

Altan derivatives of a graph

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ABSTRACT. Altan derivatives of polycyclic conjugated hydrocarbons were recently introduced and studied in theoretical organic chemistry. We now provide a generalization of the altan concept, applicable to any graph. Several earlier noticed topological properties of altan derivatives of polycyclic conjugated hydrocarbons are shown to be the properties of all altan derivatives of all graphs. Among these are results pertaining to Kekulé structures/perfect matchings, determinant of the adjacency matrix, and graph spectrum.

Keywords: altan graph, molecular graph, Kekulé structure, perfect matching, spectrum (of graph)

1. INTRODUCTION

Altan derivatives of polycyclic conjugated molecules recently came into the focus of attention of theoretical organic chemists [1-5]. The name “*altan*” is an abbreviated form of “*alternating annulene*”, which is a fragment encircling the parent conjugated system.

The altan derivative of a conjugated hydrocarbon is constructed so that each hydrogen atom is replaced by a vinyl group, and each two adjacent vinyl groups are condensed into a new cycle. The construction of altan-phenanthrene is shown in Fig. 1.

An interesting and attractive property of altan molecules is that the π -electron system of the annulene that surrounds the parent hydrocarbon is only weakly interacting with the π -electron system of the parent hydrocarbon. From the point of view of Kekulé structures, the π -electron conjugation in the annulene and the parent hydrocarbon are fully independent. In particular, the Kekulé structure count of the altan derivative is equal to the product of the Kekulé structure count of the parent hydrocarbon and the number of Kekulé structure of the annulene (which, of course is equal to two) [5,6].

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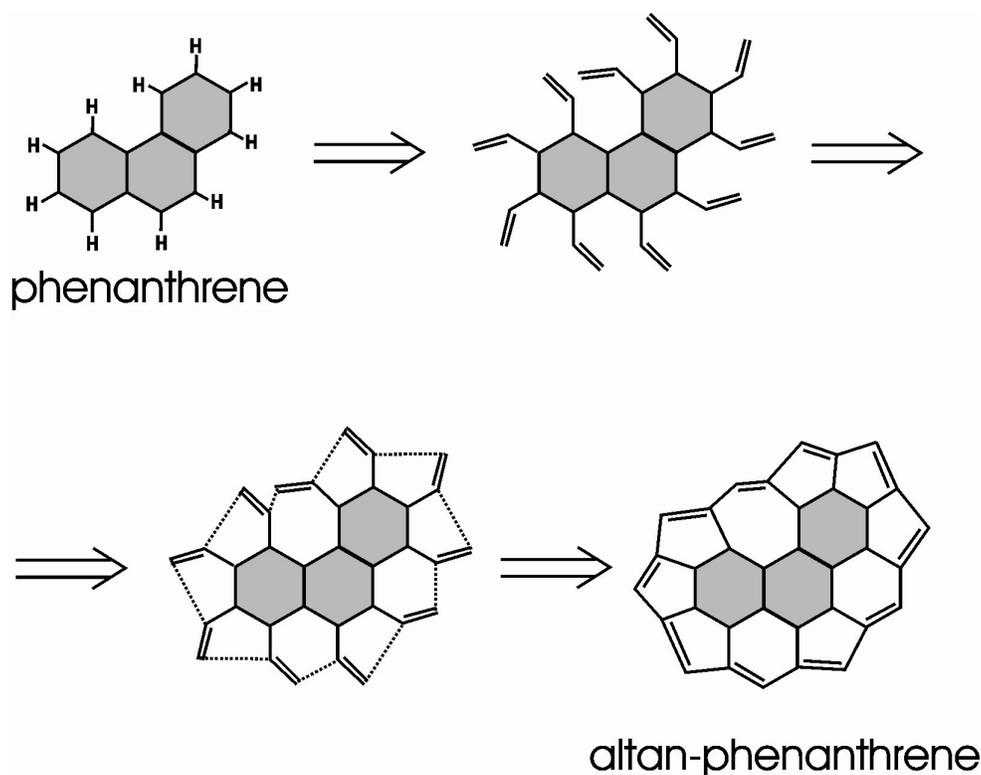


Fig. 1. Construction of altan-phenanthrene from phenanthrene. Note that the perimeter of altan-phenanthrene is a [20]annulene, encircling the phenanthrene subunit.

It is easy to see that if the number of hydrogen atoms of the parent conjugated molecule is even, then the annulene in the altan-derivative has size $4k+2$ (and thus contains $4k+2$ π -electrons). According to the Hückel $(4k+2)$ -rule [7-9], such a π -electron system contributes to antiaromaticity and possesses a paratropic ring current.

In what follows, we show that the above listed properties of altan-molecules are properties of a much more general class of graph derivatives, which we define in the subsequent section.

2. GENERALIZING THE CONCEPT OF ALTAN -DERIVATIVES

Definition 1. Let G be a graph of order n . For $2 \leq h \leq n$, let $U = (v_1, v_2, \dots, v_h)$ be an ordered h -tuple of vertices of G . The altan-derivative of the graph G with regard to U is the graph $G^\dagger = G^\dagger(U)$ constructed in the following manner. For $i=1, 2, \dots, h$, attach a new vertex x_i to the vertex v_i . Then attach a new vertex y_i to the vertex x_i . Then for $i=1, 2, \dots, h-1$, connect the vertices y_i and x_{i+1} and also connect the vertices y_h and x_1 .

As a direct consequence of Definition 1 we see that:

- 1) If the graph G has n vertices, then $G^\dagger = G^\dagger(U)$ has $n+2h$ vertices.
- 2) If the graph G has m edges, then $G^\dagger = G^\dagger(U)$ has $m+3h$ edges.

3) The degree of the vertices x_1, x_2, \dots, x_h is 3.

4) The degree of the vertices y_1, y_2, \dots, y_h is 2.

Remark 2. If G is a molecular graph of a polycyclic conjugated hydrocarbon, then in its altan-derivative $G^\dagger = G^\dagger(U)$, the vertices $U = (v_1, v_2, \dots, v_h)$ are those corresponding to carbon atoms to which a hydrogen atom is connected, arranged along the perimeter. Then h is just the number of hydrogen atoms of the underlying hydrocarbon. If so, then the cycle formed by the vertices $x_1 y_1 x_2 y_2 \cdots x_h y_h$ corresponds to the annulene encircling the parent hydrocarbon. Evidently, its size is $2h$.

In what follows, we denote by Γ_{2h} the $(2h)$ -membered cycle of $G^\dagger = G^\dagger(U)$, induced by the vertices $x_1 y_1 x_2 y_2 \cdots x_h y_h$.

3. ON PERFECT MATCHINGS OF ALTAN –GRAPHS

If u and v are two adjacent vertices of a graph, then the edge connecting them will be denoted by uv . We say that uv covers the vertices u and v . Two edges of a graph are said to be independent if they cover 4 vertices.

A *perfect matching* of a graph G is a set of mutually independent edges which cover all vertices of G . The number of perfect matchings of the graph G will be denoted by $K(G)$.

In case of molecular graphs, perfect matchings are in a one-to-one correspondence with Kekulé structures. Then $K(G)$ is just the Kekulé structure count of the underlying conjugated molecule. For details on this correspondence see [8,10].

Theorem 3. Let the vertices of the altan graph G^\dagger be labeled as in Definition 1. Then the edges $v_i x_i, i = 1, 2, \dots, h$, do not belong to any perfect matching of G^\dagger .

Proof. Suppose the contrary, namely that $M(G^\dagger)$ is a perfect matching of G^\dagger and that $v_1 x_1 \in M(G^\dagger)$. Then, in order that the vertex y_1 be covered, it must be $y_1 x_2 \in M(G^\dagger)$. Then, in order that the vertex y_2 be covered, it must be $y_2 x_3 \in M(G^\dagger)$. Continuing this argument, we see that in order that the vertex y_{h-1} be covered, it must be $y_{h-1} x_h \in M(G^\dagger)$. Then, however, the vertex y_h cannot be covered in $M(G^\dagger)$ because y_h is adjacent only to x_1 and x_h , and the edges $v_1 x_1$ and $y_{h-1} x_h$ are already in $M(G^\dagger)$. Therefore $v_1 x_1 \in M(G^\dagger)$ is not possible, and analogously $v_i x_i \in M(G^\dagger)$ is not possible for any $i = 1, 2, \dots, h$. \square

Corollary 4. For any graph G and for any h -tuple U , $K(G^\dagger(U)) = 2K(G)$.

Proof. By Theorem 3, deleting the edges $v_i x_i$ from G^\dagger does not change the number of perfect matchings. After deleting all $v_i x_i, i = 1, 2, \dots, h$, what remains is the disconnected subgraph $G \cup \Gamma_{2h}$. Corollary 4 follows from $K(G \cup \Gamma_{2h}) = K(G) \cdot K(\Gamma_{2h})$ and $K(\Gamma_{2h}) = 2$. \square

Remark 5. The Kekulé-structure equivalents of Theorem 3 and Corollary 4, valid for altan-derivatives of conjugated hydrocarbons, were noticed in all papers [1-4]. A formal proof thereof, applicable to altan-benzenoids was offered in [5]. We now see that these are just special cases of a much more general regularity.

4. DETERMINANT OF ADJACENCY MATRIX OF ALTAN –GRAPHS

Let G be a graph of order n . A Sachs graph of G is a subgraph of G whose all components are cycles and/or 2-vertex complete graphs K_2 [8,11,12]. Denote by $S(G)$ the set of all Sachs graphs that are spanning subgraphs of the graph G (i.e., that have same number of vertices as G). It is known [8,11-13] that the determinant of the adjacency matrix $A(G)$ of a graph G satisfies the relation

$$\det A(G) = (-1)^n \sum_{\sigma \in S(G)} (-1)^{p(\sigma)} 2^{c(\sigma)} \quad (1)$$

where $p(\sigma)$ and $c(\sigma)$ are, respectively, the number of components and of cycles in the Sachs graph σ .

Theorem 6. Let the vertices of the altan graph G^\dagger be labeled as in Definition 1. Then the edges $v_i x_i$, $i = 1, 2, \dots, h$, do not belong to any Sachs graph from the set $S(G^\dagger)$.

Proof. Suppose the contrary, namely that there exists a Sachs graph $\sigma \in S(G^\dagger)$, such that the edge $v_1 x_1$ belongs to one of its components. We have to distinguish between two cases: Either (a) $v_1 x_1$ belongs to a K_2 -component of σ , or (b) $v_1 x_1$ belongs to a cycle of σ .

Case (a). If $v_1 x_1$ belongs to a K_2 -component of σ , then also $y_1 x_2$ must belong to another K_2 -component of σ . Same holds for $y_2 x_3, \dots, y_{h-1} x_h$. Then, however, the vertex y_h cannot belong to any component of σ , because y_h is adjacent only to x_1 and x_h , and the edges $v_1 x_1$ and $y_{h-1} x_h$ are already in σ . Therefore the edge $v_1 x_1$ cannot belong to a K_2 -component of $\sigma \in S(G^\dagger)$, and analogously, the same holds for the edges $v_i x_i$ for all $i = 1, 2, \dots, h$.

Case (b). If the edge $v_1 x_1$ belongs to a cyclic component of σ , then either the vertices y_1, x_2 or the vertices y_h, x_h (but not both pairs!) belong to the same cycle. Without loss of generality, assume this is the pair y_h, x_h . Then the edge $y_1 x_2$ must belong to a K_2 -component of σ . Same holds for the edges $y_2 x_3, \dots, y_{h-2} x_{h-1}$. Then, however, the vertex y_{h-1} cannot belong to any component of σ , because y_{h-1} is adjacent only to x_{h-1} and x_h , and these latter vertices are already in σ . Therefore the edge $v_1 x_1$ cannot belong to a cyclic component of $\sigma \in S(G^\dagger)$, and analogously, the same holds for the edges $v_i x_i$ for all $i = 1, 2, \dots, h$. □

Corollary 7. For any graph G and for any h -tuple U , $\det A(G^\dagger(U)) = \det A(G) \cdot \det A(\Gamma_{2h})$.

Proof. By Theorem 6, and bearing in mind Eq. (1), deleting the edges $v_i x_i$ from G^\dagger does not change the determinant of the adjacency matrix. After deleting all $v_i x_i$, $i = 1, 2, \dots, h$, what remains is the disconnected subgraph $G \cup \Gamma_{2h}$. Corollary 7 follows now from $\det A(G \cup \Gamma_{2h}) = \det A(G) \cdot \det A(\Gamma_{2h})$. \square

As well known [8,11,12], and as a direct consequence of Eq. (1), the determinant of the cycle of size $2h$ is equal to -4 if h is odd, and is equal to 0 if h is even. This yields:

Corollary 8. For any graph G and for any h -tuple U , if h is even, then $\det A(G^\dagger(U)) = 0$ whereas if h is odd, then $\det A(G^\dagger(U)) = -4 \det A(G)$.

Corollary 9. For any graph G and for any h -tuple U with even h , the altan-graph G^\dagger is singular, i.e., its spectrum possesses at least one zero eigenvalue.

Remark 10. Polycyclic conjugated hydrocarbons necessarily possess an even number of hydrogen atoms. Therefore, in all chemically relevant altan-derivatives, the parameter h is even, implying that one of the graph eigenvalues is equal to zero. In the language of theoretical chemistry [8,11,14], all altan-derivatives of conjugated hydrocarbons have a non-bonding molecular orbital. This important fact was observed in all earlier papers [1-5]. We now see that this is just special cases of a much more general regularity.

The nullity $\eta(G)$ of a graph G is the multiplicity of its eigenvalue zero [14].

Corollary 11. If h is even, then $\eta(G^\dagger) \geq 1$. The nullity of G^\dagger may be greater than unity. In particular, $\eta(G^\dagger) \geq \eta(G)$, whereas the nullity of the parent graph G may assume any value between 0 and n [14]. The case $\eta(G^\dagger) = \eta(G)$ is, for example, encountered if G is the graph without edges. The case $\eta(G^\dagger) = \eta(G) + 1$ is encountered if G is non-singular.

If h is odd, then the situation with nullity is simple: $\eta(G^\dagger) = \eta(G)$ holds in all cases.

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