Clar number of catacondensed benzenoid hydrocarbons

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Abstract

A remarkably simple method is put forward for determining the Clar number CL (= number of aromatic sextets in any of the Clar formulae) of a catacondensed benzenoid hydrocarbon: CL is equal to the minimum number of straight lines required to intersect all hexagons. The connection of this result with the concept of resonance graph is outlined.

Keywords. Clar aromatic sextet theory; Clar formula; Clar number; Resonance graph; Benzenoid hydrocarbons

1. Introduction

Within the theory that was formulated [1, 2] and elaborated [3] by Erich Clar, the modes of cyclic conjugation of the π-electrons in benzenoid hydrocarbons are described by means of diagrams called *Clar aromatic sextet formulae* or, shorter, *Clar formulae*. These are obtained by drawing circles in some hexagons of the respective benzenoid system, so that the following rules are obeyed [4, 5]:

(a) circles are never drawn in adjacent hexagons;

(b) the benzenoid system must have a Kekulé structure with three double bonds in each hexagon in which the circles are drawn;

(c) as many circles as possible are drawn, taking into account the restrictions (a) and (b).

Each circle represents an "aromatic sextet" i. e., six π-electrons interacting in a similar manner as in benzene. The number CL of aromatic sextets in a Clar formula is called the *Clar number*. A benzenoid molecule may have several Clar formulae, but each of them has the same CL-value.

The main chemical implication of the Clar number is the following empirically established regularity: *If B_a and B_b are two isomeric benzenoid hydrocarbons, and if $CL(B_a) > CL(B_b)$, 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.* Examples supporting this rule are found in the books [3, 5].

In Fig. 1 are shown three benzenoid systems and some of their Clar formulas; more details on Clar formulas are found elsewhere [5].

Fig. 1 comes about here

The Clar aromatic sextet theory has numerous experimental confirmations (for details see [3, 5, 6]). Several quantum–chemical approaches were proposed, aimed at its theoretical justification [7–11]. It is commonly accepted that the Clar formulae represent some, but not all, Kekulé structures [5, 12, 13]. An illustration is provided in Fig. 2.

Fig. 2 comes about here

Whereas the drawing of Clar formulae (and thus the determination of the Clar number CL) of smaller benzenoids is easy, this task becomes prohibitively difficult as the size of the system considered increases. Much work has been devoted to learning the properties of Clar formulae of large benzenoid systems and designing procedures for their construction [14–19]; see also the related papers [20, 21]. Some time ago Hansen and Zheng [22] reported an upper bound for CL and somewhat later an algorithm for computing CL of an arbitrary benzenoid hydrocarbon, based on linear programming [23]. This algorithm is suitable for computer–aided studies, but can hardly be employed for paper–and–pencil determination of CL.

We now put forward a significantly simpler method for determining the Clar number, applicable to catacondensed benzenoid systems.

Recall that a benzenoid system is said to be *catacondensed* if no three of its hexagons share a common vertex; otherwise it is *pericondensed* [5]. All the benzenoids occurring in Figs. 1–4 and 6 are catacondensed, whereas the species depicted in Fig. 6 are pericondensed.

2. The method

An *elementary cut* or simply a *cut* C of a benzenoid system is a straight line segment intersecting the centres of some edges and being at right angles to to these edges. This line goes through the centres of some hexagons, in which case it always intersects two edges of each of these hexagons. We say that these hexagons are intersected by C.

Elementary cuts are often used in the theory of benzenoid hydrocarbons and have found numerous applications, especially in connection with Kekulé structures [24], as well as the Wiener [25], Szeged [26], and hyper–Wiener [27] topological indices [28–36].

A few illustrative examples of elementary cuts are found in Fig. 3. Of the 17 possible elementary cuts of the system B_1 only 8 are shown, which is more than the minimal number (= 3) required to intersect all hexagons. For additional explanations see the caption of Fig. 3.

Fig. 3 comes about here

We are now prepared to state the following simple rules:

Rule 1. *The Clar number of a catacondensed benzenoid system B is equal to the minimum number of elementary cuts by which all hexagons of B are intersected.*

Even for very large benzenoid systems the application of Rule 1, i. e., the finding of as few as possible cuts that intersect all hexagons, is immediate (cf. Fig. 3). In doubtful cases or for enormously large benzenoids one may employ:

Rule 2. *Let H be a terminal hexagon of a catacondensed benzenoid system B. Let B' be obtained by deleting from B the hexagon H and all hexagons that are in linear constellation with regard to H. Then $CL(B) = CL(B') + 1$.* (We say that a sequence of hexagons is in a "linear constellation" if, when their centers are joined by a line, a single straight line is obtained. Recall also that the system B' needs not be connected.)

By a successive decomposition based on Rule 2 we ultimately arrive at a linear polyacene, whose Clar number is unity. An example for such a calculation is given in Fig. 4.

Fig. 4 comes about here

In the general case Rule 1 is not applicable to pericondensed benzenoid systems. This is seen from the counterexamples shown in Fig. 5.

Fig. 5 comes about here

In what follows we will briefly outline the theoretical basis of Rules 1 and 2. For this we first need to repeat some basic notions on resonance graphs.

3. The resonance graph

The *resonance graph* is a diagrammatic representation of a model Hamiltonian in a Kekulé–structure basis, providing a rough description of the interactions between the Kekulé structures of a benzenoid molecule. The idea is that the most intense such interactions exist between Kekulé structures which differ in the positions of as small as possible (= three) double bonds whereas all other interactions are neglected. In view of this, the resonance graph is defined as follows.

Let $k_1, k_2, \ldots, k_K$ be the Kekulé structures of a benzenoid molecule B. The resonance graph of B, denoted by $R(B)$, is a graph on K vertices, each vertex of which is associated with a particular Kekulé structure. The vertices i and j of $R(B)$ are adjacent if and only if the Kekulé structure k_j is obtained from k_i by cyclically interchanging exactly three double bonds (within one hexagon). Thus, the degree (valency) of a vertex corresponding to the Kekulé structure k_i is equal to the number of Kekulé structures which differ from k_i in the position of exactly three double bonds. Using the terminology of the theory of conjugated circuits [5, 37, 38] we may say that the degree of this vertex is equal to the number of R_1-type conjugated circuits in the respective Kekulé structure.

That resonance graphs are a very natural concept is seen from the fact that in the chemical and mathematical literature they were independently conceived four times. The idea can be traced back to the work of Herndon on resonance theory [39–41]. He considered two types of interaction terms between Kekulé structures: γ_1 and γ_2, pertaining to interactions between pairs of Kekulé structures differing in the positions of exactly 3 and 5 double bonds, respectively. Herndon found that $|\gamma_1| > |\gamma_2|$, but he never neglected the γ_2-terms. By setting $\gamma_2 = 0$ and representing the interaction scheme by means of a diagram, one would arrive at resonance graphs.

The first who actually did this was Gründler in the early 1980s [42, 43]. Ten years later resonance graphs were re-invented by El–Basil [44, 45] and a few more years later by Randić [46, 47]. To be more precise: in the papers [44, 45] not all Kekulé structures were considered, but only certain restricted subsets thereof; thus El–Basil encountered only subgraphs of resonance graphs. Also in the 1980s, mathematicians Zhang, Guo and Chen [48, 49] considered precisely the same graph and established its basic properties; for the recent mathematical research along these lines see [50–52].

The name "resonance graph" for $R(B)$ was proposed by Randić [46, 47].

All authors who studied resonance graphs were fascinated by the fact that these contain many squares, often arranged into 3– or higher–dimensional cubes. A self–explanatory example is shown in Fig. 6.

Fig. 6 comes about here

4. Proof of Rules 1 and 2

The k-dimensional hypercube, denoted by Q_k, is a graph defined in the following manner. Q_k has 2^k vertices. Each vertex of Q_k corresponds to an ordered k-tuple of two symbols, say 0 and 1. Two vertices of Q_k are adjacent if the respective k-tuples differ by exactly one term.

For instance, the vertices of the 3-cube (Fig. 7) are:

$$\begin{array}{lll} v_1 & \text{corresponding to} & (0,0,0) \\ v_2 & & (0,0,1) \\ v_3 & & (0,1,0) \\ v_4 & & (0,1,1) \\ v_5 & & (1,0,0) \\ v_6 & & (1,0,1) \\ v_7 & & (1,1,0) \\ v_8 & & (1,1,1) \end{array}$$

and then v_1 is adjacent to v_2, v_3 and v_5, v_2 is adjacent to v_1, v_4 and v_6, etc, see Fig. 7

Fig. 7 comes about here

Theorem 1. Let B be a benzenoid system and $R(B)$ its resonance graph. The largest value of k, such that Q_k is a subgraph of $R(B)$ is equal to $CL(B)$.

Proof. Consider any Clar formula $f(B)$ of B and the $2^{CL(B)}$ Kekulé structures corresponding to $f(B)$, cf. Fig. 2. Let $H_1, H_2 \ldots, H_{CL(B)}$ be the hexagons of B which in the Clar formula $f(B)$ contain circles. To any Kekulé structure k_i of B (corresponding to $f(B)$) we associate a $CL(B)$-tuple $(a_1, a_2, \ldots, a_{CL(B)})$ in the following manner: For $i = 1, 2, \ldots, CL(B)$, we set $a_i = 0$ if the vertical double bond in H_i is on the left–hand side, and $a_i = 1$ if this double bond is on the right–hand side of H_i. Then from the definitions of the resonance graph and the hypercube it immediately follows that the Kekulé structures considered induce a $CL(B)$-dimensional hypercube in $R(B)$. Hence, the largest value of k, such that Q_k is a subgraph of $R(B)$ is greater than or equal to $CL(B)$.

On the other hand, k must not be greater than $CL(B)$, because, otherwise, $CL(B)$ would not be the maximum number of circles drawn in a Clar formula of B. Therefore, $k = CL(B)$.

Theorem 2. The smallest number of elementary cuts intersecting all hexagons of a catacondensed benzenoid system B is equal to the dimension of the largest hypercube that is a subgraph of the resonance graph of B.

The proof of Theorem 2 is difficult, and is based on the fact [51] that the resonance graphs of catacondensed benzenoids are median graphs. Its details were communicated elsewhere [52]. (For more information on median graphs see, for instance, [53].)

Combining Theorems 1 and 2 we arrive at Rule 1.

Rule 2 provides, in fact, an algorithm for the construction of a minimal set of elementary cuts that intersect all hexagons. The transformation $B \to B'$ is tantamount to drawing a cut through the chosen terminal hexagon H and the hexagons in linear constellation to H. This certainly is an optimal choice if we intend to intersect all hexagons of B with as few cuts as possible. In a catacondensed benzenoid a terminal hexagon does always exist. Furthermore, by eliminating the intersected hexagons from B, another catacondensed benzenoid system B' is obtained, and so the construction can be continued.

References

[1] E. Clar, C. T. Ironside and M. Zander, J. Chem. Soc., (1959) 142.

[2] E. Clar and M. Zander, J. Chem. Soc., (1958) 1861.

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

[4] I. Gutman, Bull. Soc. Chim. Beograd, 47 (1982) 453.

[5] I. Gutman and S. J. Cyvin, Introduction to the Theory of Benzenoid Hydrocarbons, Springer, Berlin, 1989, Chapter 7.

[6] M. D. Watson, A. Fechtenkötter and K. Müllen, Chem. Rev., 101 (2001) 1267.

[7] R. Pauncz and A. Cohen, J. Chem. Soc., (1960) 3288.

[8] O. E. Polansky and G. Derflinger, Int. J. Quantum Chem., 1 (1967) 379.

[9] M. Aida and H. Hosoya, Tetrahedron, 36 (1980) 1317.

[10] W. C. Herndon and H. Hosoya, Tetrahedron, 40 (1984) 3987.

[11] H. Zhu and Y. Jiang, Chem. Phys. Letters, 193 (1992) 446.

[12] I. Gutman, S. Obenland and W. Schmidt, Commun. Math. Chem. (MATCH), 17 (1985) 75.

[13] H. Hosoya, Topics Curr. Chem., 153 (1990) 255.

[14] S. El–Basil and M. Randić, J. Chem. Soc. Faraday Trans. 2, 84 (1988) 1875.

[15] F. Zhang and X. Li, Commun. Math. Chem. (MATCH), 24 (1989) 333.

[16] X. Guo and F. Zhang, J. Math. Chem., 9 (1992) 279.

[17] P. E. John, H. Sachs and M. Zheng, J. Chem. Inf. Comput. Sci., 35 (1995) 1019.

[18] M. Randić, H. Hosoya and K. Nakada, Polyc. Arom. Comp., 4 (1995) 249.

[19] H. Abeledo and G. Atkinson, in P. Hansen, P. Fowler and M. Zheng (Eds.), Discrete Mathematical Chemistry, Am. Math. Soc., Providence, 2000, pp. 1–8.

[20] M. Zheng, J. Mol. Struct. (Theochem), 231 (1991) 321.

[21] M. Zheng, J. Mol. Struct. (Theochem), 277 (1992) 1.

[22] P. Hansen and M. Zheng, J. Chem. Soc. Faraday Trans., 88 (1992) 1621.

[23] P. Hansen and M. Zheng, J. Math. Chem., 15 (1994) 93.

[24] S. J. Cyvin and I.Gutman, Kekulé Structures in Benzenoid Hydrocarbons, Springer, Berlin, 1988.

[25] H. Wiener, J. Am. Chem. Soc., 69 (1947) 17.

[26] I. Gutman and A. A. Dobrynin, Graph Theory Notes New York, 34 (1998) 37.

[27] M. Randić, Chem. Phys. Letters, 211 (1993) 478.

[28] H. Sachs, Combinatorica, 4 (1984) 89.

[29] I. Gutman and S. Klavžar, J. Chem. Inf. Comput. Sci., 35 (1995) 1011.

[30] I. Gutman and S. Klavžar, ACH Models Chem., 133 (1996) 389.

[31] W. C. Shiu and P. B. C. Lam, Congr. Numer., 126 (1997) 113.

[32] I. Gutman and S. J. Cyvin, Commun. Math. Chem. (MATCH), 36 (1997) 177.

[33] I. Gutman, L. Popović and L. Pavlović, Commun. Math. Chem. (MATCH), 36 (1997) 217.

[34] I. Gutman and S. Klavžar, ACH Models Chem., 135 (1998) 45.

[35] S. Klavžar, P. Žigert and I. Gutman, Comput. Chem. 24 (2000) 229.

[36] I. Gutman, S. Klavžar and A. Rajapakse, Int. J. Quantum Chem., 76 (2000) 611.

[37] M. Randić, Chem. Phys. Letters, 38 (1976) 68.

[38] M. Randić, J. Am. Chem. Soc., 99 (1977) 444.

[39] W. C. Herndon, J. Am. Chem. Soc., 95 (1973) 2404.

[40] W. C. Herndon, M. L. Ellzey, J. Am. Chem. Soc., 96 (1974) 6631.

[41] W. C. Herndon, J. Org. Chem., 46 (1981) 2119.

[42] W. Gründler, Wiss. Z. Univ. Halle, 31 (4) (1982) 97.

[43] W. Gründler, Z. Chem. (Leipzig), 23 (1983) 157.

[44] S. El–Basil, J. Math. Chem., 14 (1993) 305.

[45] S. El–Basil, J. Mol. Struct. (Theochem), 288 (1993) 67.

[46] M. Randić, D. J. Klein, S. El–Basil and P. Calkins, Croat. Chem. Acta, 69 (1996) 1639.

[47] M. Randić, Int. J. Quantum Chem., 63 (1997) 585.

[48] F. Zhang, X. Guo and R. Chen, Discrete Math., 72 (1988) 405.

[49] F. Zhang, X. Guo and R. Chen, Acta Math. Appl. Sin., 4 (1988) 131.

[50] R. Chen and F. Zhang, Discrete Appl. Math., 74 (1997) 191.

[51] S. Klavžar, P. Žigert and G. Brinkmann, Discrete Math., (2002), in press.

[52] S. Klavžar and P. Žigert, Appl. Math. Letters, 15 (2002) 279.

[53] W. Imrich and S. Klavžar, Product Graphs: Structure and Recognition, Wiley, New York, 2000.

Figure Captions

Fig. 1. The benzenoid systems B_1, B_2, B_3 and some of their Clar formulas. Conjugation in B_1 is represented by a total of 12 Clar formulas, of which only two are shown (f_{11}, f_{12}); B_2 has 24 Clar formulas, two of which are f_{21} and f_{22}; B_3 has a single Clar formula f_{31}. The Clar numbers of B_1, B_2 and B_3 are 3, 5 and 8, respectively.

Fig. 2. The eight $(= 2^{CL(B_4)})$ Kekulé structures of the benzenoid system B_4, corresponding to the Clar formula f_{41}. Note that the Kekulé structures k_5, k_6, k_7, k_8 are contained also in the Clar formula f_{42}. B_4 has a total of 13 Kekulé structures, see Fig. 6.

Fig. 3. Elementary cuts of the benzenoid systems B_1, B_2, B_3, B_4; the cut C_1 intersects the hexagons 3, 4, 5 and 6 of B_1, the cut C_2 intersects only the hexagon 4, etc. Three cuts (C_1, C_4 and C_8) suffice to intersect all hexagons of B_1, in harmony with $CL(B_1) = 3$. The five cuts of B_2, the eight cuts of B_3 and the three cuts of B_4 are minimal sets of cuts intersecting all hexagons, implying $CL(B_2) = 5$, $CL(B_3) = 8$ and $CL(B_4) = 3$. The choice of such minimum number of cuts needs not be unique, as in the case of B_3 and B_4.

Fig. 4. Application of Rule 2: Asterisk indicates the terminal hexagon from which the decomposition of the respective benzenoid system starts. B_5'''' is a linear polyacene and therefore $CL(B_5'''') = 1$, implying $CL(B_5''') = 2$, $CL(B_5'') = 3$, $CL(B_5') = 4$ and $CL(B_5) = 5$.

Fig. 5. Inapplicability of Rule 1 to pericondensed benzenoid systems: All hexagons of B_6 and B_7 can be intersected by three elementary cuts. Nevertheless, $CL(B_6) = 2 < 3$ and $CL(B_7) = 4 > 3$.

Fig. 6. The resonance graph of the benzenoid system B_4 and the Kekulé structures of B_4 which are not depicted in Fig. 2.

Fig. 7. The 3-cube and the labeling of its vertices; for details see text.