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A BRIEF REVIEW-ON CONTRIBUTION OF GRAPH THEORY AND WIENER INDEX TO CHEMISTRY

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Abstract

Contribution of graph theory to chemistry is outstanding, ever since the discovery of chemical trees by Arthur Cayley. Topological indices are studied, investigated, explored and analysed by chemist and mathematicians for various reasons. One such index is Wiener index. In this short survey i have presented the contribution of Graph theory and Wiener index to the world of chemistry.

Key words: Distance matrix, Graph, Hexagonal System, Molecular graph, Wiener index, Tree.

Introduction

Wiener index was introduced by Harry Wiener in his paper in the year 1947. Snapshot – 1 provides the first page of the original paper by Wiener [1].

Jan., 1947 STRUCTURAL DETERMINATION OF PARAFFIN BOILING POINTS 17

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, BROOKLYN COLLEGE]

Structural Determination of Paraffin Boiling Points

BY HARRY WIENER[1]

The boiling points of organic compounds, as well as all their physical properties, depend functionally upon the number, kind and structural arrangement of the atoms in the molecule. Within a group of isomers, both the number and the kind of atoms are constant, and variations in physical properties are due to changes in structural interrelationships alone. The study of the effect of pure structural variation upon the boiling point of the paraffins may be expected to be of some theoretical interest. It will be shown in this paper that satisfactory results can readily be obtained by this approach.

The boiling points of the paraffins are given by the linear formula

$$t_B = aw + bp + c \quad (1)$$

where a, b and c are constants for a given isomeric group, and p and w are structural variables defined below.

The polarity number p is defined as the number of pairs of carbon atoms which are separated by three carbon–carbon bonds. *E.g.*, for 2,3-dimethylpentane

Pairs 3 bonds apart: C_1C_4, C_1C_5, C_2C_5, C_2C_6, C_3C_6, C_3C_7. $p = 6$

The path number w is defined as the sum of the distances between any two carbon atoms in the molecule, in terms of carbon–carbon bonds. Brief method of calculation: Multiply the number of carbon atoms on one side of any bond by those on the other side; w is the sum of these values for all bonds. *E.g.*, for 2-methylbutane

1·4 = 4 | 2·3 = 6 | 1·4 = 4
1·4 = 4

$w = 4 + 4 + 6 + 4 = 18$

The problem is simplified by a change in notation already employed in this connection by Taylor, Pignocco and Rossini.[2] Let t_0 be the boiling point of the straight-chain member of the group of isomers, having structural variables w_0 and p_0, and let $\Delta t = t_0 - t_B$, $\Delta w = w_0 - w$, $\Delta p = p_0 - p$. Then, for an isomer with structural variables w and p, equation (1) becomes

$$\Delta t = a\,\Delta w + b\,\Delta p \quad (2)$$

Equation (2) was extended to cover the entire paraffin series. For a compound with n carbon atoms, the following relation was found to hold

$$\Delta t = \frac{k}{n^2}\,\Delta w + b\,\Delta p \quad (3)$$

Equation (3) was fitted, by means of the method of least squares, to the selected boiling point data for the thirty-seven paraffins from C_4H_{10} to C_9H_{18} in the tables of the American Petroleum Institute Research Project 44.[3]

The resulting equation is

$$\Delta t = \frac{98}{n^2}\,\Delta w + 5.5\,\Delta p \quad (4)$$

which is the form used in this paper.

The change in notation introduced by equation (2) is useful not only because of the resulting simplification, but also because it refers the boiling points of the branched isomers to the boiling points of the normal paraffins, which throughout the series have been much more intensively and accurately determined and correlated. In particular, Egloff's equation[4]:

$$t_0 = 745.42 \log (n + 4.4) - 689.4 \quad (5)$$

reproduces the data to within their experimental limits. Table I gives the reference values for the normal paraffins from *n*-butane to *n*-dodecane. For normal paraffins, the structural variables are given by

$$w_0 = \frac{1}{6}(n-1)(n)(n+1), \quad p_0 = n - 3 \quad (6)$$

TABLE I
NORMAL PARAFFINS

Cpd.	t_0	w_0	p_0
n-Butane	−0.5	10	1
n-Pentane	36.1	20	2
n-Hexane	68.7	35	3
n-Heptane	98.4	56	4
n-Octane	125.7	84	5
n-Nonane	150.8	120	6
n-Decane	174.0	165	7
n-Undecane	195.8	220	8
n-Dodecane	216.2	286	9

Example of calculation:

3-Ethylhexane: $w = 72$, $\Delta w = 12$, $p = 7$, $\Delta p = -2$, $\Delta t_{calcd.} = 7.5°$, $\Delta t_{obs.} = 7.1°$. Deviation $= -0.2°$. Calcd. b. p.: $t_B = t_0 - \Delta t = 125.7 - 7.3 = 118.4°$

Table II lists the detailed results obtained by applying equation (4) to the thirty-seven paraffins from C_4H_{10} to C_9H_{18}, for which carefully selected boiling point values are given in the A.P.I. tables,[3] and from which data the two empirical constants of equation (4) were evaluated.

(1) Present address: 5120 19th-Avenue, Brooklyn 4, N. Y.
(2) Taylor, Pignocco and Rossini, *J. Research Bur. Standards*, **34**, 413 (1945).
(3) American Petroleum Institute Research Project 44 at the National Bureau of Standards, Selected Values of Physical and Thermodynamical Properties of Hydrocarbons. Tables No. 1a, 2a, 3a and 4a, dated June 30, 1945.
(4) Egloff, Sherman and Dull, *J. Phys. Chem.*, **44**, 730 (1940).

Snapshot – 1

Ever since this great discovery by Wiener, infinite contributions are made by graph theorists and chemists independent and together on this topological index. In this short survey, i have presented a very brief note on the contribution of graph theory and Wiener index together in chemistry.

Materials and Methods

In this section a small note on the required information for comfortable reading of the survey is presented.

Wiener Index

In chemical graph theory, the Wiener index (also Wiener number) is a topological index of a molecule, defined as the sum of the lengths of the shortest paths between all pairs of vertices in the chemical graph representing the non-hydrogen atoms in the molecule [2].

Chemical Graph

In chemical graph theory and in mathematical chemistry, a molecular graph or chemical graph is a representation of the structural formula of a chemical compound in terms of graph theory. A chemical graph is a labeled graph whose vertices correspond to the atoms of the compound and edges correspond to chemical bonds. Its vertices are labeled with the kinds of the corresponding atoms and edges are labeled with the types of bonds. For particular purposes any of the labeling may be ignored [3]. In the Fig 1 the snapshot [4] on the left side is an example of a chemical graph and the graph on the right side is its respective graph structure.

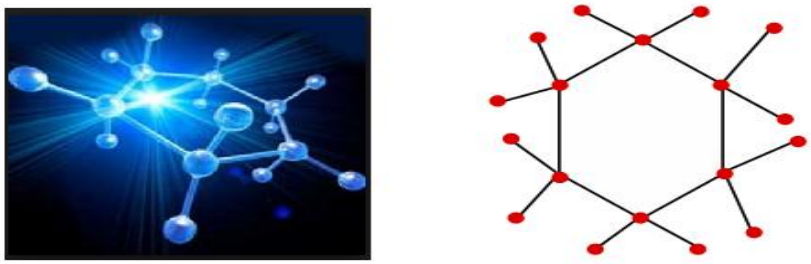


Fig. 1

Wiener Index Calculation Using Distance Matrix

Snapshot – 2 provides a method of Wiener index calculation using distance matrix [5].

The Wiener index can be defined for an arbitrary connected graph as follows. Without loss of generality, assume that G has vertices $1, 2, \ldots, n$. For each pair i, j of vertices, let d_{ij} denote the distance in G between i and j; i.e. the length of the shortest path between i and j. The distances d_{ij} form the so-called *distance matrix* $D(G) = [d_{ij}]$ of the graph G. The Wiener index of G is the number

$$W(G) = \sum_{i=1}^{n} \sum_{j=1}^{i} d_{ij} = \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} d_{ij} .$$

$UCJD_p$

	1	2	3	4	5	6	7	8	VS_i
1	0	1	1	1	1	1	1	1	7
2	7	0	3	3	3	3	7	3	29
3	5	5	0	5	5	5	5	7	37
4	3	3	3	0	6	6	3	3	27
5	2	2	2	2	0	7	2	2	19
6	1	1	1	1	1	0	1	1	7
7	1	1	1	1	1	1	0	1	7
8	1	1	1	1	1	1	1	0	7
CS_j	20	14	12	14	18	24	20	18	140

Wiener index $(W) = 70$

hyper-Cluj-distance index $(CJD_p) = 143$

D_UCJD_p

	1	2	3	4	5	6	7	8	VS_i
1	0	1	2	3	4	5	2	3	20
2	7	0	3	6	9	12	7	6	50
3	10	5	0	5	10	15	10	7	62
4	9	6	3	0	6	12	9	6	51
5	8	6	4	2	0	7	8	6	41
6	5	4	3	2	1	0	5	4	24
7	2	1	2	3	4	5	0	3	20
8	3	2	1	2	3	4	3	0	18
CS_j	44	25	18	23	37	60	44	35	286

$D^U CJD_p = 143$

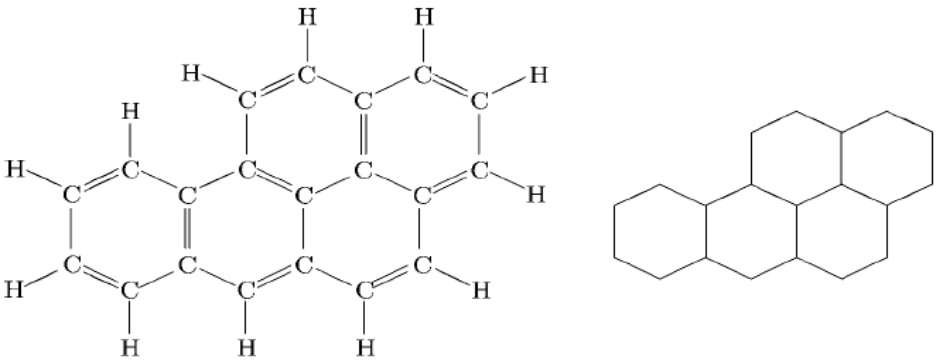
$D^2 CJD_p = 605$

Snapshot – 2

I now proceed to provide a short survey on the contribution of Graph theory and Wiener index together to chemistry. I would like to make a note here that this survey focuses on exploring Wiener index and graph theory together to chemical properties. Results relating results on properties of chemical graphs only (independent of graph theory) and their Wiener index values are omitted. Similarly the contribution on properties of Wiener index alone are omitted. Articles which use graph theory and Wiener index together into some property of chemistry is presented. Many articles and results are omitted here, as it is a short brief survey. I apologize to the authors for omitting many results due to crisp article.

Survey

In [6] Andrey A Dobrynin et. al provided a detailed analysis of hexagonal system. The paper is almost like a survey on hexagonal system. It reveals the various kinds of graph operations used in hexagonal system. A hexagonal system is a connected plane graph without cut-vertices in which all inner faces are hexagons (and all hexagons are faces), such that two hexagons are either disjoint or have exactly one common edge, and no three hexagons share a common edge. Snapshot – 3 provides a graph structure of the hexagonal system benzoil hydrocarbon benzopyrene.



Snapshot – 3

Snapshot – 4 provides the types of hexagonal systems.

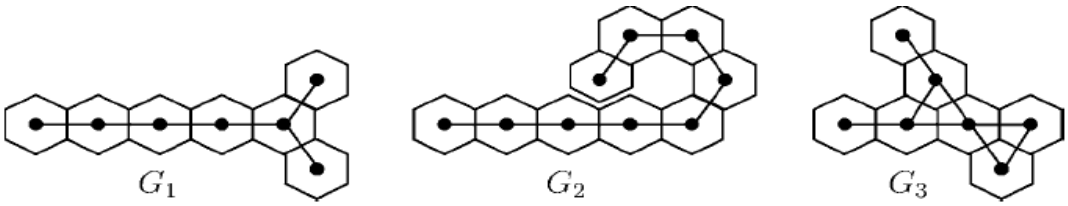


Figure 2. Simple hexagonal system G_1, jammed hexagonal system G_2, pericondensed hexagonal system G_3, and their characteristic graphs.

Snapshot – 4

Various kinds of hexagonal systems are discussed in [6] like hexagonal chains, Jammed hexagonal chains, Zigzag hexagonal chains, Fibonances, chains with given number of A-Mode Hexagons, Hexagonal chains with equal segments, catacondensed hexagonal systems, Simple catacondensed hexagonal systems, pericondensed hexagonal systems, Pericondensed hexagonal systems. Various algorithms for determination of Wiener index is discussed here. Various methods of determining the Wiener index of growing hexagonal system is discussed like Wiener index by subgraph attachment, Kink transformation of hexagonal systems, random growth of hexagonal chains. Formulas for different kinds of hexagonal systems like hexagonal chains, catacondensed hexagonal system, pericondensened hexagonal system is discussed. Also properties of Wiener index is also provided. In [7] Wen-Chung Huanga et.al have provided a classical approach to determine a nonrecursive formula for the wiener index of any given benzoid chain is derived. Interestingly here semigroup properties are used to define a string S. Then this string is associated with a graph of concatenated hexagons. The graph is designed in such a fashion that each character in the string determines the direction of the successive hexagon. Snapshot – 5 provides a sample hexagonal graph to ternary string.

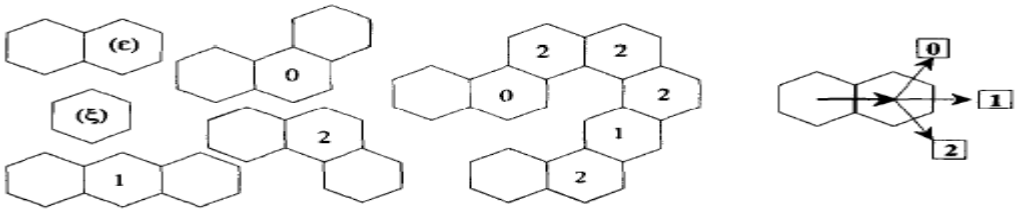
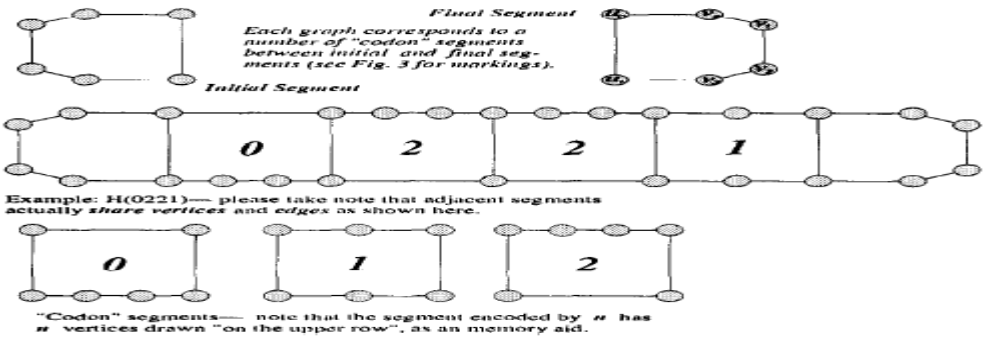


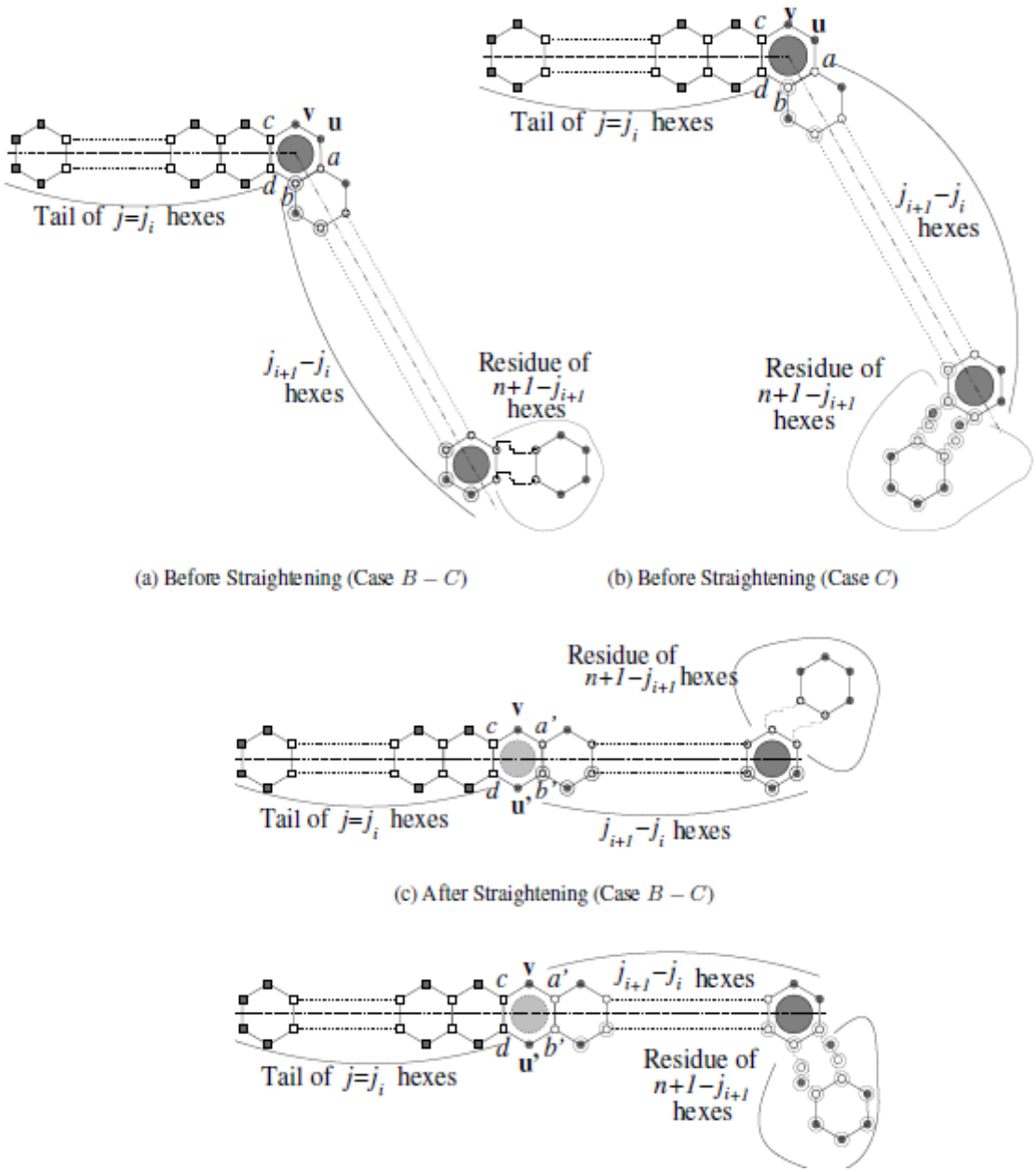
Fig. 1. Correspondence of hexagonal chain to ternary string.



Snapshot – 5

Finally the Wiener index of the given string is determined. This approach speeds up calculations rendering it manually manageable.

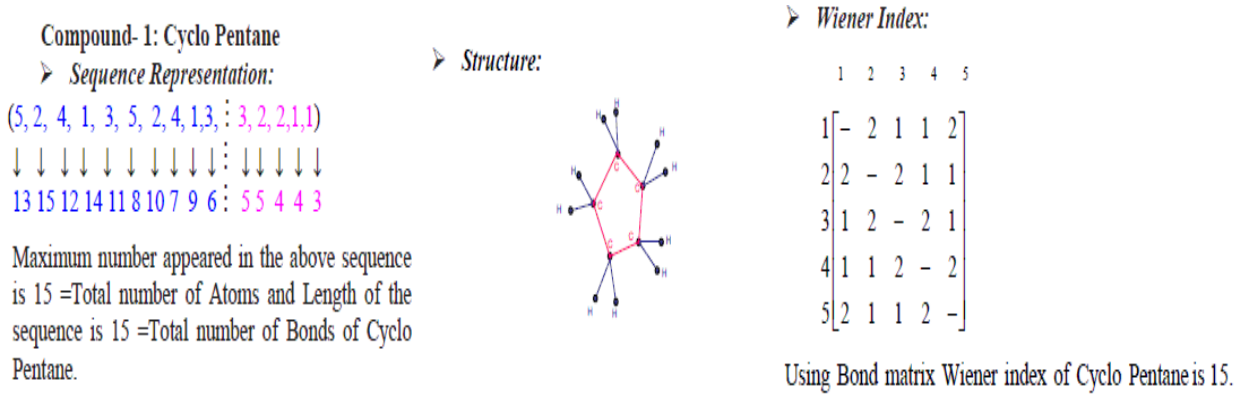
Relating to hexagonal chains in [8] a technique is presented by Sen-Peng Eu et al, which provides a much more transparent proof for computing the Wiener index. Infact it is much more than an improvement of the old method, by straightening and turning the hexagonal systems.



Snapshot - 6

A connected graph is called a motley chain. Let G be any motley chain,W1(G) = W(V2; V3;G); W2(G) := W(V2;G); W3(G) := W(V3;G); where V2 and V3 are the sets of degree-2 and -3 vertices, then W = W1 +W2 +W3; W_+ = 5W1 + 4W2 + 6W3; W_* = 6W1 + 4W2 + 9W3. They have further stated that we only need to take care ofW2 andW3, and there is no need to consider W1,since W = W1 +W2 +W3.Also they claim tha straightening out the turn at location ji hexes creates differences. The changes in W2 andW3 as we straighten out a turn position is as seen in Snapshot – 6.

In [9] A. Vijayabarathi et. al have proposed a method of calculating Wiener index of a graph using super edge matching sequence. Then a general method minimal spanning tree technique at each vertex is provided. Finally identification of chemical compounds is determined. Strange but graph labeling is used and aids in Wiener index calculations. A sample of this method is seen in Snapshot – 7



Snapshot – 7

In [10] A. Karbasioun has determined the Wiener index of carbon nanojunctions is determined. May be this is the first ever result in finding the Wiener index of carbon nanostructures opening a new area of research. This method is particularly easy to apply for graphs constructed with less number of subraphs for it applies a method of determination of the Wiener index of the graph from its subgraphs.

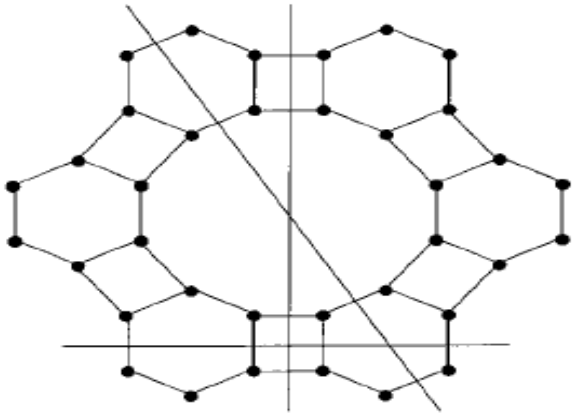
In [11] the Wiener index of spiro hexagonal chains and polyphenyl hexagonal chains is determined using cutvertex sequence. Also a relation between these two is determined. An interesting result shows that the average value of the Wiener indices with respect to the set of all such hexagonal chains is exactly the average value of the Wiener indices of three special hexagonal chains, and is just the Wiener index of the meta-chain. It is to be noted that the entire calculations is based on the cutvetex sequence for the hexagonal system.

In [12] W.C. Shiu has determined the Wiener index of hexagonal net. For this purpose a new infinite graph is defined as G = (V, E), where V = Z x Z and $\{ (x_1, y_1), (x_2, y_2)\} \in E$ if $y_1 = y_2$ and $| x_1 - x_2 | = 1$ or $x_1 = x_2$, $| y_1 - y_2 | = 1$ and $x_1 + y_1 + x_2 + y_2 \equiv 1 \pmod 4$. Using this graph they have finally proved that the Wiener index of the hexagonal net is $\frac{1}{5}(164n^5 - 30n^3 + n)$ for $n \geq 1$.

As an extension of this work in [13], W.C. Shiu et. al the Wiener index of hexagonal jagged rectangles is determined, where the difference between a jagged and normal hexagonal system is that in an usual hexagonal system all the hexagonal chains are of the same size, while in a jagged one each chain alternates between n and n – 1.

In [14] Harish Dureja et. al modified forms of Wiener index, Wiener's Topochemical index, normalized Wiener's Topochemical index, molecular connectivity Topochemical index is used for fast screening of virtual libraries having millions of molecules and providing potent therapeutic agents with high permeability through the blood-brain barrier.

A benzenoid graph is constructed in the following manner. Let H be the hexagonal (graphite) lattice and let Z be a cycle on it. Then a benzenoid graph is formed by the vertices and edges of H, lying on Z and in the interior of Z. Viewing a benzenoid graph G as a geometric figure in the plane, an elementary cut is defined as follows. Choose an edge e of G and draw a straight line through the center of e, orthogonal to e. This line intersects the perimeter of G in (at least) two points P1 and P2. The straight line segment C, the end-points of which are P1 and P2, is the elementary cut pertaining to the edge e. The set of edges intersected by an elementary cut will be called an elementary edge-cut. Snapshot – 8 provides a sample of phenylene and its cut edge.



The cyclic phenylene R_6.

Snapshot – 8

In [15] Gordon Cash considered three different methods for calculating the hyper-Wiener index of molecular graphs: the cut method, the method of Hosoya polynomials, and the interpolation method. Along the way they have obtained new closed-form expressions for the WW of linear phenylenes, cyclic phenylenes, poly(azulenes), and several families of periodic hexagonal chains. We also verify some previously known (but not mathematically proved) formulas.

In [16] Sibi S et. al, to obtain the chemical graph of a chloroalkane, replaced the edge vertex containing CH_3 group with covalently bonded chlorine atom. Introduce a constant α as the group mass ratio of Cl to CH_3 along with a molecular mass factor M =M (α,n,n_c) and a mass-modified Wiener index proposed as W= M^pW where W is the Wiener index obtained from the chemical graph, while n and n_c correspond to the number of chlorine and carbon atoms respectively in the chloroalkane molecule.

Snapshot – 9 provides the modified mass Winer index and the corresponding distance matrix. Using this new definition, the boiling point of chloroalkenes and alkenes is calculated as seen in Snapshot – 10

$$W = \frac{1}{2}\sum_{i,j=1}^{n} S_{ij}$$

$$S_{ij} = \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1n} \\ S_{21} & S_{22} & \cdots & S_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ S_{n1} & S_{n2} & \cdots & S_{nn} \end{bmatrix}$$

Snapshot – 9

Chloroalkanes		
Structure	Name	T_b (K)
	Chloromethane	248.95
	Tetrachloromethane	349.65
	1,1,2-trichloroethane	386.95
	Pentachloroethane	435.15
	Hexachloroethane	460.15

Alkanes		
Structure	Name	T_b (K)
	Ethane	184.55
	2,2-dimethylpropane	282.65
	2-methylbutane	301.05
	2,2,3-trimethylbutane	354.05
	2,2,3,3-tetramethylbutane	373.96

Snapshot – 10

Finally an approximate formula for determination of boiling point of chloroalkenes is estimated as

$$T_b = 4.3\, M^{\frac{1}{2}} W^{\frac{1}{2}} + 125.645 .$$

In [17] Sibi S et. al , using Kelman' s theorem, a previously known formula is deduced for the Wiener and Kirchoff index is deduced. It is proved that the Wiener index is correlated with the second smallest eigen value.

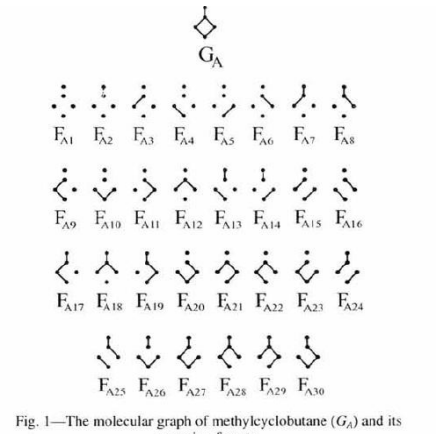


Fig. 1—The molecular graph of methylcyclobutane (G_A) and its spanning forests.

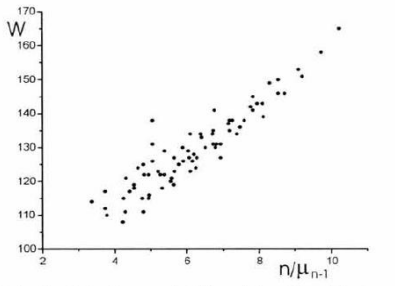


Fig. 3—Correlation between the Wiener index (W) and the term n/μ_{n-1} for chemical trees with $n=10$ vertices; μ_{n-1} is the algebraic connectivity. The outlier corresponds to the molecular graph of 4-propylheptane (cf. Fig. 5).

Snapshot – 11

Snapshot – 11 provides the molecular graph of methycyclobutane and the correlation between the Wiener index the algebraic connectivity of propylheptane.

In [18] Ivan Gutman et al proposed a review to present a cross section of the contemporary investigations of the Wiener number.

Snapshot – 12 provides a labeling of a aromatic ring in a tree like system. For an edge connecting two vertices from different hexagons in a tree-like system. They label the two end of this edge to denote where is the hexagon connected to this edge.

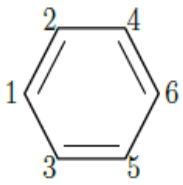


Figure 2.1: Labeling of an aromatic ring in a tree-like system

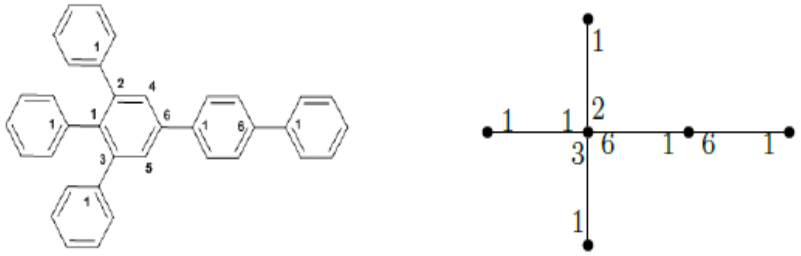


Figure 2.2: Labeling and tree representation with edge labels for Figure 1.2

Snapshot – 12

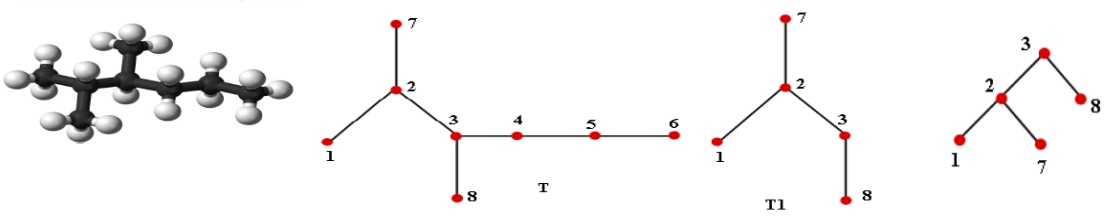
Using this method of creating trees, in [19] Tabitha N. Williford have shown that when the underlying tree structure is given, the extremal systems of tree-like polyphenyl system can be specially characterized using the Wiener index. When the systems have the same chemical molecular formula, but different structural arrangements (isomers) that possibly provides different tree structures, the study is more complicated. However, a rough algorithm to study such questions is provided. The computational results from the study are compared with physical properties of some simple chemicals that test the validity of the method.

Calculation of Wiener index is normally done using distance matrix. In [20] M. Yamuna proposed a method of determining the Wiener index of a tree by reducing the size of this distance matrix is determined. If the matrix size need to be reduced then a method of reducing the size of the tree, and hence a method of determining the original Wiener index of the tree need to be devised, which is done in [20].

Here given any tree, the longest possible path is determined, removed from the tree. Then this reduced tree is converted into a level tree, and hence the Wiener index of the original tree is calculated from this level tree using the formula.

Wiener index of T = Wiener index of T1 + Wiener index of path P_{m-1}.

Snapshot – 13 provides the method determining the Wiener index of 2, 3 dimethyl hexane, T its tree representation, T1 reduced tree, then its level tree and finally the reduced distance matrix and hence the Wiener index of T.



	1	2	3	7	8	
1	12	1	2	2	3	20
2	–	9	1	1	2	13
3	–	–	6	2	1	9
7	–	–	–	12	3	15
8	–	–	–	–	9	9

Wiener index of T1 = = 66

Wiener index of path $P_2 = 1 + 2 + 1 = 4$.

So Wiener index of T = Wiener index of T1 + Wiener index of path $P_2 = 66 + 4 = 70$.

Snapshot – 13

Conclusion

The travel in writing this short survey was an adventurous journey and travel into the spell of chemistry and graph theory. It is exciting and mesmerizing for any researcher interested in graphs and chemistry to explore the traces left behind by the contribution of two subjects, which can turn the level of research to different levels. In this crisp note i have tried to provide my experience on understanding these contributions and have presented it as a short survey on Graph and Wiener index contributions to chemistry.

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