<u>**Research Proposal:**</u>
<u>**Representing Kekule Cells in Stable Molecules**</u>
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<u>**Introduction**</u>

Carbon is the 6th element of the periodic table and backbone of all organic molecules. It is tetravalent, meaning it has 4 valence electrons available to form covalent chemical bonds. In such bonds, atoms share electrons relatively equally between them. Each possible bonding partner of carbon will contribute a single electron to the covalent bond, meaning carbon, in it's full valency will have 8 electrons. This is considered a full octet, and the stable configuration of carbon. However, 4 bonding partners is not always needed. If Carbon was bonded to 3 other atoms, but one of them was able to share 2 electrons (a double bond), carbon would still have a full valency of 8 electrons and be stable.

According to the Valence Bond Theory, such single and double bonds have different electron structure. Single bonds are named "sigma (σ) bonds", and are caused by the head-on overlapping between atomic orbitals. These are the strongest type of covalent bond. Double bonds are named "pi (π) bonds", and result from electron overlap in the nodal plane which passes through both of the bonding atoms. Double bonds are weaker, but still resilient.

Many organic molecules display alternating paths of single and double bonds. In this configuration, every atom is connected with precisely one double bond. This is named conjugation, and can increase molecular stability. Conjugation implies the possibility of different resonance structures, where every double bond shifts in one direction to obtain a different representation of the same molecule. The amount of such resonance structures is a measure of stability. The actual molecule results from the superposition of all resonance structures.

Each of the nodal lobes involved in pi bond conjugation allow their electrons to delocalize across the molecule. Since electrical current is the flow of electrons, such alternating paths are postulated to be electrically conductive [1,4]. When electricity (specifically a 'soliton') is ran through a conjugated system, all double and single bonds are alternated [4].

This allows some molecules to display a 'switching' property. A channel is defined as a path through a molecule. A channel is open when the path is alternating, and closed otherwise. When some alternating paths are toggled, other paths may be opened or closed. This resembles the behaviour of circuitry, and is proposed as a basis for molecular computation. This proposal is quite speculative.

<u>Previous Work</u>

Hesselink et al. [1,2] has previously shown that the switching behaviour can be completely described using Kekule Theory. Graph theory is first used to model cyclic unsaturated hydrocarbons, where atoms are abstracted as nodes, and edges represent chemical covalent bonds. These graphs neglect all hydrogen atoms, as they do not contribute to conjugation.

Double bonds are represented using a pairwise disjoint subgraph, where every edge in the subgraph represents a double bond. Pairwise because a double bond reaches two vertices, and disjoint because double bonds are seen at every other position in an alternating path. It is possible to give every carbon atom precisely one double bond if its graph has a 'perfect matching'. Each perfect matching corresponds to a single resonance structure.

Certain vertices are labelled 'ports' are are not required to contain a double bond. Therefore, our matchings can contain imperfections at the ports. Ports are where the molecule connects to the 'outside world'. This allows not only connectivity between molecules, but locations to observe and influence molecular behaviour. Anything can be attached to a port, as it does not affect the interchanging of bonds or the switching behaviour.

Each graph is associated with a Kekule cell, which consists of all the possible stable double bond configurations of that molecule. This is recorded by naming the ports, and labelling each configuration based on which ports contain double bonds. From this, Hesselink has classified all possible Kekule cells with ports ⪅ 5. He has also classified 210 out of 214 possible Kekule cells with 6 ports. This means nearly any molecule with 6 or less ports has the exact same 'switching property' as one of the structures found by Hesselink.

However, results obtained by Hesselink are graphs which only represent the Kekule cell, not graphs which also resemble molecules.

Motivation

"For application to carbon chemistry, it would be interesting to see whether all Kekule cells ... can be realized in stable molecules"   - Hesselink, 2013 [1]

This area of research is relatively new. To our knowledge, of the few studies that have been done, none of them have made any attempt to obtain realistic graphs. For our contribution, we would like to first, create our own software framework to confirm previous results. We would then like to attempt to find alternate more realistic structures for each one given in Hesselink's classification.

If we want a molecule with a certain switching behaviour, the search can be split into three sections:

1. Search for cells K with the required switching behavior.
2. Search for ported graphs (G, P) with K = Kp(G, P).
3. Search for suitably alternating hydrocarbon molecules that have such a ported graph.   - Hesselink, 2013 [1]

Our research attempts to bridge the gap between step 2 and 3, now that Hesselink [1] has made strong headway in step 2. We approach the problem first, by adding multiple restrictions to our resulting graphs.

"In view of the application to conjugation in carbon chemistry, we could restrict attention to graphs where all nodes degrees ⪅ 4"   - Hesselink et al., 2007 [2]

Hesselink himself has said that graphs could be restricted so nodes have degrees of 4 or less. However, we feel this is not strict enough. Every atom in such conjugated systems is involved in a double bond (or else the structure wouldn't be stable). Since double bonds are seen only in subgraphs, a node should be at maximum allowed to connect to 3 distinct vertices.

What about ports? Ports aren't required to have a double bond in order for the structure to be stable. However, in most molecules, at least one configuration involves a double bond at any given port. Additionally, ports are defined as atoms which "other chemical groups can be attached to observe and influence behaviour" [1]. This means ports must have (1) The capacity to form a double bond, and (2) One bond reserved to connect to outside chemical groups. This means ports must be at maximum allowed to connect to 2 distinct vertices.

Other than the degree of vertices, there are other inconsistencies with some of Hesselink's [1] results. Graphs are permitted to be disjoint. An unconnected graph really represents two molecules, not one, with no feasible means of conjugation between them. Therefore, results must also be limited to connected graphs. Other unstable structures such as 3 membered rings of carbon (which appear in some graphs) are sterically unfavourable.

Challenges

There are many challenges with such an approach. First off, the time complexity of searching for graphs given a Kekule cell is quite large, even without added restrictions. When searching for Kekule cells of order 6, Hesselink was not able to find graphs for 4 Kekule cells. This suggests the possibility of rather than looking for more complete structures, to obtain Hesselink's structures and alter them. The editing of a graph without changing it's Kekule cell has been studied in [1],[2], and [3]. Perhaps this approach can be taken algorithmically. Finally, we would also like to find existing organic molecules which resemble generated structures, in order to back up our claim that such results describe stable molecules.

References:

[1] W. H. Hesselink, Graph Theory for alternating hydrocarbons with attached ports. *Indagationes Mathematicae*, Elsevier, 24:115141, 2013.
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