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Graph theory for alternating hydrocarbons with attached ports

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Abstract

Properties of molecules of certain hydrocarbons give rise to difficult questions in graph theory. This paper is primarily devoted to the graph theory, but the physico-chemical motivation, which is somewhat speculative, is also presented.

Molecules of unsaturated hydrocarbons exhibit alternating paths with single and double bonds. Such alternating paths have been postulated to be electrically conductive. When used to conduct, however, such a path is toggled: the single and double bonds are interchanged. This can imply that other alternating paths appear or disappear. In this way, switching behavior arises. This suggests a possibility of molecular computing.

Molecules are represented by graphs where certain nodes, called ports, are chosen as connectors to the outside world. At these ports other chemical groups can be attached to observe and influence the behavior. A choice of single and double bonds in the molecule is represented by an almost-perfect matching in the graph—almost, in the sense that the ports and only the ports are allowed to have no double bond attached to them. The corresponding graph theory is a qualitative idealization of the molecules.

It turns out that the switching behavior is completely determined by sets of ports, called cells. The paper is devoted to the question which cells are Kekulé cells, i.e., correspond to almost-perfect matchings in graphs. We prove that every Kekulé cell is what is known as a linkable Δ-matroid (it appears that this was known).

An anonymous referee showed us the existence of a linkable Δ-matroid with 7 ports that is not a Kekulé cell. The argument is presented. We classify the linkable cells with ≤ 5 ports and show that they all are

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Kekulé cells. We also classify the linkable cells with 6 ports. There are 214 classes; 210 classes contain Kekulé cells; only 4 classes are undecided.

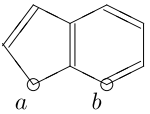
Keywords: Hydrocarbon; Undirected graph; Matching; Delta-matroid; Matroid; Group action; Classification

1. Introduction

In this paper, we propose and investigate discrete Kekulé Theory, which is a graph theory for alternating hydrocarbons with attached ports. It is a theory within discrete mathematics and graph theory, part of the theory of Δ-matroids [1,2] and close to matching theory [10]. It is inspired by chemistry [12] and first studied in [7]. The aim is to investigate and systematize qualitative switching behavior in polycyclic polyunsaturated hydrocarbons, with molecular computing as an ultimate goal.

Consider the indene molecule sketched below (indene is a constituent of indigo). In such hydrocarbons, the bonds between the carbon atoms can be single bonds and double bonds, but *ideally* every atom has precisely one double bond. In the indene molecule, however, this is not possible. By attaching other groups to the molecule at specific atoms, which are called *ports*, the rule can be weakened in the sense that at these ports the number of double bonds is *at most* one.

In the diagram, we have chosen ports at a and b, and indicated them by the little circles. Now there are three solutions, two states with no double bond at a (one of which is sketched), and one with no double bond at b.

Indene: 

The reader should realize that the single and double bonds mentioned form an idealization. When, for fixed port behavior, there are several solutions to the combinatorial problem of placing the single and double bonds, the solutions have no independent physical meaning, and are called *resonance structures*. The real quantum-mechanical state is a superposition of these resonance structures. Even worse, the graph itself is an idealization: some bonds in the graph are stronger than others, and atoms that are not connected in the graph do influence each other. In discrete Kekulé theory, however, we form a qualitative abstraction that only to some extent corresponds to the physical or chemical reality.

In a given molecule, it is possible to give every carbon atom precisely one double bond if and only if its graph has a so-called *perfect matching*. The number of perfect matchings is an indicator of the stability of the molecule [10, Section 8.7]. Our subject matter is thus an extension of classical matching theory [10]. Our matchings need not be perfect, but imperfections are only permitted at the ports.

1.1. Switching behavior

It has been postulated [13] that there is an electrically open channel through the molecule between two ports if and only if there is an alternating path between the ports, i.e., a path that alternately consists of single and double bonds (this is slightly inaccurate, see Section 2.2 for the correct definition). By sending a so-called *soliton* over the alternating path, the single and double bonds along the path are toggled [5]. In the case of indene drawn above, there is such a