http://dx.doi.org/10.5012/bkcs.2014.35.5.1413

TG Index, its Graphical Matrix Representation and Application on Polyenes

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Received October 8, 2013, Accepted January 21, 2014

A novel topological index (TG Index) has been introduced. The graphical matrix representation of the TG index includes the use of directed subgraphs for the first time in graph theory literature. The application of the TG index on certain properties of polyenes yielded very well correlation data.

Key Words : Topological indices, TG index, Graphical matrices, Polyenes, λ_{max}

Introduction

Numerical descriptors, beginning with Wiener,[1,2] and then named topological indices by Hosoya,[3] have gained gradually increasing importance along with other descriptors for use in quantitative structure property and activity relationships (QSAR and QSPR) studies. Being able to estimate the physical or chemical properties of a yet nonexistent substance as close as possible is very important due to huge consumption of time and money upon direct synthesis.

Although, there have been almost hundred topological indices so far in the chemical graph theory literature. Construction of novel molecular descriptors or topological indices has still been a chalenging subject in the area of chemical graph theory since, there is no universal numerical descriptor, in order to develop good enough quantitative structure property/activity relationships for as many properties of the chemical structures as possible. The requirement for the use of *ad hoc* combinations for many molecular descriptors makes their formulation complicated and difficult to handle.

The present research has emerged with the idea to develop a novel topological index with the desired features. The calculation of the TG Index is quite simple besides it comprises the most important graph theoretical terms, adjacency and connectivity together with the application of the T(A) graphs.[4,5] The other objectives for a good topological index are that, it should be unique for each and every molecule and correlate well with the properties of the applied molecules so that it can be used to predict the desired properties of the yet nonexistent compounds.

The TG Index

In the present study, a research has been performed to investigate a novel topological index. TG Index (Türker-Gümüş Index) is a novel topological index developed by Türker and Gümüş which is constructed on the basis of T(A) graphs. Moreover, the calculation of the topological index makes use of the concepts of both, the connectivity (branching) which was introduced by Randic,[6] and the path distances, introduced by Wiener.[2,7]

However, the application of the T(A) graphs in the case of the TG index is somewhat different from the original.[4,5] T(A) graphs, have been drawn and used to predict some properties of the completely conjugated systems. Nevertheless, it has been shown here that T(A) graphs can be exerted to all kinds of molecules independent from being totally conjugated, saturated or unsaturated. In fact, it can be implemented on both hydrocarbons and heteroatom containing species.

The TG index is defined by the following equation;

$$TG = \left(\sum_{i}^{N} \sum_{j}^{N} D_{ij}^{*} \right) \left(\sum_{i}^{N} \sum_{j}^{N} D_{ij}^{o} \right)$$

The calculation of the index is based on a novel type of matrix presently introduced that is the distance-degree matrix (D_{ij}). This matrix represents the connectivity in the structure under consideration, so that the distance between the vertices as well as the degrees of the vertices in the parent structure are taken into account.

The calculation of the topological index is presented by an example in Figure 1. One can calculate the index by following the required steps;

a) Consider a hydrogen-depleted molecular graph (A).

b) Star the molecule alternatingly (as in the case of alternant hydrocarbons).

c) Obtain $T(A^{*})$ and T(A°) graphs by connecting the started atoms and non-stared atoms for $T(A^{*})$ and T(A°), respectively, as shown in Figure 1, (the number of self loops is determined by the degree of the corresponding vertex in the original graph (A)).

d) Number the vertices of the newly obtained $T(A^{*})$ and T(A°) graphs.

e) Construct the distance-degree matrix (This is a newly developed matrix which has not been pronounced in the literature up to date.), for both $T(A^{*})$ and T(A°) graphs as follows;

$$D^{*} = \begin{bmatrix} l_{11}d_1 & l_{12}d_2 & l_{13}d_3 & l_{14}d_4 & l_{15}d_5 \\ l_{21}d_1 & l_{22}d_2 & l_{23}d_3 & l_{24}d_4 & l_{25}d_5 \\ l_{31}d_1 & l_{32}d_2 & l_{33}d_3 & l_{34}d_4 & l_{35}d_5 \\ l_{41}d_1 & l_{42}d_2 & l_{43}d_3 & l_{44}d_4 & l_{45}d_5 \\ l_{51}d_1 & l_{52}d_2 & l_{53}d_3 & l_{54}d_4 & l_{55}d_5 \end{bmatrix} \quad D^{o} = \begin{bmatrix} l_{11}d_1 & l_{12}d_2 & l_{13}d_3 \\ l_{21}d_1 & l_{22}d_2 & l_{23}d_3 \\ l_{31}d_1 & l_{32}d_2 & l_{33}d_3 \end{bmatrix}$$

Since the distance between the same atom is zero, all the diagonal elements of the matrix should be zero by definition, independent from the degree of that vertex.

f) The elements of the matrix are obtained numerically as follows; Considering the D_{35} element of the matrix,

$D_{35} = l_{35}$ (the distance between 3 and 5) $\times$ d_5 (the degree of 5) = 1 $\times$ 1 = 1

g) Sum all the elements of the each matrix to obtain

$$\sum_{i}^{N}\sum_{j}^{N} D^{*}_{ij} \text{ and } \sum_{i}^{N}\sum_{j}^{N} D^{o}_{ij}$$

Summation of half or all of the matrix elements has been frequently pronounced in the literature.[2,7,8]

h) Use the equation above to calculate the TG index for compound A.

The construction of the T(A) graphs during the formulation of the TG index makes it quite different from previously published indices. The physical meaning behind this lays on the success of the T(A) graphs for the prediction of isospectral graphs.[5]

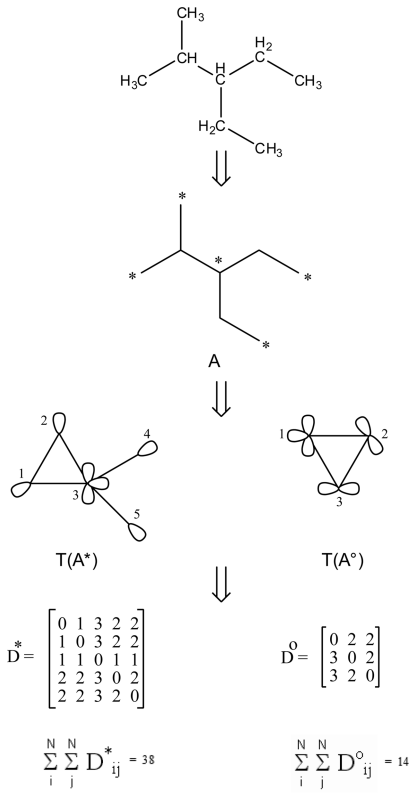


Figure 1. Illustration of how to calculate the TG index.

Graphical Matrices And The TG Index

Apart from the most popular matrices (adjacency and distance matrices) constructed by numbers related to the chemical structure, there exist graphical matrices whose elements are subgraphs of the main graph rather than numbers.

The concept of graphical matrices for the representation of molecular structures in chemistry is relatively new. Randic and co-workers introduced the first graphical matrix in 1997[9] whose elements were subgraphs made up of all the shortest paths joining vertices i and j. Since then, Randic *et al.*,[10] and Nikolic *et al.*[11,12] published their works on the subject. The idea of the necessity for the construction of the graphical matrices lies on the fact that, either, they allow the production of various novel numerical descriptors or representation of the well-known topological indices.[11,12]

The graphical matrices described up to date were all symmetrical along the matrix diagonal, therefore, drawing of either part of the graphical matrix was sufficient for the representation of the graph and the corresponding molecular structure. However, in the present case, we are reporting a

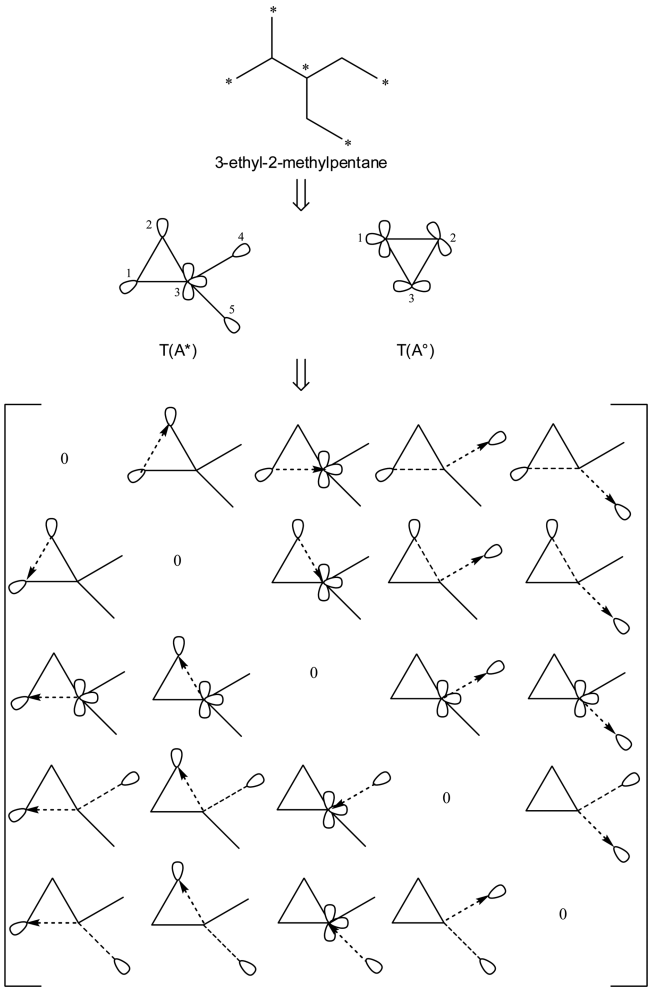


Figure 2. The graphical matrix representation of TG index. This is the graphical matrix representation for T(A*) graph of 3-ethyl-2-methylpentane.

novel type of graphical matrix whose elements are all "directed subgraphs". Hence, half-construction of the graphical matrix is not just enough, instead the complete construction of the matrix is necessary (see Figure 2).

In Figure 2, the graphical matrix representation of the TG index for 3-ethyl-2-methylpentane has been illustrated. For convenience, only the degrees of the related vertices have been indicated. The graphical form of the distance-degree matrix makes it easier to construct the numerical matrix. Therefore, for the calculation of the TG index of large systems where there is a possibility of making a mistake, it is first preferable to form the graphical representation and then reform the distance-degree matrix with numbers.

Application of the TG Index on Polyenes

Linear polyenes were first prepared and studied spectroscopically in 1930s. Their spectral properties had an important influence on the early history of molecular orbital theory. The major spectral feature of these molecules is a strongly allowed singlet-singlet transition in the near ultraviolet or visible region of the spectrum. Much of the interest has developed from a desire to understand the spectral and photochemical properties of the visual pigments.[13-16] Most of the spectral studies concentrated on the calculation or measurement of λ_{max} (maximum wavelength)[16] and $\Delta\varepsilon$ (HOMO-LUMO gap) which is very closely relevant to it. λ_{max} is one of the most important properties of such conjugated compounds since they exist as embedded in the chemical structures of some natural products.

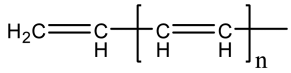
In the present work, we have considered simple linear polyenes (Figure 3) in terms of total electronic energy, HOMO, LUMO, $\Delta\varepsilon$ and λ_{max}.

The geometry optimizations of all the structures leading to energy minima were achieved by using B3LYP/6-31G(d,p) methods.[17,18] The vibrational analyses were done by using the same basis set employed in the corresponding geometry optimizations. The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface.

The B3LYP/6-31G(d,p) optimizations have been performed on Spartan 06[19] package programs, respectively.

The topological indices (TG Index) for the series of polyenes (n = 1-12) have been calculated as described before. An example of that is also presented for 1,3,5,7-octatetraene in Figure 4.

Note that T(A*) graph is just the same with T(A°) graph



n = 1, 2, ..., 12

Figure 3. General scheme for the polyenes investigated in this study.

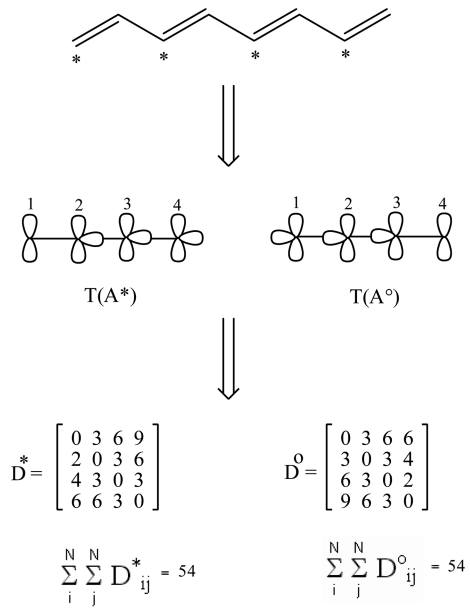


Figure 4. Calculation of the TG Index for 1,3,5,7-octatetraene.

for a symmetrical molecule with opposite numbering and thus, the sum of the elements of the distance-degree matrix yields the same score. When symmetrical compounds are under consideration, it is simply enough to draw one of the T(A) graphs and construct the distance-degree matrix. The sum of the elements of the corresponding T(A) graph should be squared to come up with the TG Index.

The TG Indices, data obtained from the computational calculations and the λ_{max}[16] values have been tabulated in Table 1.

Tha data in Table 1 demonstrate that the TG Indices, total energies (absolutely), heat of formations (obtained from PM3 calculations), lowest occupied molecular orbital energy (LUMO, absolutely) and λ_{max} values increase, whereas the highest occupied molecular orbital energy (HOMO, absolutely) and the interfrontier energy gap ($\Delta\varepsilon = \varepsilon_{LUMO}$-

Table 1. The TG Index, total energy (in Hartree), heat of formation (ΔH_f in kcal/mol), HOMO (eV), LUMO (eV), $\Delta\varepsilon$ (eV) and λ_{max} (nm) data [16] for polyene series considered in this report

n	TG	Total Energy	ΔH_f	HOMO	LUMO	$\Delta\varepsilon$	λ_{max}
1	25	–156.0017	30.91	–6.25	–0.64	5.61	203.2
2	441	–233.4113	44.88	–5.71	–1.23	4.48	242.7
3	2916	–310.8216	58.76	–5.38	–1.59	3.79	278.8
4	12100	–388.2322	72.63	–5.15	–1.83	3.32	311.5
5	38025	–465.6430	86.49	–4.98	–2.01	2.98	340.8
6	52900	–543.0538	100.35	–4.86	–2.14	2.72	366.7
7	151321	–620.4647	114.22	–4.76	–2.24	2.52	389.2
8	356409	–697.8757	128.08	–4.68	–2.33	2.36	408.3
9	736164	–775.2867	141.94	–4.62	–2.39	2.22	424.0
10	1600225	–852.6968	155.80	–4.48	–2.56	1.93	436.3
11	2722500	–930.1075	169.66	–4.37	–2.67	1.70	445.2
12	4435236	–1007.5182	183.52	–4.34	–2.83	1.50	450.7

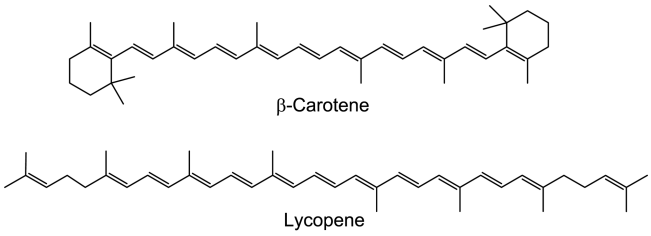


Figure 5. Chemical structures of β-Carotene (red-orange, λ_{max} = 497 nm) and Lycopene (bright red, λ_{max} = 505 nm). Both have 11 conjugated double bonds.

Table 2. The results of the correlation analysis between the TG index and certain properties of polyenes (all with 12 entries)

Property	regression equation	R^2
Total energy	y = 0.1574x + 4.5159	0.9969
ΔH_f	y = 0.1508x + 2.9077	0.9966
HOMO	y = 0.1547x – 6.6498	0.9901
LUMO	y = –0.1703x – 0.183	0.9905
$\Delta\varepsilon$	y = –0.325x + 6.4669	0.9910
λ_{max}	y = 22.331x + 114.83	0.9854

ε_{HOMO}) decrease with molecular size of the polyenes.

The results of the correlation analyses of ln(TG) with ln(Total energy), ln(ΔH_f), ε_{HOMO}, ε_{LUMO}, $\Delta\varepsilon$ and λ_{max} has been given in Table 2. As the correlation data indicate, all the properties considered here correlate very well with the TG index, which evidences that the TG index contains valuable structural information. Therefore, it can be regarded as successful so that the correlation equations can be extrapolated for the prediction of the properties of unknown polyenes or natural products that possess polyene moieties embedded in their structures such as β-Carotene and Lycopene (Figure 5). When the regression equation for the correlation of λ_{max} with the TG index has been used, we obtained 487 nm for β-Carotene and 513 nm for Lycopene. The deviations from the experimental data are –2.01% and 1.58%, respectively, which can be considered as quite acceptable.

Conclusion

In the present paper, a novel topological index has been introduced together with its graphical matrix representation. Directed subgraphs have been used during the construction of the graphical matrix for the first time in the chemical graph theory literature. The application of the index on the polyenes yielded very well correlation data.

Acknowledgments. Publication cost of this paper was supported by the Korean Chemical Society.

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