culations. No such arbitrariness is introduced in the fluctuation theory calculation, and eq 28 appears to be the correct result at low density.

Concluding Remarks

The theory described in this Account provides a new way to calculate the rates of rapid reactions in solution. It generalizes the usual Smoluchowski theory and is applicable to one-, two-, or three-dimensional problems. The theory can also be used to examine effects caused by rotational diffusion.[35] The theory separates the calculation of the bimolecular rate constant into a chemical and a physical problem. The chemistry is contained in an intrinsic reactivity function, which depends on the spatial separation of reactants. The physics is contained in the nonequilibrium radial distribution function of reactant pairs. It is calculated by using the hydrodynamic level of the mechanistic statistical theory of nonequilibrium thermodynamics.[37] Agreement between theory and experiment on the concentration dependence of fluorescence quenching rates is encouraging.[22]

An advantage of the present theory is that it is systematic. Thus, it can be applied to a variety of problems without adding ad hoc assumptions.[38] For example, to examine the effect of thermal diffusion, it is only necessary to include fluctuations in the internal energy density in the calculation.[39] Or to examine the effect of intermolecular interaction, only the effect of the potential of mean force on chemical potentials needs to be included.[15] It would be interesting to extend these calculations to include the effect of internal state relaxation, solvent density fluctuations, and other dynamic processes in solution. With use of the statistical theory of density fluctuations, calculations like these should be relatively easy to execute.

This work was supported by grants from the National Science Foundation and the National Institutes of Health.

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A Periodic Table for Polycyclic Aromatic Hydrocarbons

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The hexagon is a fundamental structure of nature. A honeycomb, for example, is made up of a cluster of hexagonal cells, and each inner billiard ball of a new setup on a pool table is surrounded by precisely six other balls. Epidermal plant cells, the grain structure in a polished/etched metallurgical cross section, the system of veins in the wing of a dragonfly, and the two-dimensional pattern formed by mud cracks all have six sides on the average.[1] The random pattern of points obtained by viewing the heavenly bodies of interstellar space has a cellular two-dimensional structure which on the average is hexagonal.[2] An example closer to chemistry is found in graphite whose hexagonal lattice resembles the honeycomb cluster of hexagonal cells.[3]

An important class of chemical compounds known as polycyclic aromatic hydrocarbons have molecular structures based on the hexagon. Polycyclic aromatic hydrocarbons or PAHs are ubiquitous chemicals which have been found even in interstellar matter.[4] Many of them are cancer initiators.[5] Burning wood, coal or petroleum, barbecuing meat, or frying foods produces PAHs via incomplete oxidation. Tar produced by the combustion of organic matter has been shown to be carcinogenic due to the presence of the polycyclic aromatic benzo[*a*]pyrene. Soot, smoke, and airborne particulates contain polycylic aromatic hydrocarbons, and in the U.S.A. alone, 900–1000 metric tons of benzo[*a*]pyrene are released annually into the environment by combustion of fossil fuels.[6] On the other hand, numerous polycyclic aromatic hydrocarbon compounds find application as synthetic intermediates, organic semiconductors and photoconductors, photochromic pigments, fluoresent and phosphorescent agents, antistatic additives for plastics, and models in theoretical studies.[7]

The development of a formula periodic table for benzenoid polycyclic aromatic hydrocarbons (Table I) has shown that the structure of the PAHs can be instrumental in systematizing them into a unified framework. This periodic table is based on the unique application of graph theoretical principles.[8] As we explain in this Account the basis of this table is that all totally fused ring graph structures having only second and third degree vertices obey a simple numerical

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

$d_s = -9$	$d_s = -8$	$d_s = -7$	$d_s = -6$	$d_s = -5$	$d_s = -4$	$d_s = -3$	$d_s = -2$	$d_s = -1$	$d_s = 0$	$d_s = 1$	$d_s = 2$	$d_s = 3$		N_{Ic}
forbidden region							most reactive		$C_{10}H_8$	$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$	...	0
									$C_{16}H_{10}$	$C_{20}H_{12}$	$C_{24}H_{14}$	$C_{28}H_{16}$	...	2
					$N_c/N_H < 2$				$C_{22}H_{12}$	$C_{26}H_{14}$	$C_{30}H_{16}$	$C_{34}H_{18}$	...	4
		$C_{00}H_{00}$						$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$	$C_{36}H_{18}$	$C_{40}H_{20}$	...	6
								$C_{30}H_{14}$	$C_{34}H_{16}$	$C_{38}H_{18}$	$C_{42}H_{20}$	$C_{46}H_{22}$	...	8
				$2 < N_c/N_H < 3$			$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$	$C_{48}H_{22}$	$C_{52}H_{24}$	...	10
							$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	$C_{50}H_{22}$	$C_{54}H_{24}$	$C_{58}H_{26}$	...	12
						$C_{40}H_{16}$	$C_{44}H_{18}$	$C_{48}H_{20}$	$C_{52}H_{22}$	$C_{56}H_{24}$	$C_{60}H_{26}$	$C_{64}H_{28}$	...	14
	$N_c/N_H > 3$				$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$	$C_{54}H_{22}$	$C_{58}H_{24}$	$C_{62}H_{26}$	$C_{66}H_{28}$	...		
					$C_{48}H_{18}$	$C_{52}H_{20}$	$C_{56}H_{22}$	$C_{60}H_{24}$	$C_{64}H_{26}$	$C_{68}H_{28}$	...			
				$C_{50}H_{18}$	$C_{54}H_{20}$	$C_{58}H_{22}$	...	...	...	...				
			$C_{52}H_{18}$	$C_{56}H_{20}$	$C_{60}H_{22}$	...								
least reactive		$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$	...									
		$C_{60}H_{20}$	$C_{64}H_{22}$	...			intermediate reactive							
	$C_{62}H_{20}$	$C_{66}H_{22}$	...											
$C_{64}H_{20}$	$C_{68}H_{22}$	..												
$C_{70}H_{22}$	...													
...														

relationship, summarized in the equation $N_{Ic} + d_s = r - 2$. Here N_{Ic} is the number internal third degree carbon vertices, d_s is the number of disconnections and/or rings among the internal C–C bond edges, and r is the number of fused rings in the molecule. This relationship becomes manifest only after one carefully distinguishes between the sets of internal edges and vertices (Q_I, P_I) according to these molecular structure parameters, which for the convenience of the reader are redefined in a glossary at the end of the text. It will become evident that d_s defines the periodic group number and that N_{Ic} defines the period in the formula periodic table.

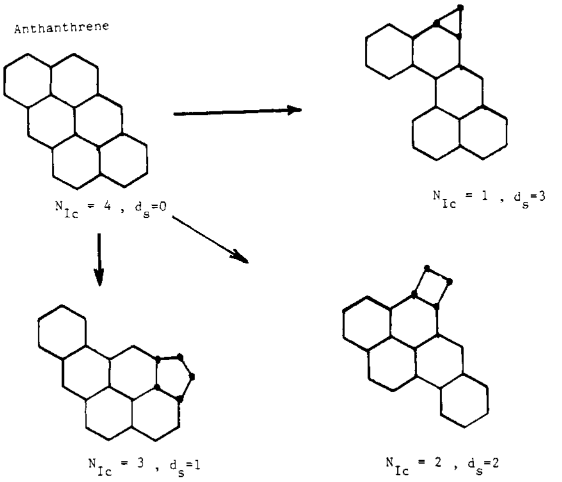
Formula Periodic Table for PAH6s

A comprehensive summary of all possible even carbon PAH formulas for compounds containing exclusively fused hexagonal rings is provided by Table I. We refer to these compounds as PAH6s. In Table I every compound in a particular column has the same d_s value, and every compound in the same row has the same N_{Ic} value. Member compounds in the same column with the same d_s value belong to the same column series. In a column the number of carbon atoms, N_c, and the number of hydrogen atoms, N_H, are related by the formula $N_c = 3N_H - 14 - 2d_s$. Member compounds in the same row with the same N_{Ic} value belong to the same row series and $N_c = 2N_H - 6 + N_{Ic}$. For example, all PAH6 isomers of the formulas $C_{16}H_{10}$ and $C_{20}H_{12}$ have the same value of $N_{Ic} = 2$, and similarly, all PAH6 isomers of the formulas $C_{20}H_{12}$ and $C_{26}H_{14}$ have the same value of $d_s = 1$. Table I extends infinitely in three directions—horizontally to the right, vertically to the bottom, and in a slanting direction to the left. The ratio of N_c/N_H for any column approaches 3 as the number of rings increases. Every formula in the column beginning with $C_{54}H_{18}$ belongs to the $N_c = 3N_H$ ($d_s = -7$) column series, and thus $N_c/N_H = 3$ for every member in this column. Columns to the left of the $N_c = 3N_H$ series have N_c/N_H ratios that approach 3 from larger values and columns to the right have ratios that approach 3 from smaller values. Similarly, the ratio of N_c/N_H for any row approaches 2 as the number of rings increases. Every formula in the row beginning with $C_{24}H_{12}$ belongs to the $N_c = 2N_H$ ($N_{Ic} = 6$) row series, and thus $N_c/N_H = 2$ for every member in this series. Rows above the $N_c = 2N_H$ series have N_c/N_H ratios that approach 2 from smaller values and the rows below have ratios that approach from larger values.

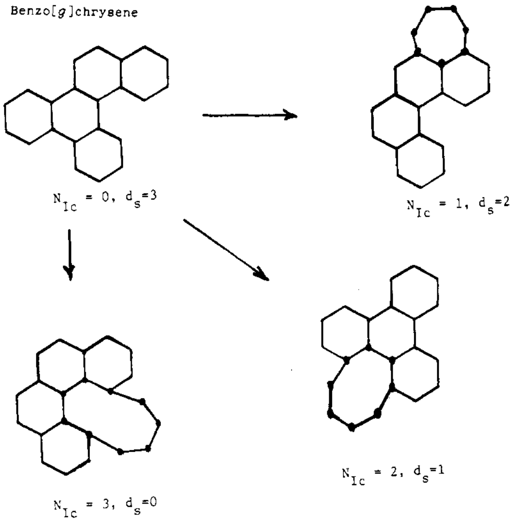
There are four quadrants to Table I, which are determined by the range of values in the ratio of N_c/N_H for the possible formulas of PAHs. The intersection of these quadrants occurs at the nonexistent formula of $C_{00}H_{00}$. The horizontal line is defined by the linear array of formulas having $N_c/N_H = 2$, 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 nonexistent $C_{xy}H_{00}$ 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 has $2 < N_c/N_H < 3$, and the upper right-hand quadrant has $N_c/N_H < 2$.

In the rows of the formula periodic table for benzenoid PAH6s (Table I), the number of formula carbons (N_c) increases from left to right according to the even residue classes of congruent modulo 4. For example, in the $N_{Ic} = 0$ and $N_{Ic} = 2$ row series, the number of formula carbons follow $N_c \equiv 2 \pmod 4$ and $N_c \equiv 0 \pmod 4$, respectively; these two respective relationships are each applicable for every other row. In the columns of the formula periodic table for benzenoid PAH6s, the number of formula carbons increases from top to bottom according to the even residue classes of congruent modulo 6. In the $d_s = 0$, $d_s = 1$, and $d_s = 2$ column series, the number of formula carbons are given by $N_c \equiv 4 \pmod 6$, $N_c \equiv 2 \pmod 6$, and $N_c \equiv 0 \pmod 6$, respectively; this sequence of congruent modulo 6 relationships successively repeats for all the columns in Table I. The basis for Table I is that all PAH structures having a common CH formula must comply with $d_s + N_{Ic}$ = constant where d_s is the net number of disconnections (or connections) of internal edges and N_{Ic} is the number of internal third degree carbon vertices (cf. with Schemes I and II). For example, anthracene/phenanthrene have two internal edges that are disconnected ($d_s = 1$) and no internal third degree vertices ($N_{Ic} = 0$) anthanthrene/benzo[*ghi*]perylene have all their

Scheme I. ($C_{22}H_{12}$)



Scheme II. ($C_{22}H_{14}$)



internal edges connected (d_s = 0) and four internal third degree vertices (N_{Ic} = 4).

Structure Correlations of the Formula Table for PAH6s

Schemes I and II illustrate key relationships that led to the formulation of several equations.[8,9] Scheme I shows that particular kinds of isomers with very different structures are actually closely related to the one another. In these kinds of isomerizations when the number of six-membered rings decreased by one and when a new smaller ring is incorporated in the structure, there is a simultaneous replacement of one internal third degree vertex to a peripheral one; in the replacement of each hexagonal ring by a tetragonal one, there is a simultaneous replacement of two internal third degree vertices to peripheral ones; and in the replacement of a hexagonal ring by a trigonal one, there is a simultaneous replacement of three internal third degree vertices to peripheral ones. Scheme II shows that in the replacement of a hexagonal ring by a larger ring, there is a simultaneous increase in the number of internal third degree vertices and a decrease in disconnection of the internal edges. In the replacement of a hexagonal ring by a heptagonal, octagonal, or nonagonal ring, there is a simultaneous decrease of one, two, or three disconnections and increase of one, two, or three internal third degree vertices, respectively. Note that $d_s + N_{Ic}$ = constant in Schemes I and II. If all the internal third degree vertices are used up in the replacement of hexagonal rings by pentagonal ones, then the maximum number of pentagonal rings ($r_{5\max}$) is given by $r_{5\max} \leq N_{Ic}(\mathrm{PAH6})$; similarly, $r_{4\max} = {}^1/_2 N_{Ic}(\mathrm{PAH6})$ and $r_{3\max} \leq {}^1/_3 N_{Ic}(\mathrm{PAH6})$. Thus using the polyhexagonal system as a frame-of-reference via Schemes I and II several important relationships have become evident. These relationships can be further verified with the representative isomers of circumcoronene in Figure 1 which have the maximum number of trigonal, tetragonal, and pentagonal rings in addition to hexagonal rings. More precisely, $r_{5\max} = r_5 + N_{Ic} = N_{Ic}(\mathrm{PAH6})$ and $r_{3\max} = r_3 + {}^1/_3 N_{Ic}$. Other relationships for the maximum number of heptagonal, octagonal, and nonagonal rings have been derived.[9] Circumcoronene cannot have isomers with larger rings in addition to hexagonal ones.

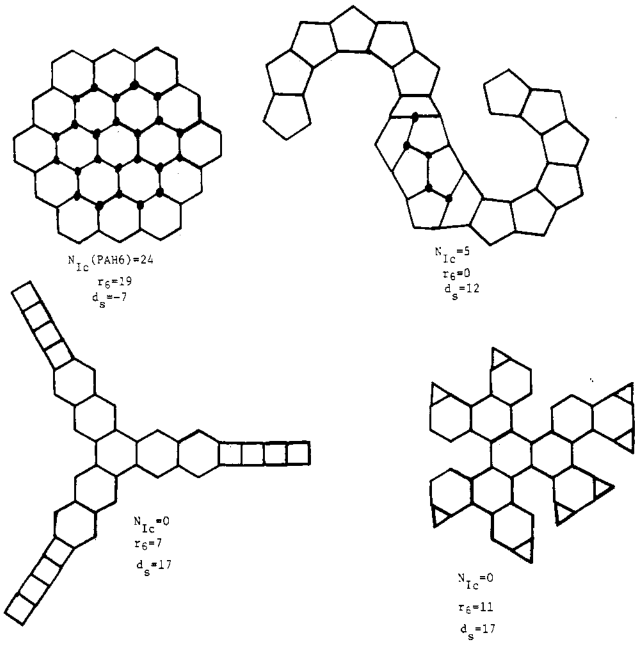


Figure 1. Isomers of circumcoronene ($C_{54}H_{18}$) having the maximum number of trigonal, tetragonal, pentagonal, heptagonal, octagonal, or nonagonal rings in addition to hexagonal rings.

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 a 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 polyhexagonal graphs the maximum number of internal third degree carbon vertices that can be contained in a 10 carbon atom peripheral cycle is zero (naphthalene), a 14-carbon atom peripheral cycle

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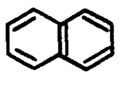
[9] J. R. Dias, *MATCH*, 14, 83 (1983).

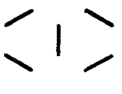
Table II.
One-Isomer Series of Polycircumnaphthalene, Polycircumpyrene, and Polycircumcoronene

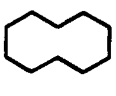
formula	no. of carbon atoms around periphery $(4\tau + 2)$	τ	N_{Ic} (max)	nomenclature
$C_{10}H_8$	10	2	0	naphthalene
$C_{16}H_{10}$	14	3	2	pyrene
$C_{24}H_{12}$	18	4	6	coronene (coronene-7)
$C_{32}H_{14}$	22	5	10	ovalene (circumnaphthalene)
$C_{42}H_{16}$	26	6	16	circumpyrene
$C_{54}H_{18}$	30	7	24	circumcoronene (coronene-19)
$C_{66}H_{20}$	34	8	32	circumovalene
$C_{80}H_{22}$	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
...	...	...	...	...

is two (pyrene), and in an 18-carbon peripheral atom 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 set of peripheral ($q_P = 4\tau + 2$; $\tau = 2, 3, 4, \ldots$) carbon atoms can contain. Table II summarizes the relevant information for these one-isomer series.[10] All PAH6 structures having formulas appearing on the left-hand diagonal boundary of Table I are called strictly peri-condensed. Strictly peri-condensed PAH6 structures have mutually connected internal structures (vide infra).

A factor of a graph G is a spanning subgraph (spans all the carbon atom vertices) which is not totally disconnected.[11] When G has a 1-factor, then p (the number of carbon atom vertices) must be even and the 1-factor lines are point disjoint. The number of different 1-factors of a PAH σ-bond graph is equal to the number of Kekule structures or structure count ($K = SC$). A graph is 2-factorable if it has spanning subgraphs that are regular of degree 2. Examples of a 1-factor and the only 2-factor of naphthalene is presented by the following:


Naphthalene


1-factor
(five components)


2-factor
(one component)

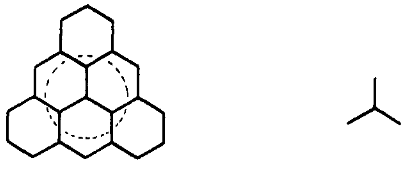


Figure 2. Triangulene and its excised internal structure, trimethylenemethane diradical.

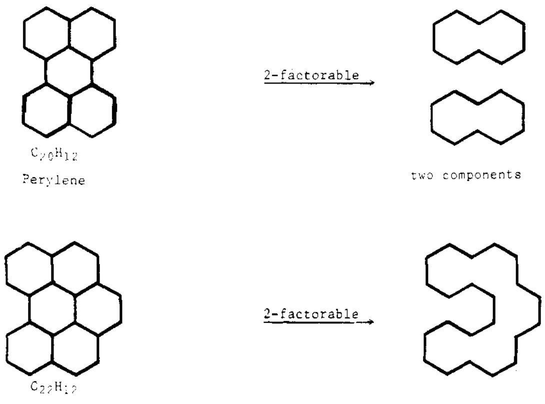


Figure 3. Example 2-factor subgraphs of some PAH6s.

Triangulene in Figure 2 is a diradical PAH6 and is not 1-factorable since it has no spanning, regular subgraph of degree 1. Perylene and benzo[*ghi*]perylene have 2-factor subgraphs shown in Figure 3. Note that all cata-condensed benzenoids have one-component, 2-factor subgraphs. Benzo[*ghi*]perylene has a one-component, 2-factor subgraph and perylene has two. The σ-bond graphs of all the cata-condensed PAH6s have a single one-component, 2-factor subgraph that corresponds to their circumference, the length of which is given by $c(\text{cata-PAH6}) = q_p = 2N_H - 6$. Not all of the isomers of peri-condensed PAH6s are 2-factorable; e.g., pyrene is not 2-factorable. The symmetrical graphs of the one isomer series of polycircumnaphthalene and polycircomcoronene (Table II) have 2-factor subgraphs comprised of concentric rings. A prerequisite for a nonsymmetrical peri-condensed PAH6 to be 2-factorable is that it must possess a concave bay region like that in perylene or benzo[*ghi*]perylene in Figure 3. The 1-factor and 2-factor subgraphs of PAH6 structures having formulas belonging to the alternate rows of $N_c = 2N_H - 6$, $N_c = 2N_H - 2$, ... [i.e., $N_c \equiv 2 \pmod 4$] of Table I have an odd number of components and an even number of components if they have formulas belonging to the other set of alternate rows [i.e., $N_c \equiv 0 \pmod 4$]. In general, PAH6 isomers having more concave bay regions are more stable and have a larger number of 1-factor and 2-factor subgraphs. A graph G is Hamiltonian if it has a single spanning cycle. The one-component 2-factor subgraph in Figure 3 is Hamiltonian. Thus PAH6 structures containing Hamiltonian subgraphs can only have corresponding formulas found in the $N_c \equiv 2 \pmod 4$ row series of Table I.[12]

Circulenes have been shown to have formulas found only below the upper right-hand quadrant in Table I.[10] Also the use of amended versions of Table I in the semiselective literature searching of polycyclic conjugated hydrocarbons having other ring sizes and/or certain hydrocarbon substitutents has been presented.[10]

According to the sextet rule all benzoid PAH6 structures having 2-factor subgraphs composed exclusively of hexagons are predicted to be more stable and have associated chemistry which tend to preserve this structural identity.[13,14] Triphenylene in Figure 4 has a 2-factor graph composed of three hexagons and is the

(10) J. R. Dias, *J. Chem. Inf. Comput. Sci.*, **24**, 124 (1984).
(11) W. Tutte, "Graph Theory", Addison-Wesley, CA, 1984.
(12) J. R. Dias, *Macromol. Sci. Chem.*, **A22**, 335 (1985).
(13) E. Clar, "The Aromatic Sextet", Wiley, London, 1972.
(14) N. Ohkami and H. Hosoya, *Theor. Chim. Acta*, **64**, 153 (1983).

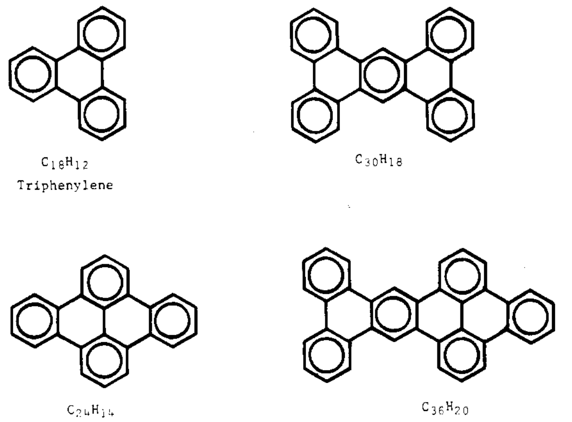


Figure 4. Sextet 2-factorable PAH6 structures from the $N_c = 3N_H - 18$ ($d_s = 2$) and $N_c = 3N_H - 24$ ($d_s = 5$) column series.

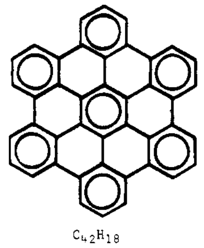


Figure 5. Sextet 2-factorable PAH6 structure belonging to the $N_c = 3N_H - 12$ ($d_s = -1$) column series.

most stable $C_{18}H_{12}$ isomer. Only the $N_c \equiv 0 \pmod 6$ column series in Table I can have PAH6 isomers possessing 2-factor subgraphs composed exclusively of hexagon components; the number of hexagon components will be odd for the $N_c \equiv 2 \pmod 4$ row series and even for the $N_c \equiv 0 \pmod 4$ row series. Figure 4 displays representative PAH6 structures from the $N_c = 3N_H - 24$ and $N_c = 3N_H - 18$ column series which have sextet 2-factor subgraphs (shown as resonant sextets).[15] All the structures in Figure 4 are the most stable isomers and are correspondingly highly branched.

The first PAH6 formula in the $N_c = 3N_H - 12$ column series having a sextet 2-factor subgraph is $C_{42}H_{18}$, and it is shown in Figure 5. Coronene ($C_{24}H_{12}$) is the first member of this column but does not have a sextet 2-factor subgraph. Since branching is necessary for the formation of isomers with sextet 2-factor subgraphs and branching decreases as the PAH6 becomes more pericondensed, fewer isomers with sextet 2-factor subgraphs exist as one goes to the left of Table I. All the sextet 2-factorable PAH6 structures in Figures 4 and 5 and others can be generated by excising them out from the $C_{114}H_{30}$ structure in Figure 6; this is illustrated by the dashed line in Figure 6 which gives the $C_{42}H_{18}$ structure of Figure 5. The exceptional stability predicted by the sextet rule probably explains why the first several benzenoid PAH6 structures ($C_{18}H_{12}$, $C_{24}H_{14}$, $C_{30}H_{18}$, and $C_{24}H_{18}$) in Figures 4 and 5 have been identified in interstellar matter.[4]

Physical/Chemical Correlations of the Formula Periodic Table for PAH6s

Expansion of the Hückel molecular orbital (HMO) secular determinant for a PAH graph gives the characteristic polynomial $P(G;X) = \det|X\mathbf{I} - \mathbf{A}|$ where $\mathbf{I}$ is the identity matrix and $\mathbf{A}$ is the adjacency matrix for the corresponding graph.[16] The characteristic polynomial of a N carbon atom system has the following form

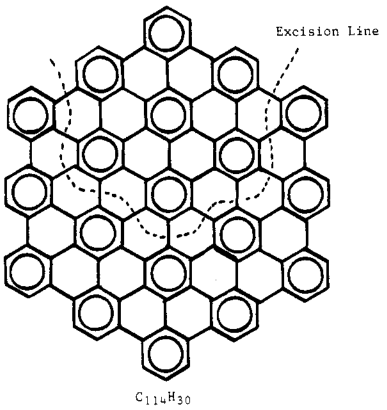


Figure 6. Sextet 2-factorable master PAH6 structure for Table I.

$$P(G;X) = \sum_{n=0}^{N} a_n X^{N-n} = 0$$

where a_n are coefficients that can be alternatively obtained by the graphical Sach's method.[15,16] The factors of this equation give the eigenvalues for the corresponding PAH graph. By definition $a_0 = 1$ but the other coefficients convey graphical and topological information. For even carbon PAH6s $a_{\text{odd}} = 0$. The number of edges (σ-bonds) in a PAH graph gives the coefficient $a_2 = -q$. For PAH6 graphs $a_N = \pm K^2$ where K is the number of Kekule structures (1-factors); for the PAH6s in Table I, the negative sign applies ($a_N = -K^2$) for the $N_c \equiv 2 \pmod 4$ row series and the positive sign ($a_N = K^2$) applies for the $N_c \equiv 0 \pmod 4$ row series. Since the a_4 coefficient is insensitive to topological changes among PAH6 isomers, a combinatorial derivation gives the following relationship which was recently derived.[15]

$$a_4 = \tfrac{1}{8}[(3N_c - N_H)^2 - 30N_c + 18N_H]$$

The difference between two a_6 coefficients corresponding to two PAH6 structural isomers equals the difference in the number of bay regions [$a_6 - a_6' = \Delta$(No. of bay regions)] associated with their graphs. For example, anthracene has no bay regions and has $a_6' = -296$ whereas phenanthrene has one bay region giving $a_6 = -297$. From these relationships for the characteristic polynomial coefficients, one can immediately write out the characteristic polynomial for benzene as being $P(C_6H_6,X) = X^6 - 6X^4 + 9X^2 - 4$. Incorporation of these relationships into computer programs which will more efficiently solve the HMO parameters for very large PAH6s is under progress; coupled with this effort is the search for other additional graphical and topological relationships hidden within the characteristic polynomial coefficients for large PAH6s.[15]

If N_H is held constant, then a comparison of the pπ energy of all the PAH6 structures having the same graph theoretical circumference ($c = q_p = 2N_H - 6$) can be made. These PAH6s lie along a formula diagonal on Table I having a positive slope. Consider the series

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(15) J. R. Dias, *Theor. Chim. Acta*, in press. J. R. Dias, *Nouv. J. Chim.*, **9**, 125 (1985).

(16) J. V. Knop and N. Trinajstić, *Int. J. Quantum Chem.*, **14**, 503 (1980); C. A. Coulson, *Proc. Cambridge Philos. Soc.*, **46** (1950).

Table III.
Comparison of Total pπ Energies of Benzenoid PAH6s of the Same Graphical Circumference

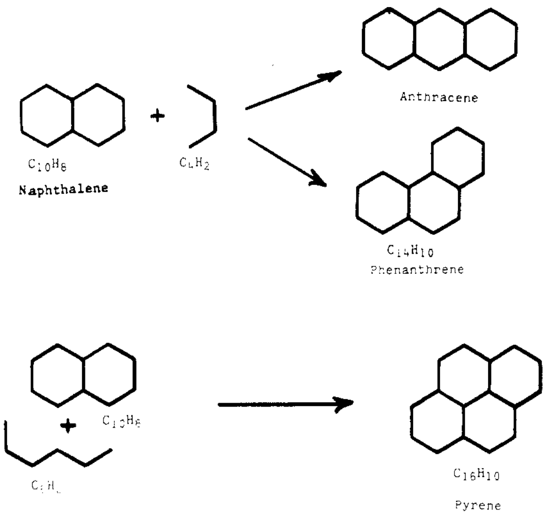
formula	E_π range for isomer set
$C_{18}H_{12}$	24.9308–25.2745β
$C_{20}H_{12}$	28.2220–28.3361β
$C_{22}H_{12}$	31.2529–31.4251β
$C_{24}H_{12}$	34.5718β
$C_{22}H_{14}$	30.5940–30.9990β
$C_{24}H_{14}$	33.7982–34.1644β
$C_{30}H_{14}$	43.1197–>43.3000β[b]
$C_{32}H_{14}$	46.4975β

[a] Zahradnik, R.; Pancir, J. "HMO Energy Characteristics"; Plenum Press: New York, 1970. [b] Data for the most stable isomer (naphtho[*bcd*]coronene) was not available.

$C_{18}H_{12}$, $C_{20}H_{12}$, $C_{22}H_{12}$, and $C_{24}H_{12}$ located in Table I sloping down from right to left from $C_{18}H_{12}$ to $C_{24}H_{12}$. For a constant graphical circumference as the number of carbon atoms increases, the pπ energy increases by more than 1.5β per carbon atom (Table III). If the number of formula carbons is held constant and the graphical circumference is allowed to increase (N_H increases), then a decrease of more than 0.4β per unit (four bonds) of increase in circumference occurs, and this is illustrated by comparing the E_π values of $C_{22}H_{12}$ vs. $C_{22}H_{14}$ and $C_{24}H_{12}$ vs. $C_{24}H_{14}$ in Table III. Holding $d_s + N_{Ic}$, p_3, and r simultaneously fixed as the number of carbon atoms increases results in a pπ energy increase of more than 1.3β per carbon atom; this is illustrated by comparing $C_{20}H_{12}$ vs. $C_{22}H_{14}$ and $C_{22}H_{12}$ vs. $C_{24}H_{14}$ in Table III. If N_{Ic} is fixed as the number of rings increases, then the pπ energy increases by more than 1.4β per carbon atom. Thus increasing the carbon atoms while holding the graphical circumference constant leads to a more rapid increase in overall pπ energy (E_π) of PAH6s. For any given number of carbon atoms, the strictly peri-condensed benzenoid hydrocarbons are the most stable.

The average pπ electron density of a PAH is defined by $N_c/q = 2N_c/(3N_c - N_H)$. All PAHs having formulas belonging to the $N_c = 3N_H$ ($d_s = -7$) column series in Table I have an isoelectrodensity (i.e., the same electron density) of $N_c/q = 0.75$. Any formula column to the left of the $N_c = 3N_H$ column have N_c/q values which approach 0.75 from smaller values, and any formula column to the right of the $N_c = 3N_H$ column have N_c/q values which approach 0.75 from larger values as the N_c/N_H ratio approaches 3. All PAHs having formulas belonging to the $N_c = 2N_H$ ($N_{Ic} = 6$) row series of Table I have an isoelectrodensity of $N_c/q = 0.8$. Any formula row above the $N_c = 2N_H$ row series have N_c/q values which approach 0.8 from larger values ($N_c/q = 0.91$ for naphthalene), and any formula row below the $N_c = 2N_H$ row series have N_c/q values which approach 0.8 from smaller values as the N_c/N_H ratio approach 2. The theoretical average pπ electron density of graphite is $N_C/q = 0.667$. Thus the PAHs with formulas found in the $N_c/N_H < 2$ quadrant of Table I have benzenoid structures with average electron density values ranging from 0.91 to 0.8, the PAHs structures found in the $2 < N_c/N_H < 3$ quadrant have N_c/q values ranging from 0.8 to 0.75, and the PAHs structures found in the $N_c/N_H < 3$ quadrant have N_c/q values ranging from 0.75 to 0.667; other things being equal, the benzenoid PAHs in the first quadrant as a group are most susceptible to electrophilic and oxidative reactions and those in the latter quadrant are least. Carcinogenic PAH6s are found only in the first quadrant of Table I with the most reactive benzenoid PAHs.

Scheme III. Illustration of Recursive Enumeration



Benzenoid Isomer Enumeration

The enumeration of all cata-condensed benzenoid hydrocarbons has been accomplished by use of a dualistic graph.[17] Recent computer algorithms have been reported for enumerating geometrically planar hexagonal graphs having the same number of rings.[18] Options for inclusion of circulenes and geometrically nonplanar helicenes in the isomer enumeration have also been developed.[19] Note that these computer results emphasized the cata-condensed benzenoids and have not yet been fully tested on totally peri-condensed benzenoids. Results have also been presented for the enumeration of PAHs having other ring sizes besides the hexagon.[9,10]

Our prior work established two concepts for enumeration of benzenoid PAH6s.[8,20] The first concept was that all benzenoid PAH6 isomers of a particular formula could be recursively enumerated from the benzenoid isomers having the corresponding formulas immediately above it and to the left of it in the formula periodic table for benzenoid PAH6s (Table I). This is illustrated in Scheme III for the enumeration of anthracene/phenanthrene ($C_{14}H_{10}$) and pyrene ($C_{16}H_{10}$) from naphthalene ($C_{10}H_8$); Figures 7 and 8 summarize this algorithmic process. Attachment of a C_4H_2 unit to naphthalene (N) gives anthracene (A) and phenanthrene (P), and continuing this process leads to all the possible cata-condensed isomers (Figure 7). From Figure 7, it is evident that only acenes beget acenes and the benzo[*a*]acenes derive from either acenes or lower benzo[*a*]acenes. Benzo[*a*]anthracene (B[*a*]A), chrysene (C), benzo[*c*]phenanthrene (B[*c*]P), and triphenylene (T) are obtained by attachment of C_4H_2 units to the four different sides of phenanthrene (P). There are 19 different attachments of C_4H_2 units onto the 5 isomers of $C_{18}H_{12}$ leading to 12 distinct $C_{22}H_{14}$ isomers, and

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(17) A. T. Balaban and F. Harary, *Tetrahedron*, **24**, 2505 (1968).

(18) J. V. Knop, K. Szymanski, Z. Jericević, and N. Trinajstić, *J. Comput. Chem.*, **4**, 23 (1983), and references therein.

(19) J. V. Knop, W. Müller, K. Szmanski, and N. Trinajstić, "Computer Generation of Certain Classes of Molecules"; SKTH/Kemija u industriji: Zagreb, 1985.

(20) J. R. Dias, *Can. J. Chem.*, **62**, 2914 (1984).

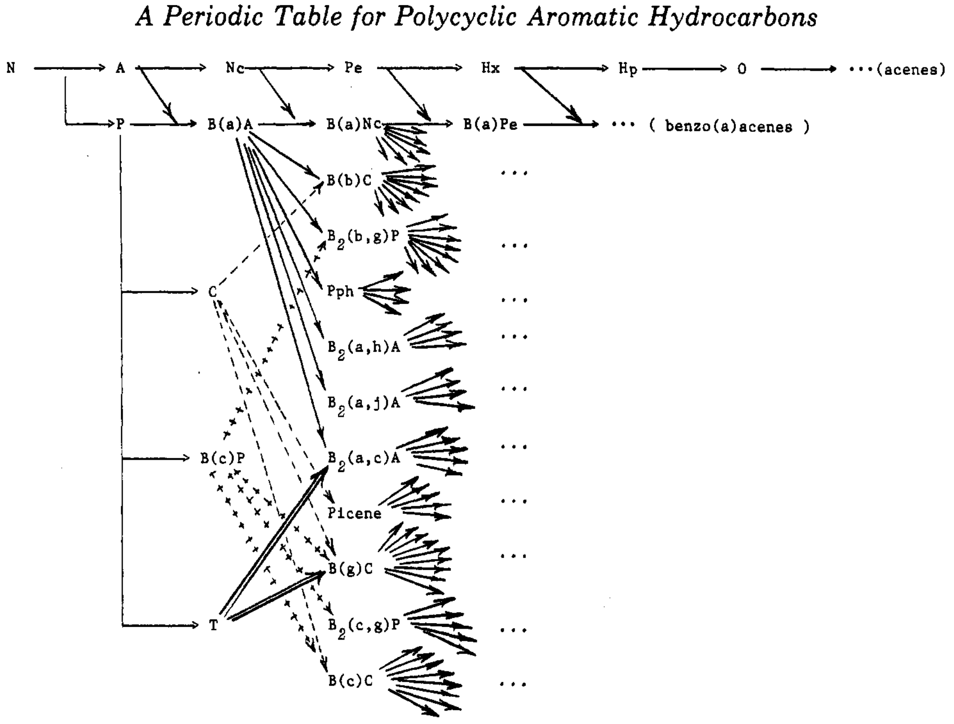

Figure 7. Scheme for recursive enumeration of the cata-condensed benzenoids.

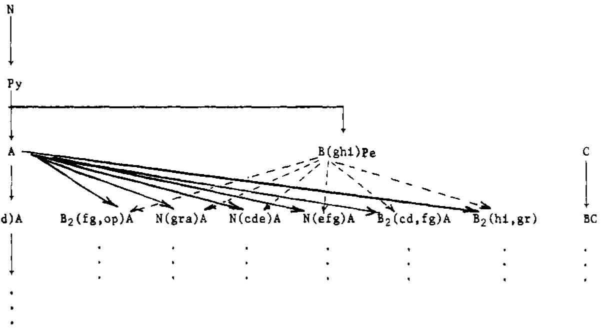

Figure 8. Scheme for recursive enumeration of some peri-condensed benzenoids.

there are 70 different attachments of C_4H_2 units onto the 12 isomers of $C_{22}H_{14}$ leading to 37 distinct $C_{26}H_{16}$ isomers and so forth. The ordering hierarchy used in Figure 7 is the magnitude of the highest occupied molecular orbital (HOMO). Acenes have the lowest E_π energy and the smallest HOMO magnitude and benzo[*a*]acenes are next. The HOMO of chrysene has a magnitude larger than benzo[*a*]anthracene but smaller than benzo[*c*]phenanthrene, and finally triphenylene has the largest HOMO magnitude and largest E_π value.

Figure 8 shows a similar pattern where pyrene is derived from naphthalene by attachment of either two C_3H units or one C_6H_2 unit. Anthanthrene (A) and benzo[*ghi*]perylene (B[*ghi*]Pe) derive from pyrene. The magnitude of the HOMO and E_π of anthanthrene is smaller than that of benzo[*ghi*]perylene. Again all less stable and symmetrical "square" peri-condensed isomers can be only derived from their lower homologues (N → Py → A → N[*bcd*]A → ...) and have the smallest HOMO values. Note that benzocoronene (BC) derives only from coronene by the attachment of a C_4H_2 unit (Figure 8).

The second concept was that strictly peri-condensed PAH6s without cata-condensed appendages have formulas along the left-hand diagonal edge of Table I and their isomers can be enumerated by enumerating the number of isomers associated with their excised internal structures.[20] Thus the number of nonradical isomers of $C_{22}H_{12}$ is two, anthanthrene and benzo[*ghi*]perylene, and the corresponding number of circumscribing isomers ($C_{52}H_{18}$) is two (Figure 9). Since circulene and helicene structures are not possible for strictly peri-condensed PAH6s, the ambiguity associated with other benzenoid isomer enumeration studies is absent in the enumeration of strictly peri-condensed PAH6s.[18] The one-isomer series presented in Table II are strictly peri-condensed PAH6s. Via this important concept the number of nonradical benzenoid isomers for $C_{38}H_{16}$, $C_{40}H_{16}$, $C_{42}H_{16}$, $C_{48}H_{18}$, $C_{50}H_{18}$, $C_{52}H_{18}$, $C_{60}H_{20}$, $C_{62}H_{20}$, and $C_{64}H_{20}$ were determined to be 10, 3, 1, 22, 7, 2, 20, 12, and 3, respectively.

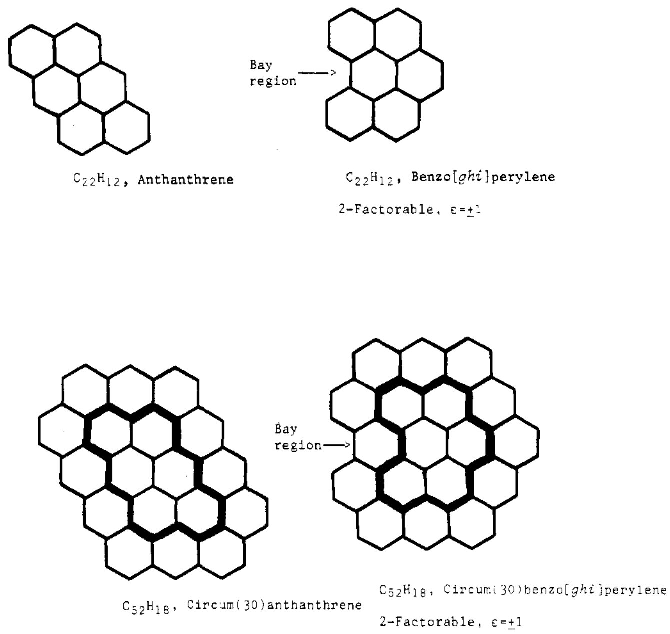

Figure 9. The corresponding parent/daughter isomers of $C_{22}H_{12}/C_{52}H_{18}$, respectively.

Application of the excised internal structure concept allows one to easily distinguish 1-factorable PAH6 structures from diradicals by the following generalization.[20] If trimethylenemethane diradical is ultimately obtained upon successive excision and pruning of a specified benzenoid hydrocarbon, then the tested benzenoid hydrocarbon is also a diradical. For example, the excised internal structures of anthanthrene, benzo[*ghi*]perylene, and triangulene ($C_{22}H_{12}$ isomers) are *s-trans*-1,3-butadiene, *s-cis*-1,3-butadiene, and trimethylenemethane diradical (Figure 2), respectively; therefore, triangulene is a diradical whereas anthanthrene and benzo[*ghi*]perylene are not. A graphite elementary carbon-bond-network defect was defined as one produced by excising out a pyrene structural unit from a perfect graphite-tessellated structure and inserting in one of the other 419 possible pyrene isomeric structural units.[3]

If the parent excised internal structure has a bay region and is 2-factorable, then the corresponding larger daughter PAH6 structure also has a bay region and is 2-factorable. Thus in Figure 9, benzo[*ghi*]perylene has a bay region and is 2-factorable and its corresponding $C_{52}H_{18}$ PAH6 structure has a bay region and is 2-factorable.[15,20] On the same basis, all the PAH6 structures having formulas belonging to the one-isomer series in Table II have no bay regions.

Concluding Remarks

A number of formula–structure and physical/chemical correlations have been established by using the formula periodic table for benzenoid polycyclic aromatic hydrocarbons. These include the average pπ-electron density, electrophilic and oxidative chemical reactivity, isomer count, and stability as predicted by the sextet rule. Although these correlations have been illustrated for even carbon benzenoid hydrocarbons in this Account, it can be shown that the reasoning on which they are based is equally applicable to odd carbon vertex polyhexes.[21] Since the hexagon seems to be a fundamental structure of nature, the relationships reviewed here may well find application beyond polycyclic aromatic hydrocarbons.

Appendix: Glossary of Terms

d_s	net tree disconnections of internal graph edges (positive values) or connections (negative values—called negative disconnection)
N_c	total number of carbon atoms in a PAH
N_H	total number of hydrogen atoms in a PAH
N_{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; also referred to as benzenoid and polyhex
$\lvert P\rvert = p = N_c$	total number of graph points
p_3	number of graph points (vertices) having a degree of 3
$\lvert Q\rvert = q$	number of graph edges (lines or C–C bonds)
q_I	number of internal graph edges
q_p	number of peripheral graph edges
r	number of rings
τ	number of rings obtained upon deletion of all internal third degree vertices from a PAH6 σ-bond graph

(21) J. R. Dias, THEOCHEM, in press.

Thermolysis of 7-Substituted Norbornadienes. Selectivity in Bond-Breaking Processes

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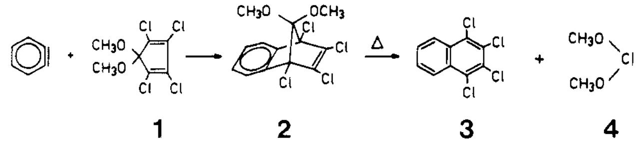
Experiments are generally carried out with the aim of obtaining certain answers. Yet our preoccupation with science would be dull if we were to obtain only those answers for which the experiments were carried out. Excitement stems from the unexpected answers, because these often lead to new insights. In this Account I would like to present unexpected insights into the thermolytic behavior of 7-substituted norbornadienes. They would not justify their presentation, if they were not to touch on a fundamental aspect: Do we understand which bond in a given molecule or intermediate is broken on thermolysis, a question related to selectivity.

Scheme I



Of course, there is the classical notion of bond strength. The weakest bond breaks first.[1] Ingeniously

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(1) Cf. H. M. Frey and R. Walsh, *Chem. Rev.*, 69, 103 (1969); C. Rüchardt, *Top. Curr. Chem.*, 88, 1 (1980).

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