

Theoretical Study of Cyclic Conjugation in Phenes: Some hitherto Unnoticed Features

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Summary. Cyclic conjugation in phenes is examined by means of the *Bosanac–Gutman–Aihara* method. In contrast to the predictions based on the analysis of *Kekulé* or *Clar* structures, we find that when going along the hexagons of a phene molecule, cyclic conjugation varies in a rather non-uniform manner. In contrast to a number of other homologous series of benzenoid hydrocarbons, the intensity of cyclic conjugation in phenes increases when going towards the center of the molecule.

Keywords. Cyclic conjugation; Phenes; Benzenoid hydrocarbons.

Theoretische Untersuchung der cyclischen Konjugation in Phenen: Einige bisher unbekannte Eigenschaften

Zusammenfassung. Die cyclische Konjugation in Phenen wird mittels der *Bosanac–Gutman–Aihara*-Methode untersucht. Im Gegensatz zu auf der Analyse von *Kekulé*- oder *Clar*-Strukturen beruhenden Voraussagen variiert die cyclische Konjugation entlang der Sechsecke eines Phenmoleküls ziemlich unregelmäßig. Anders als bei anderen homologen benzenoiden Kohlenwasserstoffen nimmt bei Phenen die Intensität der cyclischen Konjugation zum Zentrum des Moleküls hin zu.

Introduction

In 1977, *Bosanac* and one of the present authors [1,2] developed a method for calculating the effect on an individual cycle on the total π -electron energy of polycyclic conjugated molecules. At the same time, *Aihara* put forward a similar, but not identical approach [3]. Since then, the theory of cyclic conjugation, based on the consideration of the energy-effects of various cycles in conjugated molecules, was elaborated in due detail and applied to a variety of π -electron systems. One of the current directions of research in this area is the study of cyclic conjugation in benzenoid hydrocarbons [3–17]. The vast empirical material collected in Refs. [2–12, 14–17] made it possible to establish a number of general regularities for the pattern of cyclic conjugation in benzenoid systems. Of them we re-formulate the following two.

(A) The energy-effect caused by cyclic conjugation is almost always in harmony with the predictions based on the examination of the *Kekulé* and *Clar* structures. In particular, the number of times

a cycle is conjugated in the *Kekulé* structures (in the sense of the *Herndon-Radić* conjugated circuit theory [18–25]), is roughly proportional to the intensity of cyclic conjugation, as measured by the respective (stabilizing) energy-effect; cycles which are conjugated only in a few *Kekulé* structures, or are never conjugated, have small (either stabilizing or destabilizing) energy-effects. The number of times an aromatic sextet is located in a hexagon (in the sense of *Clar's* aromatic sextet theory [25, 26]) is roughly proportional to the energy-effect of that hexagon.

- (B) In catacondensed benzenoid hydrocarbons, the intensity of cyclic conjugation (as measured by the energy-effect) is maximal at the terminal hexagons, and diminishes when going towards the center of the molecule. In linear hexagonal chains, the energy-effects monotonically decrease from end towards center.

Rule (A) was found to be valid for the great majority of benzenoid systems, but in certain cases violations were observed [5, 12]. Rule (B) was verified on polyacenes [8], benzo-annelated polyacenes [9], fibonacenes [10], and some other homologous series containing chains of hexagons [12]; until now, no violation of rule (B) was discovered.

In this paper we report our findings concerning cyclic conjugation in phenes, a class of unbranched catacondensed benzenoid hydrocarbons whose structure is depicted in Fig. 1. As a kind of surprise, in the case of phenes rule (B) is not obeyed. Besides, when proceeding from the end of the molecule towards its center, some quite remarkable variations in the energy-effects occur which are not anticipated by the approaches based on the *Kekulé* and *Clar* structures.

We note in passing that the first five members of the phene series (phenanthrene ($h = 3$), tetraphene ($h = 4$), pentaphene ($h = 5$), hexaphene ($h = 6$), and heptaphene ($h = 7$)) are known compounds [27]; all are typical representatives of stable benzenoid hydrocarbons.

The formula for the number of *Kekulé* structures of phenes is easy to obtain:

$$K\{P_h\} = (m + 1)(n + 1) + 1$$

where the notation used is same as in Fig. 1. Another way of writing this expression is

$$K\{P_h\} = \lfloor [h + 1)/2]^2 \rfloor + 1$$

where $\lfloor x \rfloor$ denoting the greatest integer which is not greater than x (for example, $\lfloor 7.00 \rfloor = 7$, $\lfloor 8.50 \rfloor = 8$, $\lfloor 9.99 \rfloor = 9$).

A direct way to infer from the *Kekulé* structures about the extent of cyclic conjugation in individual cycles is to use *Randić's* local aromaticity index, defined as

$$LAI(G, Z) = 2K\{G - Z\}/K\{G\}$$

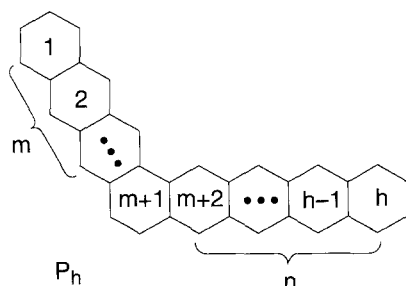


Fig. 1. The phene with h hexagons, $h \geq 3$; if h is odd, then $m = n = (h - 1)/2$ and the molecule has C_{2v} symmetry; if h is even, then $m + 1 = n = h/2$ and the symmetry is C_s ; two linear segments, embracing the hexagons 1, 2, ..., m , and $m + 2, m + 3, \dots, h$, respectively, are attached to the central hexagon ($m + 1$)

in Ref. [28]. Here, G stands for a molecular graph and $G - Z$ is the subgraph obtained by deleting from G the vertices of the cycle Z . If Z is a hexagon, then in the case of phenenes we have

$$K\{P_h - Z\} = \begin{cases} n + 1 & \text{for the hexagons } 1, 2, \dots, m \\ 1 & \text{for the hexagon } m + 1 \\ m + 1 & \text{for the hexagons } m + 2, m + 3, \dots, h \end{cases}$$

from which it follows that for the hexagons $1, 2, \dots, m$, forming the first linear segment of P_h (see Fig. 1):

$$LAI(P_h, Z) = 2[\lfloor h/2 \rfloor + 1][\lfloor [(h+1)/2 \rfloor^2 \rfloor + 1]^{-1};$$

for the central hexagon of P_h :

$$LAI(P_h, Z) = 2[\lfloor [(h+1)/2 \rfloor^2 \rfloor + 1]^{-1};$$

whereas for the hexagons $m + 2, m + 3, \dots, h$, forming the second linear segment of P_h (see Fig. 1):

$$LAI(P_h, Z) = 2[\lfloor (h+1)/2 \rfloor + 1][\lfloor [(h+1)/2 \rfloor^2 \rfloor + 1]^{-1}.$$

What is important for us is that all hexagons within a linear segment of P_h have precisely the same LAI -values (examples illustrating this fact are found already in Ref. [28]). Hence, from the analysis of the *Kekulé* structures we have to conclude that within a linear segment of the phene molecule the extent of cyclic conjugation is everywhere (approximately) the same.

Reasoning based on the *Clar* aromatic sextet theory [25, 26] yields the very same conclusions. P_h has $m \cdot n$ distinct *Clar* formulas, all possessing two aromatic sextets. One aromatic sextet is uniformly distributed in the first linear segment (occurring n times in each of the m hexagons), the other sextet is uniformly distributed in the second linear segment (occurring m times in each of the n hexagons). The central hexagon of P_h is (from the point of view of *Clar*'s theory) void of any cyclic conjugation.

Methods of Calculation, Results and Discussion

Details of the *Bosanc-Gutman-Aihara* method by which one computes the effect of a cycle Z on the total π -electron energy of a conjugated π -electron system whose molecular graph is G , can be found elsewhere [1-3, 5, 12, 29-32]. Employing HMO approximation and using β -units, this effect is evaluated by means of the formula

$$ef(G, Z) = \frac{2}{\pi} \int_0^\infty \ln \left| \frac{\phi(G, ix)}{\phi(G, ix) + 2\phi(G - Z, ix)} \right| dx$$

in which $\phi(H, x)$ stands for the characteristic polynomial of a graph H , and $i = \sqrt{-1}$.

The phene P_h contains a total of $h(h+1)/2$ cycles: h hexagons, $h-1$ ten-membered cycles, $h-2$ fourteen-membered cycles, $h-3$ eighteen-membered cycles, etc. We computed the energy-effects of all these cycles for $h=3, 4, \dots, 15$. In Table 1, the ef values of all cycles of heptaphene and octaphene are given; these may be considered as typical for the phene series. Table 2 contains the energy-effects of the hexagons of P_h , $3 \leq h \leq 15$.

Table 1. The ef values (in β units) of all cycles of heptaphene and octaphene; their hexagons are labelled according to Fig. 1; the larger cycles are denoted so that, for instance, 2+3+4 indicates the 14-membered cycle embracing the hexagons 2, 3, and 4

cycle Z	$ef(P_7, Z)$	$ef(P_8, Z)$	cycle Z	$ef(P_7, Z)$	$ef(P_8, Z)$
1	0.0946	0.0950	4+5+6	0.0029	0.0022
2	0.0630	0.0605	5+6+7	0.0215	0.0124
3	0.0661	0.0662	6+7+8	–	0.0141
4	0.0345	0.0346	1+2+3+4	0.0022	0.0020
5	0.0661	0.0617	2+3+4+5	0.0015	0.0012
6	0.0603	0.0497	3+4+5+6	0.0015	0.0010
7	0.0946	0.0531	4+5+6+7	0.0022	0.0012
8	–	0.0907	5+6+7+8	–	0.0107
1+2	0.0332	0.0334	1+2+3+4+5	0.0012	0.0010
2+3	0.0275	0.0277	2+3+4+5+6	0.0010	0.0007
3+4	0.0071	0.0070	3+4+5+6+7	0.0012	0.0007
4+5	0.0071	0.0068	4+5+6+7+8	–	0.0010
5+6	0.0275	0.0202	1+2+3+4+5+6	0.0009	0.0006
6+7	0.0332	0.0186	2+3+4+5+6+7	0.0009	0.0006
7+8	–	0.0269	3+4+5+6+7+8	–	0.0006
1+2+3	0.0215	0.0217	1+2+3+4+5+6+7	0.0009	0.0005
2+3+4	0.0029	0.0028	2+3+4+5+6+7+8	–	0.0005
3+4+5	0.0025	0.0022	1+2+3+4+5+6+7+8	–	0.0005

Table 2. The ef values (in units of $10^{-4}\beta$) of the hexagons of the first 13 members of the phene series; the hexagons are labelled according to Fig. 1

h	hexagons of P_h														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
3	1586	534	1586												
4	1717	431	796	1048											
5	1087	835	361	835	1087										
6	1104	848	352	656	596	939									
7	946	603	661	345	661	603	946								
8	950	605	662	346	617	497	531	907							
9	909	532	499	617	347	617	499	532	909						
10	910	533	499	617	349	609	474	451	510	901					
11	902	511	451	474	608	351	608	474	451	511	902				
12	902	511	451	474	608	352	609	469	434	437	505	903			
13	903	505	437	434	469	608	353	608	469	434	437	505	903		
14	903	505	437	434	469	608	354	610	469	431	422	433	505	905	
15	906	505	433	422	431	469	610	355	610	469	431	422	433	505	906

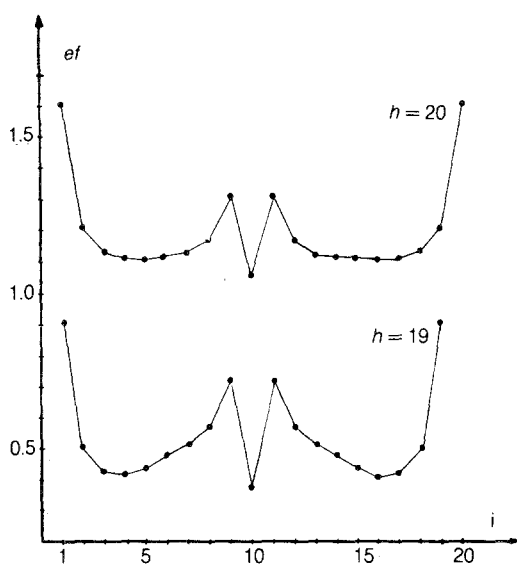


Fig. 2. The highly non-uniform nature of cyclic conjugation in phenenes: variation of the energy-effect (ef) of hexagons when going along the hexagonal chain (i = label of hexagons, according to Fig. 1); to show the details of this variation, data for two unrealistically large phenenes, P_{19} and P_{20} , are presented; the P_{20} -curve is shifted upwards by 0.7β units

A noteworthy property of cyclic conjugation in the phene series is that when going from one end of the molecule towards its center, the energy-effects of the hexagons first decrease, attain a minimum, and then increase again, reaching a new maximum at the hexagon m (or at the hexagon $m + 2$, if starting from the other end). The minimum value of the energy-effect is at the central hexagon ($m + 1$), the only detail which is in agreement with the *Kekulé-Clar* model. This usual form of conjugation is easily conceived from Table 2; a further illustrative example is given in Fig. 2.

Essentially the same triple-minimum behavior is observed also in the case of 10-, 14-, 18-, ... -membered cycles, with the only difference that their energy-effects are much smaller (see Table 1).

As already pointed out, deliberations based on *Kekulé* and *Clar* structures imply that the conjugation within each of the two linear segments of the phene molecule is more or less uniform. Our results indicate that this conclusion of the *Kekulé-Clar* model may be a drastic oversimplification.

In a number of cases it was found that cyclic conjugation is most pronounced around the end of a hexagonal chain and is minimal in its central part. This feature could be rationalized by a kind of (electrostatic?) repulsion between the aromatic sextets. In the case of phenenes, such an explanation would fail completely. Here it turns out that the positions most favorable for the aromatic sextets are the hexagons 1, m , $m + 2$, and h . Two of them (the hexagons m and $m + 2$) are second neighbors and lie next to the center of the molecule.

Concluding this paper we wish to point out some further (not unusual) properties of the energy-effects of phenenes. From Table 1 we see that all cycles in phenenes have positive (stabilizing) ef values and that the magnitude of ef (P_h, Z) decreases with the increasing size of the cycle Z . There is no noteworthy difference in the pattern of cyclic conjugation when h is odd (when the two linear segments are symmetry-equivalent) and when h is even (when the linear segments are of different length). Further, from Table 2 we see that with increasing size of the phene molecule, the

local non-uniformities in cyclic conjugation slightly decrease, but show no tendency to vanish. These, however, are properties shared by all catacondensed benzenoid molecules [2, 8–10, 12, 13].

The sum of the individual energy-effects of all cycles is known to differ from the overall (joint) effect of all cycles [32]. This is because the overall energy-effect contains collective contributions of pairs, triplets, etc. of cycles. Nevertheless, we find a very good linear correlation between the sum (σ) of individual effects and the overall energy-effect (ω). The data for the first 13 phenes ($3 \leq h \leq 15$) give the regression line

$$\omega = 1.516\sigma - 0.118$$

with a correlation coefficient of 0.9996. Besides, for all values of h , except for $h = 3$ and $h = 4$, the energy-contribution of hexagons is almost exactly 70% of the contribution of all individual cycles (σ).

Relations of the above kind were previously reported for other homologous series of catacondensed benzenoids [8, 10]. Recall that ω is just a sort of resonance energy, as put forward by *Aihara* [33] and others [34].

When we decided to examine the cyclic conjugation in phenes (after so many similar benzenoid systems have already been analyzed), we did not expect to discover anything remarkably new. However, the findings we made show that there still may exist numerous hitherto unnoticed and unexplored features in the conjugation modes of polycyclic π -electron species. This may be the case even for such exhaustively studied systems as are the benzenoid hydrocarbons.

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