Algebraic structure count of linear phenylenes

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A general combinatorial expression is deduced for the algebraic structure count (ASC) of linear phenylenes. The conditions under which ASC is equal to zero are determined. Because ASC = 0 implies that the respective conjugated system has an open-shell π-electron configuration, the results obtained enable one to distinguish between stable and unstable phenylene derivatives.

The algebraic structure count (ASC) is a concept introduced into theoretical organic chemistry by Wilcox1,2, following earlier work of Dewar and Longuet-Higgins3. It is based on the idea that each individual Kekulé structure of a conjugated molecule has a “parity”3. Then ASC is equal to the difference between the number of “even” and the number of “odd” Kekulé structures. This quantity was shown4,5 to play an important role in determining the π-electron properties of polycyclic conjugated compounds. In particular, if ASC = 0 then the respective π-electron system has an open-shell configuration and is thus extremely unstable (and nonexisting in the great majority of cases)3-5. The thermodynamic stability of conjugated hydrocarbon compounds increases with the increasing ASC-value6,7.

In the case of benzenoid hydrocarbons all Kekulé structures are of the same parity3,8. Therefore, for benzenoid species ASC coincides with the number of Kekulé structures (K).

Whereas the enumeration of the Kekulé structures (i.e., the determination of the K-value) is a classical problem in the theoretical chemistry of polycyclic conjugated molecules4,9,10 with a plethora of known counting formulae and several hundreds of published papers, there are very few works dealing with ASC. This striking dissymmetry between the research on K and ASC can be attributed to the fact that simple and powerful recursive methods exist9 for the calculation of K whereas analogous procedures seem to be inapplicable in the case of ASC11. In spite of a few efforts in this direction11-14 no efficient graphical (i.e., paper-and-pencil) technique is known for computing ASC. The only non-benzenoid conjugated hydrocarbons for which the ASC-problem is completely resolved are the unbranched cata-condensed systems15,16, for which a transfer-matrix method could be designed.

In this paper we report combinatorial expressions for ASC of linear phenylenes, namely of the class of non-benzenoid conjugated molecules whose structure is represented by the diagram $X_n$:

![Diagram](image)

The terminal groups R and S (which may, but need not exist at all) are arbitrary even benzenoid systems. If the terminal groups R and S are absent then we have the ordinary [n]-phenylene, denoted by $Y_n$:

![Diagram](image)

Another noteworthy special case of $X_n$ is obtained when both R and S are ethylene fragments:

![Diagram](image)

For the chemical properties and synthesis of the various known members of the classes $X_n$ and $Y_n$ see refs 17-21. Not a single representative of the class $Z_n$ has been obtained so far.
Algebraic structure count of \( X_1 \)

In what follows the ASC-value of a conjugated hydrocarbon \( H \) will be written as \( A[H] \); the respective number of Kekulé structures will be denoted by \( K[H] \). For brevity, instead of \( K[R] \) and \( K[S] \) we shall write \( R \) and \( S \), respectively. Further, the number of Kekulé structures of the fragments \( R \) and \( S \), in which the carbon-carbon bonds marked by arrows are chosen to be double, are denoted by \( R_\_ \) and \( S_\_ \), respectively. The number of Kekulé structures in which these marked bonds are chosen to be single are \( R_\_ \) and \( S_\_ \), respectively. Evidently,

\[ R = R_\_ + R_\_; \quad S = S_\_ + S_\_ \quad \ldots (1) \]

We can now determine \( A[X_1] \), employing the original definition of the mutual parity of Kekulé structures.

The molecule \( X_1 \) may possess several Kekulé structural formulae, depending on the actual structure of the terminal fragments \( R \) and \( S \). These Kekulé structures can be divided into 12 groups, according to the arrangement of the double bonds in the central (hatched) region of the system \( X_1 \):

Every Kekulé structure of type 2 is obtained from a Kekulé structure of type 1 by moving two double bonds within a four-membered ring. Hence they are of opposite parity, which means that their contributions to the ASC of \( X_1 \) will sum up to zero. In the same manner Kekulé structures of the type 3 and 4, 5 and 6 as well as 8 and 9 have opposite parities. Bearing in mind that the terminal fragments \( R \) and \( S \) are assumed to be benzenoid systems, we conclude that the remaining Kekulé structures (of the types 7, 10, 11 and 12) are all of the same parity. Consequently, \( A[X_1] \) is equal to the number of Kekulé structures of the types 7, 10, 11 and 12.

Now, there are \( R_\_ S_\_ \) Kekulé structures of the type 7. To see this, recall that the double bonds indicated in the diagram 7 are fixed whereas those not indicated (belonging to \( R \) and \( S \)) may occupy different positions. In every Kekulé structure of type 7 the marked bond in \( R \) is single whereas the marked bond in \( S \) is double. Since the double bonds in \( R \) and \( S \) can be rearranged independently, we see that the total number of such Kekulé structures is equal to the product \( R_\_ S_\_ \).

In an analogous way, we reach the conclusion that there are \( R_\_ S_\_ \), \( R S_\_ \) and \( R S_\_ \) Kekulé structures of the types 10, 11 and 12, respectively. This implies,

\[ A[X_1] = R S_\_ + R S_\_ + 2 R_\_ S_\_ \quad \ldots (2) \]

Using (1), we easily obtain a somewhat simpler formula:

\[ A[X_1] = R R_\_ + S S_\_ \]

Algebraic structure count of \( X_n \)

By means of an argument analogous to that used to deduce Eq. (2), one can easily prove that,

\[ A[X_n] = R_\_ S_\_ + R_\_ S_\_ + 2 R_\_ S_\_ \quad \ldots (3) \]

which combined with Eq. (1) furnishes the formula,

\[ A[X_n] = R S - R_\_ S_\_ \quad \ldots (4) \]

After similar, but much more tedious reasonings we arrive at

\[ A[X_n] = R_\_ S_\_ + R_\_ S_\_ + 3 R_\_ S_\_ \quad \ldots (5) \]

By comparing Eqs (2), (3) and (5), we can conclude that
\[ A(X_n) = R_- S_+ R_- S_- + (n+1)R_- S_- \quad \ldots (6) \]

which together with Eqs (3) and (4) yields,
\[ A(X_n) = A(X_0) + nR_- S_- \quad \ldots (7) \]
or
\[ A(X_n) = R S - R_- S_+ nR_- S_- \]

A complete proof of Eq. (6) can be obtained by mathematical induction.

The special case of Eq. (6) for \( X_n = Y_n \) is obtained by setting \( R_- = S_- = 1 \) and \( R_0 = S_0 = 0 \):
\[ A(Y_n) = n + 1 \quad \ldots (8) \]

The other special case, namely \( X_n = Z_n \) is obtained by inserting into Eq. (6) \( R_- = S_- = 0 \) and \( R_0 = S_0 = 1 \). This gives,
\[ A(Z_n) = 0. \]

From Eqs (7) and (8) we see that the algebraic structure count of \( X_n \) increases as a linear function of the parameter \( n \). This is a very slow increase, especially when compared with the \( n \)-dependency of the number of Kekulé structures (which is exponential, see the last Section). This property of \( A(X_n) \) and \( A(Y_n) \) seems to be well matched by the observed chemical behaviour of the \([n]\)-phenylenes. Whereas the \([2]\)-, \([3]\)- and \([4]\)-phenylenes are reasonably stable compounds, the only known \([5]\)-phenylene derivative is a deep red, air-sensitive substance that decomposes upon attempted melting. The highly reactive character of the \([5]\)-phenylene relative to the lower members of the \([n]\)-phenylene series is evident from its sensitivity to oxidizing agents, the facility with which it breaks through-conjugation by cycloadDITION etc. So far, despite extensive experimentation no derivative of \([6]\)-phenylene could be prepared.

**Conditions for ASC = 0**

As already mentioned, the significance of the condition \( \text{ASC} = 0 \) is that the respective conjugated species must be extremely reactive and probably very difficult to prepare in laboratory.

From Eq. (7) it is immediately clear that the algebraic structure count of \( X_n \) vanishes only if both \( A(X_0) = 0 \) and \( R_- S_- = 0 \).

Examine first the conditions for \( A(X_0) = 0 \). From Eq. (4) we see that this will occur only if both equalities \( R = R_0 \) and \( S = S_0 \) are simultaneously satisfied. In view of Eq. (1) these latter relations imply \( R_- = S_- = 0 \). Hence, if \( A(X_0) = 0 \) then also \( R_0 = S_0 = 0 \) and, therefore, \( A(X_n) = 0 \) holds then for all values of \( n \).

In the language of chemistry this means that \( X_n \) will have a zero algebraic structure count if and only if both terminal fragments \( R \) and \( S \) are attached to the central part of the molecule via fixed double bonds. An example when this happens is \( Z_n \). If \( R \) and \( S \) are required to be benzenoid systems then it is rather difficult (but still possible) to design pertinent phenylene derivatives with \( \text{ASC} = 0 \). The simplest example of this kind is given below.

![Diagram of a phenylene molecule]

We mention in passing that if either \( R_- \) or \( S_- \) (but not both) are equal to zero, then \( A(X_n) \) is a non-zero constant, independent of the actual value of the parameter \( n \).

**Number of Kekulé structures of linear phenylenes**

Recurrence relations and explicit algebraic expressions for the \( \text{K-values} \) of \( X_n, Y_n \) and \( Z_n \) can be deduced by means of standard combinatorial techniques. We report them for the sake of completeness.

The recurrence relation
\[ K[X_n] = 2 K[X_{n-1}] + K[X_{n-2}] \quad \ldots (9) \]
holds for \( W = X, Y \) and \( Z \) and for \( n \geq 2 \). Its initial conditions are:
\[ K[X_0] = R S + R_- S_-; K[X_1] = 2 R S + R_- S_+ R_0 S_- \quad \ldots (10) \]

From Eqs (9) and (10) it follows that,
\[ K[X_n] = \frac{1}{2} [K[X_0] + (K[X_1] - K[X_0]) / \sqrt{2}] (1 + \sqrt{2})^n \]
\[ + \frac{1}{2} [K[X_0] - (K[X_1] - K[X_0]) / \sqrt{2}] (1 - \sqrt{2})^n \]
whose special cases are

\[ K[Y_{n}] = \left( \frac{\sqrt{2}}{4} \right) \left[ (1 + \sqrt{2})^{n+1} - (1 - \sqrt{2})^{n+1} \right] \]

and

\[ K[Z_{n}] = \left( \frac{\sqrt{2}}{2} \right) \left[ (1 + \sqrt{2})^{n+1} - (1 - \sqrt{2})^{n+1} \right]. \]

It may be noted that \( K[Z_{n}] = 2 K[Y_{n}] \).

References