  Bull. Chem. Soc. Jpn., 65, 2011—2015 (1992)

Topological Indices of Unbranched Catacondensed Benzenoid Hydrocarbons

Haruo HOSOYA,* Ivan GUTMAN,† and Jasmina NIKOLIĆ†
Department of Chemistry, Ochanomizu University, Bunkyo-ku, Tokyo 112
†Faculty of Science, University of Kragujevac, P.O.Box 60,
YU-34000 Kragujevac, Yugoslavia
(Received February 10, 1992)

The topological indices σ (recently proposed by Merrifield and Simmons) and Z (put forward by one of the present authors, *Bull. Chem. Soc. Jpn.*, **44**, 2332 (1971)) of unbranched catacondensed benzenoid hydrocarbons are examined and their dependence on molecular structure is established. Approximate formulas are deduced, enabling an easy and accurate calculation of σ and Z.

In a recent paper[1] we have examined the mutual relation between the two variants of the topological index, namely Z, conceived twenty years ago by one of the present authors,[2] and σ, introduced somewhat later by Merrifield and Simmons.[3] We have established[1] that in the case of isomeric unbranched catacondensed benzenoid hydrocarbons a reasonably good linear correlation exists between Z and σ. In order to better understand this finding we have studied in detail the dependence of the topological indices Z and σ on the structure of the respective benzenoid molecules. The results obtained along these lines are reported in this paper.

The topological indices Z and σ are defined as

$$Z = Z(G) = \sum_{k \geq 0} p(G, k)$$

and

$$\sigma = \sigma(G) = \sum_{k \geq 0} q(G, k),$$

where $p(G, k)$ and $q(G, k)$ count the k-element sets of independent edges and vertices, respectively, of the molecular graph G. Two graph polynomials, closely related to Z and σ are

$$Q(G) = Q(G, x) = \sum_{k \geq 0} p(G, k)\, x^k$$

$$R(G) = R(G, x) = \sum_{k \geq 0} q(G, k)\, x^k.$$

Evidently, for $x=1$ the polynomials $Q(G, x)$ and $R(G, x)$ become equal to the Z and σ indices, respectively, of the graph G.

More details on the topological indices Z and σ, a survey of their numerous chemical and physicochemical applications as well as references to the underlying theoretical considerations can be found in our previous paper[1] and elsewhere.[3-6]

I. Unbranched Catacondensed Benzenoid Hydrocarbons and Their Structural Characterization

Unbranched catacondensed benzenoid systems are benzenoid hydrocarbons obeying the following structural requirements:[7]

(a) no carbon atom belongs to more than two adjacent six-membered rings;

(b) no six-membered ring has more than two adjacent six-membered rings.

In what follows six-membered rings will be called hexagons. The number of hexagons is denoted by h. Recall that all catacondensed benzenoids with h hexagons have formula $C_{4h+2}H_{2h+4}$ and are thus isomers.[7]

Unbranched catacondensed benzenoid hydrocarbons and their molecular graphs have been extensively studied in theoretical and mathematical chemistry, and quite a few of their general properties have been established so

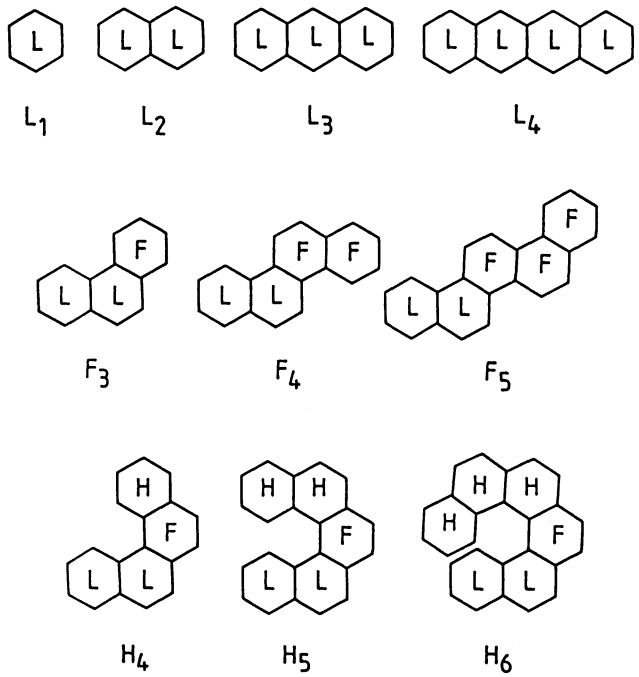

Fig. 1. The first few representatives of the linear polyacenes L_h(h=1,2,3,4), fibonaccenes F_h (h=3,4,5), and helicenes H_h (h=4,5,6). Their (L,F,H)-codes are L, LL, LLL, LLLL (linear polyacenes), LLF, LLFF, LLFFF (fibonaccenes), and LLFH, LLFHH, LLFHHH (helicenes). It is consistent to assume that $H_1=F_1=L_1$, $H_2=F_2=L_2$, and $H_3=F_3$.

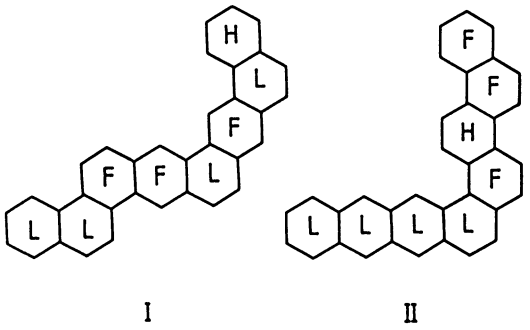

Fig. 2. Unbranched catacondensed benzenoid systems whose (L,F,H)-codes are LLFFLFLH and LLLLFHFF. Conventionally, the symbols L,F, and H are associated with the hexagons by starting from the left-hand side terminal hexagon; the codes necessarily begin with LL.

far. Of the plethora of publications devoted to this class of benzenoid molecules we mention just a few most recent.[8–15]

Now, the structure of an unbranched catacondensed system can be uniquely characterized by means of a three-digit or three-letter code, each digit or letter corresponding to a hexagon. Several such codes have been proposed,[8–10,15] the most frequently employed one being that of Balaban.[17–20] In this study we found it convenient to use the (L,F,H)-code which is essentially the same as the previously introduced[9,10] (I,J,K)-code. Here L, F, and H symbolize the annelation modes typical for linear polyacenes fibonaccenes, and helicenes (see Fig. 1). The two examples depicted in Fig. 2 should be self-explanatory; more details can be found elsewhere.[9,10]

From Fig. 1 we see that the (L,F,H)-code of a linear polyacene is $LLLLL\cdots L\equiv L^h$, of a fibonaccene is $LLFFF\cdots F\equiv L^2F^{h-2}$, whereas the code representing a helicene is $LLFHH\cdots H\equiv L^2FH^{h-3}$.

In what follows we denote the number of times the letters L, F, and H occur in the code by h_L, h_F, and h_H, respectively. Obviously, $h_L+h_F+h_H=h$.

II. Calculating the *Q*- and *R*-Polynomials and the Topological Indices of Linear Polyacenes

Applying the operator technique, invented by Hosoya and Ohkami[21] it has been shown[10] that the *Q*-polynomial of the linear polyacene L_h (cf. Fig. 1) obeys the relation

$$[Q(L_h), Q(L_{h-1}), Q(A_{h-1}), Q(B_{h-1}), Q(C_{h-1})]^t=(\boldsymbol{L}_Q)^h\boldsymbol{Q}_0 \quad (1)$$

where $\boldsymbol{Q}_0$ is the column-vector $[1+x, 1, 1, 1, 1]^t$ and

$$\boldsymbol{L}_Q=\begin{bmatrix} 1+3x+x^2 & 0 & x(2+5x+x^2) & x^2(1+2x) & x^2(1+2x) \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & x(2+x) & x^2 & x^2 \\ 1 & 0 & x & x^2 & 0 \\ 1 & 0 & x & 0 & x^2 \end{bmatrix} \quad (2)$$

and where A_{h-1}, B_{h-1}, and C_{h-1} represent auxiliary molecular graphs whose actual structures are irrelevant for the present analysis (and can be found elsewhere[10]). In Eq. 1 and later on $\boldsymbol{M}^t$ denotes the transpose of the matrix $\boldsymbol{M}$.

The characteristic polynomial of the matrix $\boldsymbol{L}_Q$ is equal to

$$\phi(\boldsymbol{L}_Q, \lambda)=\lambda(\lambda-x^2)[\lambda^3-(1+5x+3x^2)\lambda^2+x^2(1+3x+3x^2)\lambda-x^6]$$

from which it follows that $Q(L_h)$ obeys the recurrence relation[10,22,23]

$$Q(L_{h+3})-(1+5x+3x^2)\,Q(L_{h+2}) + x^2(1+3x+3x^2)\,Q(L_{h+1})-x^6Q(L_h)=0. \quad (3)$$

Setting $x=1$ in Eqs. 1, 2, and 3 we obtain, as a special case, the respective expressions for the Z index of L_h. In particular, if we define the matrices $\boldsymbol{L}_Z\equiv\boldsymbol{L}_Q(x=1)$ and $\boldsymbol{Z}_0$ as

$$\boldsymbol{L}_Z=\begin{bmatrix} 5 & 0 & 8 & 3 & 3 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 3 & 1 & 1 \\ 1 & 0 & 1 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 \end{bmatrix}$$

and $\boldsymbol{Z}_0=\boldsymbol{Q}_0(x=1)=[2, 1, 1, 1, 1]^t$ then $Z(L_h)=[(\boldsymbol{L}_Z)^h\boldsymbol{Z}_0]_{11}$. Further, the characteristic polynomial of $\boldsymbol{L}_Z$ is equal to

$$\phi(\boldsymbol{L}_Z, \lambda)=\lambda(\lambda-1)(\lambda^3-9\lambda^2+7\lambda-1)$$

and $Z(L_h)$ conforms to the recurrence relation[10,22]

$$Z(L_{h+3})-9Z(L_{h+2})+7Z(L_{h+1})-Z(L_h)=0.$$

The largest root of the equation $\phi(\boldsymbol{L}_Z, \lambda)=0$ is equal to[24]

$$\lambda_Z=3+\sqrt{80/3}\cos\left[\frac{1}{3}\arccos\sqrt{7803/8000}\right]= 8.15685606..., \quad (5)$$

which means that for large values of h, the Z index of L_h increases as $(\lambda_Z)^h$. In other words, with increasing h $\log Z(L_h)$ becomes a linear function of h and $1/h$ $\log Z(L_h)$ tends to the limit value $\log\lambda_Z$. Numerical testing shows that such a simple behavior of $Z(L_h)$ is observed already at $h\geq 3$.

We note in passing that the matrices $\boldsymbol{L}_Q$ and $\boldsymbol{L}_Z$, given by Eqs. 2 and 4, are slightly different from those reported previously.[10]

In the case of the *R*-polynomial, a fully analogous reasoning based on the operator technique[21] results in

$$[R(L_h), R(L_{h-1}), R(A_{h-1}), R(B_{h-1}), R(C_{h-1})]^t=(\boldsymbol{L}_R)^h\boldsymbol{R}_0, \quad (6)$$

where $\boldsymbol{R}_0$ is the column-vector $[1+2x, 1, 1, 1, 1]^t$ and where

$$\boldsymbol{L}_R=\begin{bmatrix} 0 & 0 & 1+4x+3x^2 & x(1+3x+x^2) & x(1+3x+x^2) \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1+2x+x^2 & x(1+x) & x(1+x) \\ 0 & 0 & 1+x & x(1+x) & x \\ 0 & 0 & 1+x & x & x(1+x) \end{bmatrix} \quad (7)$$

$$\phi(\boldsymbol{L}_R, \lambda) = \lambda^2(\lambda - x^2)[\lambda^2 - (1+4x+2x^2)\,\lambda + x^2(1+x)^2]. \quad (8)$$

Consequently, the R-polynomial of the linear polyacene satisfies the recurrence relation

$$R(\boldsymbol{L}_{h+2}) - (1+4x+2x^2)\,R(\boldsymbol{L}_{h+1}) + x^2(1+x)^2\,R(\boldsymbol{L}_h) = 0. \quad (9)$$

Setting $x=1$ in Eqs. 6—9 we obtain the expressions for the σ index of L_h. Thus the characteristic polynomial of the matrix $\boldsymbol{L}_\sigma \equiv \boldsymbol{L}_R(x=1)$,

$$\boldsymbol{L}_\sigma = \begin{bmatrix} 0 & 0 & 8 & 5 & 5 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 4 & 2 & 2 \\ 0 & 0 & 2 & 2 & 1 \\ 0 & 0 & 2 & 1 & 2 \end{bmatrix}$$

is equal to

$$\phi(\boldsymbol{L}_\sigma, \lambda) = \lambda(\lambda-1)(\lambda^2 - 7\lambda + 4)$$

from which we conclude that $\sigma(L_h)$ conforms to the recurrence relation[25]

$$\sigma(L_{h+2}) - 7\sigma(L_{h+1}) + 4\sigma(L_h) = 0.$$

The largest root of the equation $\phi(\boldsymbol{L}_\sigma, \lambda)=0$ is given by[25]

$$\lambda_\sigma = \frac{1}{2}(7+\sqrt{33}) = 6.37228132.... \quad (10)$$

In accordance with this, for large values of h, $\sigma(L_h)$ is expected to increase as $(\lambda_\sigma)^h$ i.e. the logarithm of $\sigma(L_h)$ becomes a linear function of h and $1/h \log\sigma(L_h)$ approaches the limit value $\log\lambda_\sigma$. According to our numerical testing, $\sigma(L_h)$ has such a behavior already for $h \geq 3$.

III. Calculating the Q- and R-Polynomials and the Topological Indices of Fibonaccenes and Helicenes

In the case of fibonaccenes and helicenes (cf. Fig. 1) calculations analogous to those reported in the previous section yield the following results:

$$[Q(F_h), Q(F_{h-1}), Q(A'_{h-1}), Q(B'_{h-1}), Q(C'_{h-1})]^t = (\boldsymbol{F}_Q)^{h-2}\,(\boldsymbol{L}_Q)^2\,\boldsymbol{Q}_0,$$

$$[R(F_h), R(F_{h-1}), R(A'_{h-1}), R(B'_{h-1}), R(C'_{h-1})]^t = (\boldsymbol{F}_R)^{h-2}\,(\boldsymbol{L}_R)^2\,\boldsymbol{R}_0,$$

$$[Q(H_h), Q(H_{h-1}), Q(A''_{h-1}), Q(B''_{h-1}), Q(C''_{h-1})]^t = (\boldsymbol{H}_Q)^{h-3}\,\boldsymbol{F}_Q(\boldsymbol{L}_Q)^2\,\boldsymbol{Q}_0,$$

$$[R(H_h), R(H_{h-1}), R(A''_{h-1}), R(B''_{h-1}), R(C''_{h-1})]^t = (\boldsymbol{H}_R)^{h-3}\,\boldsymbol{F}_R(\boldsymbol{L}_R)^2\,\boldsymbol{R}_0,$$

where A'_{h-1}, B'_{h-1}, C'_{h-1}, A''_{h-1}, B''_{h-1}, C''_{h-1} denote certain auxiliary molecular graphs and where

$$\boldsymbol{F}_Q = \begin{bmatrix} 1+3x+x^2 & x^2(1+3x+x^2) & x(1+2x) & x(1+4x+3x^2) & x^2(1+2x) \\ 1 & 0 & 0 & 0 & 0 \\ 1 & x^2(1+x) & x & x(1+2x) & x^2 \\ 1 & x^2 & 0 & x(1+x) & 0 \\ 1 & 0 & x & 0 & x^2 \end{bmatrix}$$

$$\boldsymbol{F}_R = \begin{bmatrix} 1+2x & x^2(1+2x) & x(1+x) & x(1+3x+x^2) & x^2(1+x) \\ 1 & 0 & 0 & 0 & 0 \\ 1 & x^2(1+x) & x & x(1+2x) & x^2 \\ 1 & x^2 & 0 & x(1+x) & 0 \\ 1 & 0 & x & 0 & x^2 \end{bmatrix}$$

$$\boldsymbol{H}_Q = \begin{bmatrix} 1+3x+x^2 & x^2(1+3x+x^2) & x(1+2x) & x^2(1+2x) & x(1+4x+3x^2) \\ 1 & 0 & 0 & 0 & 0 \\ 1 & x^2(1+x) & x & x^2 & x(1+2x) \\ 1 & x^2 & 0 & 0 & x(1+x) \\ 1 & 0 & x & x^2 & 0 \end{bmatrix}$$

$$\boldsymbol{H}_R = \begin{bmatrix} 1+2x & x^2(1+2x) & x(1+x) & x^2(1+x) & x(1+3x+x^2) \\ 1 & 0 & 0 & 0 & 0 \\ 1 & x^2(1+x) & x & x^2 & x(1+2x) \\ 1 & x^2 & 0 & 0 & x(1+x) \\ 1 & 0 & x & x^2 & 0 \end{bmatrix}$$

The respective recurrence relations read:

$$Q(F_{h+4}) - (1+5x+3x^2)\,Q(F_{h+3}) + x^2(1+2x+2x^2)\,Q(F_{h+2}) + x^4(1+3x+x^2)\,Q(F_{h+1}) - x^8 Q(F_h) = 0$$

$$R(F_{h+3}) - (1+4x+2x^2)\,R(F_{h+2}) + x^2(1+x)^2\,R(F_{h+1}) - x^4(1+2x)\,R(F_h) = 0$$

$$Q(H_{h+4}) - (1+4x+x^2)\,Q(H_{h+3}) - x(1+6x+10x^2+2x^3)Q(H_{h+2}) - x^4(1+2x-x^2)\,Q(H_{h+1}) - x^8 Q(H_h) = 0$$

$$R(H_{h+3}) - (1+3x)\,R(H_{h+2}) - x(1+5x+7x^2+x^3)R(H_{h+1}) - x^4(1+2x)\,R(H_h) = 0$$

Setting $x=1$ in the above formulas we obtain explicit expressions and recurrence relations for the topological indices Z and σ of the fibonaccenes and helicenes. It can immediately be verified that for large values of h, both $Z(F_h)$, $\sigma(F_h)$, $Z(H_h)$, and $\sigma(H_h)$ increase as exponential functions of the parameter h. Such an exponential behavior was found to begin at quite small values of h: $h \geq 6$ for the fibonaccene series and $h \geq 7$ for the helicene series.

IV. Calculating the Q- and R-Polynomials and the Topological Indices of Arbitrary Unbranched Catacondensed Benzenoid Molecules

In harmony with the previously obtained results[9,10,15] on the application of the Hosoya–Ohkami operator technique,[21] the Q- and R-polynomials of an h-cyclic unbranched catacondensed benzenoid systems U can be obtained by a successive application of the transfer matrices $\boldsymbol{L}_Q$, $\boldsymbol{F}_Q$, $\boldsymbol{H}_Q$, and $\boldsymbol{L}_R$, $\boldsymbol{F}_R$, $\boldsymbol{H}_R$. Let the (L,F,H)-code of U be $[S_1, S_2, \cdots, S_{h-1}, S_h]$ where $S_i \in \{L, F, H\}$, $i=1,2, \cdots, h$ and where S_i corresponds to the annelation mode of the i-th hexagon. (Recall that it is always $S_1=S_2=L$, cf. Fig. 2.) Then

$$Q(U, x) = [\boldsymbol{Q}_h\,\boldsymbol{Q}_{h-1} \cdots \boldsymbol{Q}_2\boldsymbol{Q}_1\boldsymbol{Q}_0]_{11} \quad (11)$$

$$R(U, x) = [\boldsymbol{R}_h\,\boldsymbol{R}_{h-1} \cdots \boldsymbol{R}_2\boldsymbol{R}_1\boldsymbol{R}_0]_{11}. \quad (12)$$

In the above formulas the matrix $\boldsymbol{Q}_i$ is equal to $\boldsymbol{L}_Q$, $\boldsymbol{F}_Q$ or $\boldsymbol{H}_Q$, depending on whether $S_i=L$, $S_i=F$ or $S_i=H$, respectively, $i=1, 2, \cdots, h$. Similarly, the matrix $\boldsymbol{R}_i$ is

equal to $\boldsymbol{L}_R$, $\boldsymbol{F}_R$ or $\boldsymbol{H}_R$ when S_i=L, S_i=F or S_i=H, respectively, i=1, 2, ···, h.

By setting x=1 in Eqs. 11 and 12 we arrive at matrix-multiplication formulas for the topological indices Z and σ. A somewhat different, but fully equivalent form of these special cases of Eqs. 11 and 12 was reported in our previous paper.[1)]

Calculations of Z and σ, based on Eqs. 11 and 12 are not too difficult, but they hardly can be done without using computers. As a consequence of this, it is not easy to see how various structural details of the benzenoid molecule influence the values of Z and σ. In order to overcome this difficulty we tried to design approximate combinatorial formulas for Z and σ, which would relate the topological indices with simple structural features of the corresponding molecules. If such formulas have a sufficiently high accuracy, then we are in the position to infer about the structure-dependency of Z and σ. In the subsequent section we report some results in this direction.

V. Structural Factors Determining the Topological Indices Z and σ

The main structural factor determining the numerical values of Z and σ of unbranched catacondensed benzenoid molecules is certainly their size i.e. the parameter h. Bearing this in mind, in the following we will be interested only in the variations of Z and σ among isomers i.e. among species having a fixed value of h.

From numerous examples studied we conclude that the second most important structural feature influencing Z and σ is the count of the symbols L, F, and H in the (L,F,H)-code i.e. the triple of the numbers h_L, h_F, and h_H. That this indeed may be the case is seen from the following example.

There are 21 unbranched catacondensed benzenoid isomers with h_L=4, h_F=3, h_H=1. Among them, the molecule I depicted in Fig. 2 has maximal Z (=47663322) and minimal σ (=7214604) whereas the molecule II from Fig. 2 has minimal Z (=47351731) and maximal σ (=7247121). Thus the observed variations of Z and σ are remarkably small. The two extremes differ only by 0.65% (in the case of Z) and by 0.45% (in the case of σ).

Similar very low variances of Z and σ are found in other families with fixed h_L, h_F, h_H values.

The form of the (approximate) functions $Z=Z(h_L, h_F, h_H)$ and $\sigma=\sigma(h_L, h_F, h_H)$ can be guessed from the known behavior of the topological indices of the linear polyacenes ($h_L=h$, $h_F=h_H=0$), fibonaccenes ($h_L=2$, $h_F=h-2$, $h_H=0$) and helicenes ($h_L=2$, $h_F=1$, $h_H=h-3$), outlined in the preceding sections. Since in these cases the dependence of Z and σ, on h_L, h_F, and h_H is exponential, we may anticipate that this dependency is maintained in all other unbranched catacondensed benzenoids. If so, then

$$Z=a_z\,(b_z)^{h_L}\,(c_z)^{h_F}\,(d_z)^{h_H} \tag{13}$$

and

$$\sigma=a_\sigma\,(b_\sigma)^{h_L}\,(c_\sigma)^{h_F}\,(d_\sigma)^{h_H} \tag{14}$$

would be the required approximate formulas. Here a_z, b_z, c_z, d_z and a_σ, b_σ, c_σ, d_σ are constants which remain to be determined.

In the subsequent section we describe in due detail how we have established that

$a_z=2.2156$	$a_\sigma=2.7945$
$b_z=8.1691$	$b_\sigma=6.3723$
$c_z=8.3314$	$c_\sigma=6.2944$
$d_z=8.3193$	$d_\sigma=6.3026$

The accuracy of the formulas (13) and (14) was tested on the set of 287 unbranched catacondensed benzenoid molecules with four to eight hexagons. Using the above listed values for the parameters $a,b,c,$ and d we could reproduce Z and σ with an average error of only 0.17% and 0.15%, respectively. The maximal observed error in this sample was 0.7% and 0.5%, respectively. The correlations between the exact and approximate Z and σ values had correlation coefficients 0.999992 and 0.999996, respectively.

Hence the accuracy and reliability of the approximate formulas (13) and (14) is fairly good. In addition to this, both Z and σ are reproduced by means of Eqs. 13 and 14 with almost equal success.

The main conclusions which can be drawn from Eqs. 13 and 14 and the established values of the parameters a,b,c,d are the following.

(i) Both Z and σ are exponential functions of h_L, h_F, and h_H. The finding that b_σ, c_σ, d_σ have significantly smaller values than b_z, c_z, d_z complies with the fact that Z is orders of magnitudes greater than σ.

(ii) Angularly annelated hexagons contribute more to the value of Z than linearly annelated hexagons. Consequently, the linear polyacenes have minimal Z values among all unbranched catacondensed benzenoids with the same number of hexagons.

(iii) Linearly annelated hexagons contribute more to the value of σ than angularly annelated hexagons. Consequently, among all unbranched catacondensed benzenoids with h hexagons, L_h has the maximal σ value.

(iv) The F- and H-character of an angularly annelated hexagon has very little influence on the magnitude by which it contributes to either Z or σ. Nevertheless, a fibonaccene-type annelation is somewhat more favorable for the Z index whereas a helicene-type annelation is slightly more favourable in the case of the σ index. These minor differences (which, however, increase exponentially) cause that fibonaccenes will have both maximal Z and minimal σ indices among all unbranched catacondensed benzenoid hydrocarbons with a given number of hexagons.

(v) The two topological indices Z and σ depend on the same structural features of the benzenoid molecule (and are thus correlated). The correlation between Z and σ

is reverse, i.e. large Z values are associated with small σ values and vice versa.

VI. Numerical Work

The parameters $a,b,c,$ and d in Eqs. 13 and 14 were computed in seven different ways.

First we determined ln a, ln b, ln c, and ln d from the straight lines obtained by plotting ln $Z(L_h)$, ln $Z(A_h)$, ln $Z(H_h)$, ln $\sigma(L_h)$, ln $\sigma(A_h)$, and ln $\sigma(H_h)$ versus h. The values thus obtained coincide completely with those which can be deduced from the eigenvalues of the transfer matrices $\boldsymbol{L}$, $\boldsymbol{F}$, and $\boldsymbol{H}$ or from the recurrence relations listed in the sections II and III.

Next we calculated $a,b,c,$ and d by least-squares fitting, using as a data base the exact Z and σ values of all 287 geometrically planar unbranched catacondensed benzenoids[7] with 4, 5, 6, 7, and 8 hexagons.

Finally we calculated $a,b,c,$ and d by least-squares fitting, using as a data base the Z and σ values of all geometrically planar unbranched catacondensed benzenoid isomers. We separately considered the isomers with four, five, six, seven, and eight hexagons.

In these latter cases the parameters $a,b,c,$ and d are not uniquely determined because the three numbers h_L, h_F, and h_H are linearly dependent if h (=their sum) is fixed. In order to avoid this difficulty we adopted for b_Z and b_σ the values λ_Z and λ_σ, respectively, given by Eqs. 5 and 10.

By all these seven procedures we obtained almost identical values for $a,b,c,$ and d. Nevertheless, the parameters determined from the set of all unbranched catacondensed molecules with $4 \leq h \leq 8$ were found to be optimal for the Z index. On the other hand, the best parameters for the σ index were determined from the set of the 7-cyclic unbranched catacondensed benzenoid isomers. These best values for the parameters $a,b,c,$ and d are listed in the preceding section. They are capable of reproducing Z and σ with a chemically insignificant error of less than 0.5%.

References

1) I. Gutman, H. Hosoya, G. Uraković, and L. Ristić, *Bull. Chem. Soc. Jpn.*, **65**, 14 (1992).

2) H. Hosoya, *Bull. Chem. Soc. Jpn.*, **44**, 2332 (1971).

3) H. E. Simmons and R. E. Merrifield, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 2616 (1977); R. E. Merrifield and H. E. Simmons, *Theor. Chim. Acta*, **55**, 55 (1980); R. E. Merrifield and H. E. Simmons, *Proc. Natl. Acad. Sci. U.S.A.*, **78**, 692 (1981); *ibid.*, **82**, 1 (1985); R. E. Merrifield and H. E. Simmons, "Topological Methods in Chemistry," Wiley, New York (1989).

4) I. Gutman and O. E. Polansky, "Mathematical Concepts in Organic Chemistry," Springer-Verlag, Berlin (1986), pp. 127—134.

5) H. Hosoya, *Discrete Appl. Math.*, **19**, 239 (1988).

6) H. Hosoya, in "Valence Bond Theory and Chemical Structure," ed by D. J. Klein and N. Trinajstić, Elsevier, Amsterdam (1990), pp. 53—80.

7) I. Gutman and S. J. Cyvin, "Introduction to the Theory of Benzenoid Hydrocarbons," Springer-Verlag, Berlin (1989).

8) I. Gutman and S. J. Cyvin, *Bull. Chem. Soc. Jpn.*, **62**, 1250 (1989).

9) O. E. Polansky, M. Randić, and H. Hosoya, *MATCH*, **24**, 3 (1989).

10) M. Randić, H. Hosoya, and O. E. Polansky, *J. Comput. Chem.*, **10**, 683 (1989).

11) S. El-Basil, *Top. Curr. Chem.*, **153**, 273 (1990).

12) I. Gutman, J. W. Kennedy, and L. V. Quintas, *Chem. Phys. Lett.*, **173**, 403 (1990).

13) I. Gutman, J. W. Kennedy, and L. V. Quintas, *J. Math. Chem.* **6**, 377 (1991).

14) R. Q. Sheng, *MATCH*, **26**, 247 (1991).

15) I. Gutman, *Rev. Roum. Chim.*, **36**, 379 (1991).

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

17) A. T. Balaban, *Pure Appl. Chem.*, **52**, 1409 (1980).

18) A. T. Balaban, *Pure Appl. Chem.*, **54**, 1075 (1982).

19) A. T. Balaban, *J. Mol. Struct. (THEOCHEM)*, **120**, 117 (1985).

20) A. T. Balaban, *J. Chem. Inf. Comput. Sci.*, **25**, 334 (1985).

21) H. Hosoya and N. Ohkami, *J. Comput. Chem.*, **4**, 585 (1983).

22) I. Gutman, E. J. Farrell, and S. A. Wahid, *J. Combust. Inf. System Sci.*, **8**, 159 (1983).

23) E. J. Farrell and S. A. Wahid, *Dicrete Appl. Math.*, **7**, 45 (1984).

24) I. Gutman, *Z. Naturforsch., A*, **43a**, 939 (1988).

25) I. Gutman and N. Kolaković, *Bull. Acad. Serbe Sci. Arts*, **102**, 39 (1990).