A  REGULARITY  FOR  THE  TOTAL  π-ELECTRON  ENERGY  OF  PHENYLENES


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*Abstract:* The total π-electron energies of a phenylene and its hexagonal
squeeze  are  closely  related:  as  a  very  good  approximation,
their difference is equal to $\sqrt{8}$ (h - 1)  β-units, where h is
the  number  of  hexagons  in  the  phenylene  or  in  its  hexagonal
squeeze.


## INTRODUCTION

A class of alternant nonbenzenoid conjugated hydrocarbons, that Pe-
ter Vollhardt named "phenylenes" [1], has recently attracted much atten-
tion. Thanks to the synthetic efforts by Vollhardt and his group, quite
a few members of the phenylene family became recently available [2,3].
Theoretical studies of the phenylenes [4-10] are mainly motivated by the
fact that phenylenes are composed of (thermodynamically stabilizing)
six-membered benzene rings, separated by (thermodynamically destabiliz-
ing) four-membered cyclobutadiene-ring fragments, which results in
rather peculiar π-electron properties [2-10]. The structural principles
according to which the phenylene systems are designed should be evident
from the examples **1** and **3**. If a phenylene has h six-membered rings, then

we say that it is an [h]phenylene. In particular, **1** is a [6]phenylene whereas **3** is an [8]phenylene.



1



2



3



4
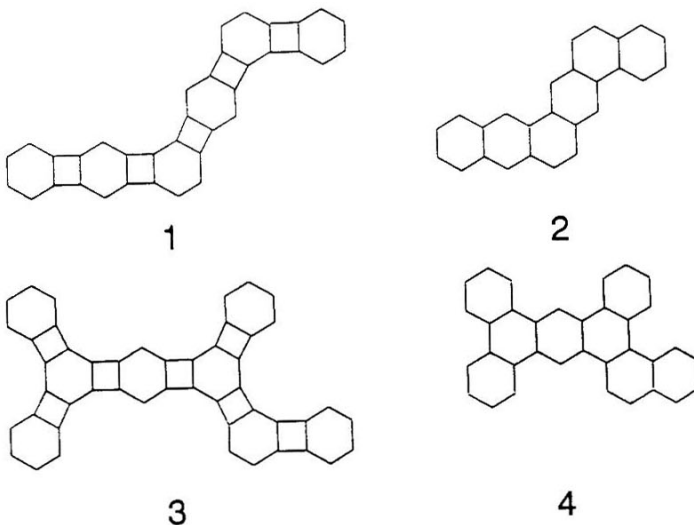
To each [h]phenylene a unique catacondensed benzenoid system with h hexagons is associated, which is referred to as the <u>hexagonal squeeze</u> of the respective phenylene [9]. For instance, the hexagonal squeezes of **1** and **3** are **2** and **4**, respectively. From these examples the construction of the hexagonal squeezes should be evident; for more details on their properties see [9].

In what follows a phenylene will be denoted by PH and its hexagonal squeeze by HS. Both are assumed to posses h hexagons.

The following remarkable relation between the properties of PH and HS was recently discovered [9]: The algebraic structure count of PH is equal to the number of Kekulé structures of HS,

$$ASC\{PH\} = K\{HS\} \ . \tag{1}$$

For instance, the [6]phenylene **1** has 191 Kekulé structures, but some of them are of even parity and some of odd parity. The molecule **1** has 104 even even Kekulé structures and 87 odd Kekulé structures, hence its algebraic structure count is 104 - 87 = 17 . This, on the other hand, is precisely equal to the number of Kekulé structures of the benzenoid hydrocarbon **2**. In our second example, the [8]phenylene **3** has a total of 1502 Kekulé structures, of which 782 are even and 720 are odd. Thus the algebraic structure of **3** is equal to 782 - 720 = 62 . The benzenoid hydrocarbon **4** has 62 Kekulé structures.

For more details on Eq. (1) and the structural relations between a phenylene (PH) and its hexagonal squeeze (HS) the reader is referred to the work [9].

Bearing in mind the result expressed by Eq. (1), one may expect that other π-electron characteristics of PH and HS are also somehow related. In this paper we show that this indeed is the case, and establish a remarkably simple and fairly accurate approximation which connects the total π-electron energies of a phenylene and its hexagonal squeeze.

## ON THE TOTAL π-ELECTRON ENERGY OF PH AND HS

The HMO total π-electron energy of conjugated molecules and its dependence on molecular structure has been studied in detail [11,12] and this work should be considered as a further contribution along the same lines. Exceptionally, this work seems to be the first which is concerned

with the total $\pi$-electron energy of phenylenes.

The HMO model is often considered as outdated and of low accuracy (see, for example, the discussion in [13]). In reality the situation is slightly different, especially when the HMO results are used and interpreted with due caution; for an extensive discussion on this matter and for numerous practical examples see the recent book [14]. In the case of HMO total $\pi$-electron energy this point was elaborated in some detail in the review [12]. Another recent example of how the results of HMO calculations can be combined with, and utilized within the unrestricted Hartree-Fock (UHF) model of conjugated polymers is found in [15].

In what follows we anyway remain within the framework of the HMO model, within which the use of graph-theoretical formalism is quite usual (see [11-15] and the references quoted therein). Thus, our $\pi$-electron energy levels are just the eigenvalues of the respective molecular graph, whereas what we call "total $\pi$-electron energy" is simply twice the sum of the positive graph eigenvalues. If G denotes a molecular graph, then the respective total $\pi$-electron energy (expressed, as usual, in units of the HMO carbon-carbon resonance integral $\beta$ [11]) is denoted by E(G) and is equal to twice the sum of the positive eigenvalues of G. In other words, E(G) is equal to twice the sum of the positive roots of the equation $\phi(G, x) = 0$ where $\phi(G)$ is the characteristic polynomial of G.

Because the molecular graph of an [h]phenylene has 6h vertices and 8h-2 edges, we have [16]

$$\phi(PH, x) = x^{6h} - (8h - 2) x^{6h-2} + \cdots + (-1)^h ASC\{PH\}^2 \quad . \qquad (2)$$

The molecular graph of the respective hexagonal squeeze has 4h+2 vertices and 5h+1 edges. Therefore [16],

$$\phi(HS, x) = x^{4h+2} - (5h + 1) x^{4h} + \cdots - K\{HS\}^2 \quad . \tag{3}$$

Bearing in mind Eq. (1), from (2) and (3) we readily conclude that

$$\phi(PH, 0) = (-1)^{h-1} \phi(HS, 0)$$

and because $K\{HS\}$ is always greater than zero [17],

$$\phi(PH, 0)/\phi(HS, 0) = (-1)^{h-1} \quad . \tag{4}$$

Define now a function $q(x)$ as follows:

$$q(x) = \phi(PH, x)/\phi(HS, x) \quad . \tag{5}$$

By performing polynomial division and by taking into account (2),(3) and (4), the right-hand side of (5) becomes

$$q(x) = x^{2h-2} - 3(h - 1) x^{2h-4} + \cdots (- 1)^{h-1} + \begin{array}{c} \text{non-polynomial} \\ \text{residuum} \end{array} \quad .$$

Denoting by $Q(x)$ the polynomial part of $q(x)$,

$$Q(x) = x^{2h-2} - 3(h - 1) x^{2h-4} + \cdots (- 1)^{h-1} \tag{6}$$

we may try to approximate the characteristic polynomial of PH as

$$\phi(PH, x) \approx \phi(HS, x) Q(x) \quad .$$

A proper consequence of this approximation would be

$$E(PH) \approx E(HS) + E[Q] \tag{7}$$

where $E[Q]$ is the "energy" obtained by formally treating $Q(x)$ as a characteristic polynomial. To be more specific, $E[Q]$ may be calculated from the coefficients of $Q(x)$ by using the Coulson integral formula [11,12], and thus by avoiding the finding of the zeros of $Q(x)$. Needless to say that there is no guarantee that the zeros of $Q(x)$ are real-valued. On the other hand, even if some of these zeros are complex numbers, $E[Q]$ remains a well-defined and real-valued quantity.

Anyway, the approximation (7) must not be accepted before being tested on concrete molecules. We will do this in a later part of this paper and based on the numerical results obtained, we may conclude that (7) is not so bad as it may look (from a formalists point of view).

A vast number of previously collected results in the theory of total $\pi$-electron energy [11,12] leads to the conclusion that the gross part (some 99.5% or more) of the total $\pi$-electron energy of an alternant hydrocarbon is determined by the following three graph-theoretical para-meters: (i) the number of vertices, i.e., the degree of the character-istic polynomial; (ii) the number of edges, i.e., the second coefficient of the characteristic polynomial, and (iii) the algebraic structure count, whose square is just equal to (plus or minus) the last coeffici-ent of the characteristic polynomial. It is plausible to expect that such kind of regularity is applicable also in the case of E[Q]. If so, then the three most significant factors influencing E[Q] would be (i) the degree [= 2 h - 2] of the polynomial $Q(x)$, (ii) the second coeffici-ent [= -3(h - 1)] of $Q(x)$ and (iii) its last coefficient [= $(-1)^h$], see Eq. (6). Notice that all three of the above factors are uniquely deter-mined by the number of hexagons, h. Hence, by considering only those co-efficients of $Q(x)$ which are explicitly given on the right-hand side of (6), we see that E[Q] will depend solely on h. By this we reach our first general conclusion:

**Rule 1.** The difference between the total $\pi$-electron energies of an [h]-phenylene and of its hexagonal squeeze depends principally on h. For series of isomeric phenylenes (all having the same value of h) this difference is nearly constant.

At this point we wish to stress that Rule 1 is not obtained by some rigorous mathematical reasoning, but by guessing, based on the form of Eq. (6) and on certain anticipated analogies with, previously establish- ed, properties of the total $\pi$-electron energy. Only numerical testing can reveal to what extent is Rule 1 in agreement with real data. As it will be shown in the subsequent section, not only Rule 1, but a much stronger statement, namely Rule 2, are sufficiently good approximations.

Rule 1 may be understood as a statement that the difference between the total $\pi$-electron energies of an [h]phenylene and of its hexagonal squeeze depends principally on local structural features of either the phenylene or its hexagonal squeeze. This seems to be a non-trivial ob- servation, because the total $\pi$-electron energy itself is known to depend on both local and non-local structural features [11,12]; typical non-lo- cal structural parameters (on which the total $\pi$-electron energy depends to a great extent) are the Kekulé structure count (K) and the algebraic structure count (ASC).

## AN APPROXIMATION FOR E[Q]

The direct way to calculate E[Q] would, of course, be via finding the zeros of the polynomial Q(x). With the limited knowledge which we have about the coefficients of Q(x) (see Eq. (6)), this can be done only by adopting further, more or less severe, approximations. Within the theory of total $\pi$-electron energy such methods for approximating the characteristic polynomial have been previously elaborated [18-21] (and in all hitherto examined cases they lead to acceptable results). Their application to Q(x) lead us to a trial formula:

$$Q(x) \approx \left(x^2 - p\right)^{(h-1)/2} \left(x^2 - \frac{1}{p}\right)^{(h-1)/2} \qquad (8)$$

where the parameter p has to be adjusted so that $coeff_{2h-4}(Q) = -3(h-1)$.

Note that one of the assumptions behind formula (8) is that all the zeros of $Q(x)$ are real-valued. Since $E[Q]$ is real-valued anyway, this assumption is of little relevance for the below consideration.

Eq. (8) implies:

$$-\left[\frac{h-1}{2} p + \frac{h-1}{2}\frac{1}{p}\right] = -3(h-1)$$

from which it is evident <u>that p is independent of h</u> and that it satisfies the equation $p + \frac{1}{p} = 6$ i.e. that $p = 3 \pm \sqrt{8}$ .

From this,

$$E[Q] \approx (h-1)\left[(3 + \sqrt{8})^{1/2} + (3 - \sqrt{8})^{1/2}\right]$$

which, by taking into account that $(3 + \sqrt{8})^{1/2} + (3 - \sqrt{8})^{1/2} = \sqrt{8}$ , results in a remarkably simple expression:

$$E[Q] \approx \sqrt{8} (h - 1) \quad ; \quad \sqrt{8} = 2.828427... \qquad (9)$$

Combining (7) and (9) we arrive at our final approximate formula

$$E[PH] \approx E[HS] + \sqrt{8} (h - 1) . \qquad (10)$$

Note that, strictly speaking, the approximation (8) can be used only if h is an odd number. However, we formally applied (8) also for even values of h. The good agreement between the left- and right-hand sides of Eq. (10), irrespective of the parity of h, provides a justification for this mathematical inconsistency.

Consider, as an example, the phenylenes $\underline{1}$ and $\underline{3}$, whose structures are shown in the introductory section and whose hexagonal squeezes are $\underline{2}$

and **4**, respectively. By using an appropriate computer program we calcu-
late that $E(\underline{1}) = 50.7113$ and $E(\underline{2}) = 36.5389$. Applying Eq.(10) and not-
ing that $h(\underline{1}) = 6$, we have $E(\underline{1}) \approx E(\underline{2}) + (6 - 1) \sqrt{8} = 50.6810$. Hence
in the case of the pair $\underline{1}/\underline{2}$ the error of the approximation (10) is only
0.03 $\beta$-units (0.06%), what from a practitioner's point of view is
negligibly small. Similarly, $E(\underline{4}) = 48.2693$ and $E(\underline{4}) + (8 - 1) \sqrt{8} =$
68.0683. On the other hand, the exact value of $E(\underline{3})$ is 67.9979 and thus
in the case of the pair $\underline{3}/\underline{4}$ the error of (10) is 0.07 $\beta$-units (0.10%).

Some more numerical data, supporting the approximation (10) are col-
lected in Table 1.

## DISCUSSION

Based on Eqs. (9) and (10) and corroborated by the data from Table 1
we can formulate the following:

**Rule 2.** The difference between the total $\pi$-electron energies of an [h]-
phenylene and of its hexagonal squeeze is approximately equal to
$\sqrt{8}$ (h - 1) and is basically independent of any other structural
feature.

In view of the fact that an [h]phenylene contains h-1 cyclobutadiene
fragments, we can interpret the above rule also in the following manner:

**Rule 3.** As a good approximation, the total $\pi$-electron energy of a phe-
nylene is equal to the total $\pi$-electron energy of its hexagonal
squeeze, plus increments coming from the four-membered rings.
These increments are basically independent of any other struc-
tural feature of the phenylene molecule, each being equal to
$\sqrt{8} = 2.83$ $\beta$-units.

As clearly seen from the data in Table 1, the accuracy of Rule 3 is
such that the E(PH)-values can be reproduced from the known E(HS)-values

Table 1. Examples illustrating the precision of the approximation (10);
for convenience, instead of the phenylenes we indicate the na-
mes of their hexagonal squeezes (recall that naphthalene cor-
responds to biphenylene, anthracene to linear [3]phenylene,
phenanthrene to angular [3]phenylene etc.); $\sqrt{8} = 2.83$

| hexagonal squeeze (HS) | h | E(PH) | E(HS) | $\frac{E(PH) - E(HS)}{h - 1}$ |
|---|---|---|---|---|
| naphthalene | 2 | 16.5055 | 13.6832 | 2.82 |
| anthracene | 3 | 25.0103 | 19.3137 | 2.85 |
| phenanthrene | 3 | 25.0822 | 19.4483 | 2.82 |
| naphthacene | 4 | 33.5144 | 24.9308 | 2.86 |
| benz(a)anthracene | 4 | 33.6019 | 25.1012 | 2.83 |
| chrysene | 4 | 33.6454 | 25.1922 | 2.82 |
| benzo(c)phenanthrene | 4 | 33.6461 | 25.1875 | 2.82 |
| triphenylene | 4 | 33.7061 | 25.2745 | 2.81 |
| pentacene | 5 | 42.0181 | 30.5440 | 2.87 |
| benzo(a)naphthacene | 5 | 42.1095 | 30.7256 | 2.85 |
| pentaphene | 5 | 42.1276 | 30.7627 | 2.84 |
| benzo(b)chrysene | 5 | 42.1624 | 30.8390 | 2.83 |
| dibenzo(b,g)phenanthrene | 5 | 42.1631 | 30.8338 | 2.83 |
| dibenz(a,h)anthracene | 5 | 42.1875 | 30.8805 | 2.83 |
| dibenz(a,j)anthracene | 5 | 42.1873 | 30.8795 | 2.83 |
| picene | 5 | 42.2141 | 30.9440 | 2.82 |
| benzo(c)chrysene | 5 | 42.2144 | 30.9386 | 2.82 |
| dibenzo(c,g)phenanthrene | 5 | 42.2150 | 30.9362 | 2.82 |
| dibenz(a,c)anthracene | 5 | 42.2347 | 30.9418 | 2.82 |
| benzo(g)chrysene | 5 | 42.2605 | 30.9990 | 2.82 |
| benzo(a)pentacene | 6 | 50.6141 | 36.3413 | 2.85 |
| dibenzo(b,k)chrysene | 6 | 50.6788 | 36.4839 | 2.84 |
| benzo(h)pentaphene | 6 | 50.7669 | 36.6142 | 2.83 |
| dibenzo(g,p)chrysene | 6 | 50.8687 | 36.7953 | 2.81 |
| dibenzo(a,l)pentacene | 7 | 59.2094 | 42.1374 | 2.85 |
| dibenzo(a,c)pentacene | 7 | 59.2495 | 42.1875 | 2.84 |
| octaphene | 8 | 67.6539 | 47.6380 | 2.86 |
| tetrabenzonaphthacene | 8 | 67.9687 | 48.2014 | 2.82 |

on at most two decimal places. In view of this, in Table 1 we give the values of $\frac{E(PH)-E(HS)}{h-1}$ also on only two decimal places.

As a concluding remark we wish to point out that for (catacondensed) benzenoid hydrocarbons the dependence of total $\pi$-electron energy on molecular structure is fairly well understood [12]. Now, Eq. (10) as well as the Rules 1-3 enable that all the results known for the total $\pi$-electron energy of benzenoids are straightforwardly transferred to the phenylene systems. Thus, for the first time, the structure-dependence of the thermodynamic stability of a class of polycyclic conjugated non-benzenoid hydrocarbons is understood to a significant degree.

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