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A Periodic Table for Polycyclic Aromatic Hydrocarbons. Part 3. Enumeration of all the Polycyclic Conjugated Isomers of Pyrene Having Ring Sizes Ranging from 3 to 9.

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Abstract. A review of graph theory relevant to polycyclic conjugated hydrocarbons is provided. All the molecular formulas corresponding to polycyclic aromatic hydrocarbons having structures composed of exclusively fused hexagonal rings (PAH6) are listed in a table according to their invariant graphical properties. Extended tables of PAH formulas having corresponding structures with other ring sizes in addition to the hexagonal ring are presented. Equations that give the possible range of the number of rings of a specified size in the isomeric conversion of a PAH6 structure to a structure including another ring size are provided. These equations are illustrated in the systematic enumeration of all 420 polycyclic conjugated hydrocarbon isomers of pyrene. Graph theoretical computation of the resonance energies (REs) of selected pyrene isomers was accomplished. Disregarding possible angle and steric strain several of these pyrene isomers have sufficient REs to warrant synthetic investigation.

Previous graph theoretical work from our laboratory has defined formula-structure parameters which allows one to systematically adduce from the formula of a polycyclic aromatic hydrocarbon (PAH) the range of possible structures.[1,2] The purpose of this paper is to review some of these results while presenting additional correlations. Also, previously formulated graph theoretical properties will be extended to include PAH's containing three- and nine-membered rings. These results will be illustrated by the enumeration of all 420 possible polycyclic conjugated hydrocarbon isomers of pyrene and their corresponding resonance energies (RE).

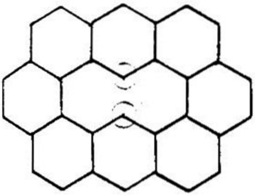
Results and Discussion

The graph structures of this study are restricted to those which have the following properties: 1) planar graphs; 2) only second and third degree vertices; 3) ring sizes of 3 to 9; 4) no bridges or cutpoints, and 5) no internal second degree vertices. A third degree vertex is bounded by three regions; a peripheral third degree vertex is bounded by two finite regions and an infinite outer region and an internal third degree vertex is bounded by three finite regions. A second degree vertex is bounded by two regions; an internal second degree vertex is bounded by two finite regions.

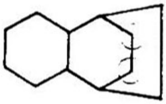
For any graph G, $m(G)=q-p+k$ where k is the number of components. If graph G has a tree subgraph connecting all the points of G (called a spanning tree), then G is connected and is comprised of one component ($k=1$). Thus for any connected graph G, $m(G)=q-p+1$.[3,4] In this paper, net disconnection (positive integers $1,2,3\cdots$) or connection (negative integers $-1,-2,-3\cdots$) is defined as $d_s=k-m(G)-1=p_3-q_I-1$.

Consider the number of edges in any PAH6. Each ring is bounded by six edges, each peripheral edge bounded by one ring, and each internal edge is bounded by only two rings; thus, $6r_6=q_p+2q_I$. Generalizing this to any PAH having other possible ring sizes gives Equation (18) in Table 2.

Circulenes have been defined as PAH's that possessed one or more "holes" larger than a hexagon each containing two or more hydrogens.[1] An example is provided below. Also, structures related to *a* are sterically unacceptable. Both these structures possess internal second degree vertices which are circled. Molecular graphs related to these structures are thus excluded in this paper.



A *circulene*



a

Table 1. Glossary of Terms

c - number of circulene holes

d_i - degree of vertex i of a graph

d_s - net tree disconnections (of internal graph edges)

d_{max} - maximum degree of any point in a molecular graph

d_{min} - minimum degree of any point in a molecular graph

ε_{max} - maximum eigenvalue (highest MO energy level) corresponding to a molecular graph

ε_{min} - minimum eigenvalue (lowest MO energy level) corresponding to a molecular graph

N_c - total number of carbon atoms in a PAH

N_H - total number of hydrogen atoms in a PAH

N_{Ic} - 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

$|P|=p=Nc$ - total number of graph points

p_3 - number of graph points (vertices) having a degree of 3

$|Q|=q$ - number of graph edges (lines or C-C bonds)

q_I - number of internal graph edges

q_p - number of peripheral graph edges

q_b - number of graph edges connecting to phenyl-like ring substituents

r - number of rings

r_{5max} - maximum number of pentagonal rings

r_{4max} - maximum number of tetragonal rings

r_{3max} - maximum number of trigonal rings

r_n - number of rings or cycles having n vertices

t_{max} - maximum number of triple bonds in a structure with ring sizes of six or less having a PAH6 formula

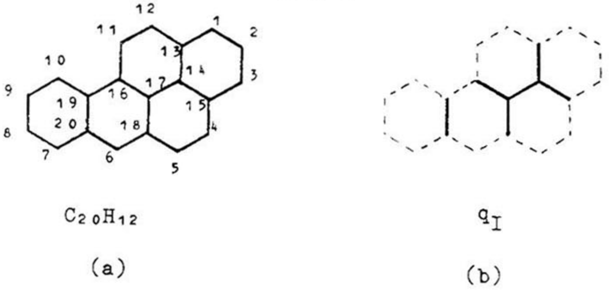
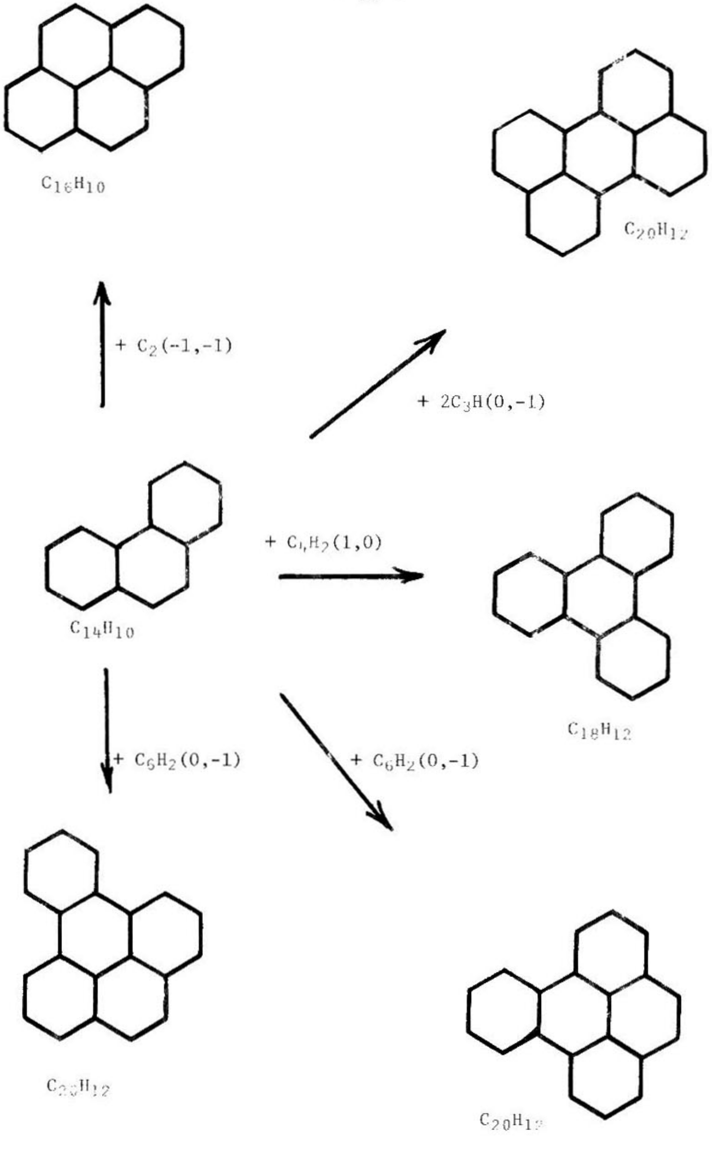


Figure 1. Graph of Benzo(a)pyrene (a) and its internal edges, q_I (b).

A glossary of terms used in this text is presented in Table 1. The meaning of these terms may be illustrated by the molecular graph of benzo(a)pyrene ($C_{20}H_{12}$) shown in Figure 1a. Vertices 1 through 12 have a degree of two (i.e., have two incident lines) and are counted by N_H. Similarly, vertices 13 through 20 have a degree of three (p_3) where the vertices 13, 15, 16, 18, 19, and 20 are counted by N_{Pc} and vertices 14 and 17 by N_{Ic}. The total number of vertices 1 to 20 is counted by N_c and the total number of edges (bonds) by q. Figure 1b presents the internal edges, q_I, as bold lines and collectively is called a broken tree (forest) with a single disconnection (d_s) between points 16 and 19. Table 2 presents a summary of equations that are applicable to totally fused PAH's. Table 3 gives all the possible formulas for polycyclic aromatic hydrocarbons composed of exclusively fused hexagonal rings (PAH6); all benzenoid (PAH6) compounds in the same column of Table 3 have the same number of disconnections (d_s) and in the same row have the same number of internal third degree carbon vertices (N_{Ic}). For a complete description of all the properties of Table 3 refer to the first paper in this series.[1] Scheme I illustrates with phenanthrene how


$C_{16}H_{10}$
$C_{20}H_{12}$
$+ C_2(-1,-1)$
$+ 2C_3H(0,-1)$
$+ C_4H_2(1,0)$
$C_{14}H_{10}$
$C_{18}H_{12}$
$+ C_6H_2(0,-1)$
$+ C_6H_2(0,-1)$
$C_{20}H_{12}$
$C_{20}H_{12}$

Scheme I

Table 2. Equations Applicable to Totally Fused PAH's

(1) $N_c=N_{Pc}+N_{Ic}+N_H$

(2) $N_{Pc}=N_H-6+3r_3+2r_4+r_5-r_7-2r_8-3r_9$

(3) $q=q_I+q_p$

(4) $q_p=q-q_I=2N_H-6+3r_3+2r_4+r_5-r_7-2r_8-3r_9$

(5) $d_s=N_{Pc}-r$

(6) $2q=\Sigma d_i=\Sigma d_2+\Sigma d_3=2N_H+3(N_c-N_H)=3N_c-N_H$

(7) $p_3=q_I+1+d_s=N_c-N_H=N_{Pc}+N_{Ic}$

(8) faces-edges+vertices=2

$(r+1)-q+p=2$ or $r=q+1-N_c=\frac{1}{2}(N_c+2-N_H)$

(9) $r_{5max} \leq N_{Ic}=N_c-2N_H+6$

(10) $r_{4max} = \frac{1}{2} N_{Ic} = \frac{1}{2}[N_c-2N_H+6]$

(11) $r_{3max} \leq {}^1/_3 N_{Ic} = {}^1/_3[N_c-2N_H+6]$

(12) $$2 \leq \frac{3N_c-N_H}{N_c} \leq -\varepsilon_{max},\ \varepsilon_{min} \leq 3$$

(13) $t_{max} \leq \frac{1}{4} N_{Ic} = \frac{1}{4}[N_c-2N_H+6]$

(14) $r_{7max} \leq d_s(PAH6)-M=\frac{1}{2}[-N_c+3N_H-14-2M]$

(15) $r_{8max} \leq \frac{1}{2}[d_s(PAH6)-M]=\frac{1}{4}[-N_c+3N_H-14-2M]$

(16) $r_{9max} \leq \frac{1}{3}[d_s(PAH6)-M]=\frac{1}{6}[-N_c+3N_H-14-2M]$

Table 2. (cont'd)

(17) $r_{10\mathrm{max}} \leq \frac{1}{4} [d_s(\mathrm{PAH6}) - M] = {}^{1}/_{8} [-N_c + 3N_H - 14 - 2M]$

M=0,1··· and corresponds to the d_s value of the first formula member of the associated now series in Table 3 or the d_s value of the first formula member of the associated row series above the $N_c = 2N_H - 6$ row in Table 7 [for Equation (14)], Table 8 [for Equation (15)], or Table 9 [for Equation (16)]; always round of fractional values to the lowest integer.

(18) $3r_3 + 4r_4 + 5r_5 + 6r_6 + 7r_7 + 8r_8 + 9r_9 = q_p + 2q_I$

(19) $N_{Ic} + d_s = \text{constant} = \frac{N_c - N_H}{2} - 1$

for any specific PAH formula.

Table 3. All the Formulas Possible for Polycyclic Aromatic Hydrocarbons having Nonradical Hexagonal Rings - PAH Periodic Table

$N_c=3N_H$	$N_c=3N_H-2$	$N_c=3N_H-4$	$N_c=3N_H-6$	$N_c=3N_H-8$	$N_c=3N_H-10$	$N_c=3N_H-12$	$N_c=3N_H-14$	$N_c=3N_H-16$		$(N_c=2N_H-6+N_{1c})$
							$C_{10}H_8$	$C_{14}H_{10}$	. . .	$N_c=2N_H-6$
							$C_{16}H_{10}$	$C_{20}H_{12}$	. . .	$N_c=2N_H-4$
							$C_{22}H_{12}$	$C_{26}H_{14}$	. . .	$N_c=2N_H-2$
						$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$	. . .	$N_c=2N_H$
						$C_{30}H_{14}$	$C_{34}H_{16}$	$C_{38}H_{18}$	. . .	$N_c=2N_H+2$
					$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$	. . .	$N_c=2N_H+4$
					$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	$C_{50}H_{22}$	. . .	$N_c=2N_H+6$
				$C_{40}H_{16}$	$C_{44}H_{18}$	. . .	$C_{52}H_{22}$	$C_{56}H_{24}$	. . .	$N_c=2N_H+8$
			$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$		$C_{58}H_{24}$	$C_{62}H_{26}$	. . .	$N_c=2N_H+10$
			$C_{48}H_{18}$	$C_{52}H_{20}$	. . .		$C_{64}H_{26}$	$C_{68}H_{28}$	. . .	$N_c=2N_H+12$
		$C_{50}H_{18}$	$C_{54}H_{20}$	. . .			$C_{70}H_{28}$	$C_{74}H_{30}$	. . .	$N_c=2N_H+14$
	$C_{52}H_{18}$	$C_{56}H_{20}$	. . .				$C_{76}H_{30}$	$C_{80}H_{32}$	. . .	$N_c=2N_H+16$
$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$					$C_{82}H_{32}$	$C_{86}H_{34}$	. . .	$N_c=2N_H+18$
$C_{60}H_{20}$	$C_{64}H_{22}$	. . .					$C_{88}H_{34}$	$C_{92}H_{36}$	. . .	$N_c=2N_H+20$
$C_{66}H_{22}$	$C_{70}H_{24}$						$C_{94}H_{36}$	$C_{98}H_{38}$	. . .	$N_c=2N_H+22$
$C_{72}H_{24}$	$C_{76}H_{26}$						$C_{100}H_{38}$	$C_{104}H_{40}$	. . .	$N_c=2N_H+24$
$C_{78}H_{26}$	. . .						$C_{106}H_{40}$	$C_{110}H_{42}$	. . .	$N_c=2N_H+26$
$C_{84}H_{28}$							$C_{112}H_{42}$	$C_{116}H_{44}$	. . .	$N_c=2N_H+28$
$C_{90}H_{30}$							. . .	. . .		$N_c=2N_H+30$
. . .										$N_c=2N_H+32$

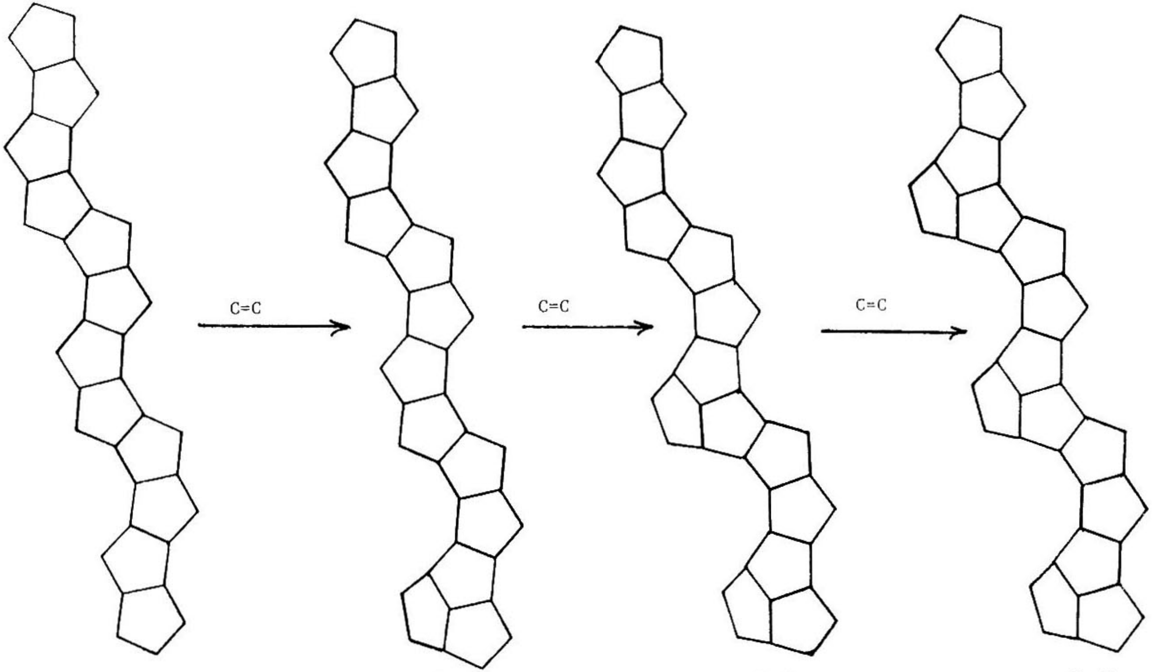
Table 4. Formulas of PAH Containing Pentagonal Rings in Addition to Hexagonal Rings

. . .	$N_c=3N_H$	$N_c=3N_H-2$	$N_c=3N_H-4$	$N_c=3N_H-6$	$N_c=3N_H-8$	$N_c=3N_H-10$	$N_c=3N_H-12$	$N_c=3N_H-14$		
						C_6H_6	$C_{12}H_8$	$C_{16}H_{10}$	. . .	$N_c=2N_H-4$
					$C_{10}H_6$	$C_{14}H_8$	$C_{18}H_{10}$	$C_{22}H_{12}$	. . .	$N_c=2N_H-2$
				$C_{12}H_6$	$C_{16}H_8$	$C_{20}H_{10}$	$C_{24}H_{12}$	$C_{28}H_{14}$	. . .	$N_c=2N_H$
			$C_{14}H_6$	$C_{18}H_8$	$C_{22}H_{10}$	$C_{26}H_{12}$	$C_{30}H_{14}$	$C_{34}H_{16}$	. . .	$N_c=2N_H+2$
		$C_{16}H_6$	$C_{20}H_8$	$C_{24}H_{10}$	$C_{28}H_{12}$	$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	. . .	$N_c=2N_H+4$
	$C_{18}H_6$	$C_{22}H_8$	$C_{26}H_{10}$	$C_{30}H_{12}$	$C_{34}H_{14}$	$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	. . .	$N_c=2N_H+6$
	$C_{24}H_8$	$C_{28}H_{10}$	$C_{32}H_{12}$	$C_{36}H_{14}$	$C_{40}H_{16}$	$C_{44}H_{18}$	. . .	$C_{52}H_{22}$	. . .	$N_c=2N_H+8$
	$C_{30}H_{10}$	$C_{34}H_{12}$	$C_{38}H_{14}$	$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$		$C_{58}H_{24}$	. . .	$N_c=2N_H+10$
	$C_{36}H_{12}$	$C_{40}H_{14}$	$C_{44}H_{16}$	$C_{48}H_{18}$	$C_{52}H_{20}$	. . .		$C_{64}H_{26}$	. . .	$N_c=2N_H+12$
. . .	$C_{42}H_{14}$	$C_{46}H_{16}$	$C_{50}H_{18}$	$C_{54}H_{20}$	. . .			$C_{70}H_{28}$	. . .	$N_c=2N_H+14$
	$C_{48}H_{16}$	$C_{52}H_{18}$	$C_{56}H_{20}$	. . .				$C_{76}H_{30}$	. . .	$N_c=2N_H+16$
	$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$					$C_{82}H_{32}$	. . .	$N_c=2N_H+18$
	$C_{60}H_{20}$	$C_{64}H_{22}$	. . .					$C_{88}H_{34}$	. . .	$N_c=2N_H+20$
. . .	. . .	. . .						. . .	. . .	. . .

all the structures corresponding to formulas in Table 3 can be successively generated starting with naphthalene by appropriate attachment of units corresponding to C_2, C_3H, C_4H_2, and C_6H_2. Note that in the schemes, the pair of numbers in parentheses are coordinates tracing the lineage of a derived formula due to specific attachments of the units adjacent to the coordinates; the origin of the coordinates is the table position of the original formula, and the first coordinate gives the number of formula columns shifted to the right (positive number) or left (negative number) and the second coordinate gives the number of formula rows shifted up (positive number) or down (negative number) in the corresponding table. For example, in Scheme I appropriate attachment of a C_2 unit to phenanthrene ($C_{14}H_{10}$) gives a formula of $C_{16}H_{10}$ corresponding to pyrene which is located one column to the left and one row down from the original formula of $C_{14}H_{10}$ in Table 3, and thus each C_2 attachment has coordinates of (-1,-1). Since the second coordinates for the various constructions illustrated in Scheme I is zero or minus one, successive generation of formulas corresponding to PAH6 structures in Table 3 from the *cata*-condensed PAHs results in a general downward movement.

If w is the largest eigenvalue of a connected graph G, then all eigenvalues of G occur within the interval (-w,w). Letting d_{max} denote the maximum degree of G, d_{min} the minimum degree, and $\bar{d}$ the average degree, then $d_{min} \leq \bar{d} \leq w \leq d_{max}$ from which Equation (12) is derived upon appropriate substitution of the respective symbols and quantities relevant to PAHs.[3]

Consider Figure 1, between the third degree-peripheral vertices 16 and 19 there are no points ($c_0=0$), between 18 and 20 there is a single second degree point ($c_1=1$) numbered 6, between 15 and 18 there are the two second degree points ($c_2=2$) of numbers 4 and 5, between 13 and 15 there are the three second degree points ($c_3=3$) of numbers 1, 2, and 3 and finally between the peripheral vertices of 19 and 20 there are four second degree points ($c_4=4$) of numbers 7, 8, 9, and 10; the quantity of each of these five different sequences of intervening second degree points between peripheral third degree vertices in a particular structure is designated by n_0, n_1, n_2, n_3, and n_4, respectively. The simple sum of the number of each of these five sequences is given by $n_0+n_1+n_2+n_3+n_4=N_{Pc}$ which for benzo(a)pyrene (Figure 1) is 1+1+2+1+1=6, i.e., there is one sequence with no intervening second degree points (between 16 and 19), one sequence with one intervening second degree point (between 18 and 20), two sequences with two intervening points (between 15 and 18 and 13 and 16), one sequence with three intervening points (between 13 and 15), and one sequence with four intervening points (between 19 and 20) and the sum of these sequences gives the number of peripheral third degree carbon atoms. When there are no intervening points $c_0=0$, one intervening point $c_1=1$, two intervening points $c_2=2$, three intervening points $c_3=3$, and four intervening points $c_4=4$. Since these intervening points correspond to second degree vertices between the outer third degree vertices, the total number of second degree vertices is given by $N_H=n_0c_0+n_1c_1+n_2c_2+n_3c_3+n_4c_4$ which for benzo(a)pyrene gives $12=1\cdot 0+1\cdot 1+2\cdot 2+1$ $3+1\cdot 4$; note that $n_1+n_3=$ even number$\leq N_H$ since $N_H \geq n_1+3n_3$.



$C_{38}H_{16}$ $C_{40}H_{16}$ $C_{42}H_{16}$ $C_{44}H_{16}$

Scheme II

Construction of Formula Tables 4,5 and 6 for Polycyclic Conjugated Hydrocarbons Containing Pentagonal, Tetragonal and Trigonal Rings, Respectively, in Addition to Hexagonal Rings.

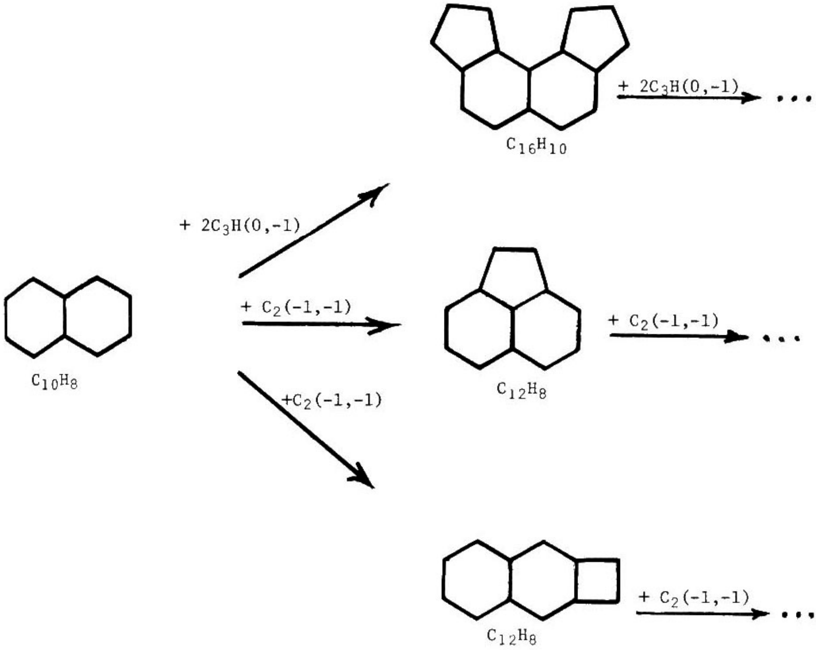
If all PAH structural isomers having the maximum number of possible pentagonal rings are considered, then those having formulas belonging to the $N_c = 3N_H-10$ column series of Table 4 (or Table 3) would have structures made up of exclusively five-membered rings and contain no internal third degree carbon vertices; whereas structures having formulas belonging to column series to the left of this column would contain exclusively five-membered rings with internal third degree carbon vertices and those to the right would contain five- and six-membered rings with no internal third degree carbon vertices. All structural isomers having PAH6 formulas to the right of the $N_c = 3N_H -10$ column of Table 4 (or Table 3) containing the maximum number of possible pentagonal rings and no internal third degree carbon vertices can be recursively generated by successive pairwise attachment of C=CH-C units to ethylene CH-CH edges of benzene or the catacondensed PAH6 structures ($C_{10+4n}H_{8+2n}$, n=0,1,···). The structural isomers containing the maximum number of possible pentagonal rings having PAH formulas belonging to the $N_c=3N_H-10$ column ($N_{Ic}=0$) Table 4 can be recursively generated by successive pairwise attachment of C=CH-C units to the CH-CH edges of pentalene (C_8H_6). All structural isomers containing exclusively pentagonal rings ($N_{Ic}=0$) with formulas to the left of the $N_c=3N_H-10$ column of Table 4 can be recursively generated by successive attachment of C=C units to 1-3 located secondary vertices as illustrated with one polypentalen isomer ($C_{38}H_{16}$) in Scheme II. Note that longitudinal growth by successive attachments of C=C units in Scheme II is limited by the number of existing

Table 5. Formulas of PAH Containing Tetragonal Rings in Addition to Hexagonal Rings

. . .	$N_c=3N_H$	$N_c=3N_H-2$	$N_c=3N_H-4$	$N_c=3N_H-6$	$N_c=3N_H-8$	$N_c=3N_H-10$	$N_c=3N_H-12$	$N_c=3N_H-14$		
						C_8H_6	$C_{12}H_8$	$C_{16}H_{10}$	. . .	$N_c=2N_H-4$
				C_6H_4	$C_{10}H_6$	$C_{14}H_8$	$C_{18}H_{10}$	$C_{22}H_{12}$	. . .	$N_c=2N_H-2$
			C_8H_4	$C_{12}H_6$	$C_{16}H_8$	$C_{20}H_{10}$	$C_{24}H_{12}$	$C_{28}H_{14}$	. . .	$N_c=2N_H$
		$C_{10}H_4$	$C_{14}H_6$	$C_{18}H_8$	$C_{22}H_{10}$	$C_{26}H_{12}$	$C_{30}H_{14}$	$C_{34}H_{16}$	. . .	$N_c=2N_H+2$
	$C_{12}H_4$	$C_{16}H_6$	$C_{20}H_8$	$C_{24}H_{10}$	$C_{28}H_{12}$	$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	. . .	$N_c=2N_H+4$
	$C_{18}H_6$	$C_{22}H_8$	$C_{26}H_{10}$	$C_{30}H_{12}$	$C_{34}H_{14}$	$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	. . .	$N_c=2N_H+6$
	$C_{24}H_8$	$C_{28}H_{10}$	$C_{32}H_{12}$	$C_{36}H_{14}$	$C_{40}H_{16}$	$C_{44}H_{18}$	. . .	$C_{52}H_{22}$	. . .	$N_c=2N_H+8$
	$C_{30}H_{10}$	$C_{34}H_{12}$	$C_{38}H_{14}$	$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$		$C_{58}H_{24}$	. . .	$N_c=2N_H+10$
	$C_{36}H_{12}$	$C_{40}H_{14}$	$C_{44}H_{16}$	$C_{48}H_{18}$	$C_{52}H_{20}$	. . .		$C_{64}H_{26}$	. . .	$N_c=2N_H+12$
. . .	$C_{42}H_{14}$	$C_{46}H_{16}$	$C_{50}H_{18}$	$C_{54}H_{20}$	. . .			$C_{70}H_{28}$	. . .	$N_c=2N_H+14$
	$C_{48}H_{16}$	$C_{52}H_{18}$	$C_{56}H_{20}$	. . .				$C_{76}H_{30}$	. . .	$N_c=2N_H+16$
	$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$					$C_{82}H_{32}$	. . .	$N_c=2N_H+18$
	$C_{60}H_{20}$	$C_{64}H_{22}$	. . .					$C_{88}H_{34}$	. . .	$N_c=2N_H+20$
. . .	. . .	. . .						. . .	. . .	. . .

Table 6. Formulas of PAH Containing Trigonal Rings in Addition to Hexagonal Rings

. . .	$N_c=3N_H$	$N_c=3N_H-2$	$N_c=3N_H-4$	$N_c=3N_H-6$	$N_c=3N_H-8$	$N_c=3N_H-10$	$N_c=3N_H-12$	$N_c=3N_H-14$		
					$C_{10}H_6$	$C_{14}H_8$	$C_{18}H_{10}$	$C_{22}H_{12}$	. . .	$N_c=2N_H-2$
		C_4H_2	C_8H_4	$C_{12}H_6$	$C_{16}H_8$	$C_{20}H_{10}$	$C_{24}H_{12}$	$C_{28}H_{14}$	. . .	$N_c=2N_H$
		$C_{10}H_4$	$C_{14}H_6$	$C_{18}H_8$	$C_{22}H_{10}$	$C_{26}H_{12}$	$C_{30}H_{14}$	$C_{34}H_{16}$	. . .	$N_c=2N_H+2$
	$C_{14}H_4$	$C_{16}H_6$	$C_{20}H_8$	$C_{24}H_{10}$	$C_{28}H_{12}$	$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	. . .	$N_c=2N_H+4$
	$C_{18}H_6$	$C_{22}H_8$	$C_{26}H_{10}$	$C_{30}H_{12}$	$C_{34}H_{14}$	$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	. . .	$N_c=2N_H+6$
	$C_{24}H_8$	$C_{28}H_{10}$	$C_{32}H_{12}$	$C_{36}H_{14}$	$C_{40}H_{16}$	$C_{44}H_{18}$	. . .	$C_{52}H_{22}$	. . .	$N_c=2N_H+8$
	$C_{30}H_{10}$	$C_{34}H_{12}$	$C_{38}H_{14}$	$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$		$C_{58}H_{24}$	. . .	$N_c=2N_H+10$
	$C_{36}H_{12}$	$C_{40}H_{14}$	$C_{44}H_{16}$	$C_{48}H_{18}$	$C_{52}H_{20}$	. . .		$C_{64}H_{26}$	. . .	$N_c=2N_H+12$
. . .	$C_{42}H_{14}$	$C_{46}H_{16}$	$C_{50}H_{18}$	$C_{54}H_{20}$	. . .			$C_{70}H_{28}$	. . .	$N_c=2N_H+14$
	$C_{48}H_{16}$	$C_{52}H_{18}$	$C_{56}H_{20}$	. . .				$C_{76}H_{30}$	. . .	$N_c=2N_H+16$
	$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$					$C_{82}H_{32}$	. . .	$N_c=2N_H+18$
	$C_{60}H_{20}$	$C_{64}H_{22}$	. . .					$C_{88}H_{34}$	. . .	$N_c=2N_H+20$
. . .	. . .	. . .						. . .	. . .	. . .



Scheme III

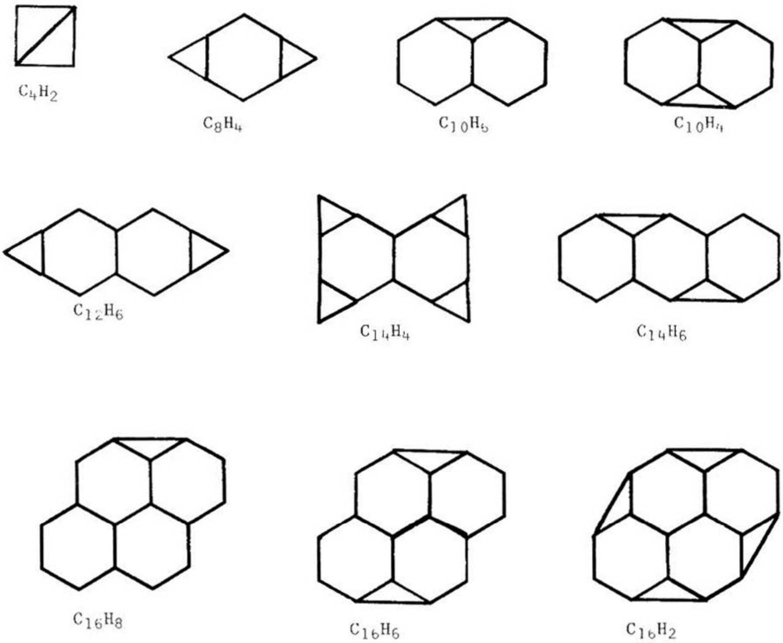
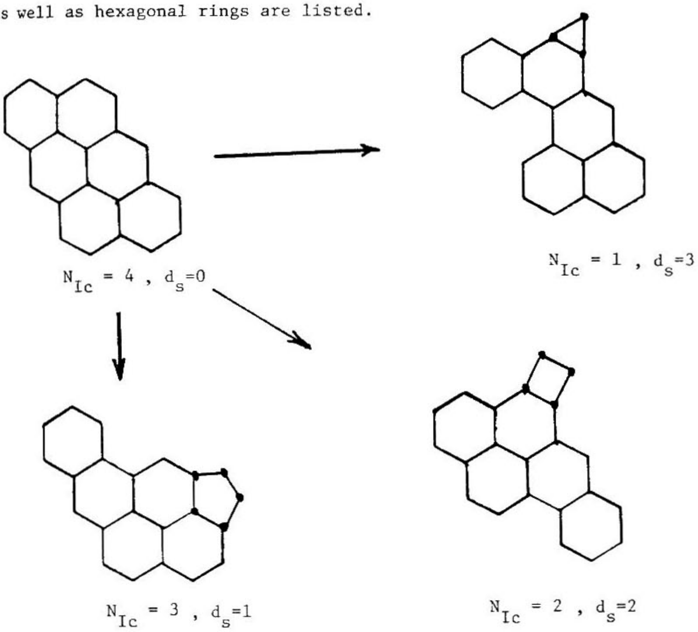


Figure 2. Polycyclic conjugated hydrocarbons possessing only trigonal and hexagonal rings.

1-3 located secondary vertices, whereas pentagonal ring growth can continue indefinitely by extending the ends of these polypentalenes if distortion of the regular pentagon is permitted. Similarly, all structural isomers having PAH6 formulas containing the maximum number of tetragonal rings and no internal third degree vertices can be recursively generated by successive attachment of C=C units to ethylene CH-CH edges of the cata-condensed PAH6 structures starting with $C_{14}H_{10}$; all of the structural PAH isomers having the maximum number of tetragonal rings possible with formulas belonging to Table 5 except the cata-condensed polycyclic tetragonal hydrocarbons

$(C_{6+2n}H_4,\ n=0,1,\cdots)$ can be recursively generated by successive attachment of C=C units to ethylene CH-CH edges of benzene and the cata-condensed PAH6 structures. Note that while structures containing exclusively pentagonal rings can also have internal third degree carbon vertices, no structure containing exclusively tetragonal rings can have internal third degree carbon vertices. Figure 2 lists some polycyclic conjugated hydrocarbon structures from which Table 6 was partly derived. Scheme III illustrates how to recursively generate structures with formulas corresponding to those in Tables 4 and 5 from the *cata*-condensed PAH's. In summary Tables 4, 5, and 6 are extensions of Table 3, where in the former formulas corresponding to structures having pentagonal, tetragonal, and trigonal rings, respectively, as well as hexagonal rings are listed.



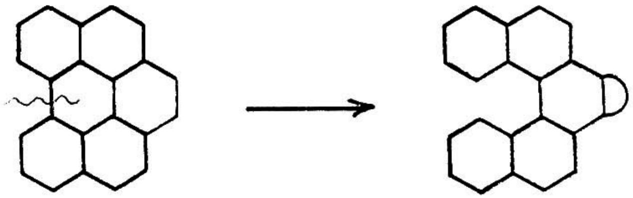
Scheme IV $(C_{22}H_{12})$

Maximum Number of Pentagonal, Tetragonal and Trigonal Ring Possible for a PAH.

Scheme IV illustrates how a PAH6 structure can be converted to other structures of the same formula by transforming a hexagonal ring to a pentagonal, tetragonal, or trigonal rings. In these transformations of a hexagonal ring to smaller ring sizes there is a simultaneous decrease in the number of third degree internal carbon vertices (N_{Ic}). In fact for a fixed PAH6 formula (Table 3), in the conversion of each hexagonal ring to a pentagonal ring, there is a simultaneous transformation of one internal third degree vertex to a peripheral one; in the conversion of each hexagonal ring to a tetragonal ring there is a simultaneous transformation of two internal third degree vertices to peripheral ones; and in the conversion of each hexagonal ring to a trigonal ring, there is a simultaneous transformation of three internal third degree carbon vertices to peripheral ones such that $p_3 = N_{Ic} + N_{Pc} = N_c - N_H$ = constant. Since the number of rings is constant in the above conversion (Scheme IV), there must be a corresponding increase in disconnection per $d_s = N_{Pc} - r$. In general, if all the internal third degree carbon vertices can be converted to peripheral third degree carbon vertices with corresponding simultaneous conversion of hexagonal rings to pentagonal, tetragonal, or trigonal rings, then the maximum number of pentagonal (r_{5max}) tetragonal (r_{4max}), or trigonal (r_{3max}) rings that a structure corresponding to a PAH6 formula can possess are given by Equations (9), (10), or (11), respectively. Note that the left of the $N_c = 3N_H - 10$ column $r_{5max} = r_5 + N_{Ic} < N_c = 2N_H + 6$ for a structure composed exclusively of fused pentagonal rings and for the $N_c = 3N_H - 10$ column and the other columns to the right

$r_{5max} = N_c - 2N_H + 6$ exactly. Since a polycyclic antiaromatic hydrocarbon composed of exclusively tetragonal rings cannot contain internal third degree carbon vertices, Equation (10) is exact. In computations using Equation (11) always round off to the lowest integer. Since the *cata*-condensed PAH6 structures have no internal third degree carbon vertices ($N_{Ic}=0$), there are no PAH structures having pentagonal, tetragonal, or trigonal rings with formulas corresponding to the $N_c=2N_H-6$ row (Table 3); also there are no PAH structures with trigonal rings having formulas corresponding to the $N_c=2N_H-4$ row (Table 3). Although, Equations (9),(10), and (11) were derived specifically from structures corresponding to formulas belonging in Table 3, they are also valid for the structures of formulas found in the extended Tables 4, 5, and 6 but not in Table 3.

In a formal sense a triple bond can be thought of as a two member ring as illustrated by the following tansformation. Thus the maximum number of triple bonds in addition to hexagonal rings that a structure having a PAH6 formula can possess is given by Equation (13).



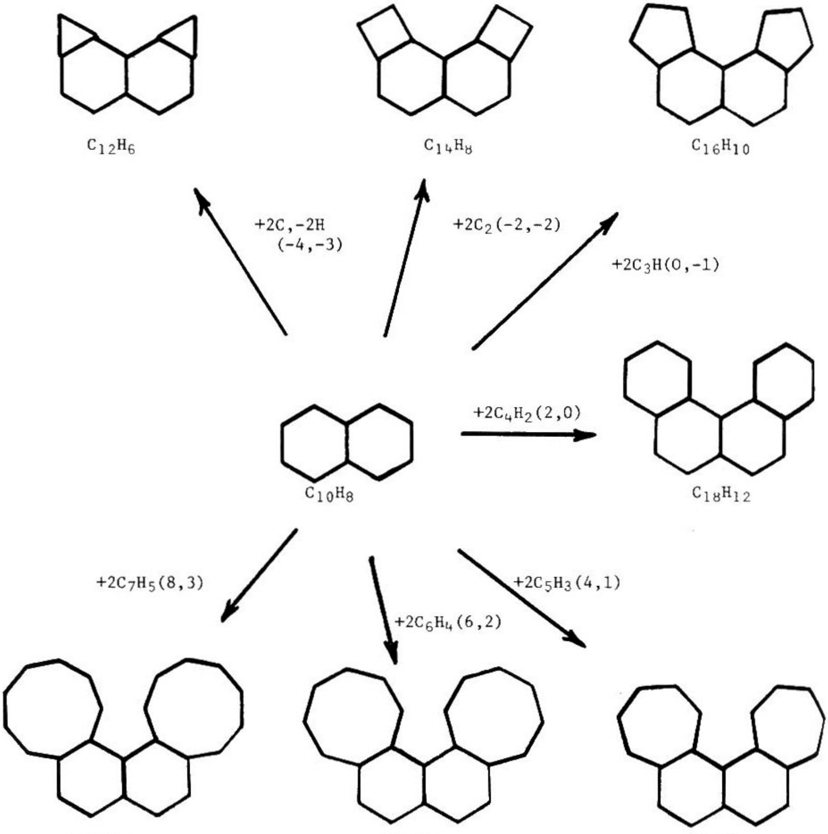
$C_{22}H_{12}$ $C_{22}H_{12}$

Table 7. Formulas of PAH Having only Hexagonal and Heptagonal Rings

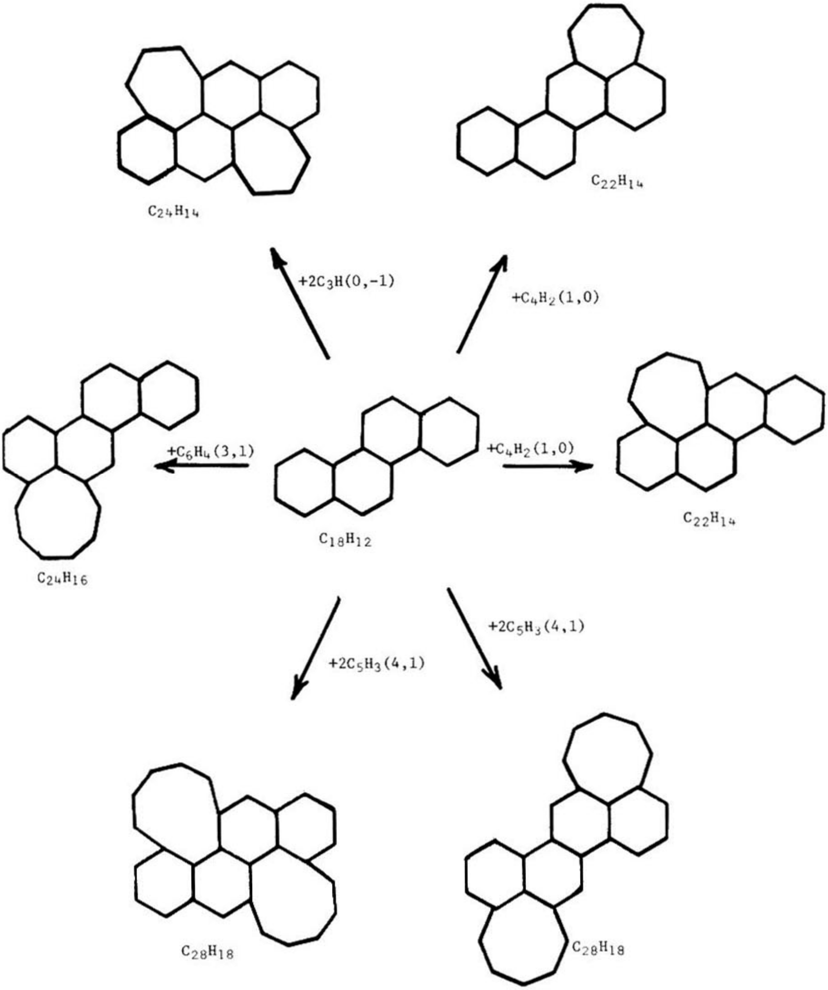
									$C_{12}H_{10}$	$C_{16}H_{12}$	$C_{20}H_{14}$	$C_{24}H_{16}$
								$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$	$C_{26}H_{16}$	$C_{30}H_{18}$
								$C_{20}H_{12}$	...	...	...	...
								$C_{26}H_{14}$				
							$C_{28}H_{14}$	$C_{32}H_{16}$				
							$C_{34}H_{16}$	$C_{38}H_{18}$				
						$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$				
						$C_{42}H_{18}$	$C_{46}H_{20}$	$C_{50}H_{22}$				
					$C_{44}H_{18}$	...	$C_{52}H_{22}$	$C_{56}H_{24}$				
				$C_{46}H_{18}$	$C_{50}H_{20}$		$C_{58}H_{24}$	$C_{62}H_{26}$				
				$C_{52}H_{20}$	...		$C_{64}H_{26}$	$C_{68}H_{28}$				
			$C_{54}H_{20}$	...			$C_{70}H_{28}$	$C_{74}H_{30}$				
		$C_{56}H_{20}$	...				$C_{76}H_{30}$	$C_{80}H_{32}$				
	$C_{58}H_{20}$	$C_{62}H_{22}$					$C_{82}H_{32}$	$C_{86}H_{34}$				
	$C_{64}H_{22}$	...					$C_{88}H_{34}$	$C_{92}H_{36}$				
$C_{66}H_{22}$	$C_{70}H_{24}$						$C_{94}H_{36}$	$C_{98}H_{38}$				
$C_{72}H_{24}$	$C_{76}H_{26}$						$C_{100}H_{38}$	$C_{104}H_{40}$				
$C_{78}H_{26}$	...						$C_{106}H_{40}$	$C_{110}H_{42}$				
$C_{84}H_{28}$							$C_{112}H_{42}$	$C_{116}H_{44}$				
$C_{90}H_{30}$							...	...				
...												

Table 7 (cont'd)

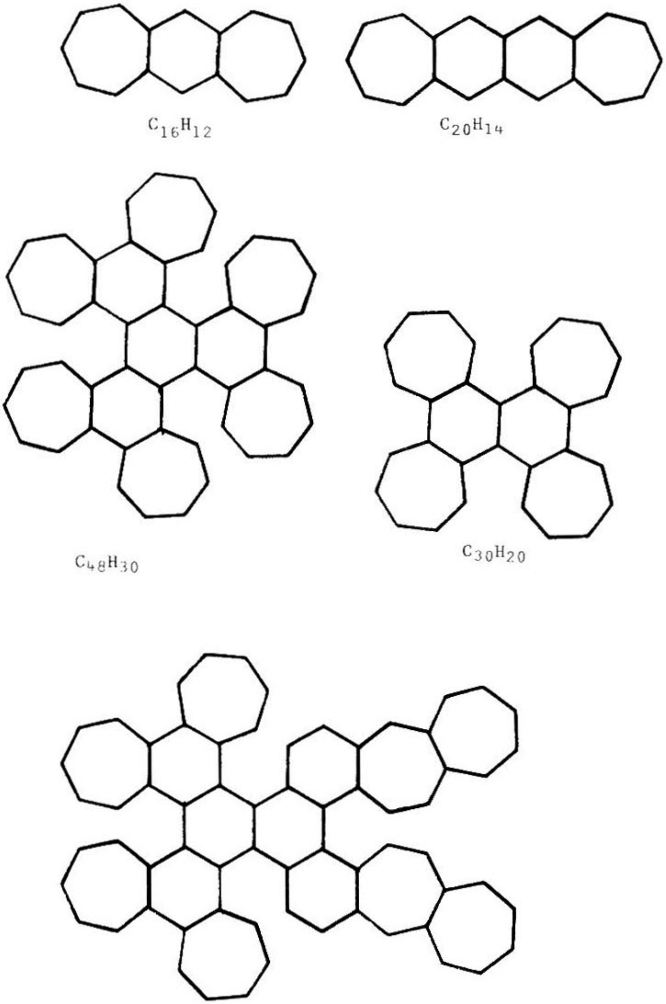
								$C_{42}H_{28}$	$C_{46}H_{30}$	...	$N_c=2N_H-14$
				$C_{32}H_{22}$	$C_{36}H_{24}$	$C_{40}H_{26}$	$C_{44}H_{28}$	$C_{48}H_{30}$	$C_{52}H_{32}$	$C_{56}H_{34}$	$N_c=2N_H-12$
$C_{22}H_{16}$	$C_{26}H_{18}$	$C_{30}H_{20}$	$C_{34}H_{22}$	$C_{38}H_{24}$	$C_{42}H_{26}$	$C_{46}H_{28}$	$C_{50}H_{30}$	$C_{54}H_{32}$	...	...	$N_c=2N_H-10$
$C_{28}H_{18}$	$C_{32}H_{20}$	$C_{36}H_{22}$	$C_{40}H_{24}$	$C_{44}H_{26}$	$C_{48}H_{28}$	$C_{52}H_{30}$	$C_{56}H_{32}$	$C_{60}H_{34}$	...		$N_c=2N_H-8$
$C_{34}H_{20}$	$C_{38}H_{22}$	$C_{42}H_{24}$	$C_{46}H_{26}$	$C_{50}H_{28}$	$C_{54}H_{30}$	$C_{58}H_{32}$	$C_{62}H_{34}$	$C_{66}H_{36}$	...		$N_c=2N_H-6$
...	...	...	...	...	...	...	...	...			$N_c=2N_H-4$
											$N_c=2N_H-2$
											$N_c=2N_H$
											$N_c=2N_H+2$
											$N_c=2N_H+4$
											$N_c=2N_H+6$
											$N_c=2N_H+8$
											$N_c=2N_H+10$
											$N_c=2N_H+12$
											$N_c=2N_H+14$
											$N_c=2N_H+16$
											$N_c=2N_H+18$
											$N_c=2N_H+20$
											$N_c=2N_H+22$
											$N_c=2N_H+24$
											$N_c=2N_H+26$
											$N_c=2N_H+28$
											$N_c=2N_H+30$
											$N_c=2N_H+32$
											$N_c=2N_H+34$
											$N_c=2N_H+36$
											$N_c=2N_H+38$
											$N_c=2N_H+40$
											$N_c=2N_H+42$
											$N_c=2N_H+44$
											$N_c=2N_H+46$
											$N_c=2N_H+48$


$C_{12}H_6$
$C_{14}H_8$
$C_{16}H_{10}$
+2C, -2H (-4,-3)
$+2C_2(-2,-2)$
$+2C_3H(0,-1)$
$+2C_4H_2(2,0)$
$C_{10}H_8$
$C_{18}H_{12}$
$+2C_7H_5(8,3)$
$+2C_6H_4(6,2)$
$+2C_5H_3(4,1)$
$C_{24}H_{18}$
$C_{22}H_{16}$
$C_{20}H_{14}$

Scheme V


$C_{24}H_{14}$
$+2C_3H(0,-1)$
$C_{22}H_{14}$
$+C_4H_2(1,0)$
$+C_6H_4(3,1)$
$+C_4H_2(1,0)$
$C_{24}H_{16}$
$C_{18}H_{12}$
$C_{22}H_{14}$
$+2C_5H_3(4,1)$
$+2C_5H_3(4,1)$
$C_{28}H_{18}$
$C_{28}H_{18}$

Scheme VI



$C_{16}H_{12}$

$C_{20}H_{14}$

$C_{48}H_{30}$

$C_{30}H_{20}$

$C_{66}H_{40}$

Figure 3. Heptagonal ring containing structures with formulas above the $N_c=2N_H-6$ row of Table 7.

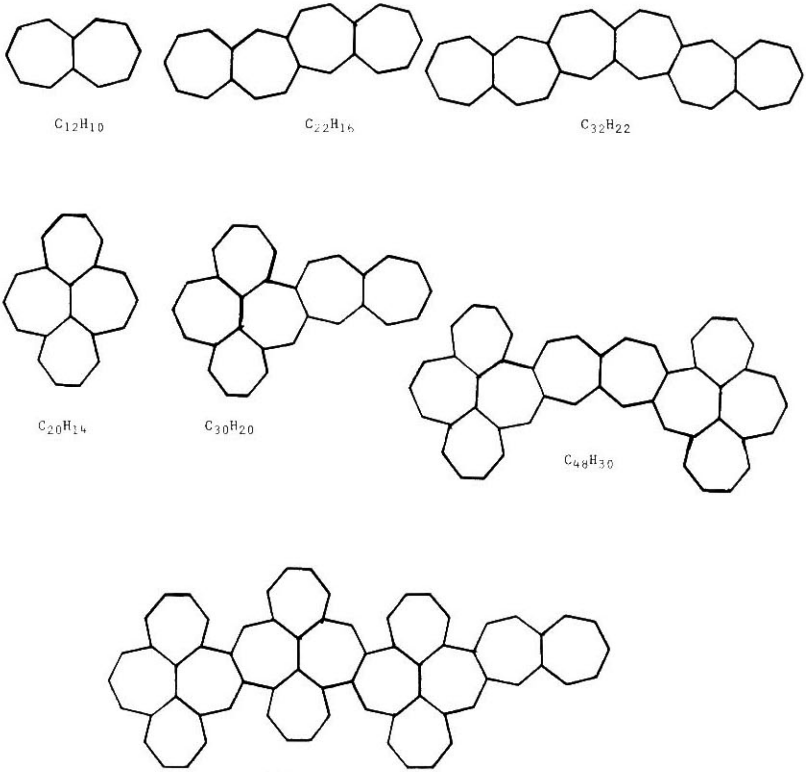
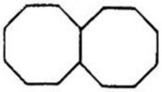


Figure 4. Structures having the maximum number of heptagonal rings possible for the specified formula above the $N_c=2N_H-6$ row of Table 7.

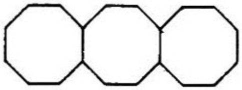
Construction of Formula Tables 7,8, and 9 for Polycyclic Conjugated Hydrocarbons Containing Heptagonal, Octagonal, and Nonagonal Rings, Respectively, in Addition to Hexagonal Rings.

Pairwise attachment of CH=C-CH-C=CH units to the CH-CH ethylene edges benzene or the *cata*-condenses PAH6 structures from the $N_c=2N_H-6$ row series in Table 3 leads to the representative structures possessing heptagonal rings shown in Figure 3. These structures in Figure 3 have formulas not contained in Table 3 but are present in the upper right hand region (above the dashed line) of Table 7 above the $N_c=2N_H-6$ row. Thus this procedure produces structures that have formulas four columns to the right and one row series higher than the precursor formula for each two C_5H_3 units connected [$2C_5H_3$ units has coordinates of (4,1)]; for example, $C_{10}H_8$ belongs in the $N_c=2N_H-6$ row and upon attachment of two C_5H_3 units gives a structure with the formula $C_{20}H_{14}$ (Scheme V) which belongs four columns to the right in the $N_c=2N_H-8$ row and attachment of two more C_5H_3 units gives a structure with the formula $C_{30}H_{20}$ (Figure 3) which belongs to the $N_c=2N_H-10$ row in Table 7. The formulas of the *cata*-condensed even carbon polycyclic conjugated hydrocarbons (C_{12+4n} H_{10+2n}) in the top row of Figure 4 define the upper diagonal formula edge of Table 7. The last four structures in Figure 3 and 4 are pairwise isomeric. Other constructions of heptagonal rings by pairwise attachment of C_3H units to concave regions of a PAH and C_4H_2 units to PAH CH-C-CH segments are shown in Scheme VI.

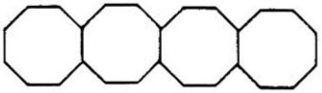
With each attachment of a C=CH-CH=CH-CH=C unit to an ethylene edge Scheme V of benzene or a PAH6 structure there is obtained an octagonal ring containing PAH with a formula three column series to the right and one row series higher than the precursor formula [a C_6H_4 unit has coordinates of (3,1)].



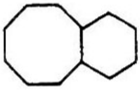
$C_{14}H_{12}$



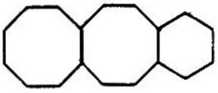
$C_{20}H_{16}$



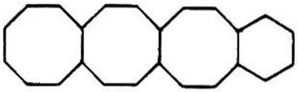
$C_{26}H_{20}$



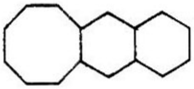
$C_{12}H_{10}$



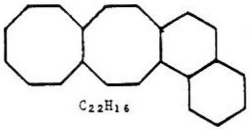
$C_{18}H_{14}$



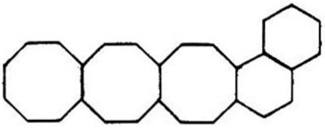
$C_{24}H_{18}$



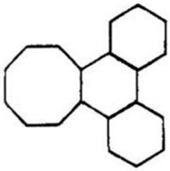
$C_{16}H_{12}$



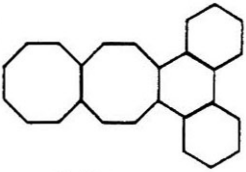
$C_{22}H_{16}$



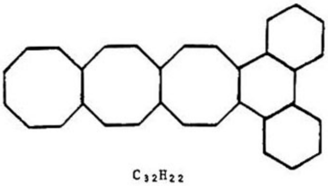
$C_{28}H_{20}$



$C_{20}H_{14}$



$C_{26}H_{18}$



$C_{32}H_{22}$

Figure 5. **Structures containing fused octagonal rings** above the $N_c = 2N_H - 6$ row series of Table 8.

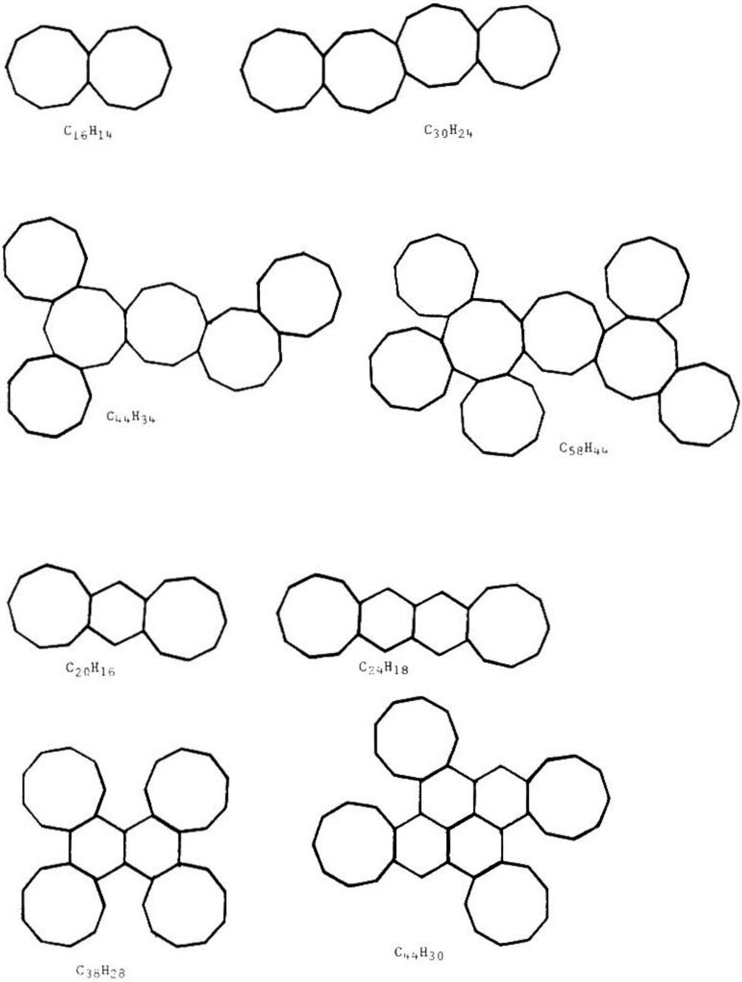
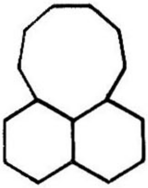
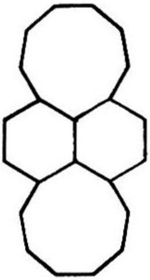


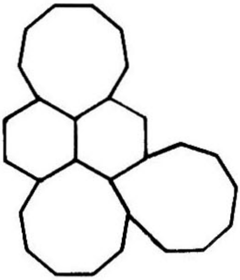
Figure 6. Nonagonal ring containing PAHs above the $N_c=2N_H-6$ row series.



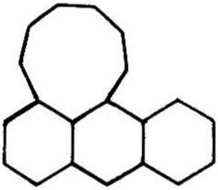
$C_{16}H_{12}$



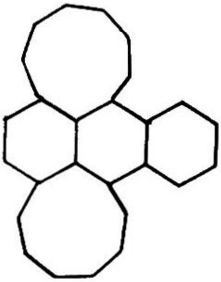
$C_{22}H_{16}$



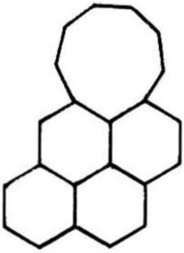
$C_{28}H_{20}$



$C_{20}H_{14}$



$C_{26}H_{18}$



$C_{22}H_{14}$

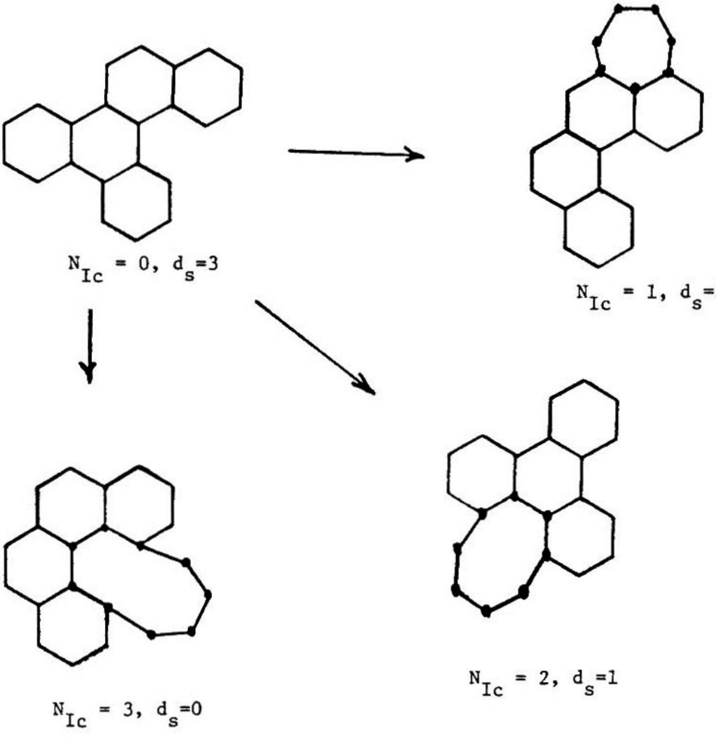
Figure 7. PAHs having the maximum number of nonagonal rings possible for the given formula.

Table 8. Formulas of PAH Having only Hexagonal and Octagonal Rings

...												
$N_c=2N_H-14$											$C_{26}H_{20}$	...
$N_c=2N_H-12$								$C_{20}H_{16}$	$C_{24}H_{18}$	$C_{28}H_{20}$	$C_{32}H_{22}$	...
$N_c=2N_H-10$					$C_{14}H_{12}$	$C_{18}H_{14}$	$C_{22}H_{16}$	$C_{26}H_{18}$	$C_{30}H_{20}$	$C_{34}H_{22}$	$C_{38}H_{24}$	...
$N_c=2N_H-8$			$C_{12}H_{10}$	$C_{16}H_{12}$	$C_{20}H_{14}$	$C_{24}H_{16}$	$C_{28}H_{18}$	$C_{32}H_{20}$	$C_{36}H_{22}$	$C_{40}H_{24}$	$C_{44}H_{26}$	...
$N_c=2N_H-6$			$C_{18}H_{12}$	$C_{22}H_{14}$	$C_{26}H_{16}$	$C_{30}H_{18}$	$C_{34}H_{20}$	$C_{38}H_{22}$	$C_{42}H_{24}$	$C_{46}H_{26}$	$C_{50}H_{28}$	...
$N_c=2N_H-4$			$C_{24}H_{14}$	$C_{28}H_{16}$	$C_{32}H_{18}$	$C_{36}H_{20}$	...	...	...	...	...	...
$N_c=2N_H-2$			$C_{30}H_{16}$	$C_{34}H_{18}$	...							
$N_c=2N_H$		$C_{32}H_{16}$	$C_{36}H_{18}$	...								
...	$C_{34}H_{16}$	$C_{38}H_{18}$	$C_{42}H_{20}$	...								
	$C_{40}H_{18}$	$C_{44}H_{20}$	...									
...	$C_{46}H_{20}$	...										
...	...											

Table 9. Formulas of PAH's Containing only Hexagonal and Nonagonal Rings.

$N_c=2N_H-18$															$C_{30}H_{24}$	$C_{34}H_{26}$	...
$N_c=2N_H-16$															$C_{36}H_{26}$	$C_{40}H_{28}$	...
$N_c=2N_H-14$															$C_{42}H_{28}$	$C_{46}H_{30}$	...
$N_c=2N_H-12$							$C_{16}H_{14}$	$C_{20}H_{16}$	$C_{24}H_{18}$	$C_{28}H_{20}$	$C_{32}H_{22}$	$C_{36}H_{24}$	$C_{40}H_{26}$	$C_{44}H_{28}$	$C_{48}H_{30}$	...	
$N_c=2N_H-10$							$C_{22}H_{16}$	$C_{26}H_{18}$	$C_{30}H_{20}$	$C_{34}H_{22}$	$C_{38}H_{24}$	$C_{42}H_{26}$	$C_{46}H_{28}$	$C_{50}H_{30}$	$C_{54}H_{32}$	...	
$N_c=2N_H-8$				$C_{16}H_{12}$	$C_{20}H_{14}$	$C_{24}H_{16}$	$C_{28}H_{18}$	$C_{32}H_{20}$	$C_{36}H_{22}$	$C_{40}H_{24}$	$C_{44}H_{26}$	...	...	...			
$N_c=2N_H-6$				$C_{22}H_{14}$	$C_{26}H_{16}$	$C_{30}H_{18}$	$C_{34}H_{20}$	$C_{38}H_{22}$	$C_{42}H_{24}$	$C_{46}H_{26}$	$C_{50}H_{28}$	...					
$N_c=2N_H-4$				$C_{28}H_{16}$	$C_{32}H_{18}$	$C_{36}H_{20}$	$C_{40}H_{22}$	...	...	...	...	...					
$N_c=2N_H-2$				$C_{34}H_{18}$	$C_{38}H_{20}$	$C_{42}H_{22}$	$C_{46}H_{24}$	...									
$N_c=2N_H$				$C_{40}H_{20}$	$C_{44}H_{22}$	$C_{48}H_{24}$	$C_{52}H_{26}$	...									
$N_c=2N_H+2$				$C_{46}H_{22}$	$C_{50}H_{24}$	$C_{54}H_{26}$	...										
$N_c=2N_H+4$				$C_{52}H_{24}$	$C_{56}H_{26}$	$C_{60}H_{28}$	...										
$N_c=2N_H+6$				$C_{58}H_{26}$	$C_{62}H_{28}$	...	...										
. . .				$C_{64}H_{68}$	$C_{68}H_{30}$	...											
			$C_{66}H_{28}$	$C_{70}H_{30}$	...												
		$C_{68}H_{28}$	$C_{72}H_{30}$	...													
	...	$C_{74}H_{30}$	...														
		...															



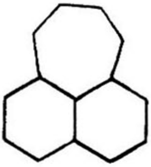
Scheme VII ($C_{22}H_{14}$)

Example structures with formulas not found in Table 3 are shown in Figure 5. The *cata*-condensed polycyclic antiaromatic hydrocarbon ($C_{12+6n}H_{12+4n}$) shown in the first row of Figure 5 defines the upper diagonal formula boundary above the $N_c=2N_H-6$ row (above the dashed line) of Table 8. Other octagonal ring constructions are illustrated in Scheme VI on chrysene.

Pairwise attachment of CH=C-CH=CH-CH-C=CH units to ethylene edges (Scheme V) of benzene or the *cata*-condensed PAH6 structures from the $N_c=2N_H-6$ row series leads to the representative nonagonal ring containing structures shown in the last two rows of Figure 6. This procedure produces structures that have formulas three rows higher and eight columns [$2C_7H_5$ units have coordinates of (8,3)] to the right of the procursor formula for each two C_7H_5 units attached. The *cata*-condensed polycyclic conjugated hydrocarbons ($C_{16+14n}H_{14+10n}$) like the ones shown in the first two rows of Figure 6 define the upper diagonal formula boundary above the $N_c=2N_H-6$ row (above the dashed line) of Table 9. Figure 7 presents other nonagonal ring containing PAHs derived by attachment of C=CH-CH=CH-CH=C units to PAH6 CH-C-CH peripheral segments per Scheme VI.

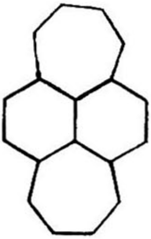
Maximum Number of Heptagonal, Octagonal, and Nonagonal Rings Possible for a PAH.

Scheme VII illustrates how a PAH6 structure can be transformed into another structure of the same formula but with heptagonal, octagonal, and nonagonal rings in addition to hexagonal rings. In these transformations of a hexagonal ring into larger ring sizes, there is a simultaneous increase in the number of third degree internal carbon vertices (N_{Ic}) and a corresponding decrease in the number of peripheral third degree vertices (N_{Pc}) and disconnections (d_s) per Equation (5). For each hexagonal ring converted to a heptagonal, octagonal, or nonagonal ring there is a simul-



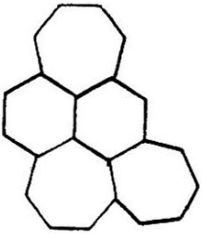
$C_{14}H_{10}$

$d_s=0$



$C_{18}H_{12}$

$d_s=0$

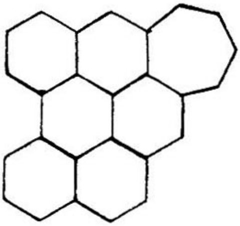


$C_{22}H_{14}$

$d_s=0$

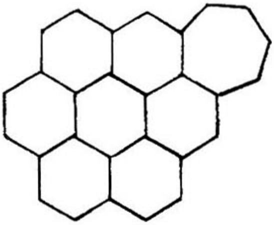
$C_{20}H_{12}$

$d_s=0$



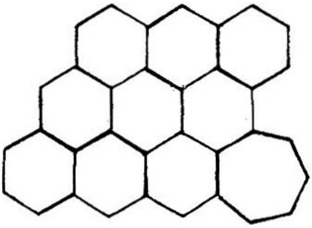
$C_{26}H_{14}$

$d_s=0$



$C_{28}H_{14}$

$d_s=-1$

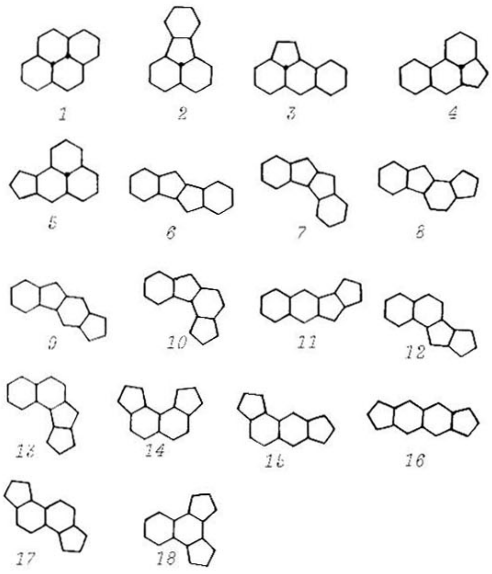


$C_{34}H_{16}$

$d_s=-1$

Figure 8. Structures in and below the $N_c=2N_H-6$ row series containing the maximum number of heptagonal rings possible for the specified formula.

taneous decrease in one, two, or three disconnections, respectively. If all the disconnections can be reduced to zero with the corresponding simultaneous conversion of hexagonal rings to heptagonal rings, then the maximum number of heptagonal rings (r_{7max}) that a corresponding PAH6 formula can possess should be given by Equation (14). In Figure 6, PAH6 isomers of anthracene ($C_{14}H_{10}$) and other *cata*-condensed PAH6 compounds (first row in Figure 8), benzo(a) pyrene ($C_{20}H_{12}$), and dibenzo(a,ghi)-perylene ($C_{26}H_{14}$) have been converted to PAHs having the maximum number of possible heptagonal rings and a minimum number of disconnections (d_s). Note that naphthalene ($C_{10}H_8$), pyrene ($C_{16}H_{10}$), and benzo(ghi)perylene $C_{22}H_{12}$) can have no isomers containing only six- and seven-membered rings since their structures already have a minimum number disconnections ($d_s=0$). If it were not for the coronene related isomers possessing negative d_s values in one region of its structure and positive d_s values in others but having an overall net $d_s$value of zero, all the structures in the column series ($N_c=3N_H-14$) having $d_s=0$ would be without possible isomers possessing heptagonal rings. Thus for PAH6 formulas belonging to the three row series of $N_c=2N_H-6$, $N_c=2N_H-4$, and $N_c=2N_H-2$, the maximum number of seven-membered rings (r'_{7max}) in addition to hexagonal rings that corresponding structures can possess is given by $r'_{7max}= d_s(\text{PAH6})=\frac{1}{2}[-N_c+3N_H-14]$. Similarly, the last two structures in Figure 8 are isomers of benzo(a)coronene ($C_{26}H_{14}$) and tribenzo(bc,g,kl)coronene ($C_{34}H_{16}$) with the maximum number of possible heptagonal rings and minimum number of disconnections ($d_s=-1$). Thus for the row series $N_c=2N_H$ and $N_c=2N_H+2$, the maximum number of seven-membered rings in addition to hexagonal rings that a structure corresponding to a PAH6 formula can possess is given by $r_{7max}=d_s(\text{PAH6})+1=\frac{1}{2}[N_c+3N_H-12]$. This process can be continued so that in general $r_{7max}=d_s(\text{PAH6})-M$ where $M=0, -1$



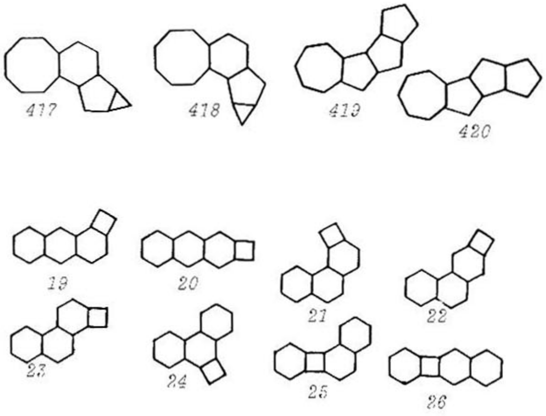
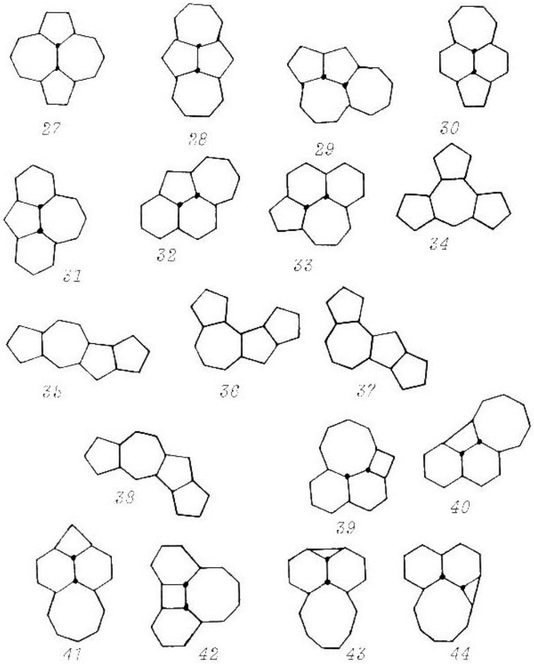


Figure 9. Isomers of Pyrene ($C_{16}H_{10}$)



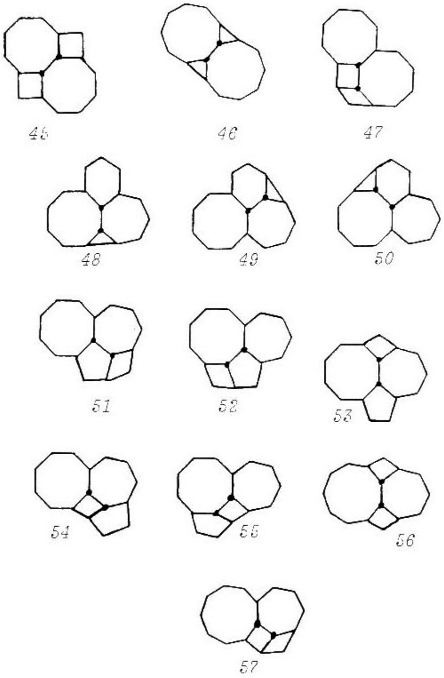


Figure 9. Isomers of Pyrene ($C_{16}H_{10}$)

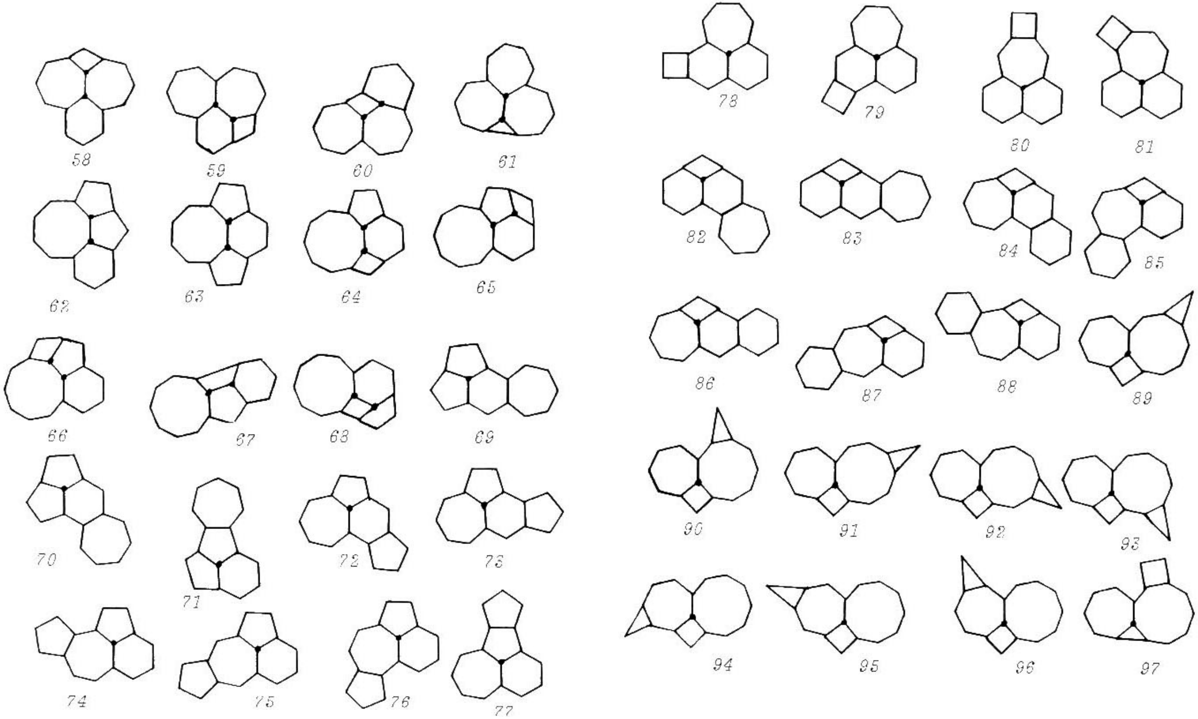
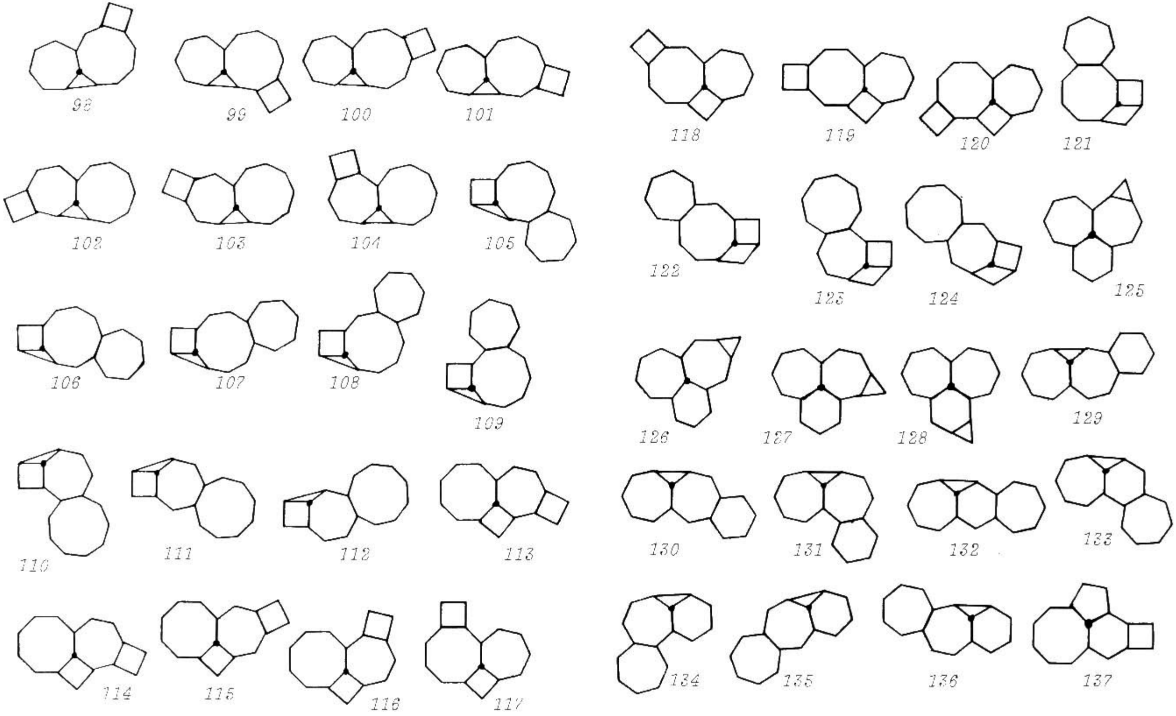


Figure 9. (cont'd).



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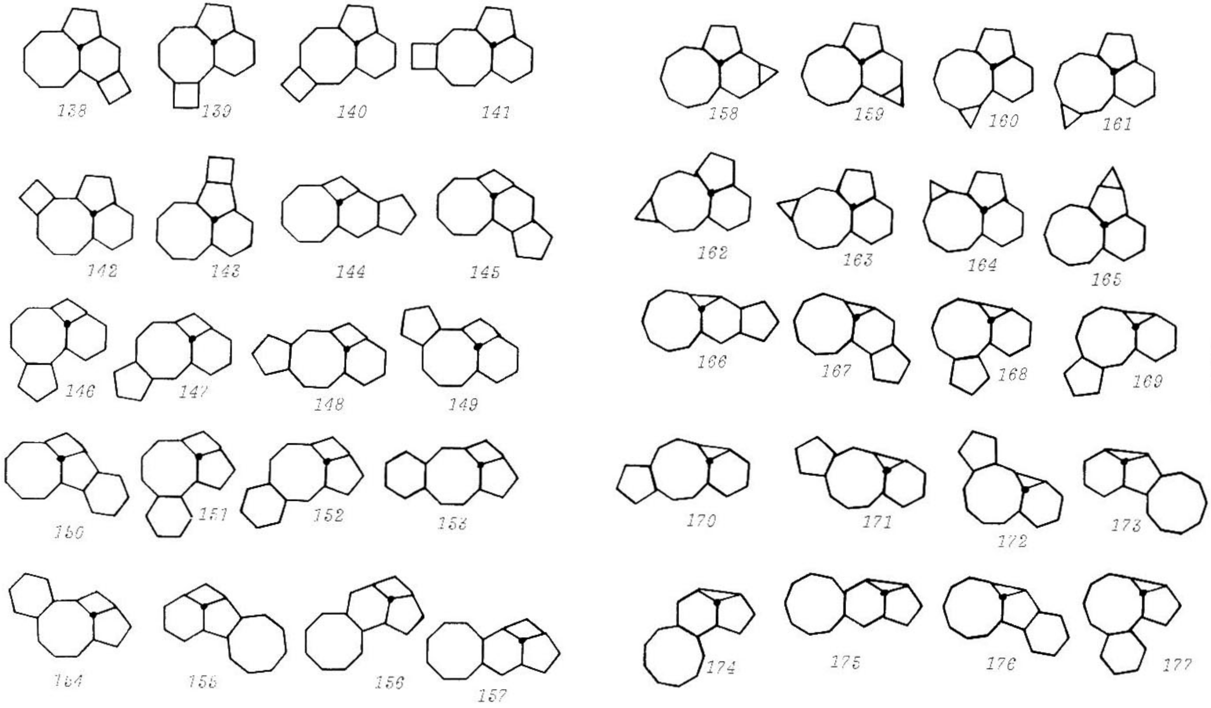

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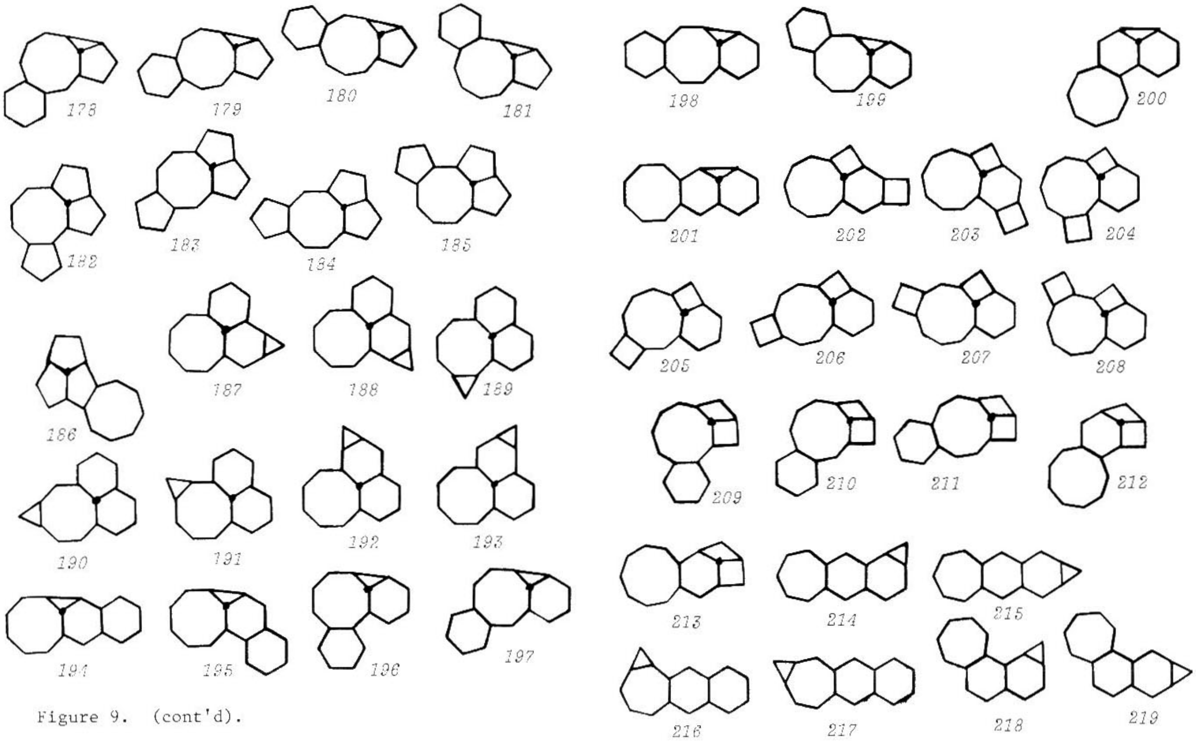

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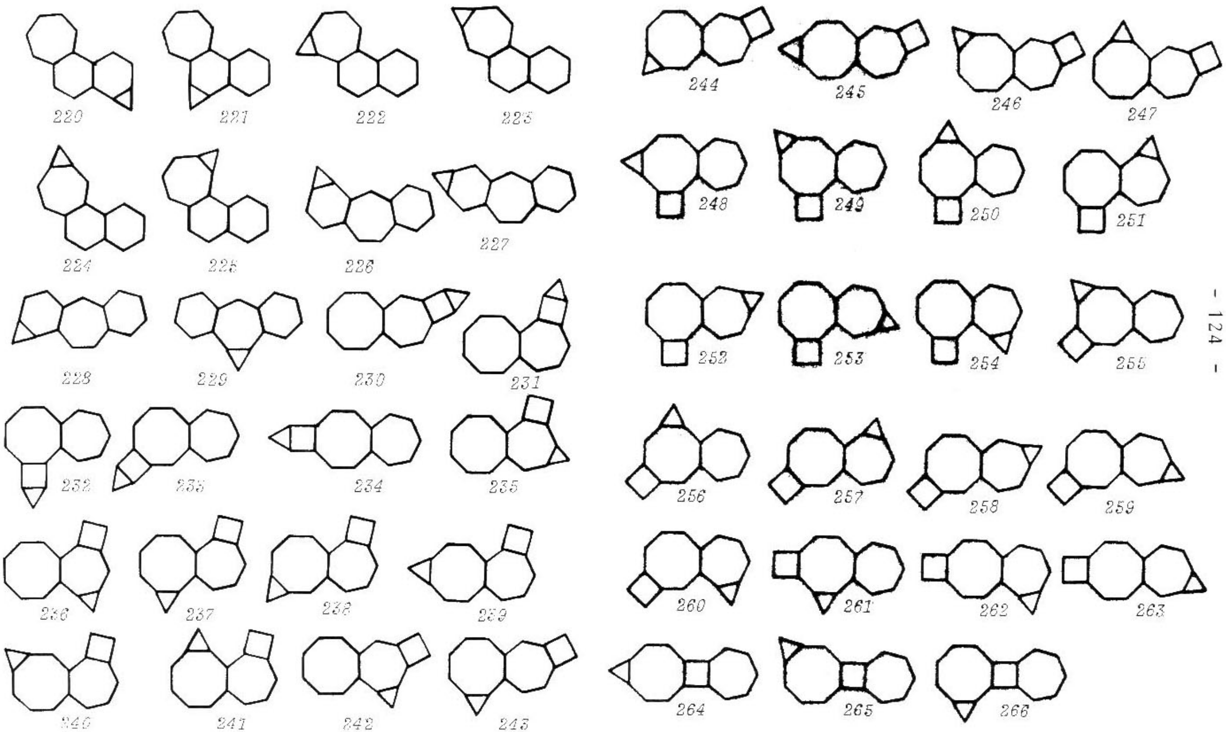

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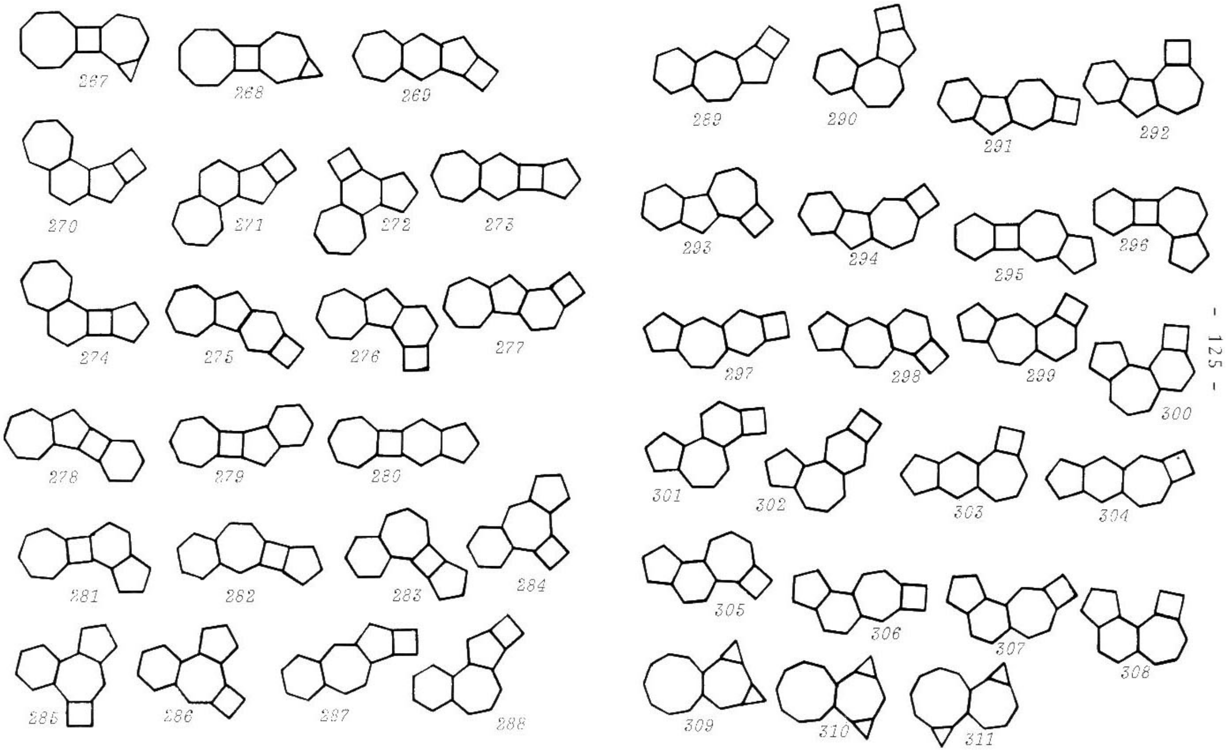

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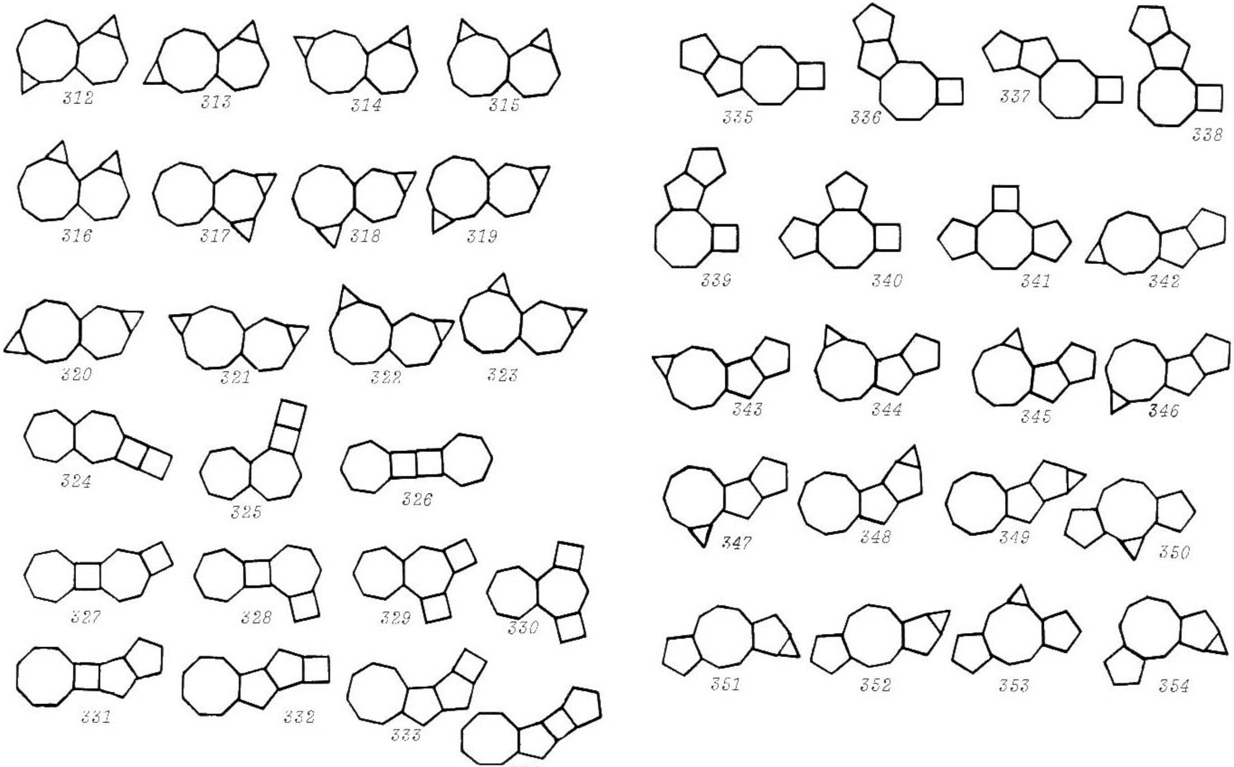

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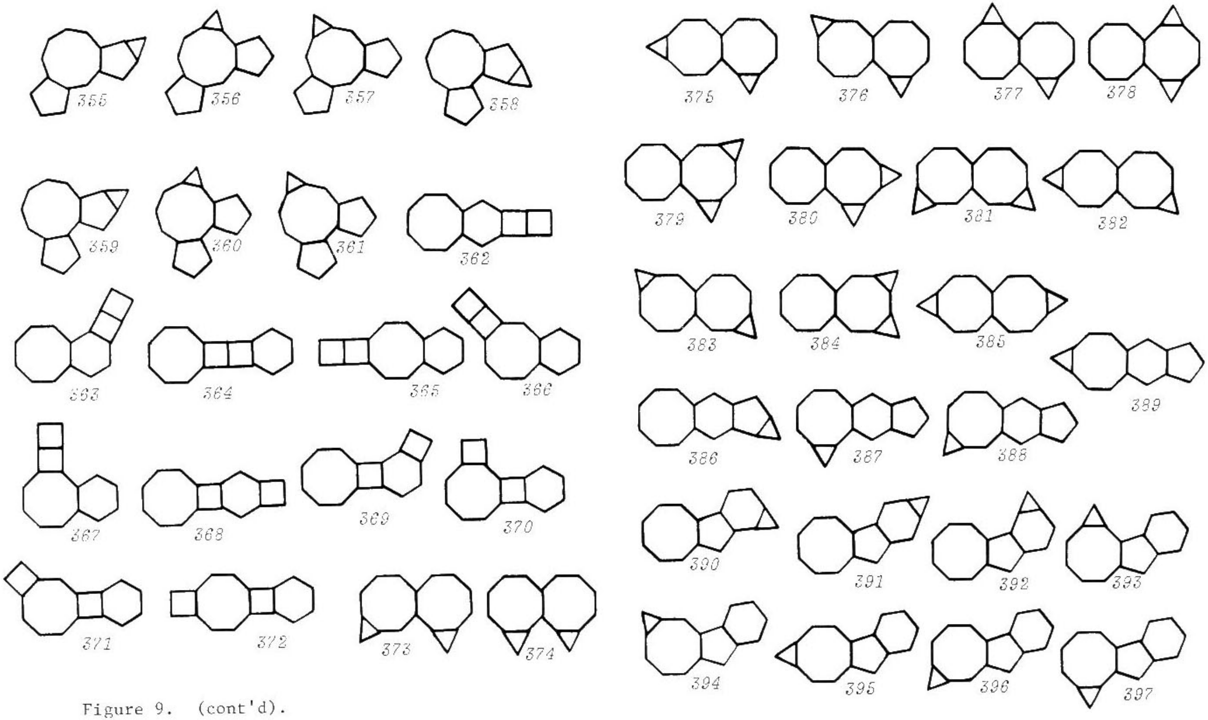

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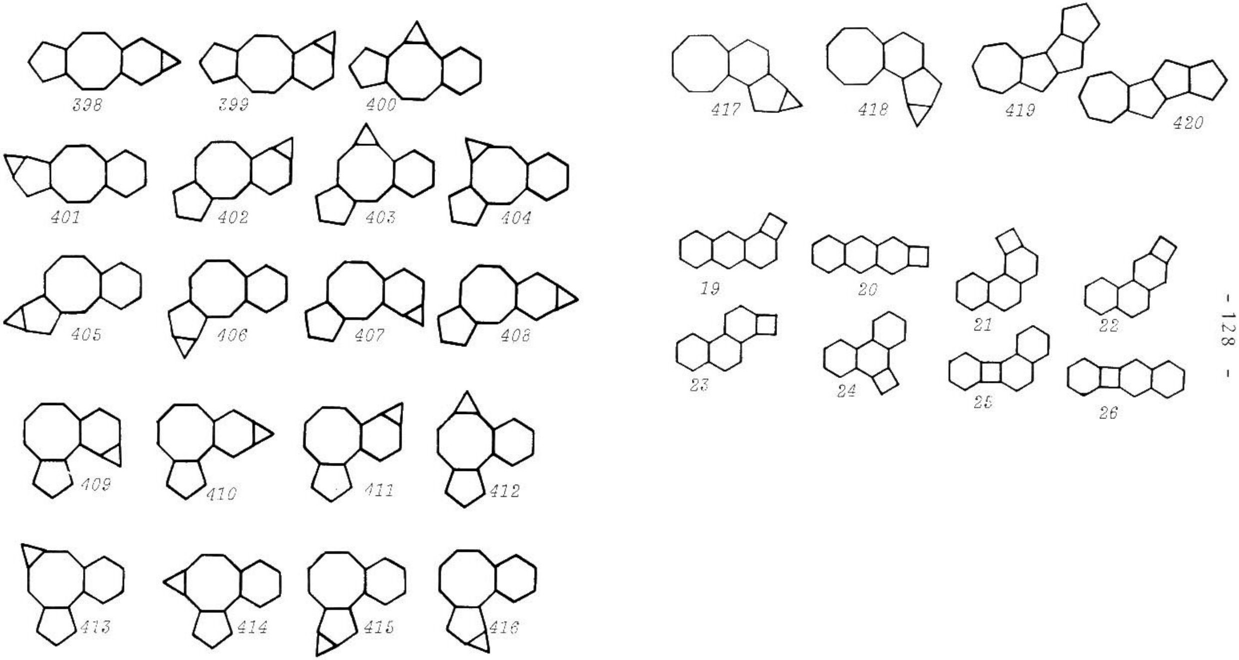


Figure 9. (cont'd).

···corresponds to the d_s value of the first member of the associated row series in Table 3 or the d_s value of the associated row series above the $N_c=2N_H-6$ row of Table 7 as defined by the *cata*-condensed polycyclic conjugated hydrocarbons of the formula $C_{12+10n}H_{10+6n}$ with n=0,1,··· (first row in Figure 4).

In analogy to the above derivation, Equation (15) gives the maximum number of octagonal rings that a structure having a PAH6 formula can contain besides hexagonal rings. Figures 6 and 7 are example structures believed to have the maximum number of nonagonal rings possible for the specified formula as computed according to Equation (16).

Polycyclic Conjugated Isomers of Pyrene.

Application of the equations in Table 2 allows one to define the range of possible polycyclic conjugated structures that have a specified PAH formula. To illustrate this, all the polycyclic conjugated structures for the formula corresponding to pyrene ($C_{16}H_{10}$) will now be enumerated (Figure 9). Solution of Equations (9),(10),(11),(14),(15) and (16) tells one that in addition to hexagonal rings up to two pentagonal rings, one tetragonal ring, and no trigonal, heptagonal, octagonal, or nonagonal rings are possible for this formula. Also since $r_5+N_{Ic}=N_c-2N_H+6$, structures with one pentagonal ring and three hexagonal rings will have one internal third degree carbon vertex (structures *2* to *5*) and there will be no internal third degree vertex for structures with two pentagonal and two hexagonal rings (structures *6* to *18*). Tetragonal ring containing structures will have no internal third degree vertex and three hexagonal rings (structures *19* to *26*) since $r_4+N_{Ic}=\frac{1}{2}[N_c-2N_H+6]$. Structures with this formula and two internal third degree carbon vertices can be composed of four hexagonal rings (structure *1*).

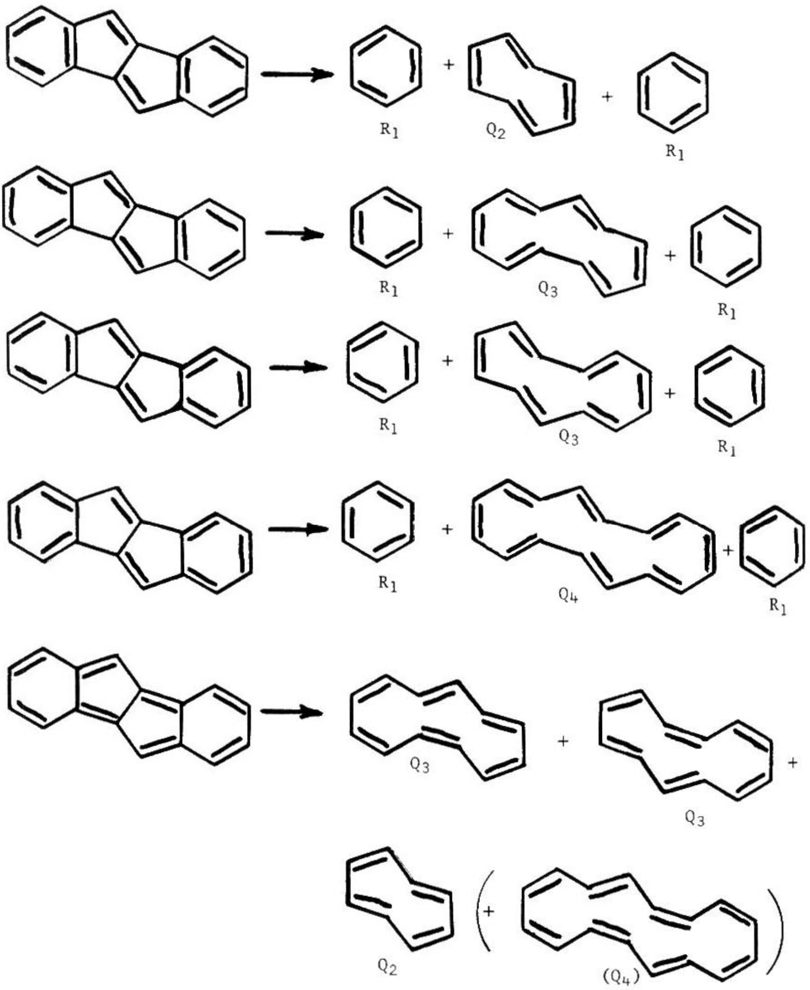
Table 10. Molecular Orbital Energy Quantities for Pyrene Isomers.

						Number of Different Ring Sizes						
Cpd	RE(eV)	CSC	Eπ(β)	HOMO	LUMO	3	4	5	6	7	8	9
1	2.133	6	22.5055	0.4450	-0.4450	0	0	0	4	0	0	0
2	2.192	6	22.5001	0.6180	-0.3709	0	0	1	3	0	0	0
3	1.600	4	22.3005	0.5166	-0.1866	0	0	1	3	0	0	0
4	1.955	5	22.3813	0.5864	-0.2913	0	0	1	3	0	0	0
5	1.323	3	22.2100	0.4328	-0.1153	0	0	1	3	0	0	0
6	1.078	3(5)[a]	22.1870	0.5441	-0.1157	0	0	2	2	0	0	0
7	0.464	0(4)	22.0037	0.2962	0.0000	0	0	2	2	0	0	0
8	0.439	-(3)	21.8889	0.3689	0.1146	0	0	2	2	0	0	0
9	0.439	-(3)	22.0195	0.4395	-0.0155	0	0	2	2	0	0	0
10	0.439	-(3)				0	0	2	2	0	0	0
11	0.662	2(4)				0	0	2	2	0	0	0
12	0.709	1(5)	22.0378	0.4361	-0.0150	0	0	2	2	0	0	0
13	0.709	1(5)				0	0	2	2	0	0	0
14	-0.060	-(2)				0	0	2	2	0	0	0
15	-0.060	-(2)				0	0	2	2	0	0	0
16	-0.060	-(2)	21.8898	0.4142	0.0000	0	0	2	2	0	0	0
17	-0.060	-(2)	21.7573	0.4879	0.2029	0	0	2	2	0	0	0
18	0.439	-(3)	21.6540	0.3501	0.2824	0	0	2	2	0	0	0
19	-0.049	1(7)				0	1	0	3	0	0	0
20	0.376	3(5)				0	1	0	3	0	0	0
21	0.274	2(8)				0	1	0	3	0	0	0
22	0.422	3(7)				0	1	0	3	0	0	0
23	0.274	2(8)				0	1	0	3	0	0	0
24	0.296	1(9)				0	1	0	3	0	0	0
25	0.686	4(8)	22.1661	0.3207	-0.3207	0	1	0	3	0	0	0
26	1.134	5(7)	22.2515	0.5021	-0.5021	0	1	0	3	0	0	0
27	0.467	-(4)	22.0515	0.4450	-0.3620	0	0	2	0	2	0	0
28	0.317	-(4)	22.0297	0.4450	-0.4450	0	0	2	0	2	0	0
29	0.119	-(4)	21.9929	0.3029	-0.3072	0	0	2	0	2	0	0
30	1.142	-(4)	22.2517	0.4450	-0.4450	0	0	1	2	1	0	0
31	0.100	2	21.9929	0.1761	-0.1323	0	0	1	2	1	0	0
32	1.215	4	22.2063	0.3291	-0.4048	0	0	1	2	1	0	0
33	1.215	4	22.2197	0.4109	-0.2815	0	0	1	2	1	0	0
34	-0.060	-(2)	21.4773	0.3565	0.2466	0	0	3	0	1	0	0
35	-0.176	-(3)				0	0	3	0	1	0	0
36	-0.176	-(3)				0	0	3	0	1	0	0
37	-0.176	-(3)				0	0	3	0	1	0	0
38	-0.176	-(3)				0	0	3	0	1	0	0
39	-0.317	2(6)				0	1	0	2	0	1	0
40	0.040	2(6)				0	1	0	2	0	1	0
41	-0.356	4				0	1	0	2	0	1	0
42	0.074	2(6)				0	1	0	2	0	1	0
43	1.142	-(4)				1	0	0	2	0	0	1
44	1.142	4				1	0	0	2	0	0	1
45	-2.072	6				0	2	0	0	0	2	0
46	0.512	-(4)				2	0	0	0	0	0	2
47	-1.565	6(6)				0	2	0	0	0	2	0

a. Total structure count (SC) is given in parentheses if different from the corrected structure count (CSC).

Table 11. Conjugated Circuit Resonance Energy Terms for 47 Polycyclic Conjugated Hydrocarbon Isomers of Pyrene

Cpd	R_n and Q_n Decomposition
1	$(12R_1+8R_2+4R_3)/6$
2	$(14R_1+4R_2)/6$
3	$(6R_1+4R_2+2R_3)/4$
4	$(10R_1+4R_2+R_3)/5$ or $(10R_1+4R_2+2R_3)/5$
5	$(4R_1+2R_2)/3$
6	$(8R_1+2Q_2+4Q_3+Q_4)/5$ or $(8R_1+2Q_2+4Q_3+2Q_4)/5$
7	$(4R_1+2Q_2+4Q_3+2Q_4)/4$
8	$(2R_1+2Q_3+2Q_4)/3$
9	$(2R_1+2Q_3+2Q_4)/3$
10	$(2R_1+2Q_3+2Q_4)/3$
11	$(4R_1+2R_2+2Q_2+2Q_3+2Q_4)/4$
12	$(6R_1+2R_2+4Q_2+2Q_3+Q_4)/5$ or $(6R_1+2R_2+4Q_2+2Q_3+2Q_4)/5$
13	$(6R_1+2R_2+4Q_2+2Q_3+Q_4)/5$ or $(6R_1+2R_2+4Q_2+2Q_3+2Q_4)/5$
14	$(2Q_4)/2$
15	$(2Q_4)/2$
16	$(2Q_4)/2$
17	$(2Q_4)/2$
18	$(2R_1+2Q_3+2Q_4)/3$
19	$(10R_1+6R_2+2R_3+6Q_1+2Q_2+Q_3+Q_4)/7$ or $(10R_1+6R_2+2R_3+6Q_1+2Q_2+2Q_3+2Q_4)/7$
20	$(6R_1+4R_2+2R_3+2Q_1+2Q_2+2Q_3+2Q_4)/5$
21	$(14R_1+6R_2+R_3+6Q_1+4Q_2+Q_3)/8$ or $(14R_1+6R_2+2R_3+6Q_1+4Q_2+2Q_3)/8$
22	$(12R_1+4R_2+R_3+4Q_1+4Q_2+2Q_3+Q_4)/7$ or $(12R_1+4R_2+2R_3+4Q_1+4Q_2+2Q_3+2Q_4)/7$
23	$(14R_1+6R_2+R_3+6Q_1+4Q_2+Q_3)/8$ or $(14R_1+6R_2+2R_3+6Q_1+4Q_2+2Q_3)/8$
24	$(18R_1+4R_2+R_3+8Q_1+2Q_2+2Q_3+Q_4)/9$ or $(18R_1+4R_2+2R_3+8Q_1+2Q_2+2Q_3+2Q_4)/9$
25	$(16R_1+4R_2+4Q_1+6Q_2+2Q_3)/8$
26	$(14R_1+4R_2+2Q_1+3Q_2+4Q_3+Q_4)/7$ or $(14R_1+4R_2+2Q_1+4Q_2+4Q_3+2Q_4)/7$
27	$(8R_2+2R_3+2Q_3)/4$
28	$(8R_2+2R_3+2Q_3)/4$
29	$(6R_2+2R_3+2Q_2+2Q_3)/4$
30	$(4R_1+2R_2+6R_3)/4$
31	$(2R_3)/2$
32	$(4R_1+4R_2+4R_3)/4$
33	$(4R_1+4R_2+4R_3)/4$
34	$(2Q_4)/2$
35	$(2R_2+2Q_2+2Q_4)/3$
36	$(2R_2+2Q_2+2Q_4)/3$
37	$(2R_2+2Q_2+2Q_4)/3$
38	$(2R_2+2Q_2+2Q_4)/3$
39	$(6R_1+4R_2+4R_3+4Q_1+4Q_2+2Q_3)/6$
40	$(6R_1+4R_2+3R_3+2Q_1+6Q_2+2Q_3+Q_4)/6$ or $(6R_1+4R_2+4R_3+2Q_1+6Q_2+2Q_3+2Q_4)/6$
41	$(4R_1+4R_3+2Q_1+4Q_2+2Q_3)/4$
42	$(8R_1+2R_3+2Q_1+6Q_2+5Q_3+Q_4)/6$ or $(8R_1+2R_3+2Q_1+6Q_2+6Q_3+2Q_4)/6$
43	$(4R_1+2R_2+6R_3)/4$
44	$(4R_1+2R_2+6R_3)/4$
45	$(8R_2+2R_3+8Q_1+3Q_2+3Q_3)/6$ or $(8R_2+2R_3+8Q_1+4Q_2+4Q_3)/6$
46	$(8R_2+2R_3+2Q_4)/4$
47	$(2R_1+4R_2+4R_3+6Q_1+6Q_2+Q_3+Q_4)/6$ or $(2R_1+4R_2+4R_3+6R_1+6Q_2+2Q_3+2Q_4)/6$



$RE=(8R_1+2Q_2+4Q_3+Q_4)/5$

Figure 10. Decomposition of the five Kekule'structures of dibenzo(b,f)-pentalene into its conjugated circuits

Equation (2) can be expoited for specific formulas. The maximum number of peripheral carbon vertices that $C_{16}H_{10}$ structures can possess within the polycyclic conjugated constraint is $N_{Pc}=6$; thus N_{Pc} can vary between 4 to 6 which corresponds to $N_{Ic}=2$ to $N_{Ic}=0$, respectively. Incorporating this information into Equation (2) leads to the following equations: All $C_{16}H_{10}$ polycyclic conjugated structures having two internal third degree carbon vertices will obey $3(r_3-r_9)+2(r_4-r_8)+(r_5-r_7)=0$, all structures having one internal third degree vertex will obey $3(r_3-r_9)+2(r_4-r_8)+(r_5-r_7)=1$, and finally all structures having $N_{Ic}=0$ will obey $3(r_3-r_9)+2(r_4-r_8)+(r_5-r_7)=2$ where $r_3+r_4+r_5+r_6+r_7+r_8+r_9=4$. Enumeration of structures *27-33*, and *39-68* were facilitated by the first of these equations; the second equation facilitated generation of structures *69* to *213*; and the latter equation facilitated the systematic enumeration of structures *214* to *418*. Another useful equation for any specific formula is $N_{Ic}+d_s=\text{const} = \frac{N_c-N_H}{2} -1$ which gives $N_{Ic}+d_s=2$ for $C_{16}H_{10}$; this relationship is the basis of the periodic tables in this paper.

Resonance Energies of the Isomers of Pyrene.

All the pertinent molecular orbital energy quantities for many of the polycyclic conjugated isomers of pyrene in Figure 9 are listed in Table 10. The resonance energy (RE) of each $C_{16}H_{10}$ isomer was computed by the conjugated circuit method.[5] The structure count (SC) and corrected structure count (CSC) was determined by a PMO method[6] or enumeration of all the Kekule' valence structures. The total pi electron energy ($E\pi$), HOMO, and LUMO quantities were obtained from the published literature;[7] the absence of these literature quantities for most of the $C_{16}H_{10}$ isomers emphasizes the need for a systematic approach for PAH isomer enumeration of which this paper addresses.

Table 11 summarizes all the conjugated circuit resonance energy terms for the 47 polycyclic conjugated hydrocarbon isomers in Figure 9. The alternative quantities following the conjunction "or" for structures *4*, *6*, *12*, *13*, *19*, *21*, *22*, *23*, *24*, *26*, *40*, *42*, *45*, and *47* were obtained by an adaptation of a method not requiring the writing down of all the Kekule' valence structures;[8] for all the other structures the circuit resonance energy terms were identical when computed by either the longhand[5] or shorthand method.[8] Nevertheless, for the structures that have slightly different terms due to the fact that the latter method does not allow one to readily recognize those extra terms which are a linear combination of the other terms, the numerical values obtained in these cases were nearly the same by either method. This is illustrated by the following example with structure *6*. Figure 10 lists the five Kekule' valence structures of *6* and their associated component circuits; the sum of the circuit terms divided by the number of Kekule' valence structures gives the RE for *6* after substituting in their appropriate numerical values.[5] In the second method, the various 4n+2 and 4n circuit terms are displayed in Figure 11 where the weighting or term coefficient is given by the number of Kekule' valence structures of the residual; multiplying all the term coefficients by two and dividing the whole sum by the number of Kekule' structures (i.e., structure count of *6*) gives the RE which differs from that determined by the first method (Figure 10) in that there are no odd coefficients. In this example the extra Q_4 term is a linear combination $(2Q_3-Q_2)$ of Q_2 and Q_3 which was recognized and consequently omitted in last Kekule' structure in Figure 10. The SC of *6* can be obtained by a PMO method and is equal to the sum of the absolute values of the unnormalized NBMO coefficients in the odd alternate hydrocarbon derived by localizing the appropriate carbon vertex (circled) as shown below which gives a value of

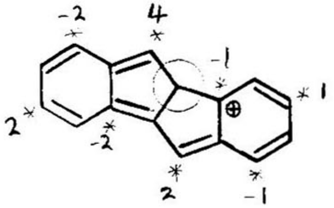
Table 12. Selected Resonance Energies for Various Pyrene Isomers.

Cpd	RE(eV)	R_n and Q_n Decompostion	Number of Different Ring Sizes						
			3	4	5	6	7	8	9
48	-0.116	$(2R_1+2R_3+4Q_2+4Q_3)/4$	1	0	0	1	1	1	0
49	-0.041	$(2R_1+2R_3+4Q_2+2Q_3)/4$	1	0	0	1	1	1	0
50	0.110	$(2R_1+2R_3+2Q_2+4Q_3)/4$	1	0	0	1	1	1	0
51	0.100	$(2R_3)/2$	0	1	1	0	1	1	0
52	0.085	$(2R_2+ 2R_3+ 2Q_2+ 2Q_3)/6$	0	1	1	0	1	1	0
53	-0.804	$(4R_2+2R_3+2Q_1+2Q_2+2Q_3)/4$	0	1	1	0	1	1	0
54	-0.556	$(4R_2+2R_3+2Q_1+2Q_2+2Q_3+2Q_4)/6$	0	1	1	0	1	1	0
55	-0.957	$(2R_2+2R_3+2Q_1+2Q_2+2Q_3+2Q_4)/4$	0	1	1	0	1	1	0
56	0.100	$(2R_3)/2$	0	2	0	0	1	0	1
57	-1.115	$(2R_1+2R_3+4Q_1)/4$	0	2	0	0	1	0	1
58	0.100	$(2R_3)/2$	0	1	0	1	2	0	0
59	-0.754	$(2R_1+4R_3+2Q_1+2Q_2+2Q_3)/3$	0	1	0	1	2	0	0
60.	-0.645	$(2R_1+2R_3+2Q_1+2Q_2+2Q_3+2Q_4)/4$	0	1	0	1	2	0	0
61	-0.550	$(2R_3+4Q_2+4Q_3)/4$	1	0	0	0	3	0	0
62	-0.116	$(2R_1+2R_3+4Q_2+4Q_3)/4$	0	0	2	1	0	1	0
63	0.246	$(2R_1+2R_3+2Q_2+2Q_3)/3$	0	0	2	1	0	1	0
64	-0.410	$(2R_1+2R_3+2Q_1+2Q_2+2Q_3)/6$	0	1	1	1	0	0	1
65	-0.377	$(2R_1+4R_3+2Q_1+2Q_2+2Q_3)/6$	0	1	1	1	0	0	1
66	0.100	$(2R_3)/2$	0	1	1	1	0	0	1
67	0.215	$(2R_1+2R_3+2Q_1+2Q_2+2Q_3+2Q_4)/12$	0	1	1	1	0	0	1
68	-0.520	$(2R_1+4R_3+2Q_1+2Q_2+2Q_4)/4$	0	1	1	1	0	0	1

Table 12. (cont'd)

Cpd	RE(eV)	R_n and Q_n Decomposition	Number of Different Ring Sizes 3	4	5	6	7	8	9
78	-0.108	$(4R_1+2R_2+2Q_1+2Q_2+2Q_3)/4$	0	1	0	2	1	0	0
79	-0.086	$(4R_1+2R_2+2Q_1+2Q_2+2Q_3)/5$	0	1	0	2	1	0	0
80	0.256	$(4R_1+2R_2+2Q_1)/3$	0	1	0	2	1	0	0
81	0.128	$(4R_1+2R_2+2Q_1)/6$	0	1	0	2	1	0	0
84	-0.108	$(4R_1+2R_2+2Q_1+2Q_2+2Q_3)/4$	0	1	0	2	1	0	0
85	-0.086	$(4R_1+2R_2+2Q_1+2Q_2+2Q_3)/5$	0	1	0	2	1	0	0
89-93	-0.419	$(2R_2+2Q_1+2Q_3)/3$	1	1	0	0	1	0	1
94-96	-1.203	$(2R_2+2Q_1+2Q_2)/3$	1	1	0	0	1	0	1
160-164	0.810	$(2R_1+2R_2+2R_3)/3$	1	0	1	1	0	0	1
165	0.743	$(2R_1+2R_2)/3$	1	0	1	1	0	0	1
168-172	0.439	$(2R_1+2Q_3+2Q_4)/3$	1	0	1	1	0	0	1
177,179	0.937	$(4R_1+2R_2+2R_3+2Q_3+2Q_4)/4$	1	0	1	1	0	0	1
178,180	0.750	$(4R_1+2R_2+2R_3+2Q_3+2Q_4)/5$	1	0	1	1	0	0	1
189-191	1.323	$(4R_1+2R_2)/3$	1	0	0	2	0	1	0
195,198	0.371	$(4R_1+2Q_2+4Q_3+2Q_4)/5$	1	0	0	2	0	1	0
197,199	0.464	$(4R_1+2Q_2+4Q_3+2Q_4)/4$	1	0	0	2	0	1	0
200	0.530	$(4R_1+2R_2+2Q_2+2Q_3+2Q_4)/5$	1	0	0	2	0	1	0
201	0.662	$(4R_1+2R_2+2Q_2+2Q_3+2Q_4)/4$	1	0	0	2	0	1	0
216,217	0.662	$(4R_1+2R_2+2Q_2+2Q_3+2Q_4)/4$	1	0	0	2	1	0	0
222-225	0.530	$(4R_1+2R_2+2Q_2+2Q_3+2Q_4)/5$	1	0	0	2	1	0	0
275-278	-0.497	$(2R_1+2R_2+2Q_1+2Q_2+2Q_4)/4$	0	1	1	1	1	0	0
297-302	-0.497	$(2R_1+2R_2+2Q_1+2Q_2+2Q_4)/4$	0	1	1	1	1	0	0
309-310	-0.06	$(2Q_4)/2$	2	0	0	0	1	0	1
311-316	-0.264	$(2R_2+2Q_2+2Q_4)/2$	2	0	0	0	1	0	1
348,349	0.439	$(2R_1+2Q_3+2Q_4)/3$	1	0	2	0	0	0	1
386	0.662	$(4R_1+2R_2+2Q_2+2Q_3+2Q_4)/4$	1	0	1	1	0	1	0
393-397	0.439	$(2R_1+2Q_3+2Q_4)/3$	1	0	1	1	0	1	0
417-418	0.530	$(4R_1+2R_2+2Q_2+2Q_3+2Q_4)/5$	1	0	1	1	0	1	0

five (|4|+|-1|). When the above two methods gave a difference, the average numerical difference between the two methods was 0.03 eV and the largest difference was 0.09 eV for the data in Table 10. All the REs for the structures in Table 12 were computed by the second method.[8]



SC =|4|+|-1|= 5

Conclusion

The largest RE obtained in this work was +2.19 eV for fluoranthene (2) and smallest RE was -2.072 eV for compound *45*; for both these compounds SC=6, but *2* is strongly aromatic and *45* is strongly antiaromatic and emphasizes that the empirical logrithmic relationship between SC and RE is limited to only those structures which have no antiaromatic conjugated circuit terms, i.e., benzenoid hydrocarbons.[9] Comparison of the data in Table 10 for those structures (*8*, *9*, and *18*; *16*, *17*, and *34*; *32* and *33*) having identical conjugated circuits (Table 11) show that there is no obvious correlation between RE, E_π, HOMO, and LUMO. Disregarding possible steric and angle strain, structures *43*, *44*, *46*, *63*, *67*, *80*, *160-165*, *168-172*, *177-180*, *189-191*, *195*, *198-201*, *216*, *217*, *222-225*, *348*, *349*, *386*, *393-397*, and *417-418* probably have sufficient REs to warrant synthetic investigation. In general for N_{Ic}=1, the pyrene isomer structures must have one or three odd ring sizes, and for $N_{Ic}=0$ there are zero, two, or four odd ring sizes present in the structure. Fusion of a conjugated trigonal ring to the outer periphery of a pentagonal, octagonal or nonagonal ring results in relative increase in REs (*cf.*, structures *160-164*, *165*, *177-180*, and *189-191*). Fusion of a conjugated trigonal ring to the periphery of a hexagonal ring results in a relative decrease in REs. An example of the relevance of this work is nicely annotated by the recent example of the thermal (500°) isomerization of azupyrene (*27*) to pyrene (1).[10] This example is probably mechanistically the simplest type of isomerization possible for these isomers; a pairwise detachment and reattachment exchange of *syn* internal bonds to the internal third degree carbon atom vertices would convert azupyrene to pyrene or vice versa.

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