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Topological properties of altan-benzenoid hydrocarbons

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Abstract: The main topological characteristics of altan-benzenoids were established. In particular, it was shown that the perimeter of Kekuléan altan-benzenoids is of size $4k$, having a destabilizing (anti-aromatic) energy effect, similar to $(4k)$ -annulenes.

Keywords: altan-benzenoid hydrocarbon; benzenoid hydrocarbon; annulene; molecular graph; cyclic conjugation.

INTRODUCTION

Altan derivatives of polycyclic conjugated molecules recently came into the focus of attention of theoretical organic chemists.^{1–4} 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.

Altan conjugated systems are interesting for two reasons. If all the cycles surrounding the parent hydrocarbon are 5- and/or 6-membered, then the altan molecule is non-planar, bowl shaped,^{1,2} thus being a distant relative of fullerenes and nanotubes. The annulene system surrounding the parent hydrocarbon⁵ may contain $4k$ cyclically delocalized π -electrons.

According to the Hückel $(4k+2)$ -rule,^{6–9} it thus contributes to anti-aromaticity and possesses a paratropic ring current.^{1–4,10,11}

The graph representation of an altan derivative of a conjugated molecule is shown in Fig. 2.

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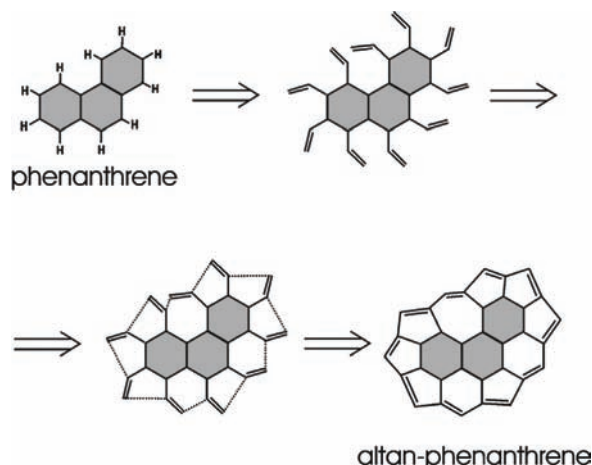


Fig. 1. Construction of altan-phenanthrene from phenanthrene. Note that the perimeter of altan-phenanthrene is a [20]annulene, encircling the phenanthrene subunit.

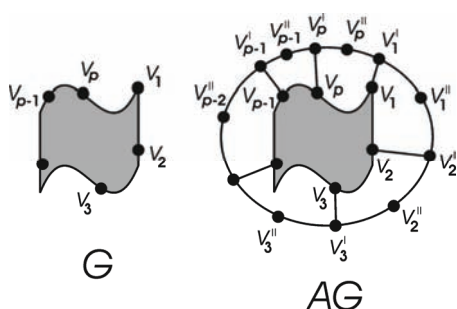


Fig. 2. The molecular graph AG of an altan, the molecular graph G of its parent hydrocarbon, and the labeling of some of their vertices; for details see text.

The molecular (Hückel) graph¹² of a polycyclic conjugated hydrocarbon is denoted by G , and is assumed to contain no $=\text{CH}_2$ groups. This graph has n vertices, all of which are of degree 2 and 3. There are p vertices of degree two, and in the diagram G in Fig. 2, these are indicated and labeled by v_1, v_2, \dots, v_p (the $n-p$ vertices of degree three are not indicated). These degree-two vertices represent carbon atoms to which hydrogen atoms are attached. Thus, the formula of the conjugated hydrocarbon represented by the graph G is C_nH_n .

The altan graph, AG , corresponding to the parent molecular graph G (see Fig. 2), consists of a central fragment identical to G , and a cycle of size $2p$, in which the vertex v'_i is connected with the vertex v_i of G , $i = 1, 2, \dots, p$. Therefore, if G has n vertices and m edges, then AG has $n + 2p$ vertices and $m + 4p$ edges.

If the distance between the vertices and of G is equal to d , then the cycle of AG embracing the vertices $v_i, v_{i+1}, v'_i, v'_{i+1}$ is of size $d + 4$.

The parent conjugated system from which the altan derivative is constructed needs not be a benzenoid hydrocarbon,¹⁻⁴ but altan-benzenoids are certainly the most interesting (and also the most realistic) members of this class. In that which

follows, the considerations will be restricted to benzenoid altans, and their main topological properties established.

STRUCTURAL FEATURES OF ALTAN-BENZENOIDS

Details on the structural characteristics of benzenoid hydrocarbons can be found in the book¹³ and the recent papers.^{14–18} In particular, on the perimeter of a benzenoid system, one distinguishes features called fissures, bays, coves, and fjords,^{13,14,19,20} cf. Fig. 3. The numbers of fissures, bays, coves, and fjords will be denoted by b_1 , b_2 , b_3 and b_4 , respectively. The frequently used “bay number” of a benzenoid system¹³ is then $b = b_2 + 2b_3 + 3b_4$.

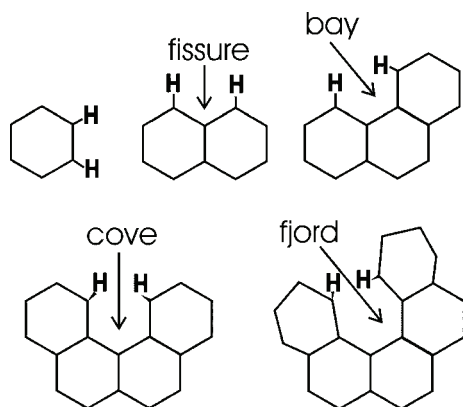


Fig. 3. The five different constellations of two nearest-lying hydrogen atoms on the perimeter of a benzenoid hydrocarbon. In order that all the rings of the altan-benzenoid be of size 5 and 6, bays, coves and fjords cannot be present. Note that in an earlier work,²¹ the hydrogen atoms attached to a fissure, bay, cove, and fjord were labeled by $H-a$, $H-a3$, $H-a4$, and $H-a5$, respectively.

In view of the above-described construction of altan derivatives, the sizes of the newly formed rings depend on the mutual constellation of the nearest-lying hydrogen atoms of the parent benzenoid system. The following regularities are immediately established.

Rule 1. a) Two nearest-lying hydrogen atoms attached to neighboring carbon atoms of the parent benzenoid system give rise to the formation of a 5-membered ring in the corresponding altan. b) Two nearest-lying hydrogen atoms separated by a fissure on the perimeter of the parent benzenoid system (see Fig. 3) give rise to the formation of a new 6-membered ring in the corresponding altan. c) Two nearest-lying hydrogen atoms separated by a bay or cove or fjord on the perimeter of the parent benzenoid system (see Fig. 3) give rise to the formation of a ring in the corresponding altan of size greater than 6.

A benzenoid system is said to be convex^{14,19,20} if there are no bays, coves or fjords on its perimeter, *i.e.*, if $b = 0$. From Rule 1, the condition under which an altan derivative consists of only 5- and 6-membered rings is evident:

Rule 2. In order that all rings of an altan-benzenoid be of sizes 5 and 6, the parent benzenoid system must be convex.

The number m_{22} of edges of a benzenoid system connecting two vertices of degree two satisfies the relation:¹³ $m_{22} = 6 + b$. Therefore, from Rule 1a, it could be concluded that the corresponding altan has $6 + b$ pentagons.

Rule 3. The number of 5-membered rings of an altan-benzenoid is 6 if and only if the parent benzenoid is convex.

Rule 4. a) If the parent benzenoid system has h hexagons, then the corresponding altan-benzenoid has $h + b_1$ hexagons. b) The numbers of 7-, 8-, and 9-membered rings in an altan are equal to b_2 , b_3 and b_4 , respectively.

Note that all altan derivatives considered until now were derivatives of convex (benzenoid or non-benzenoid) conjugated molecules, for which $b_2 = b_3 = b_4 = 0$. This is understandable, since the 7- and higher-membered rings in altan derivatives of non-convex (benzenoid or non-benzenoid) π -electron systems would cause in them high steric strain and drastic deviation from planarity (*cf.* Fig. 3).

Let G be the molecular graph of a benzenoid system with h hexagons and n_i inner vertices.¹³ Then the number of its vertices is equal to:¹³

$$n = 4h + 2 - n_i \quad (1)$$

The number of vertices of degree three in G is:¹³

$$n_3 = 2h - 2 \quad (2)$$

In addition:

$$n = n_3 + p \quad (3)$$

Combining Eqs. (1)–(3), one obtains $p = 2h + 4 - n_i$. Therefore, the size r of the annulene ring (*i.e.*, the perimeter) of the corresponding altan AG is equal to:

$$r = 4h + 8 - 2n \quad (4)$$

In order that a benzenoid system be Kekuléan (*i.e.*, to possess Kekulé structures),¹³ the number n of the vertices must be even. Then, by Eq. (1), n_i must also be even. Bearing this in mind, Eq. (4) implies the following important result:

Rule 5. The size of the annulene ring (*i.e.*, the perimeter) of an altan derivative of a Kekuléan benzenoid hydrocarbon is divisible by 4, *i.e.*, it contains $4k$ cyclically delocalized π -electrons.

The property stated here as Rule 5 was certainly known to earlier investigators of altans,^{1–4} and might have been the chief motivation for the study of this class of conjugated π -electron systems. Yet, a demonstration of the general validity of this rule seems to be offered here for the first time.

π -ELECTRON PROPERTIES OF ALTAN-BENZENOIDS

The alternating double bonds in the annulene ring of an altan can be arranged in two different ways, which causes a duplication of the Kekulé structures of the parent benzenoid system. An illustrative example is given in Fig. 4,

where the pairs k_i, k'_i ; $i = 1,2,3$ should be compared. Therefore, any altan-benzenoid has at least two times as many Kekulé structures as the parent benzenoid hydrocarbon, *i.e.*, $K(AG) \geq 2K(G)$. Now, it will be proven that in all cases, the equality $K(AG) = 2K(G)$ holds.

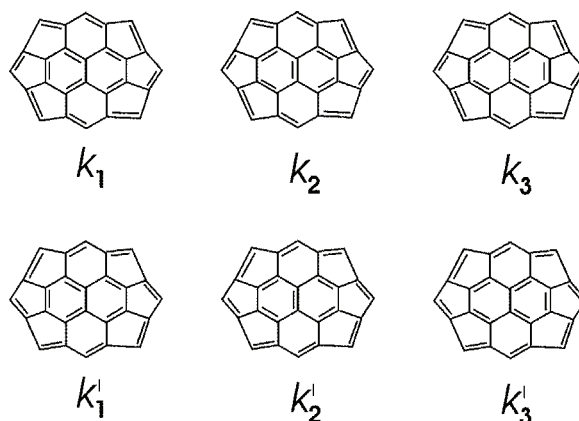


Fig. 4. Kekulé structures of altan-naphthalene.

Rule 6. The Kekulé structure count of an altan-benzenoid is exactly twice the Kekulé structure count of the parent benzenoid hydrocarbon.

In order to verify Rule 6, the altan AG in Fig. 2 is considered and the indicated labeling of its vertices is referred to. It is necessary to show that in all Kekulé structures of AG , the bonds $v_i v'_i$, $i = 1,2,\dots,p$ are single.

Suppose the opposite, namely that there is a Kekulé structure of AG in which the bond $v_1 v'_1$ is double, see Fig. 2. Then also the bond $v_1 v'_2$ must also be double, and, continuing the same argument, all the bonds $v_{i+1} v'_i$, $i = 1,2,\dots,p-1$, must be double. Then, however, the vertex v_p remains isolated, which contradicts the existence of a Kekulé structure. Therefore, the bond $v_1 v'_1$ cannot be double.

If all bonds $v_i v'_i$, $i = 1,2,\dots,p$, of AG are single in all its Kekulé structures, then the total number of Kekulé structures of AG is equal to the product of $K(G)$ and the number of Kekulé structures of the annulene ring, equal to two. This implies Rule 6.

In the terminology of Monaco and Zanasi,¹⁰ it could be stated that Rule 6 proves “K-factorization” of the parent benzenoid system and its enveloping annulene. It is possible to show that such a “K-factorization” (*i.e.*, Rule 6) holds for all altan-species (both benzenoid and non-benzenoid).

From Rule 6, it can be seen that the π -electron conjugation in the annulene ring of an altan-benzenoid is only weakly influenced by the conjugation modes of the parent benzenoid system. As a direct consequence of this, some π -electron

properties of annulenes^{6,22–24} are preserved also in altan-benzenoids. From Rule 5, it is known that these annulenes are of size $4k$. Of their properties, the most important may be that cyclic conjugation has a significant destabilizing energy effect. Some characteristic examples are presented in Table I. The energy effects of the perimeters have been computed by means of a standard procedure, the details of which were described elsewhere.^{15,25–27}

TABLE I. Energy effects (in units of the HMO resonance integral β) of the perimeters of some altan-benzenoids and their parent hydrocarbons. According to the Hückel $(4k+2)$ -rule, cycles of size 10, 14, 18, ... have a positive (stabilizing) effect, whereas cycles of size 16, 20, 24, ... have negative (destabilizing) energy effects. The destabilizing energy effects of the annulene-type perimeters of altan-benzenoid hydrocarbons are remarkably strong, and (except in the case of altan-naphthalene) exceed the stabilizing energy effect of the parent benzenoid system

Compound	Altan-benzenoid		Parent hydrocarbon	
	Size of perimeter	Energy effect	Size of perimeter	Energy effect
Naphthalene	16	-0.0565	10	+0.0709
Anthracene	20	-0.0694	14	+0.0279
Phenanthrene	20	-0.0295	14	+0.0198
Pyrene	20	-0.0196	14	+0.0128
Coronene	24	-0.0082	18	+0.0039

Another characteristic feature of the π -electron configuration of $(4k)$ -annulenes is the existence of a pair of non-bonding molecular orbitals (NBMOs).^{6,7,12} This property is also (partially) preserved in the case of altan-benzenoids. Namely, the following regularity holds.

Rule 7. Altan-benzenoid hydrocarbons have NBMOs. Kekuléan altan-benzenoids have a unique NBMO.

The form of the single NBMO of Kekuléan altan-benzenoids should be evident from the examples depicted in Fig. 5.

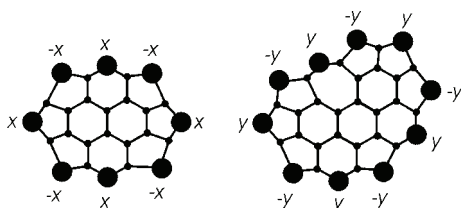


Fig. 5. The unique NBMO of altan-naphthalene ($x=1/\sqrt{8}$) and altan-phenanthrene ($y=1/\sqrt{10}$). The coefficients of the NBMOs on all other carbon atoms are equal to zero.

ИЗВОД
ТОПОЛОШКА СВОЈСТВА АЛТАН-БЕНЗЕНОИДНИХ УГЉОВОДОНИКА

ИВАН ГУТМАН

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Одређене су важније тополошке карактеристике алтан-бензеноидних угљоводоника. Између осталог, показано је да периметар Кекулеовских алтан-бензеноидних систем има величину $4k$, и да има дестабилизујући (антиароматични) енергетски ефекат, сличан $(4k)$ -ануленима.

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