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GRAPH THEORY AND MOLECULAR ORBITALS—VI[1]

A DISCUSSION OF NON-ALTERNANT HYDROCARBONS

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Abstract—Non-alternant hydrocarbons (NAH's) have been studied using a graph-theoretical approach. A number of *general* rules are given which enable one to predict several topology-dependent molecular properties (redox behaviour, charge distribution, dipole moment orientation and its approximate magnitude) only by inspection of the molecular graph. The obtained results are in agreement with experimental facts.

INTRODUCTION

In the preceding papers of this series[1-6] conjugated hydrocarbons have been studied using the graph-theoretical approach.[7] A number of general rules concerning the dependence of several physical and chemical properties (stabilities,[3,4] charge density distributions,[3] dipole moments,[3] energies[5]) on the molecular topology have been given covering, however, mainly the class of alternant hydrocarbons (AH).[2]† In the present work we give a set of rules for non-alternant hydrocarbons (NAH) describing the dependence of their redox behaviour and π-electron charge distribution on molecular topology. Rules are given in such a form that they can be straightforwardly used; i.e. a number of interesting predictions can be obtained only by the inspection of the graphs corresponding to NAH's *without going through any sort of theoretical calculations.* Some of these rules are, of course, known to organic chemists, but we quote them nevertheless here because our intention is to give a complete survey of the relation between the topology of NAH's and their topology-dependent properties. Effort is made to provide a symbolism that permits chemists to think graphically instead in terms of numbers.

Details of the graph theory and its application to the chemistry can be found elsewhere.[2,9]

The redox behaviour of NAH's

Some properties of NAH's are rather interesting. For example, charge density distribution is not uniform and NAH's exhibit large dipole moments. Similarly the MO energy levels are unsymmetrically disposed about the non-bonding orbital (NBMO) energy level.[10] The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) determine to a great extent the chemical properties, redox behaviour, etc of conjugated molecules.[11] Eight characteristic energy level patterns can arise, as shown in Fig 1 AH's have, of course, the energy level patterns of the type A, while NAH's have them of the type B and C. Molecules having the energy level distribution of the type B (e.g. methylene-cyclopropene **1** and heptalene **2**) can give away a pair of electrons under the influence of nucleophilic reagents producing a relatively stable dicationic form. This property is quite pronounced in molecules having the B_3 or B_2 energy level pattern (e.g. **2**). On the other hand, NAH's having the energy level distribution of the type C (e.g. fulvene **3** and pentalene **4**) can accept two electrons from an appropriate donor, the stability of the resulting dianion being rather considerable in the class of molecules having C_3 and C_2 (e.g. **4**) energy level pattern.


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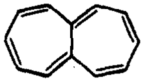
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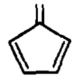
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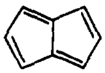
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Therefore, molecules of type B belong to the class of *electron-excessive* systems and are capable of oxidation, while those of type C to the *electron-deficient* systems which can undergo reduction under relatively mild conditions.

The problem of investigation of the energy level patterns was imposed in a series of papers by Bochvar *et al.*[12] but no general results have been obtained.[13]

The use of simple Hückel MO calculation in the present work is justified because the obtained results are *qualitative* ones. It can be shown[2] that the HMO problem is equivalent with the eigenvalue

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†This concept was introduced by Coulson and Rushbrooke.[8] AH's do not possess any odd-membered rings. On the other hand, NAH's obligatorily contain odd-membered ring systems. Graphs corresponding to AH's and NAH's are called bipartite and non-bipartite graphs, respectively.

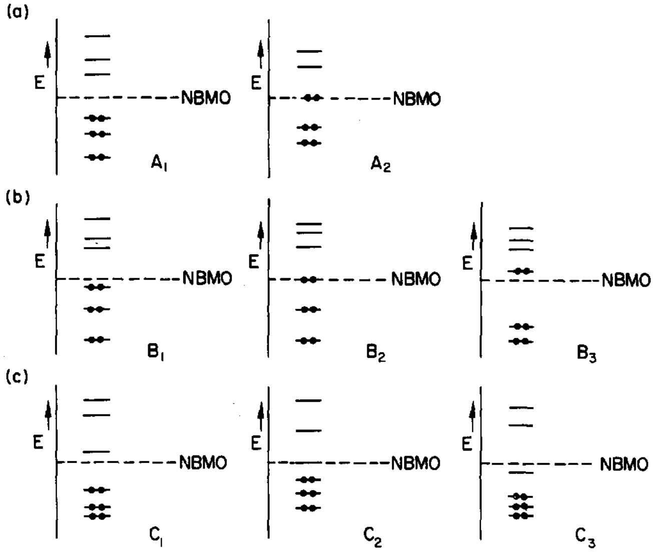


Fig 1. Characteristic energy level patterns of conjugated hydrocarbons: (a) Alternant hydrocarbons; (b) Electron-excessive non-alternant hydrocarbons; (c) Electron-deficient non-alternant hydrocarbons.

problem of the adjacency matrix of the molecular graph. Positive, negative and zero eigenvalues correspond to bonding, antibonding and non-bonding MO's, respectively. Let N_+, N_- and N_0 denote the number of these three type of eigenvalues (and MO's), and $N = N_+ + N_- + N_0$ the number of C atoms. It is obvious that the knowledge of the factors determining N_+, N_- and N_0 will give insight into the dependence of the redox behaviour of the conjugated molecules on molecular topology.

Fortunately, N_+ can be determined from the characteristic polynomial $P_G(x)$ of the molecular graph[2] due to a theorem of Descartes.[14] Let

$$P_G(x) = \sum_{j=0}^{N} a_j x^{N-j}$$

be the characteristic polynomial. Then, N_+ is equal to the number of changes of signs in the series $(a_0, a_1, \ldots, a_N)$. N_0 (and hence N_-) can be then obtained from $P_G(x)$ too.

Methods for calculating $P_G(x)$ are developed by Heilbronner[15] and recently by Hosoya.[16] The relations between the coefficients a_j and the structure of the molecular graph (the Sachs theorem[17]) are discussed in detail elsewhere.[2,3] The formulae of Sachs and Heilbronner for $P_G(x)$ combined with the mentioned theorem of Descartes can give the rules listed below, but the procedures for their derivation are rather lengthy and are omitted here. Some of the proofs are given in the parts IV and V of this series.[1,6]

Rule 1. The presence of $(4m-1)$-membered rings (m = positive integer) in molecular graphs indicates that the corresponding hydrocarbon can undergo oxidation. Similarly, the presence of $(4m+1)$ membered rings in molecular graphs indicates that the corresponding NAH's are capable of reduction. Thus, $(4m-1)$-ring systems contribute towards the C-type energy levels distribution, while $(4m+1)$-rings give the orbital energy level arrangement of the B-type.

Rule 2. The presence of $(4m-1)$-membered rings is a necessary (but, of course, not a sufficient) condition for the existence of dicationic form of a particular π-electron system. Analogously, if a dianionic form of a molecule is anticipated, the $(4m+1)$-membered ring must be present in the NAH.

If both $(4m+1)$- and $(4m-1)$-rings are contained in a particular NAH the neutral form of a molecule is the most probable one.

For illustrative examples we can use pentalene (**4**), azulene (**5**) and heptalene (**2**). Thus far **4** has not been synthetized despite many attempts.[18] It has the energy level distribution of C_2-type, i.e. eight π-electrons are accommodated in four bonding MO's. The LUMO level is a NBMO; thus **4** may be expected to accept a pair of electrons from a suitable donor. Incidentally, this molecule was predicted to be antiaromatic by various authors.[19] The pentalenyl dianion was obtained some ten years ago[20] by the action of n-butyl lithium in n-heptane on a dihydropentalene. The white crystals of dilithium pentalenide are stable in solution (in THF) at room temperature.

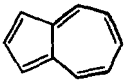
Compound **5** is stable as a neutral molecule. Discussion about the azulene chemistry and its properties as well as structure is given in several review articles[21] and books.[18a,22]

Compound **2** is a very unstable molecule. It has been prepared,[23] but readily polymerizes. Heptalene has the energy level distribution of B_2-type; i.e. ten π-electrons are accommodated in five bonding MO's, while the last two π-electrons are in the NBMO. Thus, heptalene should give up a pair of electrons to suitable electrophilic reagents and should form readily heptalenium salts. Incidentally, **2** is also predicted by various authors[19] to be antiaromatic.

Rule 3. The ring effect from rules 1 and 2 changes (decreases) quickly with the increasing of the ring size, and only 3-, 5-, and 7-membered ring systems behave really according to our rules. When ring size is greater than 7 steric effects and distortion from planarity are not any more negligible and the use of HMO approach is questionable.

Rule 4. The oxidation (or reduction) ability of a π-electron system decreases with the increase of the branching of a ring.

Therefore, it should be easier to reduce **3** (one branching) than [5]-radialene (**6**, five branchings). Similarly, it should be easier to oxidize heptafulvalene (**7**) than [7]-radialene (**8**).



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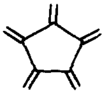

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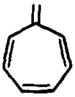

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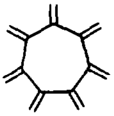

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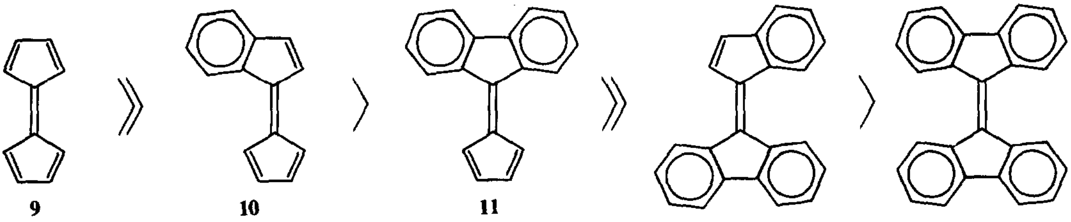
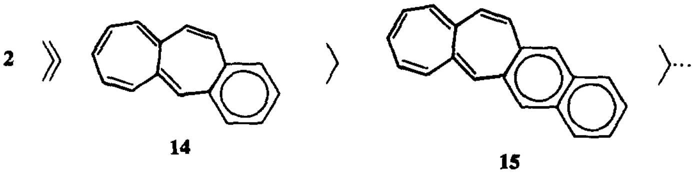
In the same way, the electron affinity in the fulvalene series should fall as follows:



9 **10** **11** **12** **13**

Rule 5. The alternant part of the molecule generally decreases the oxidation (or reduction) ability of the π-electron system. Thus, for example, the dicationic stability in the heptalene series should decrease as follows:



14 **15**

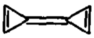
However, when the alternant part of the molecule increases, destabilisation due to small HOMO–LUMO separation can arise. A detailed discussion on this topic is recently given by Herndon.[24]

Rule 6. A necessary (but not sufficient) condition for a molecule to be of B_3 or C_3 type is to *possess at least two* (4m−1)- or (4m+1)-rings, respectively. These rings must not possess common atoms, i.e. they should not be fused. Thus, **3**, **4**, and **9** belong to the classes C_1, C_2, and C_3, respectively.

The following three rules show that some transformations on the molecular graph leave the energy level pattern invariant.[6,13]

Rule 7. Let the molecule G_2 result from the introduction of a 4-membered chain —CH=CH—CH=CH— into an arbitrary molecule G_1. Then, both G_1 and G_2 belong to the same energy level distribution class.

Example. Let us consider the molecules **16–19**.



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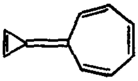

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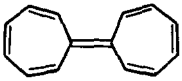

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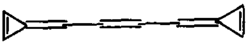

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According to rule 6 **16** belongs to the class B_3 (this can be easily checked by direct calculation of P_G). From rule 7 we can immediately deduce that also **17–19** belongs to the class B_3. However, the reduction strength of these compounds, according to rules 5 and 3, should be as follows:

$$\mathbf{16} \geqslant \mathbf{19} \gg \mathbf{17} \gg \mathbf{18}$$

Rule 8. Let the molecule G_2 result from the elimination of a $CH_2{=}C<$ group from an arbitrary molecule G_1. Then, both G_1 and G_2 belong to the same class. Exceptionally, if G_1 belongs to C_1 or B_1, G_2 may belong to the class A_1 too.

Example. Since hexatriene (**20**) obviously belongs to A_1, molecules **21** and **22** will belong to C_1 while **7** will belong to B_1 (see rule 1).

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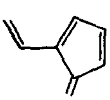

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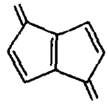

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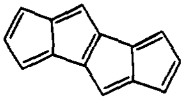
The series of compounds

4,  ,

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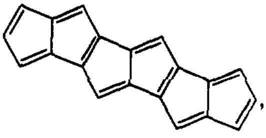 , . . ., etc.

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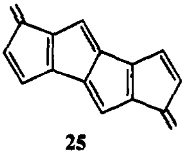
exhibit an increasing tendency of producing dianions.[12] This is also in agreement with rule 1. Similarly, the following predictions can be made using rule 8: the series of compounds:



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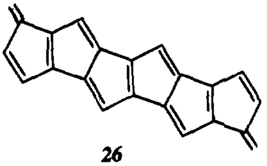 . . . etc.

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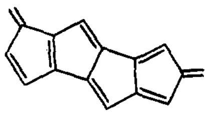
should give stable dianions, while the isomeric series:

 ,

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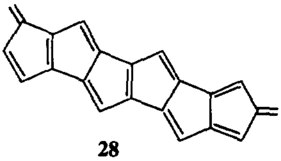
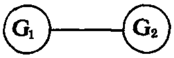
 . . . etc.

28

should not. Therefore, **25** should be more stable than **27**, **26** than **28**, etc. Note that when $CH_2{=}C<$ is replaced by $HN<$ and/or $S<$ a completely analogous situation is found.[25]

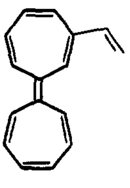
Generally speaking, an *odd chain* attached on the ring would quench the ring effect. For example, fulvene has not a pronounced electron affinity.

Rule 9. Let the molecule G be of the form



and let G_2 be an even alternant hydrocarbon radical. Then G and G_1 belong to the same class.

Using this rule a number of potential dianionic and dicationic compounds can be predicted starting from a known one. Hence, **29**, **30**, **31**, etc. should all have tendency to generate cations.



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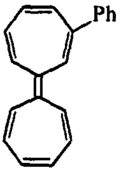

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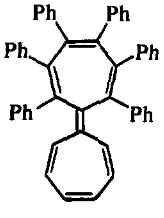

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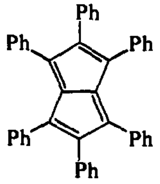

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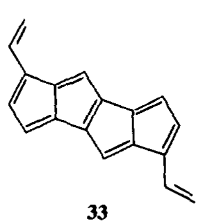
Rules 5 and 9 give the explanation for Herndon's result[24] for hexaphenylpentalene (**32**), which is a stable compound.[26] Although **32** must be of C_2 type, the relatively large alternant part of the molecule (six phenyl groups) will considerably decrease the ease of generating dianion, and, therefore, **32** is to be expected to be stable as noncharged moiety.

As a special case of rule 9 *even chains* cause only a small perturbation on the ring effect (rules 1 and 2). Thus, the electron affinities, for example, in the series **23**, **25**, **33** should be $23 \geqslant 33 \gg 25$.



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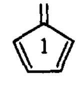
Topological rules for π-electron charge distribution and dipole moments in non-alternant hydrocarbons

Simple MO considerations for AH's lead to the following results: the π-electron charge on an arbitrary atom is equal to zero. A proper consequence of this result is the prediction of zero π-component of the dipole moments of AH's. This prediction can be, of course, checked by measurements of molecular dipole moments. Available experimental data[27] confirm this prediction.

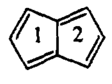
The situation with NAH's is quite different. Their dipole moments are of considerable magnitude and these results are obtained from direct measurements[27] and various calculations.[28] Although in most cases the calculated dipole moments of NAH's are of the wrong *magnitude*, the predicted *orientation* is always correct. The rules governing the charge distribution in NAH's are similar to those obtained for redox behaviour, thus showing that both effects have the same, topological origin.[1]

Rule 10. (4m − 1)-membered rings in the molecule are positively charged.* Similarly, (4m + 1)-rings are negatively charged.

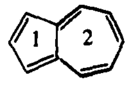
Example



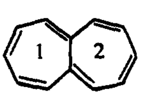
$Q_1 = -0{\cdot}38$
34



$Q_1 = Q_2 = -0{\cdot}20$
35



$Q_1 = -0{\cdot}45$
$Q_2 = +0{\cdot}39$
36



$Q_1 = Q_2 = +0{\cdot}13$
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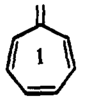

$Q_1 = +0{\cdot}31$
38

Rule 11. Smaller rings in both cases have stronger effects on the magnitude of the ring charges. As example compare **34** and **38** and also see **43**.

Rule 12. The ring charge decreases with the increase of the branching of the ring.

Example

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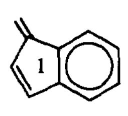
$Q_1 = -0{\cdot}38$



$Q_1 = -0{\cdot}21$
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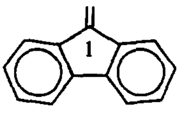

$Q_1 = -0{\cdot}11$
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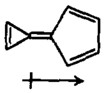
The direction of the dipole moment can be now easily predicted. For example



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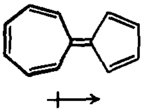

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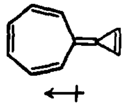

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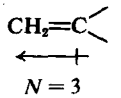
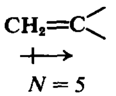
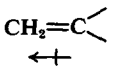
In the case of [N]-radialenes the total dipole moment is zero because of symmetry.[29] Though the dipole moments of the $CH_2 = C$ can be predicted in the manner as follows:



$N = 3$



$N = 5$



$N = 7$

Because of rule 12 the dipole moments of radialene $CH_2{=}C\langle$ fragments decrease very rapidly with increasing N.

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*The *ring charge* (Q) is the sum of the charges of all atoms belonging to a given ring. The ring charge is, of course, zero if there are symmetry reasons for it.

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