Correlations between various ways of accounting for the distribution of π-electrons in benzenoids

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The π-electrons in polycyclic benzenoid hydrocarbons can be counted in two different ways: (i) as partitions of π-electrons in each ring of the benzenoid (according to the conventions that all resonance structures contribute equally, that shared double bonds resonance structures contribute with one π-electron to each of the condensed rings, and that both π-electrons of an unshared double bond belong to the corresponding ring) and (ii) as benzenoid signature, *i.e.* a sequence of six real numbers counting for all resonance structures the numbers of times a ring is assigned according to the above conventions s_i π-electrons, where i takes integer values between 6 and 1. For bridging the gap between these two ways of accounting for the same number of π-electrons, various types of resonance structures (also called Kekule valence structures) are examined and mixed: Fries, Clar, anti-Fries, and quasi-Clar structures.

1 Introduction

Since Friedrich August Kekulé (who later adopted the name August Kekule von Stradonitz, associated with becoming admitted to nobility, and dropping the accent) advanced his famous benzene formula with the "oscillating valence hypothesis" to account for the equivalence of all CC bonds in benzene, chemists tried various ways for explaining the differences in the chemical reactivity of aromatic compounds and of non-aromatics. Initially, other structures (valence isomers of benzene,[1] put forward by Albert Ladenburg, James Dewar, Adolf Claus) had to be ruled out by cleverly devised experimental arguments. Only when quantum chemistry became widely accepted based on ideas introduced by Linus Pauling, George W. Wheland, Erich Hückel, and others, was it possible to deal with the details of aromaticity. Even recently, chemists were surprised by newer experimental facts on bond lengths in aromatic hydrocarbons that could be explained by the "tug-of-war" between the π-electrons and σ-electrons, first described by Shaik and Hiberty more than 20 years ago by means of a VB approach,[2] and confirmed by MO and DFT analysis.[3]

In the present communication, we will discuss the various representations that have been in use for polycyclic benzenoid hydrocarbons. The valence-bond representation of benzene as a resonance hybrid between two equivalent Kekule structures was summed up in a single formula with the circle symbolizing the "aromatic sextet" introduced by Robert Robinson at the end of an experimental paper.[4] Later, Eric Clar put forward arguments (based on studying the electronic absorption spectra of polycyclic benzenoids) advocating a special use of this circle[5,6] so that the following three rules should be observed:[7–9] (i) no sextet circles are allowed in adjacent rings; (ii) all rings without a circle must have a Kekule structure, *i.e.* they need to have zero, one, or two double bonds such that all carbon atoms are sp^2-hybridized; (iii) Clar structures must have maximum numbers of sextet circles subject to the above restrictions. Benzenoid rings with a high share in the π-electron partition correspond to rings with sextet circles. Apart from recent investigations of Clar's theory using various local aromaticity indices such as Krygowski's harmonic oscillator model of aromaticity (HOMA),[10] Schleyer's nucleus-independent chemical shift (NICS),[11] Aihara's π-electron current,[12] Solà's *para*-delocalization index (PDI),[13] and Hosoya's aromaticity index,[14] a special mention must be made of two papers: (1) Morikawa and Klein devised a method based on the "local capacity" for differentiating weights of Clar sextets;[15] and (2) Gutman and colleagues achieved a similar differentiation on the basis of bond-based π-electron contents and the derived π-electron excess of a ring.[16]

Clar postulated that whenever a sextet circle may occupy one of several linearly fused hexagons, it can be placed in any of these hexagons, and this may be indicated by arrow(s), as will be shown in Fig. 1 and in structure (**i**) of Fig. 3. When adjacent rows of linearly fused hexagons allow (in principle) arrows to be inscribed in adjacent hexagons, as shown in the first of the two structures shown in Fig. 1, the above rule (i) applies: once a choice is made for one of the circles, this limits the range for the second circle, as indicated in the second formula. In the following we shall refer to Char structures according to the Guman model.[7]

Benzenoids that have only sextet rings and "empty" rings were called by Clar "*fully-benzenoid hydrocarbons*", observing that they possess a remarkable thermal and chemical stability. In the book by Dias they are called *total resonant sextet benzenoids*.[17] We prefer the name *sextet resonant benzenoids*, as motivated in ref. 18. Klaus Müllen and his coworkers synthesized recently a large number of such sextet resonant

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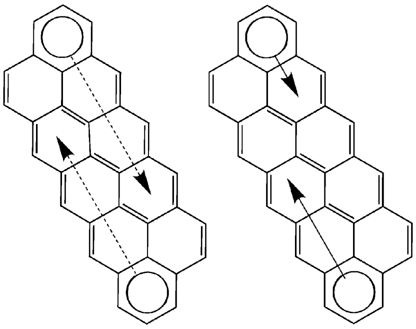

Fig. 1 Although the sextet circles might migrate to any of the available positions indicated by the dotted arrows in the first formula, once one circle defines its range, it limits the range of the other circle, as shown in the second formula.

benzenoids, including giant and dendrimeric ones, taking advantage of their stability and ease of formation *via* intramolecular dehydrogenation reactions.[19] Other features of such sextet resonant benzenoid hydrocarbons are the high resistance to sulfonation associated with insolubility in concentrated sulfuric acid, non-reactivity in diene-like cycloadditions (see below), the high melting point, *e.g.* of the highly symmetrical hexabenzocoronene (above the temperature at which glass becomes fluid), resistance to fragmentation in a mass spectrometer, strong fluorescence and phosphorescence of long life in solid solution at low temperatures, characteristic proton NMR coupling constants, hypsochromic shifts for the longest-wavelength absorption band in the electronic absorption spectrum relative to its isomers, and the highest numbers *K* of Kekule structures among their isomers.[5,6]

Clar synthesized many new polycyclic benzenoids for studying their ultraviolet and visible absorption spectra, classifying their bands according to the wavelength shifts he observed when changing the topology of annelation and addition of new rings. Clar and Zander found that isomeric benzenoids differing in the number of sextet circles reacted differently in cycloadditions.[20] The fully benzenoid tribenzo[*fg*,*ij*,*rst*]pentaphene shown as the first compound in Fig. 2 (to be discussed later under item 4.6) does not react with maleic anhydride or chloranil, whereas its isomer that cannot have five sextet rings, benzo[*qr*]naphtho[2,1,8,7-*fghi*]pentacene (the second one in Fig. 2) shows diene reactivity towards these dienophiles.[20]

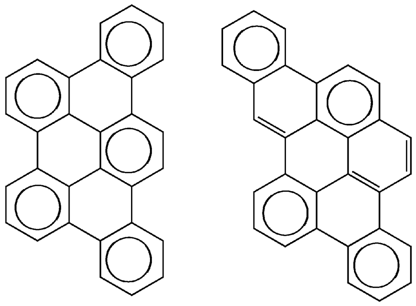

Fig. 2 Two isomeric tribenzoperylenes with different numbers of sextet rings and different reactivities in cycloadditions with maleic anhydride or chloranil.

Clar's collection of benzenoids was used by Biermann and Schmidt for studying the kinetics of Diels–Alder cycloadditions with maleic anhydride.[21] A simple graph-theoretical correlation was found for cycloaddition rates *versus* ($z + 1$), where z is the number of anthracenic subgraphs (linearly annelated benzenoid rings).[22] This parameter can also be used for other correlations of physico-chemical properties of benzenoids.[23]

2 Partitions of π-electrons and signatures of benzenoids

The present authors explored the partition of π-electrons between various rings in polycyclic benzenoids by adopting the convention[24] that a double bond contributes with one π-electron to each of the two rings sharing this bond. Another convention in calculating the π-electron partition was that all *K* resonant structures (Kekule valence structures) of benzenoid should be taken with equal weight. Thus many cata-condensed, peri-condensed and corona-condensed benzenoids (catafusenes, perifusenes and coronafusenes, respectively) were investigated.[25–30] In addition, a different inventory of the distribution of π-electrons in rings of benzenoids was also computed by summing up the number of times each ring

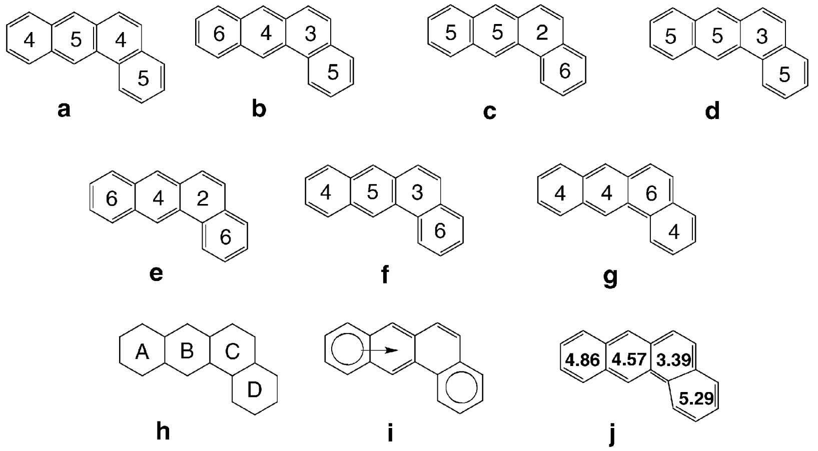

Fig. 3 The seven resonance structures of benz[*a*]anthracene or tetraphene (**a–g**) with the numbers of π-electrons assigned to each ring. The last row displays the ring denominations (**h**), the Clar structure (**i**), and the π-electron partition (**j**).

achieves a count of 6, 5, 4, 3, 2, 1 or 0 π-electrons according to the above convention.[31–34]

For any given benzenoid, one can also produce a table with h rows corresponding to each hexagonal ring (indicated by capital letters starting with A), showing on seven columns denoted by R_6 through R_0 the number of times each of the h benzenoid rings were assigned 6, 5, 4, 3, 2, 1 or 0 π-electrons. The row sum divided by K provides the above-mentioned partition, but one can also look at the column sums (the R_i sequence with $i = 6$ through 0). Obviously, $\sum_i R_i = Kh$. On dividing each R_i value by K, one obtains the r_i sequence, also with $i = 6$ through 0. Again, obviously $\sum_i r_i = h$. The *benzenoid signature* (or the s_i sequence) is a sequence of six real numbers obtained from the r_i sequence by taking into account the number of π-electrons contributed by each of the h rings: $s_i = ir_i$ with the corollary that we arrive at the total number P of π-electrons from a different summation, namely we have $P = \sum_i s_i$. For catafusenes, $P = 4h + 2$, and for perifusenes $P = 4h - int + 2$ where int denotes the number of internal carbon atoms.[17]

For illustration, we provide in Fig. 3 the seven Kekule structures of benz[*a*]anthracene or tetraphene $C_{18}H_{12}$ (**a–g**) and in Table 1 the array of numbers expressing the partitions of the 18 π-electrons. Because $R_1 = R_0 = r_1 = r_0 = s_1 = 0$, all these numbers are not shown in Table 1 for brevity.

In this example for benz[*a*]anthracene, the partition of the 18 π-electrons is shown both in the last formula of Fig. 3 and in the second column of Table 1. The D and A rings are assigned larger shares of π-electrons than the B ring, with the "kink" C-ring having the lowest share. The next five columns of Table 1 indicate the R_i sequences for each of the four rings (since there are no rings with 1 or 0 π-electrons, the corresponding columns have been omitted). The sum of R_i values is $hK = 28$. On dividing the R_i values by K, one obtains the r_i sequences for each of the four rings. Finally, by multiplying these r_i values by the respective numbers of π-electrons, one obtains for each ring the s_i sequences shown in the last five columns of Table 1. The column sum of s_i sequences is called the *signature of the benzenoid*, and it shows in a different manner how the 18 π-electrons are distributed: rings being assigned 5 π-electrons predominate, followed in turn by rings that have assigned 6, 4, 3 and 2 π-electrons.

It will be observed that both the sums of partitions and of the benzenoid signature (the numbers in **boldface**) yield the same value, which for this benzenoid is 18. The question is how to bridge these two different ways of accounting for the distribution of the π-electrons in benzenoids. In the case of tetraphene, resonance structures **c** and **e** in Fig. 3 come closest to the Clar structure, but the signature shows that the major contribution to the distribution of π-electrons originates in quintets followed by sextets and then by quartets, agreeing better with a hybrid with contributions from all structures but the anti-Fries structure **g**. The high reactivity of tetraphene is manifested in the easy hydrogenation at the *meso* (7 and 12) positions, the formation of Diels–Alder adducts with maleic anhydride and the ready oxidation affording tetraphene-7,12-quinone, a dyestuff known as Sirius Yellow G (agreeing with the dienic character of the anthracenic moiety in structures **b** and **e**). The methyl- and dimethyl-derivatives of tetraphene have a higher carcinogenic activity than the parent hydrocarbon, and the system with an annelated cyclopentane ring (cholanthrene) is one of the most potent carcinogens.

It is the purpose of the present paper to show the connection between these two ways of accounting for the π-electrons in benzenoids, and also the connection with various types of electronic structure formulas.

3 Kekule, Fries, anti-Fries, Clar and quasi-Clar electronic structures of benzenoids

We have examined above Kekule and Clar structures. Now we mention that Karl Theophil Fries expressed the view that among the Kekule valence structures, those with the most rings having three conjugated double bonds express best the electronic disposition of π-electrons; such formulas are called "Fries structures". Among all Kekule valence structures, Fries structures are those with the most shared double bonds. In the light of our convention for partitioning π-electrons, it should be stressed that although a ring may have three conjugated double bonds, it may be assigned any number of π-electrons between 6 and 3, depending on presence or absence of surrounding rings sharing double bonds.

In addition to Kekule, Fries, and Clar structures, we must mention also anti-Fries resonance structures, which have the least number of benzenoid rings with three conjugated double bonds. In most cases, anti-Fries resonance structures are one of the pair that has a perimeter of conjugated double bonds. Returning to the above example of benz[*a*]anthracene that is a cata-condensed benzenoid (catafusene), resonance structures **a**, **c** and **d** which all have three rings with three conjugated double bonds may qualify as Fries structures. Among the two resonance structures with two rings having three conjugated double bonds (**b**, **e**, **f**), the second is closer to the Clar structure (**i**), and we will call it the "quasi-Clar resonance structure" because in most cases none of the Kekule valence structures achieves the goal of duplicating the Clar structure. Finally, the anti-Fries structure is **g** because it has the lowest number (one) of rings having three conjugated double bonds, and because the ring C with the highest assigned number of π-electrons corresponds to the ring with the lowest number of π-electrons both in the Clar structure (**h**) and in the partition (**j**). One should note that there is a fairly close parallelism between the

Table 1 The partition of the 18 π-electrons in the four rings of benz[*a*]anthracene followed by the R_i-sequences, r_i-sequences and s_i-sequences

Ring	Partition	R_6	R_5	R_4	R_3	R_2	r_6	r_5	r_4	r_3	r_2	s_6	s_5	s_4	s_3	s_2
A	**4.857**	2	2	3	0	0	0.286	0.286	0.429	0.000	0.000	1.714	1.429	1.714	0.000	0.000
B	**4.571**	0	4	3	0	0	0.000	0.571	0.429	0.000	0.000	0.000	2.857	1.714	0.000	0.000
C	**3.286**	1	0	1	3	2	0.143	0.000	0.143	0.429	0.286	0.857	0.000	0.571	1.286	0.571
D	**5.286**	3	3	1	0	0	0.429	0.429	0.143	0.000	0.000	2.571	2.143	0.571	0.000	0.000
Total	**18.000**	6	9	8	3	2						**5.143**	**6.429**	**4.571**	**1.286**	**0.571**

data shown in the partition (**j**), Clar (**h**) and quasi-Clar structure (**e**).

4 Six more examples for π-electronic structures of benzenoids

We shall illustrate all these various types of π-electronic structures with two other catafusenes and four perifusenes which are Kekulean, *i.e.* which have non-zero K values. In order to avoid the less interesting "disconnected" perifusenes (such as zethrene or perylene) we will discuss only perifusenes having contiguous internal vertices.

4.1 Phenanthrene

The starting example is phenanthrene, which has $K = 5$ resonance structures, three of which are presented in Fig. 4, following the Clar structure with two sextet rings (**k**). The Fries structure with all three rings having three conjugated double bonds (**l**) is followed by the pair of resonance structures that have a perimeter of conjugated double bonds. As an exceptional case, characteristic for fibonacenes (zigzag non-branched catafusenes), the first of these structures (**m**) happens to coincide with the Clar structure (**k**), while the second one (**n**) is the anti-Fries structure with only one ring (the central ring) having three conjugated double bonds. The remaining two resonance structures of phenanthrene (not shown in Fig. 2) have each two rings with three conjugated double bonds. Again, as an exceptional case, the average of the two structures with conjugated double bonds on the perimeter happens to be the Fries structure.

The chemical behavior of phenanthrene agrees with the Clar structure in the easy additions to the central double bond between carbons 9 and 10, *e.g.* of bromine, leading to isolable 9,10-dibromo-9,10-dihydrophenanthrene. Under heating, hydrogen bromide elimination takes place affording the 9-bromophenanthrene, a fact that led to speculations (disproved later) that all aromatic electrophilic substitutions might involve intermediate addition products. Ozonolysis attacks the C-9–C-10 bond, and oxidation with chromic acid yields 9,10-phenanthrenequinone, which on further oxidation with hydrogen peroxide affords diphenic acid by fission of the C-9–C-10 bond. The Pauling bond order for the C-9–C-10 bond is 1.8, also in fair agreement with the Clar structure and the experimental bond distance, which is shorter than normal aromatic C–C bonds.

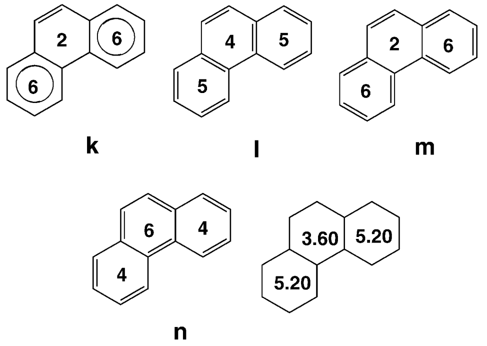

Fig. 4 Phenanthrene with its Clar structure (**k**) Fries structure (**l**), one of the two structures that have a perimeter of conjugated double bonds and coincides with the Clar structure (**m**), and the other one (the anti-Fries structure, **n**). The last formula indicates the partition of the 14 π-electrons.

However, the partition indicates a much larger share of π-electrons (almost double) than the Clar formula, and closer to the Fries structure. In Table 2 we show that averaging contributions from two or three of the resonance structures displayed in Fig. 4 leads to a fair agreement with the signature of phenanthrene (last column of Table 2).

4.2 Triphenylene

The next example is also a catafusene: triphenylene, a fully-benzenoid hydrocarbon, having $K = 9$ Kekule valence structures. From here onwards, resonance structures become so numerous that we have to designate by boldface numbers those that are shown in figures. Fig. 5 presents the Clar structure of triphenylene (**1**) which (again exceptionally) happens to coincide with a resonance structure (**2**), which is one of the two structures with conjugated double bonds on the perimeter. The Fries structure is **3**, and the anti-Fries structure is **4**, the other structure with conjugated double bonds on the perimeter. Finally, the π-electron partition is shown as formula **5**.

Again, the π-electron partition agrees better with the Fries structure (**3**, having 5 + 5 + 5 + 3 π-electrons) than with the Clar structure (**1** or **2**, having 6 + 6 + 6 + 0 π-electrons). Whereas the Clar structure has only π-electron sextets and the Fries structure has mostly π-electron quintets, a hybrid between two or three resonance structures from Fig. 5 provides a fair agreement with the signature of triphenylene (last column of Table 3). The remarkably high stability of triphenylene is manifested by its resistance to sulfonation by sulfuric acid, and by the lack of reactivity towards cycloaddition with maleic anhydride.

4.3 Pyrene

All the next examples will be for perifusenes. We start with pyrene, the smallest kekulean tetraperifusene, which has six resonance structures, all presented in Fig. 6 (**7–12**). An interesting natural source of pyrene was the fraction of polycyclic aromatic hydrocarbons accompanying the mercury ore from Idria (Slovenia), where pyrene was present in amounts of about 20%. The Clar structure **6** does not correspond to any Kekule structure, as it happens for practically all perifusenes and most catafusenes. Structures **9** and **10** are both Fries structures, and their π-electron partition averages are represented by structures **7** and **8** which are among the few numerical (algebraic) structures that do not correspond uniquely to one and only one geometrical resonance structure. Formulas **11** and **12** are the closest to anti-Fries structures with conjugated double bonds on the periphery happen to be mirror images to one another, and their average is expressed by formula **13** which does not correspond to any Kekule structure. The π-electron partition is shown in formula **14**.

There is a better agreement between the π-electron partition (**14**) of pyrene and the Fries structures (**9** and **10**) than with the Clar structure (**6**). Also, the signature indicated in Table 4

Table 2 π-Electronic data for phenanthrene with its Clar (**k**), Fries (**l**) and anti-Fries (**n**) resonance structures. The signature is shown in the last column

Ring	Clar **k** (or **m**)	Fries **l**	Anti-Fries **n**	(**k** + **l**)/2	(**k** + **l** + **n**)/3	Signature
6π	2 × 6 = 12	—	1 × 6 = 6	6.0	6.0	s_6 = 6.0
5π	—	2 × 5 = 10	—	5.0	3.3	s_5 = 3.2
4π	—	1 × 4 = 4	2 × 4 = 8	2.0	4.0	s_4 = 1.8
3π	—	—	—	0	0	s_3 = 0.8
2π	1 × 2 = 2	—	—	1.0	0.7	s_2 = 0.2
1π	—	—	—	0	0	s_1 = 0
Total	14	14	14	14.0	14.0	14.0

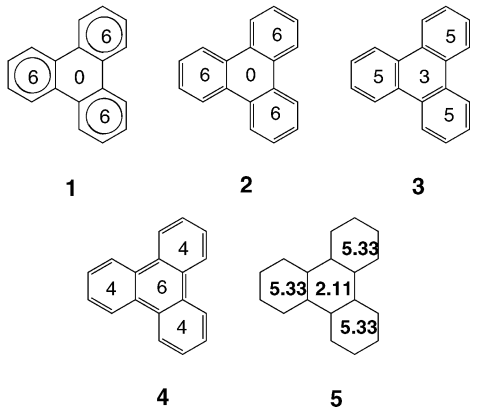

Fig. 5 The Clar structure and three from the nine resonance structures of triphenylene (**2**, **3**, **4**); its π-electron partition is indicated in formula **5**.

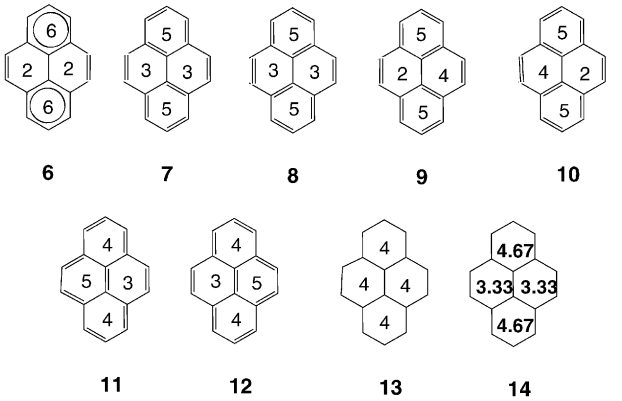

Fig. 6 The Clar structure of pyrene **6**, all resonance structures **7–12**, average (**13**) of **11** and **12**, and the π-electron partition of pyrene (**14**).

reveals that there is no contribution from π-electron sextets, but only from π-electron quintets. The signature agrees fairly well with averages of two or three resonance structures from Fig. 6.

The chemical behavior of pyrene is not in full agreement with the Clar structure (**6**), because two hydrogen atoms can add either to the 1,2-C–C bond as required by the Clar structure, or to 3,8- and 3,10-positions. Likewise, oxidation proceeds more readily in 3,8- and 3,10-positions affording the corresponding pyrenequinones, whereas ozonolysis attacks the 1,2-C–C bond.

4.4 Dibenzo[*fg*,*op*]pyrene

In Fig. 7 we present a fully-benzenoid hexaperifusene with two internal vertices, dibenzo[*fg*,*op*]pyrene, which has a quite high melting point (340–342 °C). Its Clar structure is **15**, with no correspondence to any Kekule valence structure. It has K = 20 resonance structures, four of which are displayed in Fig. 7: the Fries structure **16**, a quasi-Clar structure (**17**), and the two structures that have conjugated double bonds on the periphery, **18** and **19**, again mirror images of each other, with an average π-electron count presented as **20**. The π-electron partition is shown as **21**.

Dibenzo[*fg*,*op*]pyrene is much less reactive than pyrene, and it is insoluble in concentrated sulfuric acid. The π-electron partition (**21**) agrees better with the Fries (**16**) or quasi-Clar structure (**17**) than with the Clar structure, which contains only π-electron sextets and empty rings. The signature indicates that the major contribution to the π-electron distribution comes from π-electron quintets and not from π-electron sextets. However, the partition of π-electrons is more accurately mirrored by the quasi-Clar structure (**17**) than the Fries structure (**16**). The signature (Table 5) is not represented satisfactorily by any of the averages between two or three resonance structures from Fig. 7, because none of these structures has benzenoid rings that are assigned with three π-electrons, so that in principle one should include also other resonance structures from the set of 20.

Table 3 π-Electronic data for triphenylene with the Clar (**1**), Fries (**3**) and anti-Fries (**4**) electronic structures. The signature is shown in the last column

Ring	Clar **1** (or **2**)	Fries **3**	Anti-Fries **4**	(**1** + **3**)/2	(**1** + **3** + **4**)/3	Signature
6π	3 × 6 = 18	—	1 × 6 = 6	9.0	8.0	s_6 = 8.67
5π	—	3 × 5 = 15	—	7.5	5.0	s_5 = 6.67
4π	—	—	3 × 4 = 12	—	4.0	s_4 = 1.33
3π	—	1 × 3 = 3	—	1.5	1.0	s_3 = 0.33
2π	—	—	—	0	0	s_2 = 0.67
1π	—	—	—	0	0	s_1 = 0.33
Total	18	18	18	18.0	18.0	18.00

Table 4 Pyrene with its Clar structure (**6**) quasi-Clar (**7**) and Fries resonance structure (**9**) and averages of two or three from these last structures. The signature is displayed in the last column

Ring	Clar **6**	Quasi-Clar **7**	Fries **9**	Anti-Fries **11**	(**7** + **9**)/2	(**7** + **9** + **11**)/3	Signature
6π	2 × 6 = 12	—	—	—	0	0	s_6 = 0
5π	—	2 × 5 = 10	2 × 5 = 10	1 × 5 = 5	10.0	8.3	s_5 = 8.33
4π	—	—	1 × 4 = 4	2 × 4 = 8	2.0	4.0	s_4 = 4.00
3π	—	2 × 3 = 6	—	1 × 3 = 3	3.0	3.0	s_3 = 3.00
2π	2 × 2 = 4	—	1 × 2 = 2	—	1.00	0.7	s_2 = 0.67
1π	—	—	—	—	0	0	s_1 = 0
Total	16	16	16	16	16.0	16.0	16.0

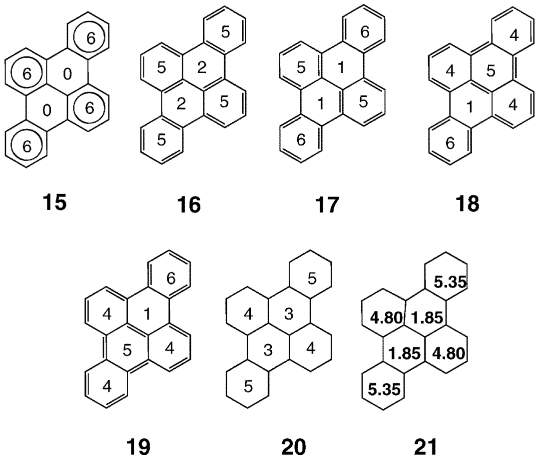

Fig. 7 Dibenzo[*fg*,*op*]pyrene with its Clar structure **15**, four of the 20 resonance structures (**16–19**), the average (**20**) of **18** and **19**, and the π-electron partition, **21**.

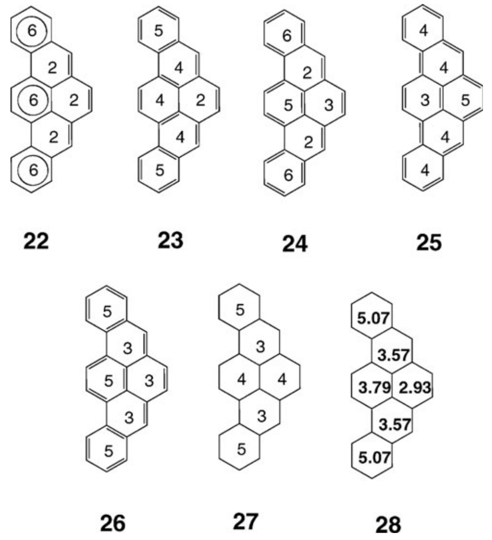

Fig. 8 Dibenzo[*a*,*i*]pyrene with its Clar structure, three of the 14 Kekule valence structures (**23–26**), the average (**27**) of **24** and **25**, and the π-electron partition, **28**.

4.5 Dibenzo[*a*,*i*]pyrene

The isomeric hexaperifusene, dibenzo[*a*,*i*]pyrene or benzo[*rst*]-pentaphene, which is not fully-benzenoid, has only $K = 14$ resonance structures, four of which are shown in Fig. 8 as formulas **23–26**, following the Clar structure **22**, which again has no correspondence to any resonance structure. The Fries structure is **23**, and the two structures that have conjugated double bonds on the periphery are **24** (the quasi-Clar structure) and **25** (the anti-Fries structure). The average of these two structures (which does not correspond to any of the 14 resonance structures is shown as **27**. The π-electron partition is presented as **28**.

This isomer is soluble in concentrated sulfuric acid, unlike the preceding hydrocarbon, can be easily hydrogenated, is present in cigarette smoke and is highly carcinogenic.

The π-electron partition (**28**) does not agree with the Clar structure (**22**) but agrees well with the Fries structure (**23**) and the quasi-Clar structure (**24**). The signature indicates that about half of the 24 π-electrons are present as quintets, a quarter as sextets, and the remaining s_i values have $i = 0$–4. None of the three averages between two or three resonance structures gives a good agreement with the signature (Table 6), but either by including more than three structures, or by considering other resonance structures from the set of 14, it may be possible to obtain better agreements.

4.6 Tribenzo[*fg*,*ij*,*rst*]pentaphene

The last example is tribenzo[*fg*,*ij*,*rst*]pentaphene, a fully-benzenoid octaperifusene with a melting point 388–389 °C, which can be sublimed, and does not react with boiling maleic

Table 5 Distribution of the 24 π-electrons in dibenzo[*fg*,*op*]pyrene according to various electronic structures presented in Fig. 7. The signature is displayed in the last column

Ring	Clar **15**	Fries **16**	Quasi-Clar **17**	**18**	(**16** + **17**)/2	(**16** + **17** + **18**)/3	Signature
6π	4 × 6 = 24	—	2 × 6 = 12	1 × 6 = 6	6.0	6.0	s_6 = 4.29
5π	—	4 × 5 = 20	2 × 5 = 10	1 × 5 = 5	15.0	11.7.0	s_5 = 7.50
4π	—	—	—	3 × 4 = 12	0	4.0	s_4 = 6.00
3π	—	—	—	—	0	0	s_3 = 4.93
2π	—	2 × 2 = 4	—	—	2.0	1.3	s_2 = 1.29
1π	—	—	2 × 1 = 2	1 × 1 = 1	1.0	1.0	s_1 = 0
Total	24	24	24	24	24.0	24.0	24.0

Table 6 Distribution of the 24 π-electrons in dibenzo[*a*,*i*]pyrene according to various electronic structures presented in Fig. 8. The signature is displayed in the last column

Ring	Clar **22**	Fries **23**	Quasi-Clar **24**	Anti-Fries **25**	**26**	(**23** + **24**)/2	(**24** + **26**)/2	(**23** + **24** + **26**)/3	Signature
6π	3 × 6 = 18	—	2 × 6 = 12	—	—	6.0	6.0	4.0	s_6 = 5.40
5π	—	2 × 5 = 10	1 × 5 = 5	1 × 5 = 5	3 × 5 = 15	7.5	10.0	10.0	s_5 = 13.50
4π	—	3 × 4 = 12	—	4 × 4 = 16	—	6.0	0	4.0	s_4 = 2.40
3π	—	—	1 × 3 = 3	1 × 3 = 3	3 × 3 = 9	1.5	6.0	4.0	s_3 = 0.60
2π	3 × 2 = 6	1 × 2 = 2	2 × 2 = 4	—	—	3.0	2.0	2.0	s_2 = 1.40
1π	—	—	—	—	—	0	0	0	s_1 = 0.70
Sum	24	24	24	24	24	24.0	24.0	24.0	24.00

Table 7 Distribution of the 30 π-electrons in tribenzo[*fg*,*ij*,*rst*]perylene according to various electronic structures presented in Fig. 9. The signature is displayed in the last column

Ring	Clar **29**	Quasi-Clar **30**	**31**	Fries **32**	(**30** + **32**)/2	(**30** + **31** + **32**)/3	Signature
6π	5 × 6 = 30	2 × 6 = 12	2 × 6 = 12	—	6.0	8.0	s_6 = 5.33
5π	—	3 × 5 = 15	2 × 5 = 10	4 × 5 = 20	17.5	15.0	s_5 = 15.33
4π	—	—	1 × 4 = 4	1 × 4 = 4	2.0	2.7	s_4 = 4.63
3π	—	1 × 3 = 3	—	2 × 3 = 6	4.5	3.0	s_3 = 1.47
2π	—	—	2 × 2 = 4	—	0	1.3	s_2 = 2.22
1π	—	—	—	—	0	0	s_1 = 1.02
Total	30	30	30	30	30.0	30.0	30.00

anhydride, as shown by Clar and Zander.[20] It is shown in Fig. 9 with its Clar structure (**29**) that does not correspond to any Kekule valence structure and five of its 45 resonance structures (**30–34**): a quasi-Clar structure (**30**), a next-to-quasi-Clar structure (**31**), the Fries structure **32**, and the two structures with conjugated double bonds on the periphery: **33** having three rings with three double bonds and the anti-Fries structure **34** with only two rings with three double bonds. The average of **33** and **34** is shown as **35**, which does not correspond to any Kekule valence structure. The π-electron partition is presented as **36**.

From all the above examples it results that the Clar theory postulates that hexagons in benzenoids have a pronounced tendency of acquiring π-electron sextets at any price, without regard to other rings, achieving perfection in fully-benzenoid hydrocarbons with rings being either sextet rings or empty rings, most often not corresponding to any resonance structure. On the other hand, Fries structure(s), which are among the resonance structures, achieve a more balanced π-electron distribution. On looking at all resonance structures, one can sometimes find "quasi-Clar" structures that have almost as many sextet rings, and leaving almost as many empty rings, as in Clar structures. On comparing the π-electron partition with Clar structures, one can observe that indeed the highest values do correspond to sextet rings, but seldom are there rings with zero π-electrons in the partition.[35]

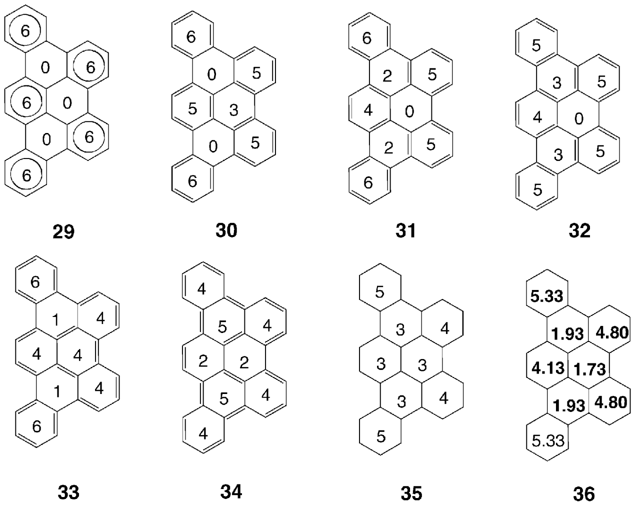

Fig. 9 Tribenzo[*fg*,*ij*,*rst*]pentaphene with its Clar structure **29**, five of its 45 resonance structures (**30–34**), the average (**35**) of the last two structures, and the π-electron partition, **36**.

In Table 7 we present in the last column the signature of tribenzo[*fg*,*ij*,*rst*]pentaphene showing that a quarter of the 30 π-electrons occur in quintet π-electron groups. Then we show how one can balance the strict and unrealistic requirements of the Clar structure **29** (five sextet rings and three empty rings) and the accommodating situation of the Fries structure (no sextet rings, but two thirds of the π-electrons in quintet π-electron groups) with a compromise situation, based on the realistic quasi-Clar structure **30**, the next-to-quasi-Clar structure **31**, and the Fries structure **32**. On comparing the last three columns, it can be seen that the signature can be satisfactorily approximated by an average of two or three electronic structures.

5 Conclusions

Clar's theory of the aromatic sextet has a sound experimental support, based mainly on the chemical reactivity of benzenoids. However, in many cases the Fries π-electronic resonance structures are closer to physical manifestations of aromaticity and to the two ways of accounting for the distribution of π-electrons in polycyclic conjugated systems developed by the present authors and based both on the simple postulate that on averaging for all resonance structures, shared double bonds contribute for each ring with one π-electron, and unshared double bonds with two π-electrons. These two ways are: (i) π-electron partition for each ring, and

(ii) the signature of the benzenoid, counting the number of times rings are assigned 6, 5, 4, 3, 2 or 1 π-electron.

A possible comparison with the John Nash's contribution to game theory may be made. Departing from the von Neumann–Morgenstern treatment of conflictual games,[36] he concluded that in cooperative or non-cooperative games or bargaining situations, mutually advantageous equilibrium points (self-countering *n*-tuples of strategies) can be reached.[37] In our case, the Clar postulate that "winner takes all π-electrons" leads to unrealistic (and most often unreachable) resonance structures, at high contradiction to the benzenoid signature. By adopting a compromise average with several resonance structures, in which the Fries structure has an important contribution, the sharing in the distribution of π-electrons can be achieved in better agreement with the benzenoid signature. Thus, whereas the Clar structure puts highest weight on 'sextet rings' (in good agreement with chemical reactivity of benzenoids, but in disagreement with some of their physical data), the signature usually indicates that 'quintet rings' have the highest contribution. The "electronic compromise" between several significant resonance structures makes it possible to bridge the gap between the partition of π-electrons among benzenoid rings and the signatures of the polycyclic aromatic hydrocarbons.

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