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Invited Review

Cyclic Conjugation Energy Effects in Polycyclic π-Electron Systems

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Summary. The fact that cyclic arrangements of double bonds have a dramatic effect on the behavior of conjugated organic molecules is known since the 19th century. The fact that in monocyclic conjugated systems the size of the cycle and the number of π-electrons involved is decisive for their stability ("aromaticity") or lack of stability ("antiaromaticity") is known since the 1930s. In polycyclic π-electron systems several cyclic effects are present simultaneously and their separation became possible only recently. A molecular orbital method has been elaborated, by means of which the energy effects of individual cycles in polycyclic π-electron systems can be estimated. This method is briefly outlined and illustrated by pertinent examples. An exhaustive bibliography of the topic considered is given.

Keywords. Cyclic conjugation; Energy-effect of cyclic conjugation; Total π-electron energy; Chemical graph theory.

Introduction

The extraordinary chemical stability of benzene and the fact that, in spite of its low hydrogen content, it does not behave like ordinary unsaturated organic compounds has fascinated chemists already in the middle of the 19th century. Until the 1930s none of the numerous theoretical attempts, put forward to give a rational explanation of this "anomaly", could be characterized as satisfactory. In 1931 *Erich Hückel* applied the (then) new quantum mechanics to the *Benzolproblem* [1, 2] and obtained the long-sought solution: *Hückel*'s molecular orbital approach revealed that the six π-electrons in benzene form a stable, closed-shell configuration.

When the very same molecular orbital reasoning was applied to other monocyclic π-electron systems, a surprising discovery was made. A stable, closed-shell configuration is encountered whenever the number of π-electrons is 2 or 6 or 10 or .... Even more surprisingly, if the number of π-electrons is 4 or 8 or 12 or ..., then an open-shell, unstable configuration is predicted. This is the famous *Hückel*

$(4k+2)$-*Rule*, whose details can nowadays be found in textbooks of Theoretical Organic Chemistry.

The original version of the $(4k+2)$-rule speaks of open- and closed-shell π-electron configurations. It seems that *Breslow* and *Mohácsi* [3] were the first to realize that the $(4k+2)$-rule has also a thermodynamic, energy-based, aspect: the closure of a cycle in an initially acyclic π-electron system lowers the energy (causes thermodynamic stabilization) if the number of π-electrons is $4k+2$, $k = 0, 1, 2, \ldots$, and increases the energy (causes thermodynamic destabilization) if the number of π-electrons is $4k$, $k = 1, 2, 3, \ldots$.

Once the thermodynamic connection of the *Hückel* rule was recognized, the stage was set for seeking for an extension of the rule from monocyclic to polycyclic conjugated π-electron species. The importance of this extension is evident: whereas there exist one or two dozens of chemically relevant monocyclic conjugated molecules and ions, there are thousands of known (and practically endless possible) polycyclic π-electron systems.

Michael Dewar attempted to cut the Gordian knot. Based on perturbation-molecular-orbital arguments, he stated the extended *Hückel* $(4k+2)$-rule, according to which the $(4k+2)$-membered cycles of a polycyclic conjugated molecule have a thermodynamically stabilizing effect, whereas the $(4k)$-membered cycles thermodynamically destabilize the system (see Chapter 6.12 in Ref. [4]). Because it only speaks of ''stabilization'' and ''destabilization'', but not how large these are, *Dewar*'s version of the extended $(4k+2)$-rule is qualitative and – as we shall see later – not generally valid. In the best case, it served as a motivation for further investigations, that started in the 1970 and eventually lead to the formulation of a quantitative theory of cyclic conjugation. In what follows we outline the details of this theory.

Of course, the theory discussed and exemplified below is not the only approach that has been put forward for quantifying cyclic conjugation in polycyclic conjugated molecules. Three other, frequently employed ones, are based on the counting of *Kekulé* structures [5, 6], analysis of conjugated circuits [7, 8], and the concept of aromatic sextet [9, 10]; their details are found in a book [11] and a recent extensive review [12].

Total π-Electron Energy and its Dependence on Molecular Structure

Because we are concerned with the energy-effects caused by a cyclic arrangement of π-electrons, it is purposeful to first briefly summarize the main known facts on the dependence of total π-electron energy on molecular structure.

The total π-electron energy E and all energy-effects considered here are computed by means of the tight-binding *Hückel* molecular orbital (*H*MO) approximation [13] and, as usual, expressed in the units of the carbon–carbon resonance integral β. Although E cannot be directly measured, it is known to be reasonably well related to the experimentally accessible thermodynamic data [14–17]. For the present considerations the actual value of the parameter β is not important, except that its value is negative. We nevertheless mention that for thermochemical purposes the recommended value of β is $-137.0\,\mathrm{kJ/mol}$, and that the heats of atomization computed by the *H*MO method are accurate to 0.1%, implying that in favorable cases E is accurate up to ± 0.005 β-units [16].

Bearing in mind that β is negative-valued, any structural factor that increases (resp. diminishes) E, causes thermodynamic stabilization (resp. destabilization) of the corresponding conjugated molecule. In this paper we restrict the consideration to (polycyclic) conjugated hydrocarbons.

In *H*MO-theoretical considerations it is advantageous to use the formalism of graph theory [14, 18]. If so, then $E = E(G)$, where G is the respective molecular graph. Therefore, in what follows we may speak about the dependence of E on the structure of the molecular graph G. (Recall that the number of vertices and edges of G are equal to the number of carbon atoms and carbon–carbon bonds, respectively, of the underlying conjugated molecule [14, 18]. Then the number of hydrogen atoms is equal to $3n - 2m$.)

The main structural factors determining E are the following:

- The gross part (over 99%) of E is determined by the size of the molecule, *i.e.*, by the parameters n and m, or – what is the same – by the number of carbon and hydrogen atoms [19, 20].
- The total π-electron energy depends on the cycles present in the conjugated system, both their number, size, and mutual arrangement; this matter is discussed in due detail in the subsequent sections.
- A direct consequence of the presence of cycles is the existence of several *Kekulé*-type structural formulas, often a very large number thereof. The relation between E and the *Kekulé* structure count K has been much investigated, especially in the case of benzenoid hydrocarbons [21, 22]. Roughly speaking, E increases as a linear function of K. Yet, a complete solution of the problem has not been obtained [23, 24].
- Another effect influencing E is the extent of branching of the carbon-atom skeleton [25, 26]. Note, however, that a quantitative relation between E and branching has never been reported, perhaps because there exists no unique numerical measure of (what intuitively is regarded as) "branching" [27, 28]. Anyway, E depends on the number of branching points, their degrees, their location in the molecular graph, and their mutual constellation.
- That non-bonding molecular orbitals have a diminishing effect on E was recognized long ago [25, 26]. However, it was demonstrated only quite recently that if all the above specified structural features are kept constant, then E is a (decreasing) linear function of the number of non-bonding molecular orbitals [29].

Total π-Electron Energy and its Dependence on Cycles. Theory

In order to give the reader an idea of how the theory of cyclic conjugation is constructed we sketch some necessary notions of graph theory and graph spectral theory. More details can be found in the books [14, 18] and elsewhere [30, 31].

A conjugated hydrocarbon is represented by its molecular graph. The construction of such a graph should be evident from the example shown in Fig. 1.

The number of vertices of a molecular graph G is denoted by n. Two vertices connected by an edge are said to be adjacent.

If the vertices of the graph G are labelled by $v_1, v_2, \ldots, v_n$, then the structure of G can be represented by the adjacency matrix $A = A(G) = ||A_{ij}||$. This is a square matrix of order n, whose elements A_{ij} are defined so that $A_{ij} = A_{ji} = 1$ if the vertices v_i and v_j are adjacent, and $A_{ij} = 0$ otherwise. The characteristic polynomial

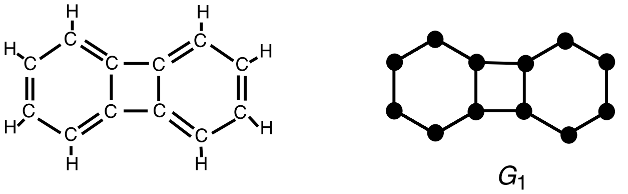


Fig. 1. The structural formula of biphenylene and the corresponding molecular graph G_1; the graph G_1 has $n = 12$ vertices and $m = 14$ edges; the vertices of G_1 represent the carbon atoms, whereas its edges represent the carbon–carbon bonds of biphenylene

of the graph G, denoted by $\phi(G, \lambda)$ is equal to the determinant $\det(\lambda I - A)$ where I stands for the unit matrix.

The first significant result in the theory of total π-electron energy was obtained by *Charles Coulson* as early as in 1940 [32] (Eq. (1)).

$$E(G) = \frac{1}{\pi}\int_{-\infty}^{+\infty}\left[n - ix\frac{\phi'(G, ix)}{\phi(G, ix)}\right]dx \tag{1}$$

In Eq. (1), ϕ' stands for the first derivative of the characteristic polynomial, and i is the imaginary unit, $i = \sqrt{-1}$.

A quarter of century later, *Horst Sachs* discovered the way in which the characteristic polynomial of a graph depends on its structure. His result, nowadays referred to as the *Sachs* theorem [30, 33] reads as follows (Eq. (2)) where the summation goes over all so-called *Sachs* graphs of the graph G. These *Sachs* graphs, essential for the present considerations, are defined as follows.

$$\phi(G, \lambda) = \lambda^n + \sum_S (-1)^{p(S)} 2^{c(S)} \lambda^{n-n(S)} \tag{2}$$

By K_2 is denoted the graph consisting of two vertices, connected by an edge. By C_n is denoted the cycle possessing n vertices, $n = 3, 4, 5, \ldots$, see Fig. 2.

A graph, the components of which are K_2 and/or C_3 and/or C_4 and/or C_5 and/or C_6 and/or ..., is called a *Sachs* graph. Some of these *Sachs* graphs are contained in the molecular graph; examples are found in Fig. 3.

In Eq. (2), $p(S)$, $c(S)$, and $n(S)$ are the number of components, cyclic components and vertices, respectively, of the *Sachs* graph S. For instance, the *Sachs* graphs S_1, S_4, S_7, and S_9 (depicted in Fig. 3), have, respectively, 1, 6, 3, and 2 components, 0, 0, 1, and 2 cyclic components, as well as 2, 12, 10, and 12 vertices.

When Eqs. (1) and (2) are combined, one arrives at an explicit expression for the structure-dependence of the total π-electron energy [34].

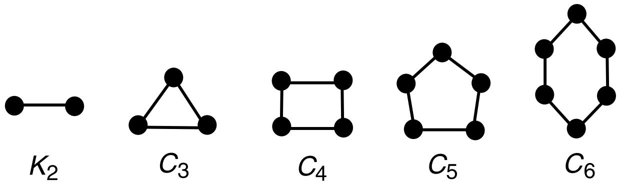


Fig. 2. Components of the *Sachs* graphs; any *Sachs* graph consists of components that are K_2 and/or C_3 and/or C_4 and/or ..., *cf.* Fig. 3

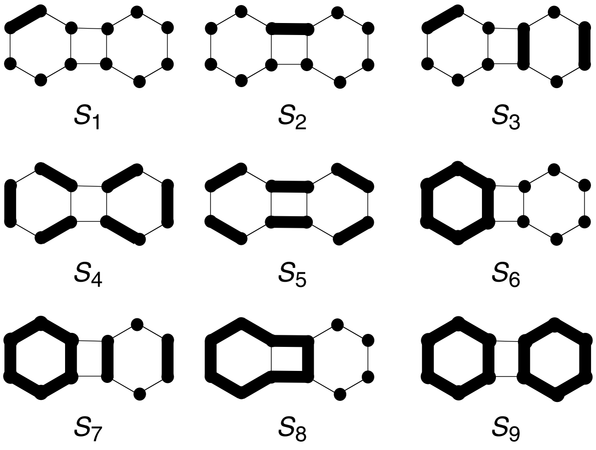


Fig. 3. Examples of *Sachs* graphs (indicated by tick lines) contained in the biphenylene graph G_1; the biphenylene graph contains a total of 514 *Sachs* graphs; each of these graphs can be understood as representing a structural feature of the respective molecule

Each *Sachs* graph can be understood as representing a particular structural detail of the underlying molecule. Using the fortunate fact that the total π-electron energy depends on *Sachs*-graph-type structural features, and that (some) *Sachs* graphs consist of cycles, it was possible to express the effect $ef(G, Z)$ of a particular cycle Z, contained in the molecular graph G, on the respective E-value [35, 36] (Eq. (3)).

$$ef(G,Z) = \frac{1}{\pi}\int_{-\infty}^{+\infty} \ln \frac{\phi(G,ix)}{\phi(G,ix) + 2\,\phi(G-Z,ix)}\,dx \tag{3}$$

In Eq. (3) $G - Z$ denotes the subgraph obtained by deleting the cycle Z from the graph G. Whenever $ef(G, Z)$ is positive, the cycle Z stabilizes the molecule; negative ef-values imply destabilization.

The theory put forward in Refs. [35, 36] was eventually further elaborated [37–40], but these mathematical details will not be discussed here.

Total π-Electron Energy and its Dependence on Cycles. Examples

In Fig. 4 are given the energy-effects, computed by means of Eq. (3), of two typical polycyclic conjugated systems.

The examples shown in Fig. 4 illustrate some basic properties of cyclic conjugation:

- Not only rings, but also larger cycles (often ignored by chemists) have their energy contributions.
- The energy-effect usually decreases with increasing size of the cycle, but has a non-negligible value also for cycles of larger size.
- Cycles of the same size may have significantly different energy-effects.
- In the examples shown in Fig. 4, the 6-, 10-, and 14-membered cycles have a stabilizing effect, and the 4-, 8-, and 12-membered cycles a destabilizing effect. This agrees with the extended $(4k + 2)$-rule. However, contrary to what chemists may expect based on their "intuition", the $(4k + 2)$-rule is not generally obeyed. For details see below.

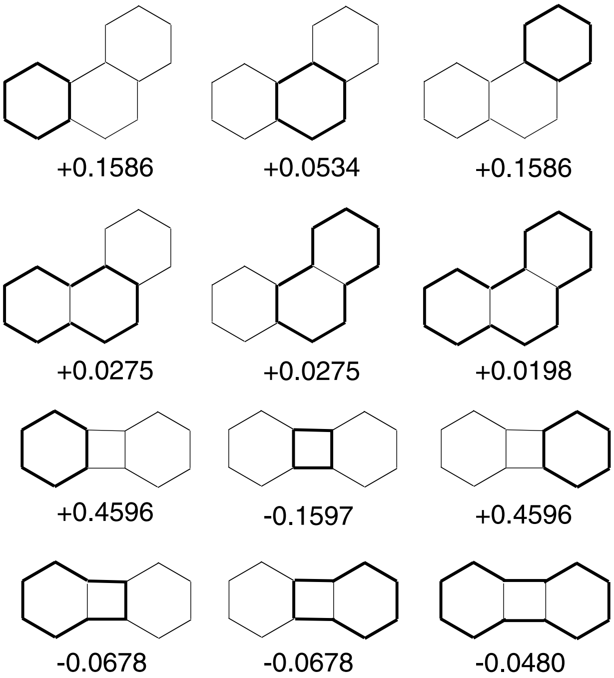


Fig. 4. Energy-effects of the cycles of phenanthrene and biphenylene, expressed in the units of the *H*MO resonance integral β

The Extended *Hückel* ($4k + 2$)-Rule Revisited

By means of Eq. (3), for each particular cycle Z in each particular conjugated system whose molecular graph is G it is possible to test if the extended $(4k+2)$-rule is satisfied. According to this rule, it should be

(a) $ef(G,Z) > 0$ whenever the size of the cycle Z is $4k+2$, *i.e.*, 6 or 10 or 14 or ...;
(b) $ef(G,Z) < 0$ whenever the size of the cycle Z is $4k$, *i.e.*, 4 or 8 or 12 or ....

A detailed mathematical analysis [41–44] revealed that only the (b)-part of the above rule is generally valid. In Ref. [42] the following result was obtained:

Rule A. *In all alternant hydrocarbons, all* $(4k)$*-membered cycles have a negative ef-value, that is have a destabilizing effect.*

The counterpart of this rule, namely that $(4k+2)$-membered cycles have a positive *ef*-value, is not always true [45–47]. Some characteristic examples of the violation of the $(4k+2)$-rule are shown in Figs. 5 and 6.

The validity of the (a)-part of the extended $(4k+2)$-rule could be verified only in some special cases:

Rule B. [48] *In all monocyclic conjugated systems both parts* (*a*) *and* (*b*) *of the extended* $(4k+2)$*-rule hold.*

Rule C. [49] *Part* (*a*) *of the extended* $(4k+2)$*-rule holds for all catacondensed benzenoid hydrocarbons. Because all cycles in catacondensed benzenoid systems are of* $(4k+2)$*-type, it follows that all cycles in catacondensed benzenoid hydrocarbons have a stabilizing effect.*

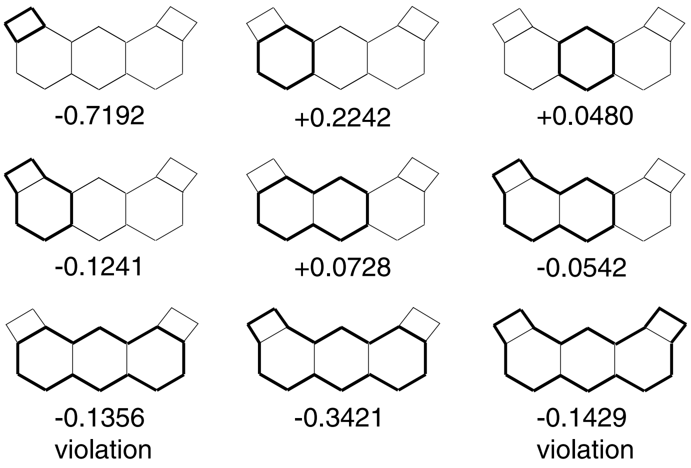


Fig. 5. Energy-effects of the cycles of 1,2,7,8-dicyclobutadienoanthracene; of the symmetry-equivalent cycles only one is shown; the 14- and the 18-membered cycles violate the *Hückel* rule, because they are of $(4k+2)$-type, but have a destabilizing effect

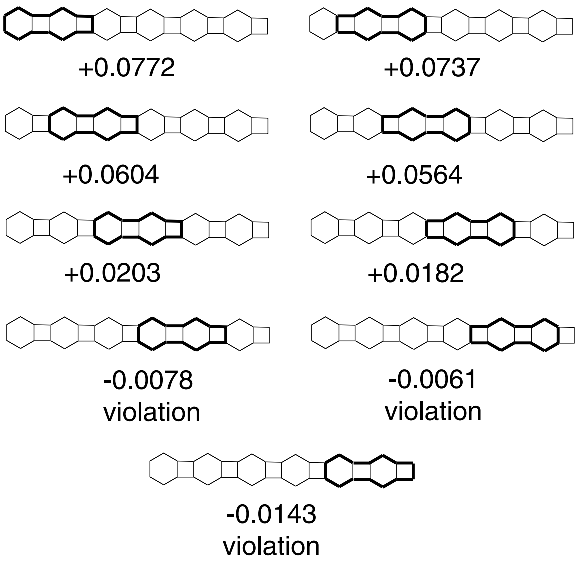


Fig. 6. Energy effects of the 14-membered cycles in a non-benzenoid conjugated molecule; three of these violate the $(4k+2)$-rule; interestingly, in the lower homologs of this molecule, possessing 4 or fewer hexagons, no violation of the *Hückel* rule is observed, whereas in the homolog with 5 hexagons there is just a single violation [46]

It seems likely that part (a) of the $(4k+2)$-rule holds for all benzenoid hydrocarbons, both catacondensed and pericondensed [49]. Yet, so far this could not be rigorously demonstrated.

Anyway, violations of the $(4k+2)$-rule occur as rare exceptions. In the vast majority of cases (*e.g.*, in the examples shown in Figs. 4, 7, and 8), the extended *Hückel* rule is obeyed.

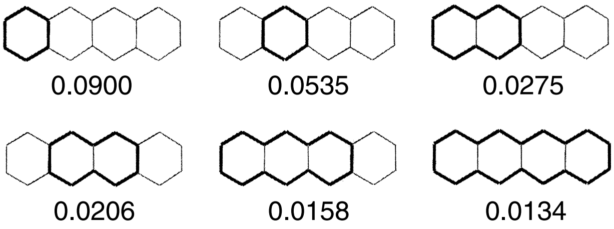


Fig. 7. Energy-effects of the cycles of tetracene; of the symmetry-equivalent cycles only one is shown; the energy-effects of the 10-membered cycles are 2–4 times smaller than the effects of the 6-membered cycles; the energy-effects of the 14- and 18-membered cycles are still smaller, but the decrease (relative to the 10-membered cycles) is slight; the 18-membered cycle forms the perimeter of the molecule

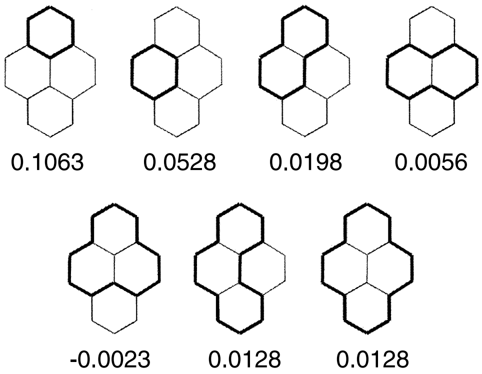


Fig. 8. Energy-effects of the cycles of pyrene; of the symmetry-equivalent cycles only one is shown; whereas the *ef*-values of the 6-membered cycles significantly exceed those of the larger cycles, the *ef*-values do not always decrease with the increasing size of the cycle; the right-hand side 14-membered cycle is the perimeter

Dependence of the Energy-Effect on the Size of the Cycle

Until now no general regularity could be discovered, concerning the dependence of *ef*-values on the size of the respective cycle. Nevertheless, numerous example show that the energy-effects usually decrease with the increase of the size of the underlying cycle. This tendency is especially pronounced in the case of benzenoid hydrocarbons. A characteristic example is given in Fig. 7. The example depicted in Fig. 8 shows that the *ef*-values need not always decrease with increasing cycle size.

The rule of thumb is that the smallest cycles (that are traditionally referred to as "rings") provide the dominant contributions to the energy-effect of cyclic conjugation of π-electrons in polycyclic conjugated compounds. The energy-effects of larger cycles are much smaller, although not always negligible. Anyway, the vast majority of the studies of cyclic conjugation reported so far [50–68], is concerned only with the energy-effects of the smallest cycles (rings). The effect of 10-membered cycles in benzenoid hydrocarbons was studied in Ref. [69].

An early attempt to rationalize the aromaticity of polycyclic conjugated molecules was the "perimeter rule" (see, for instance, Chapter 15.5 in Ref. [70]), according to which the size of the perimeter determines whether such species are aromatic or non-aromatic. If the perimeter is a $(4k+2)$-membered cycle, then the underlying molecule would be aromatic, whereas $(4k)$-membered perimeters would imply antiaromaticity. Calculations based on Eq. (3) reveal that this was a blunder [71]: the perimeter is found to have a negligibly small effect on the overall conjugation in a polycyclic molecule; for examples see Figs. 7 and 8. For a discussion on the role of the perimeter in porphin and cyclacenes see Refs. [72, 73].

Connections to *Clar* Aromatic Sextet Theory

In the 1970s *Eric Clar* proposed a peculiar diagrammatic way to represent the distribution of π-electrons in benzenoid hydrocarbons [9], nowadays referred to as *Clar* aromatic sextet (*C*AS) theory. The rules according to which *Clar* formulas are constructed are described in Refs. [9, 11, 74]; examples are found in Fig. 9. For our considerations it is important that the circles drawn in *Clar* formulas represent "aromatic sextets", namely six cyclically conjugated π-electrons. This can be understood as a claim that in these rings the intensity of cyclic conjugation is large. As seen from the examples depicted in Fig. 9, in some cases the location of the aromatic sextets is fixed, whereas in some other cases these sextets "migrate"

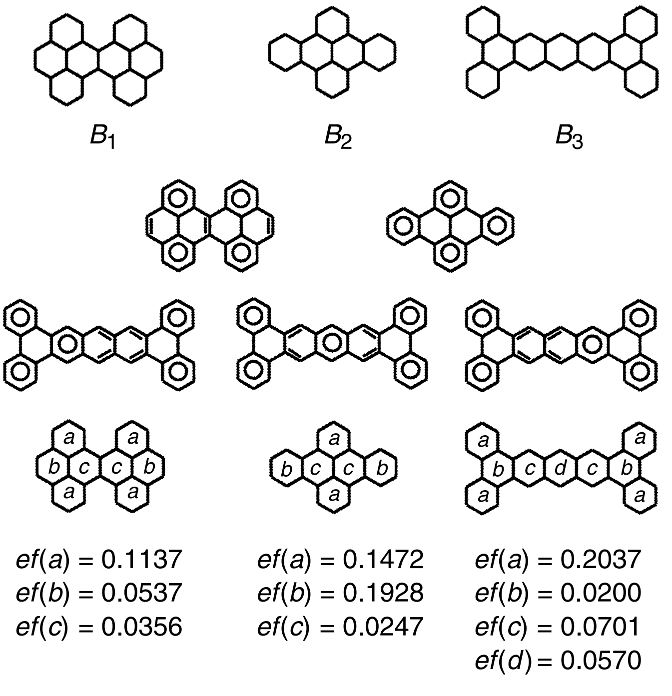


Fig. 9. Three benzenoid systems (B_1, B_2, B_3), their *Clar* formulas, and the energy-effects of their hexagons; B_1 and B_2 have unique *Clar* formulas (in which the aromatic sextets have fixed locations); B_3 is represented by three *Clar* formulas (according to which some aromatic sextets have fixed locations, but some are shared between several hexagons); B_2 is an example of a fully-benzenoid system, because in it all π-electrons (formally) belong to aromatic sextets; in these examples, the *ef*-values of the hexagons are in good agreement with the *Clar* picture

over several hexagons. Hexagons in which the aromatic sextet is present in all *Clar* formulas are referred to as "full"; hexagons into which an aromatic sextet is never drawn are said to be "empty". For instance, in the molecule B_3 (depicted in Fig. 9), the hexagons labelled by *a* are "full", those labelled by *b* are "empty" whereas the hexagons *c* and *d* are neither "full" nor "empty".

The theory of cyclic conjugation, based on Eq. (3), makes it possible to check the validity of the *C*AS theory. Indeed, in the majority of cases examined, the *ef*-values are in excellent agreement with what one would expect on the basis of *C*AS theory: "full" hexagons have large (>0.1), "empty" hexagons have small (<0.3), whereas hexagons in which the aromatic sextets "migrate" have intermediate *ef*-values. Characteristic examples are found in Figs. 9 and 10.

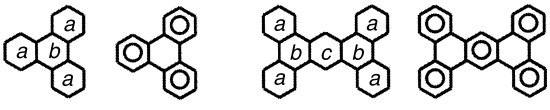
In *C*AS theory the so-called fully-benzenoid molecules are of particular importance. These are the benzenoids in which all π-electrons can be (formally) grouped into aromatic sextets. These possess a unique *Clar* formula without any double bond. Fully-benzenoid hydrocarbons are the most stable benzenoid hydrocarbons. Much experimental [75] and theoretical work [76] has recently been devoted to them.

The system B_2 in Fig. 9 is fully-benzenoid. Two more examples are given in Fig. 10.

By means of the theory of cyclic conjugation it is not only possible to test the validity of *C*AS theory, but also to envisage a number of finer details in the conjugation pattern of benzenoid hydrocarbons. For instance, reasoning based on *C*AS theory would predict an equal degree of cyclic conjugation in the *c*- and *d*-type hexagons of B_3 (see Fig. 9). On the other hand, our calculations reveal that cyclic conjugation in *c* is some 20% more intense than in *d*. Many regularities of this kind have been observed [53, 54, 61, 62, 64, 66, 67].

Whereas *C*AS theory is applicable only to benzenoid molecules with *Kekulé* structures, energy-effects can be computed also for non-*Kekulé*an species. It was found that there is no significant difference between the *ef*-values of *Kekulé*an and non-*Kekulé*an benzenoids [60].

Recently [68] certain cyclic-conjugation effects were recognized that point out the limitations of both the *C*AS theory and any *Kekulé*-structure-based theory [11, 12].



B_4 B_5

$ef(a) = 0.1910$
$ef(b) = 0.0242$

$ef(a) = 0.1939$
$ef(b) = 0.0227$
$ef(c) = 0.1380$

Fig. 10. Two fully-benzenoid hydrocarbons and the energy-effects of their hexagons; "empty" hexagons have a small and almost constant *ef*-value, equal to 0.02; the *ef*-values of the "full" hexagons are 5–10 times greater; these latter energy-effect vary significantly, depending mainly on the number of adjacent hexagons [50, 65]

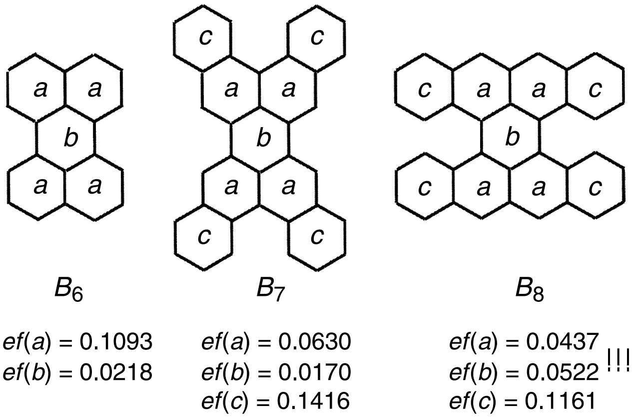


Fig. 11. Perylene (B_6) and its two tetrabenzo-annelated derivatives (B_7, B_8); as expected on the basis of *Kekulé*-structure-based classical approaches, in perylene and B_7 the *ef*-value of the central "empty" hexagon *b* is 4–5 times smaller than the *ef*-value of hexagon *a*; in the molecule B_8 we encounter the "anomaly" $ef(b) > ef(a)$

A carbon–carbon bond in a conjugated molecule is said to be "essentially single" if it is single in all *Kekulé* structures. The classical approaches to cyclic conjugation [11, 12] assume that in rings containing essentially single carbon–carbon bonds there is no cyclic conjugation at all.

The simplest benzenoid hydrocarbon with such an "empty" hexagon is perylene, see Fig. 11. In Ref. [68] benzo-annelated perylenes were examined. It was found that the extent of cyclic conjugation in their central "empty" hexagon may exceed that in the other hexagons of the same molecule. This contradicts the predictions of the *Kekulé*-structure-based approaches to cyclic conjugation, pointing out their limitations.

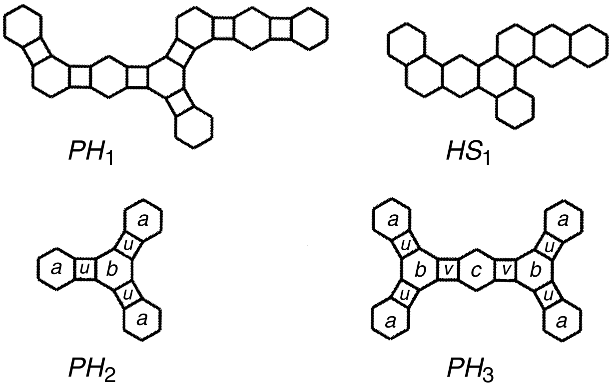
Cyclic Conjugation in Phenylenes – The Anti-*Clar* Rule

Phenylenes are polycyclic conjugated systems in which hexagons are separated by cyclobutadiene rings. Their chemistry is nowadays in rapid expansion [77–79]. These conjugated species are very interesting from a theoretical point of view because they contain both aromatic six- and antiaromatic four-membered rings. Details on the structure and number of isomers of phenylenes can be found in Ref. [80]. The examples depicted in Fig. 12 are self-explanatory.

An important concept in the theory of phenylenes is the so-called hexagonal squeeze [81]. If *PH* is a phenylene, then its hexagonal squeeze *HS* is a benzenoid system obtained from *PH* by eliminating from it (squeezing out) the four-membered rings. For an example see Fig. 12. Hexagonal squeezes are catacondensed benzenoid systems.

Numerous relations between the properties of a phenylene and its hexagonal squeeze were discovered. One such pertains to cyclic conjugation [63].

Let *PH* be a phenylene and *HS* its hexagonal squeeze, such that *HS* is fully-benzenoid. Let *X* and *Y* be two hexagons of *PH* and let X' and Y' be the corresponding hexagons of *HS*.



$ef(a) = 0.2947$
$ef(b) = 0.4570$
$ef(u) = -0.1301$

$ef(a) = 0.2912$
$ef(b) = 0.4339$
$ef(c) = 0.3295$
$ef(u) = -0.1323$
$ef(v) = -0.1359$

Fig. 12. Examples of phenylenes (PH_1, PH_2, PH_3); the benzenoid system HS_1 is the hexagonal squeeze of PH_1; the hexagonal squeezes of PH_2 and PH_3 are the benzenoid systems B_4 and B_5, respectively, depicted in Fig. 10; Rule D is applicable to PH_2 and PH_3 because their hexagonal squeezes of are fully-benzenoid; this is seen by comparing the energy-effects of the hexagons of PH_2 and PH_3 with the *ef*-values given in Fig. 10

Rule D. *If* $ef(HS, X') > ef(HS, Y')$ *then* $ef(PH, X) < ef(PH, Y)$, *and vice versa. In words: The intensity of cyclic conjugation in the hexagons of a phenylene obeys a regularity inverse to what holds for the hexagons of the respective (fully-benzenoid) hexagonal squeeze. Hexagons of PH pertaining to the "full" hexagons of HS have smaller ef-values than those pertaining to the "empty" hexagons of HS.*

Rule D, which may be called "anti-*Clar*", is illustrated by the examples depicted in Figs. 10 and 12.

Attempts were made to extend the Rule D to phenylenes whose hexagonal squeezes are not fully-benzenoid, but only some partial results along these lines could be obtained [64].

Concluding Remarks and Outlooks

In this survey we outlined the main features of a theory of cyclic conjugation based on the consideration of the energy-effects of individual cycles in polycyclic conjugated molecules. The emphasis was on practical aspects, and the underlying theory was only briefly sketched.

We wish to point out that, contrary to the other currently used such approaches [12], this theory is independent of some usual assumptions (or prejudices?), namely that the main features of cyclic conjugation can be deduced solely from the *Kekulé* or *Clar* structural formulas. Although in the majority of cases our results agree with those deduced by classical approaches [11, 12], they can sometimes refine the classical results, and sometimes point out their inadequacy.

Our theory can be equally applied to the odd-membered cycles of non-alternant hydrocarbons as well as to the cycles (of any size) in heteroatom-containing conjugated species, but until now very little work was done on these matters [72]. By slightly modifying Eq. (3) it is possible to compute the *ef*-values in conjugated ions [82, 83], and thus rationalize some surprising experimental findings obtained in this area. Yet, also here the majority of research awaits to be done.

There is no *a priori* reason why the *ef*-values should be calculated at the *H*MO level of approximation. Any other molecular orbital approach could – in principle – be used for this purpose. However, beyond the *H*MO approximation we could no more use the *Coulson* formula (Eq. (1)) and the *Sachs* theorem (Eq. (2)), which would result in a significantly more perplexed (but feasible!) mathematical formalism, and would require significantly more extensive (but feasible!) calculation techniques and computer software. Anyway, this extension of our theory of cyclic conjugation remains a task to be accomplished in the future.

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