

it seems that there is a magic point in every dissatisfied library work when he/she decides that the home library is a hostile environment. These people leave. They continue to do their work, but they do it elsewhere.

This has enormous significance for many institutions. It is no secret that even modest chemistry collections are expensive.<sup>6</sup> If they are under-utilized because the on-site users are going elsewhere, both the library and its disgruntled clients are at a disadvantage. From the chemists' point of view, that library may be seen as having failed in its mission. The library, on the other hand, may look upon the chemists as ungrateful and demanding. In the interests of improved service in an era of tight budgets and simple efficiency, it would be useful for some libraries to compare their methods with those of the

libraries those whose users feel that they are very well served.

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# Deciphering the Information Content of Chemical Formulas: Chemical and Structural Characteristics and Enumeration of Indacenes<sup>†</sup>

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Constant-isomer series for indacene-related compounds are presented. These results illustrate the generality of the previously developed algorithms and associated concepts. The indacenoid constant-isomer series exhibit a repetitive ...abac... isomer number sequence. The constant-isomer series with the same isomer number have a one-to-one matching in the symmetry distribution of their membership.

## INTRODUCTION

While numerous enumerations of benzenoid isomers have been reported (only a representative list is given herein),<sup>1-3</sup> very little work has been done on other polycyclic hydrocarbons.<sup>4,5</sup> Polycyclic hydrocarbons related to indacenes represent an important subgroup of the polycyclic group of pyrolytic pollutants,<sup>6-8</sup> and the enumeration of these isomers is the subject of this investigation. Indacene-related polycyclic hydrocarbons (indacenoids) have two pentagonal rings among otherwise hexagonal rings. Indacenoid constant-isomer series will be presented. The formula periodic table for indacenoid hydrocarbons and the enumeration studies provide the framework for understanding the limits of what we know and can learn about indacenoids. This epistemology represents an important goal in deciphering the information content of chemical formulas.

Over 25 indacenoid hydrocarbons isomeric with benzenoids have been synthesized.<sup>9</sup> Indacenoids that are not isomeric to benzenoids will be discussed here. Indacenoids are expected to be strained and frequently nonplanar. An indacenoid of 50 carbons is offered for sale by a commercial vendor.<sup>10</sup> A brief view of some noteworthy chemistry of indacenoids will be presented.

Our general approach to the enumeration of polycyclic aromatic hydrocarbons involves construction of an appropriate formula periodic table and using the aufbau principle and excised internal structure concept (see below) 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

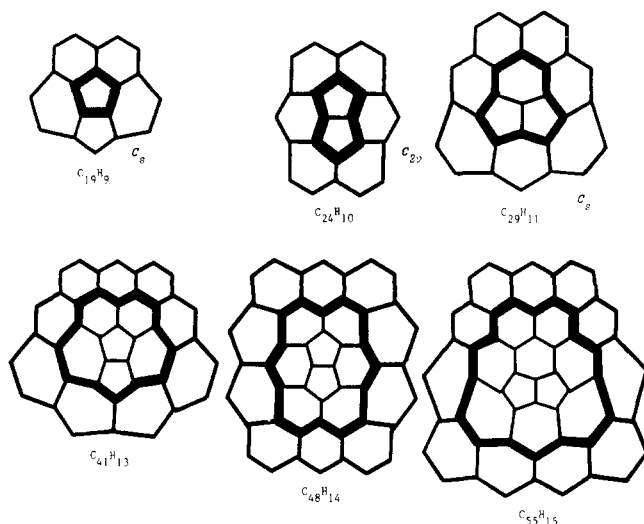
the isomer numbers alternate between singlet and doublet occurrence, and there exists a one-to-one matching in the symmetries between the member compounds with the same isomer numbers.<sup>11</sup> The isomer numbers have the same sequence of values between the strictly peri-condensed and the total resonant sextet subsets and between the monoradical, diradical, triradical, etc. subsets.<sup>12,13</sup>

In addition, this approach has shown that constant-isomer series also exist for fluorenoids/fluoranthenoids having one pentagonal ring among hexagonal ones.<sup>5</sup> Again these constant-isomer series exhibited isomer numbers that alternate between singlet and doublet occurrence and those member compounds belonging to series with the same isomer number exhibit a one-to-one matching in their symmetry distributions. We demonstrate here that indacenoid hydrocarbons also have constant-isomer series which follow the above topological paradigm, i.e., they have isomer numbers that alternate between single and pairwise occurrence with a one-to-one matching in the symmetries of the member compounds that have the same isomer numbers.

## RESULTS AND DISCUSSION

**Excised Internal Structure Concept.** If a conjugated hydrocarbon is encircled by a perimeter of carbon atoms with the appropriate number of hydrogens, this process is described as *circumscription*. The reverse process (*excision*) leads back to the excised internal structure. A polycyclic conjugated hydrocarbon may not have two or more bay regions if it is to be circumscribed. All constant-isomer series are generated by successive circumscription, are strictly peri-condensed (if the number of rings  $r > 2$ ), and correspond to formulas on the left-hand edge of the relevant formula periodic table. A constant-isomer series consists of compounds which, when circumscribed as described here, give at every step compounds

<sup>†</sup> Dedicated to former Editor Herman Skolnik, who contributed significantly to the area of chemical information.



**Figure 1.** Excised internal structure concept in the successive enumeration of indacenoid one-isomer series (the excised internal structures are shown in bold).

with the same number of isomers. For further discussion of this phenomenon, see ref 5.

If an excised internal structure has  $N_c$  carbons and  $N_H$  hydrogens and its circumscribed successor has  $N'_c$  carbons and  $N'_H$  hydrogens, then

$$N'_c = N_c + 2N_H + 6 - r_5$$

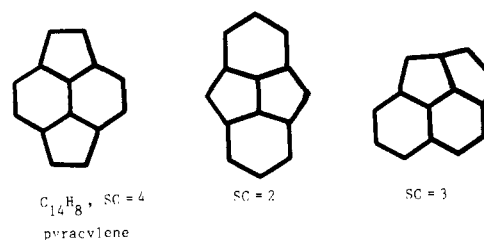
and

$$N'_H = N_H + 6 - r_5$$

represent useful recursive relationships which can be used to obtain successive strictly peri-condensed formulas. In these equations,  $r_5$  is the number of pentagonal rings in the structure. Fluorenoids and fluoranthenoids have  $r_5 = 1$  and in indacenoids,  $r_5 = 2$ . The concept of the excised internal structure is illustrated in Figure 1. Each column in this figure shows the successive generation of a one-isomer series.

**Formula Periodic Table for Indacenoid Hydrocarbons.** A formula periodic table for indacenoid hydrocarbons is given in Table I. All those formulas above and to the left of the upper zigzag dashed line correspond to polycyclic structures consisting of two (or more) pentagonal rings among hexagonal rings. All the formulas between the upper and lower dashed lines correspond to polycyclic hydrocarbons consisting of one (or more) pentagonal ring among hexagonal rings. All the formulas below and to the right of the lower dashed line have polycyclic structures that are isomeric with benzenoids that have  $N_{ic}$ (PAH6) internal third-degree vertices and may correspond to hydrocarbon structures with 0 to a maximum number of pentagonal rings of  $r_{5max} = N_{ic}$ (PAH6). In Table I,  $r_5$  is restricted to 2. Table I is a formula periodic table for indacenoid hydrocarbons and is named Table PAH5,6(I), Table II is Table I reorganized according to carbon number. The formula periodic table for fluorenoid/fluoranthenoid hydrocarbons is named Table PAH5,6(F/F),<sup>5</sup> and the formula periodic table for benzenoid hydrocarbons is named Table PAH6 and for total resonant sextet benzenoids as Table PAH6(sextet).<sup>12</sup>

Table I was constructed in exactly the same manner as Table II [Table PAH5,6(F/F)] in ref 5 for fluorenoids/fluoranthenoids and was constructed from Table PAH6. In this case, a CH is subtracted from every edge formula in Table II of ref 5 instead of Table PAH6. The formula obtained in this manner is then added to Table PAH5,6(F/F).<sup>5</sup> This preliminary table was then augmented with the formulas of the indacenoid one-isomer series, which serve as benchmarks, and the formulas missing in-between were filled in. In



**Figure 2.** First-generation members of the three-isomer indacenoid constant-isomer series.

this construction process, the version of Table I sorted by carbon number (Table II) was useful, and the formulas to the three-isomer series were needed for the even-carbon formulas. Note that no cata-condensed fluorenoid formula can occur on Table PAH5,6(I). All indacenoids in the same row of Table I have the same  $N_{ic}$  value, and all indacenoids in the same column have the same  $d_s$  value.  $N_{ic}$  is the number of internal third-degree vertices (bounded by three rings), and  $d_s$  is the net number of disconnections (negative values) and connections (positive values) among the internal edges. For example, pyracylene and its isomers in Figure 2 have  $N_{ic} = 2$  and  $d_s = 0$ .

**Isomer Enumeration.** The indacenoid isomers of a given  $C_nH_s$  formula ( $n = N_c$  and  $s = N_H$ ) were generated as follows. The fluorenoid/fluoranthenoid structures with one more CH are identified and carry out all possible combinatorial hexagonal-to-pentagonal ring contractions. In this way indenyl ( $C_9H_7$ ) gives pentalene ( $C_8H_6$ )—and the three fluorenoid isomers of  $C_{13}H_9$  give the only three indacenoid isomers of  $C_{12}H_8$ ; viz., *s*-indacene, *as*-indacene, and benzopentalene. In general, all indacenoid isomers with  $N_{ic} < 5$  can be obtained by taking all combinatorial hexagonal-to-pentagonal ring contractions of the corresponding fluorenoids/fluoranthenoids with one more CH. The excised internal structure concept was employed to obtain the one-isomer series shown in Figure 1. Other constant-isomer indacenoid series having formulas on protrusive locations of the left-hand zigzag edge of Table I were likewise generated using the excised internal structure concept. A combination of the hexagonal-to-pentagonal ring contraction process and the excised internal structure concept was used to generate the other constant-isomer series. Additionally, it is necessary to employ the aufbau  $C_4H_2$  attachment process to indacenoids having formulas located to the left of a targeted enumeration formula. Indacenoid isomers with  $8 > N_{ic} \geq 5$  can be generated by all combinatorial hexagonal-to-pentagonal ring contractions of fluorenoid/fluoranthenoid isomers with one more CH and by benzo  $C_4H_2$  attachments to isomers having formulas located to the immediate left in Table I.

**Constant-Isomer Series.** The indacenoid constant-isomer series are summarized in Table III. Note that the repeating pattern for the isomer number sequence is ...abac... (e.g., ... 6, 7, 6, 12, ...) which means that there are twice as many single isomer number sets as pairwise occurring sets. The isomer sets which occur in pairs have odd-carbon formulas, and the single occurring isomer number sets have even-carbon formulas.

Table IV gives a summary of the patterns found in the number of isomers and the matching topological characteristics observed for compounds with the same isomer number cardinalities for the various classes of polycyclic hydrocarbons. These results constitute a new topological paradigm.<sup>11-13</sup>

The first-generation formulas for constant-isomer series not listed in Table III (but see Table I) include  $C_{65}H_{17}$ ,  $C_{74}H_{18}$ ,  $C_{83}H_{19}$ ,  $C_{92}H_{20}$ , and  $C_{101}H_{21}$  where the two series beginning with  $C_{65}H_{17}$  and with  $C_{83}H_{19}$  have the same isomer number cardinality. From the recursion pattern evident in Table III,

**Table I.** Formula Periodic Table for Indacenoid Hydrocarbons [Table PAH5,6 (I)]

$d_s = -9$	$d_s = -8$	$d_s = -7$	$d_s = -6$	$d_s = -5$	$d_s = -4$	$d_s = -3$	$d_s = -2$	$d_s = -1$	$d_s = 0$	$d_s = 1$	$d_s = 2$	$d_s = 3$	...	$N_{Ic}$
														0
												$C_{20}H_{12}$	...	1
											$C_{16}H_{10}$			2
										$C_{15}H_9$	$C_{19}H_{11}$			3
										$C_{14}H_8$	$C_{10}H_{10}$	$C_{22}H_{12}$		4
										$C_{17}H_9$	$C_{21}H_{11}$	$C_{25}H_{13}$		5
										$C_{20}H_{10}$	$C_{24}H_{12}$	...		6
										$C_{23}H_{11}$	$C_{27}H_{13}$			7
										...				8
										$C_{19}H_9$				9
										$C_{22}H_{10}$				10
										$C_{25}H_{12}$				11
										$C_{28}H_{12}$				12
										$C_{31}H_{13}$				...
										$C_{34}H_{14}$				
										$C_{37}H_{15}$				
										$C_{40}H_{16}$				
										...				
										$C_{24}H_{10}$				
										$C_{27}H_{11}$				
										$C_{30}H_{12}$				
										$C_{33}H_{13}$				
										$C_{36}H_{14}$				
										$C_{39}H_{15}$				
										$C_{42}H_{16}$				
										...				
										$C_{29}H_{11}$				
										$C_{32}H_{12}$				
										$C_{35}H_{13}$				
										$C_{38}H_{14}$				
										$C_{41}H_{15}$				
										$C_{44}H_{16}$				
										...				
										$C_{34}H_{12}$				
										$C_{37}H_{13}$				
										$C_{40}H_{14}$				
										$C_{43}H_{15}$				
										$C_{46}H_{16}$				
										$C_{49}H_{17}$				
										...				
										$C_{39}H_{13}$				
										$C_{42}H_{14}$				
										$C_{45}H_{15}$				
										$C_{48}H_{16}$				
										$C_{51}H_{17}$				
										$C_{54}H_{18}$				
										...				
										$C_{41}H_{13}$				
										$C_{44}H_{14}$				
										$C_{47}H_{15}$				
										$C_{50}H_{16}$				
										$C_{53}H_{17}$				
										$C_{56}H_{18}$				
										$C_{59}H_{19}$				
										...				
										$C_{46}H_{14}$				
										$C_{49}H_{15}$				
										$C_{52}H_{16}$				
										$C_{55}H_{17}$				
										$C_{58}H_{18}$				
										$C_{61}H_{19}$				
										$C_{64}H_{20}$				
										...				
										$C_{48}H_{14}$				
										$C_{51}H_{15}$				
										$C_{54}H_{16}$				
										$C_{57}H_{17}$				
										$C_{60}H_{18}$				
										$C_{63}H_{19}$				
										$C_{66}H_{20}$				
										...				
										$C_{65}H_{19}$				
										$C_{68}H_{20}$				
										...				
										$C_{53}H_{15}$				
										$C_{56}H_{16}$				
										$C_{59}H_{17}$				
										$C_{62}H_{18}$				
										...				
										$C_{65}H_{19}$				
										$C_{68}H_{20}$				
										...				
										$C_{71}H_{21}$				
										...				

Table II. All Formulas Corresponding to Indacenoids

$N_c$	$N_H$	$N_c$	$N_H$
8	→6 <sup>a</sup>	11	→7
12	8	15	9
14	→8	17	→9
16	10	19	→9-11 <sup>c</sup>
18	10	21	11
20	10-12 <sup>b</sup>	23	11-13
22	→10-12	25	11-13
24	→10-14	27	→11-15
26	12-14	29	→11-15
28	12-16	31	13-17
30	12-16	33	13-17
32	→12-18	35	13-19
34	→12-18	37	→13-19
36	14-20	39	→13-21
38	14-20	41	→13-21
40	14-22	43	15-23
42	14-22	45	15-23
44	→14-24	47	15-25
46	→14-24	49	15-25
48	→14-26	51	→15-27
50	16-26	53	→15-27
52	16-28	55	→15-29
54	16-28	57	17-29
56	16-30	59	17-31
58	→16-30	61	17-31
60	→16-32	63	17-33
62	→16-32	65	→17-33
64	18-34	67	→17-35
66	18-34	69	→17-35
68	18-36	71	→17-37
70	18-36	73	19-37
72	18-38	75	19-39
74	→18-38	77	19-39
76	→18-40	79	19-41
78	→18-40	81	19-41
80	→18-42	83	→19-43
82	20-42	85	→19-43
84	20-44	87	→19-45
86	20-44	89	→19-45
88	20-46	91	21-47
90	20-46	93	21-47
92	→20-48	95	21-49
94	→20-48	97	21-49
96	→20-50	99	21-51
98	→20-50	101	→21-51
100	22-52	103	→21-53
102	22-52	105	→21-53
104	22-54	107	→21-55
...	...	109	→21-55

<sup>a</sup> An arrow to the left marks the formulas of the constant-isomer series. <sup>b</sup> Range of successive even numbers. <sup>c</sup> Range of successive odd numbers.

one can extend this table indefinitely. This recursion pattern is quite apparent if one notes that the first-generation formulas for each successive constant-isomer series have  $N_H$  values increasing by one and differences in successive  $N_c$  values varying according to  $\Delta N_c = 3, 3, 3, 3, 5, 5, 5, 5, 7, 7, 7, 7, 9, 9, 9, 9, \dots$ . Difference patterns, like this can be easily determined for all ordered constant-isomer series.<sup>5,11,12</sup> There are other regularities that can be used to cross-check these difference patterns.

**Topological Characteristics of Indacenoids.** Since indacenoids, like fluorenoids/fluoranthenoids, tend to be strained and nonplanar, the symmetry group classification of their planar molecular graph representations differs from that of the corresponding curved molecular structures. The former is referred to as the pseudosymmetry group classification of the latter. The symmetry group classification of  $D_{2h}$ ,  $C_{2v}$ ,  $C_{2h}$ , and  $C_s$  for planar molecular graphs becomes  $C_{2v}$ ,  $C_s$ ,  $C_2$ , and  $C_1$ , respectively, for the corresponding curved molecular structures. The molecular structures with  $C_2$  and  $C_1$  symmetries are expected to exist as enantiomeric pairs.

Table III. Indacenoid Hydrocarbon Constant-Isomer Series

series	no. of isomers	pseudosymmetry <sup>a</sup> distribution
(C <sub>5</sub> H <sub>5</sub> ) <sup>b</sup>	1	$C_{2v}$
C <sub>19</sub> H <sub>9</sub>		
C <sub>41</sub> H <sub>13</sub>		
...		
C <sub>8</sub> H <sub>6</sub>	1	$D_{2h}$
C <sub>24</sub> H <sub>10</sub>		
C <sub>48</sub> H <sub>14</sub>		
...		
C <sub>11</sub> H <sub>7</sub>	1	$C_{2v}$
C <sub>29</sub> H <sub>11</sub>		
C <sub>55</sub> H <sub>15</sub>		
...		
C <sub>14</sub> H <sub>8</sub>	3	$D_{2h}(2)$ , $C_s(1)$
C <sub>34</sub> H <sub>12</sub>		
C <sub>62</sub> H <sub>16</sub>		
...		
C <sub>17</sub> H <sub>9</sub>	6	$C_{2v}(2)$ , $C_s(4)$
C <sub>39</sub> H <sub>13</sub>		
...		
C <sub>22</sub> H <sub>10</sub>	7	$D_{2h}(1)$ , $C_{2v}(4)$ , $C_s(2)$
C <sub>46</sub> H <sub>14</sub>		
...		
C <sub>27</sub> H <sub>11</sub>	6	$C_{2v}(2)$ , $C_s(4)$
C <sub>53</sub> H <sub>15</sub>		
...		
C <sub>32</sub> H <sub>12</sub>	12	$D_{2h}(1)$ , $C_{2v}(4)$ , $C_s(7)$
C <sub>60</sub> H <sub>16</sub>		
...		
C <sub>37</sub> H <sub>13</sub>	28	$C_{2v}(5)$ , $C_s(23)$
C <sub>67</sub> H <sub>17</sub>		
...		
C <sub>44</sub> H <sub>14</sub>	26	$C_{2v}(8)$ , $C_{2h}(3)$ , $C_s(15)$
C <sub>76</sub> H <sub>18</sub>		
...		
C <sub>51</sub> H <sub>15</sub>	28	$C_{2v}(5)$ , $C_s(23)$
C <sub>85</sub> H <sub>19</sub>		
...		
C <sub>58</sub> H <sub>16</sub>	51	$D_{2h}(4)$ , $C_{2v}(6)$ , $C_{2h}(2)$ , $C_s(39)$
C <sub>94</sub> H <sub>20</sub>		
...		

<sup>a</sup> Pseudosymmetry assumes that these molecules are perfectly planar.

<sup>b</sup> To obtain successive formulas use the following recursions of  $N_c' = N_c + 2N_H + 4$  and  $N_H' = N_H + 4$ .

From Table III and Figures 1-5, it should be evident that the indacenoid constant-isomer series with the same isomer numbers possess a one-to-one matching in the symmetry distributions of their membership. Also, the unique indacenoid constant-isomer series (with a singlet occurring isomer number), in general, contain members with higher symmetries. When compared to fluorenoids/fluoranthenoids, indacenoids have a different set of possible pseudosymmetry groups. No constant-isomer fluorenoid/fluoranthenoid can belong to the  $C_{2h}$  or  $D_{2h}$  pseudosymmetry groups, whereas constant-isomer indacenoids have structures belonging to these pseudosymmetry groups. No indacenoids can belong to the pseudosymmetry groups of  $D_{5h}$ ,  $C_{5v}$ , or  $C_{5h}$ , whereas fluorenoids/fluoranthenoids can.

The perimeter topology of polycyclics with pentagonal and hexagonal rings is described by  $-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 = 6 - r_5$  where  $\eta_0$  is the number of bay regions,  $\eta_2$  is the number of duo groups,  $\eta_3$  is the number of trio groups, and  $\eta_4$  is the number of quarto groups. For the indacenoid constant-isomer series,  $\eta_4 = 0$  and  $r_5 = 2$ .

**Chemistry of Indacenoids.** Probably the most studied indacenoid is rubicene (C<sub>26</sub>H<sub>14</sub>), which is synthesized from fluorenone by treatment with Mg metal at high temperatures.<sup>14</sup> Several indacenoid isomers of coronene have been investigated theoretically as analytical candidates for the mass 300 constituent in hard-coal flue gas condensate. Dihydro derivatives of cata-condensed indacenoids have been found among the

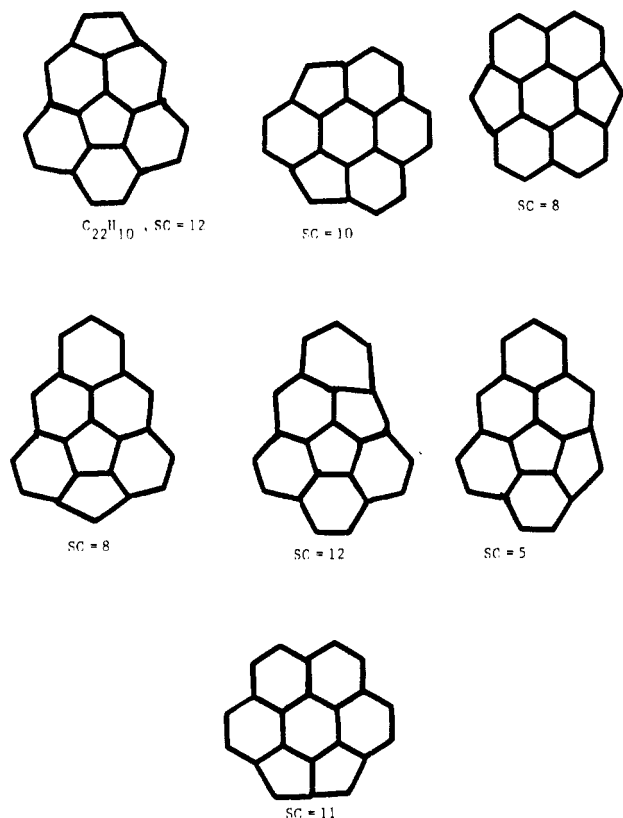
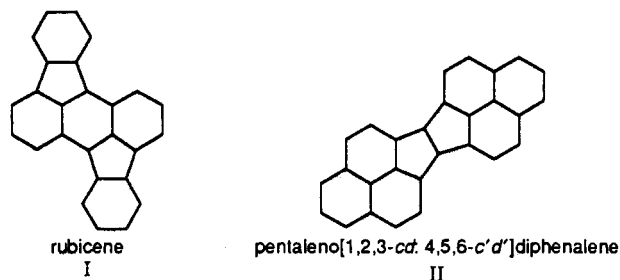
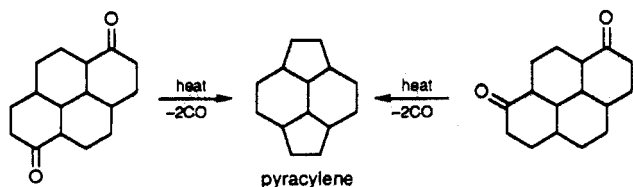


Figure 3. First-generation members of the seven-isomer indacenoid constant-isomer series.

constituents of hydrocarbon minerals,<sup>15</sup> and a  $C_{38}H_{14}$  indacenoid was theoretically studied as a candidate structure for Clar's hydrocarbon.<sup>16</sup> Dicyclopenta[*ghi,pqr*]perylene ( $C_{22}H_{10}$ ), the most symmetrical first-generation isomer of the seven-isomer series (Figure 3), has been calculated to have a resonance energy of 1.45 eV.<sup>17</sup> The ESR and ENDOR spectra of pentaleno[1,2,3-*cd*:4,5,6-*c'd'*]diphenalene ( $C_{28}H_{14}$ ) has been studied.<sup>18</sup> Neither rubicene (I) nor pentaleno[1,2,3-*cd*:4,5,6-*c'd'*]diphenalene (II) can be circumscribed.



A theoretical study of high-temperature stabilities of hydrocarbons included pyracylene, dicyclopentapyrene ( $C_{20}H_{10}$ ), dicyclopentacoronene ( $C_{28}H_{12}$ ), and dicyclopentaovalene ( $C_{36}H_{14}$ ).<sup>19</sup> Flow pyrolysis of 1,6- or 1,8-pyrenequinone leads to pyracylene,<sup>20</sup> which has been identified as an emission



constituent in heavy-oil flames by GC/MS.<sup>21</sup> A benzo[*cd*]pentalenyl cation has been detected in hydrocarbon flames by time-of-flight mass spectrometry.<sup>8</sup> The synthesis of 1*H*-benzo[*cd*]pentalene has been reported.<sup>22</sup> Electron impact induced loss of two CO molecules from benz[*h*]acepleiadylyl-

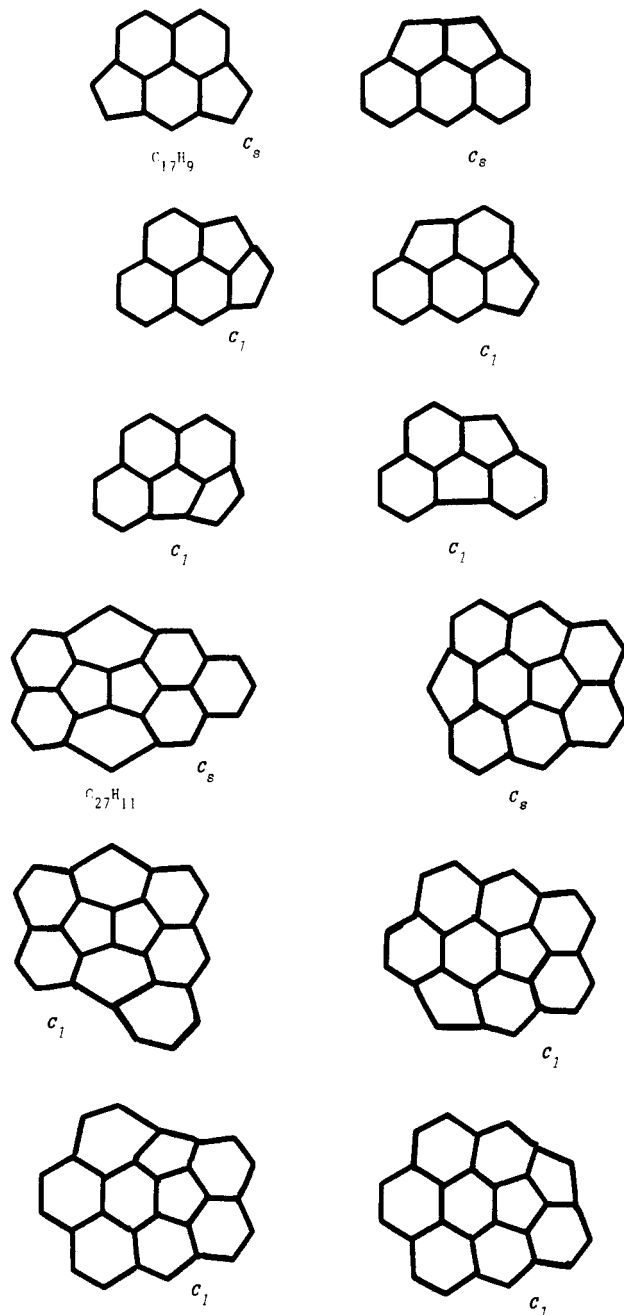


Figure 4. First-generation members of the two six-isomer indacenoid constant-isomer series.

ene-5,10-dione and naphth[2,3-*h*]acepleiadylylene has been reported to give benzo[*a*]pyracylene and naphtho[2,3-*a*]pyracylene daughter ions, respectively.<sup>23</sup> Numerous dithiophene analogues of indacenoids have been synthesized.<sup>24</sup> Although unstable, pentalene has been synthesized.<sup>25</sup> Only the aza analogue of  $C_{11}H_7$ , cyclo[3.2.2]azine, is known.

High-temperature isomerization of polycyclic aromatic compounds has been studied by Scott and co-workers.<sup>26</sup> Such rearrangements in fullerenes do not require concurrent hydrogen shifts and are conjectured to be the mechanism by which they convert to the structure of highest symmetry. For the members of the one-isomer series, this process is not permissible without changing the final ring-size distribution, but it could operate in other constant-isomer series leading to the more stable isomer of each set.

It is of interest to note that the second-generation formula of  $C_{60}H_{16}$  for the twelve-isomer series in Table III corresponds to a partially hydrogenated form of buckminsterfullerene which has more than  $2.49 \times 10^{12}$  caged isomers.<sup>27</sup> This large isomer number is a lower bound to the global number of isomers that

Table IV. Comparison of Isomer Number Sequences for Constant-Isomer Series

constant-isomer series	isomer number series	matching topological characteristics of PAH members with same isomer number
even-carbon benzenoids	...abb...	symmetry, no. of selective lineations and bay regions
odd-carbon benzenoids	...abb...	symmetry, no. of selective lineations and bay regions
polyradical benzenoids	...abb...	symmetry, no. of selective lineations and bay regions
total resonant sextet benzenoids	...abb...	symmetry, no. of solo groups
fluorenoids/fluoranthenoids	...aabc...	symmetry, no. of bay regions
indacenoids	...abac...	symmetry, no. of bay regions

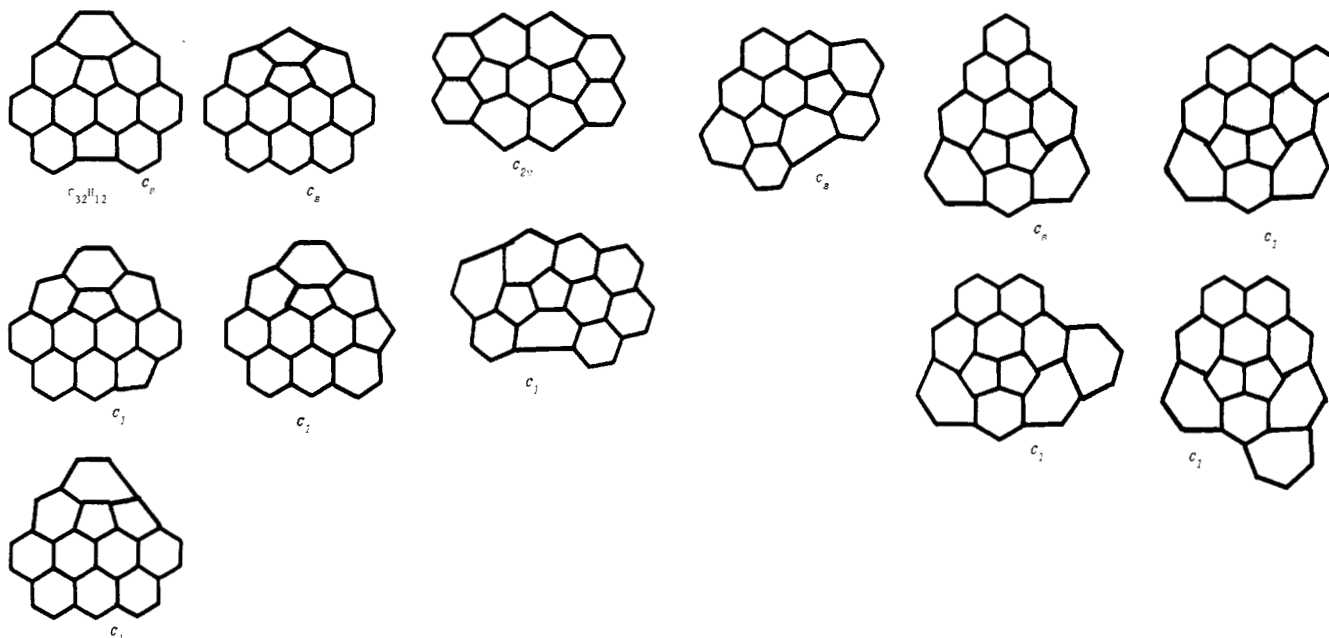


Figure 5. First-generation members of the twelve-isomer indacenoid constant-isomer series.

are possible for this formula, and its magnitude emphasizes that the constraints that we built into our framework for polycyclic hydrocarbons results in a manageable system, which we believe is ultimately governed by the mechanism and thermodynamics of their formation.

In a study of HMO energy characteristics Zahradnik and Pancir<sup>28</sup> presented some of the first practical enumerations of nonradical benzenoids ( $C_6H_6 - 1$ ,  $C_{10}H_8 - 1$ ,  $C_{14}H_{10} - 2$ ,  $C_{18}H_{12} - 5$ ,  $C_{22}H_{14} - 12$ ,  $C_{26}H_{16} - 1$ ,  $C_{30}H_{18} - 3$ ,  $C_{34}H_{20} - 2$ ,  $C_{38}H_{22} - 1$ ), odd-carbon benzenoids ( $C_{13}H_9 - 1$ ,  $C_{17}H_{11} - 1$ ,  $C_{19}H_{11} - 1$ ), fluorenoids ( $C_9H_7 - 1$ ,  $C_{13}H_9 - 3$ ,  $C_{17}H_{11} - 9$ ,  $C_{21}H_{13} - 2$ ), fluoranthenoids ( $C_{12}H_8 - 1$ ), and indacenoids ( $C_8H_6 - 1$ ,  $C_{12}H_8 - 3$ ,  $C_{16}H_{10} - 1$ ,  $C_{20}H_{12} - 3$ ). The recent synthesis of acenaphth[1,2-*a*]acenaphthylene by the coupling of 1,8-diiodonaphthalene and acenaphthylene using 5% palladium acetate catalyst has been reported.<sup>29</sup>

**Heterocyclic Isoskeletal Analogues of Indacenoids.** If a CH in an odd-carbon indacenoid formula is replaced by NH, O, or S one obtains the formula of a more stable heterocyclic isoskeletal analogue. A simple example of this is acenaphtho[1,2-*b*]thiophene ( $C_{14}H_8S$ ). The replacement of two CHs in pentalene by two divalent sulfurs leads to aromatic thienothiophenes, which are known.<sup>24</sup>

## CONCLUSION

The results in this paper again conform to the topological paradigm described for constant-isomer series of strictly peri-condensed and total resonant sextet benzenoids and fluorenoids/fluoranthenoids. We observe that the algorithmic construction of a formula periodic table using the excised internal structure concept, aufbau principle, and the hexagonal-to-pentagonal ring contraction process leads to a left-hand staircase edge on which strictly peri-condensed constant-isomer series appear. These constant-isomer series have single and

pairwise occurring isomer number cardinalities where there is a one-to-one matching of the symmetry distributions between those series having the same isomer numbers.

It should be noted that our tables [Table PAH6, Table PAH6(sextet), Table PAH5,6(F/F), and Table PAH5,6(I)] are quite complete for the chemically relevant range of formulas.<sup>5,12</sup> Nevertheless, using the Hill index versions of these tables, they can be extended indefinitely from their obvious recursion patterns. All our relevant relationships can easily be generalized. These algorithms and underlying concepts have clearly led the way to understanding the isomer/structural relationships that exist for these classes of polycyclic hydrocarbons. Like algebra, algorithmic methods is a branch of mathematics. Translating our algorithms into algebraic form and concepts into theorems may lead to additional insights, but it does not negate the force of these results as constituting the essence of inductive proofs of our concepts nor does it imply that one method is more mathematically rigorous than the other.

It was stated<sup>4</sup> that one of our goals was "... to provide a systematic framework for the grouping of polycyclic aromatic hydrocarbons according to their variant and invariant graph theoretical properties ...", and we believe that considerable results toward this objective have been achieved. The invention of the formula periodic table for benzenoids and the circumscribing principle are key elements contributing toward this progress.<sup>4,30</sup> The work of Cyvin<sup>2,31</sup> in this area has been quite instrumental in fine tuning and extending these results.

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## A Program for the Forward Generation of Synthetic Routes

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Following the skeletal dissection of a target structure, functionality and reactions may be generated either retrosynthetically back from the target to the necessary starting materials or in the forward direction from catalogue starting materials up to the target skeleton with various functionality, to be altered to the target itself after skeletal construction. The former represents the SYNGEN program; the latter is the FORWARD program described here. The FORWARD variation is important not only in being directed by available starting materials but also in solving the problem of deducing refunctionalization reactions as well as constructions.

The problem of automated synthesis design is basically one of combinatorics: the number of possible routes to any target is far greater than is generally appreciated. In principle it is simple for the computer to generate them all; the main task is to establish stringent criteria that allow for the selection of a rather small number of optimal routes.<sup>1</sup>

Our approach to automated synthesis design is centrally based on a criterion of *economy*. This dictates finding the shortest, most efficient routes to the target from real starting materials available commercially. Our developing theory of synthesis design logic takes the assembly of the target skeleton as the key to the selection of the best synthetic routes. This demands that we first separate the skeleton from its appended functionality and then derive the shortest, most efficient dissections of that skeleton to assemble it from a set of available starting material skeletons. The best syntheses are then the shortest ones, i.e., those that simply construct in the forward

direction each of the dissected skeletal bonds without stopping to refunctionalize or repair functionality on the way. Such a sequence, of construction reactions only, has been regarded as an *ideal synthesis* and is the approach taken by the SYNGEN program.<sup>1</sup>

The first task of the SYNGEN program then is dissection of the skeleton to available starting material skeletons. This is followed by a search for the necessary functionality. This search for functionality concentrates on those starting materials that are most readily convertible to target, i.e., are closest to it in the synthesis tree. When starting materials are ideal, their conversion to target is easily found as a sequence of construction reactions, but when they need refunctionalization as well as joining en route, they will not be obvious in any retrosynthetic approach. Nevertheless, a catalogue of starting materials constitutes available information for the synthesis designer and so should be incorporated in any protocol. The