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Topological Relationship Between One-Dimensional Box Model and Randić Indices in Linear Simple Conjugated Polyenes

Avat (Arman) Taherpour[1,2*] and Fatemeh Shafiei[1]

1. Chemistry Department, Faculty of Science, Arak Branch, Islamic Azad University, P. O. Box 38135-567, Arak, Iran
2. Faculty of Science, Sanandaj Branch, Islamic Azad University, P. O. Box: 618, Kurdistan, Iran

ABSTRACT

The alternative double bonds and conjugation in the polyene compounds are one of the main properties in these compounds. Each carbon-carbon bonds in a polyene compound along the chain has appreciable double-bond character. The π-electrons are therefore not localized but are relatively free to move throughout the entire carbon skeleton as an one-dimensional box. The skeleton be considered as a roughly uniform region of low potential bounded at the ends of the polyene by regions of infinitely high potential. Graph theory provides the useful natural mathematical frameworks for the quantitative codification of classical chemical bonding ideas. One of the useful indices for examination of structure-property relationship is Randić index. Some of properties here considered are associated with the molecular orbital method include and λmax, the difference energy level of the HOMO and LUMO orbitals (ΔE) and the length of the electron moving in carbon skeleton as one-dimensional box in polyene compounds (1-D box model). In this study, the difference of the length of carbon skeleton of polyenes and the length of the electron moving in the carbon skeleton will be discussed. For calculation the λmax of the compounds could use the Fieser-Kuhn rule. The interesting results of concerning among λmax, ΔE, the electron moving in carbon skeleton of simple linear polyenes by the use of 1-D box model and the above indices are presented.

Keywords: Molecular structure; Molecular topology; Randić index; Polyenes; 1-D box model; Maximum wavelength

INTRODUCTION

Topological indices are the numerical value associated with chemical constitution purporting for correlation of chemical structure with various physical properties, chemical reactivity or biological activity. Graph theory as a subdiscipline of mathematics is closely related to both topology and combinatories. A graph is a topological concept rather than a geometrical concept of fixed geometry. Therefore, Euclidean metric lengths, angles and three-dimensional spatial configurations have no significance in topological concept. Chemists employ various types of designations and formulas when they want to communicate information about chemical compounds and their structures. In spite of this fact, most of the names and formulas have no direct, immediate or explicit mathematical meaning.

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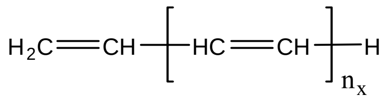
* . Corresponding author: avat_1@ Yahoo.co.uk

It has been found to be a useful tool in QSAR (Quantitative Structure Activity Relationship) and QSPR (Quantitative Structure Property Relationship).[1-6] Numerous studies have been made relating to the above mentioned fields by using what are called topological indices (TI).[6] In 1975, Randić proposed a topological index that has become one of the most widely used in both QSAR and QSPR studies.[7] Quantitative structure-activity relationships (QSAR) are mathematical models designed for the correlation of various types of biological activity, chemical reactivity, equilibrium, physical and physicochemical properties with electronic, steric, hydrophobic and other factors of a molecular structure of a given series of compounds such as substitution constants, topological indices (TI) as well as with solvent and other physicochemical parameters. In 1998, Randić reviewed that the quantitative characterization of molecular structure features have been overlooked and neglected for too long time.[3] The TIs are based on the original idea of Randić related to molecular branching, it can also be extended in accounting for contributions rooted in path clusters, clusters and chains of different lengths.[8-15]

The relationship of Randić index with λ_{max} and ΔE ($\Delta E = hc/\lambda_{max}$) were considered for the linear simple conjugated polyenes (I).[16] For calculation of the λ_{max} and ΔE of compounds (I) was utilized the Fieser-Kuhn rule and Plank's formula ($\Delta E = hc/\lambda_{max}$).[16,17]



$H_2C{=}CH\!-\![HC{=}CH]_{n_x}\!-\!H$

n_x = 1,2,3, …, 14 (I)

Each carbon-carbon bonds in the linear simple conjugated polyenes (I) along the chain has appreciable C=C character. The π-electrons are therefore not localized but are relatively free to move throughout the entire carbon skeleton if the chain of the polyenes (I) take into consideration as an one-dimensional box. The particle in a one-dimensional box model is a simple quantum mechanical model that can be used to predict the electronic energy levels for the π-electrons in long-chain conjugated unsaturated compounds. The skeleton be considered as a roughly uniform region of low potential bounded at the ends of the polyene by regions of infinitely high potential. An expression for the allowed energies of these electrons, electron-electron repulsions being ignored was obtained as below (Eq.1): [18,20]

$$\varepsilon = n^2 h^2 / 8ml^2,\ n=1,2,3,\ldots \qquad (1)$$

where "l" is the effective length of the electron moving in molecules (I), "h"(6.62×10^{-34}), and "m" (9.10×10^{-31}) are Plank's coefficient and mass of an electron. Two electrons, one with each spin direction, can be placed in each square-well orbital.

The main merit of this treatment of conjugated systems is that it offers an easy way to relate the wavelength of light absorbed to the "l_e" of conjugated system (I). In this manner was utilized from linear combination of atomic orbitals (LCAOs) that considered most in quantitative mechanical quantum studies of conjugated systems. The effective length of the electron moving in the carbon skeleton "l_e" is different from the summation of the carbon-carbon bond length "l_s" in simple linear polyenes (I). In this study, the interesting results of concerning λ_{max}, ΔE, the effective length of the electron moving "l_e" of simple linear polyenes (I) by the use of 1-D box model with the Randić indices, are presented.

MATHEMATICAL METHODS

The branching index introduced by Randić is defined as the sum of certain bond contributions calculated by applying the degree of the bonds suppressed molecular graphs. These bond contributions, named C_{ij} are calculated as:

$$C_{ij} = (\delta_i \delta_j)^{-0.5} \qquad (2)$$

Here, δ_i is the degree of the vertex representing atom "i", i.e., the number of bonds incident to this atom. Accordingly, the Randić index is defined as [1, 7, 21,22]:

$$\chi = \Sigma C_{ij} = \Sigma (\delta_i \delta_j)^{-0.5} \qquad (3)$$

Equation 2 reveals that the summation is carried out over all the bonds of linear simply conjugated polyenes (I). The inverse squared–root of the vertex degree is identified here as a measure of the relative accessible parameter of an atom from the outside. These parameters, which have length units, are proposed to be measured in a new unit called the Randić index (χ). On this basis, the bond contributions to the Randić index are relative areas of bond accessibility regarding the environment.

For two ends of polyene chains I, the Randić indices are: $C_1 = C_n = 1/(2x3)^{0.5}$, (only for ethylene: $C_1 = C_n = 1/(2x2)^{0.5}$). For each carbon atoms between the head and tail in the polyene chains I the Randić indices are: $C_2 = Cn_{x\ -1} = 1/(3x3)^{0.5}$. On the basis, the final equation for calculating the Randić indices of the linear simple conjugated polyenes (I) is:

$$\chi = 2[1/(2x3)^{0.5}] + [\,(N_B - 2) / (3x3)^{0.5}] \tag{4}$$

and:

$$\chi = 2\,[1/(6)^{0.5}] + [\,(A - 3) / 3] \tag{5}$$

In this equation, “A” is the number of conjugated carbon atoms and “N_B” is the number of atoms, the Randić indices are $1/(3x3)^{0.5}$ in the compounds I.

If “n_0” equals “A-3” (n_0=A-3), the number of nodes in the HOMO orbitals of the linear simple conjugated polyenes (I) is gained, thus:

$$\chi = 0.82 + [\,0.33\,(A\text{-}3)] \tag{6}$$

$$\chi = 0.82 + [\,0.33\,(n_0)] \tag{7}$$

For calculating the λ_{max} of polyenes I, the Fieser-Kuhn rule was used. (See Eq.-8). These maximum wave length (λ_{max}) are calculated as follows:

$$\lambda_{max}=114+5M+n_x(48.0-1.7n_x)-16.5R_{endo}-10R_{exo.} \tag{8}$$

Where, “M” is the number of alkyl substitution (in I equals to zero), “n_x” is the number of conjugated double bonds, “R_{endo}” is the number of endo double bonds (in I equals to, R_{endo}= 0) and “R_{exo}” is the number of exo double bonds (in I equals to, R_{exo} = 0). Thus, the final equation of Fieser-Kuhn rule for this study is:

$$\lambda_{max} = 114 + n_x\,(48.0 - 1.7\,n_x) \tag{9}$$

If: A=2n_x (A= The number of conjugated atoms in I), then:

$$\lambda_{max} = 114 + A/2\,[48.0 - A\,(1.7 \div 2)] \tag{10}$$

$$\lambda_{max} = 114 + A\,[(48.0 - 0.85\,A) \div 2\,] \tag{11}$$

For calculating the “ΔE” the Plank’s formula (ΔE= hc/λ_{max}) was utilized. By using and combining Eq.6 and Eq.11, we arrive at the Eq.-12. This equation describes correlation of λ_{max} and Randić index (χ) for the linear simple conjugated polyene compounds (I).

$$\lambda_{max} = 126.85 + 70.63\,(\chi) - 3.82\,(\chi)^2 \tag{12}$$

For calculating the ΔE we could combine Eq.12 and Plank’s formula (ΔE= hc/λ_{max}). Finally, Eq.-13 was obtained:

$$\Delta E = hc/[126.85+70.63(\chi)-3.82(\chi)^2] \tag{13}$$

Where, "h", "c" and "χ" are Plank’s coefficient, speed of light, and the Randić index, respectively.

The equation 1 shows the allowed energies of the conjugated π-electrons are therefore not localized but are relatively free to move throughout the entire carbon skeleton if the chain of the polyenes (I) take into consideration as an one-dimensional box. According to the free-electron model for the π-electron system, this result can be related to the energy difference (see Eq.-14):

$$\Delta E=[(\varepsilon_{n+1})-(\varepsilon_n)]=[(n_{LUMO}^2)-(n_{HOMO}^2)][h^2/8m\,l_e^{\,2}] \tag{14}$$

Substitution of numerical values leads to a value of "l_e", the length of the region in which the electrons are free to move. By using and combining Eq.12 and Eq.13, we arrive at the Eq.15. This equation describes correlation of the length "l_e" and Randić index (χ) for the linear simple conjugated polyene compounds (I) :

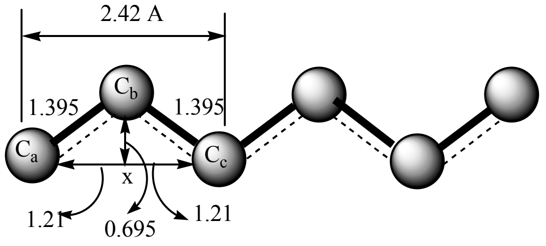
$$l_e=[(n_{LUMO}^2-n_{HOMO}^2)(126.85+70.63(\chi)-3.82(\chi)^2)/8mc]^{0.5} \tag{15}$$

Where, "l_e", "m", "c" and "χ" are the effective length of electron moving in the linear simple conjugated polyene compounds (I) according to the 1-dimentional box model, mass of electron, speed of light, and the Randić index, respectively.

In this consideration another length was determined. As we could see in Table1 and Figure1, "l_a" is the distances summation of the alternate carbon atoms in the chain of compounds (I).

The Fig.1 shows a three angle among three carbon atoms (C_a, C_b and C_c) in a linear simple conjugated polyene (I). The angle of $<C_aC_bC_c$ is equal to 120° and for $<C_bC_cC_a = <C_bC_aC_c$ are 30°. In accordance with the geometry rules the distance of the alternate carbon atoms in the chain of polyenes (I) is 2.42 Å and l_a is equal to the summation of distances between alternate carbons in the chain of compounds (I).

All structural values were calculated by ab-initio method the molecular structure of the polyenes (I) have been considered with ab initio methods by using GAUSSIAN-98 computer program that is implemented on a Pentium-PC computer. Firstly, optimizations were performed at 6-31G basis set at the Hartree–Fock (HF) level in the gas phase. To investigate further effect of electron correlation, the geometries were also optimized at the HF/6-31G** level. (See Fig.1).



$<C_aC_bC_c = 120°$

$<C_bC_cC_a = <C_bC_aC_c = 30°$

$C_aC_b = 1.21 \times 2 = 2.42$ Å $\rightarrow l_a = 6.05$ Å

Fig.1. The distance of the alternate carbon atoms in the chain of conjugated polyene compounds (I) is 2.42 Å.

Graphs

For drawing the graphs of results, the Microsoft Office Excel-2003 program has been used.

DISCUSSION

The values were shown in Table 1 demonstrate of the relative structural coefficients of the polyenes Randić index (χ) to maximum UV wave length (λ_{max}), ΔE (basis on the λ_{max}), "l_e" (basis on the one-dimensional box model and Eq.15), "l_s" (the summation of the carbon-carbon bond length) and "l_a"(distances summation of the alternate carbon atoms) in the linear simple conjugated polyene compounds (I).

As the values shown in the table, the Randić indices increase with molecular size of polyenes (I). Table1 reveals the three numerical progression indicated in the Randić indices. On this basis, the distance number of the Randić indices of {C_4H_6, $C_{10}H_{12}$, $C_{16}H_{18}$, $C_{22}H_{24}$}, {C_6H_8, $C_{12}H_{18}$, $C_{18}H_{20}$, $C_{24}H_{26}$} and {C_8H_{10}, $C_{14}H_{16}$, $C_{20}H_{22}$, $C_{26}H_{28}$}is two (2) units of Randić index.

The λ_{max} ,"l_e", "l_s" and "l_a" values increase and $\Delta E = hc/\lambda_{max}$ decrease with the Randić values of the polyenes (I). Calculations of the λ_{max} and ΔE were based on the Fieser-Kuhn rule and the Plank's formula. See Fig.2 to Fig.6 and the values of Table 1.

The values of "l_e" were calculated by the use of 1-D box model (see Eq.1 and/or Eq.15). For calculation of "l_s" and "l_a" values were utilized the summation of carbon-carbon bond length along the chain, and distances summation of the alternate carbons in compounds (I), respectively. The numbers shown in the Fig.3 to Fig.6 (extended in Table 1 for larger compounds of the family I) have simple mathematical structure. For example, in lieu of increasing each C=C bond in the linear simple conjugated polyenes (I), l_s and l_a were increased 2.79 and 2.42 Å, respectively. (Table1). For "l_e" the, difference values of two consecutive compounds in family (I), decreased by increasing the Randić indices (χ). As Table1 shows, these values between {C_4H_6 & C_6H_8} and {$C_{24}H_{26}$ & $C_{26}H_{28}$}are 1.45 and 0.83, respectively.

In Fig.2 to Fig.6, it is attempted to show two dimensional diagrams of the relationship between the main values of χ, λ_{max}, ΔE, l_e, l_s and l_a (see Table1).

The Fig.2, is a plot of the values of "χ" versus the λ_{max} of polyenes (I). There is nonlinear concerning among these values and could distinguish a curve between values of Randić indices "χ" and maximum wave length (λ_{max}) of polyenes (I). Although, perhaps not obvious from these figures, the relationship between the variables is decidedly nonlinear,

which however does not diminish their utility.

By the use of Eq.12, could achieve to the λ_{max} values.

Table 1. The values of the relative structural coefficients of polyenes **(I)**

No.	Compounds	n_x	A	*Randić* index (χ)	λ_{max} (nm)	ΔE (in Joul x10^{-19})	"l_e" (in ?)	"l_s" (in ?)	"l_a" (in ?)	$\Delta l=\lvert l_s-l_e\rvert$ (in ?)
1	C_4H_6	1	4	1.56	217.0	9.78	5.727	4.185	3.63	1.542
2	C_6H_8	2	6	2.13	242.7	8.18	7.177	6.975	6.05	0.202
3	C_8H_{10}	3	8	2.89	278.8	7.13	8.717	9.765	8.47	1.048
4	$C_{10}H_{12}$	4	10	3.46	311.5	6.38	10.188	12.555	10.89	2.367
5	$C_{12}H_{14}$	5	12	4.13	340.8	5.83	11.586	15.345	13.31	3.759
6	$C_{14}H_{16}$	6	14	4.89	366.7	5.42	12.907	18.135	15.73	5.228
7	$C_{16}H_{18}$	7	16	5.56	389.2	5.10	14.165	20.925	18.15	6.130
8	$C_{18}H_{20}$	8	18	6.13	408.3	4.87	15.325	23.715	20.57	8.390
9	$C_{20}H_{22}$	9	20	6.89	424.0	4.69	16.418	26.505	22.99	10.087
10	$C_{22}H_{24}$	10	22	7.56	436.3	4.55	17.444	29.295	25.41	11.851
11	$C_{24}H_{26}$	11	24	8.13	445.2	4.46	18.369	32.085	27.83	13.716
12	$C_{26}H_{28}$	12	26	8.89	450.7	4.41	19.198	34.875	30.25	15.677

This equation concern two important factors, i.e. Randić indices "χ" and maximum wave length (λ_{max}) in polyenes (I).

Similar to Fig.2, in Fig.3 could see a curve among the values of Randić indices "χ" and ΔE. For calculation the values of ΔE could utilize Plank's formula or Eq.14. As could see in Eq.14, two important factors, i.e. Randić indices "χ" and ΔE in polyenes (I) were concerned.

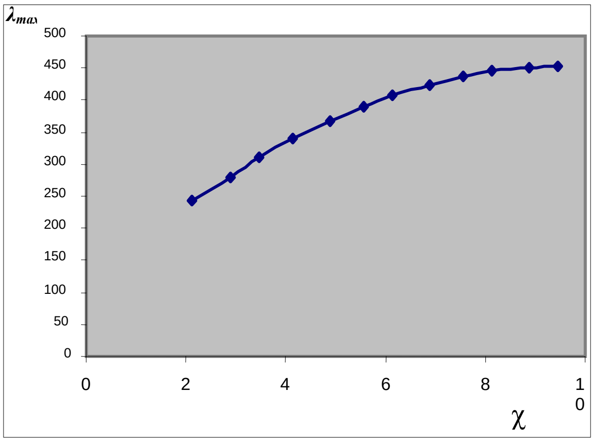


Fig.2. A plot of the Randić indices (χ) versus the maximum wave length (λ_{max} in nm) of simple linear polyenes (I).

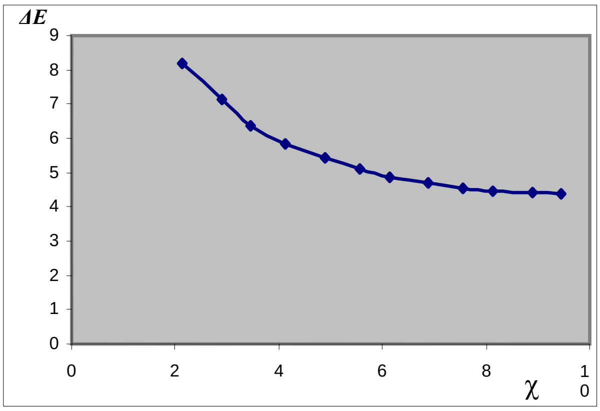


Fig.3. A plot of the Randić indices (χ) versus the ΔE (in Joul x10^{-19}) of simple linear polyenes (I).

As shown in Fig.4, there is a good linear correlations between Randic indices and the effective length of electron moving in the linear simple conjugated polyene compounds (I) according the one-dimensional box model (l_e). The high correlation (r = 0.978) of "l_e" with Randić indices "χ" is evident from Fig.4.

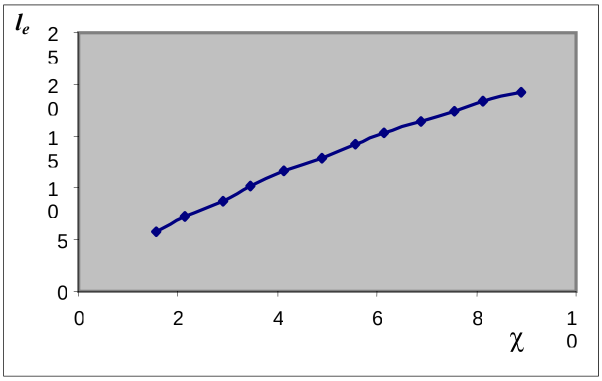


Fig.4. A plot of the Randić indices(χ) versus effective length of electron moving "l_e" (Å) in the linear simple conjugated polyene compounds (I).

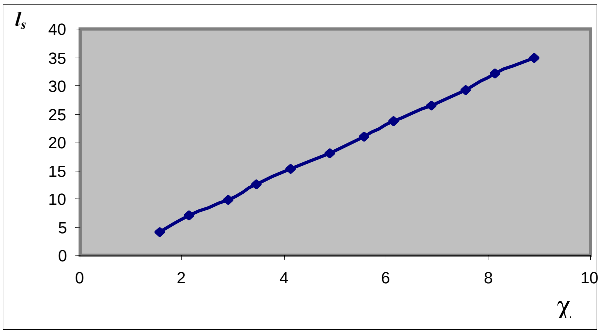


Fig.5. A plot of the Randić indices (χ) versus the summation of the carbon-carbon bond length "l_s" (Å) in the linear simple conjugated polyenes (I).

Fig.5 shows linear correlation of two values, i.e.: Randić indices (χ) and the summation of the carbon-carbon bond lengths "l_s". As shown in Fig.5, there is a good linear correlation (r = 0.993) among the values.

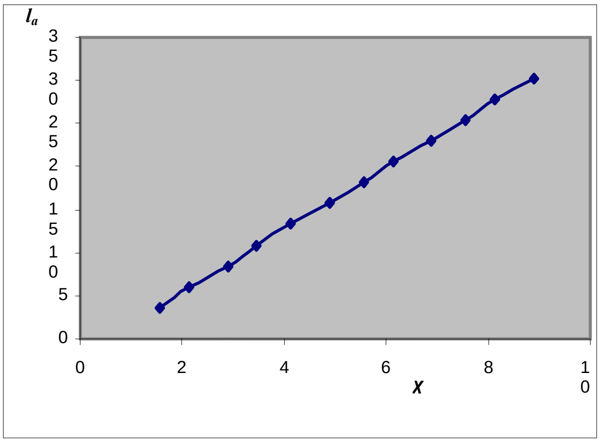


Fig.6. A plot of the Randić indices(χ) versus distances summation of the alternate carbon atoms "l_a" (Å) in the linear simple conjugated polyene compounds (I).

Fig.6 shows a plot of the Randić indices (χ) versus distances summation of the alternate carbon atoms "l_a" (Å) in the linear simple conjugated polyene compounds (I). Similar to Fig.4 and Fig.5, in Fig.6 a high correlation (r = 0.994) of "l_a" with Randić indices "χ" is evident.

In accordance with the data of Table1, except C_4H_6 from C_6H_8 to $C_{26}H_{28}$, in lieu of increasing each C=C bond in the linear simple conjugated polyenes (I) the differences of "l_s" and "l_e" ($\Delta l=|l_s-l_e|$) are increased. An important point in this series is that, by increasing the chain of family (I) the "Δl" shows greater values.

Diagram 1 shows combination of the relative values of HOMO-LUMO orbitals level ($\Delta E= hc/\lambda_{max}$), "$l_s$" and "$l_e$". As we could see in diagram1 and Table1, by increasing λ_{max} and decreasing ΔE, the values of "l_s", "l_e" and also $\Delta l=|l_s-l_e|$ were increased from C_6H_8 to $C_{26}H_{28}$. Although, the values of "l_a" are more near than "l_s" to "l_e", but the main consideration is focused on "l_s" and "l_e".

In accordance with the experimental and calculated values of ΔE and λ_{max}, it seems that, the movement of electron in a one-dimensional box model such as polyenes (I) is occurred in the effective length of electron moving "l_e" (Å) in the linear simple conjugated polyene compounds (I).

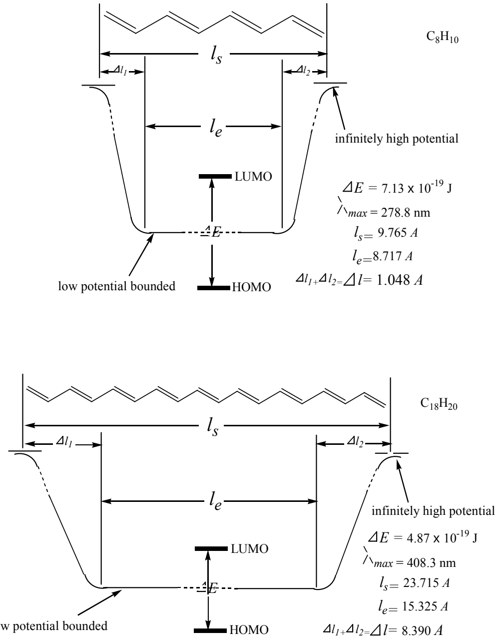


Diagram 1. The hypothetical correlation diagram of HOMO-LUMO orbitals level ($\Delta E= hc/\lambda_{max}$), "$l_s$", "$l_e$" and $\Delta l=|l_s-l_e|$ of polyenes (I).

The values of "l_e" are shorter than the summation of the carbon-carbon bond lengths "l_s". These results is agree with the values of ΔE, λ_{max} and one-dimensional box model in (I).See diagram 1.

On the other hand, according to the above mentioned, it is proposed that the motion of electron by the use of 1-D box model, occurs in the region shorter than the length of carbon-carbon chain in polyenes (I).

In C_4H_6, the "l_e" was obtained more than "l_s". Perhaps in C_4H_6 the time average motion of electron in the length "l_e" is not equal to the time of electron excitation from HOMO to LUMO. In another word, after exciting the electron from HOMO to LUMO, the electron could locomotion in the length of the chain of molecule (I) and the length for moving of electron according to the 1-D box model, is more than the length of carbon skeletal of C_4H_6. It seems that "l_e" is longer than "l_s". However, in agree with 1-D box model, ΔE and λ_{max} values the electron as a particle could move with a traffic behavior in longer region than the length of chain (l_s) in C_4H_6. But, there are enough spaces for decreasing the "l_e" in comparison with "l_s" in the longer polyenes (I).

CONCLUSION

The topological Resonance of simple linear polyenes scheme rests on the formalism of graph theory.A characteristic polynomial is constructed for the reference structure with the graphs for the given molecule taken into account. In this study, the structural relationship between Randić indices (χ), λ_{max} , ΔE, "l_a" (distances summation of the alternate carbon atoms), "l_s" (the summation of the carbon-carbon bond length) and "l_e" (the effective length of the electron moving) of linear simple conjugated polyene compounds (I) were presented and discussed. The calculations of λ_{max} and ΔE of compounds (I) are based on the concerning of these values and Randić indices. According to the results of one-dimensional box model, it is proposed that except C_4H_6, the motion of electron, occurs in the region shorter than the length of carbon-carbon chain in polyenes (I).

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