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Cyclic Conjugation in Benzo-Annelated Perylenes. How Empty is the "Empty" Ring?

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Summary. Cyclic conjugation in benzo-annelated perylenes is studied by means of the energy-effects of their six-membered rings. "Classical" theoretical approaches (based on *Kekulé* structures, *Clar* formulae, or conjugated circuits) predict that the central ring in benzo-annelated perylenes is "empty" and thus negligibly contributes to cyclic conjugation. Our calculations show that this is true only to a limited degree. In particular, rings angularly annelated relative to the central ring significantly increase the extent of its cyclic conjugation.

Keywords. Perylene; Benzo-annelated perylenes; Cyclic conjugation; Energy-effect of cyclic conjugation.

Introduction

Several theoretical approaches have been put forward for quantifying cyclic conjugation in polycyclic conjugated molecules. The three most popular ones are those based on the counting of *Kekulé* structures [1, 2], analysis of conjugated circuits [3–5], and the concept of aromatic sextet [6–8]. Details of these theories can be found in a book [9] and a recent extensive review [10]. We refer to these approaches as "classical".

When applied to benzenoid hydrocarbons, all the classical theories predict that in rings containing essentially single carbon–carbon bonds there is no cyclic conjugation or – with a reasonable caution – that the extent of cyclic conjugation is very weak. (Recall that a carbon–carbon bond of a conjugated molecule is said to be "essentially single" if it is single in all *Kekulé* structures.) Rings of this kind are usually referred to as "empty".

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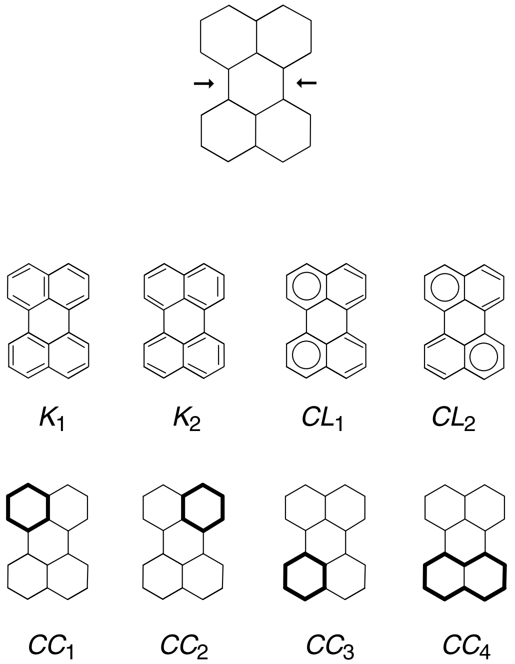

Fig. 1. Perylene, two of its *Kekulé* structures (K_1 and K_2), two of its *Clar* aromatic sextet formulae (CL_1 and CL_2), and the conjugated circuits contained in the *Kekulé* structure K_1 (indicated by heavy lines in diagrams CC_1–CC_4); the bonds marked by arrows are "essentially single" because they are single in all (nine) *Kekulé* structures, all (four) *Clar* aromatic sextet formulae, and are not contained in any of the (six) conjugated circuits of perylene; "classical" theories assume that these bonds, as well as the ring to which they belong, do not participate in cyclic conjugation

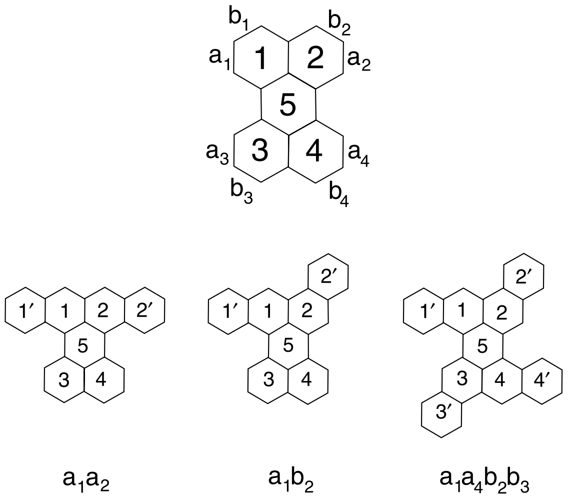

Fig. 2. Labelling of the rings of perylene and its benzo-annelated derivatives; from the point of view of the central ring 5 annelation may be either angular (in positions a_1, a_2, a_3, and/or a_4) or linear (in positions b_1, b_2, b_3, and/or b_4); the benzene ring annelated to perylene's ring 1, 2, 3, or 4 is labelled by 1′, 2′, 3′, or 4′, respectively; the way in which we denote the benzo-annelated perylenes is seen from the three self-explanatory examples

The simplest benzenoid hydrocarbon with an "empty" ring is perylene (see Fig. 1).

In this work we examine benzo-annelated perylenes and focus our attention to the extent of cyclic conjugation in their central rings. In all these benzenoid systems this central ring is "empty", in the same sense as it is "empty" in perylene (*cf*. Fig. 1). The labelling of the rings and the sites of annelation are indicated in Fig. 2.

Perylene is often considered as composed of two naphthalene units, which – from the point of view of π-electron conjugation – are almost independent. The same viewpoint would then be applicable also to its benzo-annelated derivatives.

The extent of conjugation in a cycle of a polycyclic conjugated π-electron systems can be measured by the respective energy-effect. A method for assessing the energy-effect of π-electron conjugation along a given cycle, based on the application of graph spectral theory within the *Hückel* molecular orbital (*H*MO) approximation, was put forward in the 1970s by one of the present authors [11] and was eventually elaborated and applied in numerous articles (see, for instance, Refs. [12–15] and the references quoted therein). In this approach the energy-effect of a cycle Z is computed by means of Eq. (1) where G is the molecular graph representing the π-electron system considered, $\phi(G, x)$ is its characteristic polynomial, $G - Z$ is the subgraph obtained by deleting from G the cycle Z, and $i = \sqrt{-1}$; further mathematical details are found in Refs. [16, 17].

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

Because in Eq. (1) the quantity $ef(G, Z)$ is assumed to be expressed in the units of the *H*MO carbon–carbon resonance integral β, positive ef-values indicate thermodynamic stabilization, whereas cycles with negative ef destabilize the respective π-electron system. The greater $ef(G, Z)$ is, the greater the extent of cyclic conjugation in the cycle Z is. In what follows we apply Eq. (1) to the six-membered cycles (=rings) of perylene and its benzo-annelated derivatives.

For the present considerations it is important to recall that the energy-effect-based theory of cyclic conjugation is not *a priori* restricted to the "classical" conjugation modes, implied by the *Kekulé*-type or *Clar*-type structural formulae. The fact is that in most cases the energy-effects are in harmony with the predictions of the "classical" theories. There are, however, exceptions, revealing the limitations of the "classical" approaches. One such case is being discussed below.

Results and Discussion

There exist two mono-, nine di-, eight tri-, and seven tetra-benzo-perylenes, a total of 26 distinct benzo-annelated derivatives, *cf*. Tables 1 and 2. For all rings of these benzenoid systems the ef-values, as given by Eq. (1), were computed. The results obtained are given in Tables 1 and 2.

The first regularity that easily can be seen from Tables 1 and 2 is that the extent and modes of conjugation in the region formed by the rings $1'$-1-2-$2'$ do not depend much on the conjugation in the region $3'$-3-4-$4'$, in full harmony with the "classical" picture. For instance, consider the species in which the ring $1'$, attached to ring

Table 1. Energy-effects (in β-units) of the rings 1–5 in perylene and its benzo-annelated derivatives; for notation see Fig. 2

compound	*ef*(1)	*ef*(2)	*ef*(3)	*ef*(4)	*ef*(5)
perylene	0.1093	0.1093	0.1093	0.1093	0.0218
a_1	0.0563	0.0873	0.1048	0.1091	0.0263
b_1	0.0482	0.1429	0.1094	0.1098	0.0207
a_1a_2	0.0465	0.0465	0.1040	0.1040	0.0325
a_1a_3	0.0534	0.0885	0.0534	0.0885	0.0322
a_1a_4	0.0556	0.0837	0.0837	0.0556	0.0324
a_1b_2	0.0690	0.0396	0.1058	0.1096	0.0247
a_1b_3	0.0564	0.0878	0.0464	0.1421	0.0248
a_1b_4	0.0566	0.0873	0.1369	0.0482	0.0248
b_1b_2	0.0626	0.0626	0.1101	0.1101	0.0193
b_1b_3	0.0482	0.1435	0.0482	0.1435	0.0197
b_1b_4	0.0483	0.1431	0.1431	0.0483	0.0197
$a_1a_2a_3$	0.0439	0.0465	0.0523	0.0846	0.0407
$a_1a_2b_3$	0.0465	0.0468	0.0462	0.1352	0.0304
$a_1a_3b_2$	0.0654	0.0402	0.0540	0.0888	0.0300
$a_1a_4b_2$	0.0681	0.0383	0.0844	0.0561	0.0302
$a_1b_2b_3$	0.0691	0.0398	0.0468	0.1429	0.0234
$a_1b_2b_4$	0.0693	0.0396	0.1382	0.0484	0.0234
$a_1b_3b_4$	0.0568	0.0880	0.0604	0.0625	0.0227
$b_1b_2b_3$	0.0627	0.0629	0.0484	0.1439	0.0184
$a_1a_2a_3a_4$	0.0437	0.0437	0.0437	0.0437	0.0522
$a_1a_2a_3b_4$	0.0445	0.0468	0.0641	0.0388	0.0376
$a_1a_2b_3b_4$	0.0469	0.0469	0.0599	0.0599	0.0274
$a_1a_3b_2b_4$	0.0662	0.0403	0.0662	0.0403	0.0281
$a_1a_4b_2b_3$	0.0687	0.0385	0.0385	0.0687	0.0283
$a_1b_2b_3b_4$	0.0696	0.0399	0.0608	0.0628	0.0216
$b_1b_2b_3b_4$	0.0630	0.0630	0.0630	0.0630	0.0173

1, is in angular position, and no ring is attached to ring 2. Then the *ef*-values of $1'$ in the systems a_1, a_1a_3, a_1b_3, a_1a_4, a_1b_4, and $a_1b_3b_4$ are 0.1086, 0.1130, 0.1085, 0.1111, 0.1083, and 0.1079 β-units, respectively, all being nearly equal and all insignificantly differing from 0.11β.

The next regularity that we wish to emphasize is that the energy effects of the rings annelated in a given position (either angular or linear) vary within very narrow limits. Thus, the *ef*-values of all angularly annelated rings lie between 0.1056 and 0.1232 β-units, whereas those of linearly annelated rings are between 0.1390 and 0.1653 β-units. In all cases angularly annelated rings have smaller energy-effects than the linearly annelated ones. Such a cyclic-conjugation-effect is no surprise whatsoever, and is easily rationalized (or predicted) by means of arguments from *Clar* aromatic sextet theory.

The third regularity envisaged from the data given in Table 1 is inexplicable in terms of "classical" theories.

In perylene the "empty" central ring 5 has an energy-effect of 0.0218β, significantly smaller than 0.1093β – the energy-effects of the other four rings. This is

Table 2. Energy-effects (in β-units) of the rings $1'$–$4'$ in benzo-annelated perylenes; for notation see Fig. 2

compound	$ef(1')$	$ef(2')$	$ef(3')$	$ef(4')$
a_1	0.1086	–	–	–
b_1	0.1546	–	–	–
a_1a_2	0.1066	0.1066	–	–
a_1a_3	0.1130	–	0.1130	–
a_1a_4	0.1111	–	–	0.1111
a_1b_2	0.1167	0.1647	–	–
a_1b_3	0.1085	–	0.1534	–
a_1b_4	0.1083	–	–	0.1536
b_1b_2	0.1413	0.1413	–	–
b_1b_3	0.1547	–	0.1547	–
b_1b_4	0.1547	–	–	0.1547
$a_1a_2a_3$	0.1118	0.1099	0.1163	–
$a_1a_2b_3$	0.1064	0.1062	0.1521	–
$a_1a_3b_2$	0.1206	0.1627	0.1119	–
$a_1a_4b_2$	0.1186	0.1626	–	0.1102
$a_1b_2b_3$	0.1166	0.1649	0.1538	–
$a_1b_2b_4$	0.1164	0.1649	–	0.1540
$a_1b_3b_4$	0.1079	–	0.1403	0.1404
$b_1b_2b_3$	0.1414	0.1414	0.1549	–
$a_1a_2a_3a_4$	0.1161	0.1161	0.1161	0.1161
$a_1a_2a_3b_4$	0.1105	0.1087	0.1232	0.1599
$a_1a_2b_3b_4$	0.1056	0.1056	0.1390	0.1390
$a_1a_3b_2b_4$	0.1198	0.1634	0.1198	0.1634
$a_1a_4b_2b_3$	0.1179	0.1632	0.1632	0.1179
$a_1b_2b_3b_4$	0.1161	0.1653	0.1406	0.1407
$b_1b_2b_3b_4$	0.1416	0.1416	0.1416	0.1416

a finding acceptable by the "classical" approaches (although their strict application would require a zero energy-effect in ring 5).

The annelation of a ring in angular position increases the energy-effect of ring 5 by 20%. This contradicts the "classical" picture, which would predict no (or very small) effect of such an annelation on the extent of cyclic conjugation. Only angular annelation causes a non-classical intensification of cyclic conjugation in the central ring of perylene. The analogous annelation in linear position results in a much smaller effect: it decreases the ef-value of ring 5 by only 5%.

In the case of monobenzo-perylenes the angular-annelation-effect may look small and, perhaps, negligible. However, in multiply annelated perylenes the same effect becomes remarkably stronger. With two angularly annelated rings the extent of conjugation in the central ring is by 49% greater than in the parent compound, with three by 87%, whereas in the extreme case, namely for the $a_1a_2a_3a_4$ tetrabenzo-perylene, the ef-value of ring 5 is 0.0522 β-units, implying an increase of cyclic conjugation by 140%. Moreover, in this latter molecule, cyclic conjugation in the "empty" ring 5 is found to be significantly more intense than in the rings 1, 2, 3, and 4.

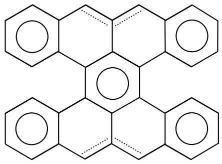

Fig. 3. A non-classical *Clar*-type aromatic sextet formula that could be used for an *ad hoc* "explanation" of the unusually high extent of cyclic conjugation found in the "empty" ring of benzo-annelated perylenes

Conclusion

Within the "classical" approaches the above described angular-annelation-effect is not anticipated and cannot be explained. In order to offer an "explanation" we must think of non-classical formulas, such as the one depicted in Fig. 3. However, it is not our aim to propose a new class of structural formulae that would compete with (and sometimes outperform) the *Kekulé*- and *Clar*-type formulae, but to call the attention to the fact that the "classical" picture of π-electron conjugation is not complete and sometimes fully unsatisfactory. As shown by our analysis of benzo-annelated perylenes, discrepancies seem to occur already in the case of benzenoid hydrocarbons, the class of polycyclic conjugated molecules whose theory has been most extensively studied in the past [9, 10].

Anyway, the central ring in perylene and its benzo-annelated derivatives, especially those in which the annelation is angular, is much less "empty" than assumed by theories based (solely) on *Kekulé* structures, *Clar* aromatic sextet formulae and/or conjugated circuits.

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