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Factors Influencing the Angle of Total Π-Electron Energies of Alternant Hydrocarbons

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Within the framework of the Hückel molecular orbital theory, the topological factors affecting the angle of total π-electron energies of alternant hydrocarbons were investigated.

Introduction

The angle of total π-electron energy (Q) is conceptually as well as practically an important topological factor[1]. Its definition covers both alternant and nonalternant hydrocarbons. In the case of the former group of compounds, Q is a function of the total π-electron energy (E), the number of bonds (e) and half the number of atoms (n) involved in the π-electron of the molecule being considered.

Many years ago, a statistical average known as McClelland's factor[2-5] was introduced into the literature in order to estimate E values of alternant hydrocarbons by means of McClelland's upper bound (E_M) (eq. 1) for E.

$$E_M = 2(ne)^{1/2} >= E \tag{1}$$

As has recently been proven, McClelland's factor is obviously a statistical average of cos Q values for alternant hydrocarbons[1].

Although n and e are the prime contributers of E, cos Q value dictates the fine topology of the system such that it differs even for positional isomers. Previously, various bounds, estimates and the usage of cos Q were reported[1,6-10]. In the present study, a deeper look is taken at the topological contributors of the angle of total π-electron energies of alternant hydrocarbons within the framework of the Hückel molecular orbital theory[11].

Theory

Although the theory developed below is for even alternant hydrocarbons, it is applicable to odd alternant hydrocarbons as well because the latter class of compounds are characterized with the highest occupied molecular orbital energy level, $X_n = 0$[12].

Assume that within the constraints of the Hückel molecular orbital theory (HMO), the molecular graph of an even alternant hydrocarbon is described by G(2n,e). Let the occupied molecular orbital energies[12] be $X_1 >= X_2 >= \cdots >= X_n$ in units of beta in HMO theory.

Now, consider an n-dimensional Euclidean linear space[13] and let vectors A and B be defined as follows:

$$A(1,1,\ldots,1) \text{ and } B(X_1,X_2,\ldots X_n)$$

Then, the scalar product of these vectors can be expressed as

$$A\cdot B=\sum_{i=1}^{n} X_i=(ne)^{1/2}\cos Q \tag{2}$$

where Q is the angle between A and B. Note that $e=\sum_{i=1}^{n} X_i^2$ for alternant hydrocarbons[12]. E of alternant hydrocarbons and eq. 2 are interrelated through eq. 3.

$$E=2(ne)^{1/2}\cos Q \tag{3}$$

where Q becomes the angle of total π-electron energy, as defined previously[1].

Components of the total π-electron energy

The vector sum of A and B constructs a parallelogram in space (Figure 1.) the lengths of whose edges are $n^{1/2}$ and $e^{1/2}$. Note that the main diagonal of the parallelogram partitions Q into angles α and β.

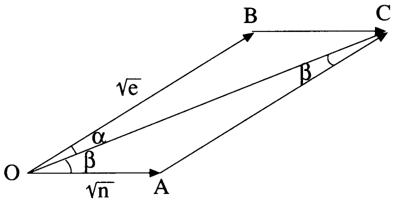

Figure 1. The vector sum of A and B.

Applying the tangent law[14] in triangle OAC, one obtains,

$$\frac{\tan((\alpha+\beta)/2)}{\tan((\alpha-\beta)/2)}=\frac{e^{1/2}+n^{1/2}}{e^{1/2}-n^{1/2}} \tag{4}$$

By inserting $(\alpha+\beta)/2=Q/2$, eq. 4 can be modified to yield

$$\tan(Q/2)=\frac{e^{1/2}+n^{1/2}}{e^{1/2}-n^{1/2}}\tan((\alpha-\beta)/2) \tag{5}$$

with elementary trigonometry, the followings can be obtained[14]

$$\cos Q = \cos^2(Q/2)-\sin^2(Q/2) \tag{6}$$
$$\cos(Q/2) = 1/(1+\tan^2(Q/2))^{1/2} \tag{7}$$
$$\sin(Q/2) = \tan(Q/2)/(1+\tan^2(Q/2))^{1/2} \tag{8}$$

Inserting eqs. (7) and (8) into eq. (6), one obtains

$$\cos Q=(1-\tan^2(Q/2))/(1+\tan^2(Q/2)) \tag{9}$$

Now, the substitution of eq. 5 into eq.9 yields

$$\cos Q = (1 - TK)/(1 + TK) \tag{10}$$

where

$$T = ((e^{1/2} + n^{1/2})/(e^{1/2} - n^{1/2}))^2 \tag{11}$$

and

$$K = \tan^2((\alpha - \beta)/2) \tag{12}$$

Note that the application of the sinus theorem[14] in triangle OAC (Figure 1) yields

$$\sin\alpha/\sin\beta = (e/n)^{1/2} \tag{13}$$

Since $e >= n$ for alternant hydrocarbons, then obviously $\alpha >= \beta$. Also it can be quite easily obtained that $\sin\beta =< 0.866(n/e)^{1/2}$ because of $Q =< 60°$ for alternant hydrocarbons[7]. On the other hand, by substituting $\cos Q >= \cos 60 = 1/2$ into eq.10 and solving for K one obtains

$$K =< 1/3T \tag{14}$$

Since eq. 13 can be converted to

$$\frac{\sin\alpha + \sin\beta}{\sin\alpha - \sin\beta} = \frac{e^{1/2} + n^{1/2}}{e^{1/2} - n^{1/2}} = T^{1/2} \tag{15}$$

By using the trigonometric conversions for the sum and the difference of sinuses of two angles, eq. 15 becomes

$$\tan((\alpha + \beta)/2)\cot((\alpha - \beta)/2) = T^{1/2} \tag{16}$$

inserting $\alpha + \beta = Q$ and $\tan((\alpha - \beta)/2) = K^{1/2}$ into eq.16 and then solving for Q, one gets

$$Q = 2\arctan(TK)^{1/2} \tag{17}$$

which yields the following partial derivatives:

$$\frac{\partial Q}{\partial K} = \frac{(T/K)^{1/2}}{1 + TK}, \quad \frac{\partial Q}{\partial T} = \frac{(K/T)^{1/2}}{1 + TK}, \quad \frac{\partial K}{\partial T} = \frac{K}{T} \tag{18}$$

Results and Discussion

The angle of total π-electron energy reflecting the contribution of the fine topology of an alternant hydrocarbon into its total π-electron energy is expressed by eq. 10, which is a function of e and n in addition to the term $\tan((\alpha - \beta)/2)$. The angle α and β should themselves be certain functions of e and n having some constraints such as $\alpha + \beta = Q, \sin\alpha/\sin\beta = (e/n)^{1/2}$, (see Fig. 1 and eq. 13) and the like. As expressed by eq. 18, $\partial K/\partial T$ is inversely proportional to T. Since $Q =< 60°\cdot$ for alternant hydrocarbons[7], which yields $\alpha - \beta)/2 =< Q/2 =< 30°\cdot$, then by using eq. 12 one obtains $K <= 0.3333$. Hence, K values for alternant hydrocarbons should be rather insensitive to topological changes. Table 1. tabulates the values of T and an upper limit of K as the n/e ratio varies.

Table 1. The variations of T and K as n/e ratio changes.

n/e	T	K=<
1	∞	0
1/2	33.07054	9.81242 10^{-3}
1/3	13.92819	2.39322 10^{-2}
1/4	9.0000	3.70370 10^{-2}

Since n/e ratios given in Table 1 span much over the possible n/e ratio for Hückel graphs then, as seen in the table, variation of K is rather limited for alternant hydrocarbons as predicted by the theory. Note that K is a positive number (see eq. 12); hence, it must be zero for n/e = 1, in which case TK becomes undetermined ($0 * \infty$). However, for ethylene possessing n/e = 1, cos Q = 1. A search for the K values of benzenoid compounds has been carried out using a pool of 106 members[15], which yields mean value of 2.21456 10^{-3}, having 2.22601 10^{-4} for the standard deviation (SDEV). In a similar way, the K values of twenty-five arbitrarily chosen alternant hydrocarbons possess a mean value of 1.80661 10^{-3} having SDEV of 9.78281 10^{-4}. Note that if Q is small, then obviously its components must be much smaller. In that case, instead of $\sin\alpha$ and $\sin\beta$, the angles themselves might be used, yielding $\alpha/\beta = (e/n)^{1/2}$.

Conclusion

In the present study, the investigation of the partitioning of the angle of total π-electron energy has unveiled some hidden topological dependence of cos Q on the numbers of edges and vertices of the corresponding chemical graphs. The investigation of the factors influencing the angles α an β will obviously lead to new perspectives on the problem.

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