MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **53** (2005) 419-426

ISSN 0340 - 6253

Towards a combinatorial efficient algorithm to solve the Clar problem of benzenoid hydrocarbons

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(Received June 1, 2004)

Abstract

The Clar problem (computing the cardinality of a maximum resonant set) of a benzenoid hydrocarbon is addressed. The concept of a maximum M-resonant set for some perfect matching M is introduced and a related result is obtained and its potential usefulness in developing an efficient combinatorial algorithm to solve the Clar problem of benzenoid hydrocarbons is discussed.

1. Introduction

A hexagonal system (also called a polyhex) is a 2-connected subgraph of the hexagonal lattice without non-hexagonal interior faces (Guo and Zhang [1992]). A hexagonal system is to be placed on the plane so that a pair of edges of each hexagon lies in parallel with the vertical axis. If no three hexagons of a hexagonal system H have a common node, H is said to be catacondensed (Gutman et al. [1977]). Hexagonal systems represent benzenoid hydrocarbons.

Let L be a non-empty set of hexagons of a hexagonal system H. We call L a set of mutually alternating hexagons of H (or a framed set of H) if there exists a perfect matching of H that contains a perfect matching of each hexagon in L (Abeledo and Atkinson [2000]) (Fig. 1). A perfect matching of a hexagon is called a sextet (Ohkami et al. [1981]). It is proper if the right vertical edge of the hexagon is in the perfect matching; otherwise it is improper.

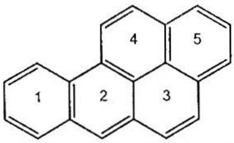

Fig. 1. {2, 4, 5} is a set of mutually alternating hexagons

Let L be a non-empty set of hexagons of a hexagonal system H. We call L a resonant set of H if the hexagons in L are pair-wise disjoint and there exists a perfect matching of H that contains a perfect matching of each hexagon in L (Abeledo and Atkinson [2000]) or equivalently (Gutman [1983]) if the hexagons in L are pair-wise disjoint and H-L has a perfect matching (H-L denotes the subgraph of H obtained by deleting from H all the nodes of the hexagons in L together with their incident edges) (Fig. 2). The cardinality of a maximum resonant set is called the Clar number (Hansen and Zheng [1992]). A Clar formula of a hexagonal system (Gutman [1982], Gutman and Cyvin [1989], Hansen and Zheng [1994]) is obtained by drawing circles in some of the hexagons according to the following rules: (a) circles are never drawn in adjacent hexagons; (b) the graph obtained by deleting the nodes of all hexagons containing a circle must have a perfect matching or must be empty; (c) the number of circles is maximum subject to (a) and (b). Hosoya and Yamaguchi [1975] were first to define Clar type formulas which are constructed by taking into account rules (a) and (b) but not the requirement (c). These are called generalized Clar formulas (Gutman [1982], Gutman and Cyvin [1989]). It is clear that Clar formulas and generalized Clar formulas are essentially pictorial representations of maximum resonant sets and resonant sets respectively.

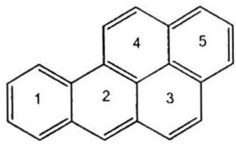

Fig. 2. {1, 5} is a resonant set

Let L be a non-empty set of hexagons of a hexagonal system H. Let M be a perfect matching of H. We call L an M-resonant set if the hexagons in L are pair-wise disjoint and the perfect matching M contains a perfect matching of each hexagon in L. A non-empty set L of hexagons is resonant if and only if it is M-resonant for some perfect matching M. A maximum resonant set is a maximum M-resonant set for some perfect matching M, but the converse is not necessarily true (Fig. 3).

The Clar problem of a hexagonal system is the problem of determining the Clar number of the hexagonal system. The Clar number is of significance in the theory of benzenoid hydrocarbons. The main chemical implication of the Clar number is the following empirically established regularity (Clar [1972]): If B_a and B_b are two isomeric benzenoid hydrocarbons, and if the Clar number of B_a is greater than the Clar number of B_b, then the compound B_a is both chemically and thermodynamically more stable; the positions of the maxima in the electron absorption spectrum of B_b are shifted towards longer wavelengths relative to B_a.

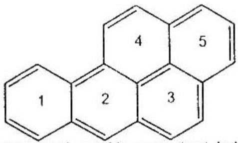

Fig. 3. {3} is a maximum M-resonant set, but not maximum resonant

2. Computing the Clar number

Hansen and Zheng [1992] reported upper bounds for the Clar number. Somewhat later, they formulated the Clar problem as an integer linear program (Hansen and Zheng [1994]). Recently, Abeledo and Atkinson showed that the problem could be solved as a linear program (Atkinson [1998], Abeledo and Atkinson [2000]). An efficient combinatorial (graph-theoretic) algorithm to solve the Clar problem in catacondensed hexagonal systems was given by Atkinson [1998, p. 5-14]. Later the algorithm was re-invented by Klavžar et al. [2002]. Its time complexity is linear (Klavžar [2003]). Also, an efficient combinatorial algorithm to solve the Clar problem in a restricted class of hexagonal systems was developed by Zhang and Li [1989].

3. A result and its potential usefulness

Theorem. Let H be a hexagonal system that has a perfect matching. Let L be a set of mutually alternating hexagons. Then the subgraph of the (inner) dual of H induced by the nodes that correspond to the hexagons in L is bipartite (Fig. 4).

Proof. Let M be a perfect matching of H that contains a sextet of each hexagon in L. The hexagons in L are either proper or improper sextets. Consider the subgraph of the (inner) dual of H induced by the nodes that correspond to the hexagons in L. Color a node black if it corresponds to a proper sextet and white if it corresponds to an improper sextet. Assume that an edge of this induced subgraph joins two nodes of the same color, then the corresponding hexagons are adjacent and they are both proper sextets or both improper sextets, a contradiction.

Q.E.D.

Remark. This theorem and its proof can be extended to a plane map of a 2-connected planar bipartite graph that has a perfect matching (Appendix).

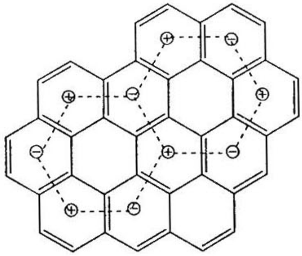

Fig. 4. The induced subgraph is bipartite

Discussion. Let H be a hexagonal system that has a perfect matching. Let M be a perfect matching of H. Let L be the set of all M-alternating hexagons. (A hexagon is M-alternating if the perfect matching M of H contains a perfect matching of the hexagon). Consider the subgraph of the (inner) dual of H induced by the nodes that correspond to the hexagons in L. A maximum M-resonant set of H corresponds to a maximum stable set of this induced subgraph. (A stable set of a graph G is a set of nodes in G, no two of which are adjacent). According to the above theorem, this induced subgraph is bipartite. Thus the maximum M-resonant set problem is a maximum stable set problem in a bipartite graph.

König's theorem states that in a bipartite graph, the maximum cardinality of a matching equals the minimum cardinality of a node cover. (A node and an edge are said to cover each other if they are incident. A set of nodes which covers all the edges of a graph G is called a node cover for G, while a set of edges which covers all the nodes is an edge cover.) A proof of König's theorem (Cook et al. [1998], p. 48) shows how a maximum flow algorithm provides an efficient combinatorial algorithm for constructing a maximum matching and a minimum node cover of a bipartite graph. The complement of a minimum node cover is a maximum stable set (Gallai [1959]). Thus the maximum stable set problem in a bipartite graph can be solved by an efficient combinatorial algorithm and so is the maximum M-resonant set problem.

A perfect matching M of a hexagonal system H is optimal with respect to the Clar problem if a maximum M-resonant set is maximum resonant. As shown above the maximum M-resonant set problem can be solved by an efficient combinatorial algorithm. Hence, solving the Clar problem by an efficient combinatorial algorithm reduces to developing an efficient combinatorial algorithm to obtain a perfect matching that is optimal with respect to the Clar problem. A criterion for a perfect matching to be optimal with respect to the Clar problem needs to be developed and also a mechanism that moves us from some (not optimal) perfect matching to a "better" one.

4. Appendix

Definitions. Let G be a plane map of a 2-connected planar bipartite graph. Since G is a 2-connected plane graph, every face boundary of G is a cycle of G (Fleischner [1990], p. III-53). We identify the faces of G with the cycles of their boundaries. Since G is bipartite, all its cycles are even (Harary [1969], p. 18). By definition of a bipartite graph, we can color the nodes of G with two colors, black and white say, so that no two nodes of the same color are adjacent.

Let L be a non-empty set of interior faces of the graph G. We call L a set of mutually alternating faces of G (or a framed set of G) if there exists a perfect matching of G that contains a perfect matching of each face in L (Abeledo and Atkinson [2000]). An alternating face f of G is proper if, by the orientation of f clockwise, the matched edges of f go from white nodes to black nodes; otherwise f is improper (Zhang and Zhang [1997]).

Theorem. Let G be a plane map of a 2-connected planar bipartite graph that has a perfect matching. Let L be a set of mutually alternating interior faces. Then the subgraph of the (inner) dual of G induced by the nodes that correspond to the faces in L is bipartite.

Proof. Let M be a perfect matching of G that contains a perfect matching of each face in L. The faces in L are either proper or improper alternating (M-alternating) faces. Consider the subgraph of the (inner) dual of G induced by the nodes that correspond to the faces in L. Color a node black if it corresponds to a proper alternating face and white if it corresponds to an improper alternating face. Assume that an edge of this induced subgraph joins two nodes of the same color, then the corresponding two faces share an edge, e say, and they are both proper M-alternating or both improper M-alternating. It is easy to see that e belongs to M and does not belong to M by considering the two proper/improper M-alternating faces, a contradiction.
Q.E.D.

Acknowledgement. The author thanks Prof. H. Abeledo (Engineering Management and Systems Engineering, The George Washington University, USA) for assisting in the proof of the result.

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