

Studies in Deciphering the Information Content of Chemical Formulas: A Comprehensive Study of Fluorenes and Fluoranthenes

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Received August 16, 1991

By use of a formula periodic table, the aufbau principle, and the excised internal structure concept an important subset of fluorenes and fluoranthenes are enumerated. Constant-isomer series for these compounds are presented for the first time. These results illustrate the generality of the previously developed algorithm and associated concepts. These results are summarized within the background of known fluorene-related heterocycles and fluoranthene hydrocarbons. Structural/theoretical properties of these compounds are detailed.

INTRODUCTION

Since fluoranthene-related polycyclic hydrocarbons represent an important subgroup of pyrolytic pollutants,¹⁻⁶ the enumeration of these isomers is the subject of this investigation. A formula periodic table for fluorenes/fluoranthenes-related hydrocarbons and an algorithm for enumerating fluorenoids/fluoranthenoids having a single pentagonal ring among otherwise hexagonal ones are presented. In our previous work on the enumeration of polycyclic conjugated polyene isomers of benzenoids with different ring sizes, it was shown that the maximum number of pentagonal rings in addition to hexagonal ones was given by $r_{5\max} = N_{1c}(\text{PAH6})$.^{7,8} Thus, cata-condensed benzenoids are incapable of having isomers composed of only pentagonal and hexagonal rings. Fluorenoid/fluoranthenoid constant-isomer series are presented for the first time. The formula periodic table for fluorenoids/fluoranthenoids [Table PAH5,6(F/F)] and enumeration studies provide the framework for understanding the limits of what we do know and can know about fluoranthenoid hydrocarbons. Thus, this epistemology also represents an important aspect of the results reported herein.

Over 70 fluoranthenoid hydrocarbons that are isomeric to benzenoids have been either synthesized or identified in the environment.⁸ Fluoranthenoid hydrocarbons that are not isomeric to benzenoids will be of principal interest in this work. Many representatives of this group have been reported.¹⁻⁶ Also, heterocyclic isoskeletal analogues of fluorenoids will be discussed.

It has been shown that corannulene ($\text{C}_{20}\text{H}_{10}$) with its central pentagonal ring and C_{5v} symmetry is bowl-shaped.⁹ In general, fluoranthenoids are expected to be strained and nonplanar. Fluoranthenoids are predominantly formed at lower combustion temperatures.³

It well known that as the number of carbons increases the number of alkane isomers increases. We have shown that there are special benzenoid series where the number of isomers remain constant as the number of carbons increases; these are called constant-isomer benzenoid series.^{10,11} Herein, it will be shown that there exist constant-isomer fluorenoid/fluoranthenoid series.

Our general approach to enumeration of polycyclic aromatic hydrocarbons involves constructing an appropriate formula periodic table and using the aufbau principle and the excised internal structure concept to enumerate the isomers found on the edges of the corresponding formula periodic tables. In this way, we have successfully enumerated even and odd carbon benzenoids having unique characteristics. In both cases, constant-isomer series have been found where the isomer numbers alternate between singlet and doublet occurrence and there exists a one-to-one matching in the symmetries between

the member compounds having the same isomer numbers. The isomer numbers have the same sequence of values between the strictly peri-condensed and the total resonance sextet subsets and between the monoradical, diradical, triradical, etc. subsets. No unique characteristics were found for circulene (coronoids) benzenoids,¹⁰ and the results reported herein for fluorenoids and fluoranthenoids with one pentagonal ring has again led to the identification of constant-isomer series where the isomer numbers alternate between single and pairwise occurrence with a one-to-one matching in the symmetries of the member compounds having the same isomer number.

RESULTS AND DISCUSSION

Terminology. In this work, conjugated polycyclic hydrocarbons having a single pentagonal ring fused to hexagonal ones are generally called *fluorenoids* if they possess an odd number of carbons and *fluoranthenoids* if they possess an even number of carbons. Herein a fluorenoid/fluoranthenoid structure is represented by a molecular graph in which all the C and H atoms and C-H and π bonds are omitted leaving only the C-C σ -bond skeleton having only second- and third-degree vertices where every vertex in the molecular graph corresponds to a carbon atom. A strictly peri-condensed fluorenoid/fluoranthenoid has no cata-condensed appendages or disconnected internal third-degree vertices. Acenaphthylene (C_{12}H_8) is a strictly peri-condensed fluoranthenoid whereas fluoranthene, an isomer of pyrene, is not. An excised internal structure of a fluorenoid/fluoranthenoid consists of all its connected internal third-degree vertices that remain after stripping off all the peripheral second- and third-degree vertices. Acenaphthylene has methyl as its excised internal structure. Since methyl is incapable of having isomers, acenaphthylene has no other fluoranthenoid isomer since it has only one arrangement of its internal third-degree vertices. Similarly, corannulene ($\text{C}_{20}\text{H}_{10}$) is a strictly peri-condensed fluoranthenoid with cyclopentadienyl as its excised internal structure (Figure 1). Since cyclopentadienyl is incapable of having other isomers within the pentagonal/hexagonal ring constraint, corannulene has no other fluoranthenoid isomer.

N_c , N_H , N_{1c} , and d_s give the number of carbons, hydrogens, internal third-degree carbon vertices, and net disconnections of the internal edges, respectively. For example, corannulene (Figure 1) has $N_c = 20$, $N_H = 10$, $N_{1c} = 5$, and $d_s = -1$ where the minus sign in the latter is a negative disconnection (connection) associated with the formation of a ring by the excised internal structure.

Formula Periodic Table for Fluorenoids/Fluoranthenoids. A periodic table set is defined as a partially ordered set (poset) forming a two-dimensional array, which complies with the triad principle where a central element has a metric property that

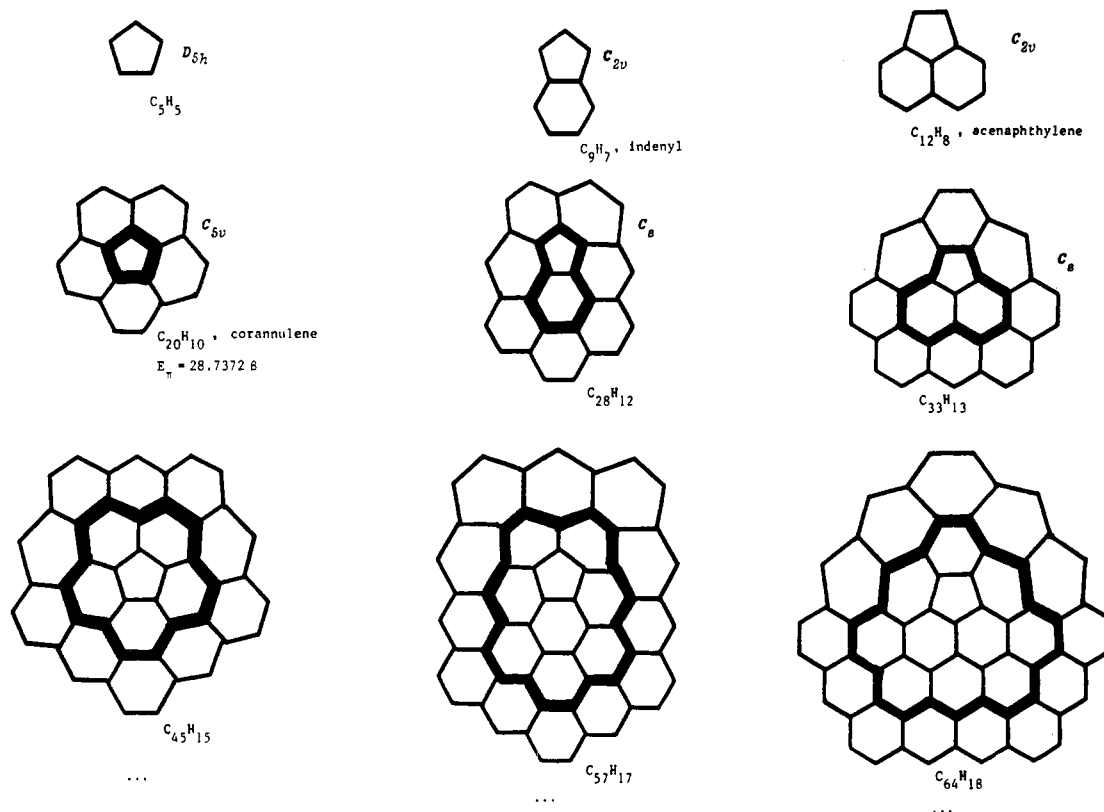


Figure 1. Fluorenoïd/fluoranthenoïd one-isomer series with their excised internal structures shown in bold.

is the arithmetic mean of two adjacent surrounding member elements. Both the periodic table of elements and the formula periodic tables are sets that obey this definition. Key features of this construction are hierarchal ordering, two-dimensionality, and edge effects. By edge effects we mean that set members located on the edge or two-dimensional boundary possess properties that are more exceptional relative to the other set members.¹¹ The constant-isomer series which have formulas on the edge of our formula periodic tables are illustrative of what we call an edge effect.

The formula periodic table for fluorenoïds/fluoranthenoïds [Table PAH5,6(F/F)] can be arranged in two different formats, shown in Tables I and II. Table I is in *index order* and Table II is in *hierarchical order*. When Table PAH5,6(F/F) is arranged in the index order format, it is referred to as Table PAH5,6(F/F)' (Table I). The advantage of the index order version is that it facilitates chemical literature searching since it orders the formulas according to the Hill system. As it will be seen in the next paragraph, the index order version also allows one to more readily identify its recursion pattern.

The formula periodic table for fluorenoïds/fluoranthenoïds was constructed as follows. As with previous periodic table sets, the one-isomer series will play a key role in this construction.¹² To obtain preliminary fluoranthenoïd even-carbon formulas, subtract one C and one H from the boundary formulas of the odd-carbon benzenoids in Table PAH6(odd). For example, the odd-carbon formula $C_{13}H_9$ for phenalenyl becomes $C_{12}H_8$, which corresponds to acenaphthylene. To obtain preliminary fluorenoïd odd-carbon formulas, subtract one C and H from the boundary formulas of the even-carbon benzenoids in Table PAH6. For example, the even-carbon formulas of $C_{10}H_8$ for naphthalene becomes C_9H_7 , which corresponds to indenyl. Note that cyclopentadienyl (C_5H_5) is not included and is regarded as having provisional status in our treatment. The formulas thus obtained are now augmented by the add-on formulas corresponding to the constant-isomer fluorenoïd/fluoranthenoïd series. This is done by noting that one needs to only know the one-isomer and

two-isomer series (Table III) for construction of Table II. For example, in the first construction step it was determined that the preliminary formulas for Table I are

N_c	N_H
...	...
58	18-30
60	20-32
62	20-32
64	20-34
66	20-34
...	...

But in the second construction step, it was found that dicircum(21,31)acenaphthylene ($C_{64}H_{18}$) has $N_H = 18$ leading to

N_c	N_H
...	...
58	18-30
60	20-32
62	20-32
64	→18-34
66	20-34
...	...

Since the leading N_H values must be identical from $N_c = 58$ to $N_c = 64$, the final form of Table I must be

N_c	N_H
...	...
58	18-30
60	→18-32
62	→18-32
64	→18-34
66	20-34
...	...

where the left arrow marks the N_H values of the constant-isomer series. In this way all the formulas in Table PAH5,6(F/F) can be deduced.

To further illustrate this algorithmic construction, subtract a CH from the relevant C_{40} , C_{42} , C_{44} , C_{46} , and C_{48} formulas in Table I found in the last citation of ref 12. This gives the following preliminary listing

N_c	N_H
...	...
39	15-21
41	15-23
43	17-23
45	17-25
47	17-25
...	...

From circum(25)corannulene ($C_{45}H_{15}$) in Table III (Figure 1), we obtain the next listing of

N_c	N_H
...	...
39	15-21
41	15-23
43	17-23
45	→15-25
47	17-25
...	...

Since the leading N_H values from $N_c = 41$ to $N_c = 45$ must be identical, the listing becomes

N_c	N_H
...	...
39	15-21
41	15-23
43	→15-23
45	→15-25
47	17-25
...	...

This is all that is needed to complete this section of Table II. However, a search of Table III shows that $C_{41}H_{15}$ is the first generation formula of the 17-isomer series. Thus, the final form of this section of Table I must be

N_c	N_H
...	...
39	15-21
41	→15-23
43	→15-23
45	→15-25
47	17-25
...	...

From these examples, it should be evident that Table I has alternating sections of leading N_H values with and without stacks of arrows. In each stack, the lower arrow always corresponds to a one-isomer or two-isomer series, the arrows immediately above are automatically filled in as one augments the N_H values in the second construction stage, and the arrows above this must be determined from higher constant-isomer series. But this latter stage is not necessary for the construction of Table II.

Table II has (x,y) -coordinates of (d_s, N_{Ic}) where $d_s + N_{Ic} = r - 2$. In general, fluorenoids have $N_{Ic} = 0, 2, 4, \dots$ and fluoranthenoids have $N_{Ic} = 1, 3, 5, \dots$. A formula table for all polycyclic conjugated polyenes with only pentagonal and hexagonal rings (Table PAH₅) has been published, and the even-carbon formulas in Table PAH_{5,6}(F/F) is a subset of it (compare with Table IV in ref 7). The formulas in Table II below and to the right of the dashed line correspond to fluorenoids/fluoranthenoids that are isomeric to benzenoids; the formulas above and to the left of this dashed line correspond to structures which must have (at least) one pentagonal ring in addition to hexagonal ones.

All structures having formulas in the same row of Table II have the same N_{Ic} values, and all structures having formulas in the same column have the same d_s values. All cata-condensed fluorenoids ($N_{Ic} = 0$) have Hamiltonian circuits (a one component two-factor subgraph spanning all the vertices). Fluorenoids have even N_{Ic} values with two-factor subgraphs occurring with an odd number of components for rows where $N_{Ic} \equiv 0 \pmod{4}$. Fluoranthenoids have odd N_{Ic} values with two-factor subgraphs occurring with an odd number of com-

Table I. All Formulas Corresponding to Fluoranthenoids (Even Carbon) and Fluorenoids (Odd Carbon)

N_c	N_H^a	N_c	N_H^b
12	→8 ^c	9	→7 ^c
16	10	13	9
18	→10	15	→9
20	→10-12	17	11
22	12	19	11
24	12-14	21	11-13
26	→12-14	23	→11-13
28	→12-16	25	13-15
30	14-16	27	13-15
32	14-18	29	13-17
34	14-18	31	→13-17
36	→14-20	33	→13-19
38	→14-20	35	15-19
40	16-22	37	15-21
42	16-22	39	15-21
44	16-24	41	→15-23
46	→16-24	43	→15-23
48	→16-26	45	→15-25
50	→16-26	47	17-25
52	18-28	49	17-27
54	18-28	51	17-27
56	18-30	53	→17-29
58	18-30	55	→17-29
60	→18-32	57	→17-31
62	→18-32	59	19-31
64	→18-34	61	19-33
66	20-34	63	19-33
68	20-36	65	19-35
70	20-36	67	→19-35
72	20-38	69	→19-37
74	→20-38	71	→19-37
76	→20-40	73	21-39
78	→20-40	75	21-39
80	→20-42	77	21-41
82	22-42	79	21-41
84	22-44	81	21-43
86	22-44	83	→21-43
88	22-46	85	→21-45
90	→22-46	87	→21-45
92	→22-48	89	23-47
94	→22-48	91	23-47
96	→22-50	93	23-49
98	24-50	95	23-49
100	24-52	97	23-51
102	24-52	99	→23-51
104	24-54	101	→23-53
106	24-54	103	→23-53
108	→24-56	105	→23-55
110	→24-56	107	25-55
112	→24-58
114	→24-58
...

^aRange of successive even numbers. ^bRange of successive odd numbers. ^cAn arrow to the left marks the formulas of the constant-isomer series.

ponents for rows where $N_{Ic} \equiv 3 \pmod{4}$.

Enumeration of Fluorenoids/Fluoranthenoids. Two problems common to most isomer enumerations are the enormous number of possible structures corresponding to the molecular formulas of all but the smallest molecules and the duplicated structure problem which attends the generation process. It is important to note that for a polycyclic aromatic hydrocarbon to serve as an excised internal structure it should be devoid of two or more proximate bay regions.

If a strictly per-condensed fluorenoid/fluoranthenoid has N_c' carbons and N_H' hydrogens and its excised internal structure has N_c carbons and N_H hydrogens, then $N_c' = N_c + 2N_H + 5$ and $N_H' = N_H + 5$ represent useful recursion relationships for obtaining successive strictly peri-condensed fluorenoid/fluoranthenoid formulas. Using these recursions, one can extend the formulas for the constant-isomer fluor- enoid/fluoranthenoid series given in Table III. Note that these

Table II. Formula Periodic Table for Fluorenoïd/Fluoranthenoïd Hydrocarbons [Table PAH5,6(F/F)]

$d_3 = -10$	$d_3 = -9$	$d_3 = -8$	$d_3 = -7$	$d_3 = -6$	$d_3 = -5$	$d_3 = -4$	$d_3 = -3$	$d_3 = -2$	$d_3 = -1$	$d_3 = 0$	$d_3 = 1$	$d_3 = 2$...	N_{IC}
										C_9H_7	$C_{13}H_9$	$C_{17}H_{11}$...	3
										$C_{12}H_8$	$C_{16}H_{10}$	$C_{20}H_{12}$...	4
										$C_{15}H_9$	$C_{19}H_{11}$	5
										$C_{18}H_{10}$	$C_{22}H_{12}$	6
										$C_{21}H_{11}$	$C_{25}H_{13}$	7
										$C_{26}H_{14}$	$C_{30}H_{16}$	8
										$C_{29}H_{15}$	$C_{33}H_{17}$	9
										$C_{32}H_{16}$	$C_{36}H_{18}$	10
										$C_{35}H_{17}$	$C_{39}H_{19}$	11
										$C_{38}H_{18}$	$C_{42}H_{20}$	12
										$C_{41}H_{19}$	$C_{45}H_{21}$	13
										$C_{44}H_{20}$	$C_{48}H_{22}$	14
										$C_{47}H_{21}$	$C_{51}H_{23}$	15
										$C_{50}H_{22}$	$C_{54}H_{24}$	16
										$C_{53}H_{23}$	$C_{57}H_{25}$	17
										$C_{56}H_{24}$	$C_{60}H_{26}$	18
										$C_{59}H_{25}$	$C_{63}H_{27}$	19
										$C_{62}H_{26}$	$C_{66}H_{28}$	20
										$C_{65}H_{27}$	$C_{69}H_{29}$	21
										$C_{68}H_{28}$	$C_{72}H_{30}$	22
										$C_{71}H_{29}$	$C_{75}H_{31}$	23
										$C_{74}H_{30}$	$C_{78}H_{32}$	24
										$C_{77}H_{31}$	$C_{81}H_{33}$	25
										$C_{80}H_{32}$	$C_{84}H_{34}$	26
										$C_{83}H_{33}$	$C_{87}H_{35}$	27
										$C_{86}H_{34}$	$C_{90}H_{36}$	28
										$C_{89}H_{35}$	$C_{93}H_{37}$	29
										$C_{92}H_{36}$	$C_{96}H_{38}$	30
										$C_{95}H_{37}$	$C_{99}H_{39}$	31
										$C_{98}H_{38}$	$C_{102}H_{40}$	32
										$C_{101}H_{39}$	$C_{105}H_{41}$	33
										$C_{104}H_{40}$	$C_{108}H_{42}$	34
										$C_{107}H_{41}$	$C_{111}H_{43}$	35
										$C_{110}H_{42}$	$C_{114}H_{44}$	36
										$C_{113}H_{43}$	$C_{117}H_{45}$	37
										$C_{116}H_{44}$	$C_{120}H_{46}$	38
										$C_{119}H_{45}$	$C_{123}H_{47}$	39
										$C_{122}H_{46}$	$C_{126}H_{48}$	40
										$C_{125}H_{47}$	$C_{129}H_{49}$	41
										$C_{128}H_{48}$	$C_{132}H_{50}$	42
										$C_{131}H_{49}$	$C_{135}H_{51}$	43
										$C_{134}H_{50}$	$C_{138}H_{52}$	44
										$C_{137}H_{51}$	$C_{141}H_{53}$	45
										$C_{140}H_{52}$	$C_{144}H_{54}$	46
										$C_{143}H_{53}$	$C_{147}H_{55}$	47
										$C_{146}H_{54}$	$C_{150}H_{56}$	48
										$C_{149}H_{55}$	$C_{153}H_{57}$	49
										$C_{152}H_{56}$	$C_{156}H_{58}$	50
										$C_{155}H_{57}$	$C_{159}H_{59}$	51
										$C_{158}H_{58}$	$C_{162}H_{60}$	52
										$C_{161}H_{59}$	$C_{165}H_{61}$	53
										$C_{164}H_{60}$	$C_{168}H_{62}$	54
										$C_{167}H_{61}$	$C_{171}H_{63}$	55
										$C_{170}H_{62}$	$C_{174}H_{64}$	56
										$C_{173}H_{63}$	$C_{177}H_{65}$	57
										$C_{176}H_{64}$	$C_{180}H_{66}$	58
										$C_{179}H_{65}$	$C_{183}H_{67}$	59
										$C_{182}H_{66}$	$C_{186}H_{68}$	60
										$C_{185}H_{67}$	$C_{189}H_{69}$	61
										$C_{188}H_{68}$	$C_{192}H_{70}$	62
										$C_{191}H_{69}$	$C_{195}H_{71}$	63
										$C_{194}H_{70}$	$C_{198}H_{72}$	64
										$C_{197}H_{71}$	$C_{201}H_{73}$	65
										$C_{200}H_{72}$	$C_{204}H_{74}$	66
										$C_{203}H_{73}$	$C_{207}H_{75}$	67
										$C_{206}H_{74}$	$C_{210}H_{76}$	68
										$C_{209}H_{75}$	$C_{213}H_{77}$	69
										$C_{212}H_{76}$	$C_{216}H_{78}$	70
										$C_{215}H_{77}$	$C_{219}H_{79}$	71
										$C_{218}H_{78}$	$C_{222}H_{80}$	72
										$C_{221}H_{79}$	$C_{225}H_{81}$	73
										$C_{224}H_{80}$	$C_{228}H_{82}$	74
										$C_{227}H_{81}$	$C_{231}H_{83}$	75
										$C_{230}H_{82}$	$C_{234}H_{84}$	76
										$C_{233}H_{83}$	$C_{237}H_{85}$	77
										$C_{236}H_{84}$	$C_{240}H_{86}$	78
										$C_{239}H_{85}$	$C_{243}H_{87}$	79
										$C_{242}H_{86}$	$C_{246}H_{88}$	80
										$C_{245}H_{87}$	$C_{249}H_{89}$	81
										$C_{248}H_{88}$	$C_{252}H_{90}$	82
										$C_{251}H_{89}$	$C_{255}H_{91}$	83
										$C_{254}H_{90}$	$C_{258}H_{92}$	84
										$C_{257}H_{91}$	$C_{261}H_{93}$	85
										$C_{260}H_{92}$	$C_{264}H_{94}$	86
										$C_{263}H_{93}$	$C_{267}H_{95}$	87
										$C_{266}H_{94}$	$C_{270}H_{96}$	88
										$C_{269}H_{95}$	$C_{273}H_{97}$	89
										$C_{272}H_{96}$	$C_{276}H_{98}$	90
										$C_{275}H_{97}$	$C_{279}H_{99}$	91
										$C_{278}H_{98}$	$C_{282}H_{100}$	92
										$C_{281}H_{99}$	$C_{285}H_{101}$	93
										$C_{284}H_{100}$	$C_{288}H_{102}$	94
										$C_{287}H_{101}$	$C_{291}H_{103}$	95
										$C_{290}H_{102}$	$C_{294}H_{104}$	96
										$C_{293}H_{103}$	$C_{297}H_{105}$	97
										$C_{296}H_{104}$	$C_{300}H_{106}$	98
										$C_{299}H_{105}$	$C_{303}H_{107}$	99
										$C_{302}H_{106}$	$C_{306}H_{108}$	100

recursions and constant-isomer series alternate from odd-carbon/hydrogen to even-carbon/hydrogen formulas, and this is why we refer to these systems as fluorenoïd/fluoranthenoïd series. The number rings is given by $r = (1/2)(N_c + 2 - N_H)$, and this is a useful equation for checking the conformance of the isomeric structures being generated via the algorithm presented herein.

In general, all fluorenoïd/fluoranthenoïd isomers with $N_{IC} < 5$ can be generated by taking all combinatorial hexagonal-to-pentagonal ring contractions of all benzenoid isomers having one more CH. To obtain fluorenoïd/fluoranthenoïd isomers with formulas on protrusive locations of the left-hand zigzag edge of Table II, one must use the excised internal structure concept. The C_4H_2 aufbau process is additionally required for formulas having fluorenoïd/fluoranthenoïd formulas to their left with structures which have $N_{IC} \geq 5$. We will now fully illustrate this algorithm in the following paragraphs.

To generate all cata-condensed fluorenoïds ($N_{IC} = 0$), one takes all combinatorial attachments of C_4H_2 units to the immediately prior set of cata-condensed fluorenoïds. Alternatively, add a CH to the target formula of the cata-condensed fluorenoïd which gives the formula of a cata-condensed benzenoid. To the corresponding benzenoid isomer set, take all combinatorial contractions of their distinct hexagonal rings possessing at least one second-degree vertex to pentagonal rings. In either process, duplicates are discarded to obtain the relevant isomer set of cata-condensed fluorenoïds.

The excised internal structure concept was used to generate the one-isomer fluorenoïd/fluoranthenoïd series (Figure 1) starting with cyclopentadienyl (C_5H_5), indenyl (C_9H_7), and acenaphthylene ($C_{12}H_8$). A combination of hexagonal-to-pentagonal ring contraction and the excised internal structure concept was used to generate the other constant-isomer fluorenoïd/fluoranthenoïd series. In fact, the one-isomer series starting with $C_{12}H_8$ can be regarded as being generated from the ultimate excised internal structure of methyl where one of the three equivalent perimeter rings in phenalenyl is contracted to a pentagonal one. Similarly, the next smallest excised internal of ethene gives pyrene, which has two distinct rings in which each in turn is contracted to give the two strictly

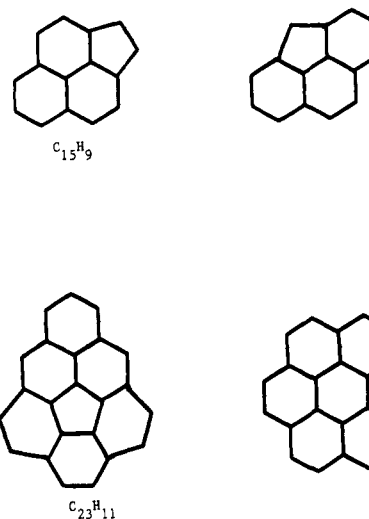


Figure 2. First generation members of the two-isomer fluorenoïd/fluoranthenoïd constant-isomer series.

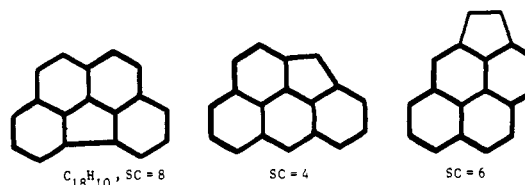


Figure 3. First generation members of the three-isomer fluorenoïd/fluoranthenoïd constant-isomer series.

peri-condensed fluorenoïd isomers of $C_{15}H_9$, which are the base members (first generation) of the corresponding two-isomer series (Figure 2). Allyl is the excised internal structure of dibenzo[def,jk]phenanthryl ($C_{19}H_{11}$), and the contraction of each of its three distinct rings leads to the three-isomer series commencing with $C_{18}H_{10}$ (Figure 3).

The number of fluorenoïd/fluoranthenoïd isomers corresponding to the constant-isomer benzenoids can be generated as follows. Note first that cata-condensed benzenoids have no fluorenoïd/fluoranthenoïd isomers.⁷ Consider phenalenyl of formula $C_{13}H_9$. Adding one CH to $C_{13}H_9$ gives $C_{14}H_{10}$

Table III. Fluorenoid/Fluoranthenoid Constant-Isomer Series

series ^a	no. of isomers	symmetry distribution ^b
(C ₅ H ₅) C ₂₀ H ₁₀ C ₄₅ H ₁₅ ...	1	D _{5h}
C ₉ H ₇ C ₂₈ H ₁₂ ...	1	C _{2v}
C ₁₂ H ₈ C ₃₃ H ₁₃ ...	1	C _{2v}
C ₁₅ H ₉ C ₃₈ H ₁₄ ...	2	C _{2v} (2)
C ₁₈ H ₁₀ C ₄₃ H ₁₅ ...	3	C _{2v} , C _s (2)
C ₂₃ H ₁₁ C ₅₀ H ₁₆ ...	2	C _{2v} (2)
C ₂₆ H ₁₂ C ₅₅ H ₁₇ ...	7	C _{2v} (3), C _s (4)
C ₃₁ H ₁₃ C ₆₂ H ₁₈ ...	7	C _{2v} (3), C _s (4)
C ₃₆ H ₁₄ C ₆₉ H ₁₉ ...	9	C _{2v} (3), C _s (6)
C ₄₁ H ₁₅ C ₇₆ H ₂₀ ...	17	C _{2v} (4), C _s (13)
C ₄₈ H ₁₆ C ₈₅ H ₂₁ ...	9	C _{2v} (3), C _s (6)
C ₅₃ H ₁₇ C ₉₂ H ₂₂ ...	31	C _{2v} (5), C _s (26)
C ₆₀ H ₁₈ C ₁₀₁ H ₂₃ ...	31	C _{2v} (5), C _s (26)
C ₆₇ H ₁₉ C ₁₁₀ H ₂₄ ...	41	C _{2v} (4), C _s (37)
C ₇₄ H ₂₀ C ₁₁₉ H ₂₅ ...	72	C _{2v} (9), C _s (63)
C ₈₃ H ₂₁ C ₁₃₀ H ₂₆ ...	41	C _{2v} (4), C _s (37)
C ₉₀ H ₂₂ C ₁₃₉ H ₂₇ ...	120	C _{2v} (9), C _s (111)
C ₉₉ H ₂₃ C ₁₅₀ H ₂₈ ...	120	C _{2v} (9), C _s (111)

^aTo obtain successive formulas in any series use these recursions: $N'_c = N_c + 2N_H + 5$ and $N'_H = N_H + 5$. ^bSymmetry classification assumes planar molecular graphs.

which corresponds to anthracene/phenanthrene. Take all combinatorial contractions (removal of one second-degree vertex) of the hexagonal rings associated with anthracene/phenanthrene; this gives benzo[e]indanyl, benzo[f]indanyl, and fluorenyl (C₁₃H₉ in Figure 4). Consider pyrene of formula C₁₆H₁₀. Adding one CH gives C₁₇H₁₁ which corresponds to benzo[a]phenalenyl (benzo[de]anthryl) having four different hexagonal rings. Contracting each one of these four different hexagonal rings in turn gives four different C₁₆H₁₀ fluorenoids shown in Figure 4. The dibenzo[def,jk]phenanthryl formula of C₁₉H₁₁ gives C₂₀H₁₂ upon adding one CH which corresponds to benzo[a]pyrene, benzo[e]pyrene, and perylene. Both benzo[e]pyrene and perylene have one hexagonal ring without any second-degree vertices that cannot be contracted to pentagonal

rings. Contracting the remaining nine distinct hexagonal rings to benzo[a]pyrene, benzo[e]pyrene, and perylene lead to nine different fluorenoids shown in Figure 4. The coronene formula of C₂₄H₁₂ gives C₂₅H₁₃ upon adding one CH which corresponds to three odd-carbon benzenoids that collectively have 18 distinct hexagonal rings, two of which have no second-degree vertices for contracting to pentagonal rings. Contracting these 16 hexagonal rings leads to 16 fluoranthenoid isomers of coronene (Figure 5). One additional isomer is obtained by attaching a C₄H₂ benzo appendage to the one-isomer fluorenoid/fluoranthenoid series C_{5v} C₂₀H₁₀ member leading to a grand total of 17 fluoranthenoid isomers of coronene. This should be compared with the 12 fluoranthenoid isomers given by Schmidt and co-workers.³

Trimethylenemethane diradical and *s-cis*- and *s-trans*-1,3-butadiene are the excised internal structures of triangulene, benzo[ghi]perylene, and anthanthrene (C₂₂H₁₂), respectively. Triangulene has two distinct rings, and both benzo[ghi]perylene and anthanthrene each have three distinct rings. Contraction of each of these 2 + 3 + 3 = 8 distinct hexagonal rings in C₂₂H₁₂ to pentagonal ones leads to eight C₂₁H₁₁ fluorenoid isomers. Fulvene and benzene are C₆H₆ isomers and circumscribing them with a perimeter of 17 carbon atoms and incrementing with 5 H's gives two C₂₃H₁₁ isomers (Figure 2); the first isomer derives directly from fulvene and has a centrally located pentagonal ring, and the second isomer derives by having one of the outer rings contracted to a pentagonal one during the circumscribing process. In a similar fashion, the seven isomers of both C₂₆H₁₂ and C₃₁H₁₃ and nine isomers of C₃₆H₁₄ and C₄₈H₁₆ were generated (Figures 6–9).

All isomers with pentagonal rings on the perimeter are obtained by all combinatorial hexagonal-to-pentagonal ring contractions of strictly peri-condensed benzenoids with one more CH, and all isomers with inner pentagonal rings are obtained from the excised internal structure concept. Thus, the above algorithm is complete and using prior benzenoid enumeration results, this algorithm will generate all possible fluorenoid/fluoranthenoid isomers. By use of this algorithm, the results in Table III were obtained.

All combinatorial hexagonal-to-pentagonal ring contractions of previously enumerated benzenoids necessarily lead to larger isomer sets. Also, Table II shows that a greater range of formulas exist for fluorenoids/fluoranthenoids than for benzenoids. Thus, one must conclude that far more fluorenoids/fluoranthenoids than benzenoids are structurally possible. The fact that fewer fluoranthenoids than benzenoids are known⁸ is suggestive that there may be a fundamental reason for this disparity.

As one goes from left to right along a row in Table II, the number of fluorenoid/fluoranthenoid isomers increases. Similarly, as one goes down in a column in Table II, the number of isomers increases. Thus, the fluorenoid/fluoranthenoid isomer numbers given in this paper can be used to obtain lower bounds for many other formulas in Table II.

Topological Characteristics. As it is evident from Table III and Figures 1–3 and 6–9, the constant-isomer fluorenoid/fluoranthenoid series with the same isomer numbers exhibit a one-to-one matching in the symmetry distribution of their fluorenoid/fluoranthenoid membership. Planar cyclopentadienyl (C₅H₅) has D_{5h} symmetry but its bowl-shaped circumscribed successor, corannulene, has C_{5v} symmetry. If the pentagonal ring did not induced curvature into the fluorenoids/fluoranthenoids, then the molecules with C_s and C₁ symmetries would have been C_{2v} and C_s, respectively, for the corresponding planar systems. The fluorenoid/fluoranthenoid isomers with C₁ symmetry will consist of enantiomeric pairs. The importance of stereochemistry in benzenoid systems has been emphasized in a recent paper by Herndon and is

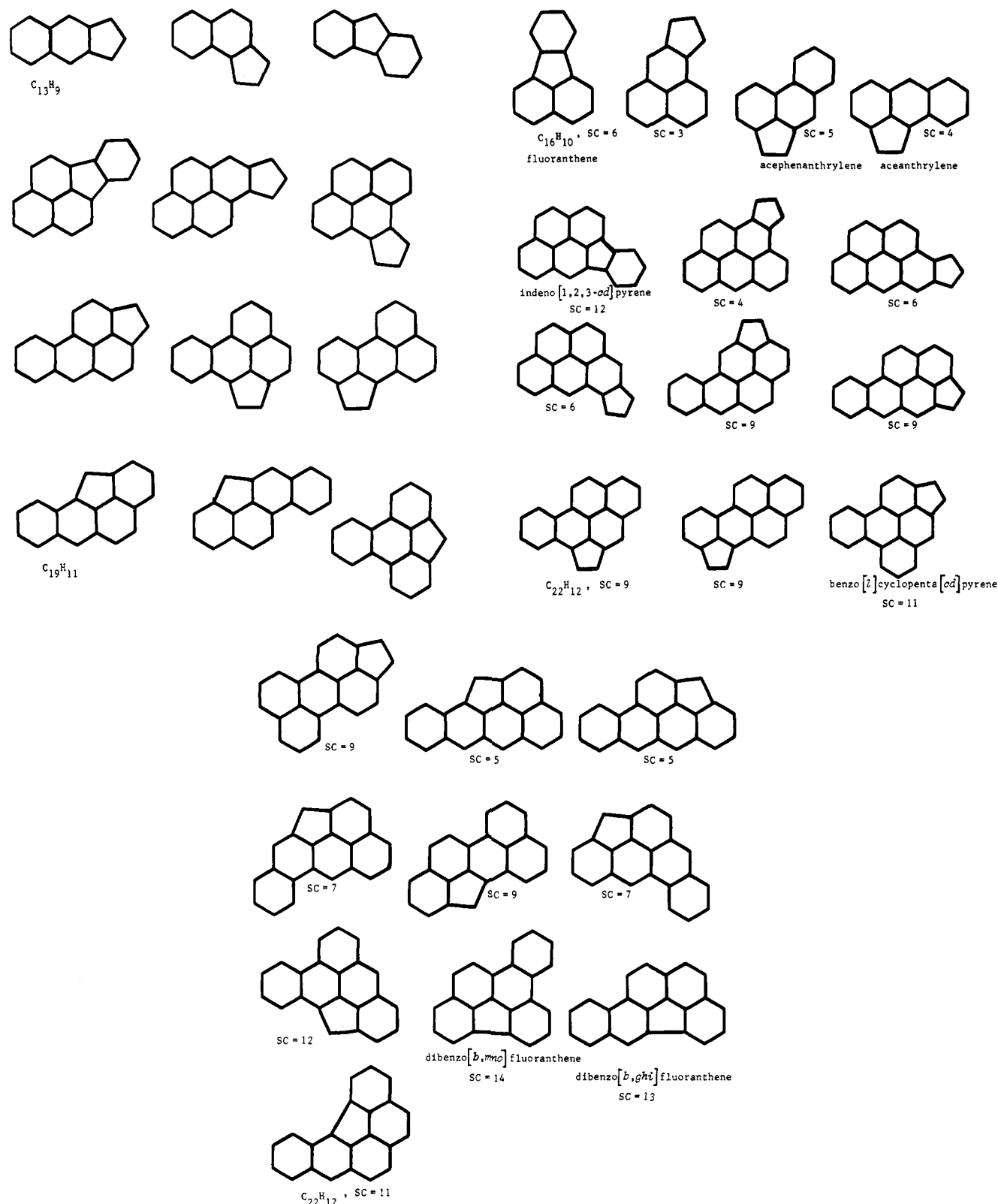


Figure 4. Some common fluorenoid ($C_{13}H_9$ and $C_{19}H_{11}$) and fluoranthene ($C_{16}H_{10}$ and $C_{22}H_{12}$) isomers.

relevant to fluorenoid/fluoranthene isomers.¹⁰

Because the energy barrier for inversion and the extent of the depth of this bowl region for large fluorenoids/fluoranthene isomers where the strain can be significantly dissipated are unknown, we chose to give the symmetry group classification for these systems assuming that they are planar. Thus, what is given in Table III is the symmetry group classification of the planar molecular graph corresponding to fluorenoid/fluoranthene hydrocarbons. Note that the repeating pattern for the isomer number sequence in Table III is ...aabcb.... This

means that there are twice as many pairwise occurring isomer number sets as there are single occurring ones. For constant-isomer benzenoid series, there are as many pairwise occurring isomer number sets as single occurring ones.

The perimeter topology of fluorenoids/fluoranthene is described by $-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 = 5$ where η_0 , η_2 , η_3 , and η_4 are the number of bay, duo, trio, and quarto regions, respectively.

Literature Examples of Fluorenoids/Fluoranthene. In a study of ions and charged soot particles in hydrocarbon flames,

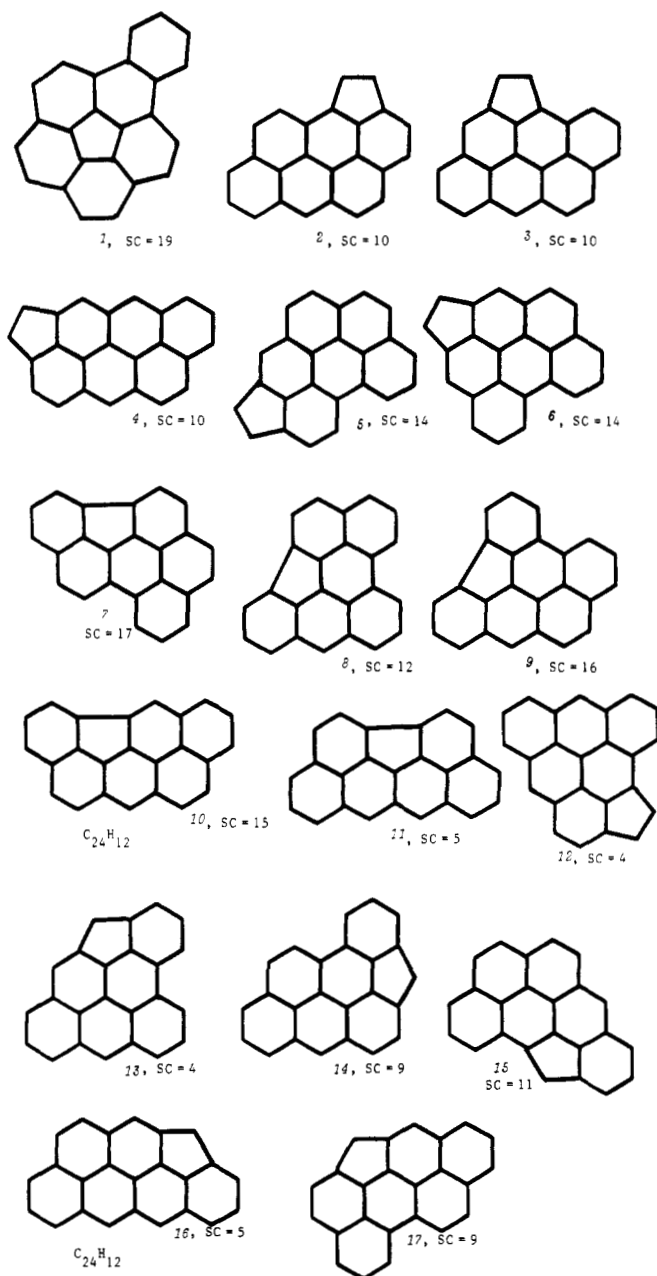


Figure 5. Fluoranthenoid isomers of coronene.

positive ions up to approximately 600 Da were analyzed by means of a time-of-flight mass spectrometer.¹ Odd-carbon fluorene ($C_9H_7^+ - 1$, $C_{15}H_9^+ - 2$, $C_{21}H_{11}^+ - 8$, $C_{23}H_{11}^+ - 2$, $C_{35}H_{15}^+ - 58$, $C_{41}H_{15}^+ - 17$) and protonated even-carbon fluoranthene ions ($C_{12}H_9^+ - 1$, $C_{18}H_{11}^+ - 3$, $C_{20}H_{11}^+ - 1$, $C_{26}H_{13}^+ - 7$, $C_{34}H_{15}^+ - 34$, $C_{36}H_{15}^+ - 9$, $C_{38}H_{15}^+ - 2$) that are not isomeric to benzenoids were detected. GC/MS was used to identify acenaphthalene ($C_{12}H_8$), benzo[ghi]fluoranthene, and cyclopenta[cd]pyrene ($C_{18}H_{10}$) that formed during combustion of heavy oils.² In the LC and MS analysis of carbon black extracts, one component having a mass of 324 ($C_{26}H_{12}$) was detected and corresponds to seven fluoranthene isomers with cyclopenta[bc]coronene and pyreno[3,4,5,6-fghi]fluoranthene being the most probable structures.⁶

In a previous analytical study of hard-coal flue gas, 53 $C_{24}H_{14}$ fluoranthene isomers were discussed.³ Only 11 of these isomers have been synthesized. In addition, this seminal paper presented theoretical HMO data on 12 of the 17 possible fluoranthene isomers of coronene (Figure 5) in an attempt to characterize four unknown GC/MS peaks of mass 300. LC microcolumns have also been reported to resolve six components of mass 300 in the extracts of carbon black.^{6,7} The five

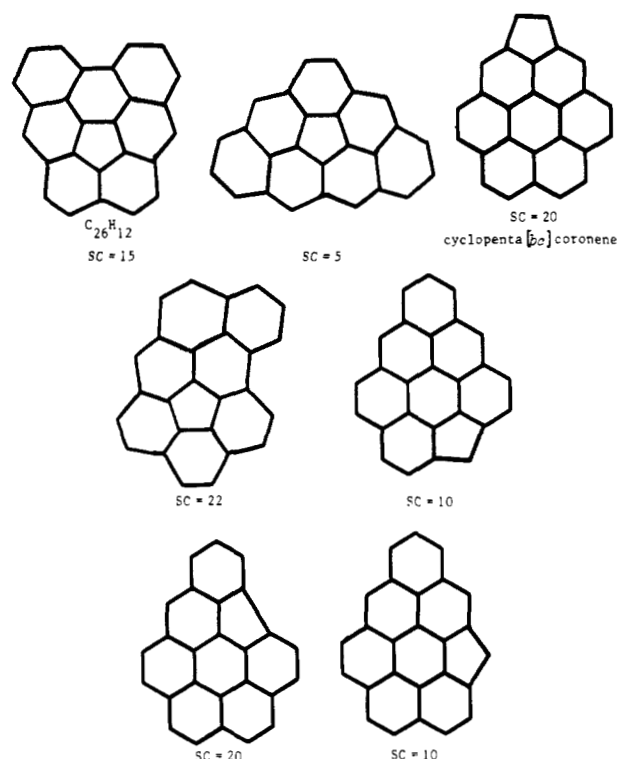


Figure 6. First generation members of the $C_{26}H_{12}$ seven-isomer fluorene/fluoranthene constant-isomer series.

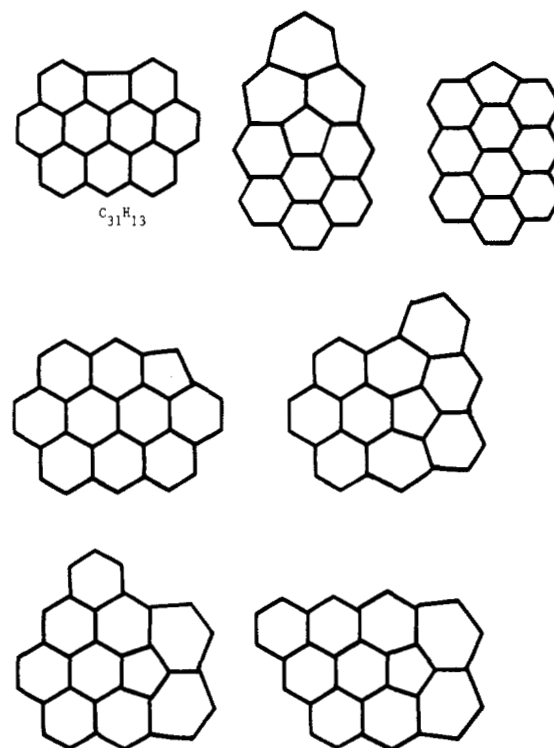


Figure 7. First generation members of the $C_{31}H_{13}$ seven-isomer fluorene/fluoranthene constant-isomer series.

absent coronene fluoranthene isomers are 12–15 and 17 in Figure 5. Two of these coronene isomers, 11 and 12, derive from diradical benzenoids. As noted previously,¹³ when formation of an odd ring in an otherwise diradical polyhex system causes pairing of two starred sites, one obtains a nonradical successor molecular system. What this means is that there are fewer radical fluoranthene isomers than even-carbon benzenoids and this kind annihilation of diradicals could provide some of the propensity for formation of fluoranthene isomers under mild combustion conditions.

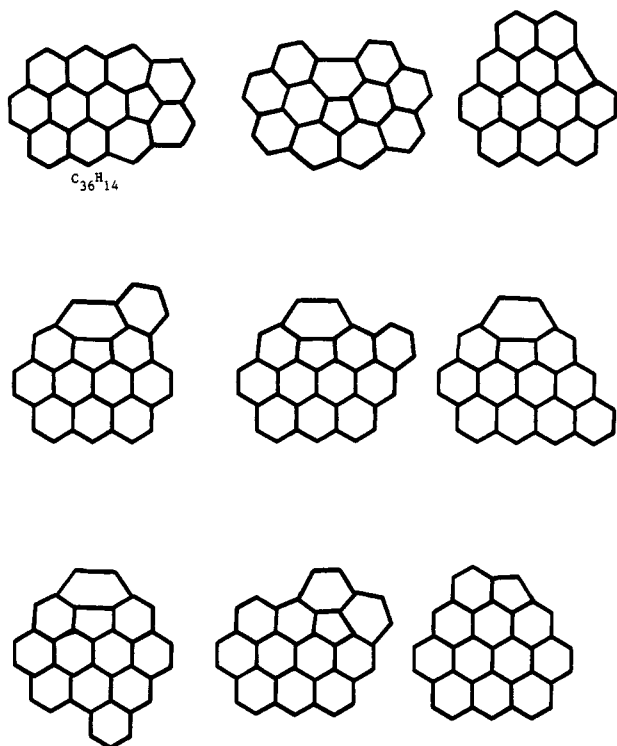


Figure 8. First generation members of the $C_{36}H_{14}$ nine-isomer fluorenoid/fluorantheneoid constant-isomer series.

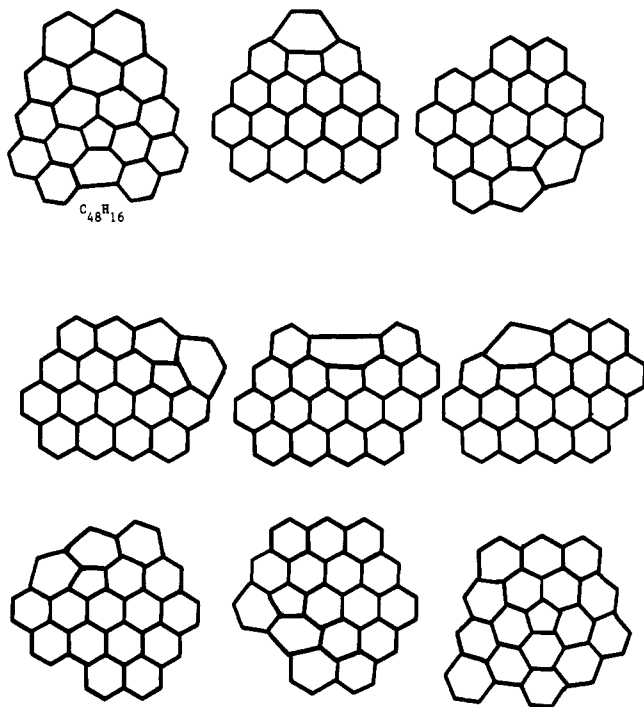
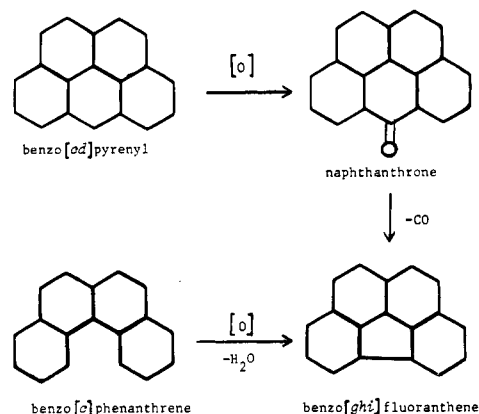


Figure 9. First generation members of the $C_{48}H_{16}$ nine-isomer fluorenoid/fluorantheneoid constant-isomer series.

Most fluorantheneoids that are isomeric to benzenoid hydrocarbons (i.e., have formulas below and to the right of the staircase dashed line in Table II) have already been compiled.⁸ The fluorantheneoids in Figures 1–4 that are known have their names given below the structures in these figures. Three of the four $C_{16}H_{10}$ fluorantheneoids in Figure 4 are known; the unknown isomer has the smallest SC (structure count), which is a measure of relative stability. Eleven of the 22 $C_{20}H_{12}$ fluorantheneoids have been synthesized by Sangaiah and Gold.^{8,14} Only 4 of the 19 $C_{22}H_{12}$ fluorantheneoid isomers (Figure 4) are known; benzo[*l*]cyclopenta[*cd*]pyrene has only recently been synthesized.¹⁵ These four $C_{22}H_{12}$ isomers have

Scheme I. Representative Pyrolytic Pathways for the Formation of Fluorantheneoids



among the largest SC values for this set. The fluorantheneoid isomers of coronene (Figure 5) and ovalene ($C_{32}H_{14}$) have been the objects of interest in several analytical investigations.^{3–6,8} Two $C_{30}H_{14}$ fluorantheneoid isomers have been reported, and the largest fluorantheneoid characterized yet is 2,12-dehydrodinaphthoperopyrene ($C_{38}H_{16}$).⁸

Fluorantheneoids that are not isomeric to benzenoid hydrocarbons represent a distinctive group of compounds. These hydrocarbons have formulas above and to the left of the staircase dashed line in Table II. Acenaphthylene ($C_{12}H_{10}$) and two of the fluorantheneoid $C_{18}H_{10}$ isomers (Figure 3) have been repeatedly detected in combustion emissions.^{2,6} Again the $C_{18}H_{10}$ isomer of lowest SC is unknown.^{8,16} Corannulene ($C_{20}H_{10}$) has been synthesized and is known to be bowl-shaped.⁹ Possible analytical detection of the protonated corannulene cation (m/z 251) has been reported.¹ Out of seven possible $C_{26}H_{12}$ fluorantheneoid isomers (Figure 6), only cyclopenta[*bc*]coronene has been suggested as being detected as a constituent of carbon black.⁵ Also, a mass spectral ion corresponding to protonated cyclopenta[*cd*]coronene has been reported.¹ Stein and Fahr have performed a theoretical thermodynamic study of polycyclic aromatic hydrocarbons which included a number of strictly peri-condensed benzenoids and fluorantheneoids belonging to constant-isomer series.¹⁷ Notable examples of the latter include cyclopenta[*cd*]pyrene, cyclopenta[*bc*]coronene, and cyclopenta[*bc*]ovalene ($C_{34}H_{14}$). This paper also depicted the five most stable $C_{24}H_{12}$ fluorantheneoid isomers out of 17 possible ones.¹⁷ Fluorenyl radicals were thermally generated from 9,9'-bifluorene and kinetically studied.¹⁷ Syntheses of 4*H*-cyclopenta[*def*]phenanthrene ($C_{15}H_{10}$), 7*H*-cyclopenta[*a*]pyrene, and 4*H*-cyclopenta[*def*]chrysene have been reported.^{18,19} Both *H*-fluorenyls and fluorantheneoids have been identified as constituents in the hydrocarbon minerals of curtisite, idrialite, and pendletonite.²⁰

Pyrolytic Formation of Fluorenyls/Fluorantheneoids. While the pyrolytic formation of benzenoid hydrocarbons has been extensively studied, less research has been pursued on the formation of fluorenyl/fluorantheneoid hydrocarbons. Ketone derivatives of odd carbon and quinone derivatives of even-carbon benzenoids are well-known pyrolytic coproducts. Scheme I shows two major reaction pathways that can lead to fluorantheneoids. It has been shown that pyrolysis at 900 °C converts phenalenone to acenaphthalene and benzanthrone to fluoranthene.²¹ By this thermal process 6,12-chrysenedione gave indeno[2,1-*a*]indene and 1,6- and 1,8-pyrenequinone gave pyracylene. Benzenoids with doublet bay regions, like benzo[*c*]phenanthrene, are known to undergo oxidative closure as shown in Scheme I. All the molecules in Scheme I are known constituents of pyrolytic emissions.^{1,5,22}

Fluorenyls, being pyrolytic odd-carbon radical species, will not continue to exist as such but will rapidly form mono-

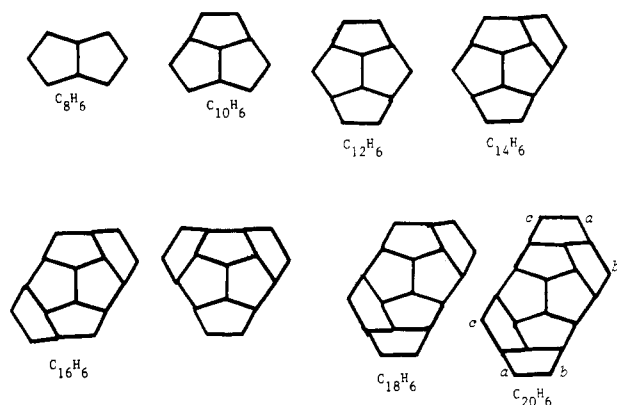


Figure 10. Polypentagonal systems having formulas found on the left-hand staircase edge of Table PAH₅.

hydrogenated or oxygenated derivatives. Various benzo-fluorenes, dibenzofluorenes, and related hydrocarbons were identified in the polycyclic aromatic hydrocarbon minerals of curtisite and idrialite.²⁰ Indene, fluorene, and benzo-fluorenes were among the hydrocarbons emitted from coal-fired residential furnaces and in heavy oil flames.^{1,22} The presence of 9-fluorenone in middle distillate fuels has been characterized.²³ Odd-carbon radical fluorenoids occur as combustion reactive intermediates¹ and may exist in interstellar space.²⁴

Heterocyclic Isoskeletal Analogues of Fluorenoids. If one replaces a CH in a fluorenoid formula by NH, O, or S, one obtains the formula of a more stable heterocyclic isoskeletal analogue. For example, both cyclopenta[def]phenanthrene (C₁₅H₉) and cyclopenta[pqr]benzo[ghi]perylene (C₂₃H₁₁) in Figure 2 have known thiophene analogues;^{2,25} also, the pyrrole analogue of the former is known. Various furan, pyrrole, and thiophene analogues isoskeletal to the C₁₃H₉, C₁₇H₁₁, and C₁₉H₁₁ fluorenoids in Figure 4 are known.^{26,27} The heterocyclic analogues of the nine C₁₇H₁₁ and nine C₁₉H₁₁ fluorenoids have been extensively studied because of their structural relationship to the carcinogenic benzo[a]anthracene and benzo[a]pyrene benzenoids. The presence of a number of large thiophene analogues of fluorenoids in carbon black has been reported.⁶ Adding H to the odd-carbon formulas in Table I or Table II gives the corresponding formulas for *H*-fluorenoids. Thus, Table I should be useful for performing semiselective literature searching for these types of heterocyclic compounds.

Stability Trends of Polyhexagonal/Polypentagonal Systems. The formulas on the extreme left-hand sloping edge of Table PAH₅ (Table IV in ref 7), all with six H's, correspond to the polypentagonal ring structures shown in Figure 10; these formulas must correspond to structures made up exclusively of pentagonal rings. The formulas between two staircase dashed lines (cf. with Table II which is a subset of Table PAH₅) must have at least one pentagonal ring and formulas below and to the right of the lower dashed line are not required to have any pentagonal rings since they are benzenoid formulas. Thus, the two staircase dashed lines are important zigzag lines of demarcation.

The polypentagonal structures in Figure 10 having formulas on the left-hand sloping edge of Table PAH₅ all have only six second-degree vertices (six formula H's). There is only one polypentagonal isomer corresponding to C₈H₆, C₁₀H₆, C₁₂H₆, and C₁₄H₆ each. There are only two isomers of C₁₆H₆ as shown in Figure 10. All the structures starting with C₈H₆ were constructed by successive aufbau attachment of C₂ units to the vee regions. However, the second C₁₆H₆ isomer with its three-fold symmetry has no vee regions and cannot continue to grow by C₂ attachment. Above C₁₆H₆, all polypentagonal structures shown again only have one isomer. From a chemical point of view, all these polypentagonal structures are probably too unstable to be synthesized and isolated. Thus, all the

structures corresponding to the extreme left-hand edge of Table PAH₅ are the least stable, all the benzenoids structures just below and to the right of the lower staircase dashed line are the most stable (as measured by relative *E_r* values), and all the structures having formulas between these two edges are of intermediate stability. Note that closing up C₂₀H₆ in Figure 10 by attaching the marked positions *a* and *a*, *b* with *b*, and *c* with *c* gives dodecahedron and that C₁₈H₆ and C₂₀H₆ cannot be circumscribed.

Those fluorenoids derivable by the hexagonal-to-pentagonal ring contraction of a sextet ring in a total resonant sextet benzenoid should be among the more stable (higher *E_r* values) fluorenoid isomers. Thus, to obtain the fluorenoid formulas having isomers of predicted higher *pπ* anionic stability, one needs only to subtract CH from each formula of our Table PAH₆(sextet).¹¹ The HMO calculations of numerous fluorenoids (and fluoranthenoids) are in agreement with this proposal.

CONCLUSION

Isomer enumeration studies are important because it gives one a list of possible structures against which all known isomers can be compared. This comparison allows one to begin to speculate why some isomers occur and others do not. Deciphering the information content of a chemical formula begins with isomer enumeration. Understanding why some isomeric structures are preferred over others as measured by the comparison of known isomers versus unknown ones is important to chemical information studies and molecular modeling. Since the chemical formula is an universal invariant, retrieval of chemical information is facilitated by formula tables which reduces the effort to searching isomer groups. Understanding the range of structure types one should encounter in this process will be an aid to the archiving, retrieving, and ultimate managing of chemical information. In molecular modeling, one would like to be able to forecast the properties of the unknown isomers from the known ones.

New enumeration results are presented herein for constant-isomer series. These results conform with the paradigm previously presented for benzenoid constant-isomer series.^{10,11} Our algorithm embodies the essence of a constructive inductive proof which has been observed for three different classes of polycyclic aromatic hydrocarbons—strictly peri-condensed benzenoids, total resonant sextet benzenoids, and now fluorenoids/fluoranthenoids. These results emphasize the generality of our algorithm and overall approach.

Five-fold symmetry is common in flowers, fruits, starfish, mystical symbols, and quasicrystals, but it is a forbidden symmetry in the world of crystals which is dominated by six-fold (and three-fold) symmetry.²⁸ Polyhex networks can be perturbed by the incursion of subunits with five-fold symmetry. The work summarized herein should contribute further to our understanding of the structural principles that are ultimately affected by these five-fold perturbations.

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Eigenvalue Distributions for the Graphs of Alternant Hydrocarbons

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Received August 16, 1991

In order to focus attention on the eigenvalue distribution for the graphs of polyhex molecules, a hypothesis is proposed about the number of eigenvalues greater than or equal to 2. From the density of states for several polymeric series of molecules it can be deduced that this hypothesis is satisfied for many molecules but in a modified form. A more general theorem on the distribution, which can be applied to any polyhex molecule, is described briefly. The calculation of the total energies of the polymeric molecules is described, and its decomposition into the sum of terms proportional to various graphical invariants is discussed. The small but significant dependence on the number of bay regions is stressed. The term proportional to the number of Kekulé structures is also strongly reduced by an exponential of the number of rings and is related to the highest occupied orbital energy.

INTRODUCTION

The importance of the highest occupied orbital energy ϵ_{HO} (and the related lowest unoccupied orbital energy ϵ_{LU}) in determining the chemical behavior and reactivity of an alternant hydrocarbon has been accepted for some time. Along with the next highest energies, these also determine the optical spectra of the molecule. The role of the remaining orbital eigenvalues is less chemical but important to various properties of the molecule as a system.

From the earliest calculations on the Hückel theory it has been known that the entire set of eigenvalues of the Hückel matrix, when referred to an origin at α and scaled by β (which makes it the adjacency matrix A of graph theory), lie within the interval

$$3 > \epsilon > -3$$

and that, for an alternant, the eigenvalues form a mirror distribution with every positive eigenvalue ϵ matched by an-

other at $-\epsilon$. Zero eigenvalues are possible and indicate that the molecular system is a radical.

In this paper some established results on the distributions will be given, and several hypotheses will be presented which are generalizations about many known molecules. Results will be stated for the positive eigenvalues, but corresponding results are true for their mirror images. Much more work is required before the distributions are fully understood.

HYPOTHESIS ABOUT THE EIGENVALUE DISTRIBUTIONS

In an attempt to generalize about the observed distributions of eigenvalues of polyhex molecules, I set up an hypothesis. This stated that the number of eigenvalues greater than or equal to 2 should be $r/2$ for a molecule with r rings where r is even and $(r+1)/2$ when r is an odd number. The number of eigenvalues less than 2 and greater than or equal to 1 should be $r+1$. The remaining positive eigenvalues lie below 1.