

Scientific paper

Algebraic Clar Formulas – Numerical Representation of Clar Structural Formula

Milan Randić¹ and Dejan Plavšić²¹ National Institute of Chemistry, Ljubljana, Hajdrihova 19, Slovenia, EU² Rudjer Bošković Institute, NMR Center, Zagreb, Bijenička cesta 54, Croatia

* Corresponding author: E-mail: mrandic@msn.com

Received: 20-02-2011

Dedicated to Professor Dušan Hadži on the occasion of his 90th birthday

Abstract

We outline the construction of an algebraic (numerical) representation for Clar's valence formulas which in their geometrical form are illustrated with π -aromatic sextets as inscribed circles in benzenoid rings.

Keywords: π -aromatic sextet; Clar formulas; Algebraic Clar's formulas

1. Introduction

With the widespread popularity of MO calculations during the last half of the previous century, and particularly with the development and expansion of *ab initio* computations using Gaussian orbitals, introduced in computational chemistry by Samuel Francis Boys in the early 1950s,¹ the use of an alternative to MO methods, namely the VB method would almost have disappeared from quantum chemistry, were it not for a few theoretical chemists who kept it alive.^{2,3} With the limited interest of quantum chemists in the theoretical chemistry research outside applied Gaussian MO computations, Kekulé valence formulas would equally fall in oblivion, as far as numerical calculations are considered in theoretical chemistry, were it not for the growing interest in Kekulé valence structures that evolved with the emergence of Chemical Graph theory in mid 1970s.^{4,5} Applications of graph theory to chemistry were not the only segment of theoretical chemistry that was largely avoided by quantum chemists. Density Functional Theory (DFT) was equally not well received by most quantum chemists (among the exceptions were Robert G. Parr and John A. Pople). There is no doubt that the *sudden* adoption of Density Functional Theory into quantum chemistry was due to the Nobel Prize in Chemistry in 1998, which was divided equally between Walter Kohn⁶ »for his development of the density-functional theory« and John A. Pople »for his develop-

ment of computational methods in quantum chemistry.«

What it will take for quantum chemists to *suddenly* adopt Chemical Graph Theory as a useful branch of theoretical chemistry is difficult to speculate, but Chemical Graph Theory is *gradually* winning recognition in some chemistry circles as it continues to offer insights on aromaticity – which remains one of the central topics of chemistry; Chemical Graph Theory cannot fade away, and can only gain in importance.

In this respect one may say that just as aromaticity is central to chemistry so are Kekulé valence structures central to aromaticity! Already in 1975 the stunning discovery of *conjugated circuits*,^{7,8} »buried« within individual Kekulé valence structures, has shown that Kekulé valence structures contain more information than their geometrical formulas may suggest. Since then a number of novel insights about Kekulé valence structures followed: the observation that a *single* Kekulé valence structure contains *information on all the remaining* Kekulé valence structures;⁹ the notion of *innate degree of freedom*^{10–12} also referred to as the *forcing number* of Kekulé valence structures,¹³ the concept of *resonance graphs*,^{14–16} which associates with the set of Kekulé valence structures of a molecule a *graph* (and its adjacency matrix); the *partition of π -electrons* to *individual rings* of polycyclic conjugated hydrocarbons;¹⁷ the representation of the set of Kekulé valence structures of a molecule by *graphical* or *alphanumeric matrix*,¹⁸ which is a special case of graphical matrices in-

produced for potential use in structure-property-activity studies about 15 years ago.¹⁹ The latest and potentially the most important use of Kekulé valence structures and conjugated circuits is development of a graph theoretical approach to the calculation of ring currents in polycyclic conjugated hydrocarbons.^{20–24} These advances have already given novel insights on aromaticity, one of the central concepts in organic chemistry. To this impressive list of accomplishments of chemical graph theory related to Kekulé valence structures, we would like to add another novelty: the Algebraic Clar formulas – to be outlined in this contribution.

1. 1. Clar Structural Formulas

An excellent introduction to Clar structural formulas and their potential in chemistry of benzenoid hydrocarbons can be found in Clar's booklet: *The Aromatic Sextet*²⁵ and its elaboration in a review on aromaticity by one of present authors.²⁶ In Fig. 1 we have illustrated two dozen Clar structures for smaller benzenoid hydrocarbons, which include all benzenoids having four and fewer fused benzene rings and a selection of smaller benzenoid hydrocarbons having from five to eight benzene rings.

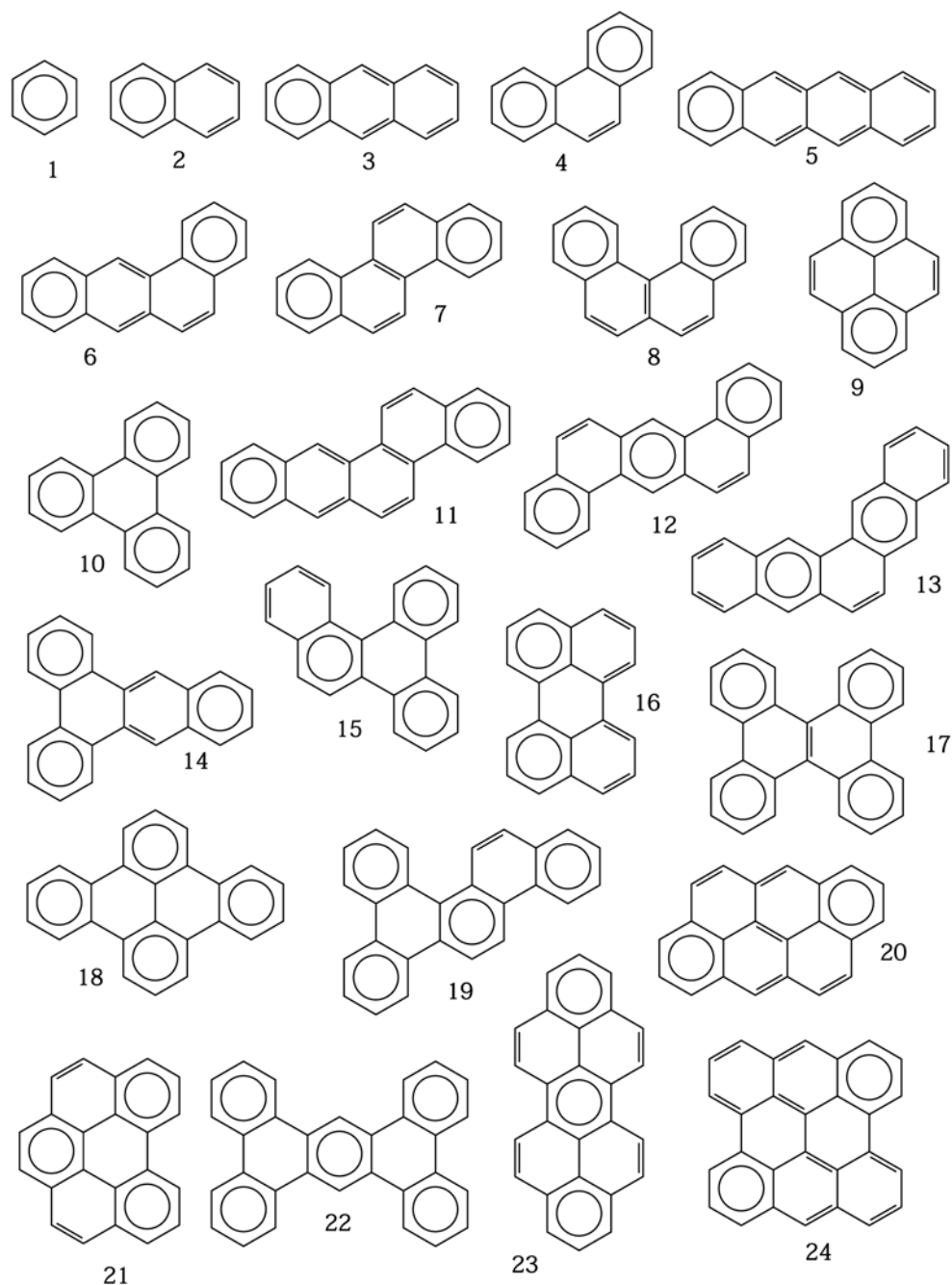


Fig. 1: Clar structures for two dozen smaller benzenoid hydrocarbons

The first important thing to notice is that aromatic π -sextets in Clar structures are never placed in adjacent benzene rings, just as two cumulated C=C bonds never occur in benzenoid hydrocarbons. The reason for not placing π -aromatic sextets in adjacent rings is that *sextets* contribute *six* electrons to the *count* of π -electrons, and if, for example, one places sextets in adjacent rings, as in both rings of naphthalene, this would give an incorrect count of π -electrons for naphthalene because the sextets in adjacent rings would contribute 12 π -electrons instead of 10, which is the count of π -electrons in naphthalene. For more on how to draw and how not to draw structural formulas for benzenoids one should consult ref.^{27, 28}

In Fig. 1 for each benzenoid only one Clar structure is shown, but it is not difficult to see that for a number of benzenoids of Fig. 1 one can write two or more Clar structures. Besides benzene, from the dozen benzenoids in Fig. 1, only an additional three benzenoids (**10**, **18**, **22**) have Clar formula in which rings have only aromatic π -sextets or are »empty«, in the terminology of Eric Clar. »Empty« rings are defined as rings which have no C=C bonds. Benzenoids which have only aromatic π -sextets and »empty« rings have $6n$ π -electrons and show unusual stability. They have been referred to by Clar as *fully aromatic benzenoid hydrocarbons*.

There is an additional group of benzenoids having only one Clar structure. They, besides sextet rings and empty rings, have one or more benzenoid rings with a *single* C=C bond. These are benzenoids **4** (phenanthrene), **9** (pyrene), **10** (triphenylene), **12** (dibenz[*a,h*]anthracene), **17**, **18**, **19**, **21**, **22**, and **23** of Fig. 1. All other benzenoids of Fig. 1 have one or more benzenoid rings with *two* C=C bonds, and consequently have more than one Clar structure.

In such molecules π -aromatic sextets can be placed in different rings, as illustrated in Fig. 2 on benzo[*b*]chrysenone (structure **11** of Fig. 1). Observe that some of Clar structures of such systems may have benzenoid rings with a single C=C bond (like rings C and D in Fig. 2). However, Clar structures with migrating sextets necessarily have benzenoid rings with pair of C=C bonds. Thus we can characterize molecules having only one Clar structure as systems that besides sextet rings and empty rings, have one or more benzenoid rings with a *single* C=C bond, and have no benzenoid rings with pair of C=C bonds.

1. 2. Algebraic Clar Formulas

In the year 2003 one of present authors has introduced the »Algebraic Kekulé valence formulas« for benzenoid hydrocarbons, i. e. the valence formulas in which numerical values have been assigned to individual benzene rings based on the partition of π -electrons to each individual ring. Depending on the number of C=C bonds within a ring and the number of C=C bonds shared between adjacent rings in the set of Kekulé valence structures of a molecule, one assigns π -electrons to individual rings.^{17, 29–42} Numerical benzenoid ring values are ring-analogous to Pauling bond orders, which count the participation of CC double bonds to individual CC bonds in a molecule in a set of Kekulé valence structures.

Is it possible to construct a numerical representation for Clar valence structures analogous to numerical representations of Kekulé valence structures? The answer is: Yes – and in this section we will outline one such construction. The goal is to arrive at algebraic (or numerical) valence formulas that would characterize the presence or

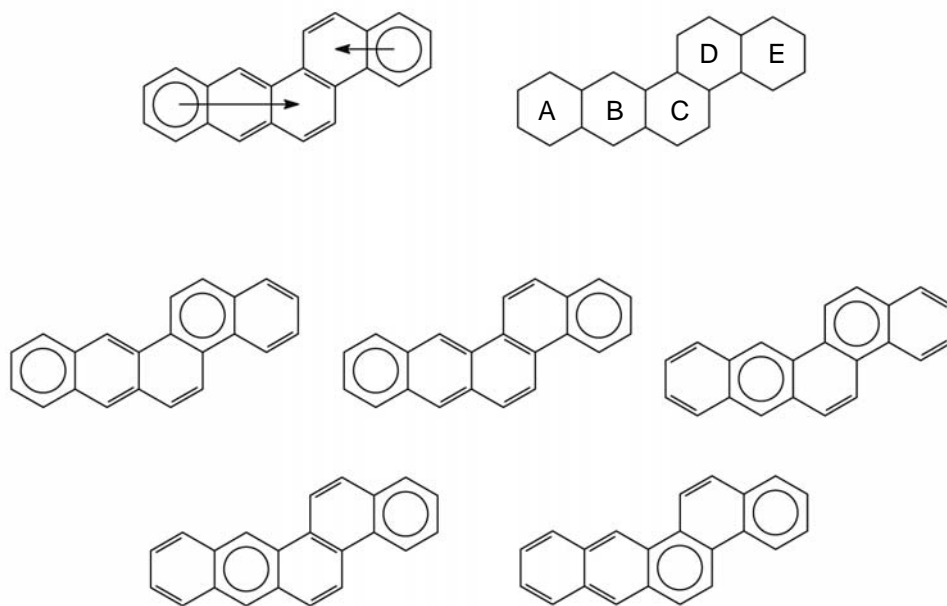


Fig. 2: The five Clar structures for **11**, naphtho[*a*]anthracene, while the first structure is representation of **11** by a single structural formula involving »migrating« sextets. Benzenoid rings are labelled A-E from left to right

the absence of π -aromatic sextets in different rings of benzenoid hydrocarbons, with a possibility of extending the approach also to non-benzenoid hydrocarbons, when appropriate. In the case of benzenoids having a single Clar structure, the numerical Clar formulas are very simple, based on the use of digits *one* for rings having π -aromatic sextet and *zero* otherwise, as illustrated in Fig. 3 for benzenoids of Fig. 1 having a single Clar structure. Observe that here there is no differentiation between fully aromatic benzenoids (the benzene rings of which are either sextet rings or empty rings) and benzenoids which have in addition to sextet rings also rings with fixed single C=C bond (structures **4**, **9**, **12**, **17**, **19**, **21** and **23** of Fig. 1). If in these structures one replaces a peripheral single C=C bond by a benzenoid ring, one obtains larger fully aromatic benzenoids. Thus from pyrene (**9**) one obtains dibenzopyrene (**18**) and from dibenz[*a,h*]anthracene (**12**) one obtains tetrabenzo[*a,c,h,j*]anthracene (**22**).

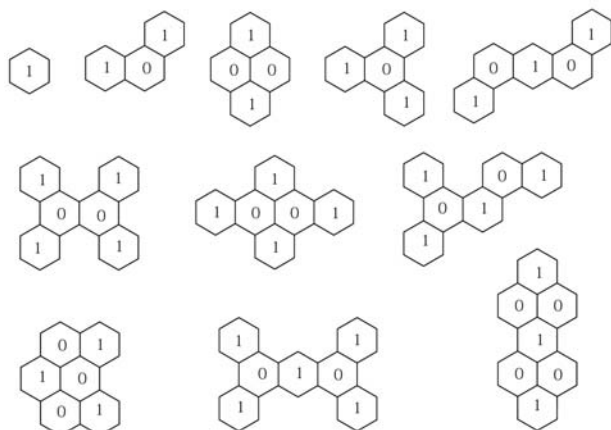


Fig. 3: Numerical representation of unique Clar structures

Of more interest are benzenoids having migrating aromatic sextets, like naphtho[*a*]anthracene of Fig. 2 with five Clar structures. Clar has depicted such benzenoids by a single structure adding one or more arrows passing through rings in which one can place aromatic sextets in alternative Clar structures of such molecules. The present challenge is that of constructing a *single* numerical structure corresponding to the *single* geometrical structure of Clar that uses π -sextets and arrows. The way how we propose to arrive at algebraic (in contrast to geometric) Clar structures is to count how many times each ring in a polycyclic benzenoid hydrocarbon has a π -aromatic circle inscribed in the set of all possible Clar structures for the molecule under consideration. By looking at Fig. 2 one can see (by viewing Kekulé structures from left to right) that the first and the second benzenoid rings and the fourth ring of naphtho[*a*]anthracene involve aromatic sextets twice, while the third ring has an aromatic sextet only in one of the five Clar structures. Finally the last ring of naphtho[*a*]anthracene has aromatic sextets in three of the five

Clar structures. On the basis of this we can assign numerical values $2/5$ to rings A, B, D, the numerical value of $1/5$ to ring C, and the value $3/5$ to ring E, as is illustrated at the end of the second row Fig. 4. Similar results for remaining benzenoids of Fig. 1 having more than a single Clar structure are shown in the rest of Fig. 4.

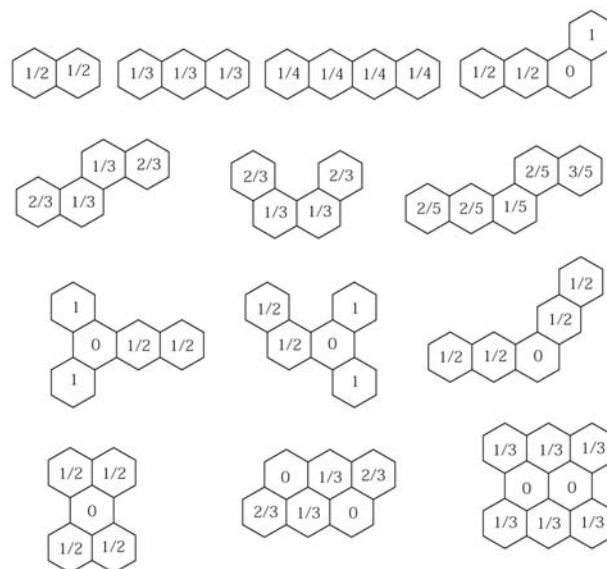


Fig. 4: Algebraic (numerical) Clar formulas for benzenoid hydrocarbons of Fig. 1 having more than one Clar structure

Before discussing the numerical Clar formulas of Fig. 4 we will report on numerical Clar formulas for additional 15 benzenoids having two or more Clar structures, illustrated in Fig. 5. Structures of Fig. 5 include all cata-condensed benzenoids having six benzenoid rings (except structures **17** and **19** of Fig. 4, already considered). A close look at the numerical Clar structures of Fig. 4 and Fig. 5 clearly shows that when a ring with zero numerical value (the ring which in none of Kekulé valence structures has been assigned π -aromatic sextet) is erased, the resulting smaller fragments have the same numerical values for their rings as are the values in the corresponding rings of smaller benzenoids. Thus when the central »zero« rings in pentaphene and perylene of Fig. 4 (structures **13** in and **16** in Fig. 1) are erased, these structures reduce to naphthalene fragments which have the same ring values as naphthalene.

In Fig. 4 and Fig. 5 several regularities in numerical ring values can be observed. The magnitude of ring values for linear acenes: naphthalene, anthracene, and tetracene, namely $1/2$, $1/3$, and $1/4$, respectively gradually decrease, having value $1/R$, where R is the number of linearly fused benzenoids. In linear fragments of angularly fused one finds constant ring values for all rings of linear fragments, except for adjacent »kink« rings, which have smaller values. This is because even though adjacent kink rings can have aromatic π -sextets they can not have aromatic sextets *simultaneously*. Finally observe the simple sum rule for

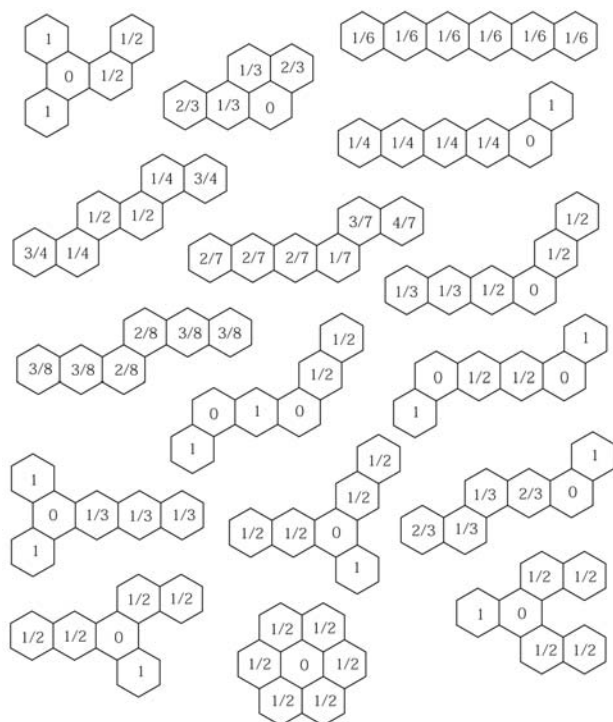


Fig. 5: Algebraic Clar structures for additional benzenoids having up to seven fused benzene rings

ring values: the ring values in linear fragments always add to 1, because each linear fragment results from the partition of a single aromatic sextet to linearly adjacent rings.

1. 2. 1. Tribenzo[*a,h,rst*]phenanthre [1,2,10-*cde*]pentaphene

We will end this outline of algebraic Clar formulas by considering tribenzo-*[a,h,rst]*phenanthro[1,2,10-*cde*]pentaphene (TPP), illustrated in Fig. 6, which has 11 fused benzenoid rings. The molecule has a center of symmetry, so we need to consider only symmetry non-equivalent carbon atoms and their rings, which are in the top right half of the molecule, all atoms of which have been numbered 1–21 in Fig. 6. The molecule has eight Clar structures with five π -aromatic sextets, which are illustrated in Fig. 7. A close look at the eight Clar structures shows that only two π -aromatic sextets have fixed positions, while the remaining three sextets are migrating sextets. If we delete the two »fixed« sextets (one at the top and one at the bottom of the molecule) and the adjacent bonds, one obtains a catacondensed 7-ring benzenoid with migrating sextets which will have the same ring values as those of the algebraic Clar structure of TPP. Observe that all five symmetry non-equivalent rings that are sites of π -aromatic sextets have in this molecule different numerical ring values: 1, 5/8, 4/8, 3/8 and 2/8. So while all benzenoid rings having »fixed« aromatic sextets always have equal numerical characterizations, this is not the case with the benzenoid rings involving migrating sextets.

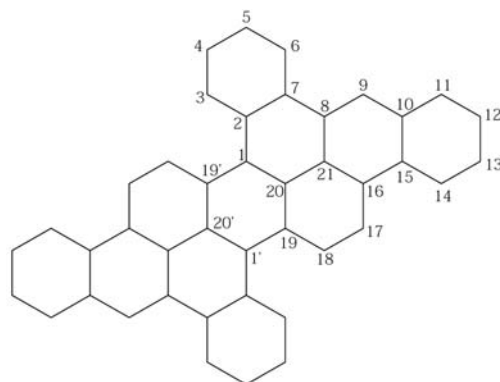


Fig. 6: The numbering of symmetry non-equivalent carbon atoms of tribenzo[*a,h,rst*]-phenanthre[1,2,10-*cde*]pentaphene

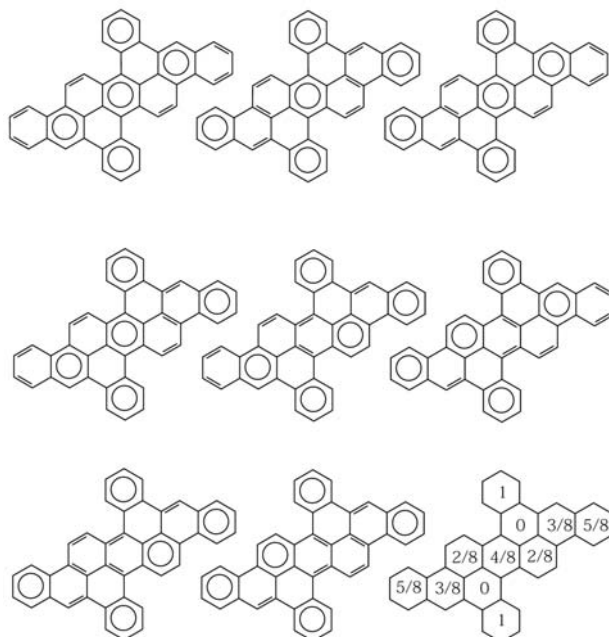


Fig. 7: Clar structures and Algebraic Clar structure for tribenzo[*a,h,rst*]-phenanthre[1,2,10-*cde*]pentaphene

The question is: Are there any computational results or experimental results that would correlate with the above variable π -aromatic ring sextet contents: 1, 5/8, 4/8, 3/8, 2/8 and 0 for the individual benzene rings in TPP? As we will illustrate below, there are in fact both computational *and* experimental data that fully agree with the trend of the relative Clar character for different benzenoid rings in tribenzo[*a,h,rst*]phenanthro-[1,2,10-*cde*]pentaphene shown above. For TPP it is no difficult to find, for example by using the approach of John and Sachs,^{43, 44} that the number of Kekulé valence structures of TPP molecule is 140. It is also not difficult to calculate the *local aromatic character* of different benzenoid rings,^{45, 46} which are given by the quotient K'/K , where K' is the number of times a ring appears in all 140 Kekulé valence structures having three C=C bonds divided by K (the total number of num-

ber Kekulé valence structures). The local aromatic character for all six non-equivalent benzenoid rings of TPP are 130/140; 96/140; 72/140; 68/140; 56/140; and 20/140; or: 0.9286; 0.6857; 0.4865; 0.4857; 0.4000 and 0.1429, for benzenoid rings having π -aromatic sextet contents: 1, 5/8, 4/8, 3/8, 2/8 and 0, respectively.

This parallelism between the algebraic Clar numbers and the local aromaticity characters, which are based on using ring contributions from *all* Kekulé valence structures, which gives even to the empty rings of TPP a local aromaticity of 20/140, is a strong support for Clar's notion of aromatic π -sextets.

Additional support for this meaningful interpretation of the numerical values of Clar's sextet occurrences in different benzenoid rings of TPP comes from a comparison of experimental bond lengths in different benzenoid rings of TPP with the π -sextet character as calculated in algebraic Clar structures. The molecular and crystal structure of tribenzo[*a,h,rst*]phenanthro[1,2,10-*cde*]pentaphene was determined by X-ray diffraction and reported by I. Oonishi, S. Ohshima, S. Fujisawa, J. Aoki, Y. Ohashi and T. M. Krygowski.⁴⁷ They found the molecule to be distorted from planar structure due to steric repulsions between the overcrowded hydrogen atoms, which results in a non-planar saddle form for the molecule. In Table 1 we show the CC bond lengths from ref.,⁴⁷ based on averaging the values for pairs of symmetry related CC bonds reported CC bonds of Oonishi *et al.*

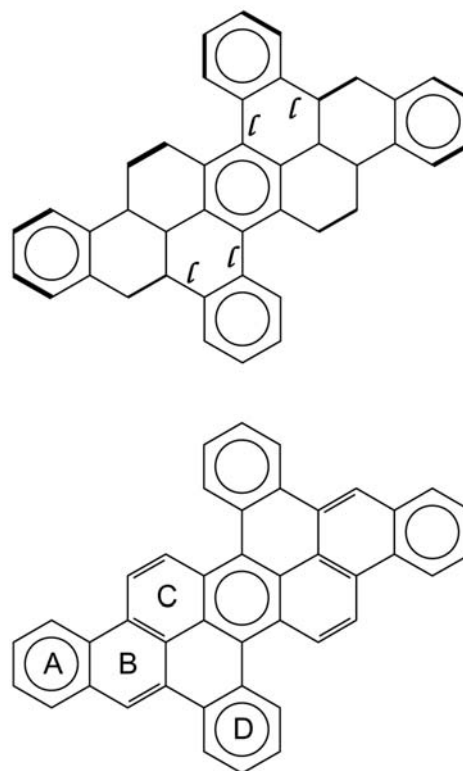


Fig. 8: CC bonds of TPP with excessive C=C bond character (bold) and excessive C-C bond character (marked by *l*) and the Clar structures consistent with changes in CC bond lengths

Table 1 Experimental bond lengths of tribenzo[*a,h,rst*]phenanthro[1,2,10-*cde*]pentaphene as reported by Oonishi *et al* [7] (the numbering of carbon atoms is given in Fig. 7)

Bond	Length	Bond	Length	Bond	Length	Bond	Length
1–2	1.467	5–6	1.372	10–15	1.414	16–21	1.405
1–19'	1.415	6–7	1.408	11–12	1.366	17–18	1.351
1–20	1.407	7–8	1.465	12–13	1.387	18–19	1.426
2–3	1.409	8–9	1.368	13–14	1.370	19–20	1.432
2–7	1.405	8–21	1.435	14–15	1.409	20–21	1.442
3–4	1.378	9–10	1.414	15–16	1.436		
4–5	1.393	10–11	1.412	16–17	1.424		

Let us look at Table 1 more closely. It is not difficult to observe that there are essentially four types of CC bonds in Table 1: »long«, »intermediate«, »aromatic« and »short«, but we have to stress that all four labels we show under quotation marks emphasize the *relative* nature of the labels used to differentiate between CC bonds which are all shorter than typical C-C bond in alkanes (saturated hydrocarbons) and longer than typical C=C bonds in alkenes (unsaturated hydrocarbons having C-C single and C=C double bonds). Here we refer to CC bonds of about 1.46 Å as »long«, to CC bonds of around 1.43 Å as »intermediate«, to CC bonds of around 1.40 Å as »aromatic«, and to CC bonds of around 1.37 Å as »short«. In Fig. 8 we have illustrated on the molecular diagram of TPP the loca-

tions of the »aromatic« CC bonds in benzene rings by inscribing π -aromatic sextets circle, the CC bonds classified as »double« are shown as bold, and CC bonds classified as »single« bonds are indicated by letter *l*.

Observe the interesting results of such a view on CC bond lengths of tribenzo[*a,h,rst*]phenanthro[1,2,10-*cde*]pentaphene, if one focuses attention to the set of »aromatic« CC bonds alone: the resulting valence structure is the second of the eight Clar structures of tribenzo[*a,h,rst*]phenanthro[1,2,10-*cde*]pentaphene! Moreover, we can account even for the minor variations of CC bonds within π -aromatic sextet rings. Let us label the three symmetry non-equivalent rings having additional C=C character (shown as bold CC bonds in Fig. 8), going from

left to right, as A, B, and C. We can relate the differences in CC bonds in these rings to bond orders of the same CC bonds in the eight Clar structures of Fig. 8.

Let us start with ring A. First let us define a *partial Pauling bond order* as the Pauling bond order calculated for a subset of Kekulé valence structures. The subset of Kekulé valence structures considered here are Kekulé valence structures that contribute to the Clar sextet in individual rings of TPP. From Fig. 7 it follows that ring A appears five times as sextet ring (having three C=C bonds) and three times as ring having only two C=C bonds. Each of five structures needs two Kekulé valence structures, which means that in 10 valence structures C=C appears five times and in addition the same CC bonds appear as C=C in additional three structures of the eight Clar structures of Fig. 7. Thus the »bold« CC bonds of Ring A have partial Pauling bond order of 8/13, while the other peripheral CC bonds of this ring have partial bond order of 5/13. The respective experimental bond lengths of Oonishi and collaborators are 1.366 Å, 1.370 Å for »bold« bonds (11, 12), (13, 14), and 1.387 Å for bond (12, 13), in agreement with expectations that larger bond order indicate shorter CC bonds.

In three Clar structures of eight of tribenzo[*a,h,rst*]phenanthro[1,2,10-*cde*]pentaphene the ring B is π -sextet ring (which involves six Kekulé structures) while in five Kekulé structures the »bold« CC bond appears as C=C bond. One obtains then the partial Pauling bond order of 8/11 and 5/11 for bonds (8, 9) and (9, 10), respectively, and the experimental length of which are: 1.368 Å and 1.414 Å, respectively. Again one sees that a larger bond order belongs to a shorter CC bond.

The situation is similarly reflected in ring C. The »bold« CC bond appears in two sextets, meaning four Kekulé valence structures and in additional six Clar structures of Fig. 8, a total of 10 structures. This gives for the »bold« CC bond a partial Pauling bond order of 8/10, and a partial Pauling bond orders of 2/10 for the other bond. The experimental CC bond length reported by X-ray are: 1.351 Å and 1.424 Å, 1.426 Å for bonds (17, 18), (16, 17) and (18,19), respectively; again the larger partial Pauling bond order belongs to a smaller CC bond length. We conclude that the experimental data of Oonishi and collaborators are consistent with expectations based on the eight Clar structures of tribenzo-*[a,h,rst]*-phenanthro-*[1,2,10-cde]*-pentaphene.

1. 3. Canonical Clar Structures

From the previous section we have seen (1) that algebraic Clar structures agree with expectations based on graph theoretically calculated *local* aromaticity in benzenoid TPP, and (2) that the particular graphical Clar formula of Fig. 7 agrees with the experimental data for CC bond lengths in TPP. These results lead to a question: Is there, among a set of symmetry unrelated Clar formulas of a

benzenoid hydrocarbon, a *single* representative Clar formula that better agrees with experimental and theoretical results, and that can be selected as *canonical*? The situation is somewhat analogous to a similar question that can be posed for the set of Kekulé valence structures: Is there, among a set of symmetry unrelated Kekulé valence structures of a benzenoid hydrocarbon, a *single* representative Kekulé structure that better agrees with experimental and theoretical results, and that can be selected as *canonical*? When there is only one Kekulé valence structure with the largest number of Kekulé benzenoid rings (rings having three C=C bonds as is in Kekulé structure of benzene) the answer to this question is known as the Fries Rule.^{48, 46} This says that the most important Kekulé valence structure for molecular stability is the structure which has the maximum number of rings having three double bonds in each ring. But the question is only partially answered, because some benzenoid hydrocarbons have more than one such so-called Fries structure. Hence the question is: Can one select among several Fries structures one as more representative than others? We will leave this open question and return to the question of Canonical Clar structure, which we define as follows:

Definition: A *canonical Clar structure* is the Clar structure in which π -sextets are assigned to non-adjacent benzenoid rings having the largest π -sextet ring values.

With this rule in the case of tribenzo[*a,h,rst*]phenanthro[1,2,10-*cde*]-pentaphene one has inscribed hexa-

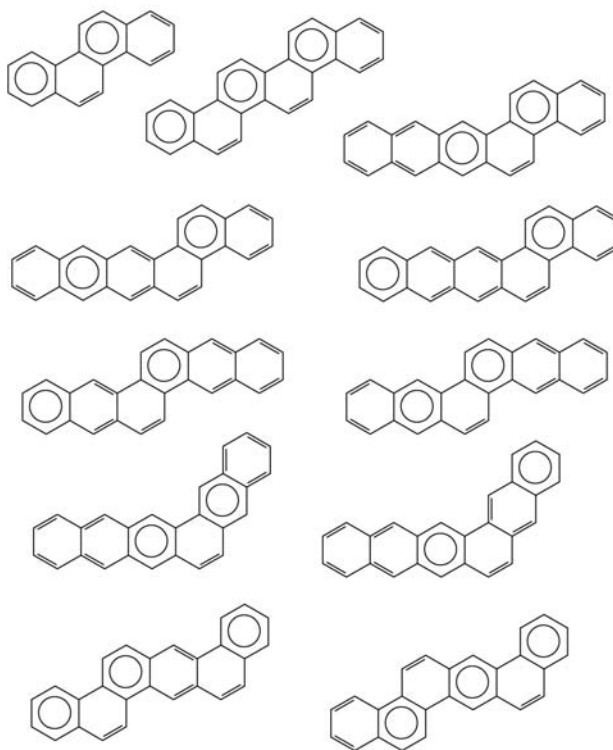


Fig. 9: Non-canonical Clar structures for selected benzenoid hydrocarbons of Fig 4. and Fig. 5

gons that have ring values $5/8$ and $4/8$, which is the case with the second Clar structure of Fig. 7. However, many benzenoid hydrocarbons have symmetry non-equivalent rings having the same π -sextet ring values (e.g., linearly fused acenes or similar fragments in branched catacondensed systems), which are not covered by the above rule; however, the rule disqualifies Clar structures, such as those of Fig. 9, in which at least one of the sextet is not placed in optimal (maximal) benzene ring.

2. Concluding Remarks

Numerical characterization of Clar structures, as we have seen, is so simple, that it appears surprising that it has not been mentioned previously in the literature. It is not uncommon in science to »rediscover« something that has been discovered earlier but may have not been widely known, particularly if published in less known journal. For example, this has been the case with resonance graphs,^{15, 16} reported by one of present authors and published in 1996. After the paper on resonance graphs has been published Professor I. Gutman, editor of *MATCH – Communication in Mathematical and Computer Chemistry*, brought to our attention the paper of W. Günther¹⁴ in which resonance graphs for smaller benzenoid compounds were outlined and discussed some 15 years before. Günther published his work in 1982 in local journal of the University of Halle, Halle, (at that time in Eastern Germany). Were it not for I. Gutman and our re-discovery of resonance graphs, which aroused considerable interest, both in mathematical^{51–55} and mathematical chemistry literature,^{56–58} the work of W. Günther would probably have passed unnoticed.

This time, therefore, we were more careful and searched »old« literature to see if something similar to numerical Clar structures has been already reported. A search for published results is today easier than it used to be, because of computers. Although even today one may never be quite sure that searching was complete, not finding relevant literature these days is more reassuring than it used to be. However, some caution is always in place. Thus though a negative search may be indicative that the work on construction of numerical formulas of Clar structures of benzenoids, reported in this article, appears here for the first time, one should not be surprised if this is not the case. Indeed, we found that in 2002 in a paper on quantum-chemical justification for Clar's valence structure⁵⁹ there was a brief mention of »frequency of π -sextet in Clar formulas«, which is the same what is called here »algebraic Clar structure«. The concept was illustrated on dibenzo[*a,f*]tetraphene (the first structure in the last row of Fig. 5) and benzo[*a*]naphtho[2,1]naphthacene (see Fig. 10). This was, however, not easy to detect, because the same concept has been named *differently* in the year 2002 and 2011! What has been surprising, however, is that the

author of the article in which the »frequency of π -sextet in Clar formulas« were outlined was one of the present authors! Apparently, this author has forgotten that in this relatively lengthy review on relating Clar structures to quantum chemical calculations, there was also a brief discussion on graph theoretical properties of Clar structures. One of the reasons, (or excuses), that one can completely forget about such »detail« in an article on 35 pages, is that with time people can shift their attention and interests to other problems. In our case we drifted to the part of bioinformatics dealing with graphical and numerical rerepresentation of biosequences, DNA, the secondary structure of RNA, proteins, and even on numerical characterization of proteomic maps and proteome.⁶⁰ So for the past decade we would return only from time to time to Kekulé valence structures, our »first love«, apparently overlooking even our own contributions in that area! In passing it is interesting to mention that the algebraic (numerical) formulas of Clar structures appeared in press about one year *before* the algebraic (numerical) formulas for Kekulé valence structures, but the latter attracted attention of several people in mathematical chemistry – hence, could not be forgotten so easily!

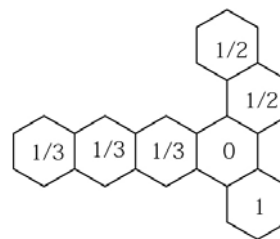


Fig. 10: Algebraic Clar formula for benzo[*a*]naphtho[2,1]naphthacene

The seminal paper on algebraic (numerical) formulas for Kekulé valence structures was followed by a series of papers on this subject in which in particular A. T. Balaban expanded the topic significantly. We may add that the interpretation of ring values in algebraic Kekulé valence is sometimes confused and viewed as a measure of local aromaticity or individual benzenoid rings. The true interpretation of partitions of π -electron to individual rings relates to π -electron ring density within polycyclic conjugated hydrocarbon molecule. This is easy to see, because when contributions in all rings are added, they give N , the number of carbon atoms and π -electrons. But some parallelism with local aromaticity may be expected. It is probably less likely that algebraic (numerical) formulas of Clar structures will attract similar attention, because the most interesting large systems, such as those giant benzenoids of Klaus Müllen and collaborators,⁶¹ are fully benzenoid hydrocarbons, and numerical representations of their Clar structures is almost trivial, having no fractions but only ones and zero values for aromatic sextets and empty rings.

However, continuing interest of chemists is likely to shift to *local* aromaticity,¹⁸ and therefore it cannot hurt to have an additional and alternative characterization of local molecular features in polycyclic conjugated hydrocarbons.

3. Acknowledgment

This work has been supported in part by the Ministry of Higher Education, Science and Technology of Republic of Slovenia, under Research Grant P1-017. Partial support for this work came also from the Ministry of Science, Education and Sport of the Republic of Croatia under Project 098-0982929-2917

4. References

1. S. F. Boys, *Proc. Roy. Soc. [London]*, **1950**, A 200, 542–554.
2. D. J. Klein and N. Trinajstić (Eds), *Valence Bond Theory and Chemical Structure*, Elsevier, Amsterdam **1990**.
3. D. J. Klein, *Topics in Current Chem.*, **1990**, 153, 57–83.
4. A. T. Balaban (Ed.), *Chemical Applications of Graph Theory*, Academic Press, New York: **1976**.
5. N. Trinajstić, *Chemical Graph Theory*, 2nd Ed., CRC Press, Boca Raton, Fl. **1992**.
6. For a views on DFT by quantum chemists prior to Nobel Award given to W. Kohn read the »Personal Introduction«, which Kohn has written for »Reviews of Modern Quantum Chemistry. A Celebration of the Contributions of Robert G. Parr«, vol 1, K. D. Sen, Ed., World Scientific, Singapore, **2002**.
7. M. Randić, *Chem. Phys. Lett.* **1976**, 38, 68–70.
8. M. Randić, *Chem. Rev.* **2003**, 103, 3449–3605.
9. I. Gutman, M. Randić, *Chem. Phys.* **1979**, 41, 265–270.
10. M. Randić, D. J. Klein, In: *Mathematical and Computational Concepts in Chemistry*, N. Trinajstić Ed., Ellis Horwood Ltd., Chichester, England, pp. 274–282.
11. D. J. Klein, M. Randić, *J. Comput. Chem.* **1987**, 8, 516–521.
12. D. Vukičević, M. Randić, *Chem. Phys. Lett.* **2005**, 401, 446–450.
13. F. Harary, D. J. Klein, T. P. Živković, *J. Math. Chem.* **1991**, 6, 295–306.
14. W. Gründler, *Wiss. Z. Univ. Halle*, **1982**, 31, 97–116.
15. M. Randić, D. J. Klein, S. El-Basil, P. Calkins, *Croat. Chem. Acta* **1996**, 69, 1639–1660.
16. M. Randić, *Int. J. Quantum Chem.* **1997**, 63, 585–600.
17. M. Randić, *J. Chem. Inf. Comput. Sci.* **2004**, 44, 365–372.
18. M. Randić, *The Open Organic Chemistry Journal*, **2011**, (in press).
19. M. Randić, M. Plavšić, M. Razinger, *MATCH – Commun. Math. Comput. Chem.* **1997**, 35, 243–259.
20. M. Randić, *Chem. Rev.* **2003**, 103, 3449–3605, pp. 3525, 3542–3543.
21. M. Randić, *Chem. Phys. Lett.* **2010**, 500, 123–127.
22. M. Randić, M. Novič, M. Vračko, D. Vukičević, D. Plavšić, *Int. J. Quantum Chemistry*, (in press).
23. M. Randić, D. Vukičević, D. Plavšić, *Ind. J. Chem.* **2011**, 88, 13–23.
24. M. Randić, D. Vukičević, D. Plavšić, (work in progress).
25. Clar, E., *The Aromatic Sextet*, Wiley: London, **1972**.
26. M. Randić, *Chem. Rev.* **2003**, 103, 3449–3605; pp. 3547–3570.
27. M. Randić, *Chem. Rev.* **2003**, 103, 3449–3605, pp. 3591–3592.
28. A. T. Balaban, D. J. Klein, *Polycyclic Arom. Comp.* **2004**, 24, 83–89.
29. M. Randić, A. T. Balaban, *Polycyclic Arom. Comp.* **2004**, 24, 173–193.
30. I. Gutman, D. Vukičević, A. Graovac, M. Randić, *J. Chem. Inf. Comput. Sci.* **2004**, 44, 296–299.
31. A. T. Balaban, M. Randić, *New J. Chem.* **2004**, 28, 800–806.
32. D. Vukičević, M. Randić, A. T. Balaban, *J. Math. Chem.* **2004**, 36, 271–279.
33. A. T. Balaban, M. Randić, *J. Chem. Inf. Comput. Sci.* **2004**, 44, 1701–1707.
34. A. T. Balaban, M. Randić, *J. Math. Chem.* **2005**, 37, 443–453.
35. M. Randić, A. T. Balaban, *J. Chem. Inf. Model.* **2006**, 46, 57–64.
36. M. Randić, A. T. Balaban, *Int. J. Quantum. Chem.* **2008**, 108, 865–897.
37. A. T. Balaban, M. Randić, *Int. J. Quantum. Chem.* **2008**, 108, 898–926.
38. A. T. Balaban, M. Pompe, M. Randić, *J. Phys. Chem.*
39. I. Gutman, A. T. Balaban, M. Randić, M., C. Kiss-Tóth, *Z. Naturforsch.* **2005**, 60a, 171–176.
40. I. Gutman, M. Randić, A. T. Balaban, B. Furtula, V. Vučković, *Polycyclic Aromat. Comp.* **2005**, 25, 215–226.
41. A. T. Balaban, M. Randić, D. Vukičević, *J. Math. Chem.* **2008**, 43, 773–779.
42. M. Randić, H. W. Kroto, D. Vukičević, *J. Chem. Inf. Modeling* **2007**, 47, 897–904.
43. P. John and H. Sachs, *Proceedings of the International Conference on Graph Theory*; Eyba, Teubner: Leipzig, **1984**; p 80.
44. I. Gutman and S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer Verlag, Berlin: **1989**.
45. M. Randić, *Pure Appl. Chem.* **1980**, 52, 1587–1596.
46. M. Randić, *Chem. Rev.* **2003**, 103, 3449–3605; pp. 3532–3539.
47. I. Oonishi, S. Ohshima, S. Fujisawa, J. Aoki, Y. Ohashi, T. M. Krygowski, *J. Mol. Structure* **1992**, 265, 283–292.
48. K. Fries, *Justus Liebigs Ann. Chem.* **1927**, 454, 121.
49. K. Fries, R. Walter, K. Schilling, *Justus Liebigs Ann. Chem.* **1935**, 516, 245.
50. W. Imrich, S. Klavžar, *Product Graphs: Structure and Recognition*, Wiley, **2000**.
51. W. Imrich, S. Klavžar, H. M. Mulder, *SIAM Journal on Discrete Mathematics* **1999**, 12, 111–118.
52. S. Klavžar, H. M. Mulder, Median graphs: characterizations, location theory and related structures, *J. Comb. Math. and Comb. Comput.* **1999**, 30, 103–127.

54. S. Klavžar, H. M. Mulder, R. Škrekovski, An Euler-type formula for median graphs, *Discrete Mathematics* **1998**, *187*, 255–258.
55. D. E. Knuth, The Art of Computer Programming, IV, *Introduction to Combinatorial Algorithms and Boolean Functions*, Addison-Wesley, **2008**, pp. 64–74.
56. S. Klavžar and P. Žigert, Preprint Univ. Ljubljana IMFM **2000**, *38*, 1–9.
57. S. Klavžar, P. Žigert, G. Brinkman, *Discrete Appl. Math.* **2002**, *253*, 35–43.
58. S. Klavžar, A. Vesel, P. Žigert, I. Gutman, *Comput. & Chem.* **2001**, *25*, 569–575.
59. M. Randić, In: *Reviews of Modern Quantum Chemistry, A Celebration of the Contributions of Robert G. Parr*, vol.1, K. D. Sen, Ed., World Scientific: Singapore, **2002**, pp. 204–239.
60. M. Randić, J. Zupan, A. T. Balaban, D. Vikić-Topić, D. Plavšić, *Chem. Rev.* **2011**, *111*, 790–862.
61. M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.*, **2001**, *101*, 1267–1300.

Povzetek

Predstavili smo konstrukcijo algebraičnih (numeričnih) predstavitev za Clarove valenčne formule, ki so v svojih geometrijskih oblikah predstavljeni z π -aromatskimi seksteti opisanih s krogi v benzenoidnih obročih.