Isomer enumeration of nonradical strictly peri-condensed polycyclic aromatic hydrocarbons

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Received January 16, 1984

A new concept for isomer enumeration of peri-condensed benzenoid hydrocarbons (PAH6) based on the enumeration of their excised internal structures is presented. Formulas corresponding only to strictly peri-condensed benzenoid hydrocarbons can be identified from a previously derived Formula Periodic Table for PAH6. The number of benzenoid PAH6 isomers having formulas C8H6, C10H8, C12H10, C14H12, C16H14, C18H16, C20H18, C22H20, and C24H22 are 10, 3, 1, 22, 7, 2, 20, 12, and 3, respectively (Fig. 1). A nomenclature for these PAH6s based on an already established nomenclature for their corresponding small-molecule, excised internal structures is proposed. The structure counts of these PAH6s, being related to their resonance energy, have been determined, and this will permit researchers to estimate the most probable structures of the macromolecular benzenoid hydrocarbons of this class formed via pyrolytic processes.


On présente un nouveau concept qui permet de faire l'énumeration des isomères d'hydrocarbures benzénoides péri-condensés (HAP6); ce nouveau concept est basé sur l'énumeration des structures internes simplifiées de ces hydrocarbures. Faisant appel à un tableau périodique des formules de HAP6 qui a été dérivé antérieurement, on peut identifier des formules qui correspondent spécifiquement à des hydrocarbures benzénoides strictement péri-condensés. Parmi les produits benzénoides de formules C8H6, C10H8, C12H10, C14H12, C16H14, C18H16, C20H18, C22H20, et C24H22, les nombres d'isomères de HAP6 sont respectivement 10, 3, 1, 22, 7, 2, 20, 12 et 3 (Fig. 1). On propose un système de nomenclature des petites molécules correspondantes et de leurs structures internes simplifiées. On a déterminé que le compte de structure de ces HAP est relié à leur énergie de résonance et ceci permettra aux chercheurs d'évaluer les structures les plus probables des hydrocarbures benzénoides macromoléculaires de cette classe qui se forment par le biais de processus pyrolytiques.

[Traduit par le journal]
have no internal third-degree carbon vertices ($N_{lc} = 0$ and $N_{c} = q_0$). Thus the two isomers of $C_{14}H_{10}$ both have a perimeter length of 14 carbon atoms, and pyrene ($C_{16}H_{10}$) has two internal third-degree carbon vertices ($N_{lc} = 2$) with a perimeter length of 14 carbon atoms, giving a total of 16 carbon atoms in its formula. Similarly, all five PAH6 isomers of $C_{18}H_{10}$ have a perimeter length of 18 carbon atoms, and the three isomers of $C_{20}H_{12}$ have $N_{lc} = 2$, the two nonradical PAH6 isomers of $C_{22}H_{12}$ have $N_{lc} = 4$, and coronene ($C_{24}H_{12}$) has $N_{lc} = 6$, all with a perimeter length of 18 carbon atoms. In hexagonal graphs the maximum number of internal third-degree carbon vertices that can be contained in a 10-carbon-atom peripheral cycle is zero (naphthalene), in a 14-carbon-atom peripheral cycle it is two (pyrene), and in an 18-carbon-atom peripheral cycle it is six (coronene). Polycircumnaphthalene, polycircumpyrene, and polycircumcoronene are three series of formulas appearing on the left-hand diagonal boundary of Table 1. Each formula of these series has only one corresponding PAH6 structure. These terminal formulas have PAH6 structures containing the maximum number of internal third-degree carbon vertices ($N_{lc}^{(min)}$) that each corresponding peripheral cycle carbons can contain. Table 2 summarizes the relevant information for these one-isomer series.

From the narration presented in the last paragraph, it is evident that PAH6s have an even number of perimeter carbon vertices, since $q_0 = N_{pc} + N_{H} = 2N_{H} - 6$ must be an even number. From this it follows that $N_{lc}$ is even for even PAH6 formulas and odd for odd radical PAH6 formulas (5). For peri-condensed PAH6s with $N_{lc}$ internal third-degree vertices, the number of PAH6 isomers is equal to the number of non-radical isomeric excised internal structures having $N_{lc}$ carbon atoms obtained by clipping $N_{pc}$ internal edges (bonds) to perimeter carbons and attaching hydrogen to $N_{pc}$ dangling bonds thus formed on the separated structures. It is important to note that all isomeric internal structures must have the same number of rings and carbon vertices ($N_{c}$ of parent), i.e., $d_{i} = \text{constant}$.

This process is illustrated by the structures in Fig. 2. Ethene, having two carbons, is the excised internal structure of pyrene ($C_{16}H_{10}$), and $C_{16}H_{10}$ ($N_{lc} = 2$) can only have one possible PAH6 isomer. $s$-trans-1,3-Butadiene, having four carbons, is the excised internal structure of anthanthrene ($C_{22}H_{12}$, $N_{lc} = 4$), and $s$-cis-1,3-butadiene is the excised internal structure of benzo(ghi)perylenne ($C_{22}H_{12}$, $N_{lc} = 4$); since triangulene and its excised structure, trimethylenemethane, (which are not shown) are diradicals, the formula of $C_{22}H_{12}$ can be represented only by the above two nonradical PAH6 isomeric structures. The excised internal structure of coronene ($C_{24}H_{12}$, $N_{lc} = 6$) is benzene, and $C_{24}H_{12}$ has only one PAH6 structure. The excised internal structure of circumcoronene ($C_{28}H_{18}$) is coronene ($C_{24}H_{12}$), and circumcoronene is the excised internal structure of dicircumcoronene ($C_{36}H_{22}$). Thus dicircumcoronene and circumcoronene have no other PAH6 isomers (7). Previously, it was shown that there were only three nonradical PAH6 isomers of the formula $C_{30}H_{18}$ (7). In Fig. 2, four PAH6 structures having the formula of $C_{30}H_{18}$ are shown, along with their corresponding excised internal structures. Styrene is the excised internal structure of naphtho(abc)coronene, 1,2-benzoquinodimethane of dibenzol be,cf)coronene, 1,3-benzoquinodimethane of the third $C_{30}H_{18}$ structure, and 1,4-benzoquinodimethane of dibenzol be,kl)coronene (dibenzoperopyrene). However, since 1,3-benzoquinodimethane is a diradical and the [22]annulene perimeter is an even alternant hydrocarbon, the third $C_{30}H_{18}$ structure shown in Fig. 2 must be a diradical.

<p>| Table 1. Formula periodic table for benzene polycyclic aromatic hydrocarbons (PAH6) $^{a,b}$ |
|---|---|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>$N_{lc}$</th>
<th>$N_{c}$</th>
<th>$d_{i}$</th>
<th>$d_{i-1}$</th>
<th>$d_{i-2}$</th>
<th>$d_{i-3}$</th>
<th>$d_{i-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>$C_{16}H_{10}$</td>
<td>$C_{18}H_{10}$</td>
<td>$C_{20}H_{12}$</td>
<td>$C_{22}H_{12}$</td>
<td>$C_{24}H_{12}$</td>
<td>$C_{26}H_{12}$</td>
<td>$C_{28}H_{18}$</td>
</tr>
<tr>
<td>$C_{30}H_{18}$</td>
<td>$C_{32}H_{22}$</td>
<td>$C_{34}H_{22}$</td>
<td>$C_{36}H_{22}$</td>
<td>$C_{38}H_{22}$</td>
<td>$C_{40}H_{22}$</td>
<td>$C_{42}H_{22}$</td>
</tr>
</tbody>
</table>

$^{a}$Number of nonradical isomers in parentheses. $^{b}$For the row series, $N_{lc} = 2N_{H} - 6$ for $N_{lc} < 3$. For the column series, $N_{lc} = 3N_{H} - 14 + 2t$.
and is not counted. In general, if the excised internal structure is a diradical which can be formed by connecting a non-starred position of a monoradical with a starred position of a second monoradical, its parent PAH6 structure will also be a diradical. Note that a strictly peri-condensed polycyclic aromatic hydrocarbon cannot have a disconnected excised internal structure. Thus perylene is not a strictly peri-condensed PAH6, nor is dibenzo(de,hi)naphthacene diradical.
Enumeration of excised internal structures

Figure 3 presents all the corresponding (primed) excised internal structures of all the parent PAH6 isomers shown in Fig. 1. The first nine substituted naphthalene structures (1'-9') and biphenyl (10'), all having twelve carbon atoms in Fig. 3, correspond in order and orientation to the ten C₃₈H₁₆ (Nᶜ = 12) isomers in Fig. 1. Only one of two possible conformers of 1-ethynl naphthalene (1') is presented, while both
possible conformers (2', 3') of 2-ethenynaphthalene appear. This is because a two-carbon-atom gap needs to exist between the s-cis-1,3-butadiene system of any excised internal structure of a PAH6 parent. Thus the other conformer of 1-ethenyl-
naphthalene has a one-carbon-atom gap and is therefore excluded. Only six of ten possible naphthoquinodimethanes (4'–9') are present in Fig. 3 because the other four are diradicals. There are only three nonradical isomeric conjugated
three-ring structures of fourteen carbon vertices (11′−13′) and, therefore, only three corresponding benzenoid PAH6 structures of the formula C_{21}H_{16} with N_c = 14 exist. The Fig. 1 formula of C_{21}H_{16} (N_c = 16) has only one possible structure, circumpyrene, since the excised internal structure corresponds to pyrene (14′), which is the only arrangement possible for sixteen carbon vertices of four hexagonal rings.

All benzenoid PAH6 structures of the formula of C_{29}H_{18} have N_c = 18 and excision of their internal structures leads to three ethenylpyrene, (15′−17′), nine nonradical pyrenylquinodimethane (18′−25′ and 36′), six perianthracenylmethylene (26′−31′), naphthacene (32′), chrysene (33′), benzo(a)anthracene (34′), and triphenylene (35′) isomers of four rings and eighteen carbon vertices. The excised internal structures (Fig. 3) corresponding to PAH6s of the formula C_{29}H_{18} (N_c = 20) lead to benzo(a)pyrene, (37′), benzo(e)pyrene (38′), four methylene-substituted isomers of naphtho[2,1,8,7-defg]anthracene (39′−42′), and perylene (43′) (C_{32}H_{22}). The formula C_{32}H_{22} (N_c = 22) has only two excised internal isomeric structures, anthanthrene (44′) and benzo(ghi)perylene (45′) (C_{28}H_{18}), and therefore the benzenoid formula of C_{32}H_{22} has only two corresponding PAH6 isomers. Finally, the formula of C_{30}H_{18} (N_c = 26) has 20 nonradical excised internal isomeric structures of twenty-six carbon vertices and seven rings (46′−65′) which correspond to 20 PAH6s.

Usually all isomers of pericondensed benzenoid PAH6 isomers without cata-condensed appendages can be enumerated by finding all excised nonradical isomeric internal structures of N_c (parent) carbon vertices. The limitations associated with this method can be illustrated by the enumeration of all eight non-radical isomers of C_{23}H_{14}. All the PAH6 isomers of C_{23}H_{14} (N_c = 6) and their corresponding excised internal structures are presented in Fig. 4. The first isomer, benzocoronene, has the same excised internal structure, benzene, as coronene and illustrates that cata-condensed appendages are not revealed by the excised internal structure method; this first C_{23}H_{14} isomer has the only excised internal structure which is a ring, suggesting an implicit disconnection elsewhere. The next four isomers have excised internal structures corresponding to all possible conformations of 1,3,5-hexatriene that do not have less than two-carbon-atom gaps. Immediately following are the two isomers having the two conformations of 3-methylene-1,4-pentadiene as excised internal structures. Finally, the last two C_{28}H_{18} benzenoid isomers have diradical excised internal structures. The first diradical can be constructed by the union of two allyl radicals through their nonstarred positions and the latter one by attaching the nonstarred position of one to the starred position of the other. Since the first diradical has two mutually exclusive pπ-electron systems and the latter one does not, the corresponding PAH6 structure of the first diradical internal structure is nonradical (closed shell) and the corresponding PAH6 structure of the latter one is also a diradical (open shell) and is not included in the isomer count.

Above it was shown that the formula C_{29}H_{18} had only two nonradical isomers, anthanthrene and benzo(ghi)perylene, with the corresponding internal excised structures of s-trans-1,3-butadiene and s-cis-1,3-butadiene (Fig. 2), respectively.
Anthanthrene and benzo(ghi)perylene are the excised internal structures of the two isomeric benzenoid hydrocarbons having the formula of C_{25}H_{18} (Fig. 1); similarly, these isomeric C_{25}H_{18} structures are the excised internal structures of the two benzenoid structures of the formula of C_{35}H_{30} (Fig. 5). There are three nonradical isomers of the formula C_{35}H_{34}, and these are the excised internal struc-
Not strictly peri-condensed

FIG. 4. All the benzenoid isomers of $C_{28}H_{14}$ and their corresponding excised internal structures.

tures of the benzenoid hydrocarbons having a formula of $C_{60}H_{30}$ (Fig. 6), which in turn are the excised internal structures associated with benzenoid hydrocarbons of the formula $C_{148}H_{30}$. Table 3 presents a summary of these polycircum two- and three-isomer series. Other polycircum isomorphic series include $C_{40}H_{16}$, $C_{78}H_{22}$, $C_{128}H_{28}$ — where each of these formulas have 3 corresponding nonradical PAH$_6$ isomers, and $C_{50}H_{18}$, $C_{92}H_{24}$, $C_{148}H_{30}$, each having 7 corresponding nonradical PAH$_6$ isomers.

Recognition of peri-condensed diradical benzenoids

Inspection of the diradical excised internal structures of triangulene, $C_{28}H_{14}$, and $C_{50}H_{18}$ reveals the following general principle for recognizing when even-carbon peri-condensed benzenoid hydrocarbons will be diradicals. If trimethylene-methane diradical is ultimately obtained upon successive excision and pruning of a specified benzenoid hydrocarbon having a formula below the $N_C = 2N_H - 4$ row series in Table 1, then that original benzenoid hydrocarbon is also a diradical. The trimethylene-methane diradical is the excised internal structure of triangulene and is also obtained by pruning off the even-carbon fragments of ethene from 2-methylene-pentadienyl diradical (Fig. 4) and $s$-trans-butadiene from 1,3-benzoquinodimethane (Fig. 2). This recognition generalization is equivalent to taking the difference in opposing triangles generated by the corresponding dualist graph where a line is drawn from every point located at the center of all hexagons (8).

A simplified nomenclature for strictly peri-condensed benzenoid hydrocarbons

Successive excision of all strictly peri-condensed PAH$_6$s usually leads to a simpler molecule which already has a standard nomenclature. Thus a straightforward nomenclature of complicated peri-condensed benzenoid hydrocarbons can be developed by using the corresponding excised internal structure for the parent name. Consider structure 60 in Fig. 1, which has structure 60' in Fig. 3 as its corresponding excised internal structure. One name for this excised internal structure could be 9-methylenylbenzo(fg)anthanthrene, and the name of the corresponding $C_{60}H_{30}$ structure could be circum(34)[9-methylenylbenzo(fg)anthanthrene] where the number in parentheses after the “circum” prefix represents the number of peripheral carbon vertices circumscribed to the parent. This nomenclature would be deductively more obvious than the perifusene/dualist graph/three-digit coding nomenclature and its graphite lattice model variant previously proposed (9—11).

Computation of the number of Kekulé structures associated with strictly peri-condensed benzenoids

Since the logarithm of the structure count (number of Kekulé structures or 1-factor subgraphs) of benzenoid PAHs has been shown to be proportional to resonance energy, the structure count ($SC = K$) of the isomers shown in Fig. 1 was determined...
### Table 3. The polycyclic isomeric series of anthanthrene/benzo-(ghi)perylene and naphtho(abc)c Coronene/dibenzo(bc,ef)c Coronene/ dibenzo(bc,kl)c Coronene

<table>
<thead>
<tr>
<th>Formula</th>
<th>Peripheral no. of carbons</th>
<th>No. of nonradical isomers</th>
<th>No. of radical isomers</th>
<th>K = SC^a</th>
</tr>
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<tbody>
<tr>
<td>C_{22}H_{12}</td>
<td>6</td>
<td>4</td>
<td>1</td>
<td>10,14</td>
</tr>
<tr>
<td>C_{22}H_{18}</td>
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<td>22</td>
<td>30</td>
<td>409,805</td>
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<tr>
<td>C_{19}H_{24}</td>
<td>36</td>
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<td>—</td>
</tr>
<tr>
<td>C_{15}H_{18}</td>
<td>60</td>
<td>94</td>
<td>54</td>
<td>—</td>
</tr>
<tr>
<td>C_{20}H_{14}</td>
<td>9</td>
<td>8</td>
<td>22</td>
<td>—</td>
</tr>
<tr>
<td>C_{19}H_{20}</td>
<td>23</td>
<td>30</td>
<td>34</td>
<td>1784,3136,3626</td>
</tr>
<tr>
<td>C_{18}H_{18}</td>
<td>43</td>
<td>64</td>
<td>46</td>
<td>—</td>
</tr>
<tr>
<td>C_{18}H_{12}</td>
<td>69</td>
<td>110</td>
<td>58</td>
<td>—</td>
</tr>
</tbody>
</table>

^aReference 17.

The computational procedure used consisted of the reduction of a given PAH into smaller PAH fragments of known structure count (13). A number of generalizations are made evident by comparison of the structure counts of the PAHs shown in Figs. 1, 2, and 6. The numerical order of the number of benzene structures associated with a set of isomers of strictly peri-condensed PAHs parallels the numerical order of their corresponding excised internal PAH structures. For example, the two benzenoid isomers of C_{22}H_{18} have K = 490 and 805 and their corresponding structures have K = 10 and 14, respectively.

Other things being equal, the more concave bay regions of benzenoid hydrocarbons have totally connected internal edges and become more predominant as one moves from right to left in Table 1.

### Acknowledgements

The author would like to express his gratitude to Professor Milan Randić, Drake University, and Dr. Robert L. Brown, National Bureau of Standards (cf. ref. 16 for a relevant computer program), for checking some of his Kekulé numbers and making other useful comments.


### Appendix: Glossary of terms

- **d_**: net tree disconnections of internal graph edges (positive values) or connections (negative values — called negative disconnection)
- **N_c**: total number of carbon atoms in a PAH
- **N_h**: total number of hydrogen atoms in a PAH
- **N_c**: number of internal carbon atoms in a PAH having a degree of 3
- **N_pc**: number of peripheral carbon atoms in a PAH having a degree of 3
- **PAH6**: polycyclic aromatic hydrocarbon containing exclusively fused hexagonal rings
- **|P| = p = N_c**: total number of graph points
- **p**: number of graph points (vertices) having a degree of 3
- **|Q| = q**: number of graph edges (lines or C—C bonds)
- **q**: number of internal graph edges
- **q_r**: number of peripheral graph edges
- **r**: number of rings
- **τ**: number of rings obtained upon deletion of all internal third-degree vertices from a PAH6 σ-bond graph