

SUMMARY

Chemical substances classified as nonstoichiometric or solid solutions confront online searchers with special problems not usually encountered with other types of materials. Search strategies for these substances must follow certain prescribed procedures or risk gross failure to capture relevant information. The searcher must also keep in mind that certain strategies will be valid only over specific time spans: both for CAS ONLINE and INSPEC this strategic dividing line occurs at the end of 1986.

In CAS ONLINE the preferred search strategy for the period 1987 to date tests on the use of the dot connected atom formulation in the /MF index of Registry File. For earlier periods in CAS ONLINE one must utilize a strategy that simultaneously searches for the co-occurrence of the end members of a solid-solution family.

Comparable searches in INSPEC over the period 1987 to date should employ the chemical index file (CI=). Searches for earlier information must use a series of molecular formula (or atom string) searches that may be quite lengthy depending on the compositional complexity of the system being searched.

Even for the period 1987+ the searcher is advised to test the completeness of retrievals obtained via use of the CI file by searching some alternative query formulations.

Finally, both in CAS ONLINE and INSPEC, searches for specific compositions or narrow compositional ranges are best initiated via use of the EXPAND file. It is far easier (and cheaper) to locate and select a given item from an EXPAND list than to search long, complex expressions that are subject to a variety of entry errors, especially mistakes in typing.

ACKNOWLEDGMENT

I acknowledge the advice and insights provided by Ken Cada of Chemical Abstracts Service and Jim Ashling of INSPEC.

REFERENCES AND NOTES

- (1) *Chemical & Numerical Indexing, Dialog Implementation*; INSPEC, The Institution of Electrical Engineers, Dec 1987; 12 pp.
- (2) *Search Guide to Superconductors in the INSPEC Database*; INSPEC, The Institution of Electrical Engineers, Feb 1988, p 5.
- (3) Coghlan, Jill. Superconducting oxides. *Database* 1989, 12, 122-127.
- (4) Note Added in Proof: The May/June 1990 issue of *CAS ONLINE* News offered a discussion about searches for nonstoichiometric compounds in the Registry File.

Benzenoid Series Having a Constant Number of Isomers. 3. Total Resonant Sextet Benzenoids and Their Topological Characteristics

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Two distinct classes of benzenoid groups having a constant number of isomers have been identified for the total resonant sextet isomer subset. One class is topologically unique and the other forms a pairwise topologically equivalent class. The numbers of isomers in these two classes are the same as those reported in Part 2 of this series for strictly peri-condensed benzenoids. This correspondence clearly signals the discovery of a fundamental topological paradigm.

INTRODUCTION

Total resonant sextet benzenoid hydrocarbons have molecular formulas whose carbon numbers are divisible by 6, and they represent a subset of the most stable isomers.¹ It is shown in this paper that unlike circulenes—benzenoids with holes—sextet benzenoids have subsets which exhibit constant-isomer series.^{2,3} It also will be shown that the number of sextet isomers and the topological features of the sextet benzenoid members of these constant-sextet-isomer series match one-for-one with the properties³ of the strictly peri-condensed constant-isomer benzenoids. This spectacular correspondence clearly points out a fundamental topological paradigm.

While compounds in the one-sextet-isomer series have only one total resonant sextet benzenoid isomer each, there are other benzenoid structures associated with these formulas.^{4,5} There are for example, 186 other benzenoid structures with the molecular formula $C_{42}H_{18}$ besides the one shown in Figure 1. Similarly, in addition to those in Figure 1, there are 5725 isomers with the molecular formula $C_{60}H_{22}$ and 123 789 with the molecular formula $C_{84}H_{26}$. This work has allowed the identification of the most stable isomers from large numbers of possible benzenoids. It is conjectured that when these constant-isomer benzenoids are formed under conditions of pyrolysis, they are more stable and both topologically and kinetically more likely to persist. Unlike many other benzenoids, total resonant sextet benzenoid isomers generally do

not give color reactions with concentrated sulfuric acid and they tend to have the least intensely colored crystals. Chemically, total resonant sextets represent a particularly important benzenoid isomer subset.^{1,6}

In a seminal paper,⁷ Stein reported a theoretical thermodynamic study of the chemical equilibria in two model systems—highly condensed to strictly peri-condensed benzenoids and total resonant sextet benzenoids. A major conclusion of this study was that for a given carbon number, the most condensed benzenoid will have the greatest thermodynamic stability. Also, the higher the temperature of formation, the larger the benzenoids tend to be. Benzenoids which are smaller than this critical size will tend to degrade, while those which are larger will tend to grow. This is because there exists a critical species, whose size increases with temperature.

In a study of the hydroprocessing of high-boiling gas oil (vacuum gas oil from the *residuum* desulfurization process), it was observed⁸ that hydrocracking of high-severity product was more difficult than for low-severity product because the former contained more highly condensed benzenoids, which belong to the constant-isomer series.

A recent mass spectral study⁹ of fuel feedstocks tabulated suggested aromatic compounds without taking into consideration the relative stability of the various isomers corresponding to a specific molecular formula. For example, the observed molecular ion of m/z 378 ($C_{30}H_{18}$) was assigned the heptacene

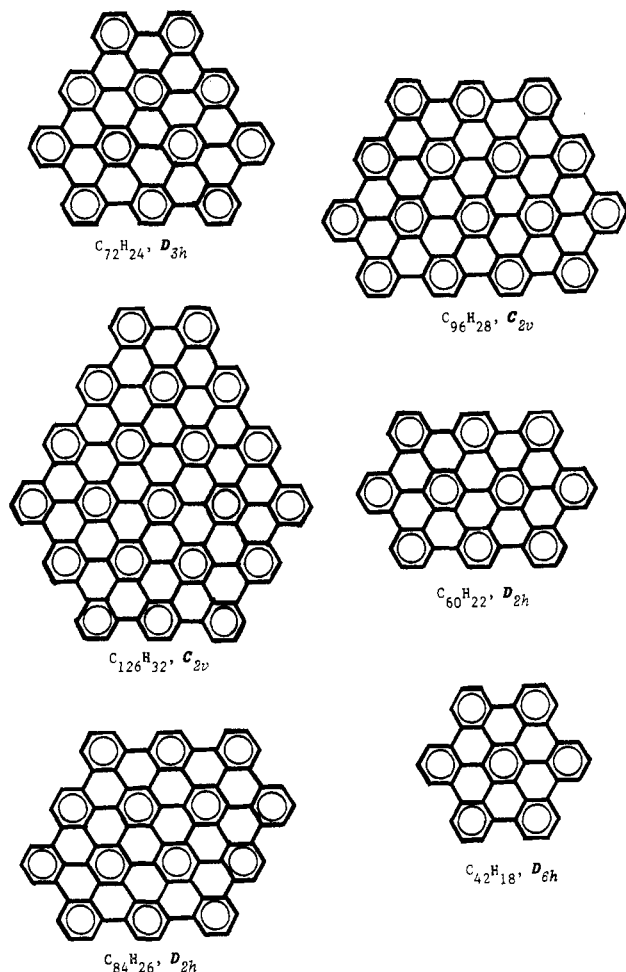
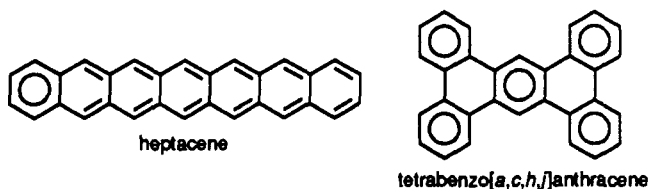


Figure 1. Second generation total resonant sextet benzenoids structures belonging to the one-sextet-isomer series.

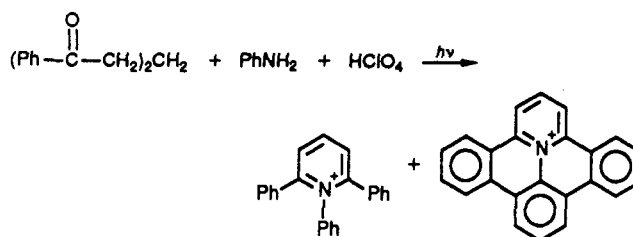
structure which is the most reactive of over 123 possible isomers. A more likely possibility would have been tetrabenzotetraphenylanthracene, which is the only essentially strain-free total resonant sextet and is the most stable $C_{30}H_{18}$ isomer.



Petroleum-derived pitch that has been heat-treated to convert it partially to mesophase and then extracted with pyridine when analyzed by GC-MS is shown to contain a component with the molecular formula $C_{54}H_{28}$.¹⁰ This molecular formula is common to more than half a million benzenoid isomers, but the five most stable strain-free total resonant sextet isomers have been postulated.^{1,4}

In a study of ions and charged soot particles in hydrocarbon flames,¹¹ positive ions with m/z values up to 600 were analyzed by means of time-of-flight mass spectrometry. Benzenoid ions with odd numbers of carbon atoms corresponding to the one-isomer D_{3h} series ($C_{13}H_9^+$, $C_{37}H_{15}^+$), the one-isomer C_{2v} series ($C_{19}H_{11}^+$), and the two-isomer C_s series ($C_{35}H_{15}^+$) were detected. Protonated even-carbon benzenoid ions corresponding to the one-isomer D_{6h} series ($C_6H_7^+$, $C_{24}H_{13}^+$), the one-isomer D_{2h} series ($C_{10}H_9^+$, $C_{32}H_{15}^+$, and $C_{16}H_{11}^+$), the three-isomer series ($C_{22}H_{13}^+$), and the four-isomer series ($C_{30}H_{15}^+$) were also detected.

A recently published¹² reaction illustrates the propensity for formation of total resonant sextet benzenoid-related species:



There are approximately 500 known benzenoids out of over 2 million with formulas that have 60 carbons or fewer.^{4,5} There are 13 known strain-free or minimally strained total resonant sextet benzenoids out of the 143 possibilities with 60 carbons or less.^{1,4} Thus there is a greater percentage of known total resonant sextet benzenoids (9%) in this range than there are known benzenoids (0.03%). Thus benzenoids belonging to the constant-isomer series represent a very important subgroup that continues to warrant special attention, both theoretical and experimental.

RESULTS AND DISCUSSION

Definition of a Total Resonant Sextet Benzenoid. The number of sextets is equal to the number of independently permutable sets of three $p\pi$ bonds, each within the hexagonal rings of a benzenoid.¹ Heptacene, for example, has only one sextet because it has only one set of three $p\pi$ bonds that can be relatively permuted at a time; the remaining $p\pi$ bonds are fixed in their position during this permutation operation. A circle is inscribed in each hexagonal ring that has a permutable set of three $p\pi$ bonds. Rings having no fixed $p\pi$ bonds or circles are said to be "empty". The sextet shown in the structure of heptacene is capable of migrating one ring at a time from left to right.

Total resonant sextet benzenoids were termed "fully benzenoid" by Clar,¹ but the term "total resonant sextet benzenoid" is more descriptive and less ambiguous because "fully benzenoid" implies that other benzenoid compounds are less benzenoid. It is clear that fluoranthrene and related polycyclic conjugated aromatics are less benzenoid or partially benzenoid. The generic use of "benzenoid" is restricted to fused polycyclic aromatic hydrocarbons composed exclusively of hexagonal rings (PAH6). Benzenoid isomers can possess a different maximum number of resonant sextets and when this maximum number totally occupies the benzenoid system, it is called a "total resonant sextet benzenoid". The subset of benzenoid hydrocarbons with numbers of carbon atoms divisible by 6 and two-factor subgraphs (spanning subgraphs having vertices of only degree 2) composed exclusively of hexagonal ring components are called "total resonant sextet benzenoids".¹³ This graph-theoretical definition was first used¹³ in 1984 and was reiterated in a subsequent paper by Knop and co-workers.¹⁴ Though the paper by Knop and co-workers contains sextet enumeration results, the work summarized herein deals with the minimally strained total resonant sextet subset and goes far beyond all prior work. For example, strained sextet benzenoids like the $C_{30}H_{18}$ isomer shown below, which should be compared with the strain-free $C_{30}H_{18}$ total resonant sextet isomer discussed above, are not considered because it is believed that they will not survive pyrolytic conditions without further self-condensation, as shown.^{1,4}

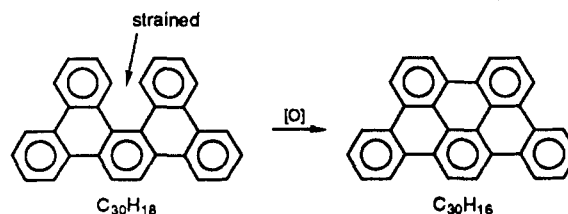


Table I. [Table PAH6(sextet)]. Formula Periodic Table for Total Resonant Sextet Benzenoid Hydrocarbons

$d_1 = -10$	$d_1 = -7$	$d_1 = -4$	$d_1 = -1$	$d_1 = 2$	$d_1 = 5$	$d_1 = 8$	$d_1 = 11$	$d_1 = 14$	N_{1c}
				$C_{18}H_{12}$	$C_{30}H_{18}$	$C_{42}H_{24}$	$C_{54}H_{30}$	$C_{66}H_{36}$	0
				$C_{24}H_{14}$	$C_{36}H_{20}$	$C_{48}H_{26}$	$C_{60}H_{32}$...	2
				$C_{30}H_{16}$	$C_{42}H_{22}$	$C_{54}H_{28}$	$C_{66}H_{34}$		4
				$C_{36}H_{18}$	$C_{48}H_{24}$	$C_{60}H_{30}$...		6
				$C_{42}H_{20}$	$C_{54}H_{26}$	$C_{66}H_{32}$			8
				$C_{48}H_{22}$	$C_{60}H_{28}$...			10
			$C_{42}H_{18}$	$C_{54}H_{24}$	$C_{66}H_{30}$				12
			$C_{48}H_{20}$	$C_{60}H_{26}$
			$C_{54}H_{22}$	$C_{66}H_{28}$					
			$C_{60}H_{24}$...					
		$C_{60}H_{22}$	$C_{66}H_{26}$						
		$C_{66}H_{24}$...						
		$C_{72}H_{26}$							
		$C_{78}H_{28}$							
		$C_{84}H_{30}$							
	$C_{72}H_{24}$...							
	$C_{78}H_{26}$								
	$C_{84}H_{28}$								
	$C_{90}H_{30}$								
	$C_{96}H_{32}$								
$C_{84}H_{26}$...								
$C_{90}H_{28}$									
$C_{96}H_{30}$									
$C_{102}H_{32}$									
$C_{108}H_{34}$									

Formula Periodic Table for Total Resonant Sextet Benzenoid Hydrocarbons. The formula periodic table for total resonant sextet benzenoids is given as Table PAH6(sextet) (Table I), which is a subset of Table PAH6. When Table PAH6(sextet) is sorted by the Hill-ordered molecular formula, it gives Table PAH6(sextet)' which is given as Table II in this paper. Table PAH6(sextet) is a true periodic table because it is a partially ordered set forming a two-dimensional array which complies with the triad principle which requires that any central element have a metric property which is the arithmetic mean of the two oppositely adjacent elements.³ For example, consider the following subsection of Table PAH6(sextet):

$C_{18}H_{12}$	$C_{30}H_{18}$	$C_{42}H_{24}$...
$C_{24}H_{14}$	$C_{36}H_{20}$	$C_{48}H_{26}$...
$C_{30}H_{16}$	$C_{42}H_{22}$	$C_{54}H_{28}$...
...	

The average of the subscripts of the outer formulas along any triad (row, column, or diagonal) gives the value of the central element subscripts. Thus, along the middle row, the central element $C_{36}H_{20}$ has 36 carbons, the average of 24 and 48, and 20 hydrogens, the average of 14 and 26, and the same relationships hold for any triad. Hierarchical ordering and edge effects are key features of Table PAH6(sextet). Set members located on the edge, or the two dimensional boundary, possess properties that are exceptional relative to the other set members, and this is known as an edge effect. Formulas corresponding to constant-sextet-isomer benzenoid series are all on the extreme left-hand staircase edge of Table PAH6(sextet), and these compounds are different from the total resonant sextet benzenoids, whose formulas are not on this boundary. It should be noted here that total resonant sextet benzenoid isomers are only subsets of the overall family of benzenoid isomers that correspond to the formulas found in Table PAH6(sextet). From the recursion pattern evident in Table II, Table PAH6(sextet)' can be extended indefinitely. The formulas on the left-hand edge or boundary of PAH6(sextet) define a very important zigzag line of demarcation in Table PAH6. Formulas to the left of this boundary in Table PAH6 cannot correspond to a total resonant sextet benzenoid structure even though their carbon numbers are divisible by 6. Formulas to the right of it cannot correspond to a strictly peri-condensed benzenoid structure. Thus it is evident that in Table PAH6 benzenoids can be segregated into two distinct

Table II. All Possible Formulas for Total Resonant Sextet^a

N_c	N_H	N_c	N_H
18	→12	180	→38-92
24	→14	186	40-96
30	→16-18 ^b	192	40-98
36	18-20	198	→40-102
42	→18-24	204	42-104
48	→20-26	210	42-108
54	22-30	216	42-110
60	→22-32	222	→42-114
66	24-36	228	44-116
72	→24-38	234	44-120
78	26-42	240	→44-122
84	→26-44	246	46-126
90	28-48	252	46-128
96	→28-50	258	46-132
102	30-54	264	→46-134
108	30-56	270	48-138
114	→30-60	276	48-140
120	32-62	282	48-144
126	→32-66	288	→48-146
132	34-68	294	50-150
138	34-72	300	50-152
144	→34-74	306	50-156
150	36-78	312	→50-158
156	36-80	318	52-162
162	→36-84	324	52-164
168	38-86	330	52-168
174	38-90	336	→52-170

^a Cata-condensed benzenoids are underlined and one-sextet-isomers are marked with an arrow (→). ^b Consecutive even numbers.

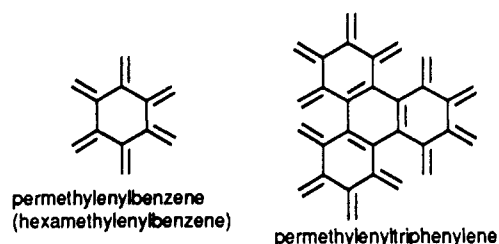
groups with discernible properties.

Enumeration of Total Resonant Sextet Benzenoids. Essentially strain-free or minimally strained total resonant sextets with 60 carbons or less have no adjacent bay regions and have all been enumerated.^{1,4} The two methods employed for the enumeration were our *aufbau* process and a different procedure which utilized a special version of our excised internal structure concept. The most condensed total resonant sextet benzenoids have formulas which are on the extreme left-hand staircase edge of Table PAH6(sextet). The excised internal structures for these total resonant sextets are constructed by taking the most condensed total resonant sextets of a given

Table III. Constant-Sextet-Isomer Series of Total Resonant Sextet Benzenoids (Analogous to Even-Carbon Strictly Peri-Condensed Benzenoid Constant-Isomer Series)

series	no. of resonant sextet isomers	symmetry distribution
(C ₆ H ₆) C ₄₂ H ₁₈ C ₁₁₄ H ₃₀ C ₂₂₂ H ₄₂ ...	1	<i>D</i> _{6h}
(C ₁₂ H ₁₀) C ₆₀ H ₂₂ C ₁₄₄ H ₃₄ C ₂₆₄ H ₄₆ ...	1	<i>D</i> _{2h}
(C ₂₄ H ₁₄) C ₈₄ H ₂₆ C ₁₈₀ H ₃₈ C ₃₁₂ H ₅₀ ...	1	<i>D</i> _{2h}
(C ₃₆ H ₁₈) C ₁₀₈ H ₃₀ C ₂₁₆ H ₄₂ C ₃₆₀ H ₅₄ ...	3	<i>D</i> _{3h} , <i>C</i> _{2v} , <i>C</i> _{2h}
(C ₅₄ H ₂₂) C ₁₃₈ H ₃₄ C ₂₅₈ H ₄₆ ...	4	<i>D</i> _{2h} , <i>C</i> _{2v} (2), <i>C</i> _s
(C ₇₈ H ₂₆) C ₁₇₄ H ₃₈ C ₃₀₆ H ₅₀ ...	4	<i>D</i> _{2h} , <i>C</i> _{2v} (2), <i>C</i> _s
(C ₁₀₂ H ₃₀) C ₂₁₀ H ₄₂ C ₃₅₄ H ₅₄ ...	9	<i>D</i> _{2h} , <i>C</i> _{2v} (2), <i>C</i> _s (6)
(C ₁₃₂ H ₃₄) C ₂₅₂ H ₄₆ ...	16	<i>D</i> _{2h} , <i>C</i> _{2v} (4), <i>C</i> _{2h} (2), <i>C</i> _s (9)
(C ₁₆₈ H ₃₈) C ₃₀₀ H ₅₀ ...	16	<i>D</i> _{2h} , <i>C</i> _{2v} (4), <i>C</i> _{2h} (2), <i>C</i> _s (9)
(C ₂₀₄ H ₄₂) C ₃₄₈ H ₅₄ ...	39	<i>D</i> _{3h} , <i>D</i> _{2h} (2), <i>C</i> _{2v} (5), <i>C</i> _{2h} (3), <i>C</i> _s (28)

number of carbons and converting them to permethylenyl derivatives.¹ The following permethylenylbenzene and permethylenyltriphenylene structures are excised internal structures of the C₄₂H₁₈ and C₇₂H₂₄ total resonant sextet benzenoids shown in Figure 1.



Consider the one-sextet-isomer series given in Tables III and IV. The second generation structures from these are shown in Figure 1. The permethylenyl derivative of benzene (C₁₂H₁₂) has only one isomer and circumscribing a 30-carbon-atom perimeter around it and incrementing the number of hydrogen atoms by 6 leads to the only C₄₂H₁₈ total resonant sextet benzenoid—the last structure in Figure 1. Multiple repetition of this process generates the first one-sextet-isomer series in Table III. Similarly, biphenyl has only one isomeric permethylenyl derivative (C₂₂H₂₀) and circumscribing it with a 38-carbon-atom perimeter and adding two hydrogens leads to the only total resonant sextet benzenoid with a molecular formula of C₆₀H₂₂. Repeating the process leads to the second

Table IV. Constant-Sextet-Isomer Series of Total Resonant Sextet Benzenoids (Analogous to Odd-Carbon Strictly Peri-Condensed Benzenoid Constant-Isomer Series)

series	no. of resonant sextet isomers	symmetry distribution
C ₁₈ H ₁₂ C ₇₂ H ₂₄ C ₁₆₂ H ₃₆ C ₂₈₈ H ₄₈ ...	1	<i>D</i> _{3h}
(C ₃₀ H ₁₆) C ₉₆ H ₂₈ C ₁₉₈ H ₄₀ C ₃₃₆ H ₅₂ ...	1	<i>C</i> _{2v}
(C ₄₈ H ₂₀) C ₁₂₆ H ₃₂ C ₂₄₀ H ₄₄ C ₃₉₀ H ₅₆ ...	1	<i>C</i> _{2v}
(C ₆₆ H ₂₄) C ₁₅₆ H ₃₆ C ₂₈₂ H ₄₈ C ₄₄₄ H ₆₀ ...	2	<i>C</i> _s (2)
(C ₉₀ H ₂₈) C ₁₉₂ H ₄₀ C ₃₃₀ H ₅₂ ...	4	<i>C</i> _{2v} , <i>C</i> _s (3)
(C ₁₂₀ H ₃₂) C ₂₃₄ H ₄₄ C ₃₈₄ H ₅₆ ...	4	<i>C</i> _{2v} , <i>C</i> _s (3)
(C ₁₅₀ H ₃₆) C ₂₇₆ H ₄₈ C ₄₃₈ H ₆₀ ...	13	<i>D</i> _{3h} , <i>C</i> _{2v} (3), <i>C</i> _s (9)
(C ₁₈₆ H ₄₀) C ₃₂₄ H ₅₂ ...	20	<i>C</i> _{2v} (4), <i>C</i> _s (16)
(C ₂₂₈ H ₄₄) C ₃₇₈ H ₅₆ ...	20	<i>C</i> _{2v} (4), <i>C</i> _s (16)
(C ₂₇₀ H ₄₈) C ₄₃₂ H ₆₀ ...	48	<i>C</i> _{3h} , <i>C</i> _{2v} (2), <i>C</i> _s (45)

one-sextet-isomer series shown in Table III. The most highly condensed arrangement of four sextet rings is found in dibenzo[*fg,op*]tetracene (C₂₄H₁₄). Circumscribing the permethylenyl derivative (C₃₈H₂₈) of this compound with a 46-carbon-atom perimeter, with removal of two hydrogen atoms, gives the only total resonant sextet benzenoid with the molecular formula C₈₄H₂₆. Continuation of this process leads to the third one-sextet-isomer series in Table III. These one-sextet-isomer series are congruent with the one-isomer series of even-carbon, strictly peri-condensed benzenoids.

In a similar fashion, compounds of the one-sextet-isomer series in Table IV are generated starting with triphenylene (C₁₈H₁₂), tribenzo[*fg,ij,rst*]pentaphene (C₃₀H₁₆), and naphtho[1,2,3,4-*cde*]circum(30)permethylenylbenzene (C₄₈H₂₀). This one-sextet-isomer series is congruent with the one-isomer series of the odd-carbon strictly peri-condensed benzenoids. The second generation structures of the one-sextet-isomer series in Figure 1 should be compared with structures of the one-isomer series of the strictly peri-condensed benzenoids in Figure 2 of ref 2. In regard to symmetry, there is a one-to-one correspondence between the structures of the one-sextet-isomer series and those of the one-isomer series of the strictly peri-condensed benzenoids. Starting with the second generation, the total resonant sextet benzenoids belonging to the constant-sextet-isomer series are strictly peri-condensed benzenoids with a maximum number of bay regions. In general, total resonant sextet benzenoids that are strictly peri-condensed

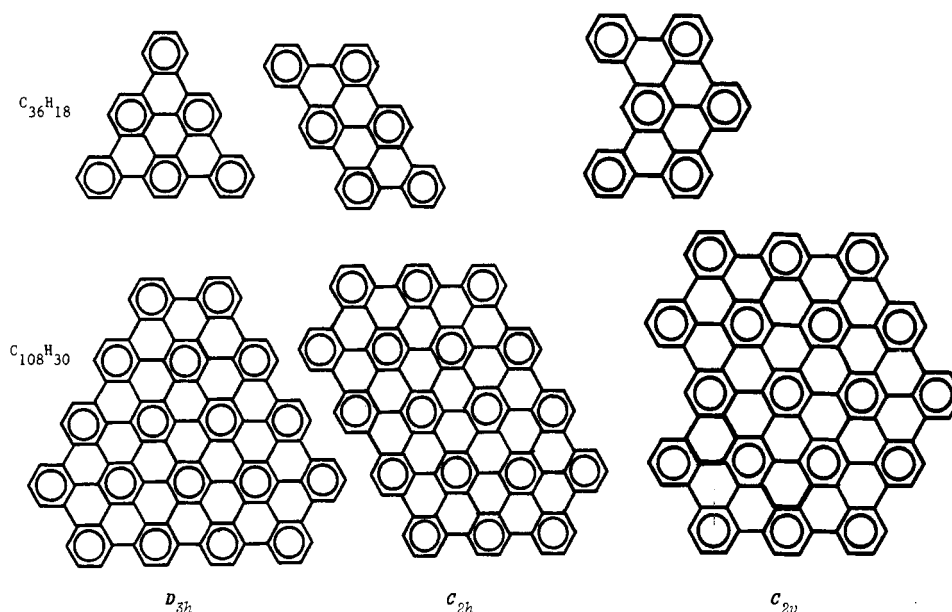


Figure 2. Total resonant sextet benzenoid structures belonging to the first and second generations of the three-sextet-isomer series.

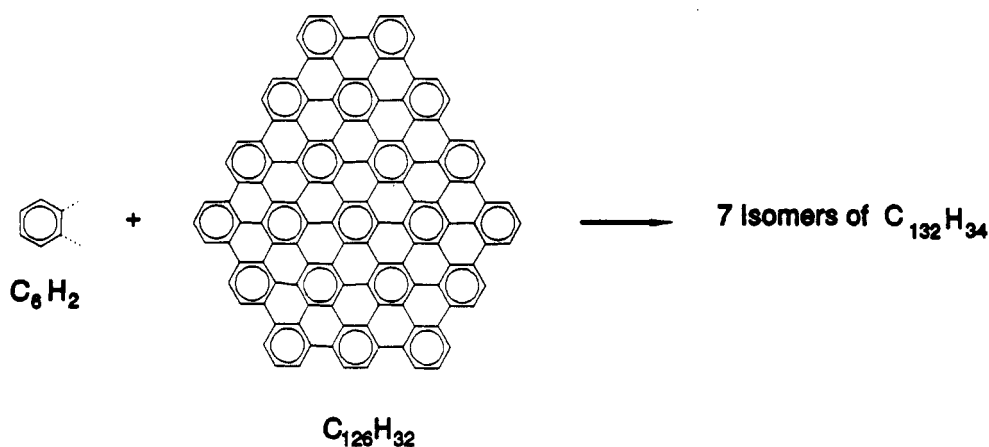


Figure 3. Aufbau attachment of the sextet C_6H_2 unit.

(N_C', N_H') have precursor total resonant sextet benzenoids (N_C, N_H) with formulas having 12 fewer hydrogen atoms ($N_H = N_H' - 12$) and numbers of carbon atoms given by:

$$N_{IC}' = N_C + N_H = N_C' - 2N_H' + 6$$

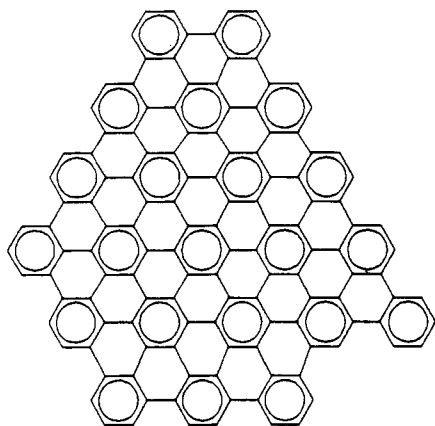
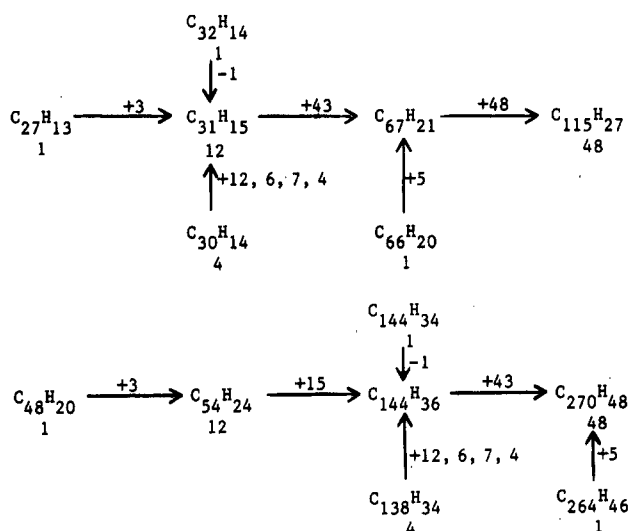
Thus, $N_H' = N_H + 12$ and $N_C' = N_C + 3N_H + 18$ are useful recursion relationships which can be used to obtain the successive molecular formulas for members of a constant-sextet-isomer series.

The benzenoids corresponding to the first formula of each constant-sextet-isomer series in Tables III and IV also correspond to the base (first generation) member of the respective series. The benzenoids corresponding to the second formula of each series correspond to the second generation, those belonging to the third formula to the third generation, and so on. If subtraction of C_6H_4 from a total resonant sextet formula such as C_xH_y leads to a formula $(C_{x-6}H_{y-4})$ which is not in Table PAH6(sextet), this means that there can be no phenyl-substituted total resonant sextet benzenoids corresponding to the molecular formula C_xH_y . With the exception of biphenyl, no phenyl-substituted total resonant sextet benzenoid has a molecular formula corresponding to a first generation constant-sextet-isomer benzenoid. No second generation constant-sextet-isomer benzenoid has a benzo appendage ($\eta_4 = 0$), and subtraction of C_6H_2 from a second generation formula leads to a successor formula which is not found in Table PAH6(sextet). This means that second generation total resonant sextet benzenoid members and higher generations

must be strictly peri-condensed benzenoids, i.e., they have connected excised internal structures.

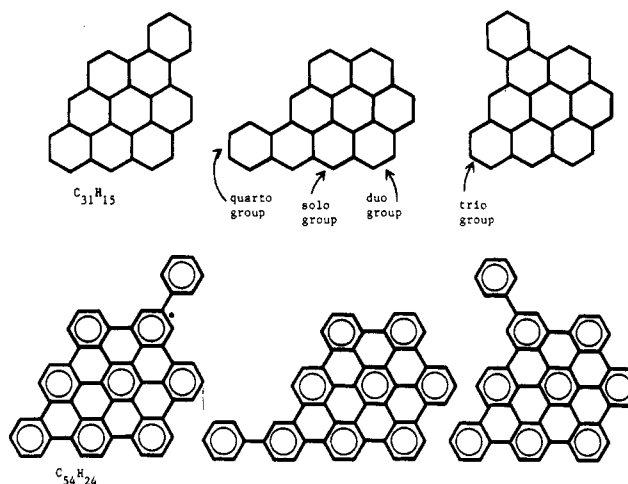
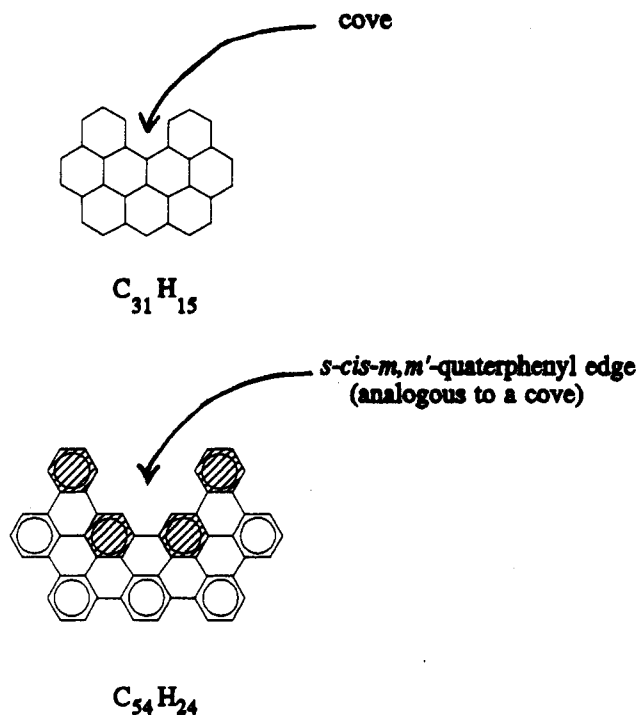
To illustrate the enumeration of the constant-sextet isomer series in Tables III and IV, consider the series beginning with $C_{132}H_{34}$ in Table III. Using the above recursion in reverse, one obtains the molecular formula $C_{48}H_{22}$, which has been shown to have eight isomers.^{1,4} Subtraction of C_6H_4 from $C_{48}H_{22}$ gives $C_{42}H_{18}$ which is the last structure in Figure 1. Thus there is one phenyl-substituted sextet with the formula $C_{48}H_{22}$ and it cannot be fused to $C_{48}H_{20}$. Conversion of these nine structures to permethylenyl derivatives and circumscription gives nine strictly peri-condensed total resonant sextet benzenoids with the molecular formula $C_{132}H_{34}$. Subtraction from this of C_6H_2 gives $C_{126}H_{32}$, which is found in Table I and which corresponds to the second generation of the third one-sextet-isomer series found in Table IV (see the third structure in Figure 1). There are seven different possible attachments of the C_6H_2 unit, as shown in Figure 3. These $9 + 7 = 16$ isomers of $C_{132}H_{34}$ comprise the first generation total resonant sextet benzenoids for this constant-sextet-isomer series. (See Chart I.)

As another example, consider in Table III the series beginning with the molecular formula $C_{204}H_{42}$. Using the recursion equations in reverse twice gives $C_{96}H_{30}$ and then $C_{24}H_{18}$. There are four relevant $C_{24}H_{18}$ quaterphenyl isomers that can be converted to permethylenyl derivatives and then circumscribed to give four strictly peri-condensed total resonant sextet benzenoids with the molecular formula $C_{96}H_{30}$. Sub-

Chart I. One of Seven Possible $C_{132}H_{34}$ Benzo IsomersScheme I. Enumeration of 48 Isomers of $C_{115}H_{27}$ Strictly Peri-Condensed and $C_{270}H_{48}$ Total Resonant Sextet Benzenoid Correspondents

tracting C_6H_2 gives $C_{90}H_{28}$, which corresponds to the first generation of the first four-sextet-isomer series in Table IV. All possible attachments of a C_6H_2 unit to each of these four $C_{90}H_{28}$ structures leads to 26 different $C_{96}H_{30}$ isomers. Conversion of the $4 + 26 = 30$ structures to the corresponding permethylenyl derivatives and circumscribing them gives 30 strictly peri-condensed total resonant sextet benzenoids with the molecular formula $C_{204}H_{42}$. Subtraction from this of C_6H_2 gives $C_{198}H_{40}$, which corresponds to the third generation of the second one-sextet-isomer series in Table IV. There are nine possible attachments of the C_6H_2 unit to this $C_{198}H_{40}$ one-sextet-isomer, and thus there are $30 + 9 = 39$ different total resonant sextet benzenoid isomers with the molecular formula $C_{204}H_{42}$.

Whenever a total resonant sextet benzenoid possess an edge section in which an *s-cis-m,m'*-quaterphenyl substructure can be embedded, then that benzenoid (e.g., $C_{54}H_{24}$ in Figure 5) cannot be circumscribed to give a strain-free resonant sextet and must be excluded by the algorithm. At each step of the enumeration, it is necessary to check Table PAH6(sextet)' to ensure that the formulas obtained from the recursion do indeed correspond to sextet benzenoids. All the series given in Tables III and IV were generated by this procedure with our earlier results.^{1,4} The recursion pattern that is evident in both Tables III and IV facilitates the extension of the tables. Additional isomer numbers for constant-sextet-isomer series can be predicted from our earlier tables.^{2,3} The one-sextet isomer series plays a pivotal role in the enumeration of other constant-sextet-isomer series.

Figure 4. Benzobenzenoid $C_{31}H_{15}$ and phenyl sextet $C_{54}H_{24}$ correspondents.Figure 5. Strictly peri-condensed $C_{31}H_{15}$ and total resonant sextet $C_{54}H_{24}$ benzenoids correspondents that are incapable of serving as excised internal structures.

To illustrate further the parallelism between the strictly peri-condensed and the total resonant sextet benzenoid isomers, the enumeration of the constant-isomer series starting with $C_{115}H_{27}$ and $C_{270}H_{48}$ will be considered (Scheme I). The first of these is strictly peri-condensed and the other is a total resonant sextet correspondent and both have 48 isomers. All 15 isomers of $C_{31}H_{15}$ have been described.⁵ There are 12 strictly peri-condensed $C_{31}H_{15}$ benzenoids as well as three benzobenzenoids, shown in Figure 4. The latter can be derived by different attachments of C_4H_2 to the sole isomer of $C_{27}H_{13}$, which is the base member of the relevant one-isomer series. All the possible attachments of a methylenyl group to the four isomers of $C_{30}H_{14}$ gives $12 + 6 + 7 + 4 = 29$ additional $C_{31}H_{15}$ isomers, for a grand total of 44 $C_{31}H_{15}$ isomers. One of the 12 strictly peri-condensed benzenoids however has a cove (an example of which is seen in Figure 5), which can be identified by the deletion of one of the two equivalent solo positions in ovalene ($C_{32}H_{14}$); this isomer cannot serve as an excised internal structure. Circumscribing the remaining 43 $C_{31}H_{15}$ isomers gives 43 strictly peri-condensed $C_{67}H_{21}$ benzenoids.

All the possible additions of a methylenyl group to the sole benzenoid isomer of $C_{66}H_{20}$ gives five more $C_{67}H_{21}$ isomers. Circumscribing these $43 + 5 = 48$ isomers of $C_{67}H_{21}$ gives all 48 strictly peri-condensed benzenoids with the formula $C_{115}H_{27}$, which are the base members of a constant-isomer series. All 12 of the $C_{54}H_{24}$ total resonant sextet benzenoids have been described.^{1,4} All possible attachments of a C_6H_4 sextet phenyl to all the available central trio and quarto positions of the base member of the one-sextet-isomer series starting with $C_{48}H_{20}$ gives three more $C_{54}H_{24}$ isomers shown in Figure 4. Converting the $12 + 3 = 15$ $C_{54}H_{24}$ resonant sextets to the permethylenyl derivatives and circumscribing them gives 15 $C_{144}H_{36}$ sextet benzenoids. All possible attachments of a C_6H_2 sextet unit to the second generation sextet benzenoids ($C_{138}H_{34}$) belonging to the four-sextet-isomer series gives $12 + 6 + 7 + 4 = 29$ additional isomers, for a total of $29 + 15 = 44$ $C_{144}H_{36}$ total resonant sextet benzenoids. One of these, the compound that emerges from circumscribing the permethylenyl derivative of the $C_{54}H_{24}$ in Figure 5, possesses a 1,6 H-H interaction, and is therefore not strain free. It can be identified by splicing in two hydrogens at the central location of one of the two equivalent edges having four linear sextets in the third generation member ($C_{144}H_{34}$) of the one-sextet-isomer series. Transforming the remaining 43 $C_{144}H_{36}$ total resonant sextet benzenoids to permethylenyl derivatives and circumscribing them gives 43 $C_{270}H_{48}$ sextet benzenoids. All attachments of a C_6H_2 unit to the fourth generation member ($C_{264}H_{46}$) of the same one-sextet-isomers above gives five more $C_{270}H_{48}$ sextet benzenoids. These $43 + 5 = 48$ $C_{270}H_{48}$ total resonant sextet benzenoids are the first generation members of the relevant constant-sextet-isomers series (Scheme 1).

From the examples in the prior paragraph, it should be noted that C_4H_2 benzo attachment in strictly peri-condensed benzenoids is analogous to the attachment of a C_6H_4 sextet unit in total resonant sextet benzenoids (Figure 4). Similarly, the attachment of a CH methylenyl unit in strictly peri-condensed benzenoids is analogous to the attachment of a C_6H_2 unit in total resonant sextet benzenoids (Figure 3). The presence of a cove in a strictly peri-condensed benzenoid and the presence of an *s-cis-m,m'*-quaterphenyl edge in a total resonant sextet benzenoid disqualifies such benzenoids from serving as excised internal structures (Figure 5). Also, note the congruency in symmetry among the strictly peri-condensed and total resonant sextet benzenoids in this example. From the above analogies, it is evident that the algorithm described here corresponds to the one used in the enumeration of strictly peri-condensed benzenoids.³

Topological Characteristics. The one-sextet-isomer series (Table III) that begins with benzene is unique in that it belongs to the singlet occurrence isomer class. It contains corresponding benzenoids with D_{6h} symmetry (see Figures 1 and 2 for examples of structures belonging to the various symmetry groups). Both of the other two one-sextet-isomer series, which start with biphenyl ($C_{12}H_{10}$) and dibenzo[*fg,op*]tetracene ($C_{24}H_{14}$), have D_{2h} symmetry. The constant-sextet-isomer series starting with $C_{36}H_{18}$ is unique (Figure 2). The constant-sextet-isomer series starting with $C_{54}H_{22}$ and that starting with $C_{78}H_{26}$ both have sextet benzenoids with corresponding symmetries of D_{2h} (one isomer each), C_{2v} (two isomers each), and C_s (one isomer each). The constant-sextet-isomer series starting with $C_{102}H_{30}$ is unique. Both the constant-sextet-isomer series starting with $C_{132}H_{34}$ and $C_{168}H_{38}$ have sextet benzenoids with corresponding symmetries of D_{2h} (one isomer each), C_{2v} (four isomers each), C_{2h} (two isomers each), and C_s (nine isomers each). It should be noted that these isomer numbers and symmetry distributions, which are shown in Table III, correspond exactly to those reported³ for the constant-

isomer series of even-carbon strictly peri-condensed benzenoids. Figure 2 can be compared with Figure 1 in ref 2.

The one-sextet-isomer series (Table IV) which begins with triphenylene ($C_{18}H_{12}$) is unique and has sextet benzenoids with D_{3h} symmetry. Both of the one-sextet-isomer series starting with $C_{30}H_{16}$ and $C_{48}H_{20}$ have sextet benzenoids of C_{2v} symmetry. The constant-sextet-isomer series beginning with $C_{66}H_{24}$ is unique. Both the constant-sextet-isomer series starting with $C_{90}H_{28}$ and $C_{120}H_{32}$ have sextet benzenoids with corresponding symmetries of C_{2v} (one isomer each) and C_s (three isomers each). The constant-sextet-isomer series starting with $C_{150}H_{36}$ is unique. Both the constant-sextet-isomer series starting with $C_{186}H_{40}$ and $C_{228}H_{44}$ have sextet benzenoids with corresponding symmetries of C_{2v} (four isomers each) and C_s (16 isomers each). These isomer numbers and symmetry distributions, shown in Table IV, correspond exactly to those observed for the constant-isomer series associated with odd-carbon strictly peri-condensed benzenoids.³

The constant-sextet-isomer series in Table III are totally analogous to the even-carbon constant-isomer series shown in Table I of ref 3, and the constant-sextet isomers in Table IV to the odd-carbon constant-isomer series shown in Table II of ref 3. Corresponding structures with the same isomer number in both the constant-sextet isomer and the constant-isomer series have the same symmetry distribution among their benzenoid members. The constant-sextet-isomer series in Table III have an even number of "empty" rings and those in Table IV have an odd number of "empty" rings, given by

$$r(\text{empty}) = r - r(\text{sextet}) = (1/6)(2N_c + 6 - 3N_H)$$

It has been observed previously³ that odd-carbon benzenoids did not have structures with symmetries belonging to the D_{6h} , D_{2h} , C_{6h} , or C_{2h} groups. Since the constant-sextet-isomer series in Table IV are analogous to the odd-carbon constant-isomer series, the total resonant sextet benzenoids found in Table IV cannot have symmetries belonging to the D_{6h} , D_{2h} , C_{6h} , or C_{2h} groups. It was also shown earlier⁴ that the perimeter topology of benzenoids obeyed the equation

$$-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 = 6$$

where η_0 is the number of bay regions, η_2 is the number of duo groups, η_3 is the number of trio groups, and η_4 is the number of quarto groups (cata-condensed appendages); this equation is independent of the number of solo groups, η_1 (see Figure 4 for examples of solo, duo, trio, and quarto peripheral groups). For constant-sextet-isomer benzenoids of second generation and higher constant-sextet-isomers, $\eta_4 = 0$. Thus, starting with the second generation, members of the constant-sextet-isomer series have a perimeter topology described by $-\eta_0 + \eta_2 + 2\eta_3 = 6$. Second generation benzenoid members of constant-sextet-isomer series of the same isomer number and symmetry will have the same η_1 and η_3 values, which remain constant when going to higher generations while $\Delta\eta_0 = \Delta\eta_2 = 6$ for each incrementation. In Figure 5, it should be noted that in going from a strictly peri-condensed benzenoid to a corresponding total resonant sextet benzenoid, solo groups become duo, duos become trios, and trios become quartos and N_{IC} becomes $r(\text{empty})$.

SUMMARY

This paper describes a spectacular congruency between the strictly peri-condensed benzenoid constant-isomer series and the total resonant sextet benzenoid constant-sextet-isomer series. Not only are the isomer numbers between these two benzenoids sets the same, but a one-to-one match exists in the symmetries between the corresponding benzenoid members. Cyvin and Brunvoll¹⁵ have recently developed a computerized algorithm which enumerates the essentially strain-free total

resonant sextet benzenoids, and further work is underway to understand fully the congruent relationships that exist between these two divergent and important subsets of benzenoids.

More than 16 total resonant sextet benzenoids and 16 isoskeletal analogues have been synthesized and characterized in the literature.^{1,4} Among these more stable compounds, some as large as $C_{48}H_{24}$, $C_{48}H_{22}$, and $C_{60}H_{30}$ ($C_{56}H_{26}N_4$) are represented. Should an analytical chemist determine, by GC-MS, for example, that an environmental sample contained a benzenoid with a molecular formula of $C_{54}H_{22}$, he would still be faced with determining the correct structure from a group of about 10 000 nonradical isomers. The four most stable structures from this group have in fact been identified,⁴ and targeted synthesis of these compounds may prove to be worthwhile. If the same sample contained a compound with the molecular formula $C_{54}H_{18}$, its structure would be immediately apparent because this molecular formula corresponds to the third generation of the strictly peri-condensed one-isomer series.³ Thus Table PAH6, together with these enumeration results, defines the epistemology of the field of benzenoid hydrocarbons and assists in an evaluation of how much is known and can be known about these compounds. The largest characterizable benzenoids will no doubt belong to those constant-isomer series that have just a few members.

Recently Kirby¹⁶ has corroborated our enumeration^{1,4} of total resonant sextet benzenoid isomers and this work greatly extends these earlier results. For examples of work in which

benzenoid resonant sextets are treated mainly as mathematical entities, the reader is referred to the work of Hosoya.⁶

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The Generation of Reaction Networks with RAIN. 1. The Reaction Generator[†]

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The formal program system RAIN is described. It generates the conceivable reaction paths that join known educts with known products of a chemical reaction. The reaction generator of this system is not based on known reactions but operates in a deductive manner. It is guided by a small number of constraints that describe the maximum complexity of a reaction step and introduce rules for the constitutional features of the generated intermediates. The chemical behavior of the elements considered is taken into account by means of transition tables representing the valence schemes and their allowed interconversions.

INTRODUCTION

This is the first of a series of articles concerning the program system RAIN. The acronym RAIN stands for **R**eactions **A**nd **I**ntermediates **N**etworks. RAIN¹ is a general system for the formal generation of reaction networks. The main task of RAIN is the production of *all formally possible reaction paths* that connect given starting materials and products of a chemical reaction, and comply with user-defined constraints. Depending on the chosen boundary conditions, the reaction paths can either form a network of mechanistic elementary reaction steps or a network of more complex "synthetic" reactions. For the elaboration of the reactions and their intermediates, RAIN uses neither a knowledge base (e.g., transforms²) nor a fixed set of formal transformations (e.g., a fixed set of R matrices,³ base transformations,⁴ or half reactions⁵). On the contrary, RAIN supplies the user with an extensive set of optional rules for the description of allowed

reactions and intermediates and generates within the user-defined boundary conditions a combinatorially complete set of solutions. The values of these constraints change according to the problem to be solved. They determine, e.g.,

- the maximum complexity (number of reacting atoms and bonds) of a reaction step
- the atomic valence schemes of the intermediates (and their interconvertibility)
- constitutional properties of the intermediates (rings, etc.)

In essence, RAIN consists of a formal reaction generator and a network management system. The reaction generator produces for a given molecule those structures that may be obtained by a chemical reaction from the molecule considered under the given boundary conditions. All generated reactions and intermediates are stored in a network file. Analogously, the reaction generator of RAIN can produce all conceivable precursors of a molecule. The successive application of this procedure to "both ends" of a chemical reaction or sequence of reactions leads to two growing "trees" of reaction pathways,

[†] Dedicated to the 60th birthday of Prof. I. Ugi.