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TOPOLOGICAL PROPERTIES OF BENZENOID SYSTEMS. XXVIII. NUMBER OF KEKULÉ STRUCTURES OF SOME BENZENOID HYDROCARBONS[1]

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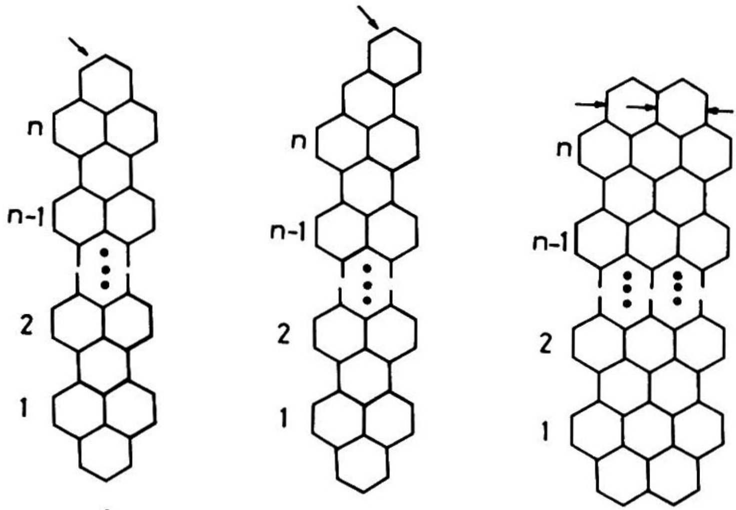
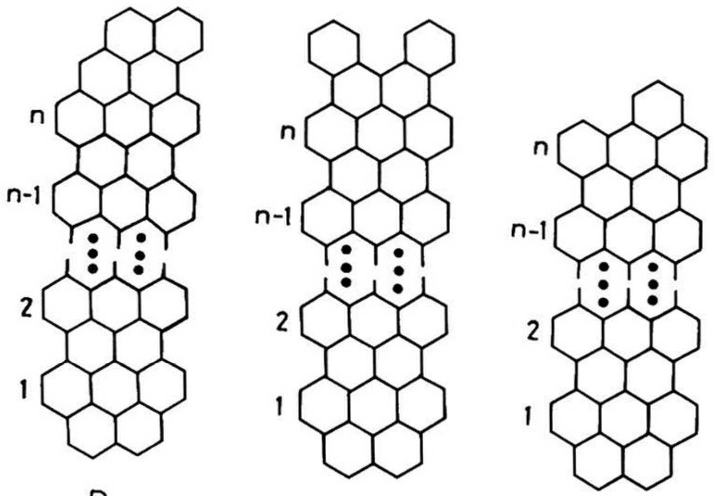
Abstract. Explicit analytical formulas for the number of Kekulé structures of six homologous series of benzenoid hydrocarbons, A_n, B_n, C_n, D_n, E_n and F_n, are deduced.

The problem of the enumeration of Kekulé structures of benzenoid molecules has attracted the attention of many scientists over more than three decades[2] and is a topic of current interest in mathematical chemistry[3]. For a great number of benzenoid systems, combinatorial formulas have been deduced[2-4], enabling the direct evaluation of the number of Kekulé structures. In the present paper we offer some more formulas of this type. In particular, we shall be concerned with the six homologous series – A_n, B_n, C_n, D_n, E_n and F_n .



A_n B_n C_n



D_n E_n F_n

The main results of the present work are summarized in the following expressions:

$$K(A_n) = 2 \cdot 3^n \quad , \qquad (1)$$

$$K(B_n) = 3^{n+1} \quad , \qquad (2)$$

$$K(C_n) = \left[(4 + \sqrt{8})^{n+2} + (4 - \sqrt{8})^{n+2}\right]/16 \quad , \qquad (3)$$

$$K(D_n) = \left[(4 + \sqrt{8})^{n+2} + (4 - \sqrt{8})^{n+2}\right]/8 \quad , \qquad (4)$$

$$K(E_n) = \left[(\sqrt{2}+1)(4+\sqrt{8})^{n+1} - (\sqrt{2}-1)(4-\sqrt{8})^{n+1}\right]/2 \quad , \quad (5)$$

$$K(F_n) = \left[(\sqrt{2}+1)(4+\sqrt{8})^{n+1} - (\sqrt{2}-1)(4-\sqrt{8})^{n+1}\right]/2 \quad , \quad (6)$$

where K(G) denotes the number of Kekulé structures of a conjugated system whose molecular graph is G.

Let e be an (arbitrary) edge of the graph G. We denote by G–e the subgraph obtained by deletion of e from G, and by G–(e) the subgraph obtained from G by deletion of the two vertices which are incident to G. Then the following well-known recursion relation[2] holds for the number of Kekulé structures of G:

$$K(G) = K(G-e) + K(G-(e)) \quad . \qquad (7)$$

An important special case of eq. (7) is obtained when the edge e is incident to a vertex of degree one. Then obviously, $K(G-e) = 0$ and thus

$$K(G) = K(G-(e)) \quad . \qquad (8)$$

In order to deduce eqs. (1) and (2), apply (7) to the edges of A_n and B_n, which are indicated by arrows. By a repeated use of (8), we easily arrive to

$$K(A_n-e) = K(B_{n-1}) \quad ,$$

$$K(A_n-(e)) = K(B_{n-1}) \quad ,$$

$$K(B_n-e) = K(B_{n-1}) \quad ,$$

$$K(B_n-(e)) = K(A_n) \quad .$$

Therefrom,

$$K(A_n) = 2\,K(B_{n-1}) \quad , \tag{9}$$
$$K(B_n) = K(A_n) + K(B_{n-1}) \quad ,$$

from which one immediately concludes that

$$K(B_n) = 3\,K(B_{n-1}) \quad .$$

Hence $K(B_2) = 3\,K(B_1)$, $K(B_3) = 3^2\,K(B_1)$, ... , $K(B_n) = 3^{n-1}\,K(B_1)$ and eq. (2) is obtained from the fact that $K(B_1) = 9$.

Eq. (1) follows from (2) and (9).

The derivation of eqs. (3)-(6) is somewhat more complicated, although based on an analogous reasoning. Consider the three edges of C_n which are indicated by arrows. Let they be denoted by e_1, e_2 and e_3. In any Kekulé structure of C_n, either e_1 or e_2 or e_3 must correspond to a double bond. On the other hand, no two of these edges can correspond to double bonds in the same Kekulé structure. Therefore, as a consequence of eq. (7), we have

$$K(C_n) = K(C_n-(e_1)-e_2-e_3) + K(C_n-e_1-(e_2)-e_3) + $$
$$+ K(C_n-e_1-e_2-(e_3)) \quad .$$

It is now easy to check (using eq. (9)), that

$$K(C_n-(e_1)-e_2-e_3) = K(D_{n-1}) \quad ,$$
$$K(C_n-e_1-(e_2)-e_3) = K(E_{n-1}) \quad ,$$
$$K(C_n-e_1-e_2-(e_3)) = K(D_{n-1}) \quad ,$$

wherefrom

$$K(C_n) = 2\ K(D_{n-1}) + K(E_{n-1}) \quad . \tag{10}$$

By similar reasoning we obtain additional three recurrence relations:

$$K(D_n) = K(C_n) + K(D_{n-1}) + K(F_n) \quad , \tag{11}$$

$$K(E_n) = 4\ K(D_{n-1}) + 4\ K(E_{n-1}) \quad , \tag{12}$$

$$K(F_n) = K(D_{n-1}) + K(E_{n-1}) \quad . \tag{13}$$

The system of coupled recurrence relations (10)-(13) can be solved in the following manner. From (12) and (13) is evident that

$$K(E_n) = 4\ K(F_n) \quad . \tag{14}$$

Substitution of (14) back into (10) and (13) yields

$$K(C_n) = 2\ K(D_{n-1}) + 4\ K(F_{n-1}) \tag{15}$$

and

$$K(F_n) = K(D_{n-1}) + 4\ K(F_{n-1}) \quad . \tag{16}$$

Subtracting (16) from (15) we get

$$K(F_n) = K(C_n) - K(D_{n-1}) \quad , \tag{17}$$

which combined with (11) gives

$$K(D_n) = 2\ K(C_n) \quad . \tag{18}$$

Another substitution of (18) into (17) gives

$$K(F_n) = K(C_n) - 2\ K(C_{n-1}) \quad . \tag{19}$$

The equations (14),(18) and (19) enable now to obtain the final solutions. Together with eq. (10) they result in the simple formula

$$K(C_n) = 8\, K(C_{n-1}) - 8\, K(C_{n-2}) \quad . \qquad (20)$$

The expression (3) follows now from (20) by standard methods of the theory of linear recursion relations, having in mind the initial conditions $K(C_1) = 20$ and $K(C_2) = 136$.

The expressions (4), (6) and (5) are immediate consequences of (3) and the relations (18), (19) and (14), respectively.

Concluding this paper we would like to emphasize the general features of the method which we used here for finding combinatorial formulas for the number of Kekulé structures of homologous series. Instead of studying one single homologous series, our approach enables (but also requires) the simultaneous consideration of a group of mutually related homologous series. If such a group is properly chosen, then a reasonable application of the formulas (7) and (8) yields a system of coupled recurrence relations. In convenient cases this system can be solved, giving thus explicit general formulas for the number of Kekulé structures. The results (1)-(6) could be viewed as examples, illustrating the power and ability of this general method. It seems likely that the same approach will enable the derivation of further combinatorial formulas for the number of Kekulé structures.

R E F E R E N C E S

1. Part XXVII see: I.Gutman, Lj.Nedeljković and A.V.Teodorović, Bull.Soc.Chim.Beograd 48, 495 (1983).
2. For review of the topological properties of benzenoid systems (including the enumeration of their Kekulé structures) see: I.Gutman, Bull.Soc.Chim.Beograd 47, 453 (1982).
3. For some recent work on the Kekulé structures of benzenoid molecules see: S.J.Cyvin, Match 13, 167 (1982); Monatsh. Chem. 113, 1127 (1982); 114, 13 (1983); S.El-Basil, Match 13, 199 (1982); I.Gutman, Match 13, 173 (1982); 14, 139 (1983); A.T.Balaban and I.Tomescu, Match 14, 155 (1983).
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