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Original Scientific Article

Ring Currents and the PCP Rule

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Abstract. According to the recently discovered PCP rule, the intensity of cyclic conjugation in the five-membered rings of polycyclic conjugated hydrocarbons related to acenaphthylene and fluoranthene increases with the number of phenyl-cyclopentadienyl (PCP) fragments present in the molecule. The validity of this regularity was first observed by studying the energy effects of cyclic conjugation in the five-membered rings of these systems. In order to show that the PCP rule is not an artifact of the method employed, it is necessary to confirm its validity by other approaches. We now show that the PCP rule is in perfect agreement with calculated topological π-electron ring-currents, ostensibly an independent, quantitative, theoretical – albeit, it is here argued, likewise also *graph*-theoretical – measure of cyclic conjugation in the individual rings of polycyclic π-electron systems. In addition, we show that the molecular-structure dependency of the ring currents in acenaphthylene and fluoranthene congeners also agrees with other, earlier-established, regularities for cyclic conjugation.

Keywords: acenaphthylene, fluoranthene, cyclic conjugation, topological ring-current, PCP rule, linear effect

INTRODUCTION

The theory of benzenoid hydrocarbons[1,2] is one of the best developed areas of theoretical organic chemistry. Motivated by recent progress in this field (see Refs. 3−13 and the citations therein), two of us (A. T. B. and I. G.), with others, have undertaken a systematic study[14–24] of a class of polycyclic conjugated systems that are closely related to the benzenoid hydrocarbons – the acenaphthylenes and fluoranthenes. These differ from 'true' benzenoids by possessing a five-membered ring; for examples, see Figures 1 and 2. A more formal definition of acenaphthylenes and fluoranthenes can be found in Ref. 14.

According to classical theories of benzenoid and similar polycyclic conjugated molecules,[1,2] there should be either no cyclic conjugation or a very weak cyclic conjugation in the five-membered ring of acenaphthylenes and fluoranthenes. In full harmony with this, what has previously been called[25,26] the 'energy effect' of the five-membered ring of acenaphthylenes and fluoranthenes, assessed by a method described in detail in two reviews,[25,26] and elsewhere,[27,28] indicates the existence of a weak cyclic conjugation. However – unexpectedly – it was found[16] that this (weak) cyclic conjugation in the five-membered ring is significantly amplified by the presence of six-membered rings connected to the five-membered ring by a single carbon-carbon bond. Two of us (I.G. and A.T.B.), with Đurđević, named this effect the *PCP rule*,[16] where *PCP* is an acronym for '***p****henyl-* ***c****yclo****p****entadienyl*'. For an illustration of this, please see Figure 3 (a & b). According to the PCP rule, the energy effect caused by cyclic conjugation in the five-membered ring increases with the number of PCP fragments present in a given structure related to acenaphthylene or fluoranthene.

A simple illustration of the PCP rule is provided by fluoranthene (**5**) and its mono-, di-, tri-, and tetrabenzo derivatives (**6**, **9**, **13** and **15**), possessing 0, 1, 2, 3, and 4 six-membered rings in PCP constellation (see Figure 1), respectively. The energy effects of their five-membered rings are 0.0031, 0.0054, 0.0105, 0.0159, and 0.0211 β-units, respectively. The two isomeric acenaphthylenes **3** and **4** have one PCP fragment and two PCP

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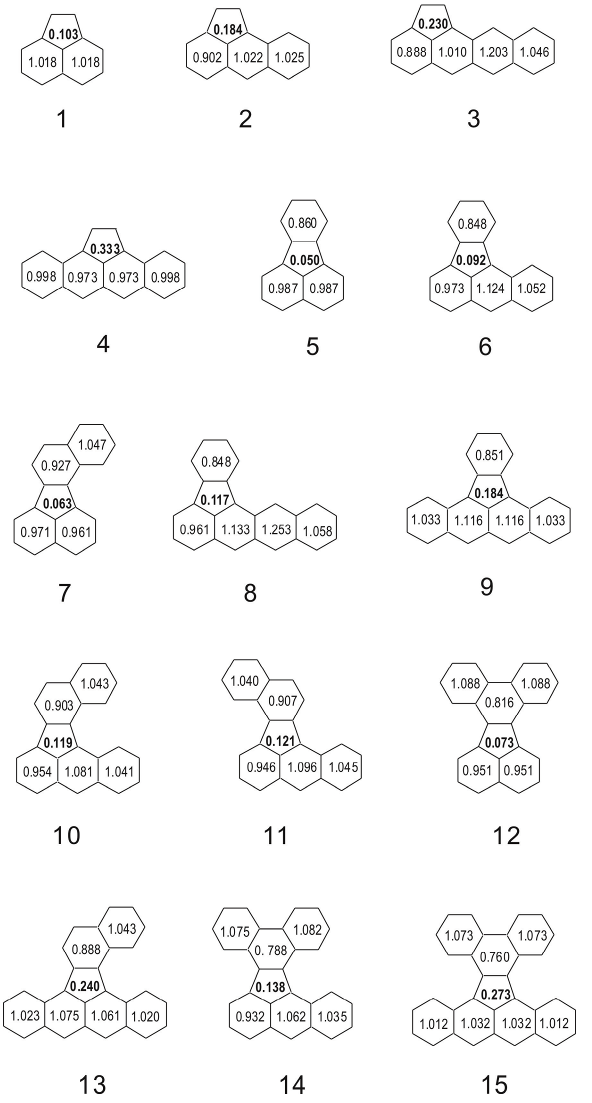

Figure 1. Acenaphthylene (**1**), fluoranthene (**5**), their derivatives containing one six-membered ring in PCP constellation (**2**, **3**, **6**, **7** and **8**), and two (**4**, **9**, **10**, **11** and **12**), three (**13** and **14**) and four (**15**) six-membered rings in PCP constellation, respectively. The values of the topological π-electron ring-current intensities borne by the several rings in these structures are inscribed (correct to three decimal places) inside the respective rings.

fragments, respectively (see Figure 1). The energy effects of their five-membered rings differ significantly: 0.0255 and 0.0390 β-units, respectively. Further examples are to be found elsewhere.[16,17,20] It should be noted that not a single violation of the PCP rule has so far been observed.

In addition to the PCP rule, several other regularities affecting the magnitude of cyclic conjugation in the five-membered ring of acenaphthylene and fluoranthene congeners have been reported.[17,20] These are much weaker than the PCP effect, and here we men-

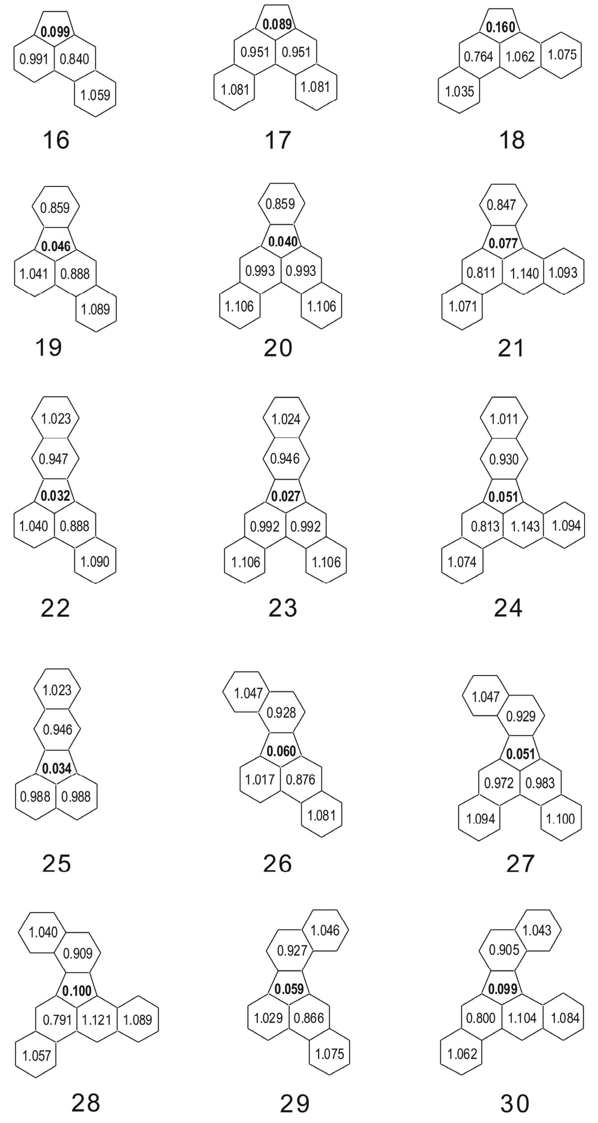

Figure 2. Derivatives of acenaphthylene and fluoranthene containing one (**16**, **18**, **19**, **21**, **25**, **26**, **28**, **29** and **30**), two (**17**, **20**, **22**, **24** and **27**) and three (**23**) six-membered rings in linear constellation, as well as one (**18**, **21**, **24**, **26**, **27** and **29**) and two (**28** and **30**) six-membered rings in PCP constellation. The values of the topological π-electron ring-current intensities borne by the several rings in these structures are inscribed (correct to three decimal places) inside the respective rings.

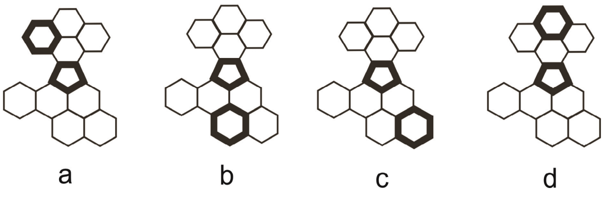

Figure 3. A molecule related to fluoranthene containing pairs of five-membered and six-membered rings (indicated by thick lines) that are in PCP constellation (a & b) and in linear constellation (c & d).

tion only the *linear effect*. A five-membered ring and a six-membered ring are said to be in a *linear constellation* if they are separated by a single six-membered ring, but are not in a PCP constellation. More precisely, a five-membered ring and a six-membered ring are in PCP constellation if the shortest path that separates them is one carbon-carbon bond in length (that is, there are no carbon atoms between them), and two such rings are in linear constellation if they are separated by two bonds (that is, there is just one carbon atom between them). For illustrative examples of the PCP and linear constellations, please see Figure 3 (a & b for the PCP constellation, and c & d for the linear constellation). According to a regularity that was named[17,20] the *linear effect*, the energy effect caused by cyclic conjugation in the five-membered ring decreases proportionally with the number of linear constellations present in the acenaphthylenes and/or fluoranthenes in question.

An illustration of the linear effect is provided by fluoranthene (**5**) and its mono-, di-, and tribenzo derivatives (**19**, **20** and **23**), possessing, respectively, 0, 1, 2, and 3 six-membered rings in linear constellation (see Figure 2). The energy effects of their five-membered rings are 0.0031, 0.0027, 0.0021, and 0.0015 β-units, respectively. From this example we see that the linear effect diminishes the magnitude of cyclic conjugation, but is much weaker than the PCP effect. Therefore, in acenaphthylene- and fluoranthene-type species in which six-membered rings in both PCP and linear constellations are present (see Figure 2), the effect of the former is the more dominant one, and thus prevails, overall.[17,20]

In view of the fact that the PCP rule was established by studying the energy effects of the five-membered rings, which themselves are computed at the level of Hückel Molecular Orbital (HMO) theory by use of an application of chemical graph-theory,[25,27] it would materially benefit belief in the validity of the rule if it could be checked by assessing it through appeal to other measures of cyclic conjugation. In two earlier papers it was shown that the PCP rule is corroborated by results based on multi-centre bond-indices,[19] Wiberg bond-orders,[24] and on *ab-initio* calculations effected in the context of Density-Functional Theory.[24] The general validity of the PCP rule was also recently confirmed by mathematical arguments,[21] albeit only at the level of the HMO approach.

In this paper we study another aspect of cyclic conjugation – topological π-electron ring-currents[29–31] – in the context of the acenaphthylene and fluoranthene congeners shown in Figures 1 and 2, in order further to assess the validity of the PCP rule.

RING CURRENTS

The topological π-electron ring-currents reported in Figures 1 and 2 were calculated by the Hückel[32]-London[33]-Pople[34]-McWeeny[35] (HLPM) method,[12] by means of the computer programs NPRC and MPRC,[36] recently revived and adapted by one of us (T.K.D.) at the University Chemical Laboratory, Cambridge (where – it is possibly of some historical interest to note – Pople[34] carried out the very first molecular-orbital ring-current calculation in the course of his classic work[34] on azulene, more than fifty years ago). The method is fully dissected, and is discussed in exhaustive detail, in Refs. 12, and 29−31. One of us (R.B.M.) has very recently argued[12] that

(a) when the HLPM method is used, and

(b) when only benzenoid hydrocarbons are considered, and

(c) when all Hückel Coulomb-integrals, α, are assigned the standard value of a carbon atom in benzene, and all resonance intergals, β, are likewise set equal to the standard value for a carbon-carbon bond in benzene, and

(d) when a geometry of standard regular-hexagons is assumed, and, finally,

(e) when ring-current intensities are expressed as a *ratio* to the ring-current intensity calculated, by the same method, for benzene,

then, once the carbon-carbon connectivity of a benzenoid molecule has been specified, the ring-current intensities so-calculated *are predetermined* and do not further depend on any subjective (or other) parameters. In that sense, the ring-current intensity that characterises each of the diverse rings in benzenoid molecules *is a purely graph-theoretical index* that depends solely on the knowledge of a vertex-adjacency matrix[37] for the graph representing the connectivity of the carbon atoms in the particular benzenoid molecule under study. The values of the topological ring-currents – though their actual numerical calculation may, in practice, be somewhat convoluted and laborious – are, in a sense, 'latent', as soon as the system's structure has been written down. Furthermore, once the eigenvectors and eigenvalues of the system's (arbitrarily labelled) adjacency-matrix[37] are known, their use for the calculation of the HMO quantities needed for the ring-current computations also requires knowledge of the ground-state π-electronic configuration for the conjugated system in question, determined by an application of the *Aufbau* Principle – a process which, it has been shown,[38–42] may itself be simulated by an entirely graph-theoretical algorithm based solely on knowledge simply of the *order* of the eigenvalues possessed by the system's adjacency matrix, arbitrarily labelled.

All the above has previously been stated and claimed only for the case of the condensed, benzenoid hydrocarbons.[12] It can, however, be argued, as we do as follows,[43] that the idea of a 'topological ring-current' can be extended from benzenoids to conjugated hydrocarbons *containing rings of more than one size.* This is because the only geometrical quantities (as distinct from 'topological' ones) that are needed for the ring-current calculations are the *ring areas* in the conjugated systems being studied.[12,30] We adopt here the simplest possible assumption (which is, indeed, the conventional assumption, originally proposed by Pople[34]) – namely, that the hexagons and rings of any other size that are in the conjugated system under study are *regular polygons of side equal in length to the standard carbon-carbon bond-length in benzene*. Simple trigonometry then determines that

$$\frac{\text{Area of a Regular } n\text{-gon}}{\text{Area of a Regular Hexagon}} = \frac{n\cot\left(\frac{\pi}{n}\right)}{6\cot\left(\frac{\pi}{6}\right)}$$

In the case of the conjugated systems containing a five-membered ring that are being studied here, the relevant ratio is

$$\frac{\text{Area of a Regular Pentagon}}{\text{Area of a Regular Hexagon}} = \frac{5\cot\left(\frac{\pi}{5}\right)}{6\cot\left(\frac{\pi}{6}\right)}$$

To calculator accuracy, this amounts to 0.66221206. It is sufficient that we curtail this to 0.6622 as, here, we quote our final ('rounded') ring-current intensities to no more than three places of decimals. Now, once the assumption has been made that the area of any five-membered ring is approximately 66% of the area of a benzenoid hexagon, then ring-currents calculated for structures such as **1**–**30** may be regarded[43] as being just as 'topological' as the ring-current intensities in benzenoid molecules that were encountered in Ref. 12.

It should be noted that structures **1**−**30** include some molecules – certainly **20**, **23**, and **27**, but there may be others – that are so severely overcrowded because of steric interactions amongst their peripheral protons that they are non-planar.[44–50] Strictly, the unmodified HLPM method should not be applied to these molecules[51–53] (though such has occasionally been done, in the past)[54–56] and — because, in the present work, the ring current is effectively being regarded purely as a mathematical, *graph-theoretical* index, and *not* as an assumed 'physical' quantity *per se* — this will again be done here (albeit with some misgivings). It is not strictly legitimate to perform HLPM ring-current calculations on such conjugated systems and then to attribute to the results any physical significance,[51–53] because 'ring-current' in the HLPM model is precisely defined as an exact quantity only for *planar* molecules; (please see refs. 51−53 for detailed discussion on this aspect). The topological ring-currents presented in Figures 1 and 2 for such geometrically non-planar molecules are thus, in effect, those for a *hypothetical* molecule having the same carbon–carbon connectivity as the actual molecule under consideration, but envisaged as if it were (geometrically) *planar*.

The topological π-electron ring-current intensities for the several rings in structures **1**−**30** – which are pure, dimensionless numbers – are displayed in Figures 1 and 2, the numerical values of the ring-current intensities being inscribed within the respective rings of the structures shown in those Figures. Data are consistently reported correct to three decimal places. It may be noted that the ring-currents for fluoranthene (**5**) and two mono-benzene derivatives of it (**19** and **25**) were published by one of us (R.B.M.) forty years ago.[57,58] The calculations reported in Figures 1 and 2 were carried out independently of that old work and the ring-currents for these three structures were found to agree precisely, to the number (three) of decimal places quoted, with those published in Refs. 57 and 58.

NUMERICAL WORK AND DISCUSSION

The most striking and immediate observation to be gleaned from an inspection of Figures 1 and 2 is that the ring currents in the five-membered rings are invariably much smaller than those in any of the six-membered rings – often smaller by more than one order of magnitude. This is consistent with the observation made some four decades ago by one of us (R.B.M.) in the context of a restricted sub-set of molecules (that included **19** and **25**) related to fluoranthene (**5**).[57,58] Ring-current considerations thus also imply that cyclic conjugation in the five-membered ring of acenaphthylenes and fluoranthenes is weak. (The fact that the ring-current values in the five-membered ring of acenaphthylenes are greater than those in fluoranthenes is easily rationalised by noting that in fluoranthenes this ring is adjacent to three six-membered rings whereas, in acenaphthylenes, it is adjacent to only two six-membered rings.) Nevertheless, the initial surprise, intuitively, when the ring-current data are first assessed is, perhaps, that the ring current in the five-membered ring can be as large as 33 % of the benzene value: it is observations of this sort that we seek to rationalise by means of the suggested PCP rule.

From the ring-current data given in Figures 1 and 2 we see that these do in fact agree perfectly with the proposed PCP rule. Consider the same illustrative examples as before: for fluoranthene (**5**) and its mono-, di-, tri-, and tetrabenzo derivatives (**6**, **9**, **13** and **15**), possessing 0, 1, 2, 3, and 4 six-membered rings in PCP constellation, respectively (see Figure 1): the ring currents in the five-membered ring are 0.050, 0.092, 0.184, 0.240, and 0.273, respectively. The five-membered rings in the two isomeric acenaphthylenes **3** and **4,** possessing one PCP fragment and two PCP fragments, respectively (see Figure 1), bear ring currents of intensity 0.230 and 0.333, respectively.

In the case of fluoranthene derivatives, a hexagon in a PCP constellation may be attached either to the naphthalene unit (as in **6**) or to the benzene unit (as in **7**). The former has a much stronger effect on the ring current in the five-membered ring. Thus, the ring currents in the five-membered rings of **6** and **7** are 0.092 and 0.063, respectively. Similarly, the analogous ring-current in **9** (equal to 0.184) is greater than those in **10** and **11** (equal to 0.119 and 0.121, respectively), which, in their turn, are greater than that in **12** (equal to 0.073). Note that **9**, **10**, **11**, and **12** all have two PCP fragments. A regularity fully analogous to this was also observed earlier in the case of energy effects.[17,20]

The structure dependency of the ring current in the five-membered ring is also in nice accord with the previously mentioned linear-effect. As before, we illustrate this by considering fluoranthene (**5**) and its mono-, di-, and tribenzo derivatives (**19**, **20** and **23**), possessing, respectively, 0, 1, 2, and 3 six-membered rings in linear constellation (see Figure 2). The ring currents in their five-membered rings are 0.050, 0.046, 0.040, and 0.027, respectively. From this example we see that the magnitude of the ring current in the five-membered ring diminishes with the number of benzene rings in linear constellation with it but, once again, this liner affect is much weaker than the PCP effect. As a consequence, in species related to acenaphthylene and fluoranthene in which six-membered rings in both PCP and linear constellations are present (see Figure 2), the ring currents are largely determined by the number of PCP constellations. For instance, the ring currents in the five-membered rings of the following structures, related to fluoranthene – **7** (1 PCP and 0 linear hexagons), **26**, **29** (1 PCP and 1 linear hexagon), and **27** (1 PCP and 2 linear hexagons) – differ only slightly: the π-electron ring-current intensities are 0.063, 0.060, 0.059, and 0.051, respectively.

More examples of the above kind are evident from further careful examination of Figures 1 and 2.

CONCLUDING REMARKS

The PCP rule is a peculiar property of acenaphthylenes and fluoranthenes, having no counterpart in the classical theory of polycyclic conjugated molecules. The whole essence of the PCP rule is that it is 'non- classical' and that it cannot be explained by means of Kekulé structures. It was discovered by studying the energy effects of the five-membered rings – *i.e.*, by means of a (chemical) graph-theoretical approach. The obvious question that emerged was whether the PCP rule was an artifact of the graph-theoretical foundation of the method used for computing the energy effects, or whether it reflects some intrinsic feature of the π-electron distribution in the molecules of this class. The present analysis, employing an independent consideration based on ring currents – albeit one also based on HMO theory and (thus[38−42]) chemical graph-theory – indicates that the latter might possibly be the case. This implies not only that the PCP rule is convincingly corroborated by arguments based on ring currents, but also that the molecular-structure dependence of the extent of cyclic conjugation, predicted by two (ostensibly) different methods, is in satisfactory agreement.

The quantum-chemical origin of the PCP rule remains obscure, but the veracity of the idea now seems, on the face of it, to be additionally verified. In concluding, however, we adopt a modicum of caution and qualify the claim just made in the previous sentence by emphasising that the topological π-electron ring-currents[12] to which we are here making appeal have themselves here been argued (indeed, in this very paper) to be purely graph-theoretical indices – even when the ring-current concept is applied to conjugated systems containing rings of more than one size.

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SAŽETAK

Struje prstenova i PCP pravilo

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Nedavno otkriveno PCP pravilo tvrdi da jakost cikličke konjugacije u peteročlanim prstenovima konjugiranih ugljikovodika acenaftilenskog i fluorantenskog tipa raste s brojem fenil-ciklopentadienilnih (PCP) fragmenata sadržanih u molekuli. Važenje ove pravilnosti je prvo bilo uočeno prilikom studija energetskih učinaka cikličke konjugacije u peteročlanim prstenovima. Da bismo pokazali da PCP pravilo nije artefakt primijenjene metode, bilo ga je potrebno potvrditi drugim postupcima. U ovom radu pokazujemo da je PCP pravilo u savršenom skladu s rezultatima izračunavanja struje prstenova, a što je jedna neovisna teorijska mjera cikličke konjugacije u prstenovima policikličkih π-elektronskih sustava. Osim toga, pokazujemo da je ovisnost struje prstenova od molekulske strukture u spojevima acenaftilenskog i fluorantenskog tipa suglasna i s drugim, ranije nađenim, pravilnostima za cikličku konjugaciju.