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On the generalized approach to the structure count

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A generalized approach to the structure count of *n*-radical-*m*-cation systems based on the properties of the acyclic polynomial is presented. The mathematical proof for the expression relating the structure count to the coefficients of the acyclic polynomial is given. The connection between the structure count of biradical structures and the number of Dewar structures is discussed and tested on some examples.

Key words: Graph theory — Acyclic polynomial, coefficients of — structure count — Sachs graphs — Kekulé structures — Dewar structures — Biradicals — Radical-cations — Canonical structures

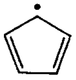
1. Introduction

Kekulé structures have found an important role in chemistry [1, 2], particularly for quick characterization of conjugated systems within the framework of qualitative valence bond theory (resonance theory) [3-6].

The interest in Kekulé structures and resonance theory has been revived after Wilcox introduced the concept of algebraic structure count, ASC [7]. Later, Herndon [8] independently introduced this concept and named it the corrected structure count. In proposing the concept of ASC Wilcox utilized the concept of parity of Kekulé structures [9]. Wilcox has shown that for polycyclic conjugated systems containing $4N$ rings (N = number of π-centers) the total number of Kekulé structures $K(G)$ of structure G (also called the structure count $SC(G)$ of structure G) [8] must be replaced by the difference between *even* (K^+) and *odd* (K^-) Kekulé structures: $ASC(G) = K^+ - K^-$; $K^+ > K^-$. The structure count is then, of course, given by $K(G) = SC(G) = K^+ + K^-$. The *ASC* was used for predicting relative stabilities and reactivities of isomeric conjugated molecules [10].

In recent years, Kekulé structures became widely used in the structure-resonance theory [8], the conjugated circuits model [11, 12], the method of significant electron structures [13, 14], the molecular orbital resonance theory [15], and the valence bond resonance energy approach [16].

However, Kekulé structures form just a special subset from the set of structures which can be generally named as n-radical-m-cation structures. Such a set would encompass, e.g. all the possible different structures of cyclopentadienyl radical:



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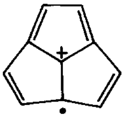
or all radical-cation structures of acepentylene:



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Formally, while Kekulé structures are generated graphically by spanning the σ-skeleton of a molecule with the appropriate number of double bonds, n-radical-m-cation structures are formed by spanning the σ-skeleton with n unpaired π-electrons and m positive charges (i.e. ionized π-electrons) balanced by the pertinent number of double bonds. Therefore, a Kekulé structure can be considered as an n-radical-m-cation structure where both n and m are equal to zero. Furthermore, monoradical structures ($n = 1, m = 0$) are to an odd-membered σ-skeleton (as in 1) the same as Kekulé structures to an even-membered σ-skeleton (e.g. benzene).

The present paper deals with the issue of enumerating n-radical-m-cation structures. The simplest approach is to manually draw all the distinct structures and count them [17], a procedure which becomes quite laborious and inconvenient even if a σ-skeleton of moderate complexity is considered. A better approach is to deal with the problem from the topological (or more correctly, from the graph theoretical) point of view [8, 18–20].

2. Mathematical approach

Let a Hückel graph [21] G (i.e. a connected graph whose vertices $v_i \in V(G)$ have degrees $d(v_i) \in \{1, 2, 3\}$, $i = 1, 2, \ldots, N$, where $N = |G|$) represent the σ-skeleton of the parent conjugated molecule.

Note, that the concept of Hückel graphs embraces *all* graphs representing conjugated molecules irrespective of the number of π-electrons they contain. Furthermore, the approach that we will describe can be applied to graphs outside of the class of Hückel graphs which in general do not necessarily need to be chemical graphs either.

Let $G(n, m)$ represent an n-radical-m-cation structure of the parent molecule. By $G(n, m)$ we understand the partition of G into three subgraphs G_1, G_2, G_3, where G_1 are acyclic Sachs graphs [22] (i.e. graphs whose only components are K_2) $s_{N-n-m} \in S^{ac}_{N-n-m}$ on $N-n-m$ vertices, while G_2 and G_3 are discrete graphs (i.e. graphs with the set of edges $E(G)=0$) such that $|G_2|=n$ and $|G_3|=m$ (see Fig. 1).

Because of

$$V(G_1) \cup V(G_2) \cup V(G_3) = V(G) \tag{1}$$

$k=n+m$ and $|G|=N$ are necessarily of the same parity (i.e. both are odd or both are even), otherwise there will exist a vertex $v \in V(G)$ such that

$$V(G_1) \cup V(G_2) \cup V(G_3) = V(G) \backslash \{v\} \tag{2}$$

The following proposition gives the relationship between the number of distinct structures $G(n, m)$ (called the structure count [8] of $G(n, m)$ or $SC[G(n, m)]$) and the coefficients a^{ac}_{N-n-m} of the acyclic polynomial [23, 24] $P^{ac}(G; x)$

$$P^{ac}(G; x) = \sum_{l=0}^{N} a^{ac}_{N-l} x^l \tag{3}$$

Proposition. *If G is a graph on N vertices*

$$SC[G(n, m)] = \binom{n+m}{m} |a^{ac}_{N-n-m}| \tag{4}$$

Proof. It is enough to realize that $|a^{ac}_{N-n-m}|$ is the number of all acyclic Sachs graphs on $N-k$ vertices (i.e. the cardinality of the set S^{ac}_{N-k}), where $N-k$ is always even and $k=n+m$. Therefore, a^{ac}_{N-n-m} enumerates all possible subgraphs G_1 of graph G which satisfy the condition $|G_1| = N-n-m$. How, for each G_1, represented by $s_{N-n-m} \in S^{ac}_{N-n-m}$, there is a set of $G(n, m)$ structures which differ only in the way the remaining $k=n+m$ vertices are partitioned into G_2 and G_3. There are exactly $\binom{k}{m}$ ways of partitioning k vertices into discrete graphs G_2 and G_3 such that the conditions $|G_2| = k-m$ and $|G_3| = m$ hold.

Comments. (i) Note the property

$$SC[G(n, m)] = SC[G(m, n)] \tag{5}$$

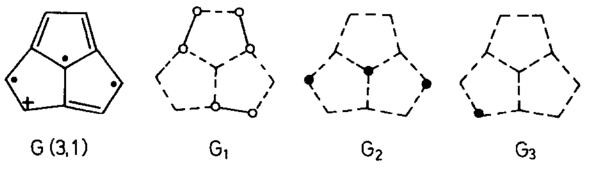


Fig. 1. The partition of a particular n-radical-m-cation structure $G(n, m)$ of graph G into subgraphs G_1, G_2, and G_3. G_1 is an acyclic Sachs graph on N-n-m vertices, while G_2 and G_3 are discrete graphs on n and m vertices, respectively

because of

$$\binom{n+m}{m}=\binom{n+m}{n}$$

This is the same as saying that the number of n-radical-m-cation structures is equal to the number of m-radical-n-cation structures for a given σ-skeleton, which is certainly true.

(ii) When we put $n=0$, $m=0$; $n=1$, $m=1$; and $n=2$, $m=0$ or $n=0$, $m=2$, the structure counts reduce to

$$\begin{aligned} &SC[G(0,0)]=|a_N^{ac}|=|K(G)| \\ &SC[G(1,1)]=2|a_{N-2}^{ac}| \\ &SC[G(2,0)]=SC[G(0,2)]=|a_{N-2}^{ac}| \end{aligned} \tag{6}$$

$K(G)$ denotes the Kekulé structures. Note that if N is odd then a_N^{ac}, $a_{N-2}^{ac}=0$

(iii) Supposing that $|G_3|=m=0$, the set S_{N-2}^{ac} can be split into two subsets such that

$$\begin{aligned} &S_{N-2}^{ac}=\bar{K}(G)\cup D(G) \\ &D(G)=\{s_{N-2}\in S_{N-2}^{ac}|\ V(G_2)\ \text{non-adjacent}\} \\ &\bar{K}(G)=\{s_{N-2}\in S_{N-2}^{ac}|\ V(G_2)\ \text{adjacent}\} \end{aligned} \tag{7}$$

where $D(G)$ symbolizes the Dewar structures (an additional edge between the two vertices of G_2 is usually added and denominated as a "long bond"). We have immediately

$$|a_{N-2}^{ac}|=|S_{N-2}^{ac}|=|\bar{K}(G)|+|D(G)| \tag{8}$$

Since

$$|\bar{K}(G)|=\frac{N}{2}|K(G)| \tag{9}$$

we obtain

$$|a_{N-2}^{ac}|=\frac{N}{2}|K(G)|+|D(G)| \tag{10}$$

which can be written as

$$|D(G)|=|a_{N-2}^{ac}|-\frac{N}{2}|a_N^{ac}| \tag{11}$$

and

$$SC[G(1,1)]=2\cdot\left(\frac{N}{2}|K(G)|+|D(G)|\right) \tag{12}$$

so that we have proven formula (5) from [25] enumerating radical-cations of graph G. Although the relation (9) is self-evident, the question arises if *every possible* $s_{N-2} \in \bar{K}(G) \subset s^{ac}_{N-2}$ can be derived from a $s_N \in S^{ac}_N \equiv K(G)$. It is easy to prove this by taking a suspect $s_{N-2} \in \bar{K}(G)$ and placing an additional subgraph $K_2(v_1, v_2)$ over the adjacent vertices $V(G_2) = \{v_1, v_2\}$. Now, if the graph $s_{N-2} \cup K_2(v_1, v_2) \equiv s_N \in S^{ac}_N$, it means that the graph s_{N-2} can be derived from the graph s_N by substituting the appropriate K_2 subgraph by two discrete vertices v_1 and v_2. If, however, the graph $s_{N-2} \cup K_2(v_1, v_2) \notin S^{ac}_N$ (i.e. it does not form a valid Kekulé structure), it means that the $(N/2-1)K_2$ components of s_{N-2} do not form a valid Sachs graph on $N-2$ vertices, i.e. obviously the tested $s_{N-2} \notin S^{ac}_{N-2}$ to begin with.

Equation (4) gives a new insight into the meaning of the coefficients of the acyclic polynomial. Namely, while $|a^{ac}_N|$ is the number of Kekulé structures (of course, if N is odd, $a^{ac}_N = 0$), $|a^{ac}_{N-1}|$ is the number of radical (or cation) structures (again, if N even, $a^{ac}_{N-1} = 0$), $|a^{ac}_{N-2}|$ is the number of biradical (or bication) structures, $|a^{ac}_{N-3}|$ is the number of triradical (or trication) structures, $|a^{ac}_{N-4}|$ is the number of tetraradical (or tetracation) structures, etc., while $|a^{ac}_2|$ is the number of $(N-2)$-radicals (or $(N-2)$-cations; or, alternatively, the number of bonds) and $|a^{ac}_0|$ is the number of N-radicals (or N-cations; i.e. the number of discrete graphs over N vertices, which is always equal to 1).

There are some interesting implications, as well. Consider a graph G (with N even) the acyclic polynomial of which has a property $a^{ac}_N = 0$. Such a graph has no Kekulé structures. However, if $a^{ac}_{N-2} \neq 0$, it means that the structures of the highest order that can be written for such a graph are of the biradical type. Thus, such a graph belongs to the family of *proper biradicals* [26, 27]. Furthermore, all the biradical structures of such a graph belong to the set of Dewar structures (because of expression (11)). Therefore, one can define a *proper biradical* as a graph with $a^{ac}_N = 0$ but $a^{ac}_{N-2} \neq 0$, or, alternatively, as a graph the highest order structures of which are Dewar structures. If, however, both $a^{ac}_N = 0$ and $a^{ac}_{N-2} = 0$, but $a^{ac}_{N-4} \neq 0$, we can talk of a *proper tetraradical* etc. If N is odd, and $a^{ac}_{N-1} \neq 0$ (which is true for most cases), we are dealing with a *proper radical*; if however, $a^{ac}_{N-1} = 0$, but $a^{ac}_{N-3} \neq 0$, we have the case of a *proper triradical*, etc.

3. Discussion

Let us now test the forwarded expressions on the examples outlined in the beginning. The needed acyclic polynomials can be obtained through one of the available computer programs [28], or one can use the recursive formula [22, 23]

$$P^{ac}(G; x) = P^{ac}(G-e; x) - P^{ac}(G-(e); x)$$

For the case *1* (cyclopentadienyl radical) the acyclic polynomial is

$$P^{ac}(\mathit{1}; x) = x^5 - 5x^3 + 5x.$$

Obviously, being an odd-membered ring, *1* does not have any Kekulé structures. From (4) we have $SC[\mathit{1}(1,0)] = |a^{ac}_4| = 5$, i.e. there are five distinct monoradical structures. Of course, because of $SC[1(2,0)] = |a_2^{ac}| = 5$ there are five triradical structures, too (Fig. 2).

The acyclic polynomial of *2* (acepentylene) is

$$P^{ac}(2; x) = x^{10} - 12x^8 + 39x^6 - 75x^4 + 39x^2 - 3.$$

Acepentylene has 3 Kekulé structures: $SC[2(0,0)] = |a_{10}^{ac}| = 3$. From (4) we have $SC[2(2,0)] = |a_8^{ac}| = 39 = SC[2(0,2)]$, i.e. there are 39 biradical structures and 39 bication structures. These will yield 78 radical-cation structures, because of $SC[2(1,1)] = \binom{2}{1}|a_8^{ac}| = 78$ (Fig. 3), etc.

It is of special interest to find the number of biradical structures where the vertices of G_2 are non-adjacent, i.e. the number of Dewar structures. From (11) it turns out that $|D(G)| = |a_8^{ac}| - N/2|a_{10}^{ac}| = 24$. Therefore, out of 39 biradical structures, there are 15 structures where the vertices of G_2 are adjacent (and consequently can be derived from Kekulé structures) and 24 structures where the vertices of G_2 are nonadjacent and cannot be derived from Kekulé structures (see Fig. 3).

A word of caution regarding $D(G)$'s is due at this point. Such structures were originally meant as "canonical first excited structures" with one "ineffective" (or "long") bond, which are important in the quantum mechanical treatment of conjugated hydrocarbons [29]. According to the original recipe [30] the orbitals (i.e. the nodes of graph G) "... are arranged formally in a circle or polygon, and all structures are drawn in which each bond lies wholly within the figure, and in which no two bonds intersect...; a structure in which one bond is 'ineffective' is called 'first excited'...". Let's add parenthetically that the σ-skeleton is not drawn during this procedure, i.e. only the π superstructure is considered. However, as Wheland himself admits [30] "... there is some arbitrariness in this [procedure] since in general the final result will depend upon the way in which the initial ordering is carried out".

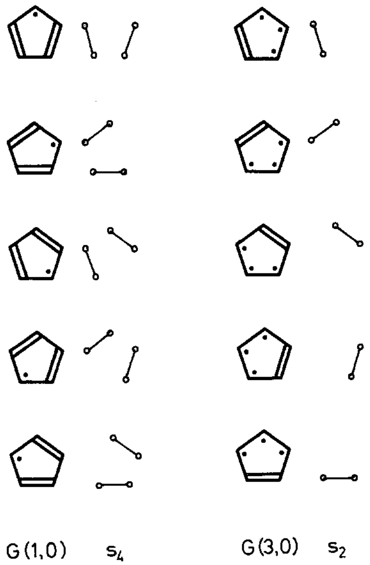


Fig. 2. The monoradical $G(1,0)$ and triradical $G(3,0)$ structures of cyclopentadienyl radical and the related Sachs graphs s_4 and s_2

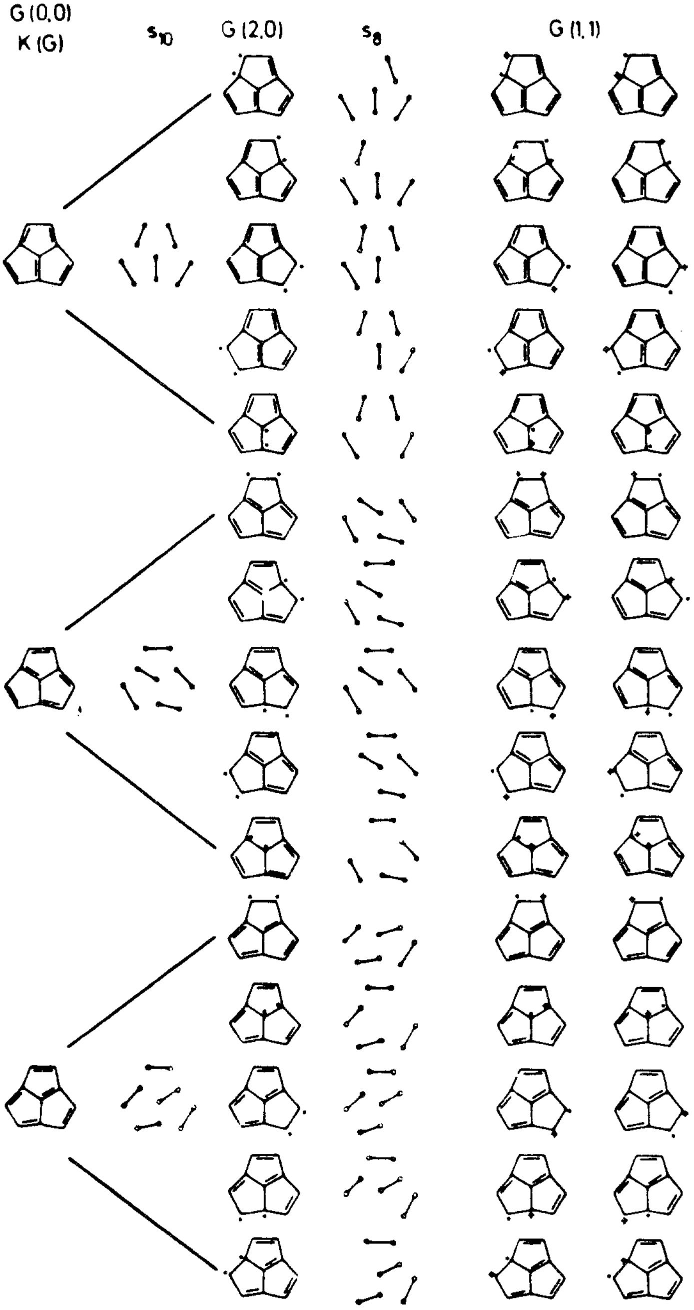


Fig. 3. The Kekulé $G(0,0)$, biradical $G(2,0)$ and radical-cation structures $G(1,1)$ of acepentylene together with the related Sachs graphs s_{10} and s_8. Out of 39 biradical structures, 15 structures can be derived from the Kekulé structures. The remaining 24 structures form the set of Dewar structures. Each biradical structure generates two radical-cation structures

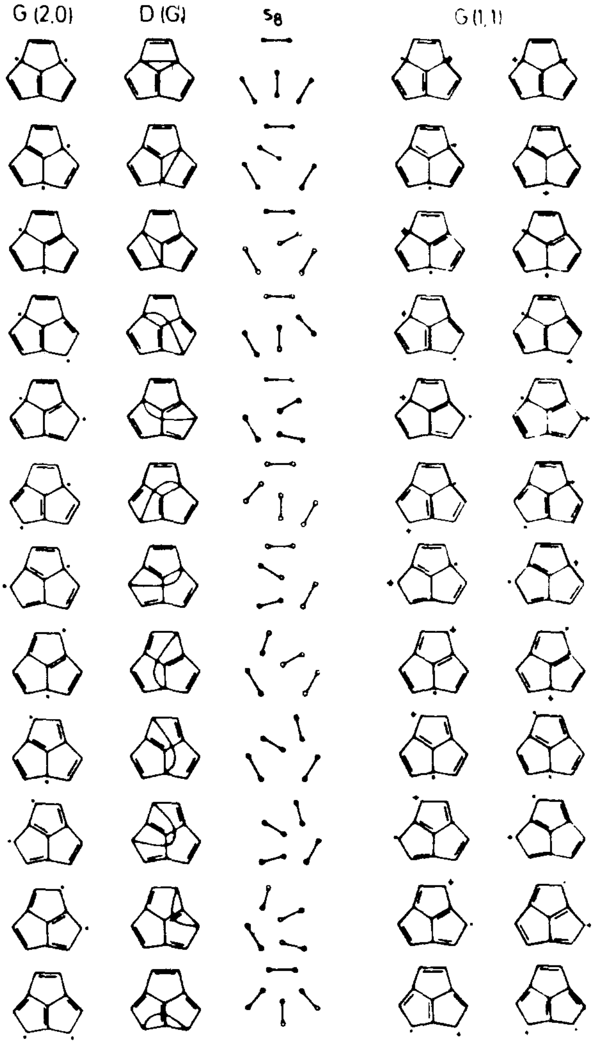
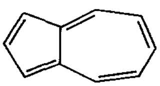


Fig. 3—(continued)

The present procedure of obtaining $|D(G)|$ counts all structures where $|G_2|=2$ and $V(G_2)$ are non-adjacent, and therefore includes all "canonical first excited structures", together with the structures where the "ineffective" bond intersects one (or more) "effective" bonds (i.e. components of the Sachs graph). It is easy to show that the latter cannot happen (when first excited structures are considered) for straight chains and mono- or polycyclic structures containing only even-membered cycles. However, bond intersection may happen in polycyclic structures with odd-membered rings. A good example of this is azulene



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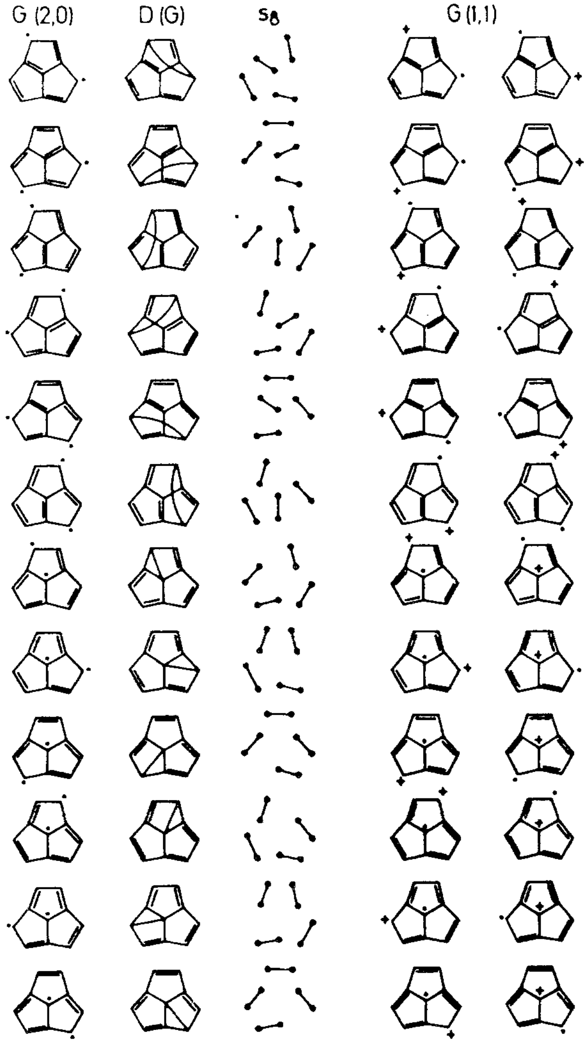


Fig. 3—(continued)

The acyclic polynomial of azulene is

$$P^{ac}(3;\, x) = x^{10} - 11x^{8} + 41x^{6} - 61x^{4} + 31x^{2} - 2.$$

From (11) we obtain $|D(G)| = 21$. All 21 structures are shown in Figs. 4b, c. However, the edge that fuses the 5-membered ring and the 7-membered ring of azulene corresponds to an essential single bond (i.e. a bond that is single in all Kekulé structures, Fig. 4a). This bond becomes a double bond in six Dewar structures (Fig. 4c). It is exactly these six structures that do not conform to the somewhat vague definition of "canonical first excited structures" because the "long bond" crossing from the 5-membered ring to the 7-membered ring intersects the K_2 edge covering the essential single bond. Obviously, the "canonical first

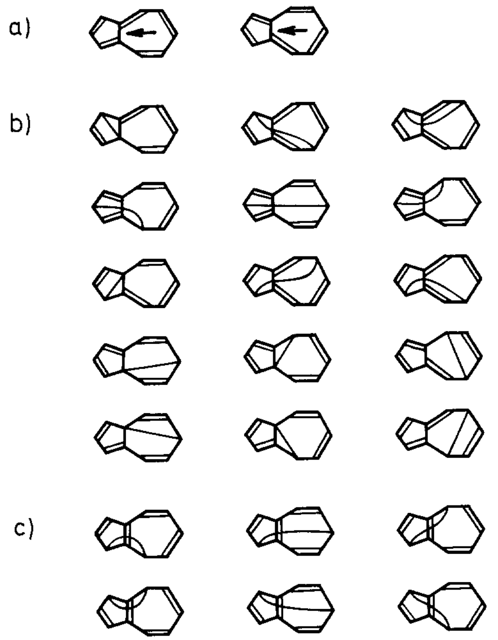
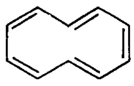


Fig. 4. Unexcited and excited structures of azulene. The *arrow* points to the essential single bond in Kekulé structures (**a**). The Dewar structures in (**b**) conform to the definition of "canonical first excited structures", those in (**c**) do not conform to the definition because the essential single bond becomes "effective" and intersects the "ineffective" bond

excited structures" of azulene can be counted by leaving out the essential single bond, i.e. considering cyclodecapentaene



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The acyclic polynomial of cyclodecapentaene is

$$P^{ac}(4;\, x) = x^{10} - 10x^{8} + 35x^{6} - 50x^{4} + 25x^{2} - 2.$$

From (11) we obtain $|D(G)| = 15$, which is the correct number of "canonical first excited structures" for both *3* and *4*. Unfortunately, the ultimate reference to the number of "canonical first excited structures", the Wheland polynomial [30–33], cannot be constructed for azulene by the usual prescriptions, so that the mismatch between $|D(G)|$ and the number of "canonical first excited structures" may be beside the point.

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