ARTICLES

A Periodic Table for Polycyclic Aromatic Hydrocarbons. 4. Isomer Enumeration of Polycyclic Conjugated Hydrocarbons. 2

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Additional work toward systematizing all polycyclic aromatic hydrocarbons (PAHs) into a unified, comprehensive data and information package by using graph theoretical principles is described. Key equations [$N_{Ic} + d_s$ = constant and $N_{Pc} = N_H - 6 + 3r_3 + 2r_4 + r_5 - r_7 - 2r_8 - 3r_9 - \cdots$] are illustrated in the enumeration of all 43 totally fused polycyclic conjugated hydrocarbon isomers of anthracene. The practical molecular size limit of the PAH6 formula periodic table was investigated. The largest literature reported PAHs are $C_{68}H_{30}$ (from pitch), $C_{62}H_{34}$, $C_{64}H_{32}$, $C_{66}H_{36}$, $C_{68}H_{34}$, and $C_{72}H_{36}$ (theoretical studies). All PAH6s with the same number of formula hydrogens (N_H) have structures with the same carbon atom perimeter length ($q_P = 2N_H - 6$ = constant) and lie along the same diagonal formula array in the PAH6 formula periodic table. The maximum number of alkynyl units (A_{max}) in addition to benzenoid rings that can exist in a molecular structure corresponding to a PAH6 formula is given by $A_{max} \leq (1/4)(2N_c - 3N_H + 6)$. An algorithm for determining the maximum number of alkyl methylene carbons that a structure corresponding to a PAH6 formula can possess is presented. The number of benzenoid PAH6 isomers having formulas $C_{38}H_{16}$, $C_{40}H_{16}$, $C_{42}H_{16}$, $C_{48}H_{18}$, $C_{50}H_{18}$, $C_{52}H_{18}$, and $C_{60}H_{20}$ are 10, 3, 1, 22, 7, 2, and 19, respectively; a method for their complete enumeration is presented. The area of polycyclic conjugated hydrocarbons needing future research emphasis has been identified, and methods for selective literature searching with PAH formulas is presented.

In this fourth paper of the series[1-3] the current and past research scope of polycyclic aromatic hydrocarbons (PAHs) is examined within the framework of graph theoretical principles. Additional graph theoretical algorithms and correlations have been developed for inclusion of alkyl-substituted and alkynyl-containing PAH6s. One eventual goal of this work is to develop a unified, comprehensive data and information package for all PAHs systematized according to Table I and the principles developed in this series.

RESULTS AND DISCUSSION

A glossary of specialized terms used herein appears in the appendix. Throughout this paper, only the σ-bond system of PAHs is shown and the $p\pi$ bonds, C-H bonds, C atoms, and H atoms are omitted.

Formula Periodic Table for PAH6. Our previous research identified a formula periodic table for PAH6 (Table I), which systematized for the first time the formula-structure relationships of PAHs.[1] The basic graphical invariant that permitted this unification was that $N_{Ic} + d_s = (1/2)(N_c - N_H) - 1$ = constant for all isomeric structures corresponding to a particular formula. If only fused hexagonal rings (PAH6) are permitted, then all the PAH6 structures corresponding to formulas found in the same row of Table I will have identical N_{Ic} values and all the PAH6 structures found in the same column would have the same d_s value. The number of internal third-degree carbon vertices (N_{Ic}) in anthracene and phenanthrene isomers ($C_{14}H_{10}$) is 0 ($N_{Ic} = 0$), and their internal edge (bond) disconnection (d_s) is 1 ($d_s = 1$). All polycyclic conjugated hydrocarbon isomers of $C_{14}H_{10}$ must have $N_{Ic} + d_s = 1$, i.e., one disconnection ($d_s = 1$) or one internal third-degree carbon vertex ($N_{Ic} = 1$); note that for larger formulas negative values are possible for d_s. The relative number of different ring sizes can be computed from $N_{Pc} = N_H - 6 + 3r_3 + 2r_4 + r_5 - r_7 - 2r_8 - 3r_9 - \ldots$. For $N_{Ic} = 0$, this equation reduces to $3r_3 + 2r_4 + r_5 - r_7 - 2r_8 - 3r_9 = 0$; structures 1-35 (Figure 1) conform to these constraints. For $N_{Ic} = 1$, $3r_3 + 2r_4 + r_5 - r_7 - 2r_8 - 3r_9 = -1$, and structures 36-43 are compliant to these latter specific equations. Since $r_{3max} \leq (1/3)N_{Ic}(PAH6) = 0$, $r_{4max} = (1/2)N_{Ic}(PAH6) = 0$, and $r_{5max} \leq N_{Ic}(PAH6) = 0$, no $C_{14}H_{10}$ isomers composed of only hexagonal and trigonal rings, hexagonal and tetragonal rings, or hexagonal and pentagonal rings are possible.[2,3] Similarly, since $r_{7max} = d_s(PAH6) - M = 1 - 0 = 1$, $r_{8max} \leq (1/2)[d_s(PAH6) - M] = 0.5$, and $r_{9max} \leq (1/4)[d_s(PAH6) - M] = 0.25$, only $C_{14}H_{10}$ isomers having one heptagonal ring in addition to hexagonal rings are possible (i.e., 36 in Figure 1). Therefore, there are only 43 totally fused polycyclic conjugated hydrocarbons isomers having ring sizes ranging from three to nine with the formula $C_{14}H_{10}$ (Figure 1). If isomers with bridging components are allowed (e.g., phenylpentalene and biphenylethyne), then far more isomers can be generated.

From a theoretical point of view, Table I extends infinitely in two dimensions, but from a practical point of view, as the size of a PAH increases so does its melting point with a corresponding decrease in solubility. As the size of a PAH increases, our ability to experimentally manipulate it into a well-defined monodispersed substance decreases. This poses the question, at what limit in molecular size does the extent of Table I become impractical? The results of a literature investigation from 1957 to 1981 are summarized in Table II. Also, no formula in Table I larger than $C_{58}H_x$ could be found in the *Chemical Abstracts 1982 Formula Index*, the *5th (1947-1956) Cummulative Formula Index*, and the *Collective (1920-1946) Formula Index*. The largest experimentally determined PAH compound in the literature[4] had a formula of $C_{68}H_{30}$ and was referred to as "Polyaromatic hydrocarbon" by Chemical Abstracts. This compound ($C_{68}H_{30}$) was one of the components in a gel-permeation chromatographic fraction isolated from pitch and was incompletely characterized by mass spectrometry. The investigators of this work noted that this was one of the largest molecular weight compounds to be identified in pitch.[4] Hexadecacene ($C_{66}H_{36}$), pentadecacene

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Table I. Formula Periodic Table for Polycyclic Aromatic Hydrocarbons (PAH6)

$N_c = 3N_H + 4$	$N_c = 3N_H + 2$	$N_c = 3N_H$	$N_c = 3N_H - 2$	$N_c = 3N_H - 4$	$N_c = 3N_H - 6$	$N_c = 3N_H - 8$	$N_c = 3N_H - 10$	$N_c = 3N_H - 12$	$N_c = 3N_H - 14$	$N_c = 3N_H - 16$	$N_c = 3N_H - 18$	$N_c = 3N_H - 20$	$N_c = 2N_H - 6 + N_{Ic}$
forbidden region									$C_{10}H_8$	$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$	$N_c = 2N_H - 6$
									$C_{16}H_{10}$	$C_{20}H_{12}$	$C_{24}H_{14}$	$C_{28}H_{16}$	$N_c = 2N_H - 4$
									$C_{22}H_{12}$	$C_{26}H_{14}$	$C_{30}H_{16}$	$C_{34}H_{18}$	$N_c = 2N_H - 2$
		$C_{00}H_{00}$						$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$	$C_{36}H_{18}$	$C_{40}H_{20}$	$N_c = 2N_H$
								$C_{30}H_{14}$	$C_{34}H_{16}$	$C_{38}H_{18}$	$C_{42}H_{20}$	$C_{46}H_{22}$	$N_c = 2N_H + 2$
							$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$	$C_{48}H_{22}$	$C_{52}H_{24}$	$N_c = 2N_H + 4$
						$C_{40}H_{16}$	$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	$C_{50}H_{22}$	$C_{54}H_{24}$	$C_{58}H_{26}$	$N_c = 2N_H + 6$
					$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{44}H_{18}$	$C_{48}H_{20}$	$C_{52}H_{22}$	$C_{56}H_{24}$	$C_{60}H_{26}$	$C_{64}H_{28}$	$N_c = 2N_H + 8$
				$C_{50}H_{18}$	$C_{48}H_{18}$	$C_{52}H_{20}$	$C_{50}H_{20}$	$C_{54}H_{22}$	$C_{58}H_{24}$	$C_{62}H_{26}$	$C_{66}H_{28}$	...	$N_c = 2N_H + 10$
			$C_{52}H_{18}$	$C_{56}H_{20}$	$C_{54}H_{20}$	$C_{58}H_{22}$	$C_{56}H_{22}$	$C_{60}H_{24}$	$C_{64}H_{26}$	$C_{68}H_{28}$	...	...	$N_c = 2N_H + 12$
		$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$	$C_{60}H_{22}$	...	...	...	...	...	...	...	$N_c = 2N_H + 14$
	$C_{62}H_{20}$	$C_{60}H_{20}$	$C_{64}H_{22}$	...	...	...	...	...	...	...	...	...	$N_c = 2N_H + 16$
$C_{64}H_{20}$	$C_{68}H_{22}$	$C_{66}H_{22}$	...	...	...	...	...	...	...	...	...	...	$N_c = 2N_H + 18$
$C_{70}H_{22}$	...	...	...	...	...	...	...	...	...	...	...	...	$N_c = 2N_H + 20$
...	...	...	...	...	...	...	...	...	...	...	...	...	$N_c = 2N_H + 22$
													$N_c = 2N_H + 24$
													$N_c = 2N_H + 26$
													...

$N_c = 3N_H - 14 - 2d_s$

$N_c = 3N_H - 22$	$N_c = 3N_H - 24$	$N_c = 3N_H - 26$	$N_c = 3N_H - 28$	$N_c = 3N_H - 30$	$N_c = 3N_H - 32$	$N_c = 3N_H - 34$	$N_c = 3N_H - 36$	$N_c = 3N_H - 38$	$N_c = 3N_H - 40$	$N_c = 3N_H - 42$	$N_c = 3N_H - 44$	...	$N_c = 2N_H - 6 + N_{Ic}$
$C_{26}H_{16}$	$C_{30}H_{18}$	$C_{34}H_{20}$	$C_{38}H_{22}$	$C_{42}H_{24}$	$C_{46}H_{26}$	$C_{50}H_{28}$	$C_{54}H_{30}$	$C_{58}H_{32}$	$C_{62}H_{34}$	$C_{66}H_{36}$	$C_{70}H_{38}$	...	$N_c = 2N_H - 6$
$C_{32}H_{18}$	$C_{36}H_{20}$	$C_{40}H_{22}$	$C_{44}H_{24}$	$C_{48}H_{26}$	$C_{52}H_{28}$	$C_{56}H_{30}$	$C_{60}H_{32}$	$C_{64}H_{34}$	$C_{68}H_{36}$	$C_{72}H_{38}$	...	...	$N_c = 2N_H - 4$
$C_{38}H_{20}$	$C_{42}H_{22}$	$C_{46}H_{24}$	$C_{50}H_{26}$	$C_{54}H_{28}$	$C_{58}H_{30}$	$C_{62}H_{32}$	$C_{66}H_{34}$	...	...	...			$N_c = 2N_H - 2$
$C_{44}H_{22}$	$C_{48}H_{24}$	$C_{52}H_{26}$	$C_{56}H_{28}$	$C_{60}H_{30}$	$C_{64}H_{32}$	$C_{68}H_{34}$	$C_{72}H_{36}$						$N_c = 2N_H$
$C_{50}H_{24}$	$C_{54}H_{26}$	$C_{58}H_{28}$	$C_{62}H_{30}$	$C_{66}H_{32}$	...	...	...						$N_c = 2N_H + 2$
$C_{56}H_{26}$	$C_{60}H_{28}$	$C_{64}H_{30}$	...	...									$N_c = 2N_H + 4$
$C_{62}H_{28}$	$C_{66}H_{30}$	...											$N_c = 2N_H + 6$
$C_{68}H_{30}$	...												$N_c = 2N_H + 8$
...													$N_c = 2N_H + 10$

$2 < N_c/N_H < 3$

$N_c/N_H < 2$

$2 < N_c/N_H < 3$

$N_c/N_H > 3$

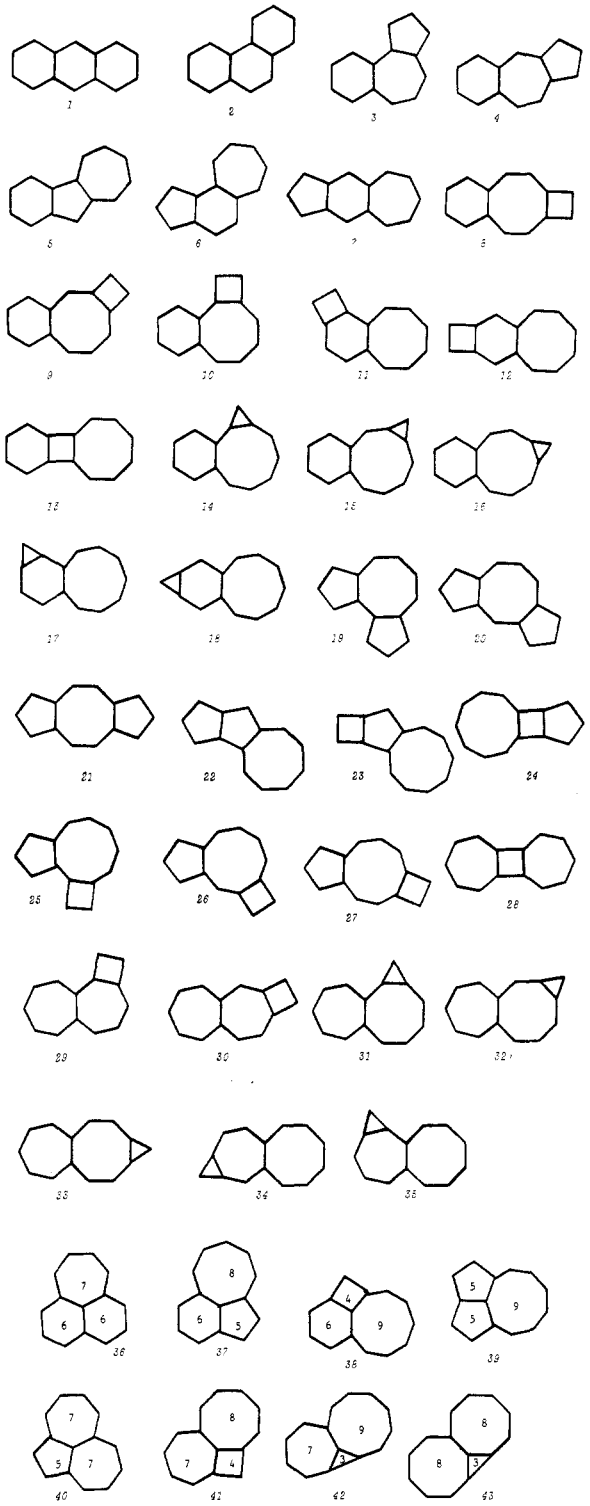


Figure 1. All the polycyclic conjugated isomers of the formula $C_{14}H_{10}$.

($C_{62}H_{34}$), and naphthaceno[2,3-*n*]undecaphene ($C_{62}H_{34}$) have only been studied theoretically by molecular orbital calculations.[5,6] Theoretical magnetic ring currents in series of circumpolyacenes (including $C_{72}H_{36}$ and $C_{68}H_{34}$) have been only calculated.[7] Thus, from Table II one can conclude that the range of formulas presently shown in Table I probably represents the current practical extent of the PAH6 formula periodic table.

There are four quadrants to Table I, which are determined by the range of values in the ratio of N_c/N_H for the possible formulas of PAHs. The intersection of these quadrants occurs at the nonexistent formula of $C_{00}H_{00}$. The horizontal line is defined by the linear array of formulas having $N_c/N_H = 2$,

Table II. Approximate Number[a] of *Chemical Abstracts* Formula Index Citations

formula	1957-1981	formula	1957-1981	formula	1957-1981
$C_{72}H_{36}$	1	$C_{46}H_{24}$	2	$C_{36}H_{16}$	10
$C_{68}H_{34}$	1	$C_{46}H_{22}$	7	$C_{34}H_{20}$	130[b]
$C_{66}H_{36}$	1[b]	$C_{46}H_{20}$	1	$C_{34}H_{18}$	80
$C_{64}H_{32}$	1	$C_{46}H_{18}$	1	$C_{34}H_{16}$	10
$C_{62}H_{34}$	2[b]	$C_{44}H_{24}$	8	$C_{32}H_{18}$	70
$C_{60}H_{30}$	1	$C_{44}H_{22}$	8	$C_{32}H_{16}$	60
$C_{58}H_{32}$	10[b]	$C_{44}H_{20}$	4	$C_{32}H_{14}$	60
$C_{56}H_{30}$	1	$C_{44}H_{18}$	3	$C_{30}H_{18}$	210[b]
$C_{56}H_{28}$	1	$C_{42}H_{24}$	40[b]	$C_{30}H_{16}$	110
$C_{56}H_{26}$	1	$C_{42}H_{22}$	20	$C_{30}H_{14}$	30
$C_{56}H_{20}$	1	$C_{42}H_{20}$	1	$C_{28}H_{16}$	>250
$C_{54}H_{30}$	10[b]	$C_{42}H_{18}$	20	$C_{28}H_{14}$	90
$C_{54}H_{26}$	1	$C_{42}H_{16}$	1	$C_{26}H_{16}$	>250[b]
$C_{54}H_{18}$	2	$C_{40}H_{22}$	20	$C_{26}H_{14}$	>130
$C_{52}H_{26}$	1	$C_{40}H_{20}$	40	$C_{24}H_{14}$	>250
$C_{50}H_{28}$	10[b]	$C_{40}H_{18}$	10	$C_{24}H_{12}$	>250
$C_{50}H_{26}$	1	$C_{40}H_{16}$	8	$C_{22}H_{14}$	>250[b]
$C_{50}H_{22}$	1	$C_{38}H_{22}$	60[b]	$C_{22}H_{12}$	>250
$C_{48}H_{26}$	3	$C_{38}H_{20}$	20	$C_{20}H_{12}$	>250
$C_{48}H_{24}$	20	$C_{38}H_{18}$	20	$C_{18}H_{12}$	>250[b]
$C_{48}H_{22}$	6	$C_{38}H_{16}$	7	$C_{16}H_{10}$	>250
$C_{48}H_{20}$	1	$C_{36}H_{20}$	30	$C_{14}H_{10}$	>>250[b]
$C_{46}H_{26}$	10[b]	$C_{36}H_{18}$	110	$C_{10}H_8$	>>250[b]

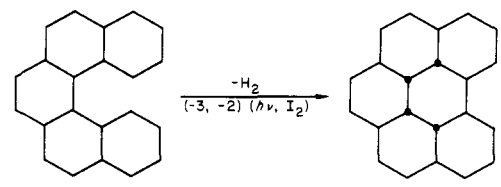
[a] Numbers above 10 are rounded off to nearest decade. [b] Formulas for cata-condensed PAHs.

and the vertical line is defined by the linear array of formulas having $N_c/N_H = 3$; these lines intersect at a hypothetical formula that should have a N_c/N_H ratio that is simultaneously equal to both 2 and 3, which is impossible ($N_c/N_H = 0/0$ for $C_{00}H_{00}$ and is undefined). In the upper left-hand corner quadrant is the forbidden region where no reasonable formula can exist, and the boundary diagonal line passes through the $C_{xy}H_{00}$ formula array, which is parallel to the diagonal linear array of formulas all having the same number of hydrogens (e.g., $C_{xy}H_{22}$). The lower left-hand quadrant contains formulas where $N_c/N_H > 3$, the lower right-hand quadrant contains formulas where $2 < N_c/N_H < 3$, and the upper right-hand quadrant contains formulas where $N_c/N_H < 2$.

An increase in the N_c/N_H ratio occurs for dehydrogenation cyclization reactions. To investigate the relationships of hexagonal benzenoid graphs having the same total number of carbon vertices but a different number of secondary carbon vertices (N_H), consider the following general process:

$$C_xH_y \xrightarrow[(-3,\,-2)]{-H_2} C_xH_{y-2}$$

Note that the process causes the original formula (C_xH_y) in Table I to shift to another formula (C_xH_{y-2}) in a new position three columns to the left and two rows down; this process has formula-shift coordinates of (−3, −2). Differentiating previously derived equations[1] shows that loss of two hydrogens ($\Delta N_H = -2$) while holding N_c constant causes the associated structure to increase by one ring ($\Delta r = -(1/2)\Delta N_H = 1$) and one edge ($\Delta q = -(1/2)\Delta N_H = 1$) and by four internal third degree vertices ($\Delta N_{Ic} = 4$). This is illustrated by the following photodehydrocyclization process that can be shown to be thermodynamically favorable:[8]

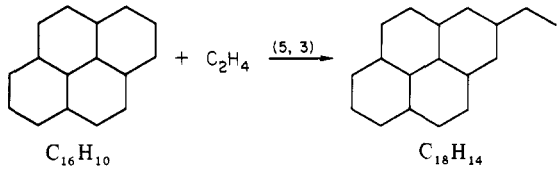


$C_{22}H_{14}$ (G) $C_{22}H_{12}$ (G + x)

Only one formula having 10, 14, 18, 16, and 20 carbons can

be found in Table I. This process having formula-shift coordinates of (−3, −2) gives a general movement of formulas from the $N_c/N_H = 2$ quadrant in Table I to the $2 < N_c/N_H < 3$ quadrant and from this latter region to the $N_c/N_H > 3$ quadrant.

Alkylated PAHs. A single methyl or an odd-carbon alkyl substituent on a PAH would give a formula with an odd number of carbons and, consequently, can be easily distinguished. To investigate how even-carbon aliphatic alkyl substituents affect the shift of a PAH6 formula in Table I, consider the following process. Take pyrene ($C_{16}H_{10}$) and attach an ethyl substituent (or two methyl substituents):



This results in a formula-position shift of five columns to the right and three rows up in Table I to a position occupied by the formula $C_{18}H_{14}$ in Table III; thus, the shift coordinates are (5, 3) for this process. Can the $C_{16}H_{10}$ be represented by an alkylated PAH6? No, since subtracting C_2H_4 from $C_{16}H_{10}$ gives $C_{14}H_6$, which does not exist in Table I. In general, no formula in Table I above the dashed zigzag line can be represented by an alkyl- (C_nH_{2n+1}) substituted PAH6, and if one has a formula below or to the right of this line, then it can. If one successively subtracts CH_2 from a formula not found in Table I that eventually gives a formula belonging to it (e.g., $C_{19}H_{14} - CH_2 = C_{18}H_{12}$), then this initial formula not belonging to Table I can also be represented by an alkyl-substituted PAH6. Table III gives the formula periodical table for even-carbon alkyl-substituted PAH6s. By use of set theory terminology, the relative complement of the set of formulas in Table III with respect to those in Table I gives the set of PAH6 formulas [(Table I)\(Table III)] that cannot have alkyl substituents (also shown above the dashed zigzag line in Table I). The relative complement of the set of formulas in Table I with respect to the set of formulas in Table III gives the set of PAH formulas [(Table III)\(Table I)] that must possess at least one even-carbon alkyl substituent (the formulas above the dashed line in Table III).

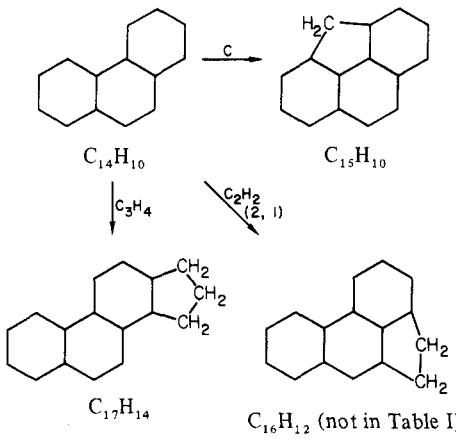
An algorithm for determining the maximum number of ethyl substituents that any structure corresponding to a particular PAH6 formula can possibly possess is given by the following. Successively subtract C_2H_4 from a PAH formula verified to be in Table I and/or Table III until the resulting formula is no longer observed in Table I; the maximum number of ethyl substituents is one less than the number of ethyl units subtracted. For example, subtracting two C_2H_4 units from $C_{46}H_{26}$ gives $C_{42}H_{18}$, which would give a nonexistent PAH6 formula of $C_{40}H_{14}$ upon subtracting a third C_2H_4 unit; thus, a PAH6 structure corresponding to $C_{46}H_{26}$ cannot possess more than two ethyl substituents (or four methyl, two methyl and one ethyl, one methyl and one propyl, or one butyl substituent). If a particular test formula has an odd number of carbons, subtract CH_2 first and check to see if this resulting even-carbon formula is on Table I and/or Table III; proceed as above if it is on Table I and/or Table III. For example, $C_{47}H_{20}$ could be a PAH6 structure with five methyl substituents or some combination of alkyl groups having a sum of five carbons.

The assumption made above was that introduction of alkyl groups into PAH6 occurred without a change in the number of rings. If cycloalkyl groups are introduced, then the number of rings also change. Three common examples, two of which are odd-carbon formulas, can be derived from phenanthrene ($C_{14}H_{10}$) and are shown in Scheme I; the formula-shift co-

Table III. Formula Periodical Table for Even-Carbon Alkyl-Substituted PAH6s

| | | |

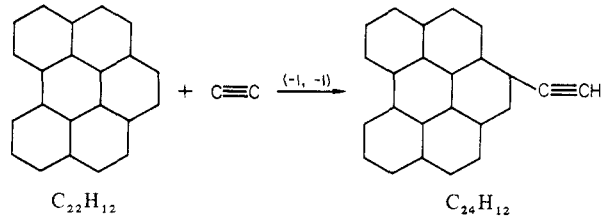
Scheme I



ordinates of (2, 1) show that the insertion of C_2H_2 leads to a shift of two columns to the right and one row up from the original formula position in Table I.

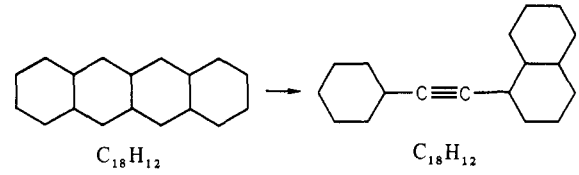
In a prior paper, a formula table was developed for phenyl-substituted PAH6 (or, in general, benzenoidyl-substituted PAH6s).[2] The relative complement of the set of formulas in this table (Table VIII in footnote 2) with those in Table I of this paper would give a set of PAH6 formulas [(Table I)\-(Table VIII)] that cannot have phenyl (or benzenoidyl) substituents. This group of formulas could have been explicitly indicated by a dashed zigzag line as used in Table I for the PAH6 formulas that cannot have alkyl substitutents, but this would have made the details of this table more complex than desired. The relative complement of the set of formula in Table I with respect to the set of formulas in Table VIII (footnote 2) would give a set of PAH formulas [(Table VIII)\(Table I)] that must possess at least one phenyl (or benzenoidyl) substituent. Bicoronene ($C_{48}H_{22}$) has a bridging bond between two coronenyl groups.[9] Using an algorithm similar to the one above,[2] one can determine the maximum number of bridging bonds that a PAH6 structure can possess if it has a formula of $C_{48}H_{22}$. By subtracting C_6H_4 from $C_{48}H_{22}$, one gets $C_{42}H_{18}$ [process has formula-shift coordinates of (−3, −1)], and by subtracting another C_6H_4, one obtains $C_{38}H_{14}$, which does not exist on Table I. Therefore, any structure comprised of linking PAH6s or phenyl groups having a formula of $C_{48}H_{22}$ cannot have more than one bridging bond ($q_b = 1$).

Polyalkynes with Terminal Aromatic Groups. A unique attribute of PAH formulas compared to other hydrocarbons is their high C to H ratio. Insertion of C≡C into a PAH6 structure shifts its formula in Table I one column to the left and one row down; the coordinates for this process are (−1, −1). This is illustrated with benzo[*ghi*]perylene ($C_{22}H_{12}$), which has a formula shifted to $C_{24}H_{12}$ in Table I as shown by the following:

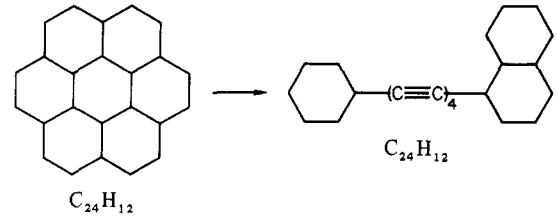


Another successive addition to a C≡C unit to $C_{24}H_{12}$ gives $C_{26}H_{12}$, which does not exist in Table I (but does exist in Table IV). All polyalkynyl polycyclic aromatic hydrocarbons must have a formula belonging to Table I or falling in the blank left-handed diagonal region of Table I. Since in this approach the pπ system of PAHs is disregarded, the C≡C unit is equivalent to a two-membered ring. An algorithm for determining the maximum number of alkynyl units that a structure corresponding to a PAH6 formula can have is given by the following procedure: successively subtract C_2 unit from the test formula until a formula is acquired that will give a formula not on Table I upon subtraction of another C_2 unit; the number of C_2 units subtracted in this process is the maximum number of alkynyl units that some structure having a PAH6 formula can contain. For example, subtraction of three C_2 units from $C_{24}H_{12}$ gives $C_{18}H_{12}$, which upon subtraction of another C_2 unit would give the formula $C_{16}H_{12}$ that does not exist on Table I; therefore, an alkynyl-substituted PAH6 structure having a formula of $C_{24}H_{12}$ can only have at most three alkynyl substituents. Note that terminal phenyl groups are excluded by this algorithm.

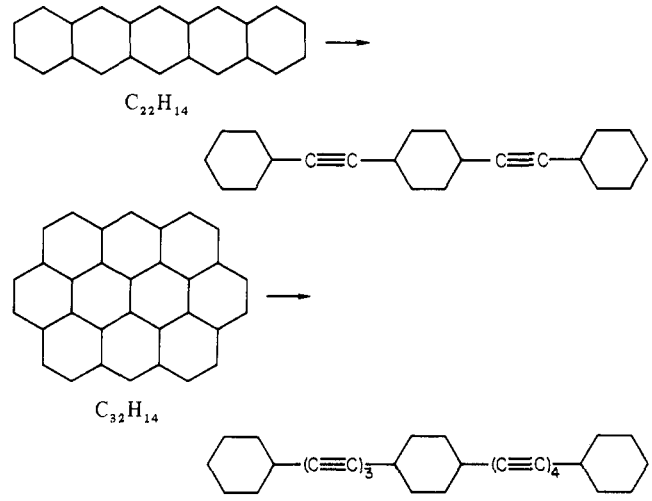
Isomeric conversion of tetracene ($C_{18}H_{12}$) to an alkyne with terminal aromatic groups is representative of the relationship that cata-condensed PAHs have with this class of compounds:



Transformation of coronene ($C_{24}H_{12}$) to a polyalkynyl isomer per the following sequence gives four triple-bonded carbon units:



Pentacene ($C_{22}H_{14}$) and ovalene ($C_{32}H_{14}$) are isomeric to the following alkynyl derivatives:



From these examples, it can be seen that for a molecular structure having a PAH6 formula, the maximum number (A_{max}) of alkynyl units that it can possess in addition to naphthyl and/or phenyl units is given by $A_{max} \leq (1/4)(2N_{Ic} + N_{Pc}) = (1/4)(2N_c - 3N_H + 6)$; note that, in general, the number of rings in the PAH6 parent isomer corresponds to the number of rings plus alkynyl units in the daughter isomer; i.e., the C≡C unit is equivalent to a two-membered ring. All PAH6 structures having the same number of formula hydrogens (N_H) will have the same number of naphthyl and/or

Table IV. Formula Periodical Table for Polyalkynyl-Substituted PAH6s

...	$N_c = 3N_H$	$N_c = 3N_H - 2$	$N_c = 3N_H - 4$	$N_c = 3N_H - 6$	$N_c = 3N_H - 8$	$N_c = 3N_H - 10$	$N_c = 3N_H - 12$	$N_c = 3N_H - 14$	$N_c = 3N_H - 16$	...	
									$C_{14}H_{10}$	...	$N_c = 2N_H - 6$
							$C_{12}H_8$	$C_{16}H_{10}$	$C_{20}H_{12}$	...	$N_c = 2N_H - 4$
						$C_{14}H_8$	$C_{18}H_{10}$	$C_{22}H_{12}$	$C_{26}H_{14}$	...	$N_c = 2N_H - 2$
					$C_{16}H_8$	$C_{20}H_{10}$	$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$	...	$N_c = 2N_H$
				$C_{18}H_8$	$C_{22}H_{10}$	$C_{26}H_{12}$	$C_{30}H_{14}$	$C_{34}H_{16}$	$C_{38}H_{18}$	...	$N_c = 2N_H + 2$
			$C_{20}H_8$	$C_{24}H_{10}$	$C_{28}H_{12}$	$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$	...	$N_c = 2N_H + 4$
		$C_{22}H_8$	$C_{26}H_{10}$	$C_{30}H_{12}$	$C_{34}H_{14}$	$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	$C_{50}H_{22}$	...	$N_c = 2N_H + 6$
...	$C_{24}H_8$	$C_{28}H_{10}$	$C_{32}H_{12}$	$C_{36}H_{14}$	$C_{40}H_{16}$	$C_{44}H_{18}$	...	$C_{52}H_{22}$	$C_{56}H_{24}$	...	$N_c = 2N_H + 8$
...	$C_{30}H_{10}$	$C_{34}H_{12}$	$C_{38}H_{14}$	$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$	...	$C_{58}H_{24}$	$C_{62}H_{26}$	...	$N_c = 2N_H + 10$
...	$C_{36}H_{12}$	$C_{40}H_{14}$	$C_{44}H_{16}$	$C_{48}H_{18}$	$C_{52}H_{20}$	...		$C_{64}H_{26}$	$C_{68}H_{28}$	...	$N_c = 2N_H + 12$
...	$C_{42}H_{14}$	$C_{46}H_{16}$	$C_{50}H_{18}$	$C_{54}H_{20}$	...			$C_{70}H_{28}$	$C_{74}H_{30}$	...	$N_c = 2N_H + 14$
...	$C_{48}H_{16}$	$C_{52}H_{18}$	$C_{56}H_{20}$	...				$C_{76}H_{30}$	...	...	$N_c = 2N_H + 16$
...	$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$					$C_{82}H_{32}$		...	$N_c = 2N_H + 18$
...	$C_{60}H_{20}$	$C_{64}H_{22}$	...					$C_{88}H_{34}$		...	$N_c = 2N_H + 20$
...	...	...						...		...	

phenyl units when transformed to their maximal alkynyl-containing isomers. Note that diphenylethyne ($C_{14}H_{10}$) is a noncondensed isomer of anthracene/phenanthrene and per the above equation ($A_{max} \leq 1$) possesses the maximum number of alkynyl units possible for a benzenoid-containing structure having the formula of $C_{14}H_{10}$.

If one successively attaches C_2 units to formulas in Table I, one obtains the formulas found in Table IV. This process has formula-shift coordinates of (−1, −1), and Table I becomes extended toward the $N_c/N_H > 3$ quadrant in order to generate Table IV. Thus, Table IV presents the formula periodical table for polyalkynyl-substituted PAH6s. Naphthalene ($C_{10}H_8$) has no alkynyl-substituted PAH6 isomers [$A_{max} \leq (1/4)(0 + 2) = 0.5$] whereas anthracene/phenanthrene ($C_{14}H_{10}$) has diphenylethyne isomers. If one confines oneself to the precise meaning of PAH6 as being composed of only fused polycyclic benzenoid hydrocarbons, then phenyl substituents should not be allowed. Thus, the previous equation for the maximum number of alkynyl units would become $A_{max} \leq (1/4)(2N_{Ic} + N_{Pc} - 4)$, and formulas $C_{14}H_{10}$ and $C_{18}H_{12}$ in Table IV would be excluded. Thus, ovalene ($C_{32}H_{14}$) is isomeric to di-2-naphthyldodecahexayne, which has a maximum number of alkynyl units [$A_{max} \leq (1/4)(20 + 8 - 4) = 6$] if phenyl groups are not allowed.[10,11] This formula gives the same answer as given by the above algorithm.

All formulas above the zigzag line of Table IV represents PAH6 that must have alkynyl substituents. This set of formulas is given by the relative complement of the set of formulas in Table I with respect to the set of formulas in Table IV [(Table IV)\(Table I)].

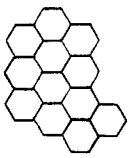
Selected PAH6 Isomer Enumeration. The enumeration of cata-condensed benzenoid hydrocarbons has been completely successful and was accomplished by use of a dualistic graph.[12] Recent computer algorithms have been reported for enumerating geometrically planar hexagonal graphs having the same number of rings.[13] However, options for inclusion of circulenes and nonplanar helicenes in the isomer enumeration need to be developed. For example, a nonplanar isomer of $C_{50}H_{28}$ and up to tetradecahelicene has been synthesized and would be excluded by restricting enumeration to planar hexagonal graphs.[14,15] The longer range goal of being able to enumerate all possible polycyclic conjugated hydrocarbon isomers is being pursued in our laboratory.[3]

All the isomers for formulas on the diagonal left-hand edge of Table I have now been enumerated (Figure 2). Previously, it was shown that coronene-7 ($C_{24}H_{12}$) and coronene-19 (synonymous to circumcoronene and dodecabenzocoronene, $C_{54}H_{18}$) both have no other PAH6 isomers.[1] Also, $C_{30}H_{14}$ was shown to have only three nondiradical isomers.[1] Ovalene ($C_{32}H_{14}$) is known to have no other PAH6 isomer. There are 10 nondiradical PAH6 isomers with the formula of $C_{38}H_{16}$, and circumanthracene ($C_{40}H_{16}$)[16] is one of three of possible isomers. Circumpyrene ($C_{42}H_{16}$) has only one PAH6 isomeric form. There are seven PAH6 isomers of the formula $C_{50}H_{18}$, two PAH6 isomers of the formula $C_{52}H_{18}$, 22 isomers for $C_{48}H_{18}$ and 19 isomers for $C_{60}H_{20}$. Figure 2 presents all these isomers.

All PAH6 formulas having the same number of hydrogens are found in a linear diagonal array of formulas (Table I) and have the same perimeter length ($q_P = 2N_H - 6$ = constant for N_H = constant). The formulas in the $N_c = 2N_H - 6$ row series have no internal third-degree carbon vertices ($N_{Ic} = 0$ and $N_c = q_p$). 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 ($N_{Ic} = 2$) with a perimeter length of 14 carbon atoms giving a total of 16 carbon atoms in its formula. Similarly, all five PAH6 isomers of $C_{18}H_{12}$ have perimeter length of 18 carbon atoms, and the three isomers of $C_{20}H_{12}$ have $N_{Ic} = 2$, the two PAH6 isomers of $C_{22}H_{12}$ have $N_{Ic} = 4$, and coronene ($C_{24}H_{12}$) has $N_{Ic} = 6$, 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 is two (pyrene), and in an 18 carbon atom peripheral cycle is six (coronene). Polycircumnaphthalene, polycircumpyrene, and polycircumcoronene are three series of formulas appearing on the left-hand diagonal boundary of Table I. 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 [$N_{Ic(max)}$] that each corresponding peripheral $q_p = 4\tau + 2$ ($\tau = 2, 3, 4, ...$) carbon atom can contain. Table V summarizes the relevant information for these one-isomer series.

The method of enumeration of these peri-condensed PAH6s will now be presented. From the narration presented in the last paragraph, it is evident that PAH6s have an even number of perimeter carbon vertices since $q_p = N_{Pc} + N_H = 2N_H - 6$ must be an even number. From this, it follows that N_{Ic} is even for even PAH6 formulas and odd for odd-radical PAH6 formulas.[2] For peri-condensed PAHs with N_{Ic} internal third-degree vertices, the number of PAH6 isomers is equal to the number of nonradical isomeric-excised internal structures having N_{Ic} 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; all isomeric internal structures have the same number of rings and carbon vertices (N_{Ic} of parent, i.e., d_s = constant). This process is illustrated by the structures in Figure 3. Ethene having two carbons is the excised internal structure of pyrene ($C_{16}H_{10}$), and $C_{16}H_{10}$ ($N_{Ic} = 2$) can only have one possible PAH6 isomer. *s-trans*-1,3-Butadiene having four

$C_{38}H_{16}$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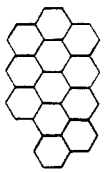
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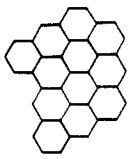
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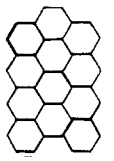
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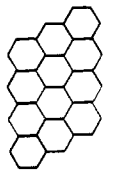
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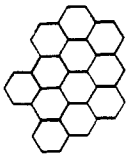
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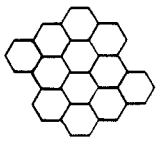
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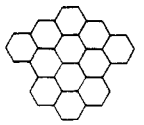
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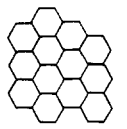
$C_{38}H_{16}$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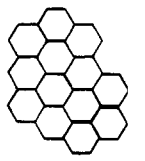
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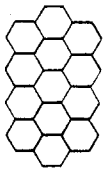
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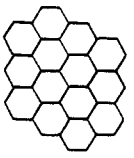
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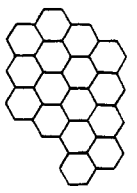
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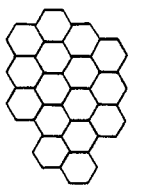
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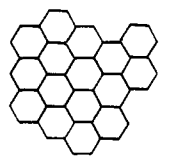
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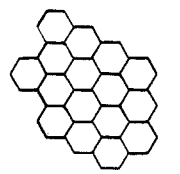
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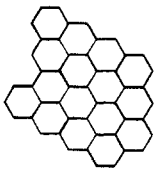
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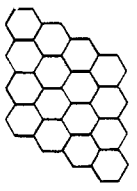
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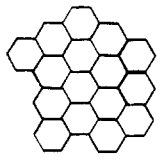
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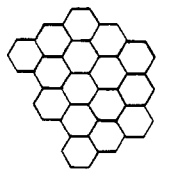
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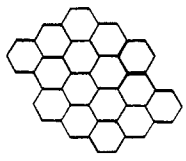
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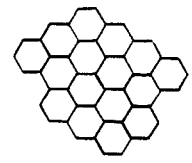
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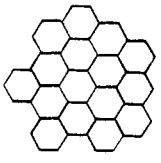
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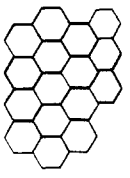
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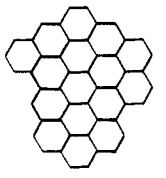
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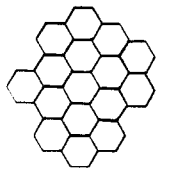
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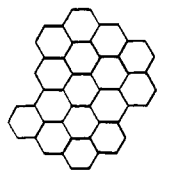
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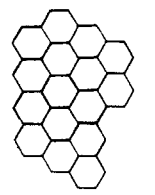
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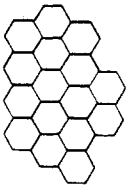
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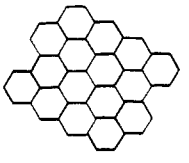
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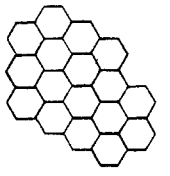
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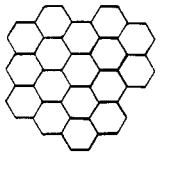
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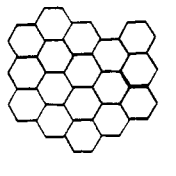
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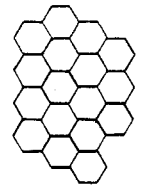
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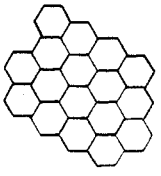
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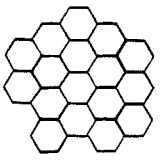
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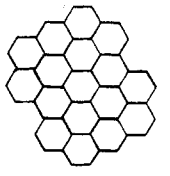
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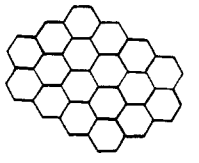
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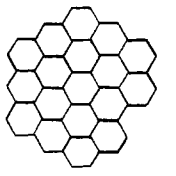
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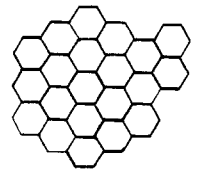
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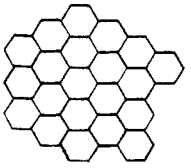
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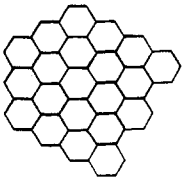
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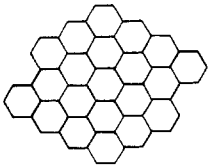
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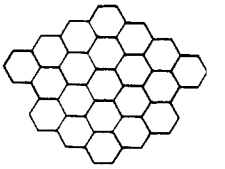
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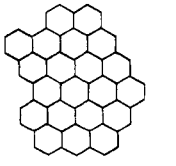
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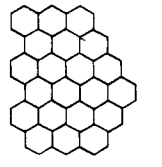
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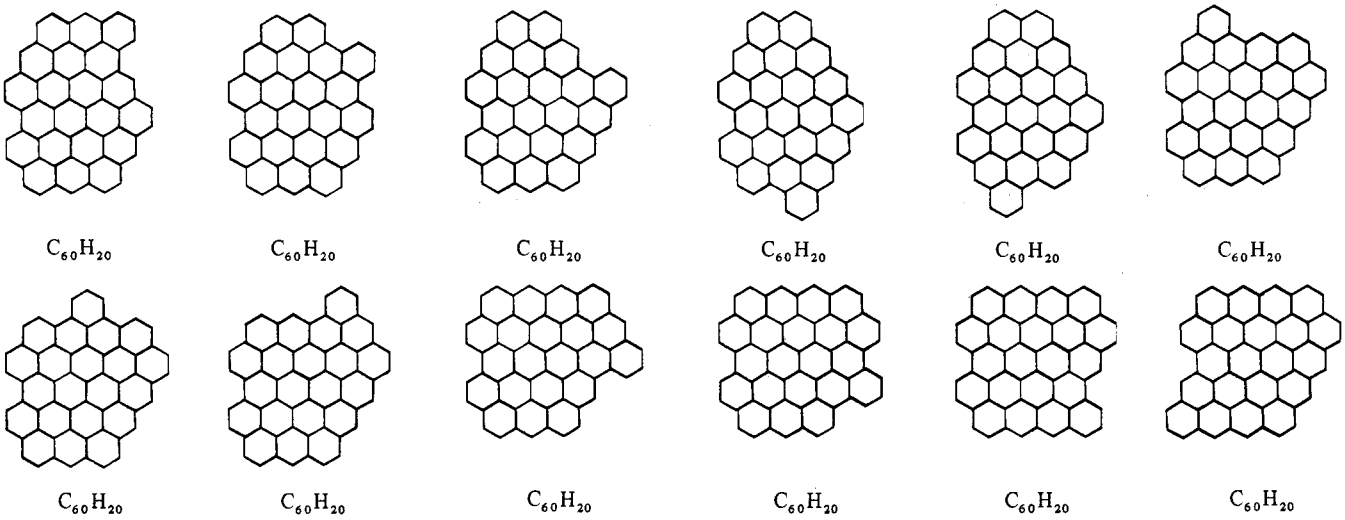


Figure 2. All the isomers of formulas on the left-hand side of the diagonal of Table I.

Table V. One-Isomer Series of Polycircumnaphthalene, Polycircumpyrene, and Polycircumcoronene

formula	no. of carbon atoms around periphery $(4\tau + 2)$	τ	$N_{Ic(max)}$	nomenclature
$C_{10}H_8$	10	2	0	naphthalene
$C_{16}H_{10}$	14	3	2	pyrene
$C_{24}H_{12}$	18	4	6	coronene (coronene-7)
$C_{32}H_{14}$	22	5	10	ovalene (circumnaphthalene)
$C_{42}H_{16}$	26	6	16	circumpyrene
$C_{54}H_{18}$	30	7	24	circumcoronene (coronene-19)
$C_{66}H_{20}$	34	8	32	circumovalene (dicircumnaphthalene)
$C_{80}H_{22}$	38	9	42	dicircumpyrene
$C_{96}H_{24}$	42	10	54	dicircumcoronene (coronene-37)
$C_{112}H_{26}$	46	11	66	tricircumnaphthalene
$C_{130}H_{28}$	50	12	80	tricircumpyrene
$C_{150}H_{30}$	54	13	96	tricircumcoronene (coronene-61)
$C_{170}H_{32}$	58	14	112	tetracircumnaphthalene
...	...	...	...	...

carbon is the excised internal structure of anthanthrene ($C_{22}H_{12}$, $N_{Ic} = 4$), and *s-cis*-1,3-butadiene is the excised internal structure of benzo[*ghi*]perylene ($C_{22}H_{12}$, $N_{Ic} = 4$); since triangulene and its excised structure, trimethylenemethane, which are not shown, are diradicals, the formula of $C_{22}H_{12}$ can be represented by only two nonradical PAH6 isomeric structures. The excised internal structure of coronene ($C_{24}H_{12}$, $N_{Ic} = 6$) is benzene, and $C_{24}H_{12}$ has only one PAH6 structure. The excised internal structure of circumcoronene ($C_{54}H_{18}$) is coronene ($C_{24}H_{12}$), and circumcoronene is the excised internal structure of dicircumcoronene ($C_{96}H_{24}$). Thus dicircumcoronene and circumcoronene have no other PAH6 isomers.[1] Previously, it was shown that there were only three PAH6 isomers of the formula $C_{30}H_{14}$.[1] In Figure 3, four PAH6 structures having the formula of $C_{30}H_{14}$ are shown along with their corresponding excised internal structures. Styrene is the excised internal structure of naphtho[*bcd*]coronene, 1,2-benzoquinodimethane of dibenzo[*bc,ef*]coronene, 1,3-benzoquinodimethane of the third $C_{30}H_{14}$ structure, and 1,4-benzoquinodimethane of dibenzo[*bc,kl*]coronene (dibenzoperopyrene). However, since 1,3-benzoquinodimethane is a diradical and the [22]annulene perimeter is an even alternate

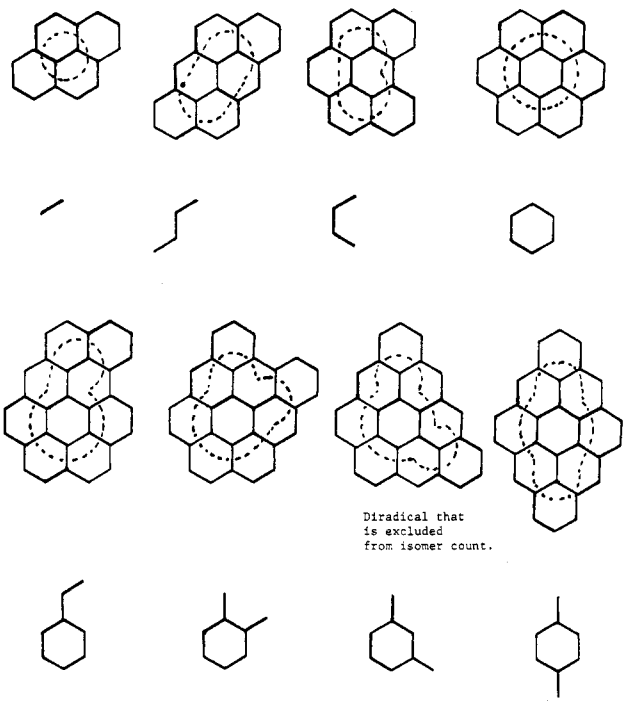


Figure 3. Excised internal structures from peri-condensed PAH6s.

hydrocarbon, the third $C_{30}H_{14}$ structure shown in Figure 3 must be a diradical and is not counted. In general, if the excised internal structure is a diradical that can be formed by connecting a nonstarred position of monoradical S with a starred position of monoradical R, its parent PAH6 structure will also be a diradical.

Figure 4 presents all the corresponding excised internal structures of all the parent PAH6 isomers shown in Figure 2. The first nine substituted naphthalene structures and biphenyl of 12 carbon atoms in Figure 4 correspond in order and orientation to the 10 $C_{38}H_{16}$ ($N_{Ic} = 12$) isomers in Figure 2. Only one of two possible conformers of 1-ethenylnaphthalene is presented while both possible conformers of 2-ethenylnaphthalene appear (first three structures in Figure 4). 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-ethenylnaphthalene has a one carbon atom gap and is therefore excluded. Only six of ten possible naphthoquinodimethanes are present in Figure 4 because the other four are diradicals. There are only three nonradical isomeric conjugated three-ring

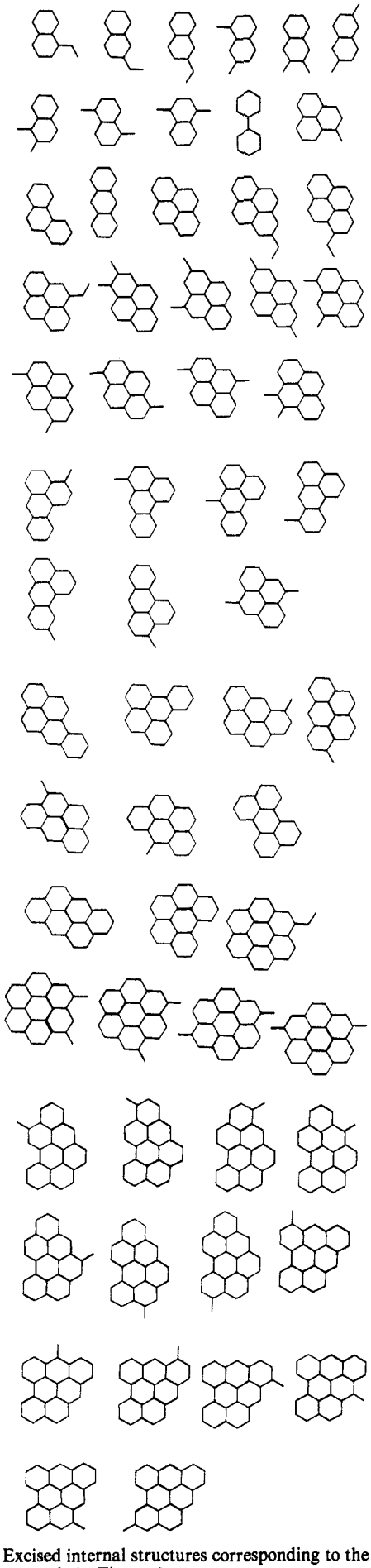


Figure 4. Excised internal structures corresponding to the benzenoid PAH6 compounds in Figure 2.

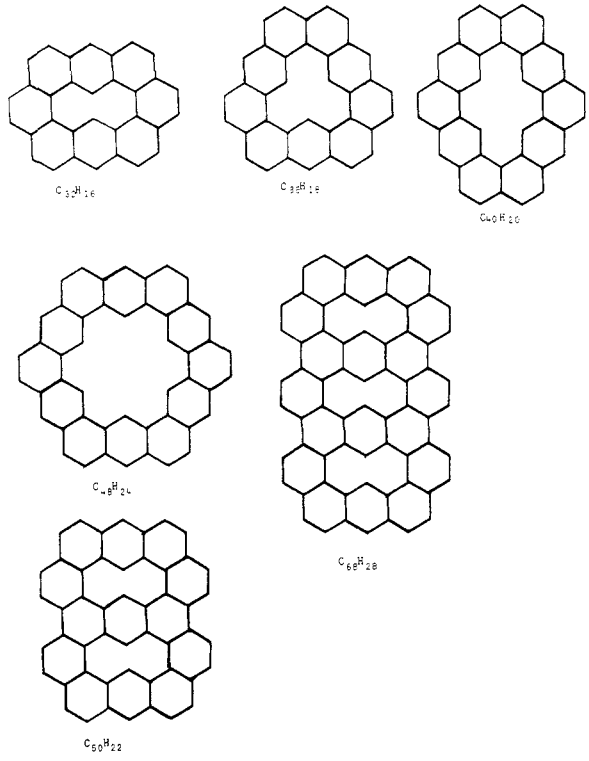


Figure 5. Class I circulenes.

structures of 14 carbon vertices as shown, and therefore, only three corresponding benzenoid PAH6 structures of the formula $C_{40}H_{16}$ with $N_{Ic} = 14$ exist. The Figure 2 formula of $C_{42}H_{16}$ ($N_{Ic} = 16$) has only one possible structure, circumpyrene, since the excised internal structure corresponds to pyrene, which is the only arrangement possible for 16 carbon vertices of four hexagonal rings.

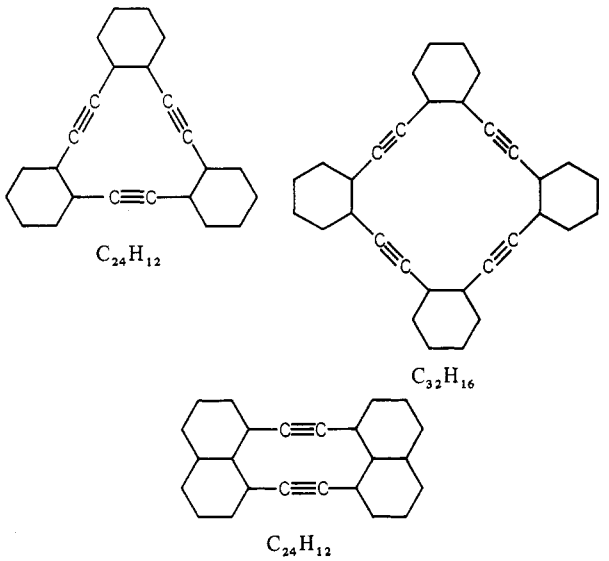
All benzenoid PAH6 structures of the formula of $C_{48}H_{18}$ have $N_{Ic} = 18$, and excision of their internal structures leads to three ethenylpyrene, nine nonradical pyrenylquinodimethane, and six methylene isomers of benzanthrene of four rings and eighteen carbon vertices. The excised internal isomeric structures (Figure 4) corresponding to PAH6s of the formula $C_{50}H_{18}$ ($N_{Ic} = 20$) lead to benzo[*a*]pyrene, benzo[*e*]pyrene, four methylene isomers of naphtho[*almn*]anthracene, and perylene ($C_{20}H_{12}$). The formula $C_{52}H_{18}$ ($N_{Ic} = 22$) has only two excised internal isomeric structures, anthanthrene and benzo[*ghi*]perylene ($C_{22}H_{12}$), and therefore, the benzenoid formula of $C_{52}H_{18}$ has only two corresponding PAH6 isomers. Finally, the formula $C_{60}H_{20}$ ($N_{Ic} = 26$) has 19 nonradical excised internal isomeric structures of 26 carbon vertices and seven rings, which correspond to 19 PAH6s. Thus, all isomers of peri-condensed benzenoid PAH6s without cata-condensed branching can be enumerated by finding all nonradical isomeric internal structures of N_{Ic}(parent) carbon vertices, i.e., finding all possible hexagonal lattice arrangement of the internal third-degree vertices.

Circulene Formulas. Previously, a monocirculene was defined as a PAH that possessed a "hole" larger than a hexagon which contained two or more hydrogens.[1] It was shown that these monocirculenes appeared in the formula region of Table I subtended and including the $N_c = 2N_H$ row series and the $N_c = 3N_H - 16$ column series. Since no formula in the $N_c = 2N_H - 6$, $2N_H - 4$, and $2N_H - 2$ row series can correspond to a circulene structure, their exclusion in benzenoid computer generation leads to no discrepancy effects in isomer counting of these PAH6s.[13] Additionally, all the formulas to the left of the $N_c = 3N_H - 16$ column will have no corresponding circulene structures. The simplest monocirculene ($C_{32}H_{16}$)

has a "hole" shaped like naphthalene and another one ($C_{36}H_{18}$) like perinaphthalene (Figure 5). Synthesis of a monocirculene ($C_{40}H_{20}$) having a hole shaped like pyrene has been attempted.[16,17] A nine-step successful synthesis of a monocirculene ($C_{48}H_{24}$) with a hole shaped like coronene, called "kekulene", has been described.[18] These and other circulenes are shown in Figure 5. Dicirculenes have two holes and formulas that first appear in Table I at the intersection of the $N_c = 3N_H - 16$ column series and the $N_c = 2N_H + 6$ row series. For example, the first dicirculene has two holes shaped like naphthalene and appears at $C_{50}H_{22}$ (Figure 5). The first tricirculene with three holes shaped like naphthalene appears at $C_{68}H_{28}$ in the $N_c = 2N_H + 12$ row series of Table I. Dimethenoheptadecacene ($C_{68}H_{34}$) is a special monocirculene called a circumpolyacene and is shaped like a wedding band.[19]

Some authors have called PAH molecules like coronene ($C_{24}H_{12}$) a circulene with a hexagonal hole. Figure 6 shows other circulenes of this second type, which are now defined as "class II" circulenes since there are no hydrogens located in the "holes". Formulas of class II monocirculenes appear in Table I or other tables previously published[2,3] subtended by and including the $N_c = 3N_H - 6$ column series and the $N_c = 2N_H$ row series. The attempted synthesis of the monocirculene ($C_{32}H_{16}$), 1.16:8.9-diethenocycloocta[1,2,3,4-*def*:5,6,7,8-*d'e'f'*]diphenanthrene, in Figure 6 has been reported.[22] The synthesis and X-ray crystal structure for the circulene $C_{20}H_{10}$ has been published;[23a] this molecule has a bowl shape, and one would expect the bowl shapes of the $C_{16}H_8$ and $C_{12}H_6$ circulenes to be progressively deeper. The recent synthesis and X-ray crystal structure determination of [7]-circulene show it to have a saddle-shaped molecular structure.[23b] By induction, it can be easily shown that the above results can be generalized to include polycirculenes of classes I and II.

Cycloalkynyl isomers of PAH6 first appear for formulas in the $N_c = 2N_H$ row series and in this regard are related to circulenes. Example structures are



The synthesis or attempted synthesis of these compounds has been reported.[24]

Selective Literature Searching with PAH Formulas. Suppose one was interested in PAHs having hexagonal rings and/or smaller rings and/or alkynyl substituents? Then the relative complement of the set of formulas in Table I (Table PAH6) with respect to the set of formulas in tables for PAHs containing trigonal rings (PAH_3), tetragonal rings (PAH_4), pentagonal rings (PAH_5), and/or alkynyl substituents (PAH_A) [(Table PAH_3, Table PAH_4, Table PAH_5, and/or Table PAH_A)\(Table PAH6)] would give a set of formulas that must contain these structural components;[2,3] these formulas all appear in the blank left-hand diagonal region of Table I. A *Chemical Abstracts Formula Index* (6th to 10th Collective editions) search of the formulas above the zigzag line in Table IV led to approximately a half dozen references for alkynyl-substituted PAH6s.[25] Only a few papers on PAHs that must possess pentagonal rings as well as hexagonal ones were found; papers on the UV spectroscopy of didehydrodinaphthoperopyrene ($C_{38}H_{14}$),[16] the synthesis of rubicene ($C_{26}H_{14}$),[26] benzo[*j*]fluoranthene ($C_{26}H_{12}$) in tobacco smoke carcinogenesis,[27] and the theoretical LCAO MO calculation of 10,5-coronene (ten pentagonal rings surrounding a decagonal ring, $C_{30}H_{10}$)[28] were found. No tetragonal or trigonal ring containing PAHs were found in this formula region of Table IV.

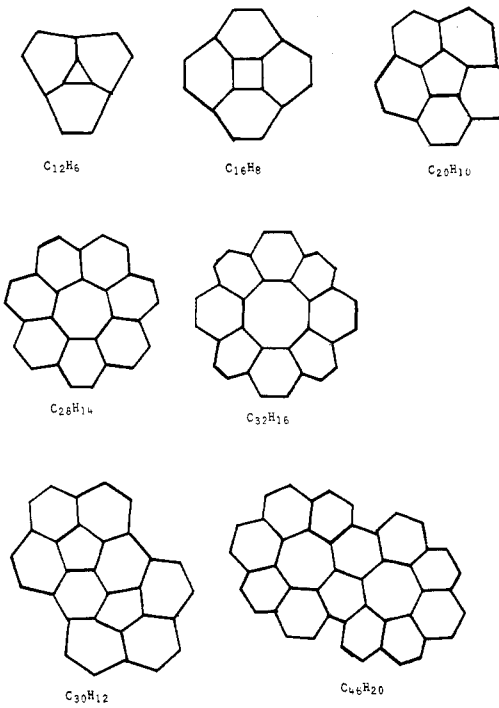


Figure 6. Class II circulenes.

If one was interested in PAHs containing hexagonal rings and/or larger rings and/or alkyl and phenyl (phenyl-like) substituents, then the relative complement of the set of formulas in Table I with respect to the set of formulas in tables for PAHs containing heptagonal rings (PAH_7), octagonal rings (PAH_8), nonagonal rings (PAH_9), phenyl (phenyl-like) substituents (PAH_{Ph}), and/or alkyl substituents (PAH_R) [(Table PAH_7, Table PAH_8, Table PAH_9, Table PAH_{Ph}, and/or Table PAH_R)\(Table PAH6)] would give the set of formulas that must contain these structural components;[2,3] these formulas all appear in the blank upper right-hand region above the $N_c = 2N_H - 6$ row series in Table I. For example, searching the *9th (1972–1976) Collective Formula Index* of *Chemical Abstracts* for $C_{52}H_{30}$ found in Table PAH_{Ph} (footnote 2) but not in Table I, one obtains a reference for 2,2'-bihexahelicyl, which contains a bridging bond ($q_b = 1$) between two hexahelicenes.[29] Of course, this formula is equally found in tables having formulas above the $N_c = 2N_H - 6$ row series for heptagonal, octagonal, and nonagonal rings and alkyl-containing PAHs. Searching the *8th (1962–1966) Collective Formula Index* of *Chemical Abstracts* for $C_{38}H_{24}$ found in Table PAH_8 but not in Table I, one obtains a paper describing the synthesis and spectra of hexabenzooctalene, which has two fused octagonal and six hexagonal rings with no internal third-degree vertices.[30] Many more references for this category of PAHs were found in the *6th Collective Formula Index* to *10th Collective Formula Index* of *Chemical Abstracts* than for the

category of PAHs discussed in the prior paragraph.

If one wishes to find the set of PAH6 formulas that cannot have molecular structures possessing other specified ring sizes in addition to the hexagon or alkyl, alkynyl, or phenyl-like substituents, then one must take the relative complements of the appropriate tables with respect to Table I. Thus, naphthalene ($C_{10}H_8$) cannot have isomeric structures possessing other ring sizes in addition to the hexagon nor isomers having alkyl, alkynyl, or phenyl substituents in addition to a PAH6 component. Previously, it was shown that no PAH6 formula associated with the cata-condensed PAH6s (i.e., formulas in the $N_c = 2N_H - 6$ row series of Table I) can have a corresponding molecular structure possessing solely trigonal, tetragonal, or pentagonal rings in addition to hexagonal rings or PAH6 components.[2,3]

CONCLUSIONS

It has been determined that there are 43 polycyclic conjugated hydrocarbon isomers of anthracene ($C_{14}H_{10}$); the two key equation assisting this enumeration are $N_{Ic} + d_s$ = constant and $N_{Pc} = N_H - 6 + 3r_3 + 2r_4 + r_5 - r_7 - 2r_8 - 3r_9 - \ldots$. The number of peri-condensed PAH6 isomers without cata-condensed branching is equal to the number of isomers associated with their excised internal structures made up of their internal third-degree carbon vertices. This correspondence was utilized to prove that the PAH6 formulas along the left-hand diagonal boundary of Table I had the following number of isomers: $C_{38}H_{16}$, 10; $C_{40}H_{16}$, 3; $C_{42}H_{16}$, 1; $C_{48}H_{18}$, 22; $C_{50}H_{18}$, 7; $C_{52}H_{18}$, 2; $C_{60}H_{20}$, 19. The maximum number of internal third-degree vertices [$N_{Ic(max)}$] that can be hexagonally fitted into various perimeter lengths having a specified number of carbon atom vertices results in the one-isomer series of polycircumnaphthalene ($C_{10}H_8$, $C_{32}H_{14}$, $C_{66}H_{20}$, $C_{112}H_{26}$, $C_{170}H_{32}$, ...), polycircumpyrene ($C_{16}H_{10}$, $C_{42}H_{16}$, $C_{80}H_{22}$, $C_{130}H_{28}$, ...), and polycircumcoronene ($C_{24}H_{12}$, $C_{54}H_{18}$, $C_{96}H_{24}$, $C_{150}H_{30}$, ...). Note that for the above formulas, helicene and class I circulene isomers are not possible.

The current practical range of the PAH6 (benzenoid) formula periodic table was determined by a literature search of *Chemical Abstracts* formula indices and is presented in Table I. Very few references were found for PAHs having formulas to the left of the coronene ($C_{24}H_{12}$) column in Table I (i.e., to the left of the $N_c = 3N_H - 12$ column). This, in part, may be due to higher insolubility associated with these higher N_c/N_H ratio compounds; these compounds are, perhaps, more graphite-like. Nevertheless, additional research is needed on PAH compounds having formulas in this region of Table I. The relative complement of the set of formulas in Table I (Table PAH6) with respect to the set of formulas in Table PAH_3, Table PAH_4, Table PAH_5, Table PAH_A (A for alkynyl), Table PAH_7, Table PAH_8, Table PAH_9, Table PAH_{Ph}, and/or Table PAH_R (R for alkyl)[(Table PAH_3, Table PAH_4, Table PAH_5, Table PAH_A, Table PAH_7, Table PAH_8, Table PAH_9, Table PAH_{Ph}, and/or Table PAH_R)\(Table PAH6)] gives the set of formulas corresponding to PAH structures that must contain trigonal rings, tetragonal rings, pentagonal rings, alkynyl groups, heptagonal rings, octagonal rings, nonagonal rings, phenyl (benzenoidyl) groups, and/or even-carbon alkyl groups. Conversely, the relative complement of the set of formulas in Table PAH_3, Table PAH_4, Table PAH_5, Table PAH_A, Table PAH_7, Table PAH_8, Table PAH_9, Table PAH_{Ph}, and/or Table PAH_R with respect to the formulas in Table I [(Table PAH6)\(Table PAH_3, Table PAH_4, Table PAH_5, Table PAH_A, Table PAH_7, Table PAH_8, Table PAH_9, Table PAH_{Ph}, and/or Table PAH_R)] gives the set of PAH6 formulas corresponding to PAH structures that cannot contain trigonal rings, tetragonal rings, pentagonal rings, alkynyl groups, heptagonal rings, octagonal rings, nonagonal rings, phenyl (benzenoidyl) groups, and/or even-carbon alkyl groups. These relationships can be used in selective literature searching with PAH formulas.

Although there are only 43 totally fused polycyclic conjugated isomers of anthracene/phenanthrene, only compounds 1–5, 36, and 40 (Figure 1) appear to have been synthesized;[31-33] the isomers that are antiaromatic may represent possible reactive intermediates. Since $N_{Ic}(PAH6) = 0$, no $C_{14}H_{10}$ isomers having only hexagonal rings and trigonal, tetragonal, or pentagonal rings are possible. Also, only one isomer having a heptagonal ring in addition to hexagonal rings is possible (36 in Figure 1) since $r_{7max} = d_s(PAH6) - M = 1$ and $r_{8max} \leq 0.5$ and $r_{9max} \leq 0.25$. An interesting combustion intermediate/product, circumcircumcoronene ($C_{96}H_{24}$, dicircumcoronene), was proposed to explain the observed kinetic data obtained for soot formation from toluene.[34] Class I circulenes obey the equation $N_{Pc} = N_H - 6 + 6c$ where c is the number of hydrogen-containing holes, and class II circulenes obey the equation $N_{Pc} = N_H - 6 + 3r_3 + 2r_4 + r_5 - r_7 - 2r_8 - 3r_9 - \ldots$ where r_n is the number of nonhexagonal "holes" of ring size n. Carbon bond network defects in graphite can be modeled by studies on small PAHs.[35] Representative examples include the tendency for the class II circulene $C_{20}H_{10}$ containing a pentagonal hole (ring) surrounded by five fused hexagonal rings to adopt a puckered structure[23] and nonplanar helicenes.[14,15] Since N_c = even number for nonradical PAHs, in the enumeration of all polycyclic conjugated hydrocarbons, one will obtain isomeric structures having an even number of odd ring sizes for $N_{Ic} = 0, 2, \ldots$ and an odd number of odd ring sizes for $N_{Ic} = 1, 3, \ldots$ (e.g., Figure 1).

APPENDIX: GLOSSARY OF TERMS

A_{max}	maximum number of alkynyl C_2 units in addition to benzenoid rings
c	number of circulene holes
d_i	degree of vertex i of a graph
d_s	net tree disconnections (of internal graph edges)
$M = 0, 1, 2, \ldots$	d_s value of the first formula member of the corresponding row series in PAH6 table
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
$\|P\| = p = N_c$	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
τ	number of rings obtained upon deletion of all third-degree vertices
r_{3max}, r_{4max}, r_{5max}	maximum number of trigonal, tetragonal, pentagonal rings, respectively, in addition to hexagonal rings
r_{7max}, r_{8max}, r_{9max}	maximum number of heptagonal, octagonal, nonagonal rings, respectively, in addition to hexagonal rings

r_n number of rings or cycles having n vertices

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Incorporating Chemical Literature and Information Retrieval into the Chemistry Curriculum at The Hebrew University†

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A chemical literature and information retrieval program has been developed at the Chemistry Teaching Division of The Hebrew University. The program is incorporated in the undergraduate chemistry curriculum for the chemistry major students. The emphasis in the whole program is on the end user, the chemist. The various problems and stages in the program development are discussed. The various parts of the programs are described in detail.

Recently, we, at the Chemistry Teaching Division of The Hebrew University, developed a teaching program in Chemical Literature and Chemical Information Retrieval. This program replaced the traditional descriptive Chemical Literature class that was given to the chemistry major students in their third year.

The whole program is divided into four parts: (a) a compulsory introductory lecture of 4 h followed by a conducted tour of our science library; (b) an elective 10-h class entitled "Chemical Information"; (c) a 4-h lecture dealing with Synthetic Organic Chemistry Literature (compulsory to all students who take the Advanced Organic Chemistry laboratory); (d) using a numeric database for the identification of an unknown (an experiment in the Advanced Organic Chemistry laboratory). In order to understand the development of the program, one should be familiar with the requirements and the curriculum at the Hebrew University, both of which are quite different from the ones in American Universities.

A student at the Hebrew University gets his BA or BSc after 3 years of studies. at present, the academic year at the University is divided into trimesters, each one of 9–10 weeks. In order to obtain a BSc in Chemistry, one has to collect 210 credit points (an hour trimester of a regular laboratory session is 0.5 credit point, an hour trimester of a lecture or an advanced laboratory is 1 credit point). Out of those 210 points, 145 are in chemistry (100 compulsory and 45 elective) and 40 are compulsory in physics, mathematics, and computer programming, while the remaining 25 points are elective ones in physics and/or biology.

DEVELOPMENT OF THE PROGRAM

Until 1977, the Chemical Literature class was given to our students in the 8th trimester under the old classical approach. The students received long lists of primary and secondary sources. No search problems were demonstrated, and very little evaluations and comparisons of the various sources were carried out. Three points guided us in renovating the curriculum: (a) to schedule the class at the earliest possible time, thus enabling the student to make use of the material covered as much as possible; (b) to use a practical approach to the subject by demonstrating in the class various examples and search problems from the various disciplines of chemistry; to teach the student the various available sources and search tools and to compare and evaluate them in selected search history cases, thus emphasizing the subject from the user's viewpoint; (c) to teach the students practical searching by giving them

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