

SOME COMBINATORIAL CONSEQUENCES OF CLAR'S RESONANT
SEXTET THEORY

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Abstract

Clar's resonant sextet theory is extended to the class of alternant non-benzenoid conjugated hydrocarbons. A number of combinatorial results have been proved, connecting the number of Clar formulas with the number of Kekulé structures and the algebraic structure count.

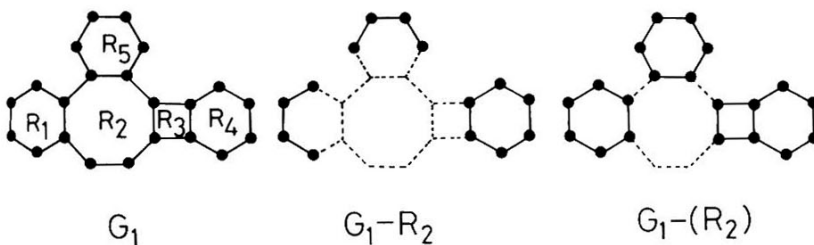
Some time ago Clar developed the concept of resonant sextet¹ in order to rationalize the theory of the aromatic benzenoid hydrocarbons and systematically explain their basic chemical and spectroscopic properties. Several authors² pointed at the fact that Clar's theory has a deeper physical meaning and that it can be justified by means of quantum theory. Hosoya and Yamaguchi³ recently discovered interesting combinatorial relations for the resonant sextet numbers and introduced the sextet polynomial of a benzenoid system. The theory of the sextet polynomial was thereafter further elaborated⁴⁻⁸.

In the present paper we shall extend Clar's formalism from benzenoid to arbitrary alternant hydrocarbons and pro-

pose a generalization of the sextet polynomial. A number of combinatorial results will be derived, which will be summarized in five theorems.

In the following we shall consider alternant hydrocarbons*. The molecular graph G of such a hydrocarbon is composed of n rings - R_1, R_2, \dots, R_n . The size of the ring R_i will be denoted by $|R_i|$. We shall assume that G contains no vertex of degree one, that is every carbon atom of the conjugated molecule under consideration has at least two adjacent carbon atoms.

For example, G_1 is the molecular graph of an alternant hydrocarbon with five rings - R_1, R_2, R_3, R_4 and R_5 and in addition, $|R_1| = |R_4| = |R_5| = 6$, $|R_2| = 8$, $|R_3| = 4$.



* A conjugated molecule is said to be alternant if the size of all its rings is even. If all rings are 6-membered, then we have a benzenoid molecule.

The subgraph $G-R_i$ is obtained by deleting all the vertices and edges of G which belong to the ring R_i . The subgraph $G-(R_i)$ is obtained by deleting all the vertices and edges of G which belong only to the ring R_i (but not to any other ring). For example, G_1-R_2 and $G_1-(R_2)$ are as given above.

The number of Kekulé structures and the algebraic structure count⁹ of G will be denoted by $K(G)$ and $ASC(G)$, respectively.

The generalized Clar formulas for G will be defined in full analogy to the Clar formulas for benzenoid systems^{1,3}. Thus if there is a Kekulé structure of G such that the ring R_i contains $|R_i|/2$ double bonds, we say that R_i is a resonant ring. Consequently, R_i is a resonant ring if and only if $K(G-R_i) \neq 0$.

Two rings R_i and R_j are mutually resonant if $K(G-R_i-R_j) \neq 0$. By definition, two adjacent rings cannot be mutually resonant. Triplets, quartets etc. of mutually resonant rings are defined in the same manner.

Resonant rings will be symbolized by circles. In order to avoid any misunderstanding, we shall use a full circle in the case of six-membered rings and a dashed circle in the case of rings whose size is different than six. Further details on Clar formulas are explained elsewhere³.

On Chart 1 are given the generalized Clar formulas of G_1 , including also the formula without resonant rings.

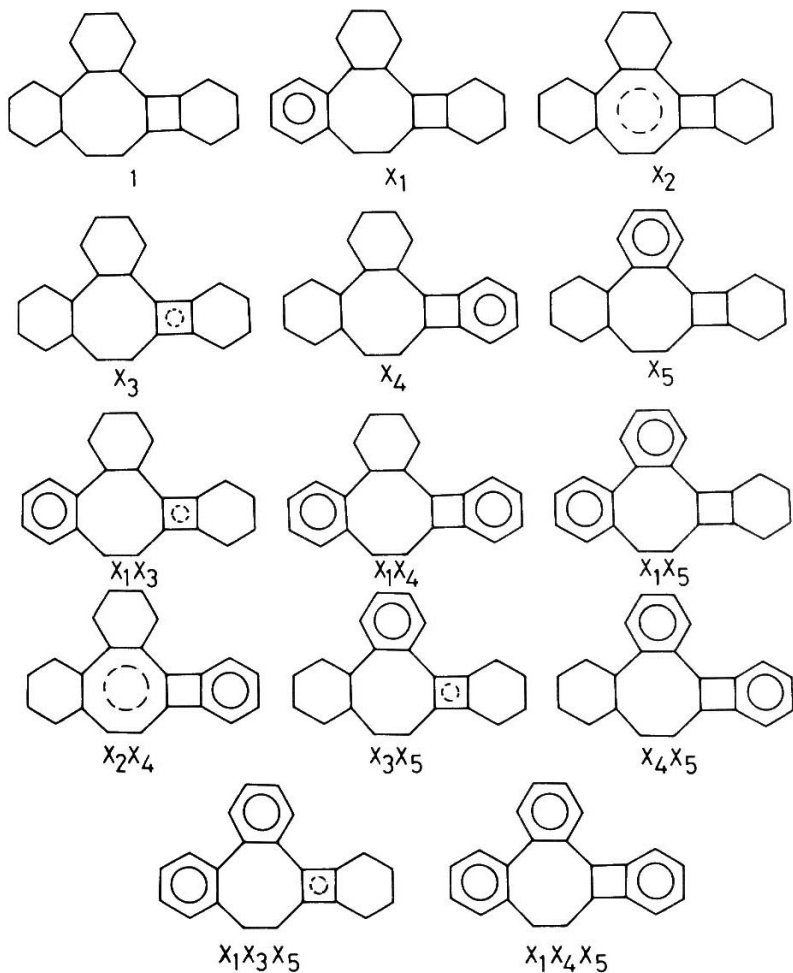


Chart 1

The generalized Clar formulas of G_1 and the corresponding resonant ring monomials

Let the Clar formulas of G be C_1, C_2, \dots, C_m . Let x_1, x_2, \dots, x_n be scalar variables. If the rings R_a, R_b, \dots are resonant in the Clar formula C_i , then we will associate a resonant ring monomial $\Xi(C_i) = x_a x_b \dots$ to this Clar formula. (The monomial $\Xi(C) = 1$ is associated to the Clar formula C without resonant rings.)

The resonant ring monomials of the Clar formulas of G_1 are also given on Chart 1.

We introduce now a multilinear form $\rho(G)$ in the following manner.

DEFINITION

If C_1, C_2, \dots, C_m are the Clar formulas of an alternant conjugated hydrocarbon G and $\Xi(C_1), \Xi(C_2), \dots, \Xi(C_m)$ are the pertinent resonant ring monomials, then

$$\rho(G) = \rho(G; x_1, x_2, \dots, x_n) = \sum_{i=1}^m \Xi(C_i) .$$

For example, $\rho(G_1) = 1 + x_1 + x_2 + x_3 + x_4 + x_5 + x_1x_3 + x_1x_4 + x_1x_5 + x_2x_4 + x_3x_5 + x_4x_5 + x_1x_3x_5 + x_1x_4x_5$.

It can be immediately verified that if G is a benzenoid system and if we set $x_1 = x_2 = \dots = x_n = x$, then $\rho(G)$ becomes identical with the Hosoya - Yamaguchi's sextet polynomial³.

T H E O R E M 1

For all rings R_i of G , such that at least one edge of R_i belongs only to R_i (but not to any other ring), the following recurrence relation holds,

$$\rho(G) = \rho(G - (R_i)) + x_i \rho(G - R_i) . \quad (1)$$

P r o o f. The Clar formulas of G can be divided into two groups. In the first group are those Clar formulas which do not contain R_i as a resonant ring. The sum of the corresponding resonant ring monomials is equal to $\rho(G-(R_i))$.

In the second group are those Clar formulas in which R_i is resonant. The corresponding resonant ring monomials must therefore contain x_i as a factor. Their sum is equal to $x_i \rho(G-R_i)$ and eq. (1) follows. Q.E.D.

Note that if the ring R_i possesses no edge as required in Theorem 1, then $G-(R_i) = G$ and eq. (1) will not be satisfied.

Eq. (1) enables an easy recursive evaluation of $\rho(G)$. For example,

$$\begin{aligned}\rho(G_1) &= \rho(G_1-(R_2)) + x_2 \rho(G_1-R_2) = \\ &= (1 + x_1)(1 + x_3 + x_4)(1 + x_5) + x_2(1 + x_4) \quad .\end{aligned}$$

A conjugated system is said to be cata-condensed¹⁰ if no three rings of it have a common atom. For example, the molecular graph G_1 represents a cata-condensed hydrocarbon.

Theorem 1 applies to all rings of cata-condensed molecules.

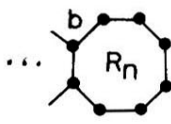
T H E O R E M 2

If G is cata-condensed, then for $x_1 = x_2 = \dots = x_n = 1$,

$$\rho(G) = K(G) \tag{2}$$

P r o o f. A ring R_1 of G will be called terminal if it has only one neighbouring ring. A cata-condensed molecule has at least two terminal rings.

Let R_n be a terminal ring of a cata-condensed system G . For convenience we will present R_n as an 8-membered ring.



G

Let $K_s(G)$ be the number of Kekulé structures of G in which b is a single bond, and let $K_d(G)$ be the number of Kekulé structures of G in which b is a double bond. Then evidently,
 $K(G) = K_s(G) + K_d(G)$.

Now, $K_s(G) = K(G-(R_n))$ and $K_d(G) = K(G - R_n)$, that is

$$K(G) = K(G-(R_n)) + K(G-R_n) \quad (3)$$

We can now prove Theorem 2 by induction. If G^0 possesses a single ring R_1 , then

$$\rho(G^0; x_1) = 1 + x_1, \quad \rho(G^0; 1) = 2 = K(G^0) \quad .$$

Thus Theorem 2 holds for monocyclic systems.

Assume that Theorem 2 is true for cata-condensed molecules with fewer than n rings. Let G be a cata-condensed

molecule with n rings and let R_n be its terminal ring. Then by eq. (1),

$$\rho(G; 1, 1, \dots, 1) = \rho(G-(R_n); 1, 1, \dots, 1) + \rho(G-R_n; 1, 1, \dots, 1) .$$

Since by the induction hypothesis $\rho(G-(R_n); 1, 1, \dots, 1) = K(G-(R_n))$ and $\rho(G-R_n; 1, 1, \dots, 1) = K(G-R_n)$, Theorem 2 follows from eq. (3). Q.E.D.

The special case of Theorem 2 for benzenoid systems has been proved previously⁶. Note that eq. (2) holds also for the majority of peri-condensed alternant molecules. Violations of eq. (2) occur if the peri-condensed system possesses a super ring. The concept of super ring was discussed in more detail elsewhere^{3,8}.

T H E O R E M 3

For those rings R_i for which Theorem 1 applies,

$$\frac{\partial \rho(G)}{\partial x_i} = \rho(G-R_i) . \quad (4)$$

P r o o f. Eq (4) follows immediately from eq. (1) and the fact that neither $\rho(G-(R_i))$ nor $\rho(G-R_i)$ depend on the variable x_i . Q.E.D.

C O R O L L A R Y 3.1

If for some i, j, k, \dots we choose $x_i = x_j = x_k = \dots = x$, then

$$\frac{\partial \rho(G)}{\partial x} = \rho(G-R_i) + \rho(G-R_j) + \rho(G-R_k) + \dots .$$

In particular, if $x_1 = x_2 = \dots = x_n = x$, then we have

COROLLARY 3.2

$$\frac{\partial \rho(G)}{\partial x} = \sum_{i=1}^n \rho(G-R_i) \quad .$$

The Theorems 2 and 3 enable us to formulate the following combinatorial result.

T H E O R E M 4

If G is cata-condensed, then for $x_1 = x_2 = \dots = x_n = 1$,

$$\frac{\partial \rho(G)}{\partial x_i} = K(G-R_i) \quad .$$

COROLLARY 4.1

If we set $x_1 = x_2 = \dots = x_n = x$, then for $x = 1$,

$$\frac{\partial \rho(G)}{\partial x} = \sum_{i=1}^n K(G-R_i) \quad .$$

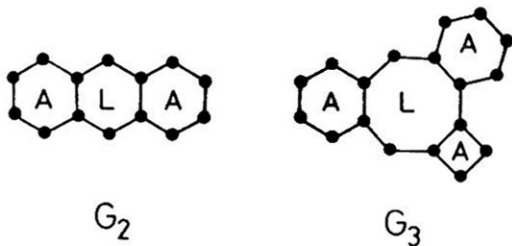
The special case of Theorem 4 was observed for benzenoid molecules by Hosoya and Yamaguchi³, but no proof has been offered until now.

Theorems 2 and 4 are more or less straightforward generalizations of previously known results^{3,7}. In the following we shall derive a combinatorial identity between $\rho(G)$ and the algebraic structure count of G . Thus we shall demonstrate that by means of the resonant ring monomials we are

able not only to determine the number of Kekulé structures, but also to obtain information about their parity⁹.

Let us consider a ring R of a cata-condensed alternant hydrocarbon and let R be adjacent to the rings R_a, R_b, \dots . We will say that R is an A-ring, or that R is of type A if its neighbouring rings R_a, R_b, \dots are all mutually resonant, that is if $K(G-R_a-R_b-\dots) \neq 0$. If this is not the case, we will say that R is an L-ring, or that R is of type L.

For example, all rings of G_1 are A-rings. The central rings in G_2 and G_3 are of type L.



Terminal rings are always of type A.

T H E O R E M 5

If G is a cata-condensed alternant molecule, such that all its rings of the size $4m$ are Λ -rings, then

$$\rho(G; s_1, s_2, \dots, s_n) = \text{ASC}(G) \quad , \quad (5)$$

where

$$s_j = +1 \quad \text{if} \quad |R_j| \equiv 2 \pmod{4} \quad (6a)$$

and

$$s_j = -1 \quad \text{if} \quad |R_j| \equiv 0 \pmod{4} \quad (6b)$$

for $j = 1, 2, \dots, n$.

P r o o f. First note that if no ring of G is of the size $4m$ (i.e. all $|R_j| \equiv 2 \pmod{4}$), then $\text{ASC}(G) = K(G)$ and Theorem 5 is true because of Theorem 2.

We proceed now to prove Theorem 5 by induction on the number k of $(4m)$ -membered rings in G . Thus Theorem 5 is true for $k = 0$.

Let us assume the validity of Theorem 5 for systems with less than k $(4m)$ -membered rings. Let R_i be a $(4m)$ -membered ring of G . Then according to the induction hypothesis,

$$\rho(G-(R_i); s_1, s_2, \dots) = \text{ASC}(G-(R_i)) \quad (7a)$$

and

$$\rho(G-R_i; s_1, s_2, \dots) = \text{ASC}(G-R_i) \quad . \quad (7b)$$

Using an analogous argument as in the proof of Theorem 2 we deduce

$$\text{ASC}(G) = \text{ASC}(G-(R_1)) - \text{ASC}(G-R_1) \quad (8)$$

if R_1 is an A-ring. (If R_1 is an L-ring, then no result analogous to eq. (8) could be obtained.) Taking into account the conditions (6) and in particular $s_i = -1$, we obtain from Theorem 1,

$$\rho(G) = \rho(G-(R_1)) - \rho(G-R_1) ,$$

which combined with eqs. (7) and (8) is further transformed into (5). Q.E.D.

For example, $\text{ASC}(G_1)$ is obtained from $\rho(G_1)$ for $x_1 = x_4 = x_5 = 1$, $x_2 = x_3 = -1$, namely

$$\rho(G_1; 1, -1, -1, 1, 1) = 2 = \text{ASC}(G_1) .$$

It is worth noting that Theorem 5 holds irrespective of whether the $(4m+2)$ -membered rings of G are of the type A or L.

For the hydrocarbon G_3 (which does not fulfil the conditions of Theorem 5) we have $\rho(G_3; x_1, x_2, x_3, x_4) = 1 + x_1 + x_2 + x_3 + x_4 + x_3x_4$, where $|R_1| = |R_3| = 6$, $|R_2| = 8$ and $|R_4| = 4$. Therefore $\rho(G_3; 1, -1, 1, -1) = 0$ whereas $\text{ASC}(G_3) = 2$. It would be of considerable interest to generalize Theorem 5 so to cover also the class of cata-condensed molecules with $(4m)$ -membered rings of the type L. Such a result is, however,

not known to the author of the present paper.

Since four-membered rings must always be A-rings, we have the following consequence of Theorem 5.

COROLLARY 5.1

If G is a cata-condensed molecule composed of 4- and 6-membered rings, then eq. (5) holds.

Combining Theorems 2 and 5 we arrive to

COROLLARY 5.2

If G satisfies the conditions of Theorem 5, then

$$K^+(G) = \frac{1}{2} [\rho(G; 1, 1, \dots, 1) + \rho(G; s_1, s_2, \dots, s_n)] ,$$

$$K^-(G) = \frac{1}{2} [\rho(G; 1, 1, \dots, 1) - \rho(G; s_1, s_2, \dots, s_n)] ,$$

where K^+ and K^- are the number of even and odd Kekulé structures, respectively⁹, and the numbers s_j are given by the eqs.(6)

From Theorems 3 and 5 we have

COROLLARY 5.3

If G satisfies the conditions of Theorem 5, then for $x_j = s_j$, $j = 1, 2, \dots, n$,

$$\frac{\partial \rho(G)}{\partial x_i} = \text{ASC}(G-R_i) .$$

This is the last combinatorial identity which we present in this paper.

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From the multilinear form $\rho(G; x_1, x_2, \dots, x_n)$ a variety of polynomials can be derived by identifying certain variables x_i . We mention here a few of these possibilities which might be of some importance in developing a general resonance theoretical formalism for the description of both benzenoid and non-benzenoid conjugated hydrocarbons.

If a unique variable λ_k is associated to all k -membered resonant rings, that is if for $j = 1, 2, \dots, n$

$$x_j = \lambda_k \quad \text{whenever} \quad |R_j| = k,$$

then we obtain from $\rho(G; x_1, x_2, \dots, x_n)$ the resonant ring polynomial¹¹ $R(G) = R(G; \lambda_4, \lambda_6, \lambda_8, \lambda_{10}, \dots)$.

Some further specializations of this polynomial are

$$R_1(G) = R_1(G; \lambda^-, \lambda^+) = R(G; \lambda^-, \lambda^+, \lambda^-, \lambda^+, \dots) \quad ,$$

$$R_2(G) = R_2(G; \lambda) = R_1(G; -\lambda, \lambda) \quad ,$$

$$R_3(G) = R_3(G; \lambda) = R_1(G; \lambda, \lambda) \quad .$$

Note that if G is a benzenoid hydrocarbon, then $R(G)$ and therefore also $R_1(G)$, $R_2(G)$ and $R_3(G)$ coincide with the sextet polynomial.

The above listed polynomials have a number of interesting algebraic properties. For instance, if G is a non-branched cata-condensed alternant hydrocarbon (either benzenoid or non-benzenoid), then all the zeros of $R_3(G; \lambda)$ are real numbers.

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The investigations of the algebraic and combinatorial content of Clar's sextet theory of benzenoid molecules were initiated by the work of Hosoya and Yamaguchi³. The present paper offers extensions and generalizations of their results. In particular we demonstrated that Clar's theory can be extended also to non-benzenoid hydrocarbons and that the formalism which we developed reflects the most essential resonance theoretical features of non-benzenoids, namely the fact that their Kekulé structures may have different parity.

Therefore we hope that the multilinear form $\rho(G)$ will become the basis for a new mathematical technique in the topological theory of conjugated molecules.

R E F E R E N C E S

1. E.Clar, *The Aromatic Sextet*, Wiley, London 1972.
2. See for example: O.E.Polansky and G.Derflinger, *Internat. J.Quantum Chem.*, 1, 379 (1967); M.Randić, *Tetrahedron*, 31, 1477 (1975); I.Gutman and S.Bosanac, *Tetrahedron*, 33, 1809 (1977).
3. H.Hosoya and T.Yamaguchi, *Tetrahedron Letters*, 4659 (1975).
4. I.Gutman, *Theoret.Chim.Acta*, 45, 309 (1977).
5. J.Aihara, *Bull.Chem.Soc.Japan*, 50, 2010 (1977).
6. I.Gutman, H.Hosoya, T.Yamaguchi, A.Motoyama and N.Kuboi, *Bull.Soc.Chim.Beograd*, 42, 503 (1977).
7. I.Gutman, *Bull.Chem.Soc.Japan*, 51, 2729 (1978).
8. N.Okhami, A.Motoyama, T.Yamaguchi, H.Hosoya and I.Gutman, *Tetrahedron*,
9. For details on the parity of Kekulé structures and algebraic structure count see: A.Graovac and I.Gutman, *Match (Mülheim)*, 6, 49 (1979).
10. See for example: A.T.Balaban, *Match (Mülheim)*, 2, 51 (1976); O.E.Polansky and D.H.Rouvray, *Match (Mülheim)*, 2, 63 (1976).
11. I.Gutman, *Bull.Soc.Chim.Beograd*, 46, (1981).