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Verifying the PCP-rule by five-center bond indices

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Abstract: According to the recently discovered PCP-rule, the (stabilizing) energy-effect of the cyclic conjugation in the 5-membered ring of acenaphthylene- and fluoranthene-type polycyclic conjugated hydrocarbons increases with the number of phenyl–cyclopentadienyl (PCP) fragments present in the molecule. It is now shown that the validity of the PCP-rule is also supported by the 5-center bond indices, an independent quantitative theoretical measure of cyclic conjugation in 5-membered rings.

Keywords: acenaphthylene-type hydrocarbons; fluoranthene-type hydrocarbons; PCP-rule; multicenter bond index; cyclic conjugation.

INTRODUCTION

The theory of benzenoid hydrocarbons[1,2] is nowadays one of the best developed areas of theoretical organic chemistry. Motivated by recent progress in this field (see the papers[3–7] and the references quoted therein), a systematic study[8–10] of a class of polycyclic conjugated systems closely related to benzenoid hydrocarbons, the acenaphthylenes and fluoranthenes, was undertaken. These differ from "true" benzenoids by possessing a five-membered ring; for examples see Fig. 1. A more formal definition of acenaphthylenes and fluoranthenes can be found in the literature.[8]

The PCP-rule

According to classical theories of benzenoid and similar polycyclic conjugated molecules,[1,2] there is no cyclic conjugation in the 5-membered ring of acenaphthylenes and fluoranthenes. Investigating the energy-effect of cyclic conjugation using the method described in detail in a review[11] and elsewhere,[3,7] it was found that a weak cyclic conjugation exists in the 5-membered ring of acena-

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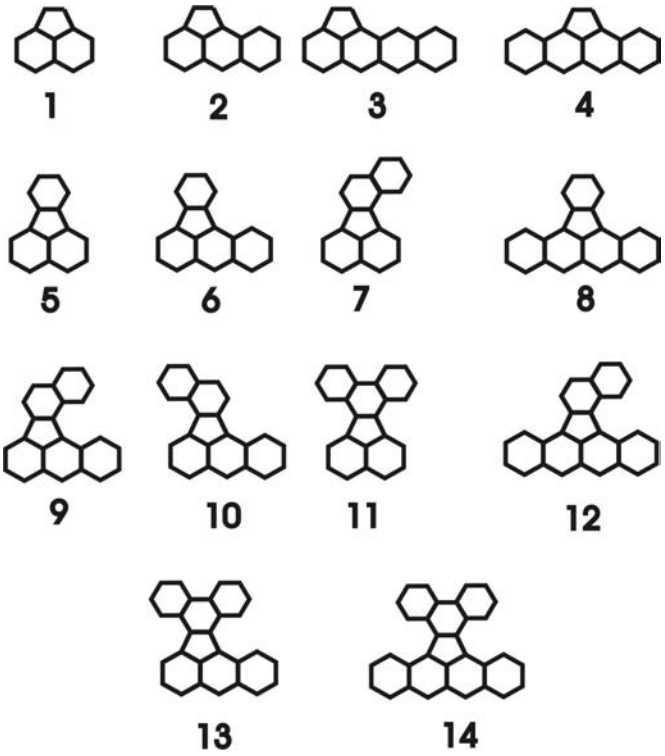

Fig. 1. Acenaphthylene (**1**) and some of its congeners (**2**–**4**), and fluoranthene (**5**) and some of its congeners (**6**–**14)**. Data on the cyclic conjugation in the 5-membered ring of these compounds are given in Table I.

TABLE I. The number of PCP fragments *(#PCP*), the five-center bond index (*5-CBI*) of the five-membered rings and the energy-effect (*ef*, in β-units) of the same rings of the acenaphthylenes and fluoranthenes depicted in Fig. 1

Compound	*#PCP*	*5-CBI*	*ef*
1	0	0.5250	0.0026
2	1	0.6124	0.0206
3	1	0.6394	0.0255
4	2	0.7281	0.0390
5	0	0.2685	0.0031
6	1	0.3062	0.0054
7	1	0.3096	0.0043
8	2	0.3566	0.0105
9	2	0.3559	0.0079
10	2	0.3558	0.0080
11	2	0.3457	0.0056
12	3	0.4181	0.0159
13	3	0.3994	0.0105
14	4	0.4716	0.0211

phthylenes and fluoranthenes. In addition, it was established[10] that this (weak) cyclic conjugation effect is amplified by the presence of 6-membered rings connected to the 5-membered ring by a single carbon–carbon bond. This effect was named the PCP-rule, where PCP is the abbreviation for "**P**henyl-**C**yclo**P**entadienyl". According to the PCP-rule, the extent of the energy-effect due to cyclic conjugation in the 5-membered ring is proportional to the number of PCP fragments present in the respective acenaphthylene and fluoranthene. These PCP fragments are indicated for two selected examples in Fig. 2.

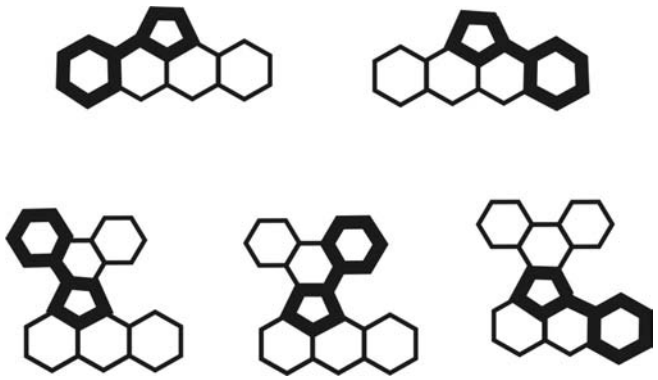

Fig. 2. The compounds **4** and **13** from Fig. 1 have two and three PCP fragments, respectively; these are indicated by thick lines.

A simple example illustrating the validity of the PCP-rule is provided by the two isomeric acenaphthylenes **3** and **4**. Whereas **3** has one PCP fragment, its isomer **4** has two PCP fragments. The energy-effects of their 5-membered rings are 0.0255 and 0.0390 β-units, respectively. Further examples are found in Table I. It should be noted that until now not a single violation of the PCP-rule has been observed.[10]

In view of the fact that the PCP-rule was established by studying the energy--effects of the 5-membered rings, it was thought purposeful to check it by other measures of cyclic conjugation. In this paper, the PCP-rule was tested by means of multicenter bond indices.

Multicenter bond indices

Multicenter bond indices are quantities specifically designed to detect and quantify the presence of delocalized multicenter bonding in molecules such as non-classical carbocations, electron deficient boranes, lithiated hydrocarbons, *etc*. The respective theory was developed in the 1990s[12–18] and was then successfully applied to a variety of types of molecules.[19–23] In view of the capability of these indices to describe non-classical three-center bonding, the idea of the multicenter bond index was recently generalized so as to be also applicable for the description of cyclically conjugated bonding extended over any number of

centers. In the general case of *k*-center bonding, the corresponding index was defined as the permutation-unique *k*-center term resulting from the partitioning of the total number (*N*) of electrons:

$$N = \frac{Tr(PS)^{\{k\}}}{2^{k-1}} = \sum_{A} \Delta_{A}^{(k)} + \sum_{A<B} \Delta_{AB}^{(k)} + \sum_{A<B<C} \Delta_{ABC}^{(k)} + \cdots + \sum_{A<B<C<\cdots<K} \Delta_{ABC\ldots K}^{(k)}$$

where *P* is the charge/bond-order matrix and *S* the overlap matrix. In this work, the 5-center bonding index (*5-CBI*), pertaining to the five carbon atoms (labeled by *A*,*B*,*C*,*D* and *E*) of the 5-membered ring in the acenaphthylene and fluoranthene species, was employed. This index, characterizing the extent of the cyclic conjugation within the particular 5-membered ring, is defined as:

$$5\text{–}CBI = 2^4 \Delta_{ABCDE}^{(5)} =$$

$$= \sum_{\mu \in A} \sum_{\nu \in B} \sum_{\lambda \in C} \sum_{\kappa \in D} \sum_{\xi \in E} \sum_{i} \Gamma_i [(PS)_{\mu\nu}(PS)_{\nu\lambda}(PS)_{\lambda\kappa}(PS)_{\kappa\xi}(PS)_{\xi\mu}]$$

where $\mu, \nu, \lambda, \kappa, \xi$ refer to the basic functions and Γ is the permutation operator that takes into account all possible (= 5!) permutations of the atomic labels. For the sake of straightforward comparability with *ef*-values, which are calculated using a generalized version of the Coulson formula[11] at the level of the simple HMO theory, the calculation of 5-center bond indices was also performed at the same level. Within such an approach, the overlap matrix is a unit matrix and the formula reduces to:

$$5\text{–}CBI = 2^4 \Delta_{ABCDE}^{(5)} =$$

$$\sum_{\mu \in A} \sum_{\nu \in B} \sum_{\lambda \in C} \sum_{\kappa \in D} \sum_{\xi \in E} \sum_{i} \Gamma_i [P_{\mu\nu} P_{\nu\lambda} P_{\lambda\kappa} P_{\kappa\xi} P_{\xi\mu}]$$

NUMERICAL WORK

The *5-CBI*-values were computed for the 5-membered rings of all acenaphthylenes and fluoranthenes depicted in Fig. 1. These data, together with the (earlier studied[10]) energy-effects, are given in Table 1.

An inspection of the *5-CBI*-data from Table I reveals that these perfectly agree with the PCP-rule. For understandable reasons, the acenaphthylenes have to be considered separately from the fluoranthenes. Within each of these two classes, when the counts of PCP fragments are equal, then the respective *5-CBI*--values are nearly the same. When a molecule X has greater number of PCP fragments than another molecule Y, then, without a single exception, *5-CBI*(X) > > *5-CBI*(Y). For instance, for the isomers **3** and **4** (possessing, respectively, one

and two PCP fragments), *5-CBI*(**3**) = 0.64 and *5-CBI*(**4**) = 0.73. Among the fluoranthenes shown in Fig. 1, the minimum and maximum *5-CBI* have, respectively, fluoranthene (**5**, no PCP fragment) and tetrabenzofluoranthene (**25**, four PCP fragments); *5-CBI*(**5**) = 0.27, *5-CBI*(**25**) = 0.47. For more examples of this kind, see Table I.

CONCLUSIONS

The PCP-rule is a peculiar property of acenaphthylenes and fluoranthenes, having no counterpart in the classical theory of polycyclic conjugated molecules. It was discovered by studying the energy-effects of the 5-membered rings contained in these molecules.[10] The obvious question that emerged at this point was whether the PCP-rule is an artifact of the graph-theory-based method used for computing the energy-effects or if the PCP-rule reflects some real feature of the π-electron distribution in the respective molecules. The analysis performed by employing a completely independent approach, based on multicenter bond indices, clearly indicates that the latter might be the case.

A reasonably good linear correlation between the five-center indices and the energy-effects of the five-membered rings exists, as seen in Fig. 3. Of course, the data-points for acenaphthylenes and fluoranthenes lie on two different lines. This implies that not only is the PCP-rule convincingly corroborated by multicenter bond indices, but also so is the molecular-structure dependence of the extent of cyclic conjugation, predicted by two different methods, in quantitative agreement.

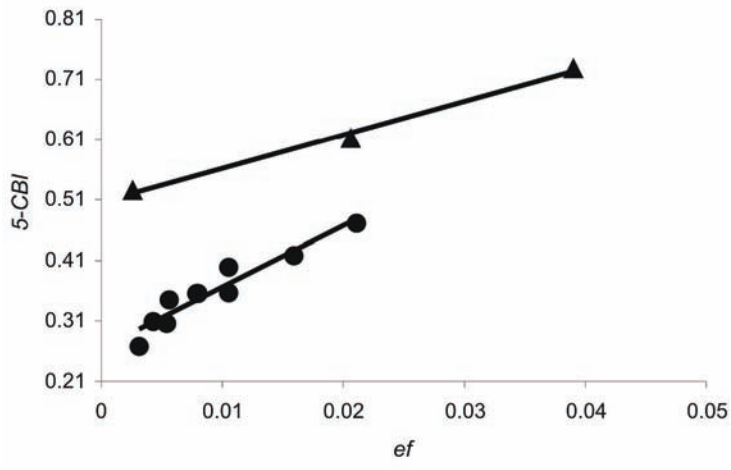

Fig. 3. The five-center bond indices (*5-CBI*) *vs*. the energy-effects (*ef*) for the acenaphthylenes (triangles) and fluoranthenes (circles) depicted in Fig. 1.

The quantum-chemical origin of the PCP-rule remains obscure, but the real existence of such a rule seems to be now additionally verified.

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И З В О Д

ПРОВЕРА PCP-ПРАВИЛА ПОМОЋУ ПЕТОЦЕНТРИЧНИХ ИНДЕКСА ВЕЗЕ

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На основу недавно откривеног PCP-правила, (стабилизујући) енергетски ефекат цикличне конјугације у петочланом прстену полицикличних конјугованих угљоводоника аценафтиленског и флуорантенског типа расте са бројем фенил-циклопентадиенилних (PCP) фрагмената садржаних у молекулу. У раду показујемо да је важење PCP-правила потврђено и помоћу петоцентричних индекса везе, који су једно независно теоријско квантитативно мерило цикличне коњугације у петочланим прстеновима.

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