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EFFECT OF BENZOCYCLOBUTADIENO-ANNELATION ON CYCLIC CONJUGATION IN PERYLENE

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Earlier studies showed that the intensity of cyclic conjugation in the central ring *R* of perylene can be significantly altered by means of benzo-annelation. In particular, linear (resp. angular) benzo-annelation was found to decrease (resp. increase) the intensity of cyclic conjugation in *R* .We now examine the analogous effect of benzocyclobutadieno-annelation, and show that linear annelation strongly increases the cyclic conjugation in *R*, whereas the effect of angular annelation is negligibly small.

Key words: polycyclic aromatic hydrocarbons; cyclic conjugation; energy effect of cyclic conjugation; perylene; benzocyclobutadieno-annelated perylene

ЕФЕКТ НА БЕНЗОЦИКЛОБУТАДИЕНСКА АНЕЛАЦИЈА ВРЗ ЦИКЛИЧНАТА КОНЈУГАЦИЈА ВО ПЕРИЛЕН

Поранешните студии укажуваат дека интензитетот на циклична конјугација во централниот прстен *R* на перилен може значително да се измени преку т.н. бензо анелација. Имено, најдено е дека линеарното (соодветно ангуларното) бензо анелирање го намалува (соодветно, го зголемува) интензитетот на цикличната конјугација во *R*. Проучуван е аналогниот ефект на бензоциклобутадиенското анелирање и најдено е дека линеарното анелирање силно ја зголемува цикличната конјугација во *R*, додека ефектот на ангуларното анелирање е незначителен.

Клучни зборови: полициклични ароматични јаглеводороди; циклична конјугација; енергетски ефект од циклична конјугација; перилен; бензоциклобутадиенски анелиран перилен

1. INTRODUCTION

Several recent studies [1–5] examined the effects of benzo-annelation on the intensity of cyclic conjugation in individual rings of benzenoid hydrocarbons. The first benzenoid systems on which these effects were considered were perylene and its benzo-annelated congeners [1]. Already in this first work, the following regularities have been observed, pertaining to the central six-membered ring:

Rule 1. Benzo-annelation in angular position to a six-membered ring increases the intensity of cyclic conjugation in this ring.

Rule 2. Benzo-annelation in linear position to a six-membered ring decreases the intensity of cyclic conjugation in this ring.

Rule 3. The effects specified in Rules 1 and 2 are proportional to the number of benzo-annelated rings.

Such a significant variation of the magnitude of cyclic conjugation in the central

ring of perylene is remarkable, because according to the standard theoretical approaches based solely on Kekulé or Clar structures [6–9], in this ring there should be no cyclic conjugation at all. As a consequence of Rules 1 and 3, cyclic conjugation in the central ring of all-angular tetrabenzoperylene is much stronger than in its four peripheral rings [1].

Eventually, the above rules were also found to hold for other benzenoids [2–5], without a single case of violation. According to the hitherto accumulated data, these rules seem to be generally valid.

In addition to attaching a benzene ring to a polycyclic conjugated molecule via benzo-annelation, it is possible to connect it also via two new carbon-carbon bonds. This mode of annelation is referred to as benzocyclobutadieno-annelation (or, abbreviated, BCBD-annelation), see Figure 1.

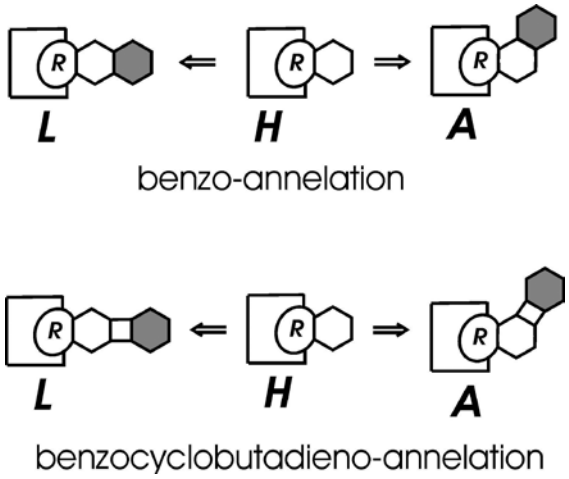

Fig. 1. Two types of annelation of a benzene ring to a polycyclic hydrocarbon (*H*) and the two modes in which this can be done: *L* = linear, *A* = angular (relative to the ring *R*)

The effect of BCBD-annelation on cyclic conjugation was until now studied only to a limited extent [10, 11], mainly for non-benzenoid polycyclic conjugated molecules. The aim of the present work was to examine it on perylene, and to see how in this case Rules 1–3 need to be modified. Our findings are a kind of surprise, because instead of Rules 1–3 we now have the following rules:

Rule 1*. BCBD-annelation in angular position to the central six-membered ring has almost no effect on the intensity of cyclic conjugation in this ring.

Rule 2*. BCBD-annelation in linear position to the central six-membered ring increases the intensity of cyclic conjugation in this ring.

Rule 3*. The effect specified in Rule 2* is proportional to the number of linearly BCBD-annelated rings. Irrespective of the number of angularly BCBD-annelated rings, their effect on cyclic conjugation remains negligible.

Rule 4*. The intensity of cyclic conjugation in the central six-membered ring is almost completely determined by the number of linear BCBD-annelations, and is almost independent on both the number of angular BCBD-annelations and on the position of the annelated BCBD-fragments.

2. METHODS

As already mentioned, if the intensity of cyclic conjugation would be assessed by means of Kekulé- or Clar-structure-based theoretical models, then the central ring of perylene and its congeners would be predicted to be void of any cyclic conjugation. In order to overcome this difficulty, we use a molecular-orbital-based and graph-theory-based method, by means of which we establish the energy contribution of an individual ring to the total π-electron energy, denoted by *ef*. Details of this approach can be found in the reviews [12, 13] and in our previous papers, e.g. in [2, 14–16]. For the present considerations it is sufficient to recall that the *ef*-values are expressed in units of the HMO carbon-carbon resonance integral β. Therefore, positive *ef*-values indicate thermodynamic stabilization caused by cyclic conjugation, and the greater is *ef*, the stronger is the cyclic conjugation in the considered ring.

3. BENZOCYCLOBUTADIENO-ANNELATED CONGENERS OF PERYLENE

In this work we are concerned with perylene and its BCBD-annelated derivatives. In Figure 2 it is shown how the annelation sites of perylene are labeled, and how its BCBD-annelated congeners are denoted. A complete list of BCBD-annelated perylenes can be found in Table 1. There are 2 mono-, 9 di-, 8 tri-, and 7 tetra-BCBD-annelated species.

As explained above, from the point of view of the theory of cyclic conjugation, the most interesting ring is the central ring of perylene and its BCBD-annelated congeners, marked by *R* in Figure 2.

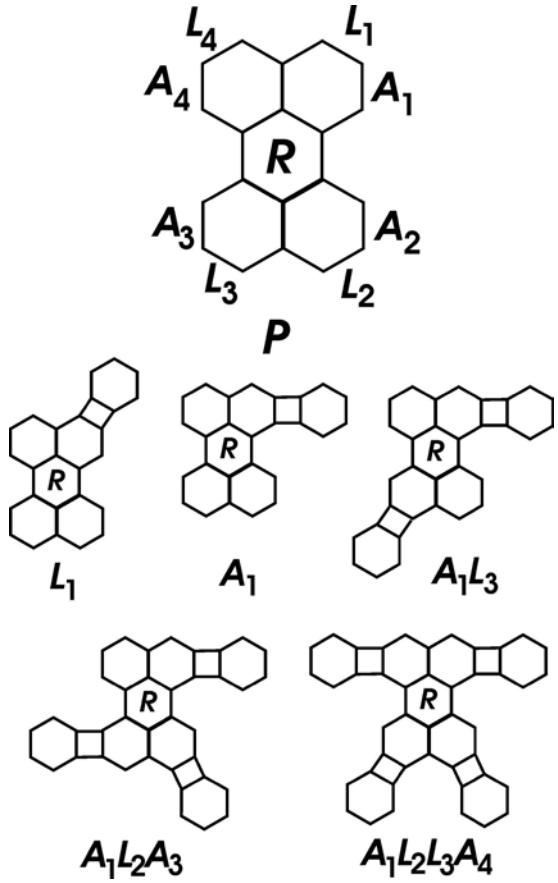

Fig. 2. Perylene (*P*) and the labeling of its annelation sites (*A* = angular, *L* = linear with regard to the central ring *R*. The benzocyclobutadieno-annelated congeners of perylene are denoted by indicating the sites of annelation; the five examples shown should be self-explanatory.

4. NUMERICAL WORK

Calculation of the *ef*-values of the ring *R* were done by means of the formula:

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

using our in-house software; for details see [12, 13, 17]. In Equation (1), $i=\sqrt{-1}$, by G is denoted the molecular graph whose characteristic polynomial is $\phi(G,x)$, and by $G–Z$ is denoted the subgraph obtained by deleting from G the cycle Z (in our case: the ring R), whose characteristic polynomials is $\phi(G-Z,x)$.

The *ef*-values were calculated for all rings of perylene and its all BCBD-annelated congeners. The *ef*-values pertaining to the central ring *R* are given in Table 1, whereas the *ef*-values of the other rings can be obtained from the authors, upon request.

5. RESULTS AND DISCUSSION

An inspection of the data collected in Table 1 leads to the conclusions formulated above as Rules 1*–4*. Rule 1* and its comparison with Rule 1 is illustrated in Figure 3, whereas Rule 2* and its comparison with Rule 2 is illustrated in Figure 4. These two figures provide also an illustrative example for Rule 3*.

From Rules 2 and 2* (as well as from Figure 4), it can be seen that linear benzo- and linear BCBD-annelations have opposite effects on the magnitude of cyclic conjugation. It is justified to ask which of the two (opposite) effects is stronger. Already by inspection of Figure 4 we may guess that the BCBD-effect is stronger. That this indeed is the case was confirmed by considering the respective *ef*-values of all derivatives obtained by attaching equal number of benzo- and BCBD-fragments in linear mode to symmetry-equivalent sites of perylene. All possible such derivatives were examined, and in all cases the effect of

BCBD-annelation prevailed. Two characteristic examples are depicted in Figure 5.

The peculiar fact that the intensity of cyclic conjugation is independent of the number of angular BCBD-annelations and depends solely on the number of linear BCBD-annelations (Rule 4*), is, for instance, confirmed by the examples: $ef(L_1) = 0.0247$, $ef(A_1L_2) = 0.0249$, $ef(A_1A_2L_3) = 0.0251$, $ef(A_1A_2A_3L_4) = 0.0249$. The other claim in Rule 4*, namely that the actual position of the annelations has little effect on the intensity of cyclic conjugation, is, for instance, confirmed by the examples: $ef(A_1A_2L_3) = 0.0251$, $ef(A_1L_2A_3) = 0.0250$, $ef(A_1L_2A_4) = 0.0247$.

T a b l e 1

Energy effects (ef, in β-units) of the central ring R of perylene and its BCBD-annelated congeners
(The way in which the BCBD-annelated species are denoted is explained in Fig. 2.)

Compound	*ef*	Compound	*ef*	Compound	*ef*
Perylene	0.0218	L_1L_2	0.0285	$A_1L_3L_4$	0.0284
A_1	0.0222	L_1L_3	0.0286	$L_1L_2L_3$	0.0339
L_1	0.0247	L_1L_4	0.0285	$A_1A_2A_3A_4$	0.0227
A_1A_2	0.0225	$A_1A_2A_3$	0.0226	$A_1A_2A_3L_4$	0.0249
A_1A_3	0.0225	$A_1A_2L_3$	0.0251	$A_1A_2L_3L_4$	0.0283
A_1A_4	0.0222	$A_1L_2A_3$	0.0250	$A_1L_2A_3L_4$	0.0284
A_1L_2	0.0249	$A_1L_2A_4$	0.0247	$A_1L_2L_3A_4$	0.0280
A_1L_3	0.0250	$A_1L_2L_3$	0.0287	$A_1L_2L_3L_4$	0.0334
A_1L_4	0.0247	$A_1L_2L_4$	0.0284	$L_1L_2L_3L_4$	0.0415

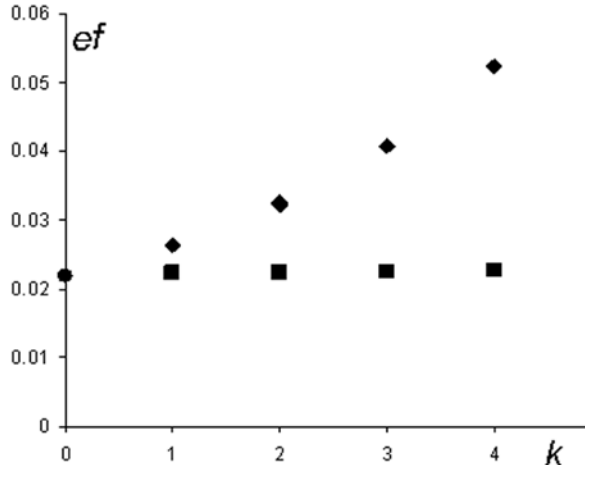

Fig. 3. The energy-effects of the central ring in perylene derivatives with k angular benzo-annelations (diamonds, cf. Rules 1 and 3) and k angular benzocyclobutadieno-annelations (squares, cf. Rules 1* and 3*). If $k = 2$, then there exist three distinct isomers for each type of angular annelation, whose *ef*-values differ insignificantly (cf. Rule 4*).

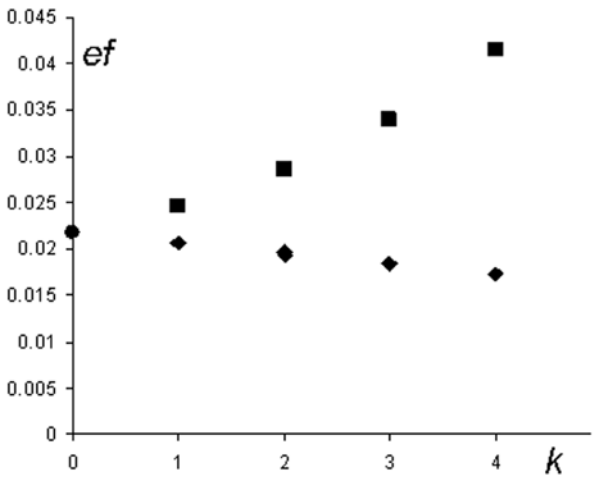

Fig. 4. The energy-effects of the central ring in perylene derivatives with k linear benzo-annelations (diamonds, cf. Rules 2 and 3) and k linear benzocyclobutadieno-annelations (squares, cf. Rules 2* and 3*). If $k = 2$, then there exist three distinct isomers for each type of linear annelation, whose *ef*-values differ insignificantly (cf. Rule 4*).

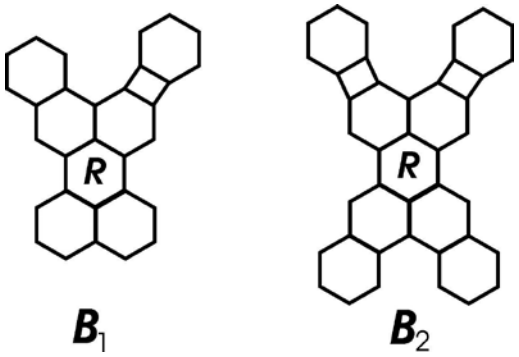

Fig. 5. Two derivatives of perylene with benzo- and BCBD-groups annelated in linear, symmetry-equivalent positions. The *ef*-values of the central ring of B_1 and \B_2, $ef(B_1) = 0.0231$ and $ef(B_2) = 0.0240$, exceed that in perylene, $ef(P) = 0.0218$, indicating that BCBD-annelation has a stronger effect on cyclic conjugation than benzo-annelation.

Comparison of Rules 1–3 (valid for benzo-annelation) with Rules 1*–4* (valid for benzocyclobutadieno-annelation, at least in the case of perylene) reveals that the two types of annelations influence the cyclic conjugation in the rings of the parent benzenoid hydrocarbon in profoundly different manner. What readily comes to mind is that these differences are caused by the 4-membered rings, known to have a destabilizing (antiaromatic) effect and negative-valued energy effect [8, 9, 12, 13].

One way of qualitatively considering these differences is as follows [18]: When benzene (which is aromatic itself) is annelated to the aromatic rings of perylene, this annelation leads to extended cyclic (aromatic) conjugation, but when benzocyclobutadiene is annelated (which is anti-aromatic itself) there is no conjugative communication between the two formally aromatic ring systems. This reasoning explains the fact that the effect of *angular* BCBD-annelation is insignificant (cf. Rule 1* and Figure 3), but then remains as a mystery why the effect of *linear* BCBD-annelation is strong, and stronger than that of benzo-annelation (cf. Rule 2* and Figure 5).

Anyway, a proper explanation or rationalization of the regularities reported in the present work remains a task for the future. Another task expected to be accomplished in our future studies is to establish how far the applicability of Rules 1*–4* can be extended. Our preliminary results indicate that contrary to Rules 1–3, which seem to be valid for all benzenoid hydrocarbons, Rules 1*–4* hold within a somewhat more restricted domain.

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