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A Method for Enumeration of the Algebraic Structure Count of Non-Branched Cata-Condensed Molecules

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An operator technique for the enumeration of the algebraic structure count (ASC) of non-branched cata-condensed molecules has been developed. General formulae for the ASC's of 16 conjugated series have been obtained.

In a recent paper[1] an operator technique has been described for the calculation of the number K of the Kekulé structures of non-branched cata-condensed (NCC) conjugated molecules. In our present study an attempt has been made to extend this technique to the calculation of the algebraic structure count (ASC) of the same class of molecules. The topological definitions of cata-condensed molecules are given in refs. 1 and 2.

The ASC is an important notion in the theoretical chemistry of conjugated molecules[3-11]. If K^+ and K^- ($K^+ + K^- = K$) are the numbers of Kekulé structures with even and odd parity respectively,[12]

$$\mathrm{ASC} = |\tilde{K}| \tag{1a}$$

where

$$\tilde{K} = K^+ - K^- \tag{1b}$$

The reason for introducing the quantity $\tilde{K}$ will be discussed later.

In alternant conjugated molecules with N carbon atoms and the graph adjacency matrix[16] $\mathbf{A}$,

$$\det \mathbf{A} = (-1)^{N/2}\,(\mathrm{ASC})^2 \tag{2}$$

while the relation between det $\mathbf{A}$ and ASC in non-alternants[17] is not so simple[5,13].

Considerations based on eq. (2) show that if ASC = O, the corresponding molecule should exhibit a biradical behaviour and be therefore extremely reactive[3,4,18-20]. Moreover, the greater the value of ASC, the stabler the molecule[7,9,11].

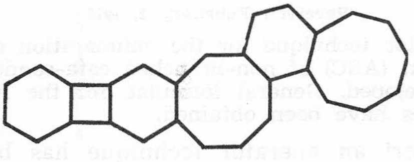
No simple and generally valid algorithm for the calculation of ASC is known. The usual way of determining ASC, *i. e.* by drawing all the Kekulé structures of a molecule is both rather tedious and unreliable for complicated polycyclic systems.

THE ALGORITHM

First we shall consider only the alternant NCC molecules. The extension of the obtained results to non-alternants will be given at the end of this section.

A ring in an alternant NCC compound is either benzenoid (that is of the size $4m + 2$) or non-benzenoid (that is of the size $4m$). We will denote these rings by R_b and R_c, respectively. Further, we say that a ring is annelated in an even (odd) manner if the number of C—C bonds between the two sites of annelation is even (odd). We denote these rings by R^+ and R^-, respectively. The terminal rings of a NCC molecule can be marked arbitrarily by R^+ or by R^-.

Thus we now distinguish four types of rings in alternant NCC molecules — R_b^+, R_b^-, R_c^+ and R_c^-. An ordered sequence of n symbols can be related to every n-cyclic NCC system; we denote such a sequence by (R). For example, the rings in the molecule 1 form a sequence $(R_1) = R_b R_c^- R_b^+ R_c^+ R_b^- R_c$.



I

Let a NCC molecule with n rings possess a ring sequence $(R) = R_1 R_2 \ldots R_n$. Let an operator $\hat{R}_j$ correspond to the ring R_j $(j = 1, 2, \ldots, n)$ and an operator sequence $\hat{R}_1 \hat{R}_2 \ldots \hat{R}_n$ to the whole molecule.

We offer the following result. If the operators $\hat{R}$ are given by

$$\hat{R}_b^+ = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 \end{bmatrix} \qquad \hat{R}_b^- = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$$\hat{R}_c^+ = \begin{bmatrix} 0 & 1 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \end{bmatrix} \qquad \hat{R}_c^- = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \tag{3}$$

then K^+ and K^- can be calculated from the relations

$$K^+ = D^+ + S^+ \tag{4a}$$

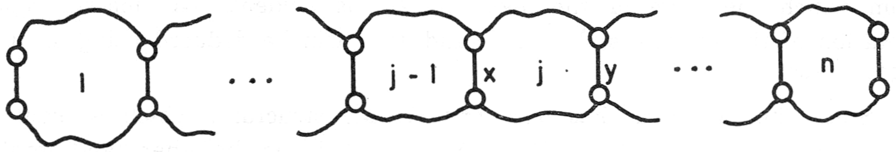
$$K^- = D^- + S^- \tag{4b}$$

where the numbers D^+, S^+, D^- and S^- follow from the equation

$$(D^+, S^+, D^-, S^-) = (1, 0, 0, 0)\, \hat{R}_1 \hat{R}_2 \ldots \hat{R}_n \tag{5}$$

From eqs. (4) one can calculate both ASC and K and, therefore, eq. (5) presents a generalization of the algorithm given in ref. 1.

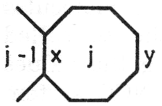
In order to prove eqs. (4) let us consider the graph[16] G_n of an n-cyclic NCC molecule.



G_n

The j-th ring is annelated to the (j—1)-th and the (j+1)-th rings through the bonds x and y, respectively. Let G_{j-1} be obtained by deletion of the rings $j, j+1, \ldots, n$ from G_n and K^-_{j-1} and K^+_{j-1} be the number of the even and odd Kekulé structures of G_{j-1}. D^+_{j-1} and S^+_{j-1} denote the number of times the bond x is double and single, respectively, in the even Kekulé structures of G_{j-1}. The quantities D^-_{j-1} and S^-_{j-1} are defined analogously for the odd Kekulé structures of G_{j-1}. Naturally, $K^+_{j-1} = D^+_{j-1} + S^+_{j-1}$ and $K^-_{j-1} = D^-_{j-1} + S^-_{j-1}$.

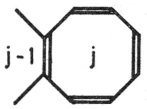
We shall consider, for example, the case when the j-th ring is of R^-_c type, let us say it is an 8-membered ring.



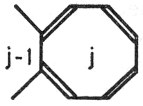
G_j

A

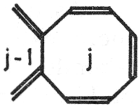
B



A_1



A_2



B_1

Let us determine the quantities D_j^+, S_j^+, D_j^- and S_j^- for the bond y of the graph G_j. If x is double in G_{j-1} (case A), two possibilities (cases A_1 and A_2) exist in G_j. If x is single in G_{j-1} (case B), only one possibility (case B_1) exists in G_j. It should be noted that the parity of the Kekulé structures A_1 is the same as the parity of A, while the structures A_2 have a parity which is the opposite of A. Similarly, B_1 and B have the same parity. Therefore,

$$D_j^+ = K^+(A_1) + K^+(B_1) = D^+_{j-1} + S^+_{j-1}$$

$$S_j^+ = K^+(A_2) = D^-_{j-1}$$

$$D_j^- = K^-(A_1) + K^-(B_1) = D^-_{j-1} + S^-_{j-1}$$

$$S_j^- = K^-(A_2) = D^+_{j-1}$$

or in matrix notation,

$$(D_j^+, S_j^+, D_j^-, S_j^-) = (D^+_{j-1}, S^+_{j-1}, D^-_{j-1}, S^-_{j-1}) \begin{bmatrix} 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \tag{6}$$

from which the form of the operator $\hat{R}_c^-$ is evident. The matrix representation of the operators $\hat{R}_b^+$, $\hat{R}_b^-$ and $\hat{R}_c^+$ can be deduced using an analogous reasoning.

Since the graph G_0 has only one Kekulé structure, which is even by definition, $D_0^+ = 1$ and $S_0^+ = D_0^- = S_0^- = 0$. This, on the other hand, implies the validity of eq. (5), where $D^+ \equiv D_n^+$, $S^+ \equiv S_n^+$, *etc.* Eqs. (4) follow now straightforwardly.

The applicability of our algorithm will be illustrated on the molecule I:

$$(1, 0, 0, 0)\, \hat{R}_b^+ \ \hat{R}_c^- \ \hat{R}_b^+ \ \hat{R}_c^+ \ \hat{R}_b^- \ \hat{R}_c^+ = (1, 1, 0, 0)\, \hat{R}_c^- \ \hat{R}_b^+ \ \hat{R}_c^+ \ \hat{R}_b^- \ \hat{R}_c^+ =$$

$$(2, 0, 0, 1)\, \hat{R}_b^+ \ \hat{R}_c^+ \ \hat{R}_b^- \ \hat{R}_c^+ = (2, 2, 0, 1)\, \hat{R}_c^+ \ \hat{R}_b^- \ \hat{R}_c^+ =$$

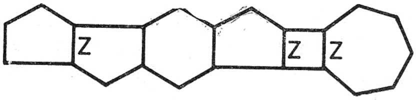
$$(0, 4, 2, 1)\, \hat{R}_b^- \ \hat{R}_c^+ = (4, 0, 3, 2)\, \hat{R}_c^+ = (3, 4, 4, 5)$$

Hence, $K^+ = 3 + 4 = 7$, $K^- = 4 + 5 = 9$ and finally $K = 16$, $\tilde{K} = -2$ and ASC = 2.

Extension to Non-Alternants

As has been discussed in detail in ref. 1, in non-alternant NCC molecules there exist C—C bonds with the zero Pauling bond oredr (the so called *z*-bonds). These *z*-bonds can be therefore erased without changing the values of K or ASC. After the elimination of all *z*-bonds an alternant NCC system will be obtained, and the previously described algorithm can be applied without difficulty. Note however that in a general case eq. (2) is no longer valid for non-alternant NCC systems[5,13].

For example, we will calculate the ASC value of compound II. Neglecting the *z*-bonds one obtains a ring sequence $(R)_{11} = R_c\, R_b^+\, R_c$, and since (1, 0, 0, 0)



II

$R_c^+\, R_b^+\, R_c^+ = (1, 1, 0, 2)$, we have finally, ASC = $|1 + 1 - 2| = 0$. Thus the compound II should be highly unstable.

GENERAL FORMULAE AND RECURSION RELATIONS FOR ASC

In this section the general formulae or recursion relations for the ASC of 16 classes of NCC molecules will be presented, the corresponding ring sequences of which are $(R)_1 - (R)_{16}$.

$(R)_1 = R_b^+ \ R_b^+ \ R_b^+ \ R_b^+ \ \ldots$

$(R)_2 = R_b^+ \ R_b^- \ R_b^+ \ R_b^- \ \ldots$

$(R)_3 = R_b^+ \ R_c^+ \ R_b^+ \ R_c^+ \ \ldots$

$(R)_4 = R_b^+ \ R_c^- \ R_b^+ \ R_c^- \ \ldots$

$(R)_9 = R_c^+ \ R_b^+ \ R_c^+ \ R_b^+ \ \ldots$

$(R)_{10} = R_c^+ \ R_b^- \ R_c^+ \ R_b^- \ \ldots$

$(R)_{11} = R_c^+ \ R_c^+ \ R_c^+ \ R_c^+ \ \ldots$

$(R)_{12} = R_c^+ \ R_c^- \ R_c^+ \ R_c^- \ \ldots$

$$(R)_5 = R_{\mathrm{b}}^{-}\ R_{\mathrm{b}}^{+}\ R_{\mathrm{b}}^{-}\ R_{\mathrm{b}}^{+}\ \ldots \qquad (R)_{13} = R_{\mathrm{c}}^{-}\ R_{\mathrm{b}}^{+}\ R_{\mathrm{c}}^{-}\ R_{\mathrm{b}}^{+}\ \ldots$$

$$(R)_6 = R_{\mathrm{b}}^{-}\ R_{\mathrm{b}}^{-}\ R_{\mathrm{b}}^{-}\ R_{\mathrm{b}}^{-}\ \ldots \qquad (R)_{14} = R_{\mathrm{c}}^{-}\ R_{\mathrm{b}}^{-}\ R_{\mathrm{c}}^{-}\ R_{\mathrm{b}}^{-}\ \ldots$$

$$(R)_7 = R_{\mathrm{b}}^{-}\ R_{\mathrm{c}}^{+}\ R_{\mathrm{b}}^{-}\ R_{\mathrm{c}}^{+}\ \ldots \qquad (R)_{15} = R_{\mathrm{c}}^{-}\ R_{\mathrm{c}}^{+}\ R_{\mathrm{c}}^{-}\ R_{\mathrm{c}}^{+}\ \ldots$$

$$(R)_8 = R_{\mathrm{b}}^{-}\ R_{\mathrm{c}}^{-}\ R_{\mathrm{b}}^{-}\ R_{\mathrm{c}}^{-} \qquad (R)_{16} = R_{\mathrm{c}}^{-}\ R_{\mathrm{c}}^{-}\ R_{\mathrm{c}}^{-}\ R_{\mathrm{c}}^{-}\ \ldots$$

The number of cycles in these molecules is n. For the sake of simplicity we will express our results in terms of $\tilde{K}$ instead of ASC (see equations (1)).

Let us first consider the sequence $(R)_1$. One can easily see that

$$(a_1, a_2, a_3, a_4)\,(\hat{\mathrm{R}}_{\mathrm{b}}^{+})^n = (a_1, na_1 + a_2, a_3, na_3 + a_4) \tag{7}$$

Therefore $K_n^{+} = (n + 1)\, a_1 + a_2$, $K_n^{-} = (n + 1)\, a_3 + a_4$ and $\tilde{K}_{\mathrm{n}} = (n + 1)\ (a_1 - a_3) + a_2 - a_4$. According to eq. (5) $a_1 = 1$ and $a_2 = a_3 = a_4 = 0$, which finally yields for $(R)_1$:

$$\tilde{\mathrm{K}}_n = n + 1 \tag{8}$$

As another example we will consider sequence $(R)_{11}$ in a greater detail. It can be proved by mathematical induction that

$$\begin{aligned} (a_1, a_2, a_3, a_4)\,(\hat{\mathrm{R}}_{\mathrm{c}}^{+})^{2j} &= (a_1, ja_1 + a_2 + ja_3, a_3, ja_3 + ja_1 + a_4) \\ (a_1, a_2, a_3, a_4)\,(\hat{\mathrm{R}}_{\mathrm{c}}^{+})^{2j+1} &= (a_3, (j + 1)\, a_1 + a_2 + ja_3, a_1, (j + 1)\, a_3 + ja_1 + a_4) \end{aligned} \tag{9}$$

Therefore one obtains for $(R)_{11}$:

$$\tilde{K}_n = \begin{cases} 1 & \text{if } n \text{ is even} \\ 0 & \text{if } n \text{ is odd} \end{cases} \tag{10}$$

A detailed but elementary analysis, analogous to the derivation of eqs. (8) and (10), gives tre following results.

$$\text{For } (R)_2\text{:} \qquad \tilde{K}_n = \begin{cases} \tilde{K}_{n-1} + \tilde{K}_{n-3} & \text{if } n \text{ is even} \\ \tilde{K}_{n-1} + \tilde{K}_{n-2} & \text{if } n \text{ is odd} \end{cases} \tag{11}$$

$$\text{For } (R)_3\text{:} \qquad \tilde{K}_n = \begin{cases} 2 & \text{if } n = 4\mathrm{j} + 1 \\ 1 & \text{if } n = 4\mathrm{j}, 4\mathrm{j} + 2 \\ 0 & \text{if } n = 4\mathrm{j} + 3 \end{cases} \tag{12}$$

$$\text{For } (R)_4\text{:} \qquad \tilde{K}_n = \begin{cases} 1 & \text{if } n \text{ is even} \\ (n + 3)/2 & \text{if } n \text{ is odd} \end{cases} \tag{13}$$

$$\text{For } (R)_5\text{:} \qquad \tilde{K}_n = \begin{cases} \tilde{K}_{n-1} + \tilde{K}_{n-2} & \text{if } n \text{ is even} \\ \tilde{K}_{n-1} + \tilde{K}_{\mathrm{n}-3} & \text{if } n \text{ is odd} \end{cases} \tag{14}$$

$$\text{For } (R)_6\text{:} \qquad \tilde{K}_n = \tilde{K}_{n-1} + \tilde{K}_{n-2} \tag{15}$$

In the recursion relations for $(R)_2$, $(R)_5$ and $(R)_6$, $\tilde{K}_0 = 1$, $\tilde{K}_1 = 2$ and $\tilde{K}_2 = 3$.

For $(R)_7$:
$$\tilde{K}_n = \begin{cases} 2 & \text{if } n = 8j+1 \\ 1 & \text{if } n = 8j, 8j+2 \\ 0 & \text{if } n = 8j+3, 8j+7 \\ -1 & \text{if } n = 8j+4, 8j+6 \\ -2 & \text{if } n = 8j+5 \end{cases} \tag{16}$$

For $(R)_8$:
$$\tilde{K}_n = \begin{cases} \tilde{K}_{n-1} - \tilde{K}_{n-2} & \text{if } n \text{ is even} \\ \tilde{K}_{n-1} + \tilde{K}_{n-2} & \textit{if } n \textit{ is odd} \end{cases} \tag{17}$$

$$\tilde{K}_0 = 1,\ \tilde{K}_1 = 2.$$

For $(R)_9$ and $(R)_{15}$:
$$\tilde{K}_n = \begin{cases} (-1)^{n/2} & \text{if } n \text{ is even} \\ 0 & \text{if } n \text{ is odd} \end{cases} \tag{18}$$

For $(R)_{10}$:
$$\tilde{K}_n = \begin{cases} 1 & \text{if } n = 8j, 8j+6, 8j+7 \\ 0 & \text{if } n = 8j+1, 8j+5 \\ -1 & \text{if } n = 8j+2, 8j+3, 8j+4 \end{cases} \tag{19}$$

For $(R)_{12}$:
$$\tilde{K}_n = \begin{cases} 0 & \text{if } n = 4j+1 \\ 1 & \text{if } n = 4j, 4j+2, 4j+3 \end{cases} \tag{20}$$

For $(R)_{13}$:
$$\tilde{K}_n = \begin{cases} 1 & \text{if } n \text{ is even} \\ 0 & \text{if } n \text{ is odd} \end{cases} \tag{21}$$

For $(R)_{14}$:
$$\tilde{K}_n = \begin{cases} \tilde{K}_{n-1} + \tilde{K}_{n-2} & \text{if } n \text{ is even} \\ \tilde{K}_{n-1} - \tilde{K}_{n-2} & \text{if } n \text{ is odd} \end{cases} \tag{22}$$

$$\tilde{K}_0 = 1,\ \tilde{K}_1 = 0.$$

For $(R)_{16}$:
$$\tilde{K}_n = \begin{cases} +1 & \text{if } n = 6j, 6j+5 \\ 0 & \text{if } n = 6j+2,\ 6j+3 \\ -1 & \text{if } n = 6j+1, 6j+4 \end{cases} \tag{23}$$

The $\tilde{K}_n$ values of the 16 studied classes of NCC molecules for $n \leqslant 10$ are given in the Table.

We would like to note the following facts. Firstly, by inspection of the Table one can see that most frequently (*e. g.* $(R)_4$, $(R)_8$, $(R)_{14}$) the annelation of a benzenoid ring causes stabilization (increases ASC) while the annelation of a non-benzenoid ring causes destabilization. However, there are exceptions to this rule, for example, molecules III and IV.

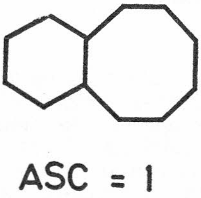
This interesting topological phenomenon has been discussed in a greater detail in ref. 20.

Secondly, according to the author's knowledge, eqs. (16), (19) and (23) are the first regularities of modulo 8 and modulo 6 in the topological theory of conjugated molecules.

TABLE

$\tilde{K}$ *values of* n-*cyclic ring sequence* $(R)_1$ — $(R)_{16}$

n	1	2	3	4	5	6	7	8	9	10
$(R)_1$	2	3	4	5	6	7	8	9	10	11
$(R)_2$	2	3	5	7	12	17	29	41	70	99
$(R)_3$	2	1	0	1	2	1	0	1	2	1
$(R)_4$	2	1	3	1	4	1	5	1	6	1
$(R)_5$	2	3	4	7	10	17	24	41	58	99
$(R)_6$	2	3	5	8	13	21	34	55	89	144
$(R)_7$	2	1	0	—1	—2	—1	0	1	2	1
$(R)_8$	2	1	3	2	5	3	8	5	13	8
$(R)_9$	0	—1	0	1	0	—1	0	1	0	—1
$(R)_{10}$	0	—1	—1	—1	0	1	1	1	0	—1
$(R)_{11}$	0	1	0	1	0	1	0	1	0	1
$(R)_{12}$	0	1	1	1	0	1	1	1	0	1
$(R)_{13}$	0	1	0	1	0	1	0	1	0	1
$(R)_{14}$	0	1	1	2	1	3	2	5	3	8
$(R)_{15}$	0	—1	0	1	0	—1	0	1	0	—1
$(R)_{16}$	0	—1	—1	0	1	1	0	—1	—1	0



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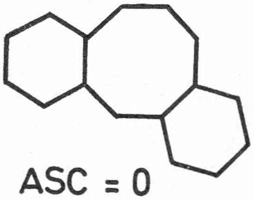

IV

Thirdly, since all the Kekulé structures of fully benzenoid molecules are of the same parity[3,14], for $(R)_1$, $(R)_2$, $(R)_5$ and $(R)_6$ we have ASC = K and hence eqs. (8), (11), (14) and (15) present, in fact recursion relations also for the number of Kekulé structures. Besides this, eqs. (11) and (14) are generalizations of the analogous results in refs. 1 and 21.

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SAŽETAK

Metoda za izračunavanje algebarskog zbroja struktura za nerazgranate kata-kondenzirane molekule

Ivan Gutman

Razvijena je operatorska tehnika za računanje algebarskog zbroja struktura (algebraic structure count, ASC) nerazgranatih kata-kondenziranih konjugiranih spojeva. Metoda je izravno poopćenje jedne ranije operatorske tehnike za određivanje broja Kekuléovih struktura za istu klasu molekula (*Croat. Chem. Acta* **46** (1974) 15), i sastoji se u pridruživanju po jedne kvadratne matrice reda 4 svakom prstenu u molekuli. Postoje 4 različite vrste takovih matrica-operatora, a ASC se dobiva njihovim množenjem za sve prstenove.

Dobivene su opće formule za ASC 16 nizova konjugiranih spojeva.

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