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ENUMERATION OF RESONANCE STRUCTURES

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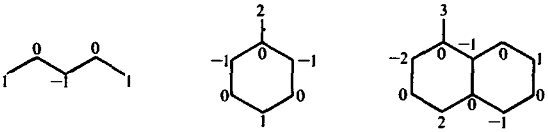
Abstract—Simple MO techniques are described that can be used to count resonance structures for unsaturated hydrocarbons, ions, and radicals. Alternant or non-alternant unsaturated species can be treated accurately and rapidly. The relationship of the structure count to the calculated values of highest filled and lowest vacant HMO energy levels is discussed. A qualitative relationship of the structure count with reactivity and stability if exemplified with several cases. A known correspondence of resonance theory and perturbational MO theory, previously limited to benzenoid and acyclic systems, is expanded to include all pi molecular systems.

The use of resonance structures and Hückel molecular orbital (HMO) theory coexist as methodologies for discussions of the chemical behaviors of π-electronic systems. For many questions of structure and reactivity, the two theoretical tools lead to identical qualitative conclusions. This is not surprising, because a congruity between the resonance structure count and the orbital amplitudes (coefficients) of zero-energy (nonbonding) molecular levels has been demonstrated for odd alternant systems that contain no rings of 4n (n = integer) orbitals.[1-3]

As examples, the unnormalized coefficients of pentadienyl, benzyl, and α-methylnaphthyl are shown in **1**. The sum of the absolute values of the coefficients is equal to the number of resonance structures which can be written for the odd system. Furthermore, the absolute value of the coefficient at any particular point is equal to the number of Kekule structures for the even, alternant molecule that would be obtained if an additional p-orbital were added to the π-system at that point. Therefore, hexatriene, styrene, and α-vinylnaphthylene have a total of one, two, and three Kekule structures respectively. Since relative stabilities and reactivities of the obtained even molecules are also related to the coefficients via a perturbational MO method, resonance theory and MO theory must give corresponding results. Some extensive discussions of these principles have been given.[4-6]



1

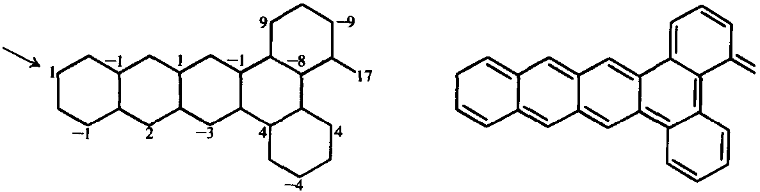
The purpose of this present paper is to show how one can extend this structure counting technique to π-systems that contain 4n rings and to non-alternant compounds. In treating some non-alternant systems, use will be made of the properties of near-zero-energy molecular orbitals, and a simplified method for writing their coefficients will be described. One will find that these methods for counting structures are fast, and the structure count information obtained is always in qualitative agreement with experimental indicators of stability and reactivity.

An analysis of resonance structures has recently appeared which is related to the work described herein.[7,8] It was shown how to obtain the product of all of the HMO eigenvalues, π_E, from an examination of the Kekule structures and the topology of a molecule.[8] A small π_E is associated with chemical instability, since it indicates one or more energy levels close to the nonbonding level of energy. For alternant hydrocarbons the square root of $|\pi_E|$ = ASC (algebraic structure count), the number of stable Kekule structures which can be written for a particular molecule. The ASC can also be obtained by actual structure counting.[7] The ASC's found for alternants in the present paper are identical to the prior results.

Structure count for odd alternants

To obtain the structure count (SC) for an odd alternant, the unnormalized coefficients of the zero-energy MO are written down and their absolute values summed. The coefficients are unique in most cases and can be written down by inspection. No bonding or antibonding orbital interactions are present, so, after carrying out the alternate starring process,[9] there must be a node (zero coefficient) at every unstarred position, and the coefficients must sum to zero around every orbital position. This last requirement is known as the zero-sum rule.

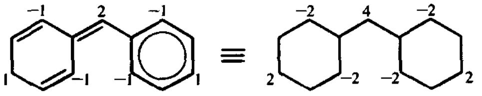
Examples are given in **1** and **2** with the arrow in **2** indicating an advantageous point to initiate



2

assignment of coefficients. Correctly counting 65 structures in **2** for the odd species, or 17 Kekule structures for the even parent molecule is not easily accomplished by sketching structures.

One pitfall must be recognized. In some systems, the smallest required unnormalized coefficient may not be unity. This circumstance can be detected by writing a single resonance structure with charge or odd electron localized at the position of smallest coefficient. If permutations of the residual double bonds are possible, the coefficients must be adjusted accordingly. To apply the procedure, it is helpful to memorize the number of Kekule structures that can be written for benzene (2), naphthalene (3), anthracene (4), and phenanthrene (5). The radicals shown in **3** and **4** are examples, and have an SC of 16 and 27 respectively. Also one notes that SC for 1,1-diphenylethylene is 4 and SC for pyrene is 6, instead of 2.



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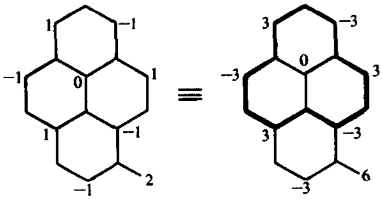


4

An important aspect of resonance theory interpretation is also illustrated in the last structure given in **4**. Two Kekule structures with odd electron localized on the upper internal atom are not contributors to the SC. These two structures contain a perinaphthenyl π-system, heavy lines in **4**, which violates the Hückel $4n+2$ rule. Another example is given in **5**, where one sees that structures containing a cyclobutadiene moiety do not contribute to the SC of 10. Therefore the SC concept is in agreement with a resonance theory modified to exclude antiaromatic structures.[10]

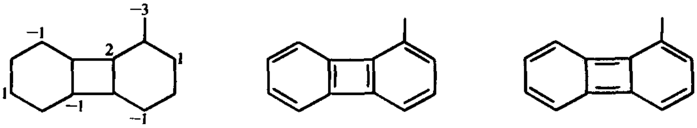
Structure count for odd non-alternants

Non-alternant radicals or ions will possess at least one zero-energy level or a near zero-energy level. The great majority of odd structures needed for discussions of even molecular systems contain one odd-membered ring. The desired wave functions can be deduced by a procedure that is best illustrated with examples.

Odd species which are obtained by removal of a p-orbital from conjugation in azulene and acenaphthylene are shown in **6**. The method to obtain the requisite wave function was developed empirically after deducing that a relationship between coefficients and resonance structures should hold for non-alternant as well as alternant systems. The procedure is as follows.

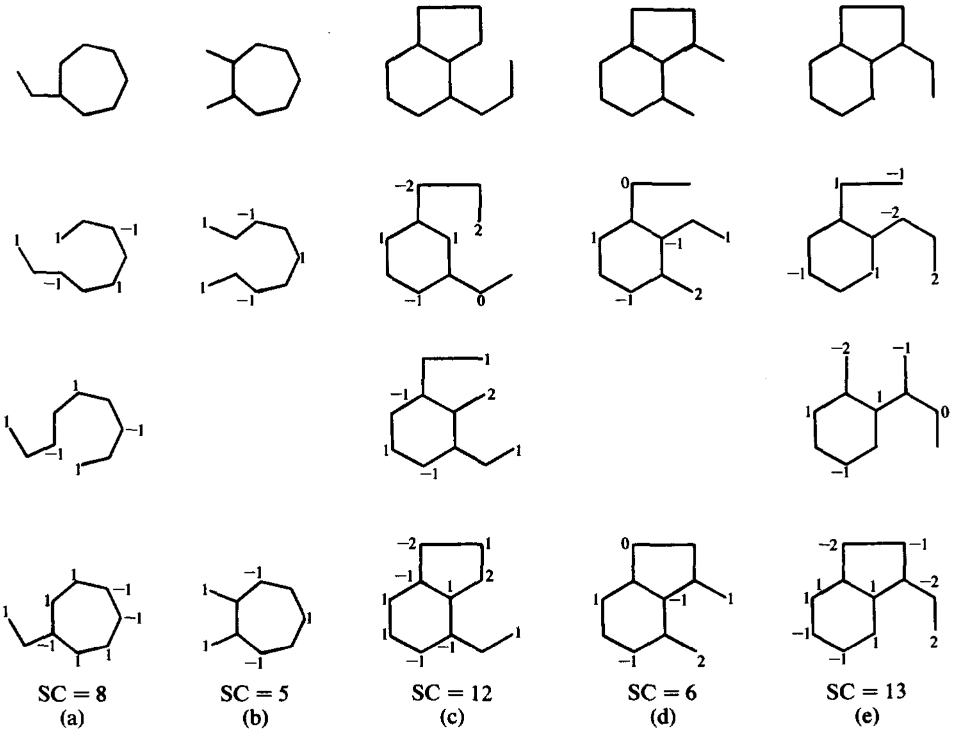
Sever the odd-membered ring at the bonds adjacent to any position in the two possible ways. Alternant systems are created for which the zero-orbital coefficients can be written using the zero-sum rule. The unnormalized coefficients of the original non-alternant system are a composite of the two severed-systems coefficients. In **6**(b) and **6**(d) application of the procedure immediately reveals the presence of a non-bonding orbital for each non-alternant structure, since a zero-energy-level for the open structure must remain if the structure is reunited at positions where there are vanishing coefficients.[4,6] Alternatively, one could have proven the presence of a non-bonding orbital in those two systems by testing with the zero-sum rule, even though the systems are not alternant hydrocarbons.

The wave-functions obtained for the near-zero-energy levels of the three remaining structures are



(not counted)

5



SC = 8 (a) SC = 5 (b) SC = 12 (c) SC = 6 (d) SC = 13 (e)

6

approximate wave functions whose eigenvalues can be calculated using simplified MO theory.[11] The values obtained, $-0{\cdot}250\beta$, $+0{\cdot}250\beta$, $+0{\cdot}211\beta$ respectively, compare well with the HMO values of $-0{\cdot}338\beta$, $+0{\cdot}263\beta$, and $+0{\cdot}224\beta$. With larger systems, the wave-functions are more accurate yielding a correspondingly more accurate energy. In all cases, the SC obtained is exactly equal to the number of resonance structures which can be written for the odd ion or radical.

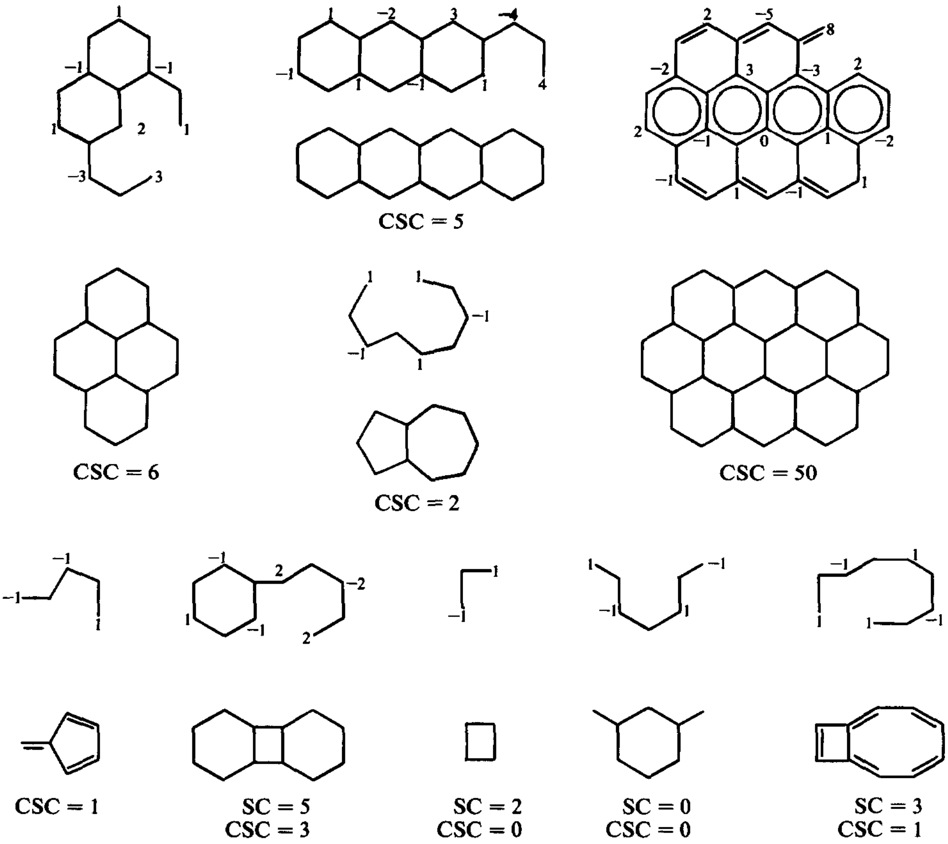
Even systems—the corrected structure count

The most useful way to obtain a structure count for even systems is to delete an orbital from the even system to obtain an odd species. Then the sum of absolute values of the unnormalized coefficients at the points adjacent to the deleted orbital is equal to the SC for the parent system. Furthermore, the absolute value of the sum of the coefficients defines a corrected structure count (CSC), that is, a structure count exclusive of structures which do not contribute to stabilizing resonance interactions.

Several examples of CSC's are given in **7**, along with the deleted orbital structures used to determine the CSC's. The numbers of structures are enumerated correctly in all cases. The CSC of 50 for ovalene has been confirmed by writing all structures.[12]

For alternant systems, CSC is exactly equivalent to the ASC defined earlier and therefore $= (|\pi_E|)^{1/2}$.[8] It necessarily follows that a neutral even alternant system with CSC = 0 must have at least two degenerate zero-energy orbitals by an HMO calculation. These zero-energy levels would be half-filled and the resulting species would be unstable and reactive. Furthermore, a relatively small CSC associated with a large molecule also indicates a reactive molecule. Energy levels for most π-systems are roughly uniformly spread in a bond of levels from about $+2{\cdot}4\beta$ to $-2{\cdot}4\beta$.[13] The smaller the CSC, the smaller the energy gap between lowest vacant and highest filled molecular levels (frontier orbitals) must be. A small energy gap of this type could indicate a thermally populated triplet state for the molecule, or a tendency toward oxidation and reduction. Finally, a non-alternant molecule with CSC = 0 must have a non-bonding orbital that may or may not be filled with electrons. Whether the orbital is filled or vacant can be determined by counting nodes in the wave function, but in either case the molecule should be reactive.

The resonance theory interpretation of the CSC gives the same conclusions. The necessity of classical Kekule structures for ground state stability is a well-known empiricism.[2,5] Also, resonance predictions of the relative stabilities of



7

isomeric species are always based on the number of structures which can be drawn. A rough division of molecular structures may be made on the basis of the CSC. A zero value, of course indicates an unstable substance not capable of isolation. A CSC = 1 is characteristic of acylic polyolefins, and so indicates a stable but reactive molecule. With CSC = 1, the larger the molecule, the more reactive. CSC greater than 1 must indicate a resonance-stabilized structure since two or more stable Kekule structures can be written.

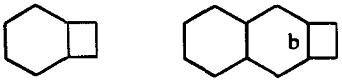
One additional use of the deleted orbital structure deserves mention. If one wishes to draw all structures for a particular parent hydrocarbon, the coefficients around the deletion point give the number of structures in which the restored atom is doubly bonded to each connected atom. One can therefore be positive that one has drawn the correct number of structures with double bonds in the correct positions.

Cyclobutadienes

SC's and CSC's for several cyclobutadiene derivatives are depicted in **8** to **11**. Exhaustive reviews[14–16] of compounds of this type have been published, and these were used as sources for experimental facts. To provide an additional crude basis for comparison of stability, the CSC for a similar vinyl-benzenoid π system has been calculated in each case, and is given in parentheses.

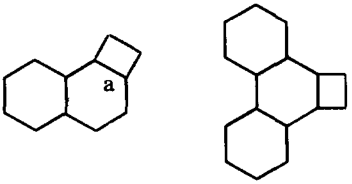
None of the compounds in **8** have been prepared, and this is in agreement with their low CSC's.[15] Naphtho[b]cyclobutadiene is predicted to be more stable than naptho[a]cyclobutadiene, which is also predicted by MO calculations[17] if one uses the total π energy or delocalization energy as a criterion of stability. The π energies are 16·20 and 15·97β respectively. This is not a large difference and one could argue whether or not the difference is meaningful. It is well-known that all condensed polycyclic systems are calculated by HMO theory to have substantial delocalization energies,[18] even those compounds which do not seem to be capable of experimental existence.

A recent review article has summarized the several possible criteria for aromaticity.[19] If the experimental criterion is taken to be stability-reactivity, then the close proximity of HMO calculated frontier orbitals or the presence of non-bonding levels is a good indicator of lack of



SC = 3
CSC = 1
(2)

SC = 4
CSC = 2
(3)



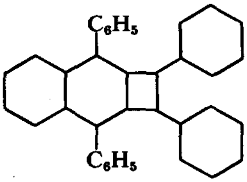
SC = 5
CSC = 1
(3)

SC = 9
CSC = 1
(5)

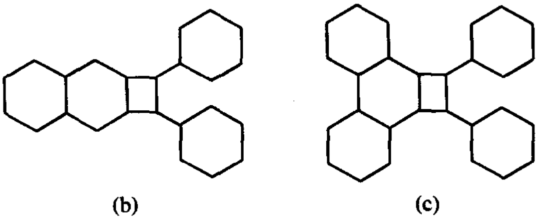
8

aromaticity. The value of the CSC is quickly obtained and highly useful in this regard.

Some attempts at the preparation of derivatives of the compounds listed in **8** have been made. Naphtho[b]cyclobutadienes, **9**(a), and **9**(b) are the only known stable hydrocarbons possessing the 4-membered ring fused to only a single aromatic residue.[20] The CSC's are in agreement. Compound **9**(b) is still reactive as a dienophile, and the CSC also indicates this aspect of its chemistry, since an addition reaction at the diphenyl substituted doulbe bond would create a structure in which the CSC has increased to 12. In contrast, diphenylphenanthro[1]cyclobutadiene, **9**(c), CSC = 2, cannot be isolated, and has been suggested to have a thermally populated triplet ground state.[21]



(a)
SC = 64
CSC = 32

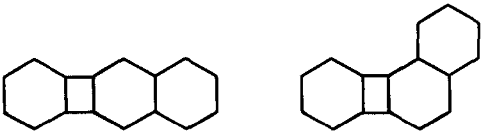


(b)
SC = 16
CSC = 8

(c)
SC = 18
CSC = 2

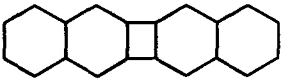
9

The linear cyclobutadienes with two fused substituents have higher CSC's than their respective angular isomers, in agreement with the known relative stabilities of these compounds.[15] Only **10**(d) is an unknown compound,* but should be capable of isolation according to its CSC. It is interesting that the dibenzobiphenylene which incorporates a phenthrene moiety into its structure **10**(g) has a CSC much higher than that of **9**(c), and it does exist.[22] It can be sublimed unchanged, whereas **10**(f) decomposes at its melting point,[23] in line with their respective CSC's. The total HMO π energies for each of the dibenzo-

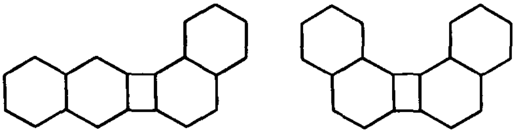


(a)
SC = 7
CSC = 5
(6)

(b)
SC = 8
CSC = 4
(6)

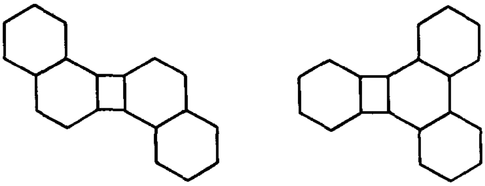


(c)
SC = 10
CSC = 8
(9)



(d)
SC = 11
CSC = 7
(9)

(e)
SC = 11
CSC = 7
(9)



(f)
SC = 13
CSC = 5
(9)

(g)
SC = 14
CSC = 6
(10)

10

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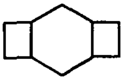
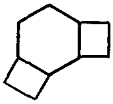
*A referee has pointed out that **10**(d) has been synthesized. J. W. Barton and S. A. Jones, *J. Chem. Soc. C*, 1276 (1967).

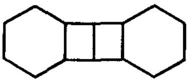
biphenylenes, **10**(c) to **10**(g) are 27·9±0·1β, which is really not indicative of their relative stabilities.

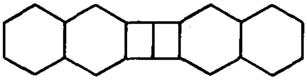
The CSC's for several compounds with two or more cyclobutadiene rings have been determined previously by structure counting.[7] The results recorded in **11** were obtained in 4 minutes using

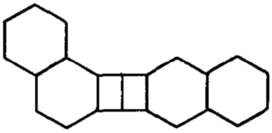

CSC = 0

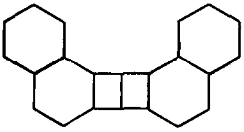

CSC = 1

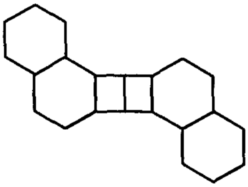

CSC = 1

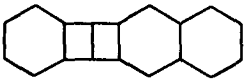

CSC = 0

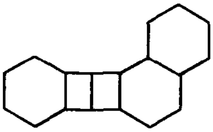

CSC = 3


CSC = 0


CSC = 3


CSC = 3


CSC = 1

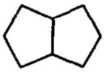

CSC = 1

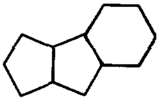
11

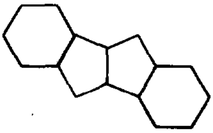
the present method, and they are identical to the prior results. Here, one cannot separate the compounds into angular or linear classes. The previous discussion[7] emphasized the fact that a finite CSC signifies a singlet ground state by an HMO calculation, the zero CSC's indicate triplet states. I would classify all of these compounds as unstable and reactive based on their low CSC's.

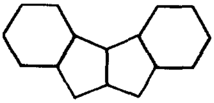
Pentalene ring system

The inferred instability of pentalene, **12**(a), can be attributed to its violation of a perimeter 4n+2 rule[24] (resonance theory), or to the fact that it has a vacant non-bonding orbital (MO theory). The CSC of zero is compatable with either theory, and also bypasses the question of whether or not a 4n+2 perimeter rule is a valid concept. Many exceptions to a perimeter rule are known.


(a)
SC = 2
CSC = 0

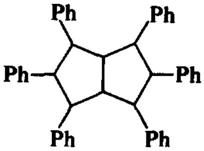

(b)
SC = 3
CSC = 1


(c)
SC = 5
CSC = 3

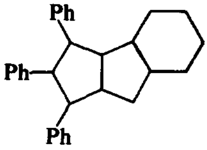

(d)
SC = 4
CSC = 0

12

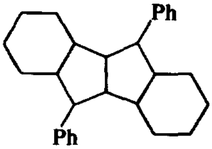
The dibenzopentalene, **12**(c), is an example since it has 16 electrons around its perimeter, and is a known compound.[25] Its CSC is nearly the same as that for 1,4-diphenylbutadiene CSC = 4, and its chemical properties are similar to those of the diene. Perhaps a better comparison would be with tetracene which has a CSC of 5 and is still quite reactive as a diene.[26] The other compounds in **12** are unknown but some derivatives which have been synthesized are shown in **13**, along with a diphenyldibenzopentalene which has been known since 1912.[27] The high CSC of 12 is suggestive of its stability.



SC = 8
CSC = 0



SC = 24
CSC = 8

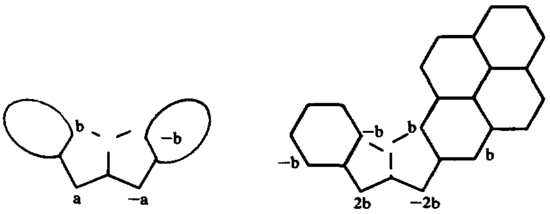


SC = 20
CSC = 12

13

The stability of the benzopentalene, CSC = 8, is consistent with its reactivity and its existence.[28] However, the existence of the hexaphenylpentalene, CSC = 0, as a stable compound[29] is a direct violation of the principles stated in this paper. However, once again, MO theory and resonance theory are in agreement, since one can use the zero-sum role to show that the pentalene does have a non-bonding orbital. Node-counting shows that this level is empty and the compound should be very easy to reduce. No ready explanation is discernable. It may be that the vacant non-bonding level being well separated from the bonding levels, the closed-shell character of the molecule leads to a relatively stable state.

Any pentalene derivative with two identical fused aromatic fragments will give a CSC of zero if the fusions are "cis" as in 12(d). This is easily demonstrated by looking at the coefficients of the nonbonding orbital in the first deleted orbital structure in 14. If the two fused substituents are not identical, a CSC = 0 will also result if the deleted atom structure has a plane of symmetry through both aromatic moities as shown in 14. Benzo and pyreno pentalenes are the only examples which come readily to mind.



SC = 2b
CSC = 0

SC = 2b
CSC = 0

14

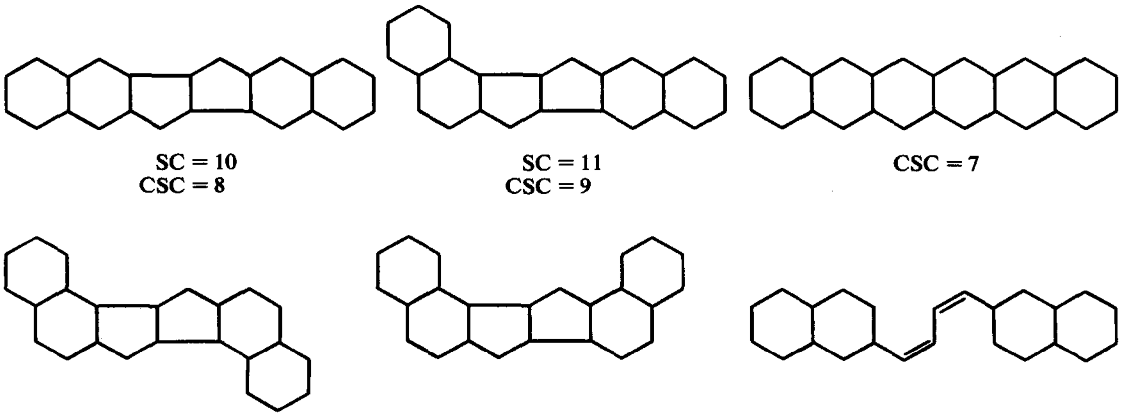
None of the "*trans*" difused substituted pentalenes can have a CSC of zero. Some dinaphthopentalenes with a "*trans*" configuration have remarkably high CSC's as shown in **15**. For comparison, hexacene has a CSC of 7, and 1,4-di-β-naphthyl-1,3-butadiene has a CSC of 9. It would be interesting to compare the properties of this series of compounds. The first two compounds in **15** should be approximately as reactive as the butadiene derivative, whereas the other two dinaphthopentalenes should be much more unstable and reactive.

Miscellaneous structures

Molecules with two non-alternant rings separated by alternant rings, or with more than two non-alternant rings are treated in analogous ways to those described above. Some examples are given in **16**, and the near bonding or non-bonding orbital of the deleted atom structure is also shown. One should choose the deleted orbital structures in such a way that the resulting non-alternant structure is as symmetrical as possible, and as structurally simple as possible. Odd non-alternant π structures with a plane of symmetry passing through a single orbital are highly apt to have a non-bonding orbital for which the coefficients can be written using the zero-sum rule.

The results depicted in **16** disagree to a certain extent with those obtained earlier.[8] The previous work gives π_E (product of the HMO eigenvalues) = 0, −4, −4, and −8 respectively for the 4 compounds in **16**. The value for the angular indacene, −4, indicates stability and is not in agreement with the CSC of zero. Note also that the CSC of 2 for the last structure in **16** is not the square root of the $|\pi_E|$. For ring systems ot this type the CSC as calculated here is not simply related to the π_E as it is for alternant systems.

A modified resonance theory including a 4n + 2 perimeter rule, and an HMO theory of reactivity based on the level of frontier orbitals, do agree with the CSC results. Both molecules with 12



SC = 10
CSC = 8

SC = 11
CSC = 9

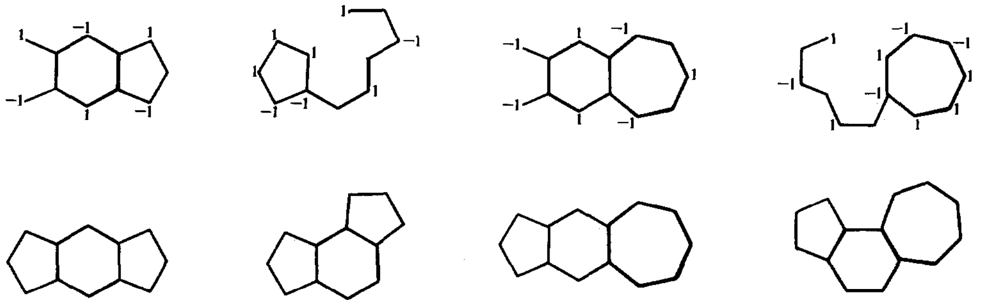
CSC = 7

SC = 13
CSC = 5

SC = 13
CSC = 5

CSC = 9

15



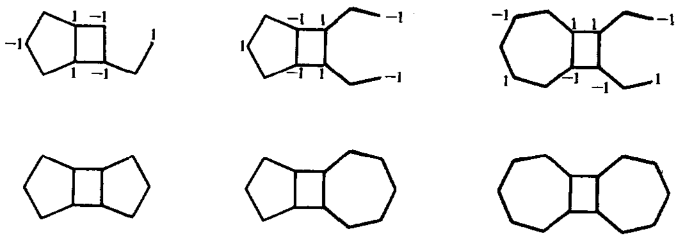
SC = 2
CSC = 0
$\pi_E = 0$

SC = 2
CSC = 0
$\pi_E = -4$

SC = 2
CSC = 2
$\pi_E = -4$

SC = 2
CSC = 2
$\pi_E = -8$

16



SC = 2
CSC = 0

SC = 2
CSC = 2

SC = 2
CSC = 0

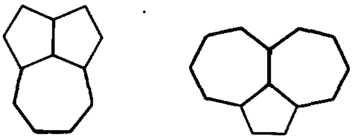
17

electrons on the perimeter have CSC's of zero, whereas the 14 electron molecules have CSC's of 2. Both 12 electron molecules are also open-shell structures according to HMO calculations, since the lowest vacant MO for linear indacene is a zero-energy level and that for angular indacene is actually a bonding level ($0{\cdot}239\beta$). Both 14 electron molecules are closed-shell structures by HMO calculations with sizable energy gaps between highest filled and lowest vacant orbitals.

However the structures in **17** do not obey a $4n+2$ perimeter rule. Two structures can be written tor each compound but both molecules with $4n+2$ orbitals and electrons are predicted to have a non-bonding orbital, and this is borne out by HMO calculations. The center structure with $4n$ electrons should and does have a closed shell of energy. None of the structures which one can draw for these three molecules incorporates a cyclobutadiene moiety, so the "instability" of the $4n+2$ molecules cannot be assigned to that factor.

The general rule seems to be that if a 4-membered ring is contained in the condensed structure, $4n$ orbital molecules should be stable, and $4n+2$ orbital molecules are not. Examples which come readily to mind are biphenylene, **7** (12 electrons, CSC = 3) or any cyclobutadiene with two tused $4n+2$ aromatic systems.

The compounds pictured in **18** will have closed shell structures, but a high degree of aromatic stability is not expected because of the low CSC to size of molecule ratio. In line with this prediction, derivatives of both structures are known compounds, and both types of compounds undergo addition reactions with dienophiles to yield azulene derivatives.[30–32]

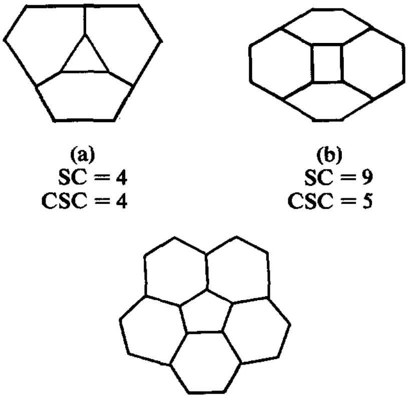


SC = 3
CSC = 3

SC = 3
CSC = 3

18

All three of the molecules shown in **19** might be capable of existence, but only **19**(c) has been synthesized.[33] The CSC's obtained must be confirmed by structure counting. Of course, those structures containing cyclobutadiene moieties in **19**(b) will not be counted by the CSC method.



(a)
SC = 4
CSC = 4

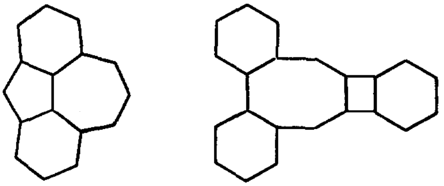
(b)
SC = 9
CSC = 5

(c)
SC = 11
CSC = 11

19

Strain in these systems could prevent the synthesis of the first two compounds, since even **19**(c) relieves some bond-angle strain by adopting a bowl shape.[33]

Two final structures ot current interest are depicted in **20**. An attempt has been made to synthesize isopyrene, **20**(a).[34] The low CSC to size ratio lends support to a suggestion of a low-lying triplet state for the compound.[35] And lastly, examples of the bicyclo[6.2.0]decapentaene system **20**(b) have been synthesized,[36,37] consistent with the high CSC. Open chain isoelectronic structures with three aromatic rings would have a CSC = 8. The unsubstituted bicyclic system with a CSC of 1 should have polyolefinic properties (see **7**).



(a)
SC = 2
CSC = 2

(b)
SC = 11
CSC = 7

20

Isomorphism of resonance and MO *theory*

Several examples have delineated the relationship between the corrected structure count for a molecule and its stability or reactivity. The CSC was obtained by examining the eigen-coefficients of a zero-energy or near-zero-energy molecular level of an odd deleted orbital structure. All π systems, alternant or non-alternant are amenable to this procedure.

The important point to remember is that the CSC could have been obtained by drawing and counting all resonance structures for the parent molecule, excluding certain unstable structures. Also, the coefficients used to find the CSC can provide a starting point for a perturbational MO treatment of structure-reactivity correlations.[2–6] Therefore, there must be a close congruity of the results of resonance theoretical explanations and perturbational MO calculations for *all* π-systems. Resonance theory is justified because of its close correspondence to MO theory.

A modified resonance theory is engendered by this work, with one point being the use of a perimeter 4n + 2 or 4n rule analogous to the empirical Hückel rule. When the parent molecule contains no (or an even number of ?) 4n moities, resonance structures with 4n electrons around the perimeter ot the molecule do not contribute to the structure count. Molecules with one 4 orbital ring will have stable resonance structures with 4n electrons on the perimeter. Other aspects of a modified resonance theory will emerge as examinations of structures using the CSC method are carried out.

One could also attempt to develop a quantitative mathematical theory of resonance,[38] but the perturbational MO theory is available, and using the principles outlined in this paper, perturbational MO theory can now be applied to non-alternant systems that could not be tested in the past. Work of this type is being carried out.[39]

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