Degeneracy of Topologic Distance Descriptors for Cubic Molecular Graphs: Examples of Small Fullerenes

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The degeneracy of topological distance sum (DS) and distance degree sequence (DDS) of small fullerenes is analyzed. The degeneracy of the two topological descriptors is determined by comparing the topological equivalence classes of the fullerene atoms with the DS and DDS classes, respectively. On the basis of DS and DDS degenerated fullerene graphs and by using two previously demonstrated theorems it is possible to generate pairs of graphs with degenerated topological indices based on DS (e.g., *W*, *J*) and on DDS (e.g., *U*, *V*, *X*, *Y*).

INTRODUCTION

In recent years many different molecular graph invariants have been proposed for characterization of structural features of chemical species. These are usually referred to in the chemical literature as Topological Indices (TI).[1−4] Such indices reflect in different ways the size and shape of the molecules they characterize and also provide some measure of the degree of molecular branching. The main area of application of TI is the development of quantitative relationships between the chemical structure and physicochemical properties. For example, the enthalpies of sublimation of fullerenes were predicted from Randić connectivity indices.[5]

One of the most used graph descriptor is the graph distance. The topological distance between the vertices v_i and v_j is denoted by d_{ij} and is equal to the number of bonds on the shortest path between the vertices v_i and v_j. Distances d_{ij} are elements of the distance matrix of G, $\mathbf{D} = \mathbf{D}(G)$. Let $d_{\max}$ be the maximum topological distance of the vertex v_i, i.e., the largest element of the ith row of the distance matrix of a molecular graph and let h_{ij} be the number of vertices in G at distance j from the vertex v_i. The sequence (h_{i0}, h_{i1}, h_{i2}, ..., h_{ij}, ...) is called the Distance Degree Sequence of the vertex v_i in G and is denoted DDS(i). Note that $h_{i0} = 1$ and $h_{i1} = \mathrm{DEG}(i)$, the degree of the vertex v_i. The number of elements in the sequence DDS(i) is equal to $d_{\max} + 1$.

The distance sum of the vertex v_i, DS(i), is the sum of the topological distances between vertex v_i and every vertex in the molecular graph:

$$\mathrm{DS}(i) = \sum_{j=1}^{N} d_{ij}$$

A number of important topological indices are defined on the basis of graph distances, DS or DDS. The index *W* was introduced in 1947 by Wiener[6,7] for predicting the alkane boiling points. In subsequent studies Wiener extended the application of the *W* index to other physical properties of alkanes such as heats of formation, heats of vaporization, molar volumes, and molar refractions. The DS set of the molecular graph was used to define the Balaban index *J*,[8] while the DDS set was used to develop the indices *U*, *V*, *X*, *Y*.[9]

The index *W* and the set of DS atomic invariants were used to study the number of lines and relative intensities of the ^{13}C NMR spectra of C_{76} fullerene isomers,[10] based on the partitioning of the carbon atoms in equivalence sets according to their DS values and on the assumption that such a partitioning will reproduce the ^{13}C NMR classes of atoms. In the present study we will demonstrate that the topological distance descriptors present a fairly high degeneracy even for small fullerenes, and their atom partitioning will not usually match the ^{13}C NMR classes of atoms. Our finding indicates that, contrary to earlier claims,[10] the topological distance descriptors cannot be used to estimate the number of lines of the ^{13}C NMR spectra of fullerenes.

The study of topological invariants of fullerene is a field in which important results were obtained in recent years,[11−19] with applications in the fullerene nomenclature, coding, structure characterization, and property prediction. The development of new structural descriptors for fullerene and fullerene derivatives can enhance the understanding of their structure−property relationships. Topological distance descriptors are widely used in characterizing the molecular structure, as indicated by recent developments.[20−24] In the present study we have demonstrated that, in certain structural conditions, two nonequivalent fullerene derivatives are characterized by the same value of distance-based descriptors. This degeneracy of distance-based descriptors for fullerene and fullerene derivatives prevents their use in fullerene nomenclature, coding, and establishing of topological equivalence classes of atoms. Fullerenes are highly complex chemical structures, and their characterization calls for the development of new structural descriptors.

THE DEGENERACY OF TOPOLOGICAL DISTANCE DESCRIPTORS

A general problem of TIs is that they are more or less degenerate, i.e., two or more nonisomorphic structures may lead to the same value for a given TI. Of course, low

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degeneracy, although highly desirable, is not sufficient to obtain good results in quantitative structure−property studies if the values of TIs do not properly reflect structural information in conjunction with the property under investigation.

Using a theorem concerning pairs of graphs with the same distance sum sequence, six pairs of molecular graphs representing alkanes with 12 carbon atoms were found to have identical index *J*.[25] Theorem 1 describes the structural conditions to construct pairs of graphs with degenerate DS sequences.

Theorem 1. Let *A* be a graph such that two topologically nonequivalent vertices a_1 and a_2 in *A* have the same distance sum. Let b_1 be a vertex in a graph B_1 and b_2 be a vertex in a graph B_2 such that b_1 and b_2 have the same distance sum in B_1 and B_2, respectively.

If *G* is the graph constructed from *A*, B_1, and B_2 by identifying vertices a_1 with b_1 and identifying a_2 with b_2 and *H* is the graph constructed from *A*, B_1, and B_2 by identifying a_1 with b_2 and identifying a_2 with b_1, then there is a one-to-one correspondence between the distance sums in the graphs *G* and *H*.

A pictorial representation of theorem 1 is given in Figure 1.

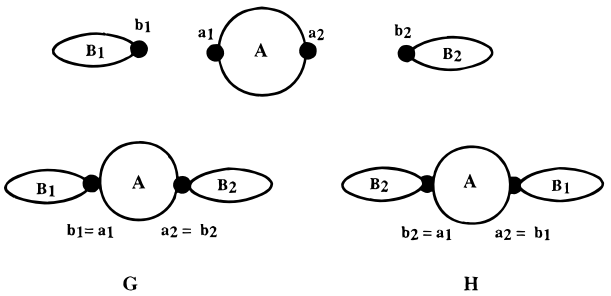

Figure 1. Pictorial representation of theorem I.

Two molecular graphs with a one-to-one correspondence between the distance degree sequences exhibit identical descriptors based on DDS, e.g., *U*, *V*, *X*, *Y*. The theorem 2 which describes the degeneracy conditions of DDS-based topological indices was recently demonstrated.[26]

Theorem 2. Let *A* be a graph such that two topologically nonequivalent vertices a_1 and a_2 in *A* have the same distance degree sequence. Let b_1 be a vertex in a graph B_1 and b_2 be a vertex in a graph B_2 such that b_1 and b_2 have the same distance degree sequence in B_1 and B_2, respectively.

If *G* is the graph constructed from *A*, B_1, and B_2 by identifying vertices a_1 with b_1 and identifying a_2 with b_2 and *H* is the graph constructed from *A*, B_1, and B_2 by identifying a_1 with b_2 and identifying a_2 with b_1, then there is a one-to-one correspondence between the distance degree sequences in the graphs *G* and *H*. The pictorial representation of theorem 2 is identical with that of theorem 1, presented in Figure 1.

In order to apply theorems 1 and 2 it is necessary to use also pairs of graphs with vertices with identical DS and DDS sequences, respectively. Some examples of pairs of trees with vertices having identical DDS sequences is presented in the Figure 2. Indicated vertices in a pair of graphs exhibit the same DDS. Below each graph, the distance degree sequence of the indicated vertices is presented.

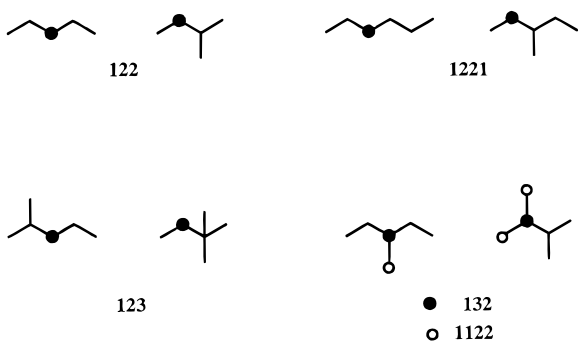

Figure 2. Examples of atoms with degenerate DDS.

DS AND DDS DEGENERACY OF SMALL FULLERENES

Knowing the structural causes of the degeneracy of topological indices, one can design new indices with better structural selectivity. Recently we have reported the topological equivalence classes of atoms and bonds in C_{20}−C_{60} fullerenes,[27] determined with a new Prolog coding program. By computing the DS and DDS atomic invariants for 18 fullerenes (between C_{24} and C_{50}) and by comparing the DS and DDS classes with the topological equivalence classes we will determine the degeneracy of the two descriptors. The distance matrix was computed with the Floyd−Warshall algorithm.[28]

We have investigated the degeneracy of the DS and DSS for the 18 fullerenes from ref 27 which have more than one class of topologically equivalent atoms. The fullerenes identified with degenerated DS and/or DDS values are reported in Tables 1 and 2, respectively. In Tables 1 and 2 fullerenes and their topological equivalence classes of atoms are numbered like in ref 27. For each atom it is indicated the topological class determined using the method described in this reference. This method makes an initial partitioning of atoms based on the list of successive extended connectivity and on the chromatism of the molecular graph. The definitive topological classes are obtained by matching all canonical labeled mapping trees exhaustively generated

Table 1. DS Degeneracy of Fullerenes

no.[a]		DS	degenerate classes[a]
3	C_{26} (D_{3h})	75	3, 4
		78	1, 2
4	C_{28} (T_d)	85	1, 2
6	C_{32} (D_3)	106	3, 4
7	C_{34} (C_{3v})	118	4, 7
8	C_{36} (D_{6h})	128	1, 3
9	C_{38} (D_{3h})	152	1, 2
10	C_{38} (C_{3v})	137	2, 3
		139	1, 7, 8
		141	5, 6
11	C_{40} (T_d)	150	1, 2, 3
12	C_{40} (C_{3v})	145	5, 9
		152	2, 4
14	C_{42} (D_3)	159	1, 3
		163	4, 6
15	C_{44} (T)	173	3, 5
		174	2, 4
17	C_{46} (C_3)	184	1, 5, 8, 13, 14
		186	2, 10
		188	3, 7, 12, 15
18	C_{48} (D_3)	201	3, 7
19	C_{50} (D_{5h})	210	1, 2

[a] The numbering of the fullerenes and of their topological equivalence classes is identical with that from the ref 27 and is indicated in the Supporting Information.

Table 2. DDS Degeneracy of Fullerenes

no.[a]		DDS								degenerate classes[a]
3	C_{26} (D_{3h})	1	3	6	7	6	3			3, 4
6	C_{32} (D_3)	1	3	6	7	7	6	2		3, 4
7	C_{34} (C_{3v})	1	3	6	7	7	6	4		4, 7
8	C_{36} (D_{6h})	1	3	6	7	8	7	3	1	1, 3
10	C_{38} (C_{3v})	1	3	6	7	8	7	4	2	5, 6
12	C_{40} (C_{3v})	1	3	6	7	8	8	5	2	2, 4
14	C_{42} (D_3)	1	3	6	8	9	8	5	2	1, 3
		1	3	6	7	9	8	5	3	4, 6
17	C_{46} (C_3)	1	3	6	8	9	9	6	4	1, 13
		1	3	6	8	9	8	7	3	1	2, 10
		1	3	6	7	9	9	6	5	3, 12
		1	3	6	8	10	8	6	3	1	5, 14

[a] The numbering of the fullerenes and of their topological equivalence classes is identical with that from the ref 27 and is indicated in the Supporting Information.

during the construction of a unique one-to-one topological code. By comparing the topological and DS classes of atoms, we have determined the fullerenes presenting nonequivalent vertices with degenerated DS values. In Table 1 we present the 14 DS-degenerated fullerenes together with the DS degenerate topological classes and the value of DS. By applying theorem 1 to the DS-degenerated fullerenes it is possible to generate pairs of fullerene derivatives with degenerate DS-based topological indices like the Wiener *W* and the Balaban *J* indices. The most DS degenerated is fullerene **17** C_{46} (C_3), which has 16 topological classes of atoms but only eight DS classes; the following classes are degenerated: 1, 5, 8, 13, 14; 2, 10; and 3, 7, 12, 15.

In the same way, in order to identify the DDS degenerated vertices in fullerenes, we have generated the distance degree sequences for all atoms of each fullerene and then, by comparing the DDS classes with the topological atom classes, we obtain the eight DDS-degenerated fullerenes reported in Table 2, together with the corresponding degenerated classes of atoms.

Again fullerene **17** C_{46} (C_3) has the highest number of degenerated classes, namely, 1, 13; 2, 10; 3, 12; 5, 14. From the collection of DDS degenerated fullerenes, by applying theorem 2 and the collection of graphs from Figure 2 it is possible to obtain pairs of fullerene derivatives with degenerate DDS-based topological indices, like indices *U*, *V*, *X*, and *Y*.

The topological distance structural descriptors of fullerenes were recently investigated for a large collection of fullerenes,[29] and a number of invariants were compared in their ability to encode the structure of fullerenes: the distance level patterns, the Wiener index, distance spectra, distance polynomial, and the sum of powers of the distance spectra. The results obtained in the present investigation allow a simple computation of the Wiener index, and our results are in perfect agreement with the results from Table 2 in ref 29. For the computation of the Wiener index one can use either the DS values or the DDS vectors reported in the Supporting Information of this paper (annexes 1 and 2, respectively). We have to mention the identity in definition between the DDS and the distance level pattern for an atom, as defined in ref 29; being a term widely used in the chemical graph theory, we have used the DDS notation in the paper.

The aim of this paper was to investigate the degeneracy of topological distance descriptors for fullerenes and fullerene derivatives, and, therefore, we have used as a comparison the topological symmetry determined with an efficient Prolog program.[27] Because the topological description is only a crude, but sometimes useful, approximation of the three-dimensional structure of molecules, recently there were developed more comprehensive methods for the generation of nuclear equivalence classes of atoms based on three-dimensional molecular structure[30,31] and for the coding and determination of topogeometrical classes of atoms.[32] When going from the topological to the three-dimensional description of a molecule, it is possible that the equivalence classes of atoms remain unchanged, like in the C_{20} (I_h) and C_{60} (I_{5h}) fullerenes. On the other hand, for chiral fullerenes or fullerenes which present geometrical isomers, the 3D partitioning will contain more classes than the 2D partitioning.

CONCLUSIONS

The degeneracy of distance based topological descriptors is not a rare case for fullerenes, and we have identified 14 fullerenes which have DS degenerated classes of atoms and eight fullerenes which have DDS degenerated vertices. By applying theorem 1 to DS degenerated fullerenes it is possible to obtain pairs of fullerene derivatives with degenerated DS-based topological indices, like *J* and *W*. Similarly, by applying theorem 2 to DDS degenerated fullerenes one can obtain pairs of fullerene derivatives with degenerated DDS-based topological indices, like *U*, *V*, *X*, and *Y*. Although the use of certain distance topological invariants was proposed for the partitioning of fullerenes in equivalence classes of atoms,[10] the results reported in the present study show that DS and DDS invariants will give unreliable predictions for a large fraction of the fullerene population.

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Supporting Information Available: Word 6 Files containing the diagrams of the 20 fullerenes investigated and the complete results of DS and DDS for all atoms (10 pages). See any current masthead page for ordering and Internet access instructions.

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