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Superaugmented Pendentic Indices: Novel Topological Descriptors for QSAR/QSPR

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Abstract

Four pendenticity based topological descriptors termed as superaugmented pendentic indices have been conceptualized in the present study. An in-house computer program was utilized to compute index values of all the possible structures (with at least one pendent vertex) containing four, five and six vertices. The sensitivity towards branching, discriminating power, degeneracy and mathematical properties of the proposed superaugmented pendentic indices were investigated. All the four proposed indices exhibited exceptionally high sensitivity towards branching, high discriminating power and extremely low degeneracy. Superaugmented pendentic index-4 ($^{SA}\int^{P}$-4) exhibited exceptionally high discriminating power of 114 in structures containing only six vertices. Statistical significance of the proposed indices was investigated using intercorrelation analysis with Wiener's index, Balaban's mean square distance index, molecular connectivity index, Zagreb indices (M_1 and M_2), superpendentic index and eccentric connectivity index. The exceptionally high sensitivity towards branching, high discriminating power amalgamated with extremely low degeneracy offer proposed indices a vast potential for isomer discrimination, similarity/dissimilarity, drug design, quantitative structure-activity/structure-property relationships, lead optimization and combinatorial library design.

Keywords

Wiener's index • Balaban's mean square distance index • Molecular connectivity index • Zagreb indices (M_1 and M_2) • Eccentric connectivity index • Superpendentic index

Introduction

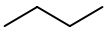
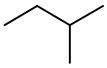
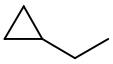
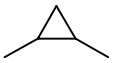
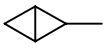
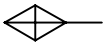
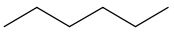
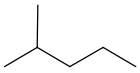
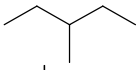
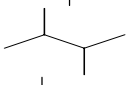
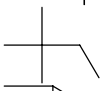
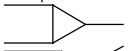
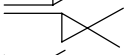
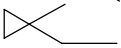
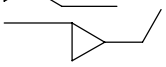
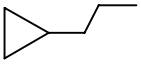
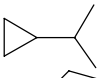
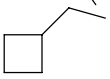
In the recent years, “Graph Theory” has been applied in an automated computer treatment of chemical structures and QSAR [1]. In chemical graph theory, molecular structures are represented by hydrogen suppressed graphs (commonly known as molecular graphs) in which vertices represent the atoms and bonds are represented by edges. The connection between atoms can be described by various types of topological matrices, which can be mathematically manipulated so as to derive a single number, usually known as graph invariant, graph-theoretical index or topological index (TI) [2]. Topological indices (TIs) are widely used as structural descriptors in QSPR/QSAR models [3]. Moreover, novel strategies are being adopted for continuous search and development of TIs [4]. During recent years, significant progress has been reported in the development of various topological, geometric, electrostatic, and quantum chemical indices as molecular descriptors. Because of the simplicity of topological structural representation, these TIs are sometime preferred over more complex geometric, electrostatic, and quantum chemical descriptors, especially in those cases where their use significantly reduces the computation time [5]. The pharmaceutical industry contributed towards increased interest in molecular descriptors because of the necessity to reduce the expenditure involved in synthesis, *in vitro*, *in vivo* and clinical testing of new medicinal compounds [6]. In recent years, a large number of topological indices have been reported and utilized for chemical documentation, isomer discrimination, study of molecular complexity, chirality, similarity/dissimilarity, QSAR/QSPR, drug design and database selection, lead optimization, rational combinatorial library design and for deriving multilinear regression models [2, 7, 8]. Estrada defined the paradigm of the use of TIs and molecular descriptors in general in QSAR studies as “it is desired to have as many molecular descriptor as possible at our disposition, but it is preferred to include as few of them as possible in the QSPR and QSAR models to be developed” [3].

In the present investigation, four pendenticity based topological descriptors termed as *superaugmented pendentic indices*, denoted by ${}^{SA}\int^{P}$ have been conceptualized and their mathematical properties studied. The sensitivity towards branching, discriminating power, degeneracy and intercorrelation of the proposed indices with regard to all the possible structures containing four, five and six vertices (with at least one pendent vertex) have been investigated.

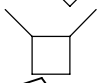
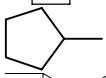
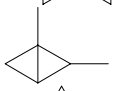
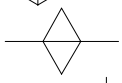
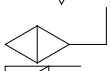
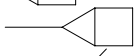
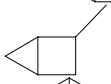
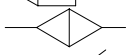
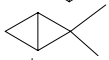
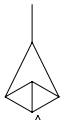
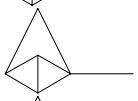
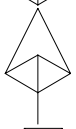
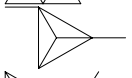
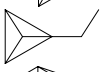
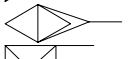
Results and Discussion

Topological descriptors have gained considerable popularity as these can be derived from molecular structures using low computational resources [9]. The use of TIs in the design and selection of novel active compounds is probably one of the most active areas of research in the application of such descriptors to biological problems [8]. In recent years a large number of topological indices have been reported and utilized for chirality, similarity/dissimilarity, QSAR/QSPR, drug design and database selection, lead optimization and for rational combinatorial library design. Though a large number of molecular descriptors of diverse nature have been reported in literature but only a small proportion of these descriptors have been successfully utilized in QSAR. As a consequence there is strong need to develop non-correlating topological indices with sensitivity towards branching, high discriminating power and extremely low degeneracy.

Tab. 1. Index values of *superaugmented pendentic indices* for all possible structures of four, five and six vertices containing at least one pendent vertex.

S.N.	Structure	$\int^{P}$	$^{SA}\int^{P-1}$	$^{SA}\int^{P-2}$	$^{SA}\int^{P-3}$	$^{SA}\int^{P-4}$
1		3.162	8.000	6.333	1.444	0.648
2		3.606	19.000	10.000	5.500	3.250
3		2.236	16.000	10.000	7.000	5.500
4		4.243	16.000	6.333	2.694	1.211
5		5.196	26.000	10.000	4.000	1.667
6		5.745	65.000	33.000	17.000	9.000
7		3.000	21.500	8.750	3.708	1.632
8		3.742	36.000	17.000	8.167	3.972
9		3.606	44.000	24.000	14.000	9.000
10		2.828	18.000	8.333	3.944	1.898
11		2.646	52.000	32.000	22.000	17.000
12		2.828	49.500	23.250	11.125	5.396
13		3.162	135.000	81.000	54.000	40.500
14		5.477	24.000	7.133	2.188	0.687
15		7.211	52.000	19.667	8.139	3.609
16		7.000	41.000	14.000	5.083	1.965
17		8.944	84.000	30.000	11.000	4.167
18		8.544	84.000	31.000	11.833	4.694
19		6.245	81.000	36.000	16.500	7.750
20		5.916	95.000	43.333	20.278	9.676
21		4.690	50.000	18.667	7.222	2.907
22		4.899	56.000	22.250	9.312	4.078
23		3.742	26.667	8.889	3.213	1.258
24		5.196	65.500	26.083	10.819	4.669
25		3.606	25.000	9.333	3.695	1.544

Tab. 1. (Cont.)

S.N.	Structure	$\int^{P}$	$^{SA}\int^{P-1}$	$^{SA}\int^{P-2}$	$^{SA}\int^{P-3}$	$^{SA}\int^{P-4}$
26		4.690	51.333	22.778	10.426	4.892
27		4.690	50.000	22.167	10.264	4.890
28		4.690	42.000	16.000	6.333	2.611
29		3.317	22.000	9.667	4.389	2.046
30		3.317	56.000	25.333	11.778	5.593
31		4.472	109.000	49.333	29.944	10.898
32		4.243	104.000	50.667	24.884	12.296
33		3.606	64.000	23.583	9.174	3.761
34		3.162	48.000	22.667	10.889	5.296
35		3.317	46.500	20.250	9.125	4.229
36		3.162	48.000	23.000	11.166	5.473
37		3.317	52.500	24.250	11.458	5.507
38		3.317	51.000	22.000	9.833	4.528
39		4.690	132.000	61.500	29.375	14.260
40		4.690	132.833	61.028	28.717	13.760
41		3.317	112.500	47.250	20.625	9.312
42		3.162	111.000	52.500	25.250	12.292
43		3.162	106.500	51.750	25.375	12.521
44		3.317	132.000	60.000	28.000	13.333
45		3.162	120.000	58.000	28.333	13.945
46		4.243	272.000	134.667	66.889	33.296
47		3.464	164.000	64.000	26.000	11.000
48		3.317	136.000	63.000	29.556	14.185
49		3.162	258.000	123.000	59.500	29.084
50		3.317	320.000	144.000	66.667	31.555
51		3.317	296.000	145.333	71.778	35.593
52		3.162	672.000	325.333	159.111	78.370

In the present study, four *superaugmented pendentic indices,* denoted by $^{SA}\int^{P}$, were conceptualized. These indices can be easily calculated from pendent matrix (Dp) and additive adjacency matrix (A^{α}). In the proposed TIs, simultaneous use of pendent-distance, degree of the vertices and eccentricity results in significant changes in the index value with a minor change in the branching of molecules.

As observed from Figure 1, the value of *superaugmented pendentic index-1* ($^{SA}\int^{P-1}$) changes by more than 4 times (from 16.0 to 65.0), the value of *superaugmented pendentic index-2* ($^{SA}\int^{P-2}$) changes by more than 5 times (from 6.333 to 33.0) and the value of *superaugmented pendentic index-3* ($^{SA}\int^{P-3}$) changes by more than 6 times (from 2.694 to 17.0) and the value of *superaugmented pendentic index-4* ($^{SA}\int^{P-4}$) changes by more than 7 times (1.211 to 9.0) following branching of five membered linear carbon structure. The *superaugmented pendentic index-4* was found to be about 2 times more sensitive to change in molecular structure when compared with *superaugmented pendentic index-1* for identical changes. These *superaugmented pendentic indices* were found to be far more sensitive towards branching using three isomers of pentane.

Researchers are striving hard to develop TIs with not only high discriminating power but also devoid of both degeneracy and correlation with existing TIs. The values of *superaugmented pendentic indices* were computed for all the possible structure of four, five and six vertices containing at least one pendent vertex using an in-house computer program. Various structures containing four, five and six vertices containing at least one pendent vertex and their corresponding index values have been presented in Table 1 whereas their comparison has been depicted in Table 2. *Superaugmented pendentic indices* have revealed high discriminating power. The discriminating power may be defined as the ratio of highest to lowest value for all possible structures of same number of vertices. The ratio of highest to lowest value for all possible structure containing six vertices with at least one pendent vertex was found to be 31 in case of *superaugmented pendentic index-1*, 46 in case of *superaugmented pendentic index-2*, 73 for *superaugmented pendentic index-3* and 114 for *superaugmented pendentic index-4* in comparison to 2.83 for $\int^{P}$. High discriminating power of the proposed indices renders them more sensitive to any change(s) in the molecular structure. Extreme sensitivity towards branching as well as exceptionally high discriminating power of all the four proposed indices is clearly evident from the respective index values (Table 1) of all the possible structures with four, five and six vertices containing at least one pendent vertex.

Degeneracy is the measure of ability of an index to differentiate between the relative positions of atom in a molecule. The *superaugmented pendentic index-2, superaugmented pendentic index-3* and *superaugmented pendentic index-4* did not exhibit any degeneracy for all possible structures with six vertices containing at least one pendent vertex, whereas the *superaugmented pendentic index-1* has very low degeneracy of five in case of all possible structures with six vertices containing at least one pendent vertex whereas The $\int^{P}$ had 22 same values out of 39 structures with all possible structures with six vertices containing at least one pendent vertex (Table 2). Extremely low degeneracy indicates the enhanced capability of these indices to differentiate and demonstrate slight variations in the molecular structure. This means that the likeliness of different structures to have same value is remote.

Intercorrelation analysis of the proposed four indices with other well-known indices revealed that *superaugmented pendentic indices* are not correlated with *Wiener's index* [10], *Balaban's mean square distance index* [11]*, molecular connectivity index* [12] and *eccentric connectivity index* [13] and superpendentic index [14] as well. Moreover, *superaugmented pendentic indices* are weakly correlated with *Zagreb indices* (M_1 and M_2) [15, 16]. These *superaugmented pendentic indices* describe the structural parameters in a different manner in comparison to other indices.

Tab. 2. Comparison of discriminating power and degeneracy of various *superaugmented pendentic* indices using all possible structures with four, five and six vertices containing at least one pendent vertex

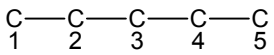
	$\int^P$	$^{SA}\int^{P-1}$	$^{SA}\int^{P-2}$	$^{SA}\int^{P-3}$	$^{SA}\int^{P-4}$
For Four Vertices					
Minimum value	2.236	8.000	6.333	1.444	0.645
Maximum Value	3.606	19.000	10.000	7.000	5.500
Ratio	1:1.61	1:2.370	1:1.580	1:4.850	1:8.490
Degeneracy	0/3	0/3	1/3	0/3	0/3
For Five Vertices					
Minimum value	2.646	16.000	6.333	2.694	1.211
Maximum Value	5.745	135.000	81.000	54.000	40.500
Ratio	1:2.17	1:8.440	1:12.790	1:20.040	1:33.440
Degeneracy	2/10	0/10	0/10	0/10	1/10
For Six Vertices					
Minimum value	3.162	22.000	7.133	2.188	0.687
Maximum Value	8.944	672.000	325.333	159.211	78.370
Ratio	1:2.83	1:30.540	1:45.610	1:72.760	1:114.080
Degeneracy	22/39	5/39	0/39	0/39	0/39

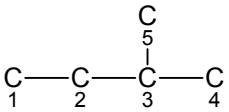
Degeneracy = Number of compounds having same values/Total number of compounds with same number of vertices

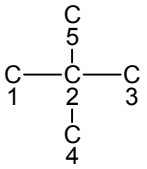
Tab. 3. Inter-correlation matrix

	W	**D**	χ	M_1	M_2	ξ^c	$\int^P$	$^{SA}\int^{P-1}$	$^{SA}\int^{P-2}$	$^{SA}\int^{P-3}$	$^{SA}\int^{P-4}$
W	1	0.731	0.840	0.114	0.141	0.661	0.511	0.017	-0.037	-0.086	-0.161
D		1	0.361	-0.477	-0.411	0.220	0.562	-0.356	-0.402	-0.447	-0.501
χ			1	0.545	0.588	0.918	0.077	0.295	0.253	0.213	0.146
M_1				1	0.983	0.545	-0.354	0.813	0.812	0.808	0.780
M_2					1	0.768	-0.403	0.796	0.791	0.783	0.753
ξ^c						1	-0.125	0.507	0.469	0.428	0.359
$\int^P$							1	-0.130	-0.170	-0.203	-0.243
$^{SA}\int^{P-1}$								1	0.996	0.983	0.943
$^{SA}\int^{P-2}$									1	0.994	0.965
$^{SA}\int^{P-3}$										1	0.965
$^{SA}\int^{P-4}$											1

Arbitrary Vertex numbering







Distance Matrices (D)

	1	2	3	4	5	e_i
1	0	1	2	3	4	4
2	1	0	1	2	3	3
3	2	1	0	1	2	3
4	3	2	1	0	1	3
5	4	3	2	1	0	4

	1	2	3	4	5	e_i
1	0	1	2	3	3	3
2	1	0	1	2	2	2
3	2	1	0	1	1	2
4	3	2	1	0	2	3
5	3	2	1	2	0	3

	1	2	3	4	5	e_i
1	0	1	2	2	2	2
2	1	0	1	1	1	1
3	2	1	0	2	2	2
4	2	1	2	0	2	2
5	2	1	2	2	0	2

Pendent Matrices (Dp)

	1	5	$p_{(ij)}$
1	0	4	4
2	1	3	3
3	2	2	4
4	3	1	3
5	4	0	4

	1	4	5	$p_{(ij)}$
1	0	3	3	9
2	1	2	2	4
3	2	1	1	2
4	3	0	2	6
5	3	2	0	6

	1	3	4	5	$p_{(ij)}$
1	0	2	2	2	8
2	1	1	1	1	1
3	2	0	2	2	8
4	2	2	0	2	8
5	2	2	2	0	8

Adjacency Matrices (A)

	1	2	3	4	5	v_i
1	0	1	0	0	0	1
2	1	0	1	0	0	2
3	0	1	0	1	0	2
4	0	0	1	0	1	2
5	0	0	0	1	0	1

	1	2	3	4	5	v_i
1	0	1	0	0	0	1
2	1	0	1	0	0	2
3	0	1	0	1	1	3
4	0	0	1	0	0	1
5	0	0	1	0	0	1

	1	2	3	4	5	v_i
1	0	1	0	0	0	1
2	1	0	1	1	1	4
3	0	1	0	0	0	1
4	0	1	0	0	0	1
5	0	1	0	0	0	1

Additive Adjacency Matrices (A^{α})

	1	2	3	4	5	m_i
1	0	2	0	0	0	2
2	1	0	2	0	0	2
3	0	2	0	2	0	4
4	0	0	2	0	1	2
5	0	0	0	2	0	2

	1	2	3	4	5	m_i
1	0	2	0	0	0	2
2	1	0	3	0	0	3
3	0	2	0	1	1	2
4	0	0	3	0	0	3
5	0	0	3	0	0	3

	1	2	3	4	5	m_i
1	0	4	0	0	0	4
2	1	0	1	1	1	1
3	0	4	0	0	0	4
4	0	4	0	0	0	4
5	0	4	0	0	0	4

Superaugmented Pendentic *Index-1*

$$^{SA}\int^{P\text{-}1} = \sum_{i=1}^{n}\sum_{j=1}^{n}\left(\frac{p_{(ij)} * m_i}{e_i}\right) = 16.0 \qquad = 26.0 \qquad = 65.0$$

Superaugmented Pendentic *Index-2*

$$^{SA}\int^{P\text{-}2} = \sum_{i=1}^{n}\sum_{j=1}^{n}\left(\frac{p_{(ij)} * m_i}{e_i^2}\right) = 6.333 \qquad = 10.0 \qquad = 33.0$$

Superaugmented Pendentic *Index-3*

$$^{SA}\int^{P\text{-}3} = \sum_{i=1}^{n}\sum_{j=1}^{n}\left(\frac{p_{(ij)} * m_i}{e_i^3}\right) = 2.694 \qquad = 4.0 \qquad = 17.0$$

Superaugmented Pendentic *Index-4*

$$^{SA}\int^{P\text{-}4} = \sum_{i=1}^{n}\sum_{j=1}^{n}\left(\frac{p_{(ij)} * m_i}{e_i^4}\right) = 1.211 \qquad = 1.667 \qquad = 9.0$$

Fig. 1. Calculation of values of *superaugmented pendentic* index-1 ($^{SA}\int^{P\text{-}1}$), *superaugmented pendentic* index-2 ($^{SA}\int^{P\text{-}2}$), *superaugmented pendentic* index-3, ($^{SA}\int^{P\text{-}3}$), *superaugmented pendentic* index-4, ($^{SA}\int^{P\text{-}4}$) for three isomer of pentane.

Theoretical

Calculation of Topological Indices

Pendenticity based topological indices termed as *superaugmented pendentic* indices i.e. *superaugmented pendentic index*-1 ($^{SA}\int^{P\text{-}1}$), *superaugmented pendentic index*-2 ($^{SA}\int^{P\text{-}2}$), *superaugmented pendentic index*-3 ($^{SA}\int^{P\text{-}3}$), *superaugmented pendentic index*-4 ($^{SA}\int^{P\text{-}4}$) have been developed in the present study.

Throughout, let G = (V, E) be a simple connected graph with vertex set V = $\{v_1, v_2, \ldots\ldots, v_n\}$ and edge set E. Let d_i be the degree of vertex v_i for i = 1, 2, …..,n and Δ, the highest degree of a graph G. Denote by i ~ j, vertices v_i and v_j are adjacent. For two vertices v_i and v_j ($i \neq j$), d (i, j), the topological distance between v_i and v_j is the number of edges in a shortest path joining v_i and v_j. The diameter of a graph is the maximum distance between any two vertices of G. The graphs having at least one pendent vertex were denoted by $G_{k,n}$, where k ($k \geq 1$) is the number of pendent vertices and n (> 4) is the order of the graph.

Superpendentic index ($\int^{p}$):

The *superpendentic index*, denoted by $\int^{P}$, is defined as square root of the sum of products of non-zero row elements in the pendent matrix in the hydrogen suppressed molecular graph [14]. It is expressed as,

$$\int P(G) = \left(\sum_{i=1,j=1}^{n,m} \prod d(v_i, v_j) \right)^{1/2} \quad (1)$$

where *m* and *n* are maximum possible number of *i* and *j* respectively. For a molecular graph (*G*) if $v_1, v_2, \ldots, v_n$ are its vertices. Then, the topological distance $d(v_i, v_j \mid G)$ between the vertices v_i and v_j of *G* is length of the shortest path connecting v_i with v_j.

A pendent vertex is defined as a vertex of degree one or an endpoint. The eccentricity e_i of a vertex v_i in *G* is the length of shortest path from v_i to the vertex v_j that is farthest from v_i (e_i = max d (v_i, v_j; *j* / *G*) [16].

*Superaugmented pendentic index-**1**:*

The *superaugmented pendentic index-1*, denoted by ${}^{SA}\int^{P-1}$, is defined as the summation of quotients, of the product of non-zero row elements in the pendent matrix and product of adjacent vertex degrees; and eccentricity of the concerned vertex, for all vertices in the hydrogen suppressed molecular graph. It is expressed as,

$${}^{SA}\int^{P-1}(G_{k,n}) = \sum_{i=1}^{n} \frac{p_i m_i}{e_i}, \quad (2)$$

where $p_i = \prod_{j:\, dj=1; p_{ij} \neq 0} p_{ij}$, $m_i = \prod_{j:j\sim i} d_j$, and p_{ij} is the length of the path that contains the least number of edges between vertex v_i and vertex v_j in graph $G_{k,n}$, m_i is the product of degrees of all the vertices (v_j), adjacent to vertex *i and can be easily obtained by multiplying all the* non-zero row elements in additive adjacency matrix, d_i is the degree of the vertex v_i, e_i is the eccentricity of vertex v_i.

*Superaugmented pendentic index-**2**:*

The *superaugmented pendentic index-2*, denoted by ${}^{SA}\int^{P-2}$, is defined as the summation of quotients, of the product of non-zero row elements in the pendent matrix and product of adjacent vertex degrees; and squared eccentricity of the concerned vertex, for all vertices in the hydrogen suppressed molecular graph. It is expressed as,

$${}^{SA}\int^{P-2}(G_{k,n}) = \sum_{i=1}^{n} \frac{p_i m_i}{e_i^2}, \quad (3)$$

where $p_i = \prod_{j:\, dj=1; p_{ij} \neq 0} p_{ij}$, $m_i = \prod_{j:j\sim i} d_j$, and p_{ij} is the length of the path that contains the least number of edges between vertex v_i and vertex v_j in graph $G_{k,n}$, m_i is the product of degrees of all the vertices (v_j), adjacent to vertex *i and can be easily obtained by*

multiplying all the non-zero row elements in additive adjacency matrix, d_i is the degree of the vertex v_i, e_i is the eccentricity of vertex v_i.

*Superaugmented pendentic index**-3:***

The *superaugmented pendentic index-3*, denoted by ${}^{SA}\int^{P-3}$, is defined as the summation of quotients, of the product of non-zero row elements in the pendent matrix and product of adjacent vertex degrees; and cubic eccentricity of the concerned vertex, for all vertices in the hydrogen suppressed molecular graph. It is expressed as,

$$ {}^{SA}\int^{P-3}(G_{k,n}) = \sum_{i=1}^{n} \frac{p_i m_i}{e_i^3}, \qquad (4) $$

where $p_i = \prod_{j:dj=1; p_{ij}\neq 0} p_{ij}$, $m_i = \prod_{j:j\sim i} d_j$, and p_{ij} is the length of the path that contains the least number of edges between vertex v_i and vertex v_j in graph $G_{k,n}$, m_i is the product of degrees of all the vertices (v_j), adjacent to vertex *i and can be easily obtained by multiplying all the* non-zero row elements in additive adjacency matrix, d_i is the degree of the vertex v_i, e_i is the eccentricity of vertex v_i.

*Superaugmented pendentic index**-4:***

The *superaugmented pendentic index-4*, denoted by ${}^{SA}\int^{P-4}$, is defined as the summation of quotients, of the product of non-zero row elements in the pendent matrix and product of adjacent vertex degrees; and fourth power of eccentricity of the concerned vertex, for all vertices in the hydrogen suppressed molecular graph. It is expressed as,

$$ {}^{SA}\int^{P-4}(G_{k,n}) = \sum_{i=1}^{n} \frac{p_i m_i}{e_i^4}, \qquad (5) $$

where $p_i = \prod_{j:dj=1; p_{ij}\neq 0} p_{ij}$, $m_i = \prod_{j:j\sim i} d_j$, and p_{ij} is the length of the path that contains the least number of edges between vertex v_i and vertex v_j in graph $G_{k,n}$, m_i is the product of degrees of all the vertices (v_j), adjacent to vertex *i and can be easily obtained by multiplying all the* non-zero row elements in additive adjacency matrix, d_i is the degree of the vertex v_i, e_i is the eccentricity of vertex v_i.

Superaugmented pendentic indices (${}^{SA}\int^{P}$) can be easily calculated from pendent matrix (Dp) and additive adjacency matrix (A^{α}) obtained by modifying distance matrix (D) and adjacency matrix (A), respectively. Pendent matrix (Dp) of a graph *G* is a sub-matrix of distance matrix (D) obtained by retaining the columns corresponding to pendent vertices. The additive adjacency matrix (A^{α}) is obtained from adjacency matrix by substituting the degree of corresponding vertex (of the vertices adjacent to vertex *i*) of a molecular graph *G*. The product of the non-zero row elements in additive adjacency matrix represents the m_i. Calculation of *superaugmented pendentic index-1* (${}^{SA}\int^{P-1}$), *superaugmented pendentic index-2* (${}^{SA}\int^{P-2}$), *superaugmented pendentic index-3* (${}^{SA}\int^{P-3}$) and *superaugmented pendentic index-4* (${}^{SA}\int^{P-4}$) for three isomer of pentane has been exemplified in Fig.1.

The sensitivity of *superaugmented pendentic indices* to branching was investigated using three isomers of pentane (Fig. 1). Discriminating power and degeneracy of the *superaugmented pendentic indices* were investigated using all possible structures with four, five and six vertices containing at least one pendent vertex (Table 1) and compared for discriminating power and degeneracy (Table 2).

The intercorrelation of four proposed *superaugmented pendentic indices* with *Wiener's index* (W), *Balaban's mean square distance index* (D), *molecular connectivity index* (χ), *Zagreb indices* (M_1 and M_2), superpendentic index ($\int^P$), and *eccentric connectivity index* (ξ^c) was investigated (Table 3). This intercorrelation has been determined with respect to index values of all possible structures containing four, five and six vertices (with at least one pendent vertex). The degree of correlation was appraised by the correlation coefficient r. Pairs of indices with r ≥ 0.97 are considered highly inter-correlated, those with 0.90 ≤ r ≤ 0.97 are appreciably correlated, those with 0.50 ≤ r ≤ 0.89 are weakly correlated and finally the pairs of indices with low r-values (< 0.50) are not inter-correlated [17].

Properties on Superaugmented Pendentic Indices of Graphs

Here we study *superaugmented pendentic index*-1 of graph $G_{k,n}$, denoted by ${}^{SA}\int^{P-1}(G_{k,n})$ and defined as

$$ {}^{SA}\int^{P-1}(G_{k,n}) = \sum_{i=1}^{n} \frac{p_i m_i}{e_i}, \qquad (2) $$

where $p_i = \prod_{j:dj=1;p_{ij}\neq 0} p_{ij}$, $m_i = \prod_{j:j\sim i} d_j$, and p_{ij} is the length of the path that contains the least number of edges between vertex v_i and vertex v_j in graph $G_{k,n}$, d_i is the degree of the vertex v_i, e_i is the eccentricity of vertex v_i.

Denote star $K_{1,n-1}$, and path P_n. Now we calculate ${}^{SA}\int^{P-1}$ for star $K_{1,n-1}$, and path P_n ($n > 3$):

$$ {}^{SA}\int^{P-1}(K_{1,n-1}) = \underbrace{2^{(n-3)}(n-1) + 2^{(n-3)}(n-1) + ...2^{(n-3)}(n-1)}_{n-1} + 1 $$

$= 2^{(n-3)}\,(n-1)^2 + 1.$

$$ {}^{SA}\int^{P-1}(P_n) = 2+2+2.4+3.4+.....+\left(\left[\frac{n-1}{2}\right]-1\right).4+\left[\frac{n-1}{2}\right].4+\left[\frac{n-1}{2}\right].4+\left(\left[\frac{n-1}{2}\right]-1\right).4+.....+3.4+2.4+2+2 $$

if n is even

$= n(n-2)$ if n is even.

$$ {}^{SA}\int^{P-1}(P_n) = 2+2+2.4+3.4+4.4+.....+\left(\left[\frac{n-1}{2}\right]-1\right).4+\left[\frac{n-1}{2}\right].4+\left(\left[\frac{n-1}{2}\right]-1\right).4+.....+3.4+2.4+2+2 \text{ if } n $$

is odd

$= (n-1)^2$ if n is odd.

Suppose that vertices v_i, i=1, 2, ……,*k* are pendent vertices and vertex v_n is the highest degree vertex corresponding degree Δ in $G_{k.n}$. Let v1 be only one pendent vertex in $G_{1,n}$, and we define $p_1 = 1$ in $G_{1,n}$. Denote by $H_{1,n}$, which is constructed by the complete graph K_{n-1} of order *n*-1 with one pendent vertex. Now we calculate $(H_{1,n}) \rightarrow {}^{SA}\int^{P-1} (H_{1,n})$:

$$(H_{1,n}) = \frac{1}{2}(n-1) + (n-2)^{n-2} + \underbrace{(n-2)^{n-3}(n-1) + (n-2)^{n-3}(n-1) + ...(n-2)^{n-3}(n-1)}_{n-2}$$

$$= \frac{1}{2}(n-1) + n(n-2)^{n-2}.$$

Lemma 1.1. *If $a_1, a_2, ……...,a_n$ are positive numbers, then:*

$$\left(\frac{a_1 + a_2 + ... + a_n}{n}\right)^n \geq a_1 a_2 .....a_{n.}$$

Equality holds if and only if $a_1 = a_2 = ……...=a_n$.

Theorem 1.2. *Let T be a tree of order n with k pendent vertices. Then*

$$^{SA}\int^{P-1}(T) \leq k\Delta D^{k-2} + (n-k)(D-1)^{k-1}\mu^{\Delta}, \qquad (6)$$

where μ is the maximum average degree of all non-pendent vertices and D is the diameter of T. *Moreover, the equality holds in (6) if and only if T is a star $K_{1, n-1}$.*

Proof: First let v_i, i=1, 2,……,*k* be the pendent vertices of tree *T*. Also let μ_i be the average degree of the vertices adjacent to vertex v_i, that is, $\mu_i = \frac{\sum_{j:j\sim i} d_j}{d_i}$, and let μ be the maximum average degree of all non-pendent vertices. For i = *k* + 1, *k* + 2,……..,*n*;

$$m_i = \prod_{j:j\sim i} d_j,$$

$$\leq \left(\frac{\sum_{j:j\sim i} d_j}{d_i}\right)^{d_i}, \text{ by Lemma 1.1}$$

$$\leq \mu_i^{\Delta} \leq \mu^{\Delta}, by \mu_i \leq \mu, d_i \leq \Delta. \qquad (7)$$

For any *i*, we have

$D \geq e_i \geq d(i, j)$ for all v_j.

Using this we have

$$P_i/e_i \leq D^{k-2}, \text{ and } m_i \leq \Delta \text{ for } i = 1,2,……,k. \qquad (8)$$

For $i = k + 1, k + 2, \ldots\ldots\ldots, n$; we have

$$P_i/e_i \leq (D\text{-}1)^{k-1}. \quad (9)$$

We have

$$^{SA}\int^{P\text{-}1}(T) = \sum_{i=1}^{k} \frac{p_i m_i}{e_i} + \sum_{i=k+1}^{n} \frac{p_i m_i}{e_i}$$

$$\leq \sum_{i=1}^{k} D^{k-2}\Delta + \sum_{i=k+1}^{n} (D-1)^{k-1} m_i, \text{ by (8) and (9)}$$

$$\leq kD^{k-2}\Delta + (n-k)(D-1)^{k-1}\mu^{\Delta}, by(7). \quad (10)$$

First part of the proof is over.

Now suppose that equality in (6) holds. Then all inequalities in the above argument must be equalities. From equality in (7) and (10), we get:

for each non-pendent vertex v_i, $d_l = d_k$ for all k, l such that $k \sim i$, $l \sim i$ and $d_i = \Delta$, $\mu_i = \mu$.

We can see easily that for any non-pendent vertex v_i, $d(i, j) \leq D\text{-}1$ (v_j is any vertex) in any tree. From equality in (9), we must have

$d(i, j) = D - 1$ for any non-pendent vertex v_i and any pendent vertex v_j.

Since T is a tree, from above result we conclude that $k = n - 1$ and hence T is star $K_{1, n-1}$.

Conversely, one can see easily that the equality holds in (6) for star $K_{1, n-1}$.

Corollary 1.3. *Let $T (\neq P_n)$ be a tree of order n with k pendent vertices. Then*

$$^{SA}\int^{P\text{-}2}(T) \leq k\Delta D^{k-3} + (n-k)(D-1)^{k-2}\mu^{\Delta}, \quad (11)$$

where μ is the maximum average degree of all non-pendent vertices and D is the diameter of T.

Proof: Since tree T is not a path P_n, we have that at least three pendent vertices in T. Thus we have

$$p_i/e_i^2 \leq D^{k-3}, \text{ for } i = 1, 2, \ldots\ldots, k. \quad (12)$$

For $i = k+1, k+2, \ldots\ldots, n$; we have

$$p_i/e_i^2 \leq (D\text{-}1)^{k-2}. \quad (13)$$

We have

$$^{SA}\int^{P\text{-}2}(T) = \sum_{i=1}^{n} \frac{p_i m_i}{e_i^2}, \tag{14}$$

Using (12), (13) in (14) and from Theorem 1.2, we get the required result.

Remark 1.4. *In Theorem 1.2, we have that star $K_{1,\,n-1}$ is the maximum superaugmented pendentic index-I of trees. Also we believe that path P_n is the minimum superaugmented pendentic index-I of trees.*

Now we will see that $H_{1,n}$ is the maximum *superaugmented pendentic index*-1 of $G_{k,n}$ graphs ($k \geq 1$, $n > 4$).

Theorem 1.5. *Let $G_{k,n}$ ($k \geq 1$, $n > 4$) be a connected simple graph of order n with k pendent vertices. Then*

$$^{SA}\int^{P\text{-}1}(G_{k,n}) \leq \frac{1}{2}(n-1) + n(n-2)^{n-2}, \tag{15}$$

with equality holding if and only if $G_{k,\,n} \cong H_{1,\,n}$.

Proof: We consider two cases (i) $k = 1$, (ii) $k \geq 2$.

Case (*i*) : $k = 1$. In this case graph has exactly one pendent vertex. Let v1 and *vn* be the pendent vertex and the highest degree vertex of $G_{1,n}$, respectively. If $G_{1,n} = H_{1,n}$, then the equality holds in (15). Otherwise, $G_{1,\,n} \neq H_{1,\,n}$. First we suppose that $G_{1,n}$ has highest degree $d_n = \Delta$. Thus we have $d_i \leq n\text{-}2$, $i = 2, 3, \ldots, n\text{-}1$ and at least one vertex has degree d_i ($i \in [2, n\text{-}1]$) strictly less than n-2. For each vertex $i \in [2, n]$ in $G_{1,\,n}$, we have

$$p_1/e_1 \leq \tfrac{1}{2} \text{ and } p_i/e_i \leq 1, \text{ as } p_1 = 1,\ p_i = d(i,1) \leq e_i. \tag{16}$$

Since $d_i \leq n - 2$ and $m_i < (n - 1)(n - 2)^{n-3}$, for all $i \in [2, n - 1]$. Now, we have

$$\frac{p_i m_i}{e_i} \leq m_i < (n-1)(n-2)^{n-3}, \text{ for all } i \in [2, n - 1], \text{ by (16)}, \tag{17}$$

$$\text{and} \quad \frac{p_1 m_1}{e_1} \leq \frac{1}{2} m_1 \leq \frac{1}{2}(n-1),\ \frac{p_n m_n}{e_n} \leq m_n < (n-2)^{n-2}. \tag{18}$$

From (2), we have

$$^{SA}\int^{P\text{-}1}(G_{1,n}) = \sum_{i=1}^{n} \frac{p_i m_i}{e_i},$$

$< \frac{1}{2}(n-1) + n(n-2)^{n-2}$, by (17) and (18)

$= {}^{SA}\int^{P\text{-}1}(H_{1,n})$.

Case (*ii*) : $k \geq 2$. Now we suppose that $G_{k,n}$ has highest degree $d_n = \Delta$ with diameter D. If $D = n$ -1, then $G_{k,n} \cong P_n$ and hence $\int^{PC\text{-}1}(G_{k,n}) < \int^{PC\text{-}1}(H_{1,n})$. Otherwise, $D \leq n$ - 2.

If $\Delta \leq n - 2$, then we have

$p_i/e_i \leq (n\text{-}2)^{k\text{-}2}$, as $d(i, j) \leq e_i \leq n$ -2, $i,j = 1, 2, \ldots\ldots, k$. (19)

and $p_i/e_i \leq (n\text{-}2)^{k\text{-}1}$, as $d(i, j) \leq e_i \leq n$ -2, $i = k+1, k+2, \ldots\ldots, n$; $j = 1, 2, \ldots, n$. (20)

Thus, ${}^{SA}\int^{P\text{-}1}(G_{1,n}) = \sum_{i=1}^{n} \frac{p_i m_i}{e_i}$,

$\leq k(n-2)^{k-2}\Delta + (n-k)(n-2)^{k-1}\Delta^{n-k-1}$, by (19) and (20)

$\leq n(n-2)^{n-2}$ as $\Delta \leq n$-2, $k \leq n$-1

$< {}^{SA}\int^{P\text{-}1}(H_{1,n})$.

We have remain the case $\Delta = n$-1 and $D \leq n$-2. In that case

$p_i/e_i = 2^{k\text{-}2}$, $i = 1, 2, \ldots\ldots, k$; $p_i/e_i = 2^{k\text{-}1}$, $i = k+1, k+2, \ldots\ldots, n$-1,

and $p_n/e_n = 1$.

Using these results, we have that

${}^{SA}\int^{P\text{-}1}(G_{1,n}) = \sum_{i=1}^{n} \frac{p_i m_i}{e_i}$,

$\leq k2^{k-2}(n-1) + (n-k-1)2^{k-1}(n-3)^{n-k-2}(n-1) + (n-3)^{n-k-1}$

$< n(n-2)^{n-2}$ as $n \geq 5$

$< {}^{SA}\int^{P\text{-}1}(H_{1,n})$.

Hence the theorem.

Conclusion

The simplicity, high sensitivity towards branching, exceptionally high discriminating power coupled with extremely low degeneracy render proposed *superaugmented pendentic indices* promising tools for quantitative structure-activity/property relationships, isomer discrimination, similarity/dissimilarity, drug design, lead optimization and combinatorial library design.

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Authors' Statement

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