A Study on the properties of various bicyclic alkanes-An Application to graph theory

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Abstract.
The objective of this paper is to explore the application of graph theory in determining the structural as well as the physical properties of various bicyclic alkanes. Here we evaluate the Wiener Index and correlate with molecular mass and boiling points of various bicyclic compounds and their properties are studied. In the application level, we came to the conclusion that Wiener index can be used as a guideline to predict the structural compactness and thus the physical properties of bicyclic and polycyclic alkanes.

Keywords : Wiener index, topological descriptors, structural compactness.

\1.Introduction

Interrelation between Mathematics and Chemistry has been developed tremendously during the last few decades. Major areas of research in mathematical chemistry include chemical graph theory, which deals with topology such as the mathematical study of isomerism and the development of topological descriptors or indices which find application in quantitative structure-property relationships; and chemical aspects of group theory, which finds applications in stereochemistry and quantum chemistry. Graph theory is a branch of mathematics started by Euler [1] as early as 1736. It has been made contributions in chemical documentation, structural chemistry, physical chemistry, inorganic chemistry, quantum chemistry, organic chemistry, chemical synthesis, polymer chemistry, medicinal chemistry, genomics and DNA studies.A molecular topology determines a large number of molecular properties.[2]It was found in the last years that some biological activities of molecules [2] , and even carcinogenicity[3] are closely related to a molecular topology. Thus, it is of a pertinent interest for chemistry (as well as for other natural sciences) to have some quantitative measure reflecting the essential features of a given topological structure. Such measures are usually called topological indices in chemical graph theory. A lot of such indices have been suggested in the last 50 years. They have been usually correlated more or less satisfactorily with the molecular properties but could not discriminate well between structural isomers, often providing the same index for different isomers [4]. The first topological index reflecting the topological structure of a molecular graph was proposed by Harry Wiener in 1947. The Wiener number W was defined as the sum of all edges between all pairs of carbon atoms in hydrocarbons [5]. It gives a good correlation with the thermodynamic properties of saturated hydrocarbon molecules but doesn't discriminate well among structural isomers [6].Basically topological index expresses in numerical form the topology of the chemical species it presents. Topological indices are designed by transforming a molecular graph into a number and possess the remarkable ability of being able to correlate and predict a very wide spectrum of properties for a vast range of molecular species. The carbon-number index is well known to provide an effective measure of the molecular volume; for the members of

homologous series, the molecular volume is known to be directly proportional to the carbon-number index. The construction and investigation of topological indices that could uniquely characterize molecular topology is one of the main directions of chemical graph theory. The isomer discrimination, structure-property relationships and structure-activity correlations, and the design of compounds of desired properties are the most important trends in chemical graph theory where topological indices are commonly used.The paper is organized as follows. In section 2, we recollect the preliminaries needed for graph theory and chemistry. Section 3 deals with the graph theory concepts and Wiener index to determine boiling point of alkanes. In section 4, we present the analysis and evaluation of the Wiener Index with molecular mass and boiling points of various bicyclic compounds.

2. Preliminaries

Graphs in [7] are mathematical structures used to model pair-wise relations among objects from a certain collection. A graph G consists of a vertex set V (G) and an edge set
E (G), where each edge is an unordered pair of vertices. A loop is a self edge within vertex itself. A link has two distinct end vertices. An edge is multiple if there is another edge with the same end vertices; otherwise it is simple. The multiplicity of an edge is the number of multiple edges sharing the same end vertices. A graph is a simple graph if it has no multiple edges or loops, a multi-graph if it has multiple edges, but no loops, and a multi-graph or pseudo-graph if it contains both multiple edges and loops.

Definition 2.1 [8]

Two nodes of a graph are called *adjacent* if these nodes are the end nodes of a member. A member is called *incident with a node* if it is an end node of that member. Two members are called *incident* if they have a common end node. The *degree* (valency) of a node of a graph, denoted by deg (ni), is the number of members incident with that node.

Two graphs S1 and S2 are called *isomorphic* if there exists a one-to-one correspondence between their node sets and adjacency is preserved.

Definition 2.2 [8]

A graph S is called *planar* if it can be drawn (embedded) in the plane in such away that no two members cross each other. A planar graph S drawn in the plane divides the plane into regions all of which are bounded and only one is unbounded. If S is drawn on a sphere, all the regions will be bounded; however, the number of regions will not change. The cycle bounding a region is called a *regional cycle*. Obviously the sum of the lengths of regional cycles is twice the number of members of the graph. There is an outstanding formula that relates the number of regions, members and nodes of a planar graph, in the form,

$$R(S) - M(S) + N(S) = 2$$

Here, R(S), M(S) and N(S) are the numbers of regions, members and nodes of planar graph S, respectively. This formula shows that for different drawings of S in the plane, R(S) remains constant.

Definition 2.3 [9]

A tree is a connected acyclic simple graph. Walk is a sequence of vertices and edges, where each edge's endpoints are the preceding and following vertices in the sequence. The degree, or *valency*, $d_G(v)$ of a vertex v in a graph G is the number of edges incident to v, with loops being counted twice. A degree sequence is a list of degrees of a graph in non-increasing order (e.g. $d_1 \geq d_2 \geq \ldots \geq d_n$). A sequence of non-increasing integers is realizable if it is a degree sequence of some graph. Two vertices u and v are called adjacent if an edge exists between them. We denote this by $u \sim v$ or $u \downarrow v$. The set of neighbours of v, that is, vertices adjacent to v not including v itself, forms an induced sub graph called the (open)

neighborhood of *v* and denoted $N_G(v)$. When *v* is also included, it is called a closed neighbourhood and denoted by $N_G[v]$.

Connectivity extends the concept of adjacency and is essentially a form (and measure) of *concatenated adjacency*. If it is possible to establish a path from any vertex to any other vertex of a graph, the graph is said to be connected; otherwise, the graph is disconnected. A graph is totally disconnected if there is no path connecting any pair of vertices.

3. Graph theory concepts and Wiener index to determine boiling pointof alkanes

Alkanes are the simplest organic compounds with single bonds that consist only of the elements carbon (C) and hydrogen (H) in proportions according to the general formula: $C_nH_{(2n+2)}$with *n* number of carbon atoms in each molecule. In general, the chemical structures of alkanes are of three types: linear, branched and cyclic. Of these, linear alkanes are the simplest to draw and explain. One example of linear alkane is ethane. Branched alkanes are derived from linear alkanes, but instead of having just a straight chain in their chemical structure, it is branched with one or more alkyl groups as in isobutane. Cyclic alkanes or cycloalkanes consist of hydrogen and carbon atoms bonded together with single bonds, where the carbon atoms are joined up in a ring. The smallest cycloalkane is cyclopropane.Each carbon atom has four chemical bonds and each hydrogen atom has one chemical bond. Therefore, the hydrogen atoms can be removed without losing information about the molecule. This carbon tree can be represented as a graph by replacing the carbon atoms with vertices and chemical bonds as an edge in the graph. Chemical Graph theory is used to model physical properties (property of a compound that can change without involving a change in chemical composition) of molecules like alkanes since the structural features of an alkane determines its physical properties. Indices based on the graphical structure of the alkanes are defined in [10] and used to model both the boiling point and melting point of the molecules.The boiling point of alkanes is determined by the geometric structure of the alkane, which is a measure of the forces of attraction between like molecules. For essentially non polar compounds such as alkanes, these forces are London dispersion forces [11] due to instantaneous dipole-induced dipole attractions. Dispersion forces are very short range forces which are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes. The alkane boiling point should also depend on how well the molecules pack together, which is related to the geometry of the molecule. The dependence on the geometry is complex, but the boiling point should decrease in a general way as the compactness of the molecule increases if the relative molecular mass stays the same.

3.1. Wiener index measurements

Topological indices in [12] have been used as a convenient abstraction of chemical structures and have experimentally shown strong correlations with the physical properties of molecules. Throughout the years, numerous such indices are proposed, known as the chemical indices, for various categories of chemical structures. One of the most well-known indices is due to and later named after Wiener. This index in [13] is defined as the sum of the lengths of the shortest paths between all pairs of vertices in a chemical graph by [14]. In other words, Wiener index measures how compact a molecule is for its given weight. Therefore, it has predictive value and chemists and physics have found many uses for the Wiener index.

Definition 3.2 [10]

Let *G* be an undirected connected graph without loops or multiple edges with *n* vertices. It is represented as *G* = (*V,E*) where *V* is the set of vertices and *E* is the set of edges. The topological distance between a pair of vertices *u* and *v* of *V*, which is denoted by $d_G(u,v)$ is the number of edges of the shortest path joining *u* and *v*.

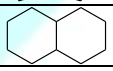
The Wiener Indexof any connected graph G is defined as:

$$w(G) := \sum_{\{u,v\} \subset V(G)} dG(u,v)$$

4. Analysis and evaluation of the Wiener index with molecular mass and boiling points of various bicyclic compounds

1. Here we consider the bicyclic and poly cyclic alkane compounds. A bicyclic molecule is a molecule that features two fused rings. They occur widely in organic and inorganic compounds. In order to analyse the validity of Wiener index values by correlating with the boiling point or melting point of various bicyclic alkane molecules, we selected the following compounds (Table 1).

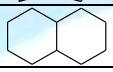
Table 1

Sl. No.	Name of the molecule	Molecular Formula	Chemical Structure
1.	Norbornane (bicyclo[2.2.1]heptane)	C_7H_{12}	
2.	*cis*-Bicyclo[3.3.0]octane	C_8H_{14}	
3.	Bicyclo[2.2.2]octane	C_8H_{14}	
4.	Spiro[4.4]nonane	C_9H_{16}	
5.	Adamantane	$C_{10}H_{16}$	
6.	*trans*-Decalin(bicyclo[4.4.0]decane)	$C_{10}H_{18}$	

The Wiener indices for the above given compounds were calculated and directly analysed the linear relation with their molecular weight and the observed boiling or melting points. The index values are calculated based on the definition and the mathematical equation in [10].

Table 2. Wiener index and boiling points of various bicyclic compounds

Sl. No.	Molecular Formula	Chemical Structure	Molecular Weight	Wiener Index	Observed Boiling Point

1.	C_7H_{12}		96.17	36	88 °C
2.	C_8H_{14}		110.20	55	136°C
3.	C_8H_{14}		110.20	54	140.5±7.0 °C
4.	C_9H_{16}		124.22	78	173.1°C
5.	$C_{10}H_{16}$		136.23	96	[a]270 °C
6.	$C_{10}H_{18}$		138.25	109	187 °C

[a] refers melting point

The tabulated data shows good correlation between Wiener index and molecular weight of the bicyclic compounds. It is also evident that the values show a linear relation with the standard boiling point of the alkanes. In the case of compounds 2, and 3, even though they have the same molecular weights, their boiling points are slightly different and Weiner index as well. The slight difference in Wiener index and boiling point can be attributed to their diversity in molecular geometry.Adamantane, which shows remarkable change in the index value, gives exceptionally high melting point. The molecule has tetrahedral (Td) symmetry and the fourcyclohexane units are all held rigidly in the preferred chair conformation. The molecule must therefore have negligible angle andtorsional strain. The highly symmetric molecule can thus be arranged closely and becomes solid.

Conclusion

The Wiener index is a good foundation for determining the correlation between a molecule's structure and physical properties because it takes into account the distances between atoms, more specifically their electron clouds. Herein, we have shown that when the molecular mass increases, the Wiener index also increases. As a rule, the Wiener index measures the compactness of a molecule. In the present study, we have also shown that there is a linear correlation between the Wiener index value and the boiling points of alkanes except for adamentane. Therefore, it is clear that the value of Wiener index can be used as a guideline to predict the structural compactness and thus the physical properties of bicyclic and polycyclic alkanes.

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