of graphene). Müllen and his coworkers perfected cycloaddition and subsequent cyclo-dehydrogenaion reactions, synthesizing such large PBHs [43]. They are almost insoluble, therefore are difficult to purify, but substation with alkyl groups increases their solubility. No systematic name exists for them, therefore our proposed code nay assume this function.

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