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The Number of Kekulé Structures in Conjugated Systems Containing a Linear Polyacene Fragment*

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The number of Kekulé structures of all conjugated systems containing a linear polyacene chain of length n is a linear function of the parameter n and is given by eq. (8).

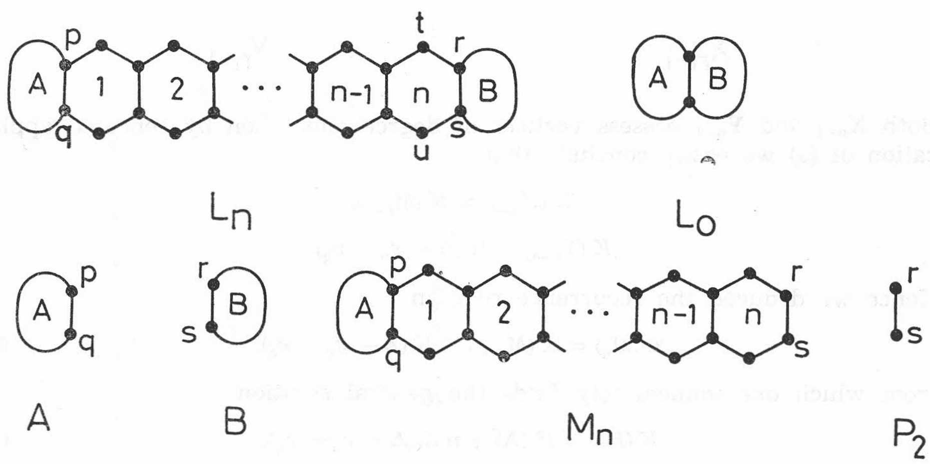
In a recent paper[1] Eilfeld and Schmidt reported closed formulae for the number of Kekulé structures for a variety of homologous series of benzenoid hydrocarbons containing a linear polyacene fragment. All their formulae were of the form

$$K_n = a + b\,n \tag{1}$$

with a and b being constants, depending on the homologous series considered. In the present paper we demonstrate that formulae of the form (1) hold for *all conjugated molecules* (not necessarily benzenoid), containing a linear polyacene fragment. In addition, we will clarify the topological nature of the constants a and b.

We will use standard graph-theoretical notation and terminology[2].

The molecular graph of a conjugated system containing a linear polyacene fragment of the length n is represented by L_n.



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The subgraphs A and B symbolize certain (but arbitrary) terminal groups. Hence L_n can be understood as being obtained by annelation of the fragments A and B to both ends of an n-cyclic linear polyacene molecule. The positions where the annelations occur will be labelled by p, q and r, s, respectively.

In the special case when the subgraph B is isomorphic to the graph P_2 (possessing just two vertices r and s), instead of L_n we have the molecular graph M_n. The molecular graph of the n-cyclic linear polyacene is of course, also a special case of M_n and L_n.

The number of Kekulé structures of a conjugated system, whose molecular graph is G will be denoted by $K(G)$. Let v_r and v_s be two adjacent vertices of G and let the edge between them be denoted by e_{rs}. Then according to a well known result[3], $K(G)$ conforms to the following recurrence relation

$$K(G) = K(G - e_{rs}) + K(G - v_r - v_s) \tag{2}$$

If the vertex v_r is of degree one (i. e. if v_s is the unique neighbour of v_r), then from (2) we obtain

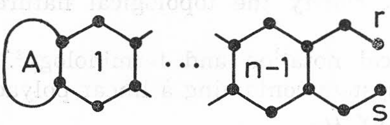
$$K(G) = K(G - v_r - v_s) \tag{3}$$

Hence, the deletion of a vertex of degree one and of its first neighbour will not alter the number of Kekulé structures.

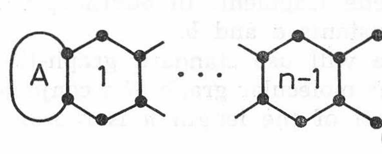
We determine first the number of Kekulé structures of the system M_n. Applying eq. (2) to the vertices v_r and v_s of M_n we get

$$K(M_n) = K(X_{n-1}) + K(\mathbf{Y}_{n-1}),$$

where the graphs X_{n-1} and $\mathbf{Y}_{n-1}$ are given as follows.



X_{n-1}



Y_{n-1}

Both X_{n-1} and $\mathbf{Y}_{n-1}$ possess vertices of degree one. Then by repeated application of (3) we easily conclude that

$$K(X_{n-1}) = K(M_{n-1}),$$

$$K(\mathrm{Y}_{n-1}) = K(\mathrm{A} - v_p - v_q). \tag{4}$$

Hence we deduced the recurrence relation

$$K(M_n) = K(M_{n-1}) + K(A - v_p - v_q), \tag{5}$$

from which one immediately finds the general solution

$$K(M_n) = K(\mathrm{A}) + \mathrm{n}\, K(\mathrm{A} - v_p - v_q), \tag{6}$$

since for $n = 0$, M_n coincides with A.

Using the auxiliary result (6) we can now calculate the number of Kekulé structures of the system L_n. The application of the identity (2) first to the edge e_{rt} and then to the edge e_{su} of L_n gives

$$K(L_n) = K(Y_{n-1})\,K(B) + K(Y_{n-1} - v_t)\,K(B - v_r) + K(Y_{n-1} - v_u)\,K(B - v_s) + $$
$$+ K(M_{n-1})\,K(B - v_r - v_s).$$

The graphs $Y_{n-1} - v_t$ and $Y_{n-1} - v_u$ possess vertices of degree one and eq. (3) can be repeatedly applied. Finally we get

$$K(Y_{n-1} - v_t) = K(A - v_q) \quad \text{and} \quad K(Y_{n-1} - v_u) = K(A - v_p),$$

which together with (4) gives

$$K(L_n) = K(A - v_p - v_q)\,K(B) + K(A - v_p)\,K(B - v_s) +$$
$$+ K(A - v_q)\,K(B - v_r) + K(M_{n-1})\,K(B - v_r - v_s).$$

Therefore,

$$K(L_n) - K(L_{n-1}) = [K(M_{n-1}) - K(M_{n-2})]\,K(B - v_r - v_s)$$

and because of (5),

$$K(L_n) = K(L_{n-1}) + K(A - v_p - v_q)\,K(B - v_r - v_s). \tag{7}$$

The general solution of the recurrence relation (7) is

$$K(L_n) = K(L_0) + n\,K(A - v_p - v_q)\,K(B - v_r - v_s). \tag{8}$$

Note that the above equation is a generalization of (5). In fact, for $B = P_2$, eq. (5) follows from (8) because of $K(B - v_r - v_s) = 1$ and $L_0 = A$.

Hence we proved that the formula (1) is the general expression for the number of Kekulé structures of all linear polyacene derivatives, irrespective of the nature of the terminal groups.

In practice it often happen that we know the number of Kekulé structures of L_n for certain values of n. If we know $K(L_n)$ for two fixed values of n, say for $n = g$ and $n = f$, then we can use the formula

$$K(L_n) = \frac{f\,K(L_g) - g\,K(L_f) + [K(L_f) - K(L_g)]\,n}{f - g}. \tag{9}$$

In particular, in the most usual case when $g = 0$ and $f = 1$, we have

$$K(L_n) = K(L_0) + [K(L_1) - K(L_0)]\,n. \tag{10}$$

Comparing the formulae (8)—(10) with eq. (1) we see that

$$a = K(L_0) \quad \text{and} \quad b = K(A - v_p - v_q)\,K(B - v_r - v_s) \tag{11}$$

or

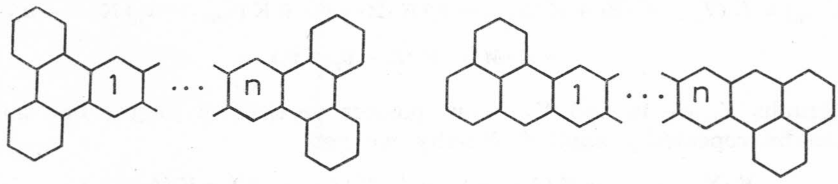
$$a = \frac{f\,K(L_g) - g\,K(L_f)}{f - g} \quad \text{and} \quad b = \frac{K(L_f) - K(L_g)}{f - g} \tag{12}$$

or

$$a = K(L_0) \quad \text{and} \quad b = K(L_1) - K(L_0). \tag{13}$$

Of course, (13) is a special case of (12).

The equations (11) provide an elementary route for the construction of closed expressions for the number of Kekulé structures of any particular homologous series. As an example, consider the tetrabenzacenes, T_n.



T_n Z_n

Here A and B are isomorphic with the phenanthrene graph, $A - v_p - v_q$ and $B - v_r - v_s$ are isomorphic with the biphenyl graph and T_O is the molecular graph of 1,2,7,8-dibenzochrysene. Since $K(T_O) = 24$ and $K(A - v_p - v_q) = K(B - v_r - v_s) = 4$, we immediately obtain the formula $K(T_n) = 24 + 16\,n$, which is in full agreement with ref. 1.

We would also like to point out the following special case. If any two members of a homologous series have an equal number of Kekulé structures, then by eq. (12), $b = 0$ and therefore all members of this homologous series must have an equal number of Kekulé structures. Similarly, if either $A - v_p - v_q$ or $B - v_r - v_s$ (or both) have no Kekulé structures, then the recurrence relation (7) becomes

$$K(L_n) = K(L_{n-1})$$

and thus the number of Kekulé structures of L_n is independent of the length of the polyacene chain. This always happens when the terminal groups A and B have an odd number of vertices. A typical example is the zethrene series (Z_n), all members of which have nine Kekulé structures.

REFERENCES

1. P. Eilfeld and W. Schmidt, *J. Electron Spectr. Rel. Phenom.* **24** (1981) 101.
2. See for example: A. Graovac, I. Gutman, and N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules*, Springer-Verlag, Berlin 1977.
3. M. Randić, *J. Chem. Soc. Faraday II*, **72** (1976) 232.

SAŽETAK

Broj Kekuléovih struktura konjugiranih sustava koji sadrže linearni poliacenski fragment

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Za sve konjugirane sustave koji sadrže linearni poliacenski lanac duljine n, broj Kekuléovih struktura je linearna funkcija parametra n i određen je jednadžbom (8).