

EQUIVALENT BOND INDEX

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Abstract:

The equivalent bond index is defined especially for the topology of the molecular skeleton of a saturated hydrocarbon, i. e., branching and ring-closure in a molecule.

This index has such a remarkable characteristic that it can show the topological nature of equivalent bond orbitals in saturated hydrocarbons. The recursion formula of the characteristic polynomials having relation with the index is explained. The general expression for the value of this index is also discussed.

1. INTRODUCTION

Many graph theoretical investigations have been performed to study the total π -electronic energy of unsaturated

hydrocarbons¹⁻⁵) or thermodynamic quantities of hydrocarbons¹³⁻¹⁷).

On the other hand, the electronic energy of saturated hydrocarbons has not been well studied graph-theoretically, because there are many parameters which are not suitable for the graph-theoretical treatments.

Heilbronner et al. applied the equivalent bond orbital method to calculate the ionization energy of saturated hydrocarbons.⁶⁻⁸) At that time they supposed Koopmans' theorem. According to them this simple method gave better results than they had thought, because the calculated orbital energy showed good agreement with the observed C_{2s} ionization potential.

They did not calculate the total equivalent bond orbital energy, E , because E depends only on the number of equivalent bonds but not on the topology of the molecular skeleton of a saturated hydrocarbon, i.e., branching and ring-closure in a molecule.

Therefore instead of the total equivalent bond orbital energy, E , we calculate the quantity σ .

The quantity, σ , corresponds to the total π -electronic energy index Z^* which has been introduced for π -electronic systems.²) Let us call the index σ the *equivalent bond index*.

A simple explanation is given in Section 2 and the equivalent bond index is introduced in Section 3. The σ -values of many saturated hydrocarbons are shown and discussed in Section 4.

The recursion formula of characteristic polynomials having relation with this value are explained in section 5 and the general expression of the σ -values is discussed in Section 6.

2. OUTLINE OF THE EQUIVALENT BOND ORBITAL METHOD

Heilbronner et al.⁶⁻⁸⁾ applied the equivalent bond orbital method to calculate the electronic energy of saturated hydrocarbons. First the outline of their method will be explained.

It is assumed that the delocalized molecular orbital φ_j is expressed as the linear combination of the equivalent bond orbitals χ_{uv} 's.

$$\varphi_j = \sum_{u,v} C_{uv,j} \chi_{uv} \quad (1)$$

where χ_{uv} is localized between two atoms u and v which are bonded in the hydrocarbon molecule.

There are three kinds of the determinantal elements with respect to the Hamiltonian H , i.e., the self-energy, interaction element, and overlap integral:

$$H_{uv,uv} = \langle \chi_{uv} | H | \chi_{uv} \rangle = A_{uv} \quad (2)$$

$$H_{uv,u'v'} = \langle \chi_{uv} | H | \chi_{u'v'} \rangle = B_{uv,u'v'} \quad (3)$$

$$S_{uv,u'v'} = \langle \chi_{uv} | \chi_{u'v'} \rangle \quad (4)$$

Let us apply the Hückel approximation to $S_{uv,u'v'}$.

$$S_{uv,u'v'} = \delta_{uv,u'v'} \quad (5)$$

Now suppose that all kinds of the self-energy are equivalent:

$$A_{CC} = A_{CH} = A = \text{constant} \quad (6)$$

Assume that all the adjacent interactions are equivalent,

$$B_{CC,CC} = B_{CC,CH} = B_{CH,CH} \quad (7)$$

If we neglect higher interactions,

$$C_{CC,CC} = C_{CC,CH} = C_{CH,CH} = 0. \quad (8)$$

From Eqs.(6)~(8) we have

$$\mathbf{H} = a \mathbf{E} + b \mathbf{A}, \quad (9)$$

where E is the unit matrix of order n (the number of orbitals) and $\mathbf{A}=[A_{\mu\nu}]$ is the adjacency matrix. Let us assume as follows:

$$A_{\mu\nu} = \delta_{\mu\nu} \begin{cases} = 1 & \mu, \nu \text{ adjacent} \\ = 0 & \text{otherwise} \end{cases} \quad (10)$$

If we define the orbital energy as

$$\varepsilon_i = a + bX_i, \quad (11)$$

we have

$$|\mathbf{A} - X \mathbf{E}| = 0, \quad (12)$$

To solve Eq.(12) means to calculate a characteristic value of graph G. In this case a vertex of graph G represents an equivalent bond orbital of a given saturated hydrocarbon.

3. EQUIVALENT BOND INDEX

After solving Eq. (12) we can express the characteristic polynomials as follows:

$$P(X) = \sum_{k=0}^n a_k X^{n-k} \quad (13)$$

with the definition that $a_0=1$ and n is the number of equivalent bond orbitals in a hydrocarbon. Using n roots of X P(X) can be expressed as

$$P(X) = \prod_{k=1}^n (X - X_k) \quad (14)$$

Define the index Z^* as

$$Z^* \equiv |P(i)| = \left| \sum_{k=0}^n a_k i^{n-k} \right| \quad (15)$$

Let us call the square of Z^* *equivalent bond index* (EBI) σ ,¹

$$\sigma \equiv Z^{*2} = |P(i)|^2 \quad (16)$$

From Eqs. (14) and (16) we have

$$\sigma = \left| \prod_{k=1}^n (i - X_k) \right|^2 = \prod_{k=1}^n (1 + X_k^2), \quad (17)$$

where n is generally expressed by the numbers of carbons (N) and rings (r) as

$$n = 3N + 1 - r. \quad (18)$$

One can compute Z^* and σ from Eqs. (13)-(17).

Decompose $P(X)$ into the sum of even and odd functions,

$S(X)$ and $A(X)$, as

$$P(X) = S(X) + A(X). \quad (19)$$

For odd n

$$S(X) = \sum_{k=0}^{\lfloor n/2 \rfloor} a_{2k+1} X^{n-(2k+1)} \quad (20a)$$

$$A(X) = \sum_{k=0}^{\lfloor n/2 \rfloor} a_{2k} X^{n-2k}, \quad (20b)$$

while for even n

$$S(X) = \sum_{k=1}^{n/2} a_{2k} X^{n-2k} \quad (20c)$$

¹ Aihara calls Z^* the total π -electron energy index (See Ref. 2).

$$A(X) = \sum_{k=0}^{n/2-1} a_{2k+1} X^{n-(2k+1)}. \quad (20d)$$

According to Eqs. (16) and (19)

$$Z^* = \left\{ |S(i)|^2 + |A(i)|^2 \right\}^{1/2} \text{ or} \\ \sigma = |S(i)|^2 + |A(i)|^2 \quad (21)$$

For alternant hydrocarbons Z^* is an integer, while for non-alternant hydrocarbons not an integer.²⁾ On the other hand σ is always an integer because a_k 's, a_{2k} 's and a_{2k+1} 's in Eqs. (15) and (20) are all integers.

We use the EBI, σ , as an index which represents the energy state of a hydrocarbon molecule instead of the total sum, E , of the equivalent bond energies. The reason why we do not apply E is that E cannot express the topological characteristic of a saturated hydrocarbon, as follows. Namely, E is shown to be merely the product of the number, n , of equivalent bonds and Coulomb integral or self-energy a . Namely,

$$E = 2(\epsilon_1 + \epsilon_2 + \dots + \epsilon_n) \\ = 2na + 2b(X_1 + X_2 + \dots + X_n) \\ = 2na \quad (22)$$

Let us explain the case of ethane C_2H_6 ($N=2$, $n=7$), (See FIGS. 1 and 2). FIGURE 1 shows the traditional chemical structure of C_2H_6 which has 7 equivalent bonds and $n=7$. FIGURE 2 shows the interaction among the 7 equivalent bonds orbitals.

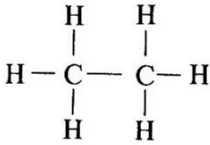


FIG.1 Ethane

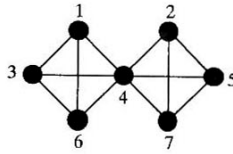


FIG.2 The Interaction of Equivalent Bond Orbitals

where a block circle expresses a bond orbital. In the case of the graph in FIG. 2, Eq. (12) is as follows:

$$\begin{vmatrix}
 -x & 0 & 1 & 1 & 0 & 1 & 0 \\
 0 & -x & 0 & 1 & 1 & 0 & 1 \\
 1 & 0 & -x & 1 & 0 & 1 & 0 \\
 1 & 1 & 1 & -x & 1 & 1 & 1 \\
 0 & 1 & 0 & 1 & -x & 0 & 1 \\
 1 & 0 & 1 & 1 & 0 & -x & 0 \\
 0 & 1 & 0 & 1 & 1 & 0 & -x
 \end{vmatrix} = 0$$

The characteristic polynomials, $P(X)$, $S(X)$, and $A(X)$, of this acyclic saturated hydrocarbon are given by developing the above determinant:

$$P(X) = X^7 - 12X^5 - 16X^4 + 21X^3 + 60X^2 + 46X + 12$$

$$S(X) = -16X^4 + 60X^2 + 12$$

$$S(i) = -64$$

$$A(X) = X^7 - 12X^5 + 21X^3 + 46X$$

$$A(i) = 12i$$

$$\sigma \equiv Z^{*2} = |S(i)^2| + |A(i)|^2 = 4240$$

The eigenvalues $\{X_1, X_2, \dots, X_n\}$ are $\{3.6458, 2.000, (-1.0000)^4, -1.6458\}$, therefore $\sigma = Z^{*2} = \prod_{k=1}^7 (1 + X_k^2) = 4240$.

Both values are naturally the same.

4. THE VALUES OF σ 'S

The numbers of carbons (N) and orbitals(n), the components, S(i) and A(i)/i, of the characteristic polynomial, and EBI of acyclic and cyclic saturated hydrocarbons are shown in TABLES 1 and 2, respectively.

TABLES 1 and 2 show that the EBI increases rapidly with the number, N, of carbon atoms.

For the case with equal N and n, the highly the graph is branched, the smaller the EBI, as in the following fashion.

$\log \sigma = -0.31586 + 0.56161n$ ($r=0.99986$, acyclic paraffins),

$\log \sigma = 0.26550 + 0.54875n$ ($r=0.99748$, cyclic paraffins), where r is a correlation coefficient. Except for the rapid increase this inclination resembles to that of Hosoya's Z index.⁹⁻¹¹⁾

In the case of acyclic hydrocarbons EBI, σ , is nearly proportional to 10^{2N-1} , but for N=5 and 6 it is a little bit smaller than this. In the case of cyclic hydrocarbons the value σ is nearly proportional to 10^{2N-2} except for the case of N=3.

For acyclic and cyclic hydrocarbons the magnitudes of |S(i)| and |A(i)| are comparable. On the other hand, as seen in TABLE 3 the term A(i)/i is zero for the π -electronic systems

TABLE 1. The S(i),A(i)/i and σ of Chain Paraffins in Equivalent Bond Orbital Method

N	n	Compounds*	S(i)	A(i)/i
1	4	1	4	-8
2	7	2	-64	12
3	10	3	344	304
4	13	4	192	-3232
		2m3	120	-3088
5	16	5	-18784	12992
		2m4	-17632	12848
		22m3	-14896	12416
6	19	6	153856	47808
		2m5	148096	42048
		3m5	148384	41472
		22m4	134560	27360
		23m4	142912	35856

N	n	σ	b.p.(K)
1	4	80	111.6
2	7	4240	184.5
3	10	210752	231.0
4	13	10482688	272.6
		9550144	261.4
5	16	521630720	309.2
		475958528	300.9
		376047872	282.6
6	19	25757273560	341.8
		23700459520	333.4
		23737738240	336.4
		18854963200	322.8
		21709492480	331.1

*2m3 means 2-methyl propane, for example.

TABLE 2. $S(i), A(i)/i$ and σ of the Cycloparaffins in EBO Method.

N	n	Compounds	$S(i)$
3	9	Cyclopropane	320
4	10	Tetrahedrane	135
	11	Bicyclo[1.1.0]butane	-1344
	12	Cyclobutane	-2224
	12	Methylcyclopropane	-2016
5	14	Bicyclo[2.1.0]pentane	11696
	15	1,1-dimethyl cyclopropane	3200
	15	1,2-dimethyl cyclopropane	2768
	15	Ethyl cyclopropane	2624
	15	Methyl cyclopropane	3632
	15	Cyclopentane	3136
6	17	Bicyclo[2.2.0]hexane	-43520
	18	1,1-Methyl-Ethyl cyclopropane	62848
	18	1,2,3-Trimethyl cyclopropane	66352
	18	1,1-Dimethyl Cyclobutane	61728
	18	1,2-Methyl-Ethyl cyclopropane	71920
	18	Isopropyl cyclopropane	71872
	18	Propyl cyclopropane	77824
	18	1,3-Dimethyl Cyclobutane	70800
	18	1,2-Dimethyl Cyclobutane	70368
	18	Methylcyclopentane	75264
	18	Ethyl Cyclobutane	76032
	18	Cyclohexane	81920
	7	21	Cycloheptane
8	24	Cyclooctane	5050368

TABLE 2. S(i),A(i)/i and σ of the Cycloparaffins in EBO Method(continued)

N	n	A(i)/i	σ
3	9	-128	118784
4	10	1080	1184625
	11	948	2705040
	12	-1152	6273280
	12	-1120	5318656
5	14	2688	144021760
	15	13952	204898304
	15	15176	237972800
	15	16064	264937472
	15	16576	287955200
	15	17120	302928896
6	17	-79360	8192000000
	18	-79488	10268213248
	18	-78936	10633480000
	18	-88576	11656053760
	18	-81792	11862417664
	18	-83136	12077178880
	18	-84480	13193445376
	18	-90880	13271814400
	18	-91456	13315855360
	18	-90080	13779076096
	18	-92704	14374896640
	18	-92160	15204352000
7	21	-53120	755523731456
8	24	5050368	37593910149120

TABLE 3. $|S(i)|$ and σ for Typical Alternant Hydrocarbons (π -electron system)

N	Compounds	$ S(i) $	σ
4	Cyclobutadiene	5	25
6	Dimethylene cyclobutane	13	169
6	Benzene	20	400
8	Cyclo - octatetraene	45	2025
8	Benzocyclobutadiene	49	2401
10	[10]Anulene	125	15625
10	Naphthalene	170	28900
12	Biphenyl	464	215296
12	Biphenylene	481	231361
14	Anthracene	1440	2073600
14	Phenanthrene	1489	2217121
16	Pyrene	4810	23136100

$$|A(i)| = 0, \sigma = Z^* = |S(i)|^2$$

TABLE 4. $|S(i)|$, $|A(i)|$ and σ for Typical Non-alternant Hydrocarbons. (π -electron systems)

N	Compounds	$ S(i) $	$ A(i) $	σ
6	Fulvene	16	2	260
8	Pentalene	54	12	3060
10	Azulene	149	10	22301
12	Heptalene	384	32	148480
12	Cyclopent[cd]azulene	464	66	219652
12	s-Indacene	469	108	231625
12	Acenaphthylene	522	52	275188
14	Aceheptylene	1236	28	1528480

$$\sigma = Z^{*2} = |S(i)|^2 + |A(i)|^2$$

of alternant hydrocarbons.

In TABLE 4 the $|A(i)|$ values are shown for the π -electronic systems of typical non-alternant hydrocarbons. In this respect the situation is the same as in the case of saturated hydrocarbons in TABLES 1 and 2.

According to TABLE 2 the σ values of cyclic saturated hydrocarbons are governed by some complicated rules with respect to the size of rings and branching.

All the graphs in TABLES 1 and 2 are strongly non-alternant and eigenvalues of them satisfy the following inequality, because the maximum order of the vertices (i.e., the equivalent bond orbitals) is six. From This we have

$$1 < 1 + X_k^2 < 37. \quad (23)$$

Therefore $1 < \prod_{k=1}^n (1 + X_k^2) < 37^n$. Namely,

$$1 < \sigma < 37^n \quad (24)$$

The above equation gives the roughest upper limit of σ 's.

However actual values of EBI, σ , are smaller than this and are almost 10^{2N-1} in acyclic hydrocarbons.

The value of EBI, σ , of the linear unbranched saturated hydrocarbon is the biggest of the isomers.

The reason why the EBI is sensitive towards the branching and ring-closure of molecular skeleton is probably associated with the largest weight of X_1 (the largest eigenvalue) in Eq. 17 (See Ref. 18).

The following relation between the boiling points T(K) and EBI of chain paraffins is obtained from Table 1:

$$T=89.12 + 23.98 \log \sigma$$

$$1 \leq N \leq 6; \quad r=0.9858$$

The correlation coefficient $r=0.9858$ shows that there is a good linear relation between the logarithm of σ and one of physico-chemical quantities, i.e., boiling points of chain paraffins.

5. RECURSION FORMULA OF CHARACTERISTIC POLYNOMIALS

Hosoya and Ohkami¹²⁾ developed a new method which gives recursion formula of the characteristic polynomial $P(x)$. When the method is applied to the $P(x)$'s of some saturated hydrocarbons the following expressions are obtained:

In linear saturated hydrocarbons

$$P_N = \sum_{i=1}^2 q_i P_{N-i} \quad (25)$$

where $q_1 = x^3 - 5x - 4$

$$q_2 = -(x^4 + 4x^3 + 6x^2 + 4x + 1)$$

In 2-methyl or 3-methyl acyclic saturated hydrocarbons

$$P_N = \sum_{i=1}^3 r_i P_{N-i} \quad (26)$$

where $r_1 = x^3 - 7x - 6$

$$r_2 = x^4 - 2x^3 - 16x^2 - 22x - 9$$

$$r_3 = -(2x^5 + 10x^4 + 20x^3 + 20x^2 + 10x + 2)$$

In 2,2-dimethyl acyclic saturated hydrocarbons $P_N(x)$ is shown as

$$P_N = \sum_{i=1}^6 c_i P_{N-i} \quad (27)$$

where it can be shown that c_i 's are expressed by the functions of x , q_i 's and r_i 's.

In the case of cyclic paraffines the following equation is obtained:

$$P_N = \sum_{i=1}^3 d_i P_{N-i} \quad (28)$$

where $d_1 = (x + 1)(x^2 - 3)$

$$d_2 = -(x + 1)^3(x^2 - 3)$$

$$d_3 = (x + 1)^6$$

The above equation shows that the coefficients of the recursion formula of cyclic paraffins have not special relations with the ones of linear hydrocarbons or branched acyclic hydrocarbons.

6. GENERAL EXPRESSION OF THE σ -VALUES

Let us find the general expressions of $P_N(i)$ which appears in

$$\sigma_N = |P_N(i)|^2.$$

Only the simplest case of linear saturated hydrocarbons is considered here. If pure imaginary number i is substituted for x in Eq.(25) the $P_N(x)$ is expressed as:

$$P_N(i) = cP_{N-1}(i) + c'P_{N-2}(i) \quad (29)$$

where $c = -6i-4$ and $c'=4$. If the above equation is treated as Fibonacci series, the formula corresponding to Binet's one is obtained:

$$\begin{aligned} \rho P_N(i) = c' [\{(c - \rho)/2\}^{N-2} - \{(c + \rho)/2\}^{N-2}] P_1(i) \\ + \{[(c - \rho)/2]^{N-1} - [(c + \rho)/2]^{N-1}\} P_2(i) \end{aligned} \quad (30)$$

where $\rho = \sqrt{c^2 + 4c'}$, $P_1(i) = 4 - 8i$ and $P_2(i) = -64 + 12i$.

On the other hand $P_N(i)$ is expressed as

$$P_N(i) = (\alpha + \beta) P_{N-1}(i) - \alpha\beta P_{N-2}(i) \quad (31)$$

where α and β are the roots of $t^2 - ct - c' = 0$, and $\alpha + \beta = c$ and $\alpha\beta = -c'$.

The following equation is obtained as in the case of Fibonacci series:

$$(\alpha - \beta) P_N(i) = -\alpha\beta (\alpha^{N-2} - \beta^{N-2}) P_1(i) + (\alpha^{N-1} - \beta^{N-1}) P_2(i) \quad (32)$$

For example, in the case of $N=4$ the following formula is obtained from Eq. (32);

$$P_4(i) = -\alpha\beta (\alpha + \beta) P_1(i) + \{(\alpha + \beta)^2 - \alpha\beta\} P_2(i) \quad (33)$$

From this we obtain

$$\sigma_3 = [P_4(i)]^2 = 36864 + 10445624 = 10482688.$$

This value coincides with the one which was calculated by a computer and shown in TABLE 1.

General cases are treated as in the same way as the above simplest case according to the general treatment of the recursion formula.

As a conclusion of this section physical meaning and mathematical relation of σ should be considered. As shown in Eq. (17), σ equals to the n times product of the quantity which is composed of one plus the square of eigenvalue X_k of the equivalent bond orbitals, where n is the number of orbitals.

In Eq. (21), when $A(i)$ is zero or is neglected compared

with $S(i)$, Z^* becomes equal to π -energy index \tilde{Z} of Hosoya.

According to TABLE 1, in the case of N greater than 5 of acyclic saturated hydrocarbons $|S(i)| > |A(i)|$ is established.

According to TABLE 2, in the case of $N=3$ or 4 of cyclic saturated hydrocarbons $|S(i)| > |A(i)|$ is found except for one example. However in the case of $N=5$ or 6 $|S(i)| < |A(i)|$ is shown except for one example.

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