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Aromaticity of Some Polycyclic Hydrocarbons

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Abstract : Based on Perturbation Molecular Orbital (PMO) calculations of some even alternant hydrocarbons an 'aromatic index' is defined. This index could be used as a measure of the aromaticity of a particular position of the ring or of the ring itself. It is useful in comparing the aromaticity of these hydrocarbons and in understanding certain properties of these compounds. It was also observed that the K-region of the polycyclic hydrocarbons which were carcinogenic had an aromatic index less than 0.3. When calculating this index, another index 'Dewar number' which is a useful reactivity index too, can be calculated.

1. Introduction

The idea of aromaticity originally began in relation to the chemical behaviour of particular compounds such as benzene in a wide range of reactions and to some extent in connection with physical properties like diamagnetic susceptibility. That is, it was bound with distinct type of reactivity and not with properties of isolated molecules. The development of valence bond (VB) and molecular orbital (MO) theories permitted the calculation of thermochemical resonance energies, a quantity which could be measured. This is a property of the ground state of molecules with only a secondary influence on reactivity. There are many objections to using chemical reactivity as a criterion of aromaticity. There are many polycylic benzenoid compounds which are much less stable and much more reactive than benzene, but undergo addition reactions rather than substitution reactions. Thus the criteria of aromaticity shifted from a chemical to a physical point of view.

The possession of large resonance energy has generally been accepted as a diagnosis of the aromatic character of a compound. Dewar[2] has defined an aromatic compound as follows :— An aromatic compound is a cyclic compound with a large resonance energy where all the annular atoms take part in a single conjugated system. Hückel[6] using MO theory showed that a monocyclic coplanar system consisting of trigonally hybridized atoms which contain $(4n + 2)$ π electrons will have a closed shell configuration and therefore possesses electronic stability. The Hückel rule however is limited in applicability as it is concerned with monocyclic systems only. The Hückel rule depends on the existence of degenerate MOs, and therefore a molecule should have at least a threefold symmetry axis for the rule to be applicable. Further, the theoretical work of Longuet Higgins and Salem[8,9] have shown that as the ring becomes larger the $(4n + 2)$ rule does not apply since the ring system will consist of alternate single and double bonds.

Craig[1] has also proposed an empirical rule, which could be applied only to hydrocarbons in which at least two centres lie on a symmetry axis that converts one Kekulè structure to another. The structural formula is first labelled with equal numbers of spin symbols α and β, as far as possible alternately, different symbols being given to the ends of all the double bonds in the Kekulè type structure. The sum is then taken of the number (f) of symmetrically related π centres not on the symmetry axis and the number (g) of interconversions of α and β by rotation about the axis. If this sum, $f + g$, is even, the VB ground state is symmetric and the compound may be expected to be aromatic. If the sum is odd, it is expected to be non-aromatic.

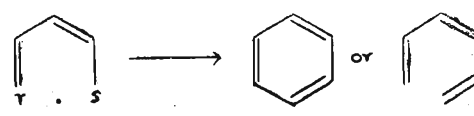
In this paper, the PMO[3] method is utilised and an index termed 'aromatic index' which is the difference in the energy between the compound and the corresponding polyene is defined. The calculations themselves are very simple for even alternant systems, without the necessity to solve secular equations as in the Hückel method.

2. PMO method

The first order change in π energy in the union of two odd alternant hydrocarbon (odd AH) radicals R and S to form RS where there is a non-bonding MO (NBMO) Φ_o of R and Ψ_o of S which are degenerate is given by

$$\delta E = \Sigma\, 2\, a_{or}\, b_{os}\, \beta_{rs}$$

where a_{or} and b_{os} are coefficients in the NBMOs Φ_o and Ψ_r of R and S respectively, and where the sum is over all the pairs of atoms r in R and s in S through which R is linked to S in RS. β_{rs} is the resonance integral between atoms r and s. This simple result can be used in the calculation of resonance energies of even alternant hydrocarbon (even AH) systems. Let us illustrate this for an even AH system. This can be formed by the union of an odd AH and methyl where both the odd AH and methyl have NBMOs. The change in π energy is then given by $\delta E = 2\Sigma\, a_{or}\, \beta_{rs}$. Thus benzene and hexatriene can both be formed by the union of 2, 4 pentadienyl with methyl where the methyl is being represented here as a dot.



Assuming β_{rs} to be constant and equal to β,

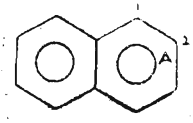
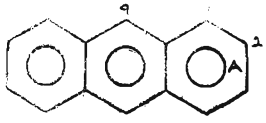
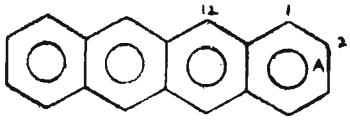
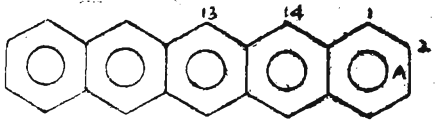
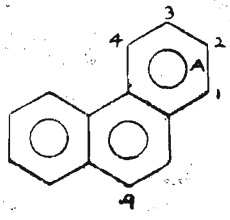
$$\Delta E \text{ (benzene)} = 2\beta\,(a_{or} + a_{os})$$

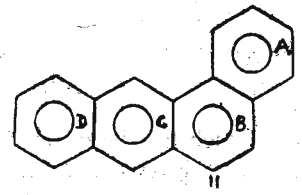
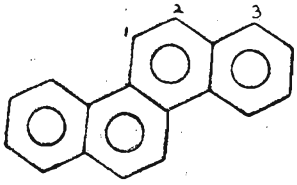
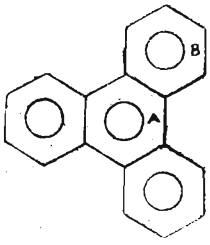
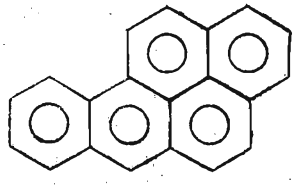
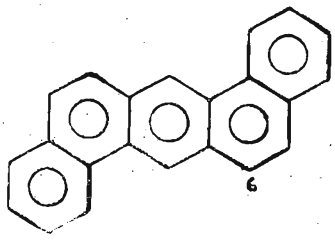
$$\Delta E \text{ (hexatriene)} = 2\beta a_{or} \text{ or } 2\beta a_{os}$$

depending whether the bond formed is with atom r or s. a_{or} and a_{os} are the coefficients of the non-bonding MO of 2—4 pentadienyl on atoms r and s respectively. The 'aromatic index' is then defined by $W = 2\,a_{or}$ or $2a_{os}$, whichever is the smaller value. The aromatic index is in effect the extra energy released or what one calls the resonance energy. If the aromatic index is <0, the compound is antiaromatic.[4]

The Dewar number $N = 2\,(a_{or} + a_{os})$ is another index which can be calculated simultaneously with the calculation of the aromatic index, which gives the reactivity of a particular centre to electrophillic substitution. The smaller the value of N, the easier would be the electrophillic substitution at the centre.

3. Results

Compound		*Aromatic Index*	
	(benzene)	1.15	
	(napthalene)	0.603	(1)
		0.707	(2)
		0.655	(A)†
	(anthracene)	0.392	(1)
		0.471	(2)
		0.432	(A)†
		0.632	(9)
	(naphthacene)	0.283	(1)
		0.338	(2)
		0.311	(A)†
		0.410	(12)
	(pentacene)	0.217	(1)
		0.256	(2)
		0.237	(A)†
		0.295	(14)
		0.400	(13)
	(phenanthrene)	0.743	(1)
		0.873	(2)
		0.816	(3)
		0.874	(4)
		0.824	(A)†
		0.359	(9)

Compound			*Aromatic Index*	
	(*)	(benzanthracene)	0.848	(A)†
			0.237	(B)†
			0.237	(11)‡
			0.598	(C)†
			0.514	(D)†
		(chrysene)	0.475	(1)
			0.417	(2)
			0.675	(3)
		(triphenylene)	0.242	(A)
			0.916	(B)†
	(*)	(benzpyrene)	0.244	(7)‡
	(*)	(dibenzanthrancene)	0.286	(6)‡

†A.I. of a ring is taken as the average of the A.I.'s of the non-fused position.

*These compound are carcinogenic.

‡K region position.

4. Discussion

When one observes the aromatic indices of benzene, napthalene, anthracene, naphthacene and pentacene, it is seen that its value decreases along the series. (The maximum values are 1.15, 0.707, 0.632, 0.410, 0.400). This is in accordance with the observed increase in unsaturation of these compounds, as one traverses along the series. The reactions of benzene are mainly electrophillic substitution while anthracene, naphthacene do take part in addition reactions. Another feature that emerges from these calculations is that as one goes towards the centre of the molecule, the aromatic index increases. This could be understood in terms of the usual resonance structures. Fries[5] formulated the rule that the most stable arrangement of a polynuclear compound is that which has the maximum number of rings in the benzenoid condition. For anthracene, therefore, the important resonance structures are as follows :—

This indicates that the middle ring has more benzenoid character than the end rings, which is precisely what the calculated aromatic index predicts. Likewise, the variation of the aromatic indices of the various rings could be explained.

Another feature which emerged from the calculations on linear polynuclear hydrocarbons is that cyclisations at the 2(β) position is preferred to the 1(α) position.

When one compares the aromatic indices of the constituent rings in phenanthrene and anthracene, one observes that the difference in the indices of rings A and **B** in phenanthrene is 0.465 while that in anthracene is 0.200. This indicates that delocalisation is reduced due to angular fusion and is more localised in the outer rings. This is borne out again from the aromatic indices of the constituent rings in naphthacene and benzanthracene and triphenylene. The differences in the aromatic indices of rings A and **B** in naphthacene is 0.10 while that in benzanthracene is 0.611 and 0.674 in triphenylene. In benzanthracene, the differences in the indices between rings **B**, C and D is only 0.361 and 0.084 respectively, showing that in benzanthracene there is greater delocalisation amongst rings **B**, C and D and not among ring A. Further experimental evidence of this is that naphthacene is orange yellow while triphenylene is colourless. Hence, when angular fusion takes place one observes a hypsochromic shift.

Certain polycyclic aromatic hydrocarbons show carcinogenic activity. This carcinogenic activity was correlated with the reactivity towards addition reactions such as epoxidation. Pullman[10] showed that these reactions take place in regions

termed as K regions, where the bond order is exceptionally high. In our calculations the polycyclic hydrocarbons which are carcinogenic (these are labelled*) have at these K regions aromatic indices less than 0.3. Thus the K regions can also be characterised by low aromatic indices of values less than 0.3.

The calculations of the aromatic indices for these even alternant polycylic hydrocarbons are very simple and do not require more than pencil and paper. It must however be stressed that these aromatic indices cannot predict the position of attack of a electrophile, for which the Dewar number would be more useful. The Dewar number can be calculated simultaneously with that of the aromatic index so that there is no additional labour involved. For non-alternant hydrocarbons to calculate these indices, separate Hückel calculations must be done on the hydrocarbon and the corresponding non-cyclic hydrocarbon.

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