A NOVEL FORMULA FOR THE TOTAL Π-ELECTRON ENERGY OF ALTERNANT HYDROCARBONS

LEMİ TÜRKER

Middle East Technical University
Department of Chemistry
Ankara, Turkey

Abstract. A novel total π-electron energy formula for alternant hydrocarbons is derived which is equivalent to the smaller root of a parabolic function of E in parametric form. The topological parameter, R, is found to be confined into a narrow range. An upper bound for E which is linear in form is obtained.

1.Introduction

The total π-electron energy (E) of conjugated hydrocarbons varies depending on topological variations occuring among them. So far, very many topological formulas have been suggested (1-15) for E (or bounds for E) of conjugated systems, especially for alternant hydrocarbons. The topic has been frequently appeared in the literature (9,16).

Various theoretical considerations of the total π-electron energy , using quite dissimilar approaches

resulted in topological formulas of the McClelland-type (1) and it has been unequivocally established that the gross part of E is determined by only two topological invariants, namely the number of carbon atoms (N) and the number of carbon-carbon bonds (e) (9,16). The role of other graph invariants is much more obscure and their effects are collectively included in the angle of total π-electron energy (13,17). Many years ago, Hall reported (10,11) a formula for E of benzenoid hydrocarbons which exhibits a linear dependence on N, e and the number of Kekule structures. Obviously, it is different from the McClelland-type formulas which are nonlinear in N and e.

In the present study, within the Hückel molecular orbital (HMO) approach a parametric formula for the total π-electron energy of alternant hydrocarbons has been derived which is linear in N and e.

2.Theory

Let G(2n,e) be the graph of a conjugated hydrocarbon represented in the usual manner (18). Let $X_1 \geqslant X_2 \geqslant ... \geqslant X_n$ be the eigenvalues of the adjacency matrix (standing for the occupied molecular orbitals (19)). The total π-electron energy (in β units) conforms to the relation

$$E = 2\sum_{i=1}^{n} X_i \qquad (1)$$

where n is half the number of carbon atoms .

Now , let vectors A and B in an n-dimensional Euclidean

linear space be defined as

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

Then, the scalar product (20) of these vectors is equal to $E/2$, hence it yields (13)

$$E = 2(en)^{1/2} \cos O_\pi \tag{2}$$

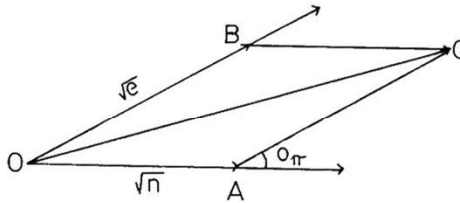where O_π is the angle between vectors A and B (Fig.1).

Fig.1 . The relation between e, n and O_π .

By using the cosine theorem one gets

$$\overline{OC}^2 = n + e + 2(ne)^{1/2} \cos O_\pi \tag{3}$$

$$\overline{AB}^2 = n + e - 2(ne)^{1/2} \cos O_\pi \tag{4}$$

then by adding eqs.3 and 4 one obtains

$$\overline{OC}^2 + \overline{AB}^2 = 2(e+n) \tag{5}$$

whereas substracting eq.4 from eq.3 and considering eq.2, eq.6 is produced.

$$\overline{OC}^2 - \overline{AB}^2 = 4(en)^{1/2} \cos O_\pi = 2E \qquad (6)$$

Now , construct a right angle triangle which possesses $\overline{OC}$ as the base, $\hat{C} = \beta$ (Fig.2) and $\overline{BC} = (2(e+n))^{1/2}$. Then, evidently due to the theorem of Pythagoras the height, $\overline{OB}$, is equal to $\overline{AB}$ because of eqs.3 and 5. Finally, construct another right angle triangle such that $\overline{OC}$, this time is the hypotenus , $\hat{C} = \alpha$ and $\overline{CB}' = (2E)^{1/2}$ (Fig.2) . Then, obviously, eq.6 necessitates $\overline{OB}' = \overline{AB}$. Note that $\overline{AB}^2 = n + e - E$, $\overline{OC}^2 = n + e + E$ (see eqs.2,3 and 4) and from Fig.2, evidently $\sin \alpha = \tan \beta$.
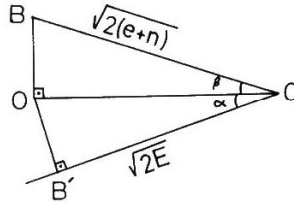

Fig.2   A different geometrical relation between e,n and E.

Since, in triangle OCB , $\tan \beta = \overline{OB}/\overline{OC}$, inserting the equivalents of $\overline{OB}$ and $\overline{OC}$ (eqs. 3 and 4) into the above expression for $\tan \beta$ and then squaring both sides of the equation one gets

$$\tan^2\beta = (e + n - E)/(e + n + E) \qquad (7)$$

solving for E results in

$$E = (e + n)(1 - \tan^2\beta)/(1 + \tan^2\beta) \qquad (8)$$

or

$$E = (e + n)(1 - \tan^2\beta)/ \sec^2\beta \qquad (9)$$

Note that $\tan^2\beta \leqslant 1$ due to eq.7 .

On the other hand, squaring both sides of eq.7 and then adding the denumerator to the numerator and substracting numerator from the denumerator , one gets

$$\frac{(\tan^4\beta + 1)}{(1 - \tan^4\beta)} = \frac{(e + n)^2 + E^2}{2E(e + n)} \equiv R \qquad (10)$$

Note that $R \geqslant 1$. By rearranging eq.10, one obtains an equation for a parabola in the parametric form.

$$E^2 - 2(e + n)RE + (e + n)^2 = 0 \qquad (11)$$

and

$$\tan\beta = ((R - 1)/(R + 1))^{1/4} \qquad (12)$$

Eq.11 yields

$$E = (e + n)(R - (R^2 - 1)^{1/2}) \qquad (13)$$

Note that the other solution of eq.11 has to be discarded for E (see the appendix).

A Lower Bound For R.

Combining eqs.2 and 13, solving for $\cos O_\pi$ and using the property that $\cos O_\pi \leqslant 1$ one obtains

$$\cos O_\pi = ((e+n)/2(en)^{1/2})(1-(1-1/R^2)^{1/2})R \leqslant 1 \quad (14)$$

Rearanging ineq.14 yields

$$R \leqslant (2(ne)^{1/2}/(e+n))(1-(1-1/R^2)^{1/2})^{-1} \qquad (15)$$

Note that $R \geqslant 1$ (see eq.10). Hence, the right hand side of ineq.15 becomes

$$(2(ne)^{1/2}/(e+n))(1-(1-1/R^2)^{1/2})^{-1} \geqslant 1 \qquad (16)$$

Solving for R yields

$$R \geqslant (1-(1 - 2(en)^{1/2}/(e+n))^2)^{-1/2} \qquad (17)$$

An Upper Bound For R.

Since, for alternant hydrocarbons $\cos O_\pi \geqslant 0.5$ (13,14), ineq.14 can be modified to yield

$$\cos O_\pi = ((e+n)/2(en)^{1/2})(1-(1-1/R^2)^{1/2})R \geqslant 0.5 \qquad (18)$$

Solving ineq.18 for R one obtains

$$R \leqslant ((e+n)^2 + en)/2(e+n)(en)^{1/2} \qquad (19)$$

Estimation of E.

Since, $R \geqslant 1$, let $R = 1+a$ where a represents a small perturbation. Then, express eq.13 in terms of a.

$$E = (e+n)(1 + a - (a^2 + 2a)^{1/2}) \qquad (20)$$

Taking the first derivative it can be shown that eq.20 is monotonically decreasing function of a and its maximum value is for a=0. Thus, an upper bound for E is obtained .

$$E \leqslant (e+n) \qquad (21)$$

Hence, one can estimate E as

$$E \approx (e+n)P \qquad\qquad (22)$$

where $0 < P \leqslant 1$.

3. Results and Discussion

Eq.11 represents a parabola where R is a parameter characteristic for the molecule being considered. The solution of eq.11 is highly dependent on R . For instance , ethylene possesses R=1 and double roots are produced. For other alternant hydrocarbons two distinct roots exist. Of these, the smaller root yields E value. The other root is a complementary one (E_c) (see the appendix).

Table 1. tabulates the upper and the lower bounds for R as e/n ratio changes between 1 through 3. As it is seen, the variation of R is very limitted.

Table 1.

The upper and the lower bounds for R as e/n varies.

e/n	Upper bound (Eq.19)	Lower bound (Eq.17)
1	1.2500	1.0000
2	1.2963	1.0016
3	1.3712	1.0090

A search for R values of various alternant hydrocarbons revealed that R is closer to its lower bound expressed by ineq.17. For instance, a set of benzenoid hydrocarbons (21) possesses the mean value of R as 1.01781 (SDEV: 1.80074

10^{-3}). For annulenes of up to 2n=30, R varies between 1.0069 (benzene) and 1.0833 (cyclobutadiene). In the case of homologous annulenes R alternatingly increases or decreases depending on whether 4m or 4m+2 type annulene being considered.

On the other hand, the value of P is close to 1. A set of benzeneoid hydrocarbons (21) possesses 0.828535 (SDEV: 0.008752) as the mean of P. In general, P is comparable to McClelland's factor, 0.92 which is suitable for the nonlinear E formula (eq.2) and stands for cos O_π .

4.Conclusion

In the present study, a parabolic function of E is derived which gives E of the alternant hydrocarbons as a function of e,n and R. The later one is a parameter and its variation produces E of the isomers if e and n are kept constant. Actually, R changes in a rather narrow range, hence it stands for very fine topological contributions into E . On the other hand, the physical importance of E_c , the other root of eq.11 , ought to be investigated.

Appendix

The other root of eq.13 is not a proper value for E because E_c is equal to

$$E_c= (e+n)(R+(R^2-1)^{1/2}) \qquad (23)$$

Since, R>=1 (see eq.10) then eq.23 requires

$$E_c>= e+n \qquad (24)$$

On the other hand, McClelland's bound ($E =< 2(ne)^{1/2}$) holds for E . Hence, $E = E_c$ requires that

$$e+n =< E_c =< 2(ne)^{1/2} \qquad (25)$$

Squaring the right and leftmost sides of ineq.25 and then rearranging one obtains

$$(e-n)^2 =< 0 \qquad (26)$$

Obviously, ineq.26 is invalid for real numbers. Hence, the possibility of $E = E_c$ has to be discarded.

REFERENCES

1. B.J.McClelland, J.Chem.Phys., 54,640 (1971).

2. I.Gutman, M.Milun and N.Trinajstic', J.Chem.Phys., 59,2772 (1973).

3. A.Groavac, I.Gutman and N.Trinajstic, Chem.Phys.Lett., 35,555 (1975).

4. I.Gutman, Chem.Phys.Lett., 50,488 (1977).

5. L.Türker, Match, 16, 83 (1984).

6. J.Cioslowski , Match, 20,95 (1980).

7. J.Cioslowski, Z.Naturtforsch, 40a, 1167 (1985).

8. I.Gutman, L.Türker and J.R.Dias , Match, 19,147 (1986).

9. I.Gutman, Topics Curr. Chem., 162, 29 (1992).

10. G.G.Hall, Int.J.Math.Educ.Sci.Technol., 4,233 (1973).

11. G.G.Hall, Bull.Inst.Math.Appl., 17,70 (1981).

12. I.Gutman and G.G.Hall, Int.J. Quantum Chem.,41,667 (1992).

13. L.Türker, Match, 28,261 (1992).

14. L.Türker, Polycyclic Aromatic Compounds, 4,107 (1994).

15. I.Gutman, Match, 29,61 (1993).

16. I.Gutman, Lj.Nedeljkovic', A.V.Teodorovic', Bull.Soc.Chim. Beograd, 48,495 (1983).

17. L.Türker, Match, 30,243 (1994).

18. I.Gutman and O.E.Polansky, "Mathematical Concepts in Organic Chemistry" , Springer-Verlag, Berlin, 1986.

19. E.Heilbronner and H.Bock ,"The HMO-Model and Its Application", Verlag,Weinheim, 1976.

20. P.Gusyatnikov and S.Reznichenko, "Vector Algebra", Mir Publishers, Moscow,1988.

21. R.Zahradnik and J.Pancir, "HMO Energy Characteristics", Plenum Press, New York, 1970.