The Clar formulas of a benzenoid system and the resonance graph

Khaled Salem [1]

The British University in Egypt
El Shorouk city, Postal code 11837, Egypt
ksalem@bue.edu.eg

Sandi Klavžar

Department of Mathematics, University of Ljubljana
Jadranska 19, 1000 Ljubljana, Slovenia
sandi.klavzar@fmf.uni-lj.si

Aleksander Vesel

Department of Mathematics and Computer Science, University of Maribor
PeF, Koroška cesta 160, 2000 Maribor, Slovenia
vesel@uni-mb.si

Petra Žigert

Faculty of Chemistry and Chemical Engineering, University of Maribor
Smetanova 17, 2000 Maribor, Slovenia
petra.zigert@uni-mb.si

Abstract

It is shown that the number of Clar formulas of a Kekuléan benzenoid system B is equal to the number of subgraphs of the resonance graph of B isomorphic to the $Cl(B)$-dimensional hypercube, where $Cl(B)$ is the Clar number of B.

Key words: Benzenoid system, resonance graph, resonant set, Clar formula

[1] corresponding author

1 Introduction

Benzenoid systems are interesting graphs in chemical graph theory [1,2] since they represent the chemical compounds known as benzenoid hydrocarbons. A necessary condition for a benzenoid hydrocarbon to be (chemically) stable is that it possesses Kekulé structures, which describe the distribution of so called π-electrons i.e. double bonds in a benzenoid hydrocarbon. Consequently, Kekuléan benzenoid systems pertain to those benzenoid hydrocarbons that are of main chemical interest [3]. Replacing the three alternating double bonds in a single hexagon of a Kekulé structure with a circle such that circles are not drawn in adjacent hexagons, one obtains a generalized Clar formula of a benzenoid system. As a consequence an invariant of a Kekuléan benzenoid system called Clar number can be introduced. It was Clar [4] who noticed the significance of this number in the chemistry of benzenoid hydrocarbons.

The resonance graph [5] of a Kekuléan benzenoid system models interactions among its Kekulé structures. The vertices of the resonance graph are the Kekulé structures; two vertices are adjacent if the corresponding Kekulé structures interact, that is if one Kekulé structure is obtained from the other by rotating three double bonds in a hexagon.

This concept of resonance graphs was first put forward by Gründler [6] and was then re-invented by El-Basil [7,8] and, independently, by Randić [9,10]. In addition to this, without any reference to chemistry, Zhang, Guo and Chen introduced resonance graphs and established their basic mathematical properties [5,11,12]. For some recent developments, see the review article [13] and [14–16].

The main motivation for the present paper is the following theorem from [17].

Theorem 1.1 *Let B be a Kekuléan benzenoid system and $R(B)$ its resonance graph. Then there exists a surjective mapping from the set of subgraphs of $R(B)$ isomorphic to hypercubes onto the family of nonempty resonant sets of B.*

Here, we take a closer look to this. As a consequence, we prove our main result: the number of Clar formulas of a Kekuléan benzenoid system B is equal to the number of subgraphs of the resonance graph of B isomorphic to the $Cl(B)$-dimensional hypercube, where $Cl(B)$ denotes the Clar number of B.

2 Preliminaries

A *benzenoid system* (also called a *hexagonal system*) is a 2-connected plane graph such that its each inner face is a regular hexagon of side length 1. A benzenoid system is *Kekuléan* if it has a Kekulé structure, i. e., it has a perfect matching.

Let P be a set of hexagons of a Kekuléan benzenoid system B. We call P a *resonant set* of B (or a *generalized Clar formula* of B) if the hexagons in P are pair-wise disjoint and there exists a perfect matching of B that contains a perfect matching of each hexagon in P [18,19]. The latter condition can be replaced by the subgraph $B - P$ (obtained by deleting from B the vertices of the hexagon in P) is either empty or has a perfect matching. Let us recall here that every perfect matching of B contains a perfect matching of a hexagon of B [20]. The maximum of the cardinalities of all the resonant sets is called the *Clar number* [21] and denoted $Cl(B)$. A *maximum cardinality* resonant set (or a *Clar formula*) is a resonant set whose cardinality is the Clar number. A resonant set P such that the subgraph $B - P$ is either empty or has a unique perfect matching is called a *canonical* resonant set [2,22]. Fig. 1 illustrates these concepts.

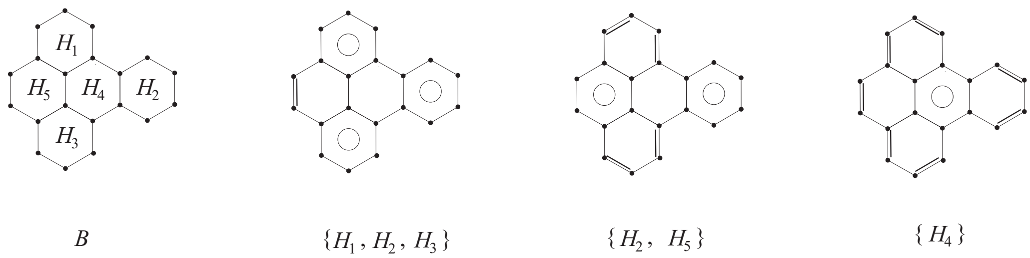

Fig. 1. A Kekuléan benzenoid system, the (unique) Clar formula and the remaining two canonical resonant sets.

The *resonance graph* [5] of a Kekuléan benzenoid system B (also called the *Z-transformation graph*) is the graph whose vertices are the perfect matchings of B and where two perfect matchings are adjacent provided that their symmetric difference is the edge set of a hexagon of B. Fig. 2 presents the resonance graph of the Kekuléan benzenoid system from Fig. 1.

The *k-dimensional hypercube*, where k is a positive integer, is the graph whose vertex set is the set of all binary sequences of length k and where two vertices are adjacent provided that they differ in exactly one position. For graph theoretical terminology the reader is referred to [23].

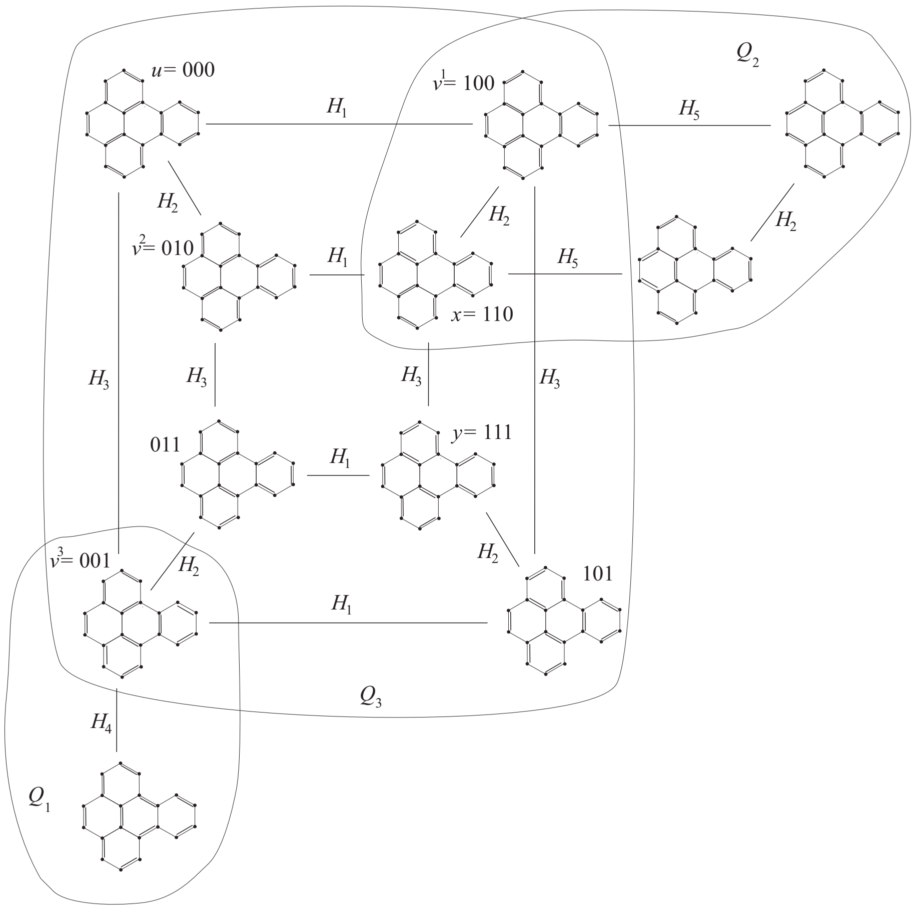

Fig. 2. The resonance graph of B.

3 The number of Clar formulas of a benzenoid system

In order to prove our main theorem some preparation is needed.

Let B be a Kekuléan benzenoid system and $R(B)$ its resonance graph. Let Q be a subgraph of $R(B)$ isomorphic to the k-dimensional hypercube for some positive integer k. We may assume that the vertices of Q (considered as the vertices of $R(B)$) are labelled with the binary sequences of length k such that two vertices of Q are adjacent in Q if and only if their binary sequences differ in exactly one position. Consider the following vertices of Q:

$$u \equiv \langle 000\ldots 0\rangle, v^1 \equiv \langle 100\ldots 0\rangle, v^2 \equiv \langle 010\ldots 0\rangle, \ldots, v^k \equiv \langle 000\ldots 1\rangle.$$

By the definition of the resonance graph, each of the edges $uv^1, uv^2, \ldots, uv^k$ corresponds to a unique hexagon of B. More precisely, for each $j = 1, 2, \ldots, k$, let H_j denote the symmetric difference of u and v^j. Then it was proved in [17] that, given arbitrary vertices x and y of Q whose binary sequences differ only at the j-th place for some $j = 1, 2, \ldots, k$, then the symmetric difference of x

and y is the hexagon H_j, as seen on Fig. 2. Moreover [17], the set

$$\mathcal{R}_Q = \{H_1, H_2, \ldots, H_k\}$$

is a resonant set of B of cardinality k. Therefore, we call $\mathcal{R}_Q$ the resonant set *associated with* a subgraph Q of $R(B)$ isomorphic to a hypercube, see Figs. 1 and 2.

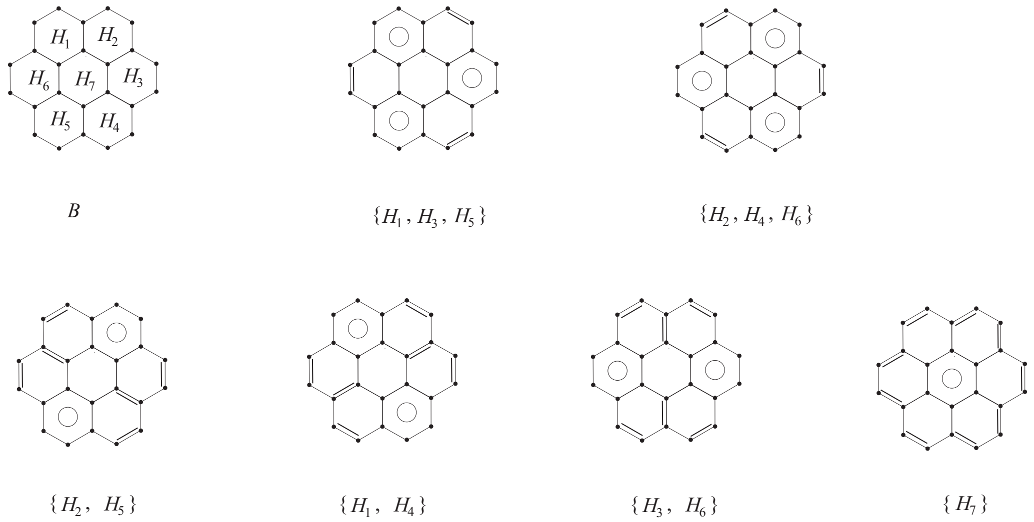

Fig. 3. A Kekuléan benzenoid system (coronene), both its Clar formulas, the remaining three canonical resonant sets and the resonant set $\{H_7\}$.

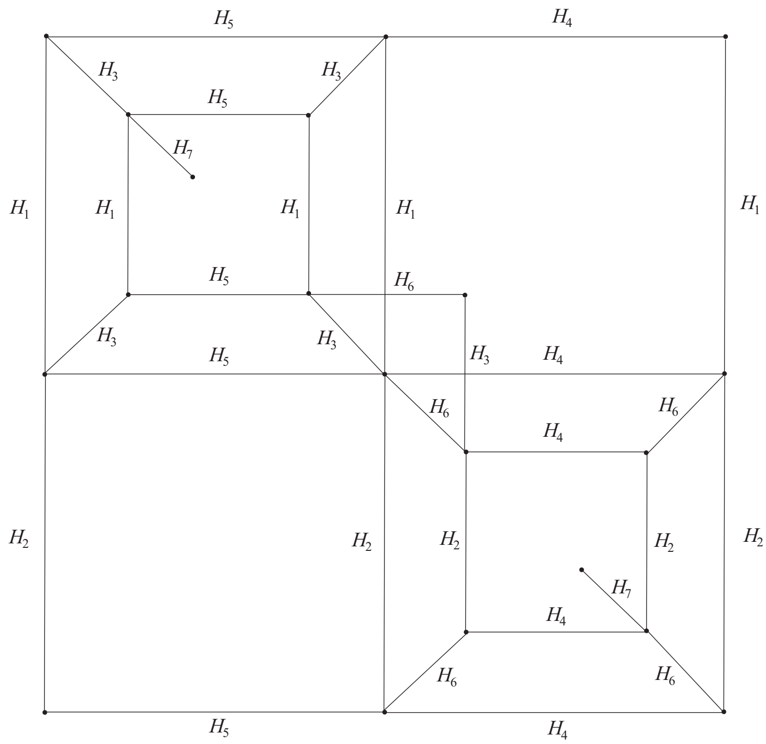

Fig. 4. The resonance graph of coronene.

Let B be a Kekuléan benzenoid system and $R(B)$ be its resonance graph. Let P be a resonant set of B of cardinality k for some positive integer k. If the subgraph $B - P$ is empty, let M be the empty set, otherwise, let M be a perfect matching of $B - P$. For each choice of M, the 2^k perfect matchings of the hexagons in P produce 2^k perfect matchings of B. It is clear that for each choice of M, the set of 2^k perfect matchings of B can be coded with integer sequences of length $k + 1$ where the first integer in the sequence denotes the choice of M and the remaining k integers are binary digits. Hence, the subgraph of $R(B)$ induced by each such set of 2^k perfect matchings of B is isomorphic to the k-dimensional hypercube.

Thus, given a resonant set of B of cardinality k for some positive integer k, this procedure associates a unique subgraph of $R(B)$ isomorphic to the k-dimensional hypercube if P is a canonical resonant set, otherwise, it associates as many (vertex-disjoint) subgraphs of $R(B)$ isomorphic to the k-dimensional hypercube as the number of perfect matchings of $B - P$. This allows the definition of the set of subgraphs of $R(B)$ isomorphic to a hypercube *associated with* a resonant set. For a resonant set P, let us denote the associated set of hypercubes with $\mathcal{H}_P$.

The above concept is illustrated with Figs. 3 and 4. The resonance graph of coronene has a unique 2-dimensional hypercube associated with the canonical resonant set $\{H_2, H_5\}$. However, it has two 1-dimensional hypercubes associated with the resonant set $\{H_7\}$ which is not a canonical resonant set. In fact, the subgraph of coronene obtained by removing the vertices of H_7 is a cycle, thus, it has two perfect matchings.

We need some more notation for our first result. Let B be a Kekuléan benzenoid system and $R(B)$ be its resonance graph. Let $\mathcal{H}(R(B))$ be the set of subgraphs of $R(B)$ isomorphic to hypercubes and $\mathcal{RS}(B)$ be the family of nonempty resonant sets of B.

Theorem 3.1 *Let B be a Kekuléan benzenoid system and let $f : \mathcal{H}(R(B)) \to \mathcal{RS}(B)$ be a mapping defined with $f(Q) = \mathcal{R}_Q$ for $Q \in \mathcal{H}(R(B))$. Then the inverse image of a nonempty resonant set P under the mapping f is $\mathcal{H}_P$.*

PROOF. Let P be a resonant set of B of cardinality k for some positive integer k. It is clear that $\mathcal{H}_P$ is a subset of the inverse image of P under the mapping f. Let Q be an element of the inverse image of P under the mapping f, i.e., Q is a subgraph of $R(B)$ isomorphic to the k-dimensional hypercube and P is the resonant set associated with Q. It follows from the remarks at the beginning of this section that for each vertex w of Q, w contains a perfect matching of each hexagon in P. Also, those remarks imply that for each two adjacent vertices of Q, their symmetric difference is a hexagon in P. Since Q

is connected, the vertex set of Q is the vertex set of a subgraph in the set of subgraphs of $R(B)$ isomorphic to a hypercube associated with the resonant set P. Hence, Q is an element of $\mathcal{H}_P$. $\square$

Note that Theorem 3.1, in particular, asserts that the mapping f is surjective, a result first proved in [17] and here stated as Theorem 1.1.

Here is our main result.

Theorem 3.2 *Let B be a Kekuléan benzenoid system. Then there exists a bijective mapping from the set of subgraphs of $R(B)$ isomorphic to the $Cl(B)$-dimensional hypercube into the family of maximum cardinality resonant sets of B.*

PROOF. It is clear that the image of a subgraph of $R(B)$ isomorphic to the $Cl(B)$-dimensional hypercube under the mapping defined in Theorem 3.1 is a resonant set whose cardinality is $Cl(B)$, i.e., a maximum cardinality resonant set. Also, a maximum cardinality resonant set is a canonical resonant set [24,25]. Hence, by Theorem 3.1 and the remarks preceding it, the inverse image of a maximum cardinality resonant set under the mapping defined in Theorem 3.1 is a singleton set containing a subgraph of $R(B)$ isomorphic to the $Cl(B)$-dimensional hypercube. $\square$

As illustrated in Fig. 3, coronene has exactly two Clar formulas (maximum cardinality resonant sets) and its Clar number is 3. Indeed its resonance graph (see Fig. 4) has exactly two 3-dimensional hypercubes.

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References

[1] I. Gutman, S. J. Cyvin, Introduction to the Theory of Benzenoid Hydrocarbons, Springer-Verlag, Berlin, 1989.

[2] M. Randić, Aromaticity of polycyclic conjugated hydrocarbons, Chem. Rev. 103 (2003) 3449–3605.

[3] G. Brinkmann, C. Grothaus, I. Gutman, Fusenes and benzenoids with perfect matchings, J. Math. Chem. 42 (2007) 909–924.

[4] E. Clar, The Aromatic Sextet, Wiley, London, 1972.

[5] F. Zhang, X. Guo, R. Chen, Z-transformation graphs of perfect matchings of hexagonal systems, Discrete Math. 72 (1988) 405–415.

[6] W. Gründler, Mesomerie und Quantenmechanik, Z. Chem. (Leipzig) 23 (1983) 157–167.

[7] S. El-Basil, Kekulé structures as graph generators, J. Math. Chem. 14 (1993) 305–318.

[8] S. El-Basil, Generation of lattice graphs. An equivalence relation on Kekulé counts of catacondensed benzenoid hydrocarbons, J. Mol. Struct. (Theochem) 288 (1993) 67–84.

[9] M. Randić, Resonance in catacondensed benzenoid hydrocarbons, Int. J. Quantum Chem. 63 (1996) 585–600.

[10] M. Randić, D. J. Klein, S. El-Basil, P. Calkins, Resonance in large benzenoid hydrocarbons, Croat. Chem. Acta 69 (1996) 1639–1660.

[11] F. Zhang, X. Guo, R. Chen, The connectivity of Z-transformation graphs of perfect matchings of hexagonal systems, Acta Math. Appl. Sinica (English Ser.) 4 (1988) 131–135.

[12] R. Chen, F. Zhang, Hamilton paths in Z-transformation graphs of perfect matchings of hexagonal systems, Discrete Appl. Math. 74 (1997) 191–196.

[13] H. Zhang, Z-transformation graphs of perfect matchings of plane bipartite graphs: a survey, MATCH Commun. Math. Comput. Chem. 56 (2006) 457–476.

[14] A. Taranenko, A. Vesel, On elementary benzenoid graphs: new characterization and structure of their resonance graphs, MATCH Commun. Math. Comput. Chem. 60 (2008) 193–216.

[15] H. Zhang, P. C. B. Lam, W. C. Shiu, Resonance graphs and a binary coding for the 1-factors of Benzenoid systems, SIAM J. Discrete Math. 22 (2008) 971–984.

[16] H. Zhang, H. Yao, D. Yang, A min-max result on outerplane bipartite graphs, Appl. Math. Lett. 20 (2007) 199–205.

[17] K. Salem, S. Klavžar, I. Gutman, On the role of hypercubes in the resonance graphs of benzenoid graphs, Discrete Math. 306 (2006) 699–704.

[18] H. Hosoya, T. Yamaguchi, Sextet polynomial. A new enumeration and proof technique for the resonance theory applied to the aromatic hydrocarbons, Tetrahedron Lett. 52 (1975) 4659–4662.

[19] I. Gutman, Some combinatorial consequences of Clar's resonant sextet theory, MATCH Commun. Math. Comput. Chem. 11 (1981) 127–143.

[20] I. Gutman, Covering hexagonal systems with hexagons, in: 4th Yugoslav Seminar on Graph Theory, Institute of Mathematics, University of Novi Sad, Novi Sad, 1983, pp. 151–160.

[21] P. Hansen, M. Zheng, Upper bounds for the Clar number of a benzenoid hydrocarbon, J. Chem. Soc. Faraday Trans. 88 (1992) 1621–1625.

[22] W. C. Herndon, H. Hosoya, Parametrized valence bond calculations for benzenoid hydrocarbons using Clar structures, Tetrahedron 40 (1984) 3987–3995.

[23] R. Diestel, Graph theory, 3rd Edition, Vol. 173 of Graduate Texts in Mathematics, Springer-Verlag, Berlin, 2005.

[24] I. Gutman, Topological properties of benzenoid systems. XIX. Contributions to the aromatic sextet theory, Wiss. Z. Thechn. Hochsch. Ilmenau 29 (1983) 57–65.

[25] M. Zheng, R. Chen, A maximal cover of hexagonal systems, Graphs Combin. 1 (1985) 295–298.