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Resonance Topology of Polynuclear Aromatic Hydrocarbons

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Equations for the determination of the number of unexcited resonance forms (N) for several lattice systems of polynuclear aromatic hydrocarbons have been developed, e.g., for the square (parallelogram) model, $S[m, n]$, the symmetric circular systems $C[m, n]$, and the rectangular model $R[m, n]$, using combinatorial mathematics. Equations for the three major classes (R, C, S) of polynuclear aromatic hydrocarbons can be reduced to a generalized formula.

An additional form, the skew strip model, $Z[m, n]$, is also described, for which N may be determined by an independent formula. However, an addition of one ring to the $R[m, n]$ series will result in a $Z[m+1, n]$ series. Thus, ring addition may transfer a lattice from one geometrical system to another, both subject to description by the same set of internally consistent equations for the calculation of N. The successive coupling of benzene rings to a specific series is general, so that an explicit formula for N of an intermediate lattice, e.g., the peropyrene type molecule, $PP[m, n]$, can be derived from a known model type, e.g., $C[m, n]$. The four major models (R, C, S, and Z) discussed are descriptive of most polynuclear aromatic hydrocarbons frequently encountered.

Gordon and Davison [1] have calculated the number of unexcited forms, N, of the square (parallelogram) model, $S[m, n]$ (Fig. 1a),

$$N = {}^{m+n}C_m \tag{1}$$

and the symmetric circular model (hexagonal assemblages of hexagons) $C[m, n]$, $m = n$ (Fig. 1b)

$$N = \frac{\prod_{a=n}^{2n-1} {}^{n+a}C_n}{\prod_{a=1}^{n-1} {}^{n+a}C_n} \tag{2}$$

from the consideration of the possible paths in a dot diagram of the hexagonal lattice.

Based on combinatorial mathematics, we have developed a formula for the N of the rectangular model [2], $R[m, n]$ polynuclear aromatic hydrocarbons (Fig. 1c)

$$N = (n+1)^m \tag{3}$$

e.g., for the polyphenylenes, $R[m, 1]$, N is 2^m; and for the polyacenes, $R[1, n]$, N is $n+1$. The polyrylene series is $R[m, 2]$ and N is 3^m. This series includes hydrocarbons such as perylene ($m = 2$), terylene ($m = 3$), and quarterylene ($m = 4$) etc. The polyanthene series is $R[m, 3]$ and N is 4^m, which includes hydrocarbons

such as bisanthene ($m=2$) tetraanthene ($m=3$), etc. For hydrocarbons of the circular model, $C[m, n]$.

$$N = \frac{\binom{m+n}{n}\binom{m+n+1}{n}\cdots\binom{m+n+(m-1)}{n}}{\binom{n+1}{n}\cdots\binom{n+(m-1)}{n}} \tag{4}$$

This expression is also applicable for circular hydrocarbons, $m \neq$ n, whose shape deviates from that of an array of the hexagonal assemblages. For the square model, $S[m, n]$ or $S[n, m]$, Eq.(1) can be written as

$$N = \binom{m+n}{n}. \tag{5}$$

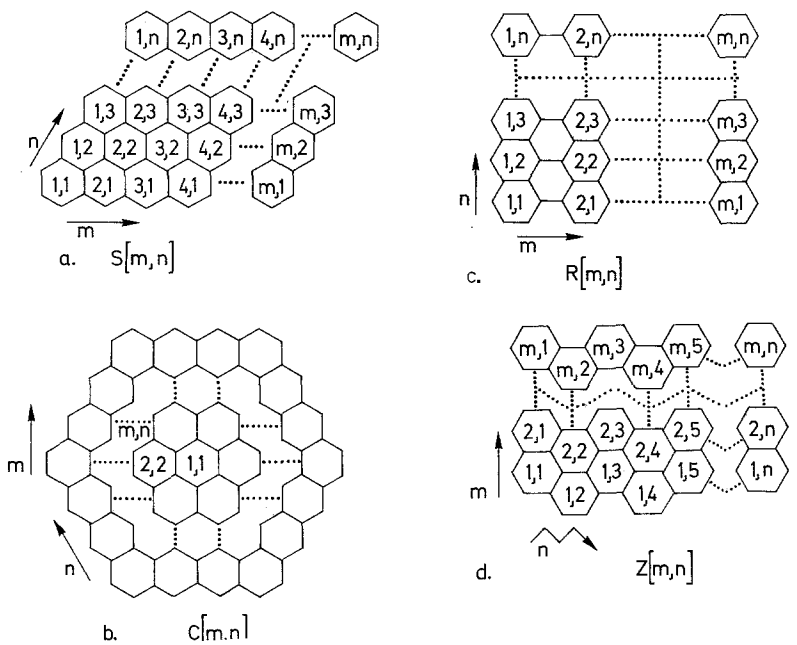

Fig. 1. a The square or parallelogram model, $S[m, n]$, where m and n are interchangable. $S[1, 1]$ is benzene, $S[2, 1]$ or $S[1, 2]$ is naphthalene, $S[2, 2]$ is pyrene, etc. Both m and n units expressed are in the naphthalene type linkage. Hydrocarbons of $C=2[m(n+1)+n]$, $H=2(m+n+1)$ belong to this class. b The circular model $C[m, n]$ where m is expressed in units of the biphenyl type linkage along the axis (y) perpendicular to the horizontal acene type axis (x) and n is along the 4-edges of the molecule. $C[1, 1]$ is benzene, $C[2, 2]$ is coronene, $C[2, 1]$ is pyrene, $C[1, 2]$ is naphthalene, $C[2, 3]$ is ovalene, etc. Hydrocarbons of $C=2m(m+2n)$ and $H=2(2m+n)$ belong to this class. c The rectangular model $R[m, n]$ originated by Coulson (Ref. 2). Index m indicates units of the biphenyl type linkage along the x-axis and n, the naphthalene type linkage along the y-axis. $R[1, 1]$ is benzene, $R[2, 1]$ is naphthalene, $R[1, 2]$ is biphenyl, $R[2, 2]$ is perylene, etc. Hydrocarbons of $C=2m(2n+1)$ and $H=2(2m+n)$ belong to this model. d The skew strip model is $Z[m, n]$. Index m is units of naphthalene type linkage along the zig-zag path of the x-axis and n is that along the straight-line path of the y-axis. $Z[1, 1]$ is benzene, $Z[2, 1]$ is naphthalene, $Z[3, 1]$ is phenanthrene, $Z[2, 2]$ is pyrene, $Z[3, 2]$ is 1,12-benzoperylene, etc. See Ref. [3]

The above Eqs. (3), (4), and (5) can be reduced to a generalized formula for three major classes (R, S, and C) of polynuclear aromatic hydrocarbons.

$$N = \binom{n+b}{n}^{c} \prod_{q=1}^{m-1} \binom{m+n+q}{n} \Big/ \binom{n+a+q}{n}$$

for

$$\begin{aligned} R[m,n]&: a=m, b=1, \ c=m, \\ S[m,n]&: a=m, b=m, c=1, \\ C[m,n]&: a=0, \ b=m, c=1. \end{aligned} \tag{6}$$

Another important model is the skew strip, $Z[m,n]$ series (Fig. 1d). For $Z[m,1]$, N takes the form of the Fabonacci series, 2, 3, 5, 8, 13 ... or the recurrence form, $f(0)=0, f(1)=1, f(k)=f(k-1)+f(k-2)$ for $k=2,3\ldots$ and $m+2=k$. This series also can be expressed by the golden section ratio τ, $1+\tau^{-1}=\tau$ or $\tau^2=1+\tau$, upon solving $\tau=(a+1)/2$ where $a=5^{\frac{1}{2}}$; i.e., $\tau^k=f(k-1)+f(k)\tau$ and $(-\tau)^{-k}$ $=f(k-1)+f(k)(1-\tau)$. Therefore, $f(k)=\dfrac{\tau^k-(-\tau)^{-k}}{\tau+\tau^{-1}}$ which can be written as

$$N = a^{-1}2^{-(m+2)}[(1+a)^{m+2}-(1-a)^{m+2}]. \tag{7}$$

This form can be modified by expansion of $(1+a)^{m+2}$ and $(1-a)^{m+2}$ based on Newton's formula and then simplified as

$$\begin{aligned} N &= 2^{-(m+1)} \sum_{k=1}^{(m+2)/2} \binom{m+2}{2k-1} 5^{(k-1)}, \quad m=\text{even}, \\ N &= 2^{-(m+1)} \sum_{k=1}^{(m+3)/2} \binom{m+2}{2k-1} 5^{(k-1)}, \quad m=\text{odd}. \end{aligned} \tag{8}$$

The above expression is a general form for N with any m for $Z[m,1]$. On the other hand, the $Z[1,n]$ series is identical to the polyacene series $R[1,n]$. The two-tier type, the $Z[2,n]$, is the series containing naphthalene, $Z[2,1]$, pyrene, $Z[2,2]$, anthanthrene $Z[2,3]$, etc. For this series, N can be calculated from $\sum_{k=1}^{n+1} k$, and, after expansion, N is given by $(n+1)(n+2)/2$ which is essentially $\binom{n+2}{n}$, derived from Eq. (6) from $S[2,n]$.

The next sequence, $Z[3,n]$, has a three tier strip with one end indented and is pentagonally shaped (in the form of chevron). $Z[3,1]$ is phenanthrene; $Z[3,2]$ is 1,12-benzoperylene, etc. Derivation of N yields

$$N = \sum_{k=1}^{n+1} k^2 = (n+1)(n+2)(2n+3)/6. \tag{9}$$

Eq. (9) can also be derived by adding one benzene ring to the $R[2,n]$ series, e.g., the addition of one benzene ring to biphenyl, $R[2,1]$, yields phenanthrene, $Z[3,1]$; adding, in the same manner, one benzene ring to perylene, $R[2,2]$, becomes 1,12-benzoperylene, $Z[3,2]$; etc.

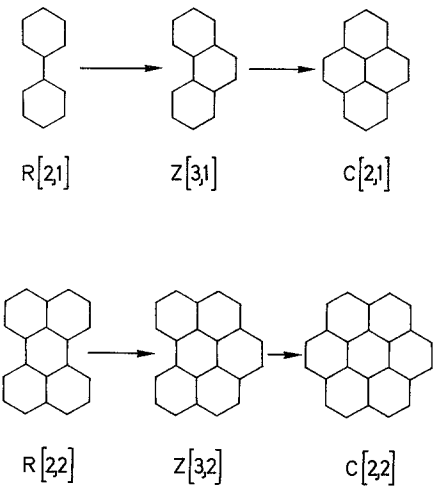

Fig. 2

In general, the addition of one benzene ring to the $R[2, n]$ series will result in the $Z[3, n]$ series. The formula for the $R[2, n]$ series is $N=(n+1)^2$. When one ring is coupled to $R[2, n]$, Eq.(10) is obtained for $Z[3, n]$.

$$\begin{aligned} N &= 1+\sum_{1}^{n}(n+1)^2 \\ &= 1+n(n+1)(2n+1)/6+n(n+1)+n \\ &= (n+1)(n+2)(2n+3)/6\,. \end{aligned} \tag{10}$$

To verify Eq. (10), another benzene ring is coupled to the $Z[3, n]$ series to produce the $C[2, n]$ series, e.g., from phenanthrene, $Z[3, 1]$ to pyrene, $C[2, 1]$; from 1,12-benzperylene, $Z[3, 2]$, to coronene, $C[2, 2]$

$$\begin{aligned} N &= 1+\sum_{1}^{n}(n+1)(n+2)(2n+3)/3\,! \\ &= (n+1)(n+2)^2(n+3)/12 \\ &= \binom{n+2}{n}\binom{n+3}{n}\Big/\binom{n+1}{n}. \end{aligned} \tag{11}$$

Eq. (11) gives a formula for $C[2, n]$ identical to that obtained from Eq. (6).

Apparently the successive coupling of the benzene ring to a specific series is quite general, e.g., if we want to write an explicit form of N for the 5-tier strip, i.e., the peropyrene type of molecule, $PP[m, n]$, we could derive it from a known model type, e.g., the C-model.

From Eq. (6), the N for $C[3, n]$ should be $\dfrac{\binom{n+3}{n}\binom{n+4}{n}\binom{n+5}{n}}{\binom{n+1}{n}\binom{n+2}{n}}$.

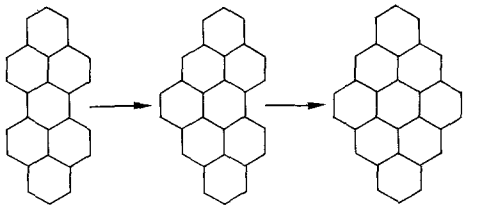

Fig. 3

After considering the numbers of $n=1$ to $n=3$, one can construct a table predicting the values for the $PP[3,n]$ series.

n	$PP[3,n]$	$BP[3,n]$	$C[3,n]$
1	18	19	20
2	136	155	175
3	650	805	980

By inspection, one can deduce the column of values from right to left as $1+\underline{19}=20$; $1+19+\underline{155}=175$; $1+19+155+\underline{805}=980$; etc. Hence we can write $BP[3,n]$ as

$$\frac{\binom{n+3}{n}\binom{n+4}{n}\binom{n+5}{n}}{\binom{n+1}{n}\binom{n+2}{n}}-\frac{\binom{n+2}{n-1}\binom{n+3}{n-1}\binom{n+4}{n-1}}{\binom{n}{n-1}\binom{n+1}{n-1}}$$

or for the $PP[3,n]$ series,

$$\frac{\binom{n+3}{n}\binom{n+4}{n}\binom{n+5}{n}}{\binom{n+1}{n}\binom{n+2}{n}}-\frac{2\binom{n+2}{n-1}\binom{n+3}{n-1}\binom{n+4}{n-1}}{\binom{n}{n-1}\binom{n+1}{n-1}}+\frac{\binom{n+1}{n-2}\binom{n+2}{n-2}\binom{n+3}{n-2}}{\binom{n-1}{n-2}\binom{n}{n-2}}$$

which can be abbreviated as

$$\begin{aligned}N_{PP[3,n]}&=\sum_{m=1}^{3}\binom{n+m}{n+m-3}\prod_{q=1}^{2}\binom{n+m+q}{n+m-3}\Big/\binom{n+m+q-3}{n+m-3}\\&\quad-3\binom{n+2}{n-1}\sum_{q=1}^{2}\binom{n+q+2}{n-1}\Big/\binom{n+q-1}{n-1}\\&=(n+1)(n+2)^3(n+3)(n^2+4n+5)/5!\,.\end{aligned}\tag{12}$$

It can be shown that

$$N_{BP[3,n]}=1+N_{PP[3,n]}\,.\tag{13}$$

and

$$N_{C[3,n]}=1+N_{BP[3,n]}\,.\tag{14}$$

The four major models (*R*, *C*, *S*, and *Z*) discussed will cover most polynuclear hydrocarbons frequently encountered, either kata- or pericondensed. Physically, since *N* is related to certain resonance forms with a specified degree of excitation, it is to be anticipated that *N* will correlate with a number of properties such as delocalization energy, boiling point, etc.

N-values obtained for a few aromatic hydrocarbons of the four models are included in the Table.

Table. *N-Values of some polynuclear aromatic hydrocarbons*

Shape	Hydrocarbon	*N*
R[1, 11]	Undecacene	12
C[2, 2]	Coronene	20
R[2, 2]	Perylene	9
C[2, 4]	Circumanthracene	105
R[6, 1]	Sexiphenyl	64
S[3, 3]	5,6,12,13-Dibenzoperopyrene	20
Z[5, 1]	Picene	13
R[4, 2]	Quaterylene	81
C[3, 3]	Circumcoronene	980
Z[3, 2]	1,12-Benzoperylene	14
C[2, 3]	Ovalene	50
C[4, 4]	—	232, 848

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