

1-1-1996

Validity of a Linear Estimator for the Total π -Electron Energy of Alternant Hydrocarbons

Lemi TÜRKER

Follow this and additional works at: <https://journals.tubitak.gov.tr/chem>

 Part of the [Chemistry Commons](#)

Recommended Citation

TÜRKER, Lemi (1996) "Validity of a Linear Estimator for the Total π -Electron Energy of Alternant Hydrocarbons," *Turkish Journal of Chemistry*. Vol. 20: No. 2, Article 1. Available at: <https://journals.tubitak.gov.tr/chem/vol20/iss2/1>

This Article is brought to you for free and open access by TÜBİTAK Academic Journals. It has been accepted for inclusion in Turkish Journal of Chemistry by an authorized editor of TÜBİTAK Academic Journals. For more information, please contact academic.publications@tubitak.gov.tr.

Validity of a Linear Estimator for the Total π -Electron Energy of Alternant Hydrocarbons

Lemi TÜRKER

Middle East Technical University,

Department of Chemistry,

Ankara-TURKEY

Received 18.7.1995

The validity of a linear topological estimator formula which possesses a slope k such that $0 < k < 1$, where k is dependent on the topology of the system, is proved for the total π -electron energy of alternant hydrocarbons.

Introduction

So far, numerous topological formulas have been derived¹⁻¹⁵ for the total π -electron energy, E , (or bounds of E) of alternant hydrocarbons. Although, starting from different standing points and using quite dissimilar approaches, most of these derivations resulted in McClelland-type¹ topological formulas (eq. $E = g(ne)^{1/2}$, g is a constant) in which E is determined by only two topological invariants, namely, the number of carbon atoms, N , and the number of carbon-carbon bonds^{9,16}, e . So far, the role of other graph invariants preserve their mystery and their effects collectively made use of in the angle of total π -electron energy^{13,17}. On the other hand, Hall's formula^{10,11} for E of benzenoid hydrocarbons has linear dependence on N , e and the number of Kekule structures. In that sense, it differs from the McClelland-type formulas which are known as nonlinear E formulas. Below, within the Hückel molecular orbital (HMO) framework, a novel linear estimator for E of alternant hydrocarbons is derived and tested for its validity.

Theory

Let, $G(2n, e)$ be a molecular graph¹⁸ of an even alternant hydrocarbon, A . Suppose, the occupied molecular orbital energies of A are $X_1 = < X_2 = < \dots = < X_n$ and its total π -electron energy, E , is defined¹⁸ as

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

where n is half the number of carbon atoms, N .

Suppose, E is linear in n and e such as

$$E = k(e + n), \quad (2)$$

where $k > 0$ is a topological parameter. Squaring both sides of Eq. 2 one obtains

$$k^2(e + n)^2 = E^2 \quad (3)$$

Now, using a property of ratios, namely adding the right hand side of Eq. 3 into the left hand side one gets

$$(k^2(e + n)^2 + E^2)/2 = E^2 \quad (4)$$

Dividing both sides of Eq. 4 by E^2 yields

$$(k^2(e + n)^2 + E^2)/2E^2 = 1 \quad (5)$$

Now, substitute Eq. 2 in the denominator of Eq. 5 as follows:

$$(k^2(e + n)^2 + E^2)/2E(e + n)k = 1. \quad (6)$$

An Upper Bound For k

To estimate the value of k , let

$$((e + n)^2 + E^2)/2E(e + n) = R \quad (7)$$

Note that Eq. 7 is the limit of Eq. 6 for $k = 1$. It is quite easily proved that $R \geq 1$. By rearranging Eq. 7, one obtains an equation for a parabola in the parametric form:

$$E^2 - 2(e + n)RE + (e + n)^2 = 0. \quad (8)$$

One can easily prove that only the smallest root of Eq. 8 stands for E value of alternant hydrocarbons, that is

$$E = (e + n)(R - (R^2 - 1)^{1/2}) \quad (9)$$

thus

$$k = R - (R^2 - 1)^{1/2} \quad (10)$$

Since $R \geq 1$, let $R = 1 + p$ where p stands for a small perturbation, $p \geq 0$. Then, express Eq. 9 in terms of p :

$$E = (e + n)(1 + p - (p^2 + 2p)^{1/2}). \quad (11)$$

using the binomial expansion¹⁹ of the term in the square root, Eq. 11 becomes

$$E = (e + n)(1/2(1 + p)^2 + 1/8(1 + p)^4 + 1/16(1 + p)^6 + \dots). \quad (12)$$

Since p is positive then each summand in the parenthesis is smaller than the corresponding term obtained by inserting $p = 0$. So the whole sum in Eq. 12 is less than

$$S = \lim_{t \rightarrow \infty} \sum_{i=1}^t (1/t!) \prod_{i=1}^{t-i} (i - 1/2), \quad (13)$$

which can be derived quite easily by using the binomial expansion¹⁹. Then, obviously, Eq. 12 becomes

$$E = \langle (e + n)S \quad (14)$$

On the other hand, substitution of $p = 0$ into Eq. 11 reveals that $S = 1$. Hence, by using Eq. 14, one can indeed satisfactorily estimate E as

$$E = (e + n)k, \quad (15)$$

where it is expected to be $0 < k \leq 1$.

Topological Bounds For k

Since, for alternant hydrocarbons Eq. 16 holds¹³ as

$$e = 2(en)^{1/2} \cos Q, \quad (16)$$

where Q is the angle of total n -electron energy, inserting Eq. 16 into Eq.15 one obtains

$$2(ne)^{1/2} \cos Q = (e + n)k, \quad (17)$$

Rearranging Eq.17 it becomes

$$\cos Q/k = \left((e)^{1/2} - (n)^{1/2} \right)^2 / 2(ne)^{1/2} + 1. \quad (18)$$

Since $\cos Q \leq 1$ Eq. 18 clearly shows that k cannot be equal to 1. On the other hand, it is known¹⁷ that $\cos Q \geq 1/2$. inserting this value into Eq. 17 and solving for k yields

$$k \geq (ne)^{1/2} / (e + n). \quad (19)$$

A better but more complicated lower bound for k is obtained by inserting Eq.20 (see Ref. 13) into Eq. 17 and solving for k

$$\cos Q \geq ((e + 2(a_4)^{1/2}) / ne)^{1/2} \quad (20)$$

where a_4 is expressed⁴ as

$$a_4 = \binom{e}{2} - V_2 - 3V_3 - 2R_4, \quad (21)$$

where V_2, V_3 and R_4 stand for the number of vertices of degree 2,3 and the number of 4-membered rings, respectively. Thus,

$$k \geq 2 \left(e + 2(a_4)^{1/2} \right)^{1/2} / (e + n) \quad (22)$$

On the other hand, it is known¹³ that

$$\cos Q = \left[\left[e + 2(ma_4)^{1/2} \right] / ne \right]^{1/2}, \quad (23)$$

where m is given ⁴ as $m = \binom{n}{2}$. Inserting Eq. 23 into Eq.17 and solving for k yields

$$k = 2(e + 2(ma_4)^{1/2})^{1/2} / (e + n) \quad (24)$$

Results and Discussion

Eq. 15 is a linear topological formula for E of alternant hydrocarbons based on invariants of the molecular graph being considered. The slope, k which lies between 0 and 1 is also dependent on topology. The upper and lower bounds, in eqs. 19, 22 and 24 enable one to estimate the range of k of a system. In general, the value of k is close to 1. For instance, a set of benzeneoid hydrocarbons (20) possesses 0.828535 (SDEV : 0.008752) as the mean of k . All of these imply that eq 15 can be used as a good estimator for E of alternant hydrocarbons.

On the other hand, Eq. 15 clearly shows that variations of E values of isomeric compounds which possess obviously the same e and n values are dictated by k values only. Since, the range of k is quite narrow, E values of isomeric compounds should not differ much from each other.

References

1. B. J. McClelland, **J. Chem. Phys.**, **54**, 640-643 (1971).
2. I. Gutman, **Chem. Phys. Lett.**, **50**, 488-490 (1977).
3. I. Gutman, L. Türker and J. R. Dias, **Match**, **19**, 147-161 (1986).
4. L. Türker, **Match**, **16**, 83-94 (1984).
5. I. Gutman, M. Milun and N. Trinajstić, **J. Chem. Phys.**, **59**, 2772-2774 (1973).
6. J. Cioslowski, **Match**, **20**, 95-98 (1980).
7. J. Cioslowski, **Z. Naturforsch.**, **40a**, 1167-1169 (1985).
8. A. Groavac, I. Gutman and N. Trinajstić, **Chem. Phys. Lett.**, **35**, 555-557 (1975).
9. I. Gutman, **Topics Curr. Chem.**, **162**, 29-63 (1992).
10. G. G. Hall, **Int. J. Math. Educ. Sci. Technol.**, **4**, 233-238 (1973).
11. G. G. Hall, **Bull. Inst. Math. Appl.**, **17**, 70-73 (1981).
12. I. Gutman and G. G. Hall, **Int. J. of Quantum Chem.**, **41**, 667-672 (1992).
13. L. Türker, **Match**, **28**, 261-276 (1992).
14. L. Türker, **Polycyclic Aromatic Compounds**, **4**, 107-114 (1994).
15. I. Gutman, **Match**, **29**, 61-69 (1993).
16. I. Gutman, Lj. Nedeljković, A. V. Teodorović, **Bull. Soc. Chim. Beograd**, **48**, 495-498 (1983).
17. L. Türker, **Match**, **30**, 243-252 (1994).
18. I. Gutman and O. E. Polansky, "Mathematical Concepts in Organic Chemistry", Springer-Verlag, Berlin, 1986.
19. M. Vygodsky, "Mathematical Handbook", Mir Publishers, Moscow, 1975.
20. R. Zahradnik and J. Pancir, "HMO Energy characteristics", Plenum Press, New York, 1970.