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Herndon's Structure-Resonance Theory. On the Valence Structure Count for Conjugated Radical Cations

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Enumeration of valence structures for conjugated radical cations is of interest in estimating the first ionization potentials of conjugated hydrocarbons. Alternative routes for enumeration are reviewed and a novel method, based on the properties of the acyclic polynomials of conjugated structures, is outlined. The method is illustrated for several molecules and results reported for a number of conjugated systems involving either 14 or less carbon atoms.

INTRODUCTION

The first (adiabatic) ionization potential, *IP*, of a conjugated molecule may be estimated from the known molecular resonance energy, *RE*, and the resonance energy for the corresponding radical cation. Recently Herndon[1,2] proposed the following linear relationship based on the above,

$$IP = A + RE\,(G) - RE\,(G^{\cdot+}) \tag{1}$$

where *A* is an empirical constant (to be determined from the least-squares procedure on selected standard compounds), while *G* and $G^{\cdot+}$ stand for a molecule and the corresponding radical cation, respectively. There are several alternative ways available for calculating the resonance energies of conjugated hydrocarbons. Particularly simple and instructive are schemes based on graph-theoretical concepts such as the concept of conjugated circuits,[3–5] or those based on Hückel molecular orbital considerations[6–9] and subsequent graph-theoretical interpretations.[10] An especially simple way of obtaining resonance energies follows from the proportionality,[11]

$$RE\,(G) = B \ln\,[CS\,(G)] \tag{4}$$

between *RE* (*G*) and *the structure count, SC* (*G*), i. e. the number of Kekulé valence structures, *K* (*G*), for the molecule[12–16] The constant *B* was found[11] to

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be 1.185 eV for benzenoid hydrocarbons. The structure count for a conjugated molecule is defined as the sum of the *even* (K^+) and the *odd* (K^-) structures,[12-17]

$$SC(G) = K^+ + K^- \tag{3}$$

A similar proportionality to (2) holds also for conjugated radical cations,

$$RE(G^{\cdot+}) = C \ln [CS(G^{\cdot+})] \tag{4}$$

where C is an empirical constant found[1,2] to be 1.044 eV, while $SC(G^{\cdot+})$ indicates the structure count for the radical cation. Enumeration of valence structures, be it for a neutral hydrocarbon or for a conjugated radical ion, is not a difficult task. However, even for relatively small systems, involving a dozen or more carbon atoms, the number of valence structures can be quite large. This is particularly true for radical cations, where the number of valence structures proliferates very fast. Hence, finding an algorithm for the enumeration of valence structures is of special interest. A number of approaches for the enumeration of Kekulé valence structures have been proposed in the literature.[15,18-32] The enumeration of valence forms of »excited« structures, i. e. structures involving so called »long« bonds, such as those in Dewar structures of benzene, and the evaluation of valence structures associated with ions and radical ions has received little attention. An interesting formula to enumerate $SC(G^{\cdot+})$ has been proposed,[33]

$$SC(G^{\cdot+}) = 2\,[SC(G)\, n_{C=C}(G) + SC(G^*)] \tag{5}$$

where $n_{C=C}(G)$ is the number of carbon-carbon double bonds in the parent structure G, while $SC(G^*)$ is the number of singly excited valence forms, i. e. the number of Dewar structures for G, for which we will use the symbol $D(G)$.

After collecting eqs. (2) and (4) into (1) we arrive at the formula for predicting ionization potentials,

$$IP = A + B \ln [SC(G)] - C \ln [SC(G^{\cdot+})] \tag{6}$$

This formula is not easy to use, because the number of Dewar structures is not a readily available datum. However, we wish to point out that for benzenoid hydrocarbons Wheland[34] has outlined the enumeration of excited valence forms, where the coefficients of counting polynomials[35] give the number of valence structures of different degrees of excitation. Recently the recursive formulae for the construction of Wheland polynomials became available.[37,38]. Nevertheless, the construction of Wheland polynomials for an arbitrary conjugated hydrocarbon remains unsolved, so in practice such an approach can be used only in the study of benzenoid systems. We will consider the problem of the valence structure count for conjugated radical cations in its generality and will demonstrate a practical route for the enumeration of valence structures involving radical ions, based on the properties of acyclic (reference, matching) polynomials.[39-48]

ENUMERATION PROCEDURE

The acyclic polynomial is a novel concept developed from the graph-theoretical considerations of the chemical theory of aromaticity.[10,16,39-41,49] Briefly, comparing π-electron energies in conjugated systems upon cyclization, the total energy may increase or decrease with respect to a standard structure which is non-cyclic. In order to avoid ambiguities and arbitrariness in selecting standards it appears that deleting all terms in the characteristic polynomial (which in the Hückel model would correspond to the Hückel polynomial whose eigenvalue spectrum produces the π-electron energy for the structure)[16,50] which arise due to cyclic components, as a consequence of using the Sachs theorem,[52] uniquely defines the reference »structure«. This »structure« is a mathematical object and not some real or hypothetical molecule. The acyclic polynomial has some interesting properties; in particular, it has been shown that its roots are real.[42,43,46–48,53]

For a given conjugated system the acyclic polynomial $P^{ac}(G; x)$ is defined as,[10,39,54]

$$P^{ac}(G; x) = \sum_{n=0}^{N} a_n^{ac}(G)\, x^{N-n} \tag{7}$$

where $a_n^{ac}(G)$ are the coefficients of the polynomial, which in general depend on the molecular graph G and implied connectivity. The coefficients $a_n^{ac}(G)$ can be constructed analogously to the construction of the coefficients of the characteristic polynomials,[52,55] with proper modifications for deleting the terms of cyclic origin. The construction formula takes the form,[10,54]

$$a_n^{ac}(G) = \sum_{K_2 \in S_n^{ac}} (-1)^{c(K_2)} \tag{8}$$

where K_2 *is the complete graph on two vertices,*[55] *i. e. an isolated edge, while* S_n^{ac} represents the set of all K_2 disjoint subgraphs, i. e. $c(K_2) = n/2$. Thus, no odd-power coefficients are possible in the acyclic polynomials, while the even-power coefficients will in general differ from the corresponding coefficients in the characteristic polynomial due to the exclusion of ring contributions. Expression (8) in principle resolves the problem of finding $a_n^{ac}(G)$, but in practice the number of combinatorial possibilities proliferates very fast with an increase in the size of molecule, so that it soon becomes tedious and impractical to carry out the calculation indicated in (8). The difficulty is, we should emphasize, inherent in a procedure which uses the Sachs theorem for construction, and applies equally to coefficients of the characteristic polynomial as to coefficients of the acyclic polynomial. The explosive growth of combinations limits even the usefulness of computers.[56].

An alternative way to construct acyclic polynomials is to use the recurrence relation,[41]

$$P^{ac}(G; x) = P^{ac}(G - e; x) - P^{ac}[G - (e); x] \tag{9}$$

where $G - e$ and $G - (e)$ denote subgraphs of G obtained by deleting an edge e, and an edge e with the incident vertices, respectively, from G. This procedure has been found very suitable for computer construction of the acyclic polynomials[57] and the necessary computer program is available.[58] This appears to be the most practical way to derive acyclic polynomials for any conjugated sistem.[59–61]

The coefficients of acyclic polynomials have some pleasing properties. The absolute magnitudes of the last two coefficients can be directly related to the structure count for singly excited forms as follows,

$$|a_N^{ac}(G)| = SC(G) \quad \text{or} \quad K(G) \tag{10}$$

$$|a_{N-2}^{ac}(G)| = SC(G)\, n_{C=C}(G) + D(G) \tag{11}$$

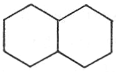
Formula (11) may be obtained by considering in detail the construction of the $a_{N-2}^{ac}(G)$ coefficient by means of the Sachs formula.[52,54] Only graphs with N = even can be considered. The K_2 subgraphs cover a given graph G in such a way that $N - 2$ vertices are covered, while two vertices are always left free. However, these uncovered vertices are either adjacent or separated by a certain number of K_2 fragments. This is illustrated below for the case of naphthalene.

a

b

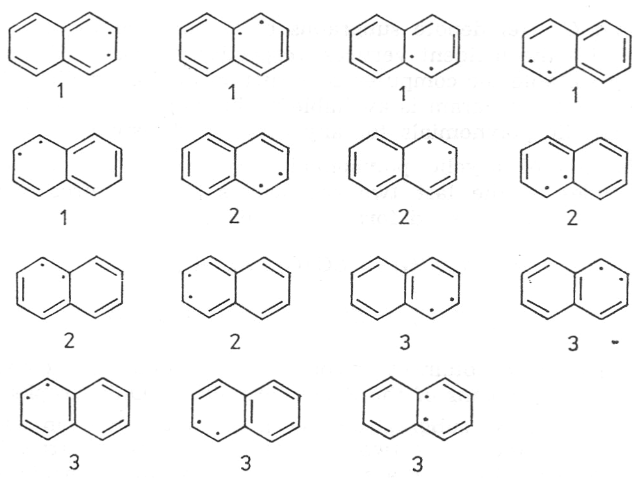
Inspection of these structures immediately reveals that structure α needs only *one* additional K_2 fragment to generate a Kekulé form, while structure *b* resembles a Dewar structure missing the »long« bond connecting two non-adjacent vertices, and, of course, cannot be used for generating Kekulé forms. It turns out that the number of structures *a* is simply equal to the number of permutations of $^1/_2\,(N - 2)$ K_2 fragments on the graphs with N vertices, always leaving two *adjacent* vertices unconnected. Since each permutation leads to a structure which upon addition of a K_2 graph produces a single Kekulé form, the total number of structures *a* is given by $SC\,(\mathrm{G}) \cdot n_{\mathrm{C=C}}\,(\mathrm{G})$.

Example



$N = 10,\ n_{\mathrm{C=C}}\,(\mathrm{G}) = 5$
$SC\,(\mathrm{G}) = 3$

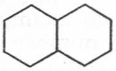
G



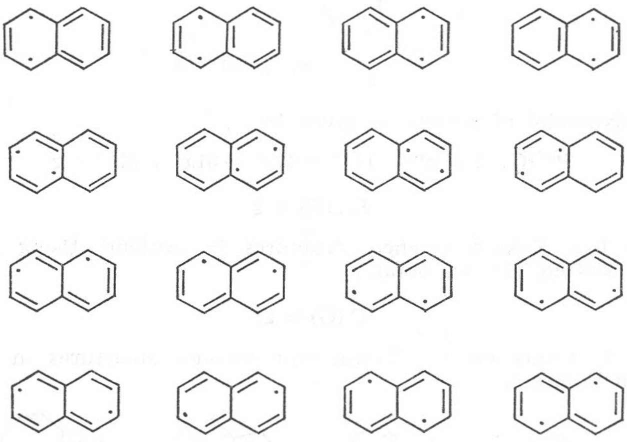
$$SC\,(\mathrm{G}) \cdot n_{\mathrm{C=C}} = 3 \cdot 5 = 15$$

The number of structures *b* is equal to the number of permutations of $\frac{N-2}{2}K_2$ fragments on the graphs with *N* vertices, always leaving two *non-adjacent* vertices disconnected. Since each permutation leads to a structure which upon addition of a »long« bond generates a single Dewar form of a molecule, the total number of structures *b* is equal to $D(G)$.

Example



G



$D(G) = 16$

$|a_8^{ac}(G)| = 15 + 16 = 31$

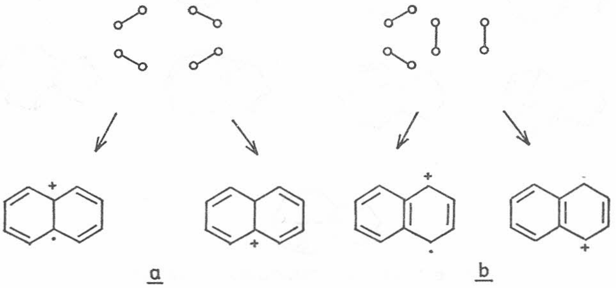
The rearrangement of formula (11) into a somewhat different form leads to the expression for the enumeration of Dewar structures of a given conjugated system *G*,

$$D(G) = |a_{N-2}^{ac}(G)| - SC(G) n_{C=C}(G) \tag{12}$$

Finally, by combining eqs. (5) and (12) we arrive at a rather simple expression for the enumeration of valence structures for radical cations,

$$SC(G^{\cdot+}) = 2|a_{N-2}^{ac}(G)| \tag{13}$$

The origin of factor two in the upper statement may be confirmed by considering the generation of radical cations from structures *a* and *b*.

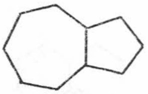


Every structure a and every structure b always generates two different forms of radical cations.

Let us now obtain the structure count for the naphthalene radical cation, since above we have derived the value of the coefficient $|a_8^{ac}(G)|$,

$$SC(G^{\cdot +}) = 2\,|a_8^{ac}(G)| = 62$$

Formulae (11)—(13), besides being used for benzenoids, may also be used directly for azulenoids,[1,2] because the structure count in this class is identical to that of the germane $(4m + 2)$ periphery. Let us consider, as an example, the evaluation of the number of Dewar structures for azulene and the number of valence structures for the azulene radical cation. The molecular graph and the number of carbon-carbon double bonds of azulene are,



G $\qquad n_{C=C}(G) = 5$

The acyclic polynomial of azulene is given by,

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

Hence,

$$SC(G) = 2$$

i. e. there are two Kekulé valence structures in azulene. Using the coefficient $a_{N-2}^{ac}(G) = 31$ and eq. (12) we obtain,

$$D(G) = 21$$

i. e. there are 21 singly excited Dewar-type valence structures in azulene which are decipted in Figure 1.

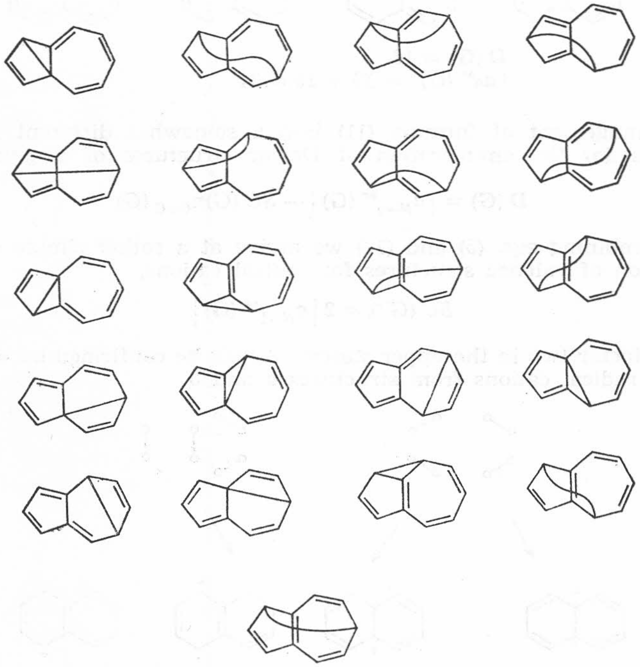


Figure 1. Dewar structures of azulene

From eq. (13) we can now derive the structure count for the azulene radical cation,

$$SC(G^{\cdot+}) = 2 \cdot 31 = 62$$

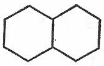
In order to take cyclobutadienoids into consideration, the structure count, $SC(G)$, should be replaced by *the algebraic (corrected) structure count*,[12-16] $ASC(G)$ or $CSC(G)$. In what follows we will use the former symbol. The algebraic structure count is defined[12] as the difference between even and odd Kekulé structures,

$$ASC(G) = |K^{+} - K^{-}| \tag{14}$$

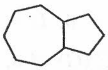
The $ASC(G)$ values of cyclobutadienoids may be determined by, for example, Wilcox's method,[12,13] or by Herndon's method,[15] or by the superposition technique.[62,63]

Note that for benzenoid and azulenoid structures, $ASC(G)$ is identical to $SC(G)$,[64] because for afternant π-network with $N/2 =$ odd, $K^{-} = 0$. In addition, $ASC(G)$ is equal to $SC(G)$ for polyenes, because these systems have only one Kekulé structure.

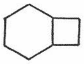
Example



G



G



G

$K^{+} = 3$; $K^{-} = 0$	$K^{+} = 2$; $K^{-} = 0$	$K^{+} = 2$; $K^{-} = 1$
$SC(G) = 3$	$SC(G) = 2$	$SC(G) = 3$
$ASC(G) = 3$	$ASC(G) = 2$	$ASC(G) = 1$

Therefore, if we want to treat cyclobutadienoids, the $SC(G)$ and $SC(G^{\cdot+})$ values must be replaced by the $ASC(G)$ and $ASC(G^{\cdot+})$ values in eq. (6),

$$IP = A + B \ln[ASC(G)] - C \ln[ASC(G^{\cdot+})] \tag{15}$$

and the Randić's relation (5) should be modified accordingly,

$$ASC(G^{\cdot+}) = 2\,[SC(G) \cdot n_{\mathrm{C=C}}(G) - L + CDSC(G)] \tag{16}$$

where L is the number of structures a with opposite parity, while $CDSC(G)$ stands for a corrected Dewar structure count. The parity correction is taken into account only when structures a contain $4m$ ring components containing exactly $4m$ paired π electrons. Only some of the structures a will contain fully conjugated $4m$ rings. There will be exactly $4m/2$ of these structures of positive parity and exactly $4m/2$ of these structures of negative parity. Therefore, the structures with the opposite parity will not contribute to eq. (16) and they should be taken away from it. Thus, the first part of relation (16) equals the algebraic structure count of structures a,

$$ASC(a) = SC(G) \cdot n_{\mathrm{C=C}}(G) - L \tag{17}$$

The L correction can be simply obtained by considering only those Kekulé structures of a cyclobutadienoid which contain four paired π electrons in the 4-memebered cycle. Then the total number of double bonds in the adjacent rings, not participating in the π system of 4-membered rings, in each such a Kekulé structure is L.

Since the Dewar structures of cyclobutadienoids have also parity, $CDSC\,(G)$ values should be considered instead of $D\,(G)$ for this class of conjugated radical cations. $CDSC\,(G)$ is defined as,

$$CDSC\,(G) = D^{+}\,(G) - D^{-}\,(G) \tag{18}$$

where $D^{+}\,(G)$ and $D^{-}\,(G)$ are Dewar structures of positive and negative parity, respectively.

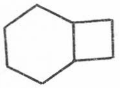
The working formula for predicting the ionization potentials of benzenoids, azulenoids, polyenes and cyclobutadienoids is then given by,

$$IP\,(\mathrm{eV}) = 11.277 + 1.185\ \ln\,[ASC\,(G)] - 1.044\ \ln\,[ASC\,(G^{\cdot+})] \tag{19}$$

Herndon[1,2] stated that this formula works well and that it gives an average deviation between the calculated and experimental IP's of ± 0.16 eV, the correlation coefficient being[1] 0.995.

Example

Enumeration of valence structures for benzocyclobutadiene radical cation



G

$$N = 8,\ L = 4,\ n_{C=C}\,(G) = 4$$

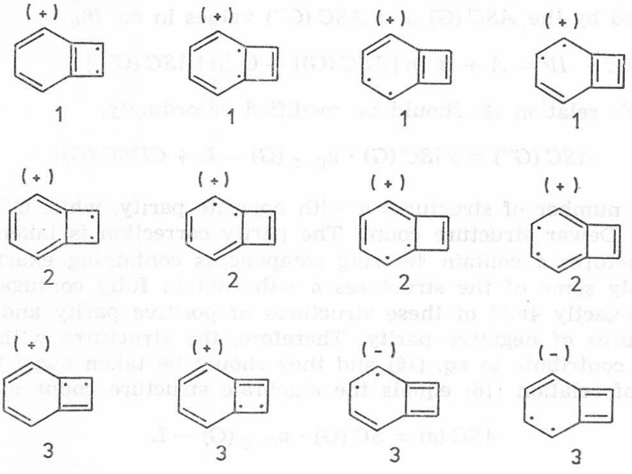
$$SC\,(G) = 3,\ ASC\,(G) = 1$$

$$P^{\mathrm{ac}}\,(G; x) = x^{8} - 9x^{6} + 24x^{4} - 20x^{2} + 3$$

$$|\,a_{N-2}{}^{\mathrm{ac}}\,(G)\,| = 20$$

$$D\,(G) = |\,a_{N-2}{}^{\mathrm{ac}}\,(G)\,| - SC\,(G) \cdot n_{C=C}\,(G) = 20 - 3 \cdot 4 = 8$$

Structures *a*

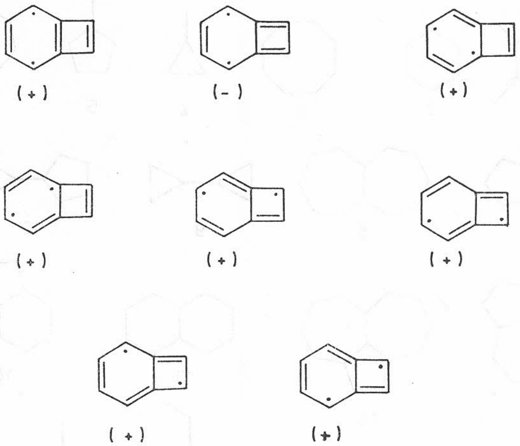


$$ASC\,(a) = SC\,(G) \cdot n_{C=C}\,(G) - L = 3 \cdot 4 - 4 = 8$$

The meaning of this value is that 10 structures above are of positive parity and 2 of negative parity. (Parity assignment is given above each structure in brackets).

Structures *b*

(Parity sign is given in brackets)



$$D(G) = 8$$

$$CDSC(G) = 6$$

Then, the valence structure count for the benzocyclobutadiene radical cation is,

$$ASC(G^{\cdot+}) = 2\,[ASC(a) + CDSC(G)] = 2\,(8 + 6) = 28$$

The corresponding structures are presented in Figure 2.

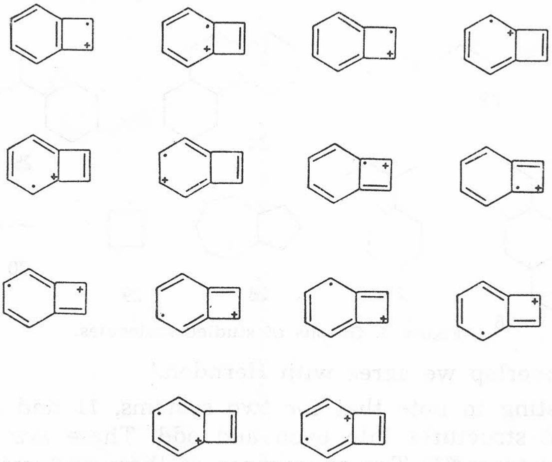


Figure 2. Half of the valence structures for benzocyclobutadiene radical cation. The other half can be simply obtained by exchanging the positions · and +.

RESULTS AND DISCUSSION

We have evaluated the number of Dewar structures for several conjugated hydrocarbons and the number of valence structures for the corresponding radical cations. Molecular skeletons for the hydrocarbons studied are given in Figure 3, while the acyclic polynomials and the parameters *D*(*G*), *CDSC* (*G*), *SC* (*G*), *ASC* (*G*), *SC* ($G^{\cdot+}$) and *ASC* ($G^{\cdot+}$) are listed in Table I.

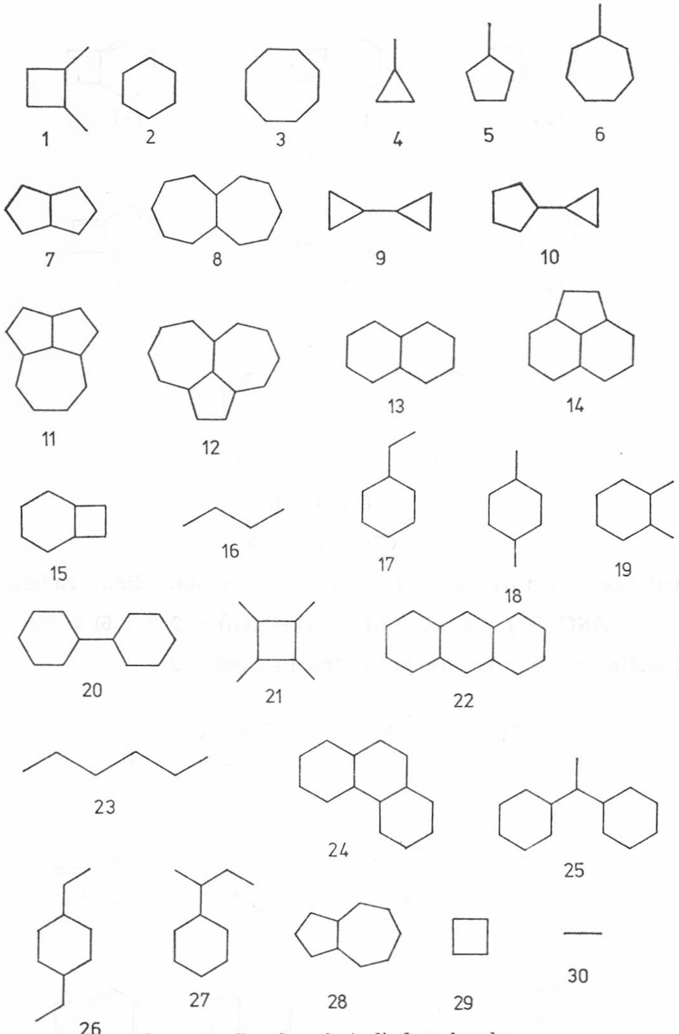


Figure 3. Graphs of studied molecules.

In all cases of overlap we agree with Herndon.[1]

It is interesting to note that for two systems, *11* and *12*, we could not partition Kekulé structures into even and odd. These are cases of Kekulé-inseparable structures.[63,65] The appearance of these systems limits the range of the structure-resonance theory. Therefore, in order to widen the use of Herndon's resonance-structure theory, the concept of algebraic (corrected) structure count must be generalised. Some work in this direction is in progress.[66]

CONCLUSION

The acyclic polynomial is a very versatile mathematical structure. It has found applications in statistical physics,[42,43] in the theory of aromatic-

TABLE I

Acyclic polynomials, the number of Dewar structures, and the (algebraic) structure counts for several conjugated molecules and their cation radicals

Molecule[a]	Acyclic polynomial	$D(G)$	$CDSC(G)$	$SC(G)$	$ASC(G)$	$SC(G^{\cdot+})$	$ASC(G^{\cdot+})$
1	$x^6 - 6x^4 + 7x^2 - 1$	4	2	1	1	14	10
2	$x^6 - 6x^4 + 9x^2 - 2$	3	3	2	2	18	18
3	$x^8 - 8x^6 + 20x^4 - 16x^2 + 2$	8	8	2	0	32	32
4	$x^4 - 4x^2 + 1$	2	2	1	1	8	8
5	$x^6 - 6x^4 + 8x^2 - 1$	5	5	1	1	16	16
6	$x^8 - 8x^6 + 19x^4 - 13x^2 + 1$	9	9	1	1	26	26
7	$x^8 - 9x^6 + 24x^4 - 20x^2 + 2$	12	12	2	0	40	40
8	$x^{12} - 13x^{10} + 62x^8 - 134x^6 + 129x^4 - 45x^2 + 2$	33	33	2	0	90	90
9	$x^6 - 7x^4 + 11x^2 - 1$	8	8	1	1	22	22
10	$x^8 - 9x^6 + 24x^4 - 19x^2 + 1$	15	15	1	1	38	38
11	$x^{12} - 14x^{10} + 71x^8 - 161x^6 + 160x^4 - 56x^2 + 3$	38	38	3	—	112	—
12	$x^{14} - 16x^{12} + 98x^{10} + 434x^8 - 301x^6 + 76x^2 - 3$	55	55	3	—	152	—
13	$x^{10} - 11x^8 + 41x^6 - 61x^4 + 31x^2 - 3$	16	16	3	3	62	62
14	$x^{12} - 14x^{10} + 71x^8 - 165x^6 + 180x^4 - 56x^2 + 3$	38	38	3	3	112	112
15	$x^8 - 9x^6 + 24x^4 + 3$	8	6	3	1	40	28
16	$x^4 - 3x^2 + 1$	1	1	1	1	6	6
17	$x^8 - 8x^6 + 19x^4 - 14x^2 + 2$	6	6	2	2	28	28
18	$x^8 - 8x^6 + 18x^4 - 10x^2 + 1$	6	6	1	1	20	20
19	$x^8 - 8x^6 + 18x^4 - 11x^2 + 1$	7	7	1	1	22	22
20	$x^{12} - 13x^{10} + 62x^8 - 134x^6 + 129x^4 - 45x^2 + 4$	21	21	4	4	90	90
21	$x^8 - 8x^6 + 16x^4 - 8x^2 + 1$	4	4	1	1	16	16
22	$x^{14} - 16x^{12} + 98x^{10} - 290x^8 + 429x^6 - 294x^4 + 76x^2 - 4$	48	48	4	4	152	152
23	$x^6 - 5x^4 + 6x^2 - 1$	3	3	1	1	12	12
24	$x^{14} - 16x^{12} + 98x^{10} - 291x^8 + 435x^6 - 305x^4 + 82x^2 - 5$	47	47	5	5	164	164
25	$x^{14} - 15x^{12} + 86x^{10} - 238x^8 + 329x^6 - 211x^4 + 52x^2 - 4$	24	24	4	4	104	104
26	$x^{10} - 10x^8 + 33x^6 - 42x^4 + 20x^2 - 2$	10	10	2	2	40	40
27	$x^{10} - 10x^8 + 33x^6 - 42x^4 + 18x^2 - 2$	8	8	2	2	36	36
28	$x^{10} - 11x^8 + 41x^6 - 61x^4 + 31x^2 - 2$	21	21	2	2	62	62
29	$x^4 - 4x^2 + 2$	0	0	2	0	8	8
30	$x^2 - 1$	0	0	1	1	2	2

[a] Numbers correspond to graphs in *Figure 1*

ity,[10,39–41,49,58–60] in pure mathematics,[44,45] etc. We have shown here that acyclic polynomials play a role in the enumeration of valence structures for radical cations, which in turn are of interest in estimating the first ionization potentials of certain classes (e. g. benzenoids) of conjugated hydrocarbons.

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Note added in proof: After this paper was in print a work by P. Eilfeld and W. Schmidt appeared (*J. Electron Spectr. Rel. Phenom.* **24** (1981) 101) in which these authors proposed a computer-oriented method for the valence structure count of conjugated radical cations. Their method requires only the Hückel (adjacency) matrix of a conjugated molecule as a input information.

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SAŽETAK

Herndonova strukturno-rezonancijska teorija. Prebrojavanje valentnih struktura konjugiranih radikalskih kationa

M. Randić, B. Ruščić, i N. Trinajstić

Prebrojavanje valentnih struktura za konjugirane radikalske katione potrebno je kod proračunavanja prvih ionizacijskih potencijala konjugiranih ugljikovodika. Navedene su poznate metode prebrojavanja i predložena je nova, koja se temelji na svojstvima acikličkih polinoma konjugiranih struktura. Metoda je ilustrirana na nekoliko primjera, a prikazani su rezultati za skup konjugiranih sustava s 14 ili manje ugljikovih atoma.

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