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A New Approach to the Aromaticity of Conjugated Hydrocarbons

R. A. THURAISINGHAM AND S. H. M. NILAR
Department of Chemistry, University of Colombo, Colombo, Sri Lanka.

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Abstract : The aromaticity of conjugated hydrocarbons was studied using a variable 'β' self-consistent technique. Two indices, the Resonance Energy per pi electron (REPE) and 'δ', defined as the sum of the squares of the difference in the adjacent bond orders divided by the number of bond pairs are used to predict the aromatic nature of these compounds. In calculating the REPE, the reference structure is chosen as one having the same geometry as that calculated, but whose pi energy is evaluated on the basis of the additivities of the single and double bond energies which are functions of the bond distances. These two indices gave good agreement with the observed nature of the conjugated hydrocarbons.

1. Introduction

Despite its many shortcomings, the Hückel Molecular Orbital (HMO) method has been much used in the calculation of resonance stabilities of conjugated hydrocarbons. Most of the work in this field,[7,8,9] was facilitated by the epoch making theory proposed by Dewar *et al*[5] and later developed by Dewar *et al.*[3,4] The basic result of this work was that the energy of an acyclic polyene can be obtained as an additive function of individual bond energy terms.

Criticisms of the HMO method are many; one is the exclusion of bond distance variation in the parametrisation of the Resonance Integral 'β'.

Calculations involving variation in 'β' with bond distance have been reported[6,11] but the reference structure used in these calculations to obtain the Resonance Energy (RE) has not been clearly defined[7,8,9] and this to us appears to nullify the usefulness of the calculations reported. In our calculation, we have incorporated the variation in 'β' with bond distance and defined the resonance structure as one having the same geometry as the actual structure, but whose pi energy is calculated on the basis of the additivities of the single and double bond pi energies where these are now functions of bond length. This method of calculating the energy of the reference structure makes the RE a measure of extra stabilisation over and above that based on additivities and which results in the special properties of the molecules termed 'aromatic'. With the reference structure defined as mentioned, we have carried out a series of variable 'β' calculations on molecules usually classified as Benzenoid, Non-Benzenoid and Olefinic and obtained the Resonance Energy per pi electron (REPE). A new index for Aromaticity 'δ' was defined as the sum of squares of the difference in adjacent bond orders divided by the number of bond pairs in the Carbon skeleton. This 'δ' could be understood as a measure of the square of the distortion of the pi electron density per bond in the carbon skeleton. The values obtained will then reflect the deviation of the pi electron cloud from complete delocalisation as observed in Benzene.

2. Method

A HMO calculation is first performed and the bond orders p_{ij} obtained in the usual manner. The bond distances r_{ij} are then obtained from p_{ij} by:

$$r_{ij} = 1.52 - 0.186 * p_{ij}. \quad \ldots \quad 1^{\text{(ref 10)}}$$

and the corresponding Resonance Integrals 'Bij' from :

$$\beta_{ij} = \beta_o \exp(4.599 * (1.397 - r_{ij})) \quad \ldots \quad 2^{\text{(ref 10)}}$$

With the new 'β' obtained, the secular determinant within the HMO approximations is set up and diagonalised and the new set of bond orders p_{ij} obtained and hence the corresponding 'β'_{ij}'. This process is repeated till self-consistency in the total pi energy is obtained. This pi energy is taken as that of the actual molecule.

The reference structure is defined here as that structure having the same geometry as the actual structure obtained by our variable 'β' method. In other words, the bond alternation parameter 'k', ($k = \beta_{ij} / \beta_o$ where β_{ij} is the Resonance Integral between carbon atoms i and j and 'β_o' that of Benzene) for the reference structure is the same as that obtained for the Carbon skeleton from the self-consistent HMO calculation. The pi energy of this localised structure is obtained as the sum of the pi energy contribution of the single and double bonds where these are now functions of bond distance.

These are evaluated as follows:

The molecule is first dissected into 'butadiene' like systems and the energy of each butadiene structure calculated using the same 'β_{ij}' as obtained from our self-consistent calculation. As the pi energy for a localised double bond between centers i and j is $2\beta_{ij}$, the pi energy of the single bond can then be evaluated.

Let us illustrate this method of calulating the REPE for Benzene. Our variable 'β' self-consistent calculation gave 'k, to be 1.0000 for all the bonds in Benzene and the pi energy to be 8.0000 β_o. The energy of the reference structure is calculated as follows :

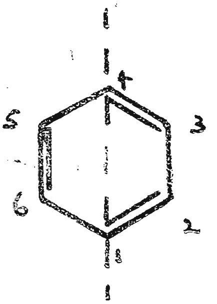

Figure 1. Reference structure for Benzene.

The energy of a 'butadiene' structure where all the bonds have the same 'β' as obtained from our self-consistent calculation is 4.47206 β_0. The energy of a double bond having a 'β' equal to 'β_0' is $2\beta_0$. Thus the energy of the single bond in butadiene, where the butadiene is one having the same 'β' for all the bonds is 0.47206 β_0. Thus the reference structure given in Fig. 1 has a pi energy of $3{*}2\beta_0 + 3{*}0.47206\ \beta_0$ which is $7.4162\beta_0$. Thus the Resonance Energy of Benzene is 0.5838 β_0 and the REPE is 0.0973 β_0. This method of calculating the double bonds and single bond energies which are functions of bond distance appears to us to be of paramount importance, more than the contributions due to the environment of the pi bond. [7,8,9] In addition, we have also defined a quantity 'δ', which is given below:

$$`\delta' = \frac{\text{sum of squares of differences in adjacent bond orders}}{\text{number of bond pairs in the carbon skeleton.}}$$

'δ' thus defined gives a measure of the mean square bond order fluctuation per bond in a molecule.

The molecules studied are given in Figure 2 (Overleaf)

3. Results

Table I gives the values for REPE and 'δ'.

TABLE 1.

Molecule	REPE (inβ_0)	δ
Benzene XVI	.0973	.0000
Biphenyl X	.0938	.0006
Biphenylene XIII	.0853	.0883
Naphthalene IX	.0618	.0176
Azulene XI	.0614	.0233
Calicene IV	.0413	.1333
Sesquifulvalene V	.0174	.1181
s-Indacene XV	.0138	.2508
Heptalene XIV	.0084	.2991
Heptafulvene II	.0023	.3392
Fulvalene VI	.0019	.2239
Fulvene I	.0015	.3371
Pentalene XII	.0006	.3196
Dimethylene Cyclobutene VIII	—.0070	.3847
Triafulvene III	—.0123	.3063
Cyclobutadiene VII	—.0597	1.0000

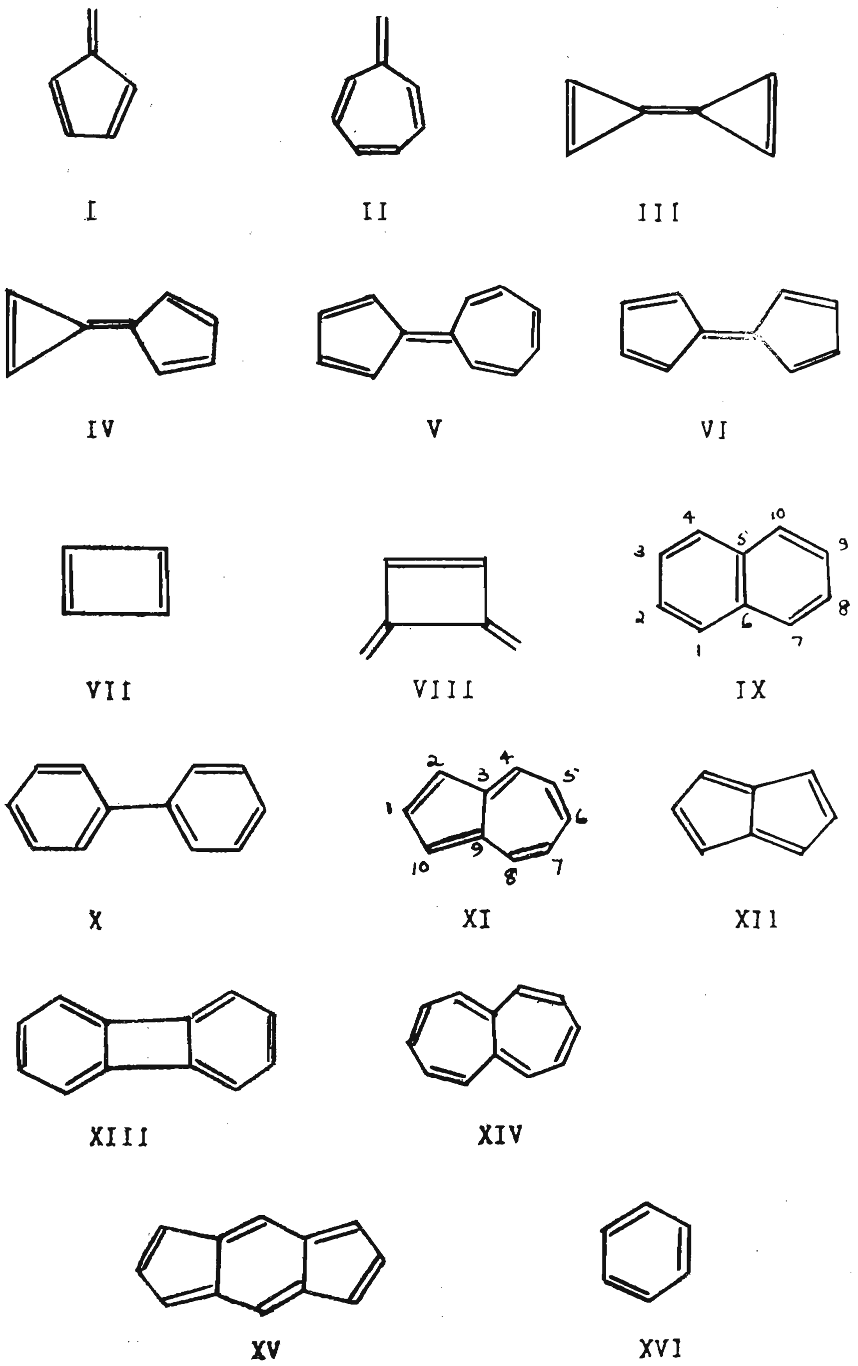

Figure 2. Conjugated Hydrocarbons studied for their Aromaticity

TABLE 2 Bond distances for some of the molecules studied.

Molecule	Observed (Å) (10)	Calculated (Å)
Naphthalene IX		
1—2	1.363	1.3794
2—3	1.425	1.4152
4—5	1.421	1.4280
5—6	1.418	1.4180
Azulene XI		
1—2	1.39	1.3983
2—3	1.42	1.4058
3—4	1.38	1.4088
4—5	1.39	1.3958
5—6	1.39	1.4014
3—9	1.48	1.4585

4. Discussion

The results of Table 2 give the bond lengths of two hydrocarbons calculated by our variable 'β' method, along with the experimental values. Although one can calculate the pi energy using the experimental geometry, this would limit our calculations to compounds whose geometries are known and therefore cannot be used as a predictive tool. The values obtained for the bond lengths are in agreement with experiment. Although other optimisation methods like the Complete Neglect of Differential Overlap (CNDO) may give better results, the cost associated with such techniques makes their application prohibitive within the framework of the computer systems available in Sri Lanka.

From Table 1 it is clear that molecules can be broadly classified into two groups one with high REPE and low 'δ' and the other with low REPE and high 'δ'. In the first group is found the Benzenoid hydrocarbons, while the other includes the compounds usually classified as olefinic. In other words, molecules having values above 0.06 for REPE and 'δ' below 0.02 are usually classified as aromatic, while a REPE below 0.02 and 'δ' greater than 0.12 indicates that such molecules are olefinic. For example, molecules such as Fulvalene, s-Indacene, Heptalene, etc, are predicted to be olefinic in nature in agreement with experiment.

Between these extremes, an interesting class of compounds emerge - those with a reasonably large value for REPE together with an appreciable 'δ'. i.e. we find a sharp change in the REPE and 'δ' in going from the aromatic to the non-aromatic region.

Hess and Schaad[7,8,9] obtained a value for the REPE for Calicene about two-thirds that of Benzene; Sesquifulvalene has a value almost equal to that of Azulene. Based on these deductions, we would expect these two molecules to be stable and isolatable. However, both molecules have evaded synthesis.

Our calulations give the REPE for Calicene to be less than half that for Benzene, while Sesquifulvalene has a REPE much lower tha than of Azulene, closer to that of the olefinic compounds. Further, both Calicene and Sesquifulvalene have high 'δ' values compared to the Benzenoid hydrocarbons which show the olefinic nature of these compounds. Magnetic Exaltation measurements (Λ) are by far the best experimental index for Aromaticity. These values are however dependant on the geometry of the system,[1] although isoconjugate systems having similar geometries are comparable. Exaltation ratios (Σ), (where $\Sigma = \Lambda$ compound/ Λ Benzene) quoted[1] clearly show that Σ Azulene $<$ Σ Naphthalene. The values for REPE and 'δ' obtained by our method give the same trend as these experimental observations. Even for other molecules where values are available[1] the trend indicated is similar to that obtained by our REPE and 'δ'.

In conclusion, it is seen that a combination of both indices, REPE calculated as illustrated here and 'δ' give a very good measure of the aromatic nature of the hydrocarbons studied with no exceptions or inconsistencies in the observed and predicted aromatic nature of these molecules.

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