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Anomalous cyclic conjugation in benzenoid molecules with a small number of Kekulé structures

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The currently used Kekulé-structure-based models for assessing the extent of cyclic conjugation in benzenoid hydrocarbons predict that there is no or very little cyclic conjugation in the rings possessing "fixed" double and single carbon-carbon bonds. With the example of a suitably chosen class of benzenoid systems with a small number of Kekulé structures, we show that the cyclic conjugation in the rings with "fixed" bonds (measured by its energy-effect) may be unexpectedly high, contradicting the results of standard Kekulé-structure-based considerations. Consequently, our study reveals that the analysis of the conjugation modes of polycyclic aromatic compounds, based solely on Kekulé structures, may sometimes be insufficient and may lead to erroneous conclusions.

It was discovered recently[1] that cyclic conjugation in certain benzenoid hydrocarbons may significantly deviate from the predictions made by means of the currently used Kekulé-structure-based approaches (Clar theory[2,3], conjugated circuit theory[3,4], partitioning of π-electrons in rings[5-7] and other measures of local aromaticity[8,9]). In particular, six-membered rings that according to the Kekulé-structure-based models are devoid of any cyclic conjugation, may exhibit very strong cyclic conjugation effects, exceeding the extent of cyclic conjugation in "regularly conjugated" rings. This phenomenon was first observed in the case of benzo-annelated perylenes[1]. According to the Kekulé-picture, the ring A in perylene (**I**, see Fig. 1) and in any of its benzo-annelated derivatives (e.g., **II**) is "empty", i.e., it possesses essentially single carbon-carbon bonds and thus no cyclic conjugation is envisaged in it. In harmony with this, the energy-effects of the cyclic conjugation in the rings A and B of **I** are computed to be equal to 0.0218 and 0.1093 β-units. On the other hand, the energy-effect of the "empty" ring A in tetrabenzo-perylene (II) is 0.0522 β, exceeding the analogous energy-effect of ring B (= 0.0437 β). It could be shown[10] that this apparent anomaly is caused by the fact that the linearly annelated benzo-derivatives of perylene have a very small number of Kekulé structures.

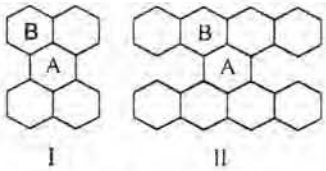


Fig. 1 — Perylene (**I**) and its linearly annelated tetrabenzo-derivative (**II**). In compound **II** the cyclic conjugation in ring A is more intense than in ring B, in spite of the fact that A is "empty" whereas B is not.

In order to examine in more detail the occurrence of anomalous cyclic conjugation in benzenoid hydrocarbons, and in order to collect more empirical data on this phenomenon, we have undertaken a systematic study of a class of benzenoid systems $Z_n(i_1,i_2,\ldots,i_k)$, whose structure is explained in Fig. 2.

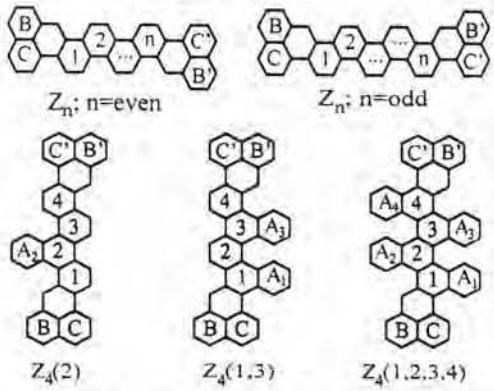
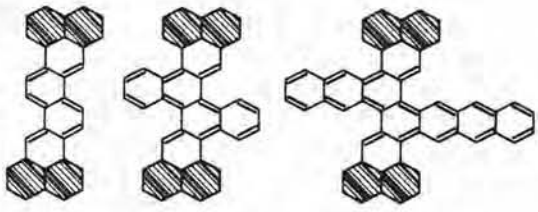


Fig. 2 — The homologous series Z_n whose benzo-annelated derivatives are considered in this work. The six-membered rings marked by $1,2,\ldots,n$ are those to which benzo-annelation is possible. The species obtained from Z_n by attaching six membered rings to the rings $i_1,i_2,\ldots,i_k$, is denoted by $Z_n(i_1,i_2,\ldots,i_k)$. The rings attached are denoted by $A_{i_1}, A_{i_2},\ldots,A_{i_k}$. The three examples illustrating this notation, namely, $Z_4(2)$, $Z_4(1,3)$ & $Z_4(1,2,3,4)$, should be self-explanatory. B, C and B', C' mark the six-membered rings belonging to the two naphthalene fragments.



III=Z_2 IV=Z_2(1,2) V

Fig. 3 — From the point of view of Kekulé structures, the molecule Z_n and its annelated congeners are viewed as consisting of two naphthalene units (indicated by shading), joined by essentially single and essentially double carbon-carbon bonds. According to the Kekulé-picture, the π-electrons in the naphthalene fragments are delocalized, with three Kekulé structures in each naphthalene unit (resulting in a total of 3×3=9 Kekulé structures). All other carbon-carbon bonds are either essentially single (i.e., single in all Kekulé structures) or essentially double (i.e., double in all Kekulé structures), as indiactated in diagrams **III**, **IV** & **V**.

The species $Z_n(i_1,i_2,...,i_k)$ belong to the class of so-called "essentially disconnected" benzenoid systems[3]. A benzenoid system is said to be "essentially disconnected" if it possesses "essentially single" carbon-carbon bonds, i.e. carbon-carbon bonds that are single in all Kekulé structures. Essentially disconnected benzenoids may, but need not, possess also "essentially double" carbon-carbon bonds, i.e. carbon-carbon bonds that are double in all Kekulé structures. The structural features and π-electron characteristics of essentially disconnected benzenoids were much studied[11-15]. Their main property is the fact that after formally deleting from them the essentially single bonds they decompose into two or more disjoint conjugated domains, each consisting of at least two hexagons[14].

In accordance with this, the Kekulé structures of the benzenoid systems Z_n and their benzo-annelated derivatives $Z_n(i_1,i_2,...,i_k)$ have the remarkable property that, except in two naphthalene domains, all their π-electrons are formally localized in fixed double bonds[11,13,14] (for illustrative examples see Fig. 3). Consequently, according to Kekulé-structure-based reasonings[2-9], non-negligible cyclic conjugation is expected only within the naphthalene fragments (that in Fig. 3 are indicated by shading), and there should be no (or in a more cautious interpretation: very little) cyclic conjugation in the rings $A_{i_1}, A_{i_2}, ..., A_{i_k}$.

In view of the fact that, irrespective of their size, all these benzenoid systems have only 9 Kekulé structures, we anticipated that in them pronounced deviations from the Kekulé-structure-based predictions of cyclic conjugation effects would be observed. In particular, we expected that the extent of cyclic conjugation in the rings $A_{i_1}, A_{i_2}, ..., A_{i_k}$ will exceed that in the rings belonging to the two naphthalene fragments of $Z_n(i_1,i_2,...,i_k)$. As shown below, this indeed was found to be the case.

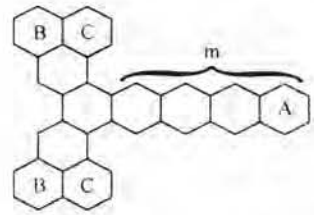


Fig. 4 — The system Z_1 to which m hexagons are attached in a linear manner, and the labeling of its hexagons.

Table 1 — Energy-effects of the rings A, B and C of the benzenoid system shown in Fig. 4, calculated according to Eq. (1). The intensity of cyclic conjugation in ring A is a decreasing function of the parameter m, i.e., it decreases with the increasing length of the linear hexagonal chain

m	$ef(A)$	$ef(B)$	$ef(C)$
0	—	0.0914	0.1066
1	0.1364	0.0897	0.1003
2	0.1038	0.0892	0.0985
3	0.0948	0.0891	0.0979
4	0.0922	0.0891	0.0977
5	0.0915	0.0891	0.0976
6	0.0913	0.0891	0.0976
7	0.0913	0.0891	0.0976
8	0.0913	0.0891	0.0976
9	0.0913	0.0891	0.0976
10	0.0913	0.0891	0.0976

The present investigations deal with cyclic conjugation (via its energy-effect ef, see below) in the six-membered rings $A_{i_1}, A_{i_2}, ..., A_{i_k}$ of the benzenoid molecules $Z_n(i_1,i_2,...,i_k)$, aimed at the species in which these energy-effects are maximal. The natural question is what would happen if longer linear hexagonal chains would be attached to the corresponding sites of Z_n. Our calculations show that with the increase of the length of such attached chains, the observed cyclic conjugation effects decrease. A characteristic example is provided by the benzenoid systems whose structure is depicted in Fig. 4. In Table 1 are given the energy-effects of the rings A, B & C, for various values of the parameter m. Because of this attenuation of the $ef(A)$-values, in what follows we focus our attention only to the case when single six-membered rings are attached to particular sites of Z_n.

Theory

In order to test the applicability of Kekulé-structure-based approaches, we need to use a method for assessing the extent of cyclic conjugation that is independent of Kekulé structures. Such a method was developed some time ago by one of the present authors[16,17] and, in a slightly different form, by Aihara[18].

The extent of conjugation in a ring of a polycyclic conjugated π-electron system can be measured by its energy-effect, computed within the framework of the Hückel molecular orbital (HMO) approximation. The energy-effect of a ring R of a (polycyclic) conjugated molecule whose molecular graph is G satisfies the expression

$$ef(R) = ef(R,G) = \frac{2}{\pi}\int_0^\infty \ln \frac{\phi(G,ix)}{\phi(G,ix) + 2\phi(G-R,ix)}\,dx \qquad \ldots (1)$$

where $\phi(G,x)$ is the characteristic polynomial of G. The subgraph G-R is obtained by deleting R from G, and $i = \sqrt{-1}$. For details see the recent review[19] and elsewhere[20-22]. In view of the fact that in Eq. (1), the quantity $ef(R)$ is expressed in the units of the HMO carbon-carbon resonance integral β, positive ef-values indicate thermodynamic stabilization, whereas rings with negative ef destabilize the respective π-electron system. Consequently, the greater is $ef(R)$, the greater is the extent of cyclic conjugation in the ring R.

Results and Discussion

Table 2 shows the energy-effects of the A-type rings of all benzo-derivatives of Z_n for n=1,2,3,4, together with the energy-effects of the corresponding "regularly conjugated" rings B and C (Fig. 2).

The search for the benzenoid system $Z_n(i_1,i_2,\ldots,i_k)$ in which $ef(A)$ is maximal (and in which the modes of cyclic conjugation maximally violate the predictions inferred from the Kekulé-structure-based theories) revealed the following regularities.

Rule 1 — In all benzenoid systems $Z_n(i_1,i_2,\ldots,i_k)$, the energy-effects of the A-type rings significantly exceed those of the B- and C-type rings (see also Rules 2 and 3).

Rule 1 implies that cyclic conjugation in the A-type rings (in which according to the Kekulé structures there would be no cyclic conjugation) is much stronger than in the B- and C-type rings (in which, according to the Kekulé structures there should be a high degree of cyclic conjugation).

Table 2 — The energy-effects of the A-type rings of the benzo-derivatives of Z_n for n = 1, 2, 3, 4, and the energy-effects of the rings B and C (*cf.* Fig. 2), calculated according to Eq. (1). Of the pairs of symmetry-equivalent species (e.g., $Z_3(1,2)$ and $Z_3(2,3)$), only one is included in Table 2. The ef-value of the ring B' either coincides with $ef(B)$ (if B and B' are symmetry-equivalent) or is nearly equal to $ef(B)$ (if B and B' are not symmetry-equivalent). The same holds for the rings C and C'. Therefore, the $ef(B')$- and $ef(C')$-values are not given in the table

Molecule	$ef(A_1)$	$ef(A_2)$	$ef(A_3)$	$ef(A_4)$	$ef(B)$	$ef(C)$
$Z_1(1)$	0.1364	—	—	—	0.0897	0.1003
$Z_2(1)$	0.1457	—	—	—	0.0872	0.0997
$Z_2(1,2)$	0.1472	0.1472	—	—	0.0851	0.0999
$Z_3(1)$	0.1540	—	—	—	0.0860	0.0988
$Z_3(2)$	—	0.1572	—	—	0.0834	0.1058
$Z_3(1,2)$	0.1525	0.1514	—	—	0.0843	0.0993
$Z_3(1,3)$	0.1616	—	0.1616	—	0.0853	0.0980
$Z_3(1,2,3)$	0.1576	0.1476	0.1576	—	0.0839	0.0987
$Z_4(1)$	0.1576	—	—	—	0.0851	0.0984
$Z_4(2)$	—	0.1597	—	—	0.0825	0.1056
$Z_4(1,2)$	0.1546	0.1570	—	—	0.0837	0.0990
$Z_4(1,3)$	0.1637	—	0.1665	—	0.0847	0.0978
$Z_4(1,4)$	0.1595	—	—	0.1595	0.0845	0.0982
$Z_4(2,3)$	—	0.1558	0.1558	—	0.0820	0.1050
$Z_4(1,2,3)$	0.1589	0.1511	0.1603	—	0.0835	0.0986
$Z_4(1,2,4)$	0.1557	0.1630	—	0.1648	0.0833	0.0989
$Z_4(1,2,3,4)$	0.1595	0.1552	0.1552	0.1595	0.0833	0.0985

Rule 2 — The energy-effects of the *A*-type rings vary within rather narrow intervals. In particular,

for n=3, $ef(A) \in (0.151\ ,\ 0.162)$;

for n=4, $ef(A) \in (0.151\ ,\ 0.166)$;

for n=5, $ef(A) \in (0.152\ ,\ 0.178)$;

for n=6, $ef(A) \in (0.152\ ,\ 0.180)$.

In other words, the extent of cyclic conjugation in all *A*-type rings in all benzenoid systems $Z_n(i_1,i_2,...,i_k)$ is practically the same.

Rule 3 — The energy-effects of the *B*- and *C*-type rings are practically constant and vary within very narrow intervals, for instance:

for n=3, $ef(B) \in (0.083\ ,\ 0.086)$; $ef(C) \in (0.098\ ,\ 0.106)$;

for n=4, $ef(B) \in (0.082\ ,\ 0.085)$; $ef(C) \in (0.098\ ,\ 0.106)$;

for n=5, $ef(B) \in (0.081\ ,\ 0.085)$; $ef(C) \in (0.098\ ,\ 0.106)$.

Rule 4 — In the monobenzo-derivatives of Z_n, the $ef(A)$-values monotonically decrease when going from the end of the chain towards its middle:

$$ef(A, Z_n(1)) < ef(A, Z_n(2)) < ef(A, Z_n(3)) < ef(A, Z_n(4)) \ldots$$

As an illustration of Rule 4 we have:

$ef(A, Z_6(1))=0.1617$; $ef(A, Z_6(2))=0.1640$; $ef(A, Z_6(3))=0.1675$;

and, by symmetry,

$ef(A, Z_6(4))= ef(A, Z_6(3))$; $ef(A, Z_6(5))= ef(A, Z_6(2))$; $ef(A, Z_6(6))= ef(A, Z_6(1))$.

Rule 5 — In multiply annelated derivatives of Z_n, if other structural influences (e.g. the one described in Rule 6) can be disregarded, then the *ef*-values of *A*-type rings lying closer to the middle of the chain are greater than the *ef*-values of the *A*-type rings lying at the ends of the chain.

Rule 6 — Annelation of *A*-type rings on opposite sides of the Z_n-chain diminishes the $ef(A)$-values. Annelation of A-type rings on the same side of the Z_n-chain increases the $ef(A)$-values.

A characteristic example illustrating Rule 5 is the following: For annelation on opposite sides of Z_6:

$ef(A_1, Z_6(1,2)) = 0.1570$; $ef(A_2, Z_6(1,2)) = 0.1596$

$ef(A_2, Z_6(2,3)) = 0.1635$; $ef(A_3, Z_6(2,3)) = 0.1635$

which should be compared with the analogous results for annelation on the same side of Z_6:

$ef(A_1, Z_6(1,3)) = 0.1662$; $ef(A_3, Z_6(1,3)) = 0.1731$

$ef(A_2, Z_6(2,4)) = 0.1689$; $ef(A_4, Z_6(2,4)) = 0.1727$

$ef(A_1, Z_6(1,3,5)) = 0.1671$; $ef(A_3, Z_6(1,3,5)) = 0.1779$; $ef(A_5, Z_6(1,3,5)) = 0.1698$.

Conclusions

From Table 2, we see that the energy-effect of a ring with "fixed" double bonds can significantly exceed the energy-effect of a "regularly conjugated" ring. Thus, π-electrons that are represented by "fixed" double bonds seem to be much more mobile than implied by the Kekulé structures (this is the reason why we use quotation marks when referring to such bonds).

It is evident that the conjugation pattern of the benzenoid systems studied in this work cannot be satisfactorily described solely by means of Kekulé structures. Our results clearly point at the limits of applicability of either the conclusions drawn from the energy-effects of rings [as computed by Eq. (1)], or the hitherto and presently widely used Kekulé-structure-based theories, in particular, of Kekulé-structure-based resonance theory[4,23], Clar aromatic sextet theory[2,24] and the conjugated circuit model[4]. Which of these two options is closer to reality should be decided by further investigations, preferably by experiments.

Anyway, our studies reveal that the benzenoid systems of the type $Z_n(i_1,i_2,...,i_k)$ are worth of attention of experimental chemists. Because at the present moment, only zethrene (denoted here by Z_0) and dibenzo[*de,kl*]pentaphene (denoted here by Z_1), as well as the closely related dibenzo[*pq,uv*]pentaphene, are known compounds[25], further experimental, primarily synthetic, work would be needed.

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