Graph Applications on Chemical Bonds and Structures

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Graph is an old mathematical problem that used in so many areas of sciences. Graph is used to represent discrete objects and the relation between them. The application of graph can be used in so many areas of knowledge. One of many important applications from graph is in chemistry. Chemical bonds use graph to represent the relation between one element to another with the appropriate bond. Some uses of graph in chemistry are : to determine the isomorphic bond between carbon compounds, to show how chemical bonds can react to another substances, the polarity of chemical element, to represent chemical reactions, etc. This paper will focus on the application of graph in chemical bonds, including it's nature, the correlation to chemical reaction, and the bonds structure.

***Index Terms* : graph, chemical graph, chemical bonds, geometrical structures**

I. INTRODUCTION

[7]Graph is one of the prime objects study in discrete mathematics. The first problem in history that used graph is the problem of Königsberg bridge. This is a problem about how to pass seven bridges and every bridge can only be passed once. The question is : Is it really possible? So many people say that is impossible but they can't explain why. This problem was solved by L.Euler, a mathematician from Swiss. The answer is because the degree of every vertex must in even quantity. Graphs have so many applications in many areas. It can be used to show the shortest path between certain place (node), to show some algorithm process, to show how a network do it's work, to show the bonds between atom in chemistry, etc.

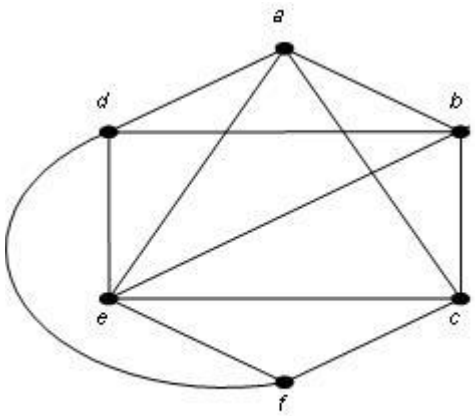
The definition of Graph is set mate between vertices and edges (V,E). In this term :

V = Not empty set from vertices (can be said as nodes)
= $(v_1, v_2, \dots, v_n)$

E = Edges from set that connect a pair of vertices. (can be said as arcs)
= $(e_1, e_2, \dots, e_n)$

The graph vertices must not empty, but the edges can. It can be said that it's possible that a graph doesn't have any edges but have the vertices at least one. The graph that only has one vertex is said as trivial graph. Every vertex in a graph can have a number or alphabet sign that represent certain vertex The edge that connects vertex v_i and v_j is written as (v_i, v_j). So we can say that an edge e that connect vertex v_i and v_j can be written as :

$e = (v_i, v_j)$



Picture 1.1 Example of graph with six vertices and 12 edges.

In the study of chemistry, graph is used in so many writing, to show chemical bonds. A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The graph can show the relation between one atom to another in the chemical bond. Molecules in chemical compounds are built by linking together atoms of various kinds. The use of graph in chemistry is written as chemical graph. Chemical graph is written as undirected weighted graph (V, E, μ). With V is atoms, E is bonds between one atom to another, $\mu : E \rightarrow N$ a weight function. In the chemical reaction the graph structure for the substrate (reactant) is (V, E, σ) and for the product is (V, E, π).[8]

Graph can be used to analyze some geometric structure in chemistry and it's characteristic. There are so many structures of molecule in chemistry and every single of them has it's own characteristic. Graph can help the comprehension of the geometric structure by using it as 3D graph to illustrate it.

II. SOME THEORIES

2.1. Basic Graph Terminologies

[7]Graph has some terminologies that will be used in the discussion of graph. Some terminologies that will be useful in this paper is :

2.2.1. Adjacent

Two vertices in undirected graph G can be said adjacent if two of them connected directly with an edge. It can be said that v_i is adjacent to v_j if and only if (v_i,v_j) is an edge in graph G. The example in picture 1.1 is a and b but not a and c.

2.2.2. Incident

To any edge e = (v_i,v_j), the edge e can be said incident with vertex v_i and v_j. From the picture 1.1, the edge that connect a and b (v_a,v_b) is incident to the vertex a and vertex b.

2.2.3. Isolated Vertex

Isolated vertex is a vertex that doesn't have any edge that incident to it. Or, it can be said that isolated vertex is an vertex that have no adjacent vertex.

2.2.4. Degree

A vertex degree is the number of edges that is incident to that vertex. From the picture 1.1, the degree from the vertex a is 4.

2.2.5. Path

Path that has length n from start vertex to the direction vertex is a row that alternately between edge and vertex. The form of path is : $v_0,e_1,v_1,e_2,...$

For a simple graph, it's enough if we write the row of vertices from the graph because, between two vertices in the path there will be only one edge.

2.2.6. Subgraph

If G = (V,E) is a graph, then G1 = (V1, E1) is subgraph from G if Vi $\subseteq$ V and E1 $\subseteq$ E.

2.2.7. Weighted Graph

Weighted Graph is a graph that on every edge is given a value.

2.2.8. Bipartite Graph

Bipartite Graph is Graph G that the set from it's vertices can be separated into two parts : V_1 and V_2. So in the bipartite graph, every edge in graph G connects one vertex in V_1 to one vertex in V_2. The bipartite graph is written as $G(V_1,V_2)$ and it can be said that every pair of vertices in V_1 aren't adjacent so that in V_2. If every vertices in V_1 adjacent to every vertices in V_2, graph $G(V_1,V_2)$ is called as complete bipartite graph represented by $K_{m,n}$. The amount of edges in complete bipartite graph is mn. The bipartite graph is used in matching application in some areas. In chemistry, bipartite graph is used in the matching of Kekulé structure of an aromatic compound to show the location of double bonds in chemical structure.

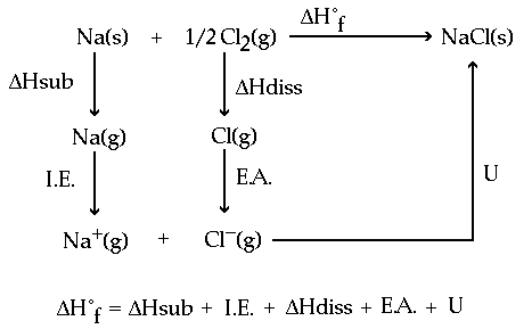
2.2.9. Circuit / Cycle

Circuit (Cycle) is a path that start and end on the sampe vertex. The length of the circuit is the amount of edges in that circuit.

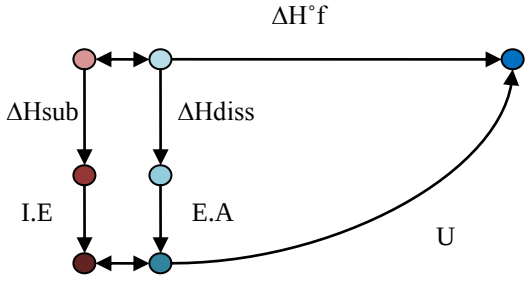
2.2. Chemical Bonds

The chemical bonds contain of some bonds between one atom to another atoms, it describes the nature of attractions in chemical properties.[9] The important thing that exist in every atom that must be known is valence electrons. Valence electrons are the electrons of an atom that can participate in the formation of chemical bonds with other atoms. There are some types of chemical bonds: the ionic bond is the bond between positive ion and negative ion sometimes said as the bond metal and non metal; covalence bond is the bond between non metal and non metal.

The chemical bonds are happened because of the electrons transfer between one atom to another. This process is called as chemical reaction. Of course the transfer of the electrons needs energy and the amount of energy needed is different in every bonds. The bonds can be separated too and of course it needs energy to separate one atom from another. In the gaseous ion, the energy is called lattice energy. Lattice energy is the energy required to completely separate the ions in one mole of a solid compound from each other to form a cloud of gaseous ion. The energy needed in every process of chemical reaction can be written as a value on the edges in weighted graph. The process that happened in the forming or breaking the chemical bonds in the chemical reactions can be pictured as a direct weighted graph.



Picture 2.1. Born Haber process in chemical reaction to form NaCl(s)



Picture 2.2. Born Haber process pictured as a direct weighted graph, the double edge process means the reaction between atom Na and Cl. The graph coloring is used to describe the different atoms.

The theory that useful in the chemical bond is domain theory. Domain theory provides the molecule type, geometric form, and characteristic from molecule. Domain is pair of electron around the center atom. The domain in chemical bond has two types. First is bonding domain (X), bonding domain is pair of electron that can be single covalence bonds, double covalence bonds, triple covalence bonds, or coordinate covalent bonds. Second is free domain(E), free domain is pair of free electrons around center atom. The amount of free domains in a molecule can be calculated with formula :

$$E = \frac{VE - \sum e(bd)}{2}$$

Where E is the sum of free domains, VE is the sum of valence electrons around center atom, e(bd) is the sum of the atom electrons in the bonding domain. As an example, the molecule SCl_2. The sum of VE of S is 6 because 6 is the amount of valence electrons around atom S, the sum of e(bd) is 2 that is the electron from atom S that have bonds with electron from Cl. So we can calculate :

$$E = \frac{6-2}{2} = 2$$

So the amount of free electrons in SCl_2 molecule is two pair of electrons.

The amount of domain, type of domain, type of molecule, and its geometric form is shown in table 2.1.

Amount of Domain	Domain Type		Molecul Type	Geometric Form
	Bonding	Free		
2	2	-	AX2	Linear
3	3	-	AX3	Planar triangular
	2	1	AX2E	V
4	4	-	AX4	Tetrahedral
	3	1	AX3E	Triangle pyramidal
	2	2	AX2E2	V
5	5	-	AX5	Trigonal bipyramidal
	4	1	AX4E	Distorted tetrahedral
	3	2	AX3E2	T
	2	3	AX2E3	Linear
6	6	-	AX6	Octahedral
	5	1	AX5E	Square pyramidal
	4	2	AX4E2	Square planar

Table 2.1. Domain in Chemical Bonds

2.3. Graphs in Chemistry

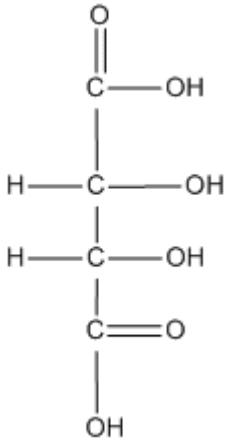
The application of graph in chemistry is by modeling chemistry bonds, structures, process, etc into the form of graph. The modeling of graphs in chemistry provides : rules that predict chemical properties, easy classification of compounds, computer simulations, and computer assisted design of new compounds. There are many terms in graph theory that have different names in chemistry.[3] That differences is shown in table 6.2 :

Graph Theory	**Chemistry**
Graph	Structural Formula
Vertex	Atom
Edge	Chemical Bond
Degree of Vertex	Valency of Atom
Tree	Acyclic Structure
Bipartite Graph	Alternant Structure
Perfect Matching	Kekulé Structure
Adjacency Matrix	Huckel Matrix
Characteristic polynomial	Secular polynomial

Table 2.2 Different Terms in Graph Theory and Chemistry

The graph in chemistry is called Chemical graph. Chemical graph is a weighted graph (V, E, μ), where (V,E) is an undirected graph (without multiple edges or self-loops) all whose nodes are labeled by means of chemical elements, and $\mu : E \rightarrow N$ is a weight function. The valence of a node in a chemical graph is the total weight of the edges incident to it. There are some rules from chemistry that can't be forgotten when we draw a chemical graph. In the graph, the valence electrons is called as vertex degree as written in table 2.2. The degree and edge from a vertex in chemical graph must fulfill the rule that the number of chemical bonds is eternal. It means that the number of degree and edge must remain fixed. Also, the draw of chemical graph mustn't change the structure of every atom in chemical bonds.

One type of chemical bonding that so many used is Carbon compounds. Carbon compounds exist in so many chemical bonds. This compound is really suitable to be modeled as graph. The picture below shows one of carbon compound the tartrate acid that can be found in grapes.



Picture 2.3 Tartrate Acid

Every atom can be represented as a vertex in graph. The structure of tartrate acid above has 12 vertices and 10 edges. Sometimes the atoms beside atom C are drawn as one vertex with atom C. This method can be used when the structure of molecules are not complex enough such as some molecules in hydrocarbon. When used to draw more complex molecules, the use of graphs to represent it can

be harder, so it's needed to keep chemical graph accurate enough to represent the chemical bonds with keep evaluate the graph that has been drawn. Sometimes, more complex theory is needed to draw complex molecules. The property such as double bonds or more complex bonds can't be represented with a simple way of drawing graph. The classical theory that pictures compounds as atoms with single or multiple bonds between them doesn't explain several experimental observations. There are many ways that have been found to solve these problems such as Kekule's theory, Quantum Chemistry, Schrödinger Equation, etc. Every one of them is really a complex theory that outside the scoop of this paper.

III. APPLICATION OF GRAPHS IN CHEMICAL BONDS AND STRUCTURES

3.1. Zagreb Indices

Zagreb Indices are the theory using weighted graph to represent molecules. The Zagreb M1 and M2 indices were introduced and applied to the branching problem. The Zagreb indices and their variants have been used to study molecular complexity and chirality, various researchers also use the Zagreb indices in their QSPR and QSAR studies. [5]

The Zagreb indices are defined as :

$$M1 = \sum_{vertices} d(i)d(i) \qquad (1)$$

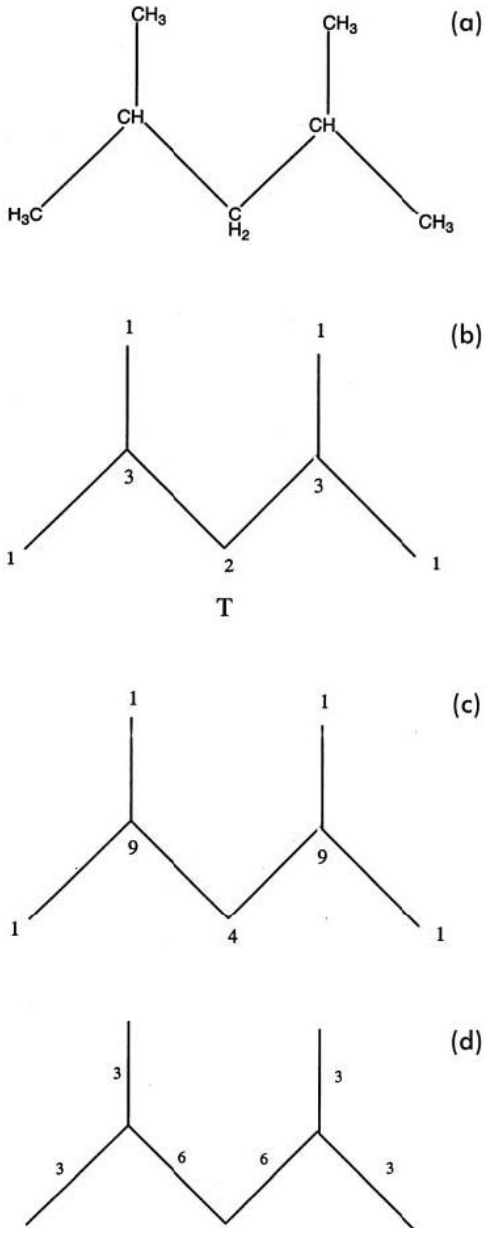
$$M2 = \sum_{edges} d(i)d(j) \qquad (2)$$

where d(i) is the degree of vertex i and d(i) d(j) is the weight of edges i-j. Sometimes the M1 is described as the square value from the degree of vertex i. The M2 value is represent the weight of edges that be obtained from the multiplication of vertex i's degree and vertex j's degree. The problem in Zagreb indices is in the molecules, the contributing parts give greater weight to the inner (interior) vertices and edges than to the outer (terminal) vertices and edges of a graph. Whereas, the outer atoms and bonds should have greater weights because the outer atoms and bonds are connected to larger parts of molecular surfaces. With Zagreb indices, it can be shown that the weight to the outer vertices and edges can be greater.

To show the weight to the outer vertices and edges can be greater, we use the modified Zagreb indices amended by S. Nikolić. The modified Zagreb indices is formed by putting inverse values of the vertex-degrees into Eqs (1) and (2). The modified Zagreb indices (^{m}M1 and ^{m}M2) is shown by the equation below :

$$^{m}M1 = \sum_{vertices} [d(i)d(i)]^{-1} \qquad (3)$$

$$^{m}M2 = \sum_{edges} [d(i)d(j)]^{-1} \qquad (4)$$



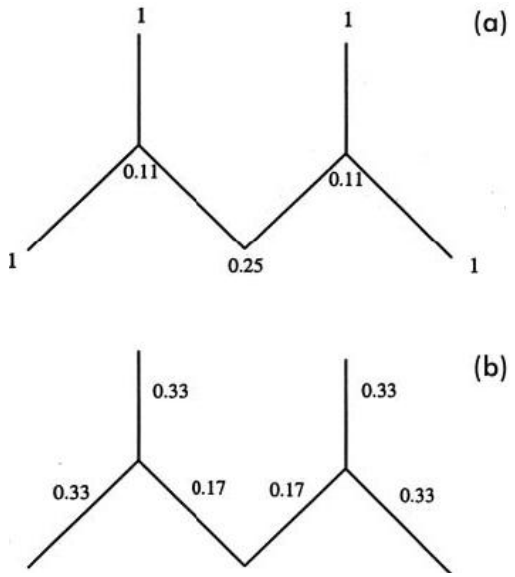
Picture 3.1 Contributing weights to the M1 and M2 indices of 2,4-dimethylpentane. (a) The structure of 2,4-dimethylpentane. (b) The vertex degrees (valence electrons) of 2,4-dimethylpentane. (c) The weights to M1 from the vertices. (d) The weights to M2 from the edges.

The applied of modified Zagreb indices is shown in Picture 3.2. It can be seen that comparing to M1 and M2, the ^{m}M1 and ^{m}M2 give greater weights to outer vertices and edges than to the inner vertices and edges.

The equations (1) and (3) and equations (2) and (4) can be collectively expressed as:

$$^{v}M1 = \sum_{vertices}[d(i)d(i)]^{\lambda} \quad (5)$$

$$^{v}M2 = \sum_{edges}[d(i)d(j)]^{\lambda} \quad (6)$$



Picture 3.2 *Contributing weights to the $^{m}M1$ and $^{m}M2$ indices of 2,4-dimethylpentane. (a) Contributing weights to $^{m}M1$ from the vertices. (b) Contributing weights to $^{m}M2$ from the edges.*

Where ^{v}M1 and ^{v}M2 denote variable Zagreb M1 and M2 indices. For λ=1, equation (5) can be changed to equation (1) and equation (6) can be changed to equation (2). For λ=-1, equation (5) can be changed to equation (3) and equation (6) changed to equation (4). This formulas is used by using the optimal value of λ. The value is used by figuring the right alkanes and their boiling points. The variable Zagreb indices can give the structure of molecules with their boiling point characteristics.

3.2. Hückel Theory

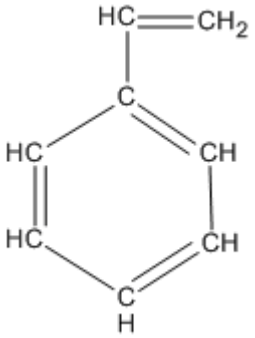
The vast majority of polyatomic molecules can be thought as collection of bonds between atoms. The bonds is consist of two kinds : bonding (σ and π) and antibonding, this is called MO (Molecular Orbital). The Hückel theory provides the framework for sophisticated MO treatments. Hückel theory is used in determining the system of σ and π orbitals. It can be used to determine the total electronic energy of molecule.

What is the correlation between Hückel theory and graph theory? Hückel theory use one-one relationship using adjacency matrix. It provides the equation : H=αI+βA. Where α is the energy of π atomic-orbital and β is π bond strength parameter. The simple example is in molecule ethylene which has two π electrons :

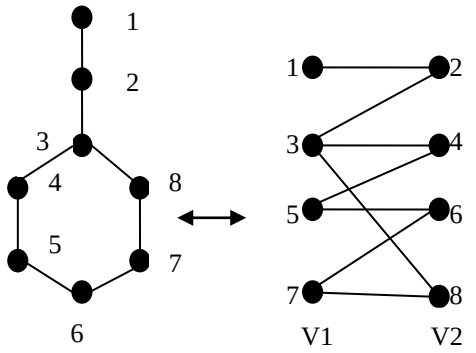
$$H = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

The molecular orbital energy value is -1 (bonding), 1 (antibonding). For the molecule energy is -2.[4] To calculate the energy, we need to put α and β on certain places in matrix. After that, calculate the eigen values and determine the eigen vectors from that matrix. Then, the total energy is the energy that is used from the number of MO that has electrons. How to calculate the Hückel theory in the aromatic compounds is outside the scoop of this paper and won't be explained.

Hückel theory uses the integral of Hamilton circuit. [6] It uses the bipartite graph for the aromatic compound of hydrocarbons. There is no need to decide whether or not a Hückel graph is bipartite because there is already a theorem that said "a graph is bipartite if, and only if, all it cycles (rings) are even membered". We take example of styrene (vinilbenzene)[1] :



Picture 3.3 Styrene (vinilbenzene)



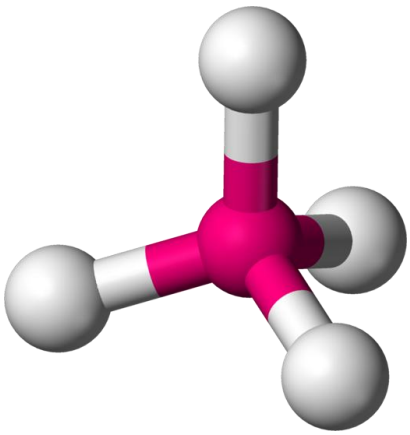
Picture 3.4. Styrene graph (Left) and the proof that styrene is bipartite (Right)

The Styrene can be divided into two subsets the V1 and V2. Every edge on graph connect one vertex in V1 to one vertex in V2, so that's why the styrene graph is bipartite. The adjacency matrix for styrene is shown below :

	1	2	3	4	5	6	7	8
1	0	1	0	0	0	0	0	0
2	1	0	1	0	0	0	0	0
3	0	1	0	1	0	0	0	1
4	0	0	1	0	1	0	0	0
5	0	0	0	1	0	1	0	0
6	0	0	0	0	1	0	1	0
7	0	0	0	0	0	1	0	1
8	0	0	1	0	0	0	1	0

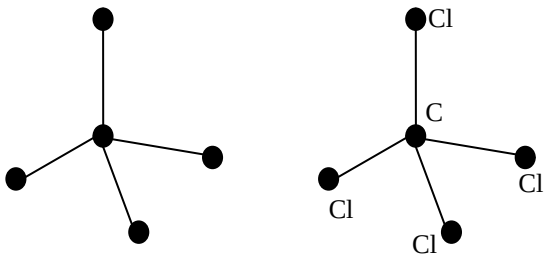
3.3. Molecular Geometry

The molecular geometry can also be represented as graph. Graph can help to analyze the molecules characteristics. For the example, the tetrahedral geometry:



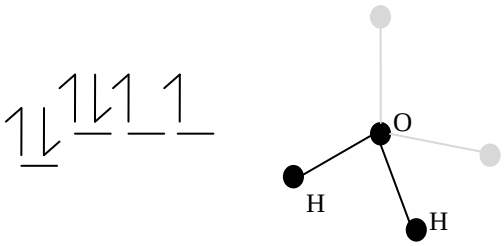
Picture 3.5. Tetrahedral

We can simplify the shape by picture it as a graph :



Picture 3.6. The tetrahedral drawn as a graph (Left); The CCl_4 molecule that has tetrahedral geometry (Right).

From the picture 3.6, it can be seen that graph can represent the geometric form of molecules. Tetrahedral has the molecule type of AX4, then what about other geometric forms that also have four domain but have less bonding domain? We can draw it as a subgraph from AX4 graph. Let see for the molecule H_2O, it has the hybridization sp3 so it also has the basic form of tetrahedral. Atom O in the molecule H_2O has two pairs of free bonding, so the molecule type is AX2E2. The geometric form of H_2O is shown in the picture 3.7. It can be seen from the graph that H_2O has lost two vertices from the AX4 graph, so it has two free electron pairs and the shape of the molecule is asymmetric. These circumstances sign that the H_2O molecule is polar. For the non-polar molecules, the geometric shape will be symmetric. If the molecules have no free electron pairs then the molecules are sure to be non-polar. The free electron pairs can also be drawn as an isolated vertex.



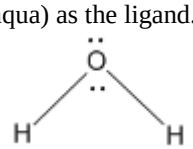
Picture 3.7. Hybridization sp3 of H_2O (Left) and the geometric form of H_2O (Right)

3.4. Complex Ion

Most chemical compounds contain one or more nonmetals. In compounds involving metals, nonmetals occur as either simple anions or in polyatomic anions.[2] Metals have some complex properties. Complex ions are substances formed when molecules or anions become bonded covalently to metal ions to form more complex species. Complex ions are formed by many metals, this is why metals have complex properties which differentiate them from others. We need to know the basic terminology that will be used. The molecules or ions that become attached to a metal ion are called ligands.

Ligands have three types : monodentate, bidentate, and polydentate. Every ligand can only provide finite and constant amount of electron pairs that determined by the length of ligands. For the monodentate, it can only provide one electron pairs, bidentate provide two electron pairs, polydentate provides more than two electron pairs but still in finite amount.

Let take example of monodentate ligands by using H_2O (aqua) as the ligand.

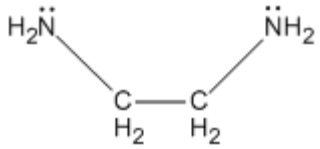


Picture 3.8. H_2O molecule

H_2O molecule is monodentate ligand and has two lone

pairs. From two lone pairs, why it can only provide one? Let use graph theory to describe it. It can be said that O is a vertex. To provide more than one pair, the path lengths have to be far enough and of course it needs more than one vertex.

Let take another example, the bidentate ligand ethylenediamine.

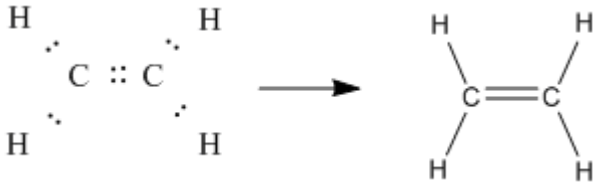


Picture 3.9. Ethylenediamine (en)

Ethylenediamine can provide two electron pairs it's because the path length from one N to another N is far enough. Let say that from the left, first N is vertex a, first C is vertex b, second C is vertex c, and second N is vertex d. The path a-b-c-d is the path from first N to second N and it's far enough to enable ethylenediamine to provide two pairs of electrons. The context 'far enough' can be said that the length between one vertex to another that contains lone pair(s) must be greater or equal to two. It needs chemical intuition to know it more than just an explanation.

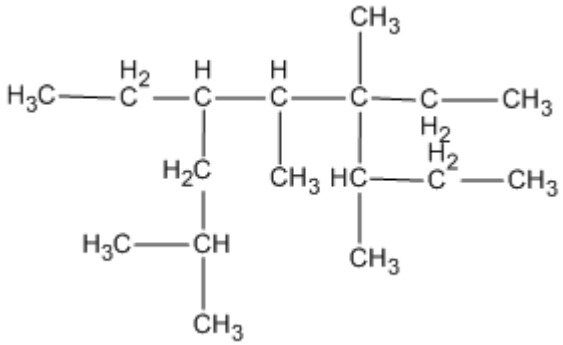
3.5. Other Applications in Chemical Bonds

Graphs represent the chemical bonds in chemistry. Naturally, graphs model molecules. Graphs are modeled from the Lewis structure as shown in picture 3.10.

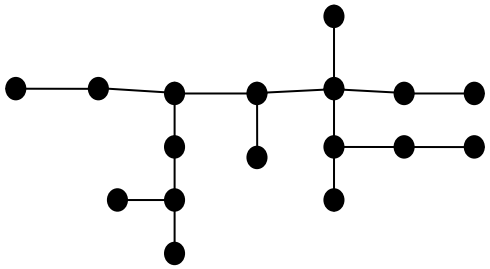


Picture 3.10. Lewis structure (Left) to graph structure (Right)

Hydrocarbon structures are really suitable to be modeled as graph[3]. That's why it's simple enough to show the graph that represents molecules using hydrocarbon bonds.



Picture 3.11. 4,6-dietil-2,5,6,7-tetrametil Nonana



Picture 3.12. 4,6-dietil-2,5,6,7-tetrametil Nonana in graph structure

The graph structures are used to model the relation between one carbon atom to another carbon atom in hydrocarbon. Sometimes the structure can also show the connection between atom carbon to atom hydrogen around it. To show the main chain in hydrocarbon bonds, we can search for the path that through the most vertices.

For other structures in chemistry, the graph can also represent the bonds between atoms in molecules. The adjacent vertices show atoms that have connections with certain atom. The incident edges show the relation between two atoms. The graphs can also show the isomorphic relation between compounds.

IV. CONCLUSION

Graph theory can be used in chemistry aspect. All bonds and structural formulas in chemistry are modeled by graph. There are some differences between some terms in chemistry and in graph but they still have the same meaning. The lines in chemical bonds symbolize the electron bonds (edge in graph) and the points symbolize atoms (vertex in graph).

By using graph, it will make the analysis of chemical bonds and structure easier. The weighted graph can be used to see the weights from atoms or chemical bonds to inner and outer elements (vertices in graph) by using Zagreb indices. We can see the characteristic molecules in chemical structures by using graph to represent the structure. We can also use Hückel theory to provide the framework for sophisticated MO treatments. Hückel theory uses the Hamilton circuit as basic principle to describe aromatic compounds, because aromatic compounds have circuit in it. The graphs that describe the aromatic compounds is called Hückel graph which is always bipartite. We can see that in molecular geometry, the molecules that have lone pair(s) on the central atom, if represent in graph can be the subgraph of the molecules that have the same domain but have no lone pair on their central atom. Graphs can also be used to show the ability to provide electron pairs in ligand.

The use of graph in chemistry is really important. Chemical bonds and structures are described by graphs and graphs can be used to analyze some aspects in them.

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PERNYATAAN

Dengan ini saya menyatakan bahwa makalah yang saya tulis ini adalah tulisan saya sendiri, bukan saduran, atau terjemahan dari makalah orang lain, dan bukan plagiasi.

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