Indian Journal of Chemistry
Vol. 48A, May 2009, pp. 658-662

Notes

Extending the phenyl-cyclopentadienyl rule

Ivan Gutman*, Svetlana Jeremić & Vladimir Petrović

Faculty of Science, P.O. Box 60, 34000 Kragujevac, Serbia
Email: gutman@kg.ac.rs

Received 26 February 2009; accepted 8 April 2009

By examining the energy effect of cyclic conjugation in individual rings of acenaphthylene- and fluoranthene-type polycyclic conjugated molecules, a peculiar regularity - named the "PCP rule" - was recently discovered [Gutman, I, Đurđević J & Balaban A T, *Polycycl Arom Comp*, 29 (2009) 3]. According to the PCP rule, a six-membered ring which is connected to the five-membered ring by a single carbon-carbon bond increases the cyclic conjugation in the five-membered ring. An analogous regularity also exists in polycyclic conjugated species possessing an odd-membered ring of size greater than five.

Keywords: Theoretical chemistry, Graph theory, PCP rule, Energy effects, Cyclic conjugation, Polycyclic conjugation

The π-electron properties of benzenoid hydrocarbons have been investigated in theoretical chemistry for almost an entire century, and have been discussed in books[1-4], reviews[5-8], research papers[9-15], and the references cited therein. In a striking contrast to this, the class of structurally closely related polycyclic conjugated systems, in which one ring is odd-membered (usually five-membered) has been almost completely ignored. Very recently we have initiated a systematic research along these lines[16-21]. One of the remarkable and fully unexpected discoveries made was the so-called PCP rule (or PCP effect)[20]. We found that in acenaphthylene- and fluoranthene-type conjugated hydrocarbons the magnitude of cyclic conjugation in the five-membered ring is significantly increased if the molecule possesses one or more six-membered rings which are connected to the five-membered ring by exactly one carbon-carbon bond. (The underlying five- and six-membered rings form a phenyl-cyclopentadienyl fragment, hence the name PCP). The magnitude of cyclic conjugation was assessed by its energy effect (*ef*)[20,21]. However, the PCP effect has eventually been corroborated by a variety of other theoretical approaches[22,23] also. The PCP effect is illustrated in Fig. 1.

Acenaphthylene, fluoranthene and their congeners are polycyclic conjugated systems in which one or two benzenoid fragments are attached to the five-membered ring[16]. An immediate extension of these polycyclic conjugated molecules are the systems in which one or more benzenoid fragments are attached to an odd-membered ring of size R, ($R \geq 5$).. In what follows we denote this class by Γ_R . Thus, a polycyclic conjugated molecule belonging to class Γ_R possesses a single odd-membered ring of size R and all its other rings are six-membered. In Fig. 2 are given characteristic examples illustrating the structure of the members of the class $\Gamma_{R,}$ and explanations of the terminology used below. Acenaphthylene, fluoranthene and their congeners belong to the class Γ_5 whereas pleiadiene and its congeners (shown in Fig. 3) to the class Γ_7.

At this point the natural question is: Is the PCP rule limited to the members of the class Γ_5 or can its validity be extended? Herein we report our findings which show that the latter is true, and that cyclic conjugation in the odd-membered ring of any member of Γ_R, $R \geq 5$, is amplified by six-membered rings connected to it by a single carbon-carbon bond. In Fig. 3 this is illustrated by pleiadiene and its congeners.

On the energy effect of a ring

In the present work we have used the standard method for assessing the magnitude of cyclic conjugation in a ring of a polycyclic conjugated molecule, based on the effect that this ring has on the total π-electron energy. For the details of this

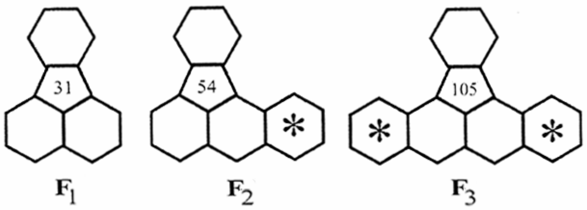

Fig. 1 – Examples illustrating the PCP effect[20,21]. [Fluoranthene (**F**$_1$); benzo[*a*]fluoranthene (**F**$_2$); dibenzo[*a,f*]fluoranthene (**F**$_3$). The six-membered rings which are in PCP constellation to the five membered ring are indicated by asterisks. The *ef*-value of the five-membered ring (multiplied by 10,000 and expressed in the units of the HMO carbon-carbon resonance integral β) is inscribed into this ring; for details see text].

approach see the review,[24] the recent papers[25,26] and the references cited therein. In nutshell, if G is the molecular graph of a polycyclic conjugated molecule and Z is a cycle contained in G, then the energy effect of this cycle is computed as

$$ef = ef(G,Z) = \frac{2}{\pi}\int_{0}^{\infty} \ln\left|\frac{\phi(G,ix)}{\phi(G,ix)+2\phi(G-Z,ix)}\right| dx \qquad \ldots (1)$$

In Eq. (1) G-Z is the subgraph obtained by deleting the cycle Z from the molecular graph G, $\phi(H,x)$ denotes the characteristic polynomial of the graph H (in our case: H=G and H=G-Z), and $i=\sqrt{-1}$. In Eq. (1), the quantity ef is expressed in the units of the Huckel molecular orbital (HMO) carbon-carbon resonance integral β. Since β<0, positive *ef*-values imply thermodynamic stabilization (caused by the cycle Z). Therefore, the larger is the *ef*-value of a ring, the stronger is the (stabilizing) cyclic conjugation in this ring.

The fact that *ef* provides a reliable quantitative measure of cyclic conjugation in a ring of a polycyclic conjugated molecule has been confirmed by several independent studies, for instance[27,28].

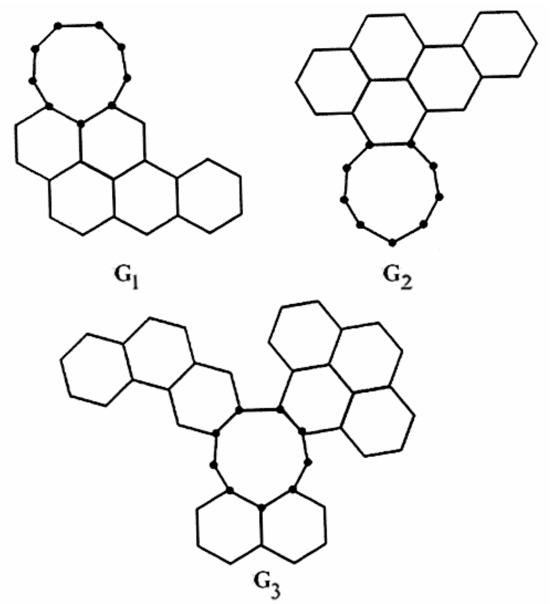

Fig. 2 – Three members of the class Γ_R for R=9. In $\mathbf{G}_1$ and $\mathbf{G}_2$ a single benzenoid fragment (benzo[*a*]pyrene) is attached to the 9-membered ring, in $\mathbf{G}_3$ three benzenoid fragments are attached (naphthalene, phenanthrene and pyrene). Benzo[*a*]pyrene in $\mathbf{G}_1$ and naphthalene in $\mathbf{G}_3$ are attached in a “female” mode, whereas the mode of attachment of benzo[*a*]pyrene in $\mathbf{G}_2$ and of phenanthrene and pyrene in $\mathbf{G}_3$ is referred to as “male”[21].

Cyclic conjugation in odd-membered ring of conjugated molecules of class Γ_R

The currently most frequently employed theoretical methods for describing the behaviour of polycyclic conjugated π-electron systems are based on the examination of their Kekulè structures, conjugated circuits or Clar aromatic sextet formulas[1-4,7]. These methods work reasonably well for benzenoid hydrocarbons. However, in the case of molecules from the class Γ_R these theories predict that cyclic conjugation in the odd-membered ring is zero. (Such a prediction is based on the fact that in Γ_R-type molecules some carbon-carbon bonds of the odd-membered ring are single while some are double

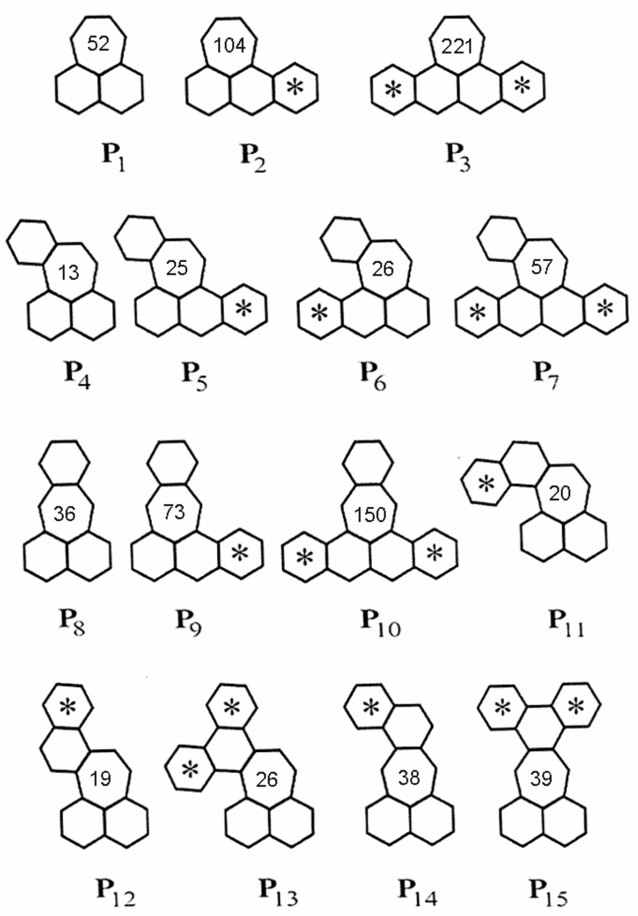

Fig. 3 – PCP effect illustrated for pleiadiene ($\mathbf{P}_1$) and its congeners. These examples illustrate the validity of the POR effect in the case when the size of the odd-membered ring is 7. With the increasing number of rings marked by asterisks, the *ef*-values increase in the homologous series $\mathbf{P}_1 - \mathbf{P}_2 - \mathbf{P}_3$ „ $\mathbf{P}_4 - \mathbf{P}_5 - \mathbf{P}_6 - \mathbf{P}_7$ „ $\mathbf{P}_8 - \mathbf{P}_9 - \mathbf{P}_{10}$ „ $\mathbf{P}_4 - \mathbf{P}_{11} - \mathbf{P}_{12} - \mathbf{P}_{13}$ and $\mathbf{P}_8 - \mathbf{P}_{14} - \mathbf{P}_{15}$. Notice that six-membered rings in the “male” benzenoid fragment have a much weaker influence than the six-membered rings in the “female” benzenoid fragment.

in all Kekulè structures. This gives the impression that the π-electrons in the odd-membered ring are localized and therefore cyclic conjugation is absent).

More subtle theoretical considerations, such as those based on Eq. (1), show that although the cyclic conjugation in the odd-membered ring is much weaker than in the other six-membered rings, it is far from negligible. Furthermore, its magnitude is rather sensitive to the structural details in the vicinity of the odd-membered ring. Examples illustrating this fact are given in Figs 1 and 3.

Examining in more detail the cyclic conjugation in the five-membered ring of Γ_5-type molecules[20,21], we envisaged a regularity, named the PCP rule[20] (*cf.* Fig. 1). We are now in a position to formulate a somewhat more general regularity, of which the PCP rule is a special case for R=5. We propose to name it the POR rule, from phenyl-odd-membered-ring.

If a six-membered ring in a Γ_R-type molecule is connected to the odd-membered ring via a single carbon-carbon bond, then we say that it is in a POR constellation to the odd-membered ring (see the rings marked by asterisks in Figs 1, 3 and 4).

The POR rule

In a molecule belonging to the class Γ_R, six-membered rings in POR constellation increase the magnitude of cyclic conjugation in the odd-membered ring. The greater is the number of six-membered rings in POR constellation, the stronger is the cyclic conjugation in the odd-membered ring. The fact that the POR rule is applicable to odd-membered rings of any size is illustrated by the data given in Table 1.

Only the six-membered rings in POR constellation influence, significantly, the cyclic conjugation in the odd-membered ring. Other types of six-membered rings have a much weaker effect, as seen from the examples shown in Fig. 5.

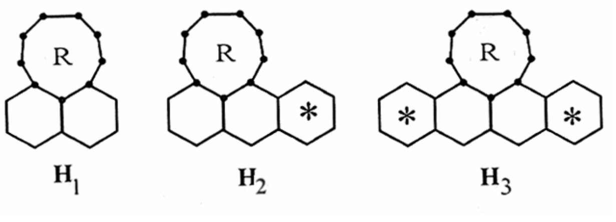

Fig. 4 – Members of the class Γ_R whose *ef*-values for the odd-membered ring are given in Table 1. The six-membered rings in POR constellation to the odd-membered ring are indicated by asterisks.

According to the above formulated POR rule, six-membered rings in POR constellation increase the magnitude of cyclic conjugation in the odd-membered ring. If so, then a carbon-carbon bond which is single in all Kekulè structures should acquire a certain amount of double-bond character and thus become shorter. Analogously, a carbon-carbon bond which is double in all Kekulè structures should lose some of its double-bond character and thus become longer. This geometry change, caused by the POR effect was checked, on pleiadiene (**P**$_1$), benzo[*a*]pleiadiene (**P**$_2$) and dibenzo[*a,f*]pleiadiene (**P**$_3$) (*cf.* Fig. 3). Their ground-state geometries were determined by density functional theory at the B3LYP/6-311G(dp) level, using the GAUSSIAN 03W package[29], ver. 6.1. The geometries of the species **P**$_1$, **P**$_2$ & **P**$_3$ are shown in Fig. 6. The bond lengths relevant for the present

Table 1 – The *ef*-values (in β units) of the odd-membered ring of size R in the molecules depicted in Fig. 4. [In **H**$_1$ there are no POR constellations, whereas in **H**$_2$ and **H**$_3$ there are, respectively, one and two POR constellations. In harmony with the POR rule, for all values of R, $ef(\mathbf{H}_1) < ef(\mathbf{H}_2) < ef(\mathbf{H}_3)$]

R	$ef(\mathbf{H}_1)$	$ef(\mathbf{H}_2)$	$ef(\mathbf{H}_3)$
5	0.0114	0.0206	0.0390
7	0.0052	0.0104	0.0221
9	0.0028	0.0062	0.0141
11	0.0017	0.0040	0.0097
13	0.0011	0.0027	0.0070
15	0.0008	0.0020	0.0053
17	0.0006	0.0015	0.0041
19	0.0004	0.0011	0.0032
21	0.0003	0.0009	0.0026

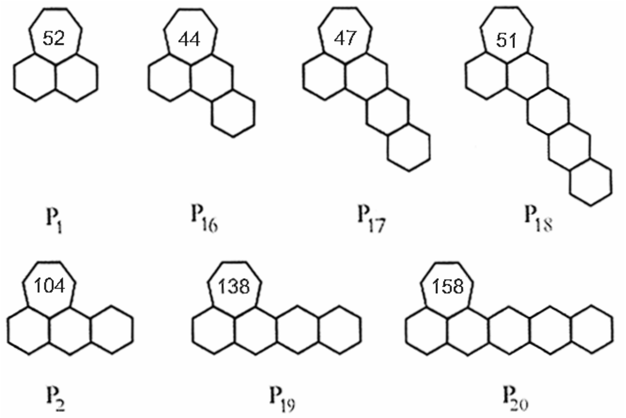

Fig. 5 – PCP effect illustrating that six-membered rings that are not in POR constellation only weakly influence the *ef*-value of the odd membered ring in pleiadiene congeners. Analogous results are obtained for systems with odd-membered rings of larger size.

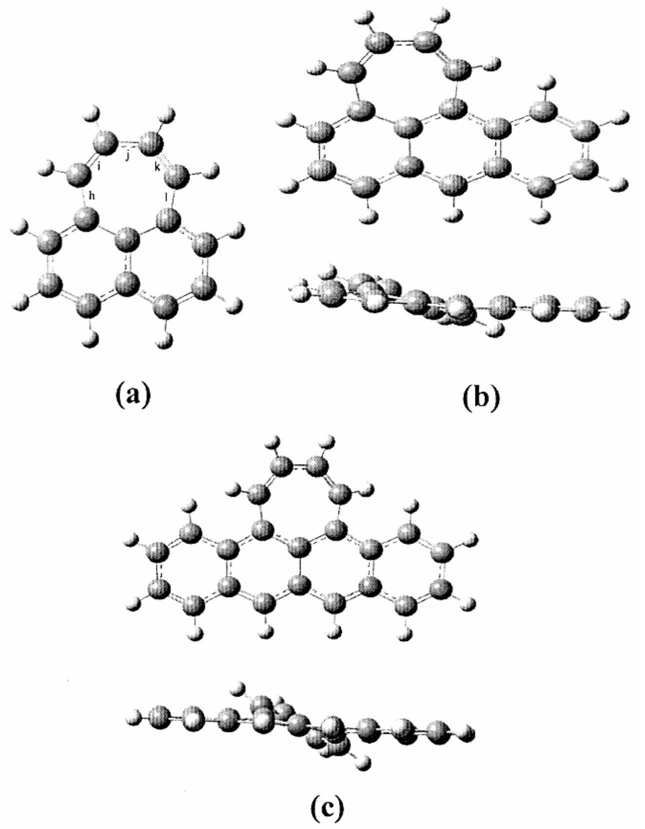

Fig. 6 – The geometry as determined by the B3LYP/6-311G(dp) *ab initio* method. [(a) pleiadiene ($\mathbf{P}_1$), The molecule was found to be perfectly planar; (b) benzo[*a*]pleiadiene ($\mathbf{P}_2$); (c) dibenzo[*a,f*]pleiadiene ($\mathbf{P}_3$). The lengths of the carbon-carbon bonds *h, i, j, k, l*, labeled as in (a), are given in Table 2].

considerations are given in Table 2. Other details of the respective geometries can be obtained from the authors upon request.

In pleiadiene ($\mathbf{P}_1$) and its derivatives ($\mathbf{P}_2$ & $\mathbf{P}_3$), the lengths of the carbon-carbon bonds *h, i, k, l* (as well as of other bonds, not reported herein) are found to be greatly influenced by the steric interaction (repulsion) between the near-lying hydrogen atoms (Fig. 6). Therefore, the best bond for testing the POR effect would be *j*, which in the Kekulè-structure picture is single. Indeed, as seen from Table 2, its length decreases with the increasing number of POR constellations.

Much less convincing is the finding that (in agreement with the POR rule) the bond *h* is shorter in $\mathbf{P}_2$ than in $\mathbf{P}_1$. The fact that it is extended in $\mathbf{P}_3$ is to be expected on the basis of increased steric repulsion caused by the near-lying hydrogen atoms. Why the double bond, *I*, is slightly shorter in $\mathbf{P}_2$ than in $\mathbf{P}_1$ is not easy to explain. This certainly contradicts what we would expect on the basis of the POR rule. Therefore, the fact that in $\mathbf{P}_3$ this bond is significantly longer than in $\mathbf{P}_1$ and $\mathbf{P}_2$ cannot be taken as a persuasive argument in favour of the POR rule. As already explained, the length of the bonds *k* and *l* is so much affected by steric repulsion that the influences of the POR effect (if any) are fully obscured.

Table 2 – Lengths (in pm) of the carbon-carbon bonds, *h,i, j,k, l* (as indicated in Fig. 6) of pleiadiene ($\mathbf{P}_1$), benzo[*a*]pleiadiene ($\mathbf{P}_2$) and dibenzo[*a,f*]pleiadiene ($\mathbf{P}_3$), as determined by the B3LYP/ 6-311G(dp) *ab initio* method

Bond	Type	$\mathbf{P}_1$	$\mathbf{P}_2$	$\mathbf{P}_3$
h	single	146.22	146.17	146.38
i	double	134.66	134.61	134.74
j	single	143.99	143.78	143.77
k	double	134.66	134.80	134.74
l	single	146.22	146.36	146.84

Anyway, the calculated geometries of $\mathbf{P}_1$, $\mathbf{P}_2$ and $\mathbf{P}_3$, especially the length of the steric-strain free bond *j*, provide evidence of the validity of the POR rule, at least in the case of pleiadiene derivatives.

The results and examples presented herein are just a selection of a much greater number of *ef*-values calculated by us. Without a single exception, these *ef*-values obey the POR rule. Our calculations indicate that the POR effect is strongest in acenaphthylene- and fluoranthene-derivatives (i. e., in the class Γ_5), somewhat weaker in pleiadiene-derivatives (i. e., in the class Γ_7), and is gradually attenuated in the analogous molecules with larger odd-membered rings (classes Γ_R for R=9,11,…). This is clearly seen from the data given in Table 1.

Another peculiar feature needs to be pointed out here. Although the POR effect exists in all cases when hexagons in POR constellation are present, its magnitude is visibly greater in cases when the respective hexagon belongs to the "female" benzenoid fragments (*cf.* Fig. 3). This phenomenon, first noticed in the case of Γ_5-type molecules[21], deserves to be examined in more detail.

In our opinion, the polycyclic conjugated molecules belonging to the classes Γ_R, R = 5,7,9,…, provide an interesting, natural and non-trivial extension of the earlier much studied class of benzenoid hydrocarbons. Some properties of benzenoid hydrocarbons are preserved also in Γ_R-type species. On the other hand, some properties of the Γ_R-type species are new and some are also unexpected[19,20]. We hope to have contributed to the better understanding of these latter properties, and intend to continue along the same lines.

Acknowledgement

The authors thank the support by the Serbian Ministry of Science, through Grant no. 144015G, and Project Graph Theory and Mathematical Programming with Applications to Chemistry and Engineering.

References

1 Clar E, *The Aromatic Sextet*, (Wiley, London) 1972.
2 Gutman I & Cyvin S J, *Introduction to the Theory of Benzenoid Hydrocarbons*, (Springer-Verlag, Berlin) 1989.
3 *Advances in the Theory of Benzenoid Hydrocarbons*, edited by I Gutman & S J Cyvin, (Springer-Verlag, Berlin) 1990.
4 *Advances in the Theory of Benzenoid Hydrocarbons II*, edited by I Gutman, (Springer-Verlag, Berlin) 1992.
5 Balaban A T, *Pure Appl Chem,* 54 (1982) 1075.
6 Gomes J A N F & Mallion R B, *Chem Rev*, 101 (2001) 1349.
7 Randić M, *Chem Rev,* 103 (2003) 3449.
8 Balaban A T, Schleyer R v R & Rzepa H S, *Chem Rev* 105 (2005) 3436.
9 Gutman I, *Indian J Chem*, 43A (2004) 1615.
10 Furtula B, Gutman I & Turković N, *Indian J Chem*, 44A (2005) 9.
11 Gutman I, Milosavljević S, Furtula B & Cmiljanović N, *Indian J Chem*, 44A (2005) 13.
12 Gutman I, Stanković S, Kovačević R, Đurđević J & Furtula B, *Indian J Chem*, 44A (2005) 1751.
13 Gutman I, Vodopivec A, Radenković S & Furtula B, *Indian J Chem*, 45A (2006) 347.
14 Gutman I, Turković N & Furtula B, *Indian J Chem*, 45A (2006) 1601.
15 Furtula B & Gutman I, *Indian J Chem*, 47A (2008) 220.
16 Gutman I & Đurđević J, *MATCH Commun Math Comput Chem*, 60 (2008) 659.
17 Gutman I, Đurđević J, Furtula B & Milivojević B, *Indian J Chem*, 47A (2008) 803.
18 Đurđević J, Radenković S & Gutman I, *J Serb Chem Soc*, 73 (2008) 989.
19 Gutman I, Đurđević J, Radenković S & Burmudžija A, *Indian J Chem*, 37A (2009) 194.
20 Gutman I, Đurđević J & Balaban A T, *Polycycl Arom Comp*, 29 (2009) 3.
21 Đurđević J, Gutman I, Terzić J & Balaban A T, *Polycycl Arom Comp*, 29 (2009) (in press).
22 Đurđević J, Gutman I & Ponec R, *J Serb Chem Soc*, 74 (2009), in press.
23 Đurđević J, Radenković S, Gutman I & Marković S, Unpublished results.
24 Gutman I, *Mon Chem*, 136 (2005) 1055.
25 Gutman I, Stanković, S, Đurđević J & Furtula B, *J Chem Inf Model*, 47 (2007) 776.
26 Gutman I & Stanković S, *Mon Chem*, 139 (2008) 1179.
27 Aihara J, *J Am Chem Soc*, 128 (2006) 2873.
28 Ponec R, Fias S, Van Damme S, Bultinck P, Gutman I & Stanković, *Coll Czech Chem Commun*, 74 (2009) 147.
29 *Gaussian 03, Rev. E.01-SMP*, (Gaussian Inc., Pittsburgh, PA) 2003.