Clar theory and resonance energy

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Abstract

A mathematical model, referred here as the Zhang–Zhang polynomial $\zeta(x)$, that embraces all the main concepts encountered in the Clar aromatic sextet theory of benzenoid hydrocarbons, was recently put forward by H. Zhang and F. Zhang. We now show that $\zeta(x)$ is related to resonance energy (RE), and that $\ln \zeta(x)$ and RE are best correlated when $x \approx 1$. This indicates that $\zeta(1)$ could be viewed as a (novel) structure–descriptor, playing a role analogous to the Kekulé structure count in Kekulé–structure–based theories. Some basic properties of $\zeta(1)$ are established.

1. Introduction

In a series of papers [1–4] Heping Zhang and Fuji Zhang introduced a mathematical object, related to the Clar aromatic sextet theory of benzenoid hydrocarbons [5–7], that in the following will be referred to as the *Zhang–Zhang polynomial*.

The Zhang–Zhang polynomial

$$\zeta(x) = \zeta(B, x) = \sum_{k \geq 0} z(B, k) \, x^k$$

of a benzenoid system B is defined via its coefficients $z(B, k)$, that count the number of ways in which the vertices of B can be covered by k mutually isolated hexagons and edges.

An example illustrating the definition of the Zhang–Zhang polynomial is shown in Fig. 1. In the case of phenanthrene, $z(B, 0) = 5$ (diagrams C_1–C_5), $z(B, 1) = 5$ (diagrams C_6–C_{10}), $z(B, 2) = 1$ (diagram C_{11}), and $z(B, k) = 0$ for $k \geq 3$. Consequently, the Zhang–Zhang polynomial of phenanthrene is $5 + 5\,x + x^2$.

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Further examples as well as details of the theory of the Zhang–Zhnag polynomial, in particular, on its relations to other combinatorial polynomials of Clar theory, can be found in the papers [1–4]; recall that in [1–4] $\zeta(x)$ is called "*Clar covering polynomial*".

Originally [1–4] no physical meaning was attributed to x in $\zeta(B, x)$. In principle, x may be any real–valued number, not necessarily an integer. Yet, for some particular values of the variable x, the polynomial $\zeta(B, x)$ is, or may be, related to certain chemically interesting features of the underlying benzenoid molecule.

Some straightforward properties of the Zhang–Zhang polynomial are the following:

(a) The power of $\zeta(B, x)$ is equal to $Cl(B)$, the Clar number of B (= the number of aromatic sextets in any of the Clar formulas [7,8]).

(b) The coefficient $z(B, Cl)$ is equal to $C(B)$, the number of Clar aromatic sextet formulas of B.

(c) The coefficient $z(B, 1)$ is equal to the number of greatest off-diagonal matrix elements γ_1 in Herndon's resonance–theoretical approach [6,9,10]. Also, $z(B, 1)$ is equal to the number of edges of the resonance graph $RG(B)$, associated with B [11].

(d) The coefficient $z(B, 0)$ is equal to $K(B)$, the number of Kekulé structures of B.

In the chemical literature a variety of "resonance energies" was introduced and considered; for details see the recent reviews [7,12,13]. Each of the quantities mentioned in points (a)–(d) was previously related to some kind of resonance energy: Cl and C in [14,15], γ_1 in [9], RG in [11,16], K in [17,18]. Bearing this in mind, it is reasonable to expect that also the Zhang–Zhang polynomial will be somehow connected with resonance energy [19]. That this indeed is the case is demonstrated in the subsequent section.

2. Relation between the Zhang–Zhang polynomial and resonance energy

If $B_1 \cup B_2$ is the molecular graph of two disconnected π-electron systems, then

$$RE(B_1 \cup B_2) = RE(B_1) + RE(B_2)$$

holds for any of the numerous kinds of resonance energies. Observing that

$$K(B_1 \cup B_2) = K(B_1) \cdot K(B_2)$$

and postulating that the resonance energy is some function of the Kekulé structure count, one readily arrives at [17,18]

$$RE \approx a_0 \ln K \tag{1}$$

with a_0 being a constant, whose actual value depends on the kind of RE considered, and on the class of benzenoid systems to which formula (1) is applied. Now, because the Zhang–Zhang polynomial obeys an analogous relation, viz.,

$$\zeta(B_1 \cup B_2, \, x) = \zeta(B_1, x) \cdot \zeta(B_2, x)$$

it is purposeful to seek for an approximation of the form

$$RE \approx a \ln \zeta(x) \tag{2}$$

where a is a fitting parameter, to be understood as a function of the variable x. In view of property (d), formula (1) is a special case of (2), for $x = 0$.

3. Numerical work

In this paper we report the results of the examination of the relation between the logarithm of the Zhang–Zhang polynomial and the so-called "topological resonance energy", TRE [20,21]. Recall that TRE is just a variant of the Dewar resonance energy [13], designed so as to require no (additional) parameters for the computation of the energy of the reference structure.

For fixed values of x, especially for those lying in the interval $[0, \, 2]$, we found good linear correlations between TRE and $\ln \zeta(x)$. A characteristic example is shown in Fig. 2.

Fig. 2 comes about here

For different groups of isomers the slopes of the regression lines differ, and the regression lines do not go through the origin. Therefore instead of (2) we have used relations of the form

$$RE \approx a \ln \zeta(x) + b \,. \tag{3}$$

The obvious question is how the quality of the approximation (3) depends on the variable x, and for which value of x is it optimal. Typical x-dependencies of the correlation coefficient (R) and of the average relative error (ARE) are shown in Figs. 3 and 4.

Figs. 3 & 4 come about here

We found that in all examined cases (i. e., for all examined classes of isomeric benzenoids) R attains a maximum and ARE attains a minimum for some x that considerably differs from zero. The respective results for catacondensed benzenoids with h hexagons, $h = 4, 5, 6, 7$, are collected in Table 1.

Table 1 comes about here

The fact that R becomes maximal and ARE becomes minimal for some x greater than zero is no surprise whatsoever. The unexpected finding is that the optimal value of x is always remarkably close to unity. As seen from Table 1, there is no statistically significant difference between the accuracy of the approximation (3) for optimal x and for $x = 1$. This points towards the conclusion that $\zeta(1)$ is a quantity of some importance in the theory of benzenoid molecules, and that the problem of its interpretation and structure–dependence deserves attention.

Anyway, according to our numerical studies, there is a good linear correlation between resonance energy and $\ln \zeta(x)$, $x = 1$, and the quality of this correlation cannot be improved (in a statistically significant manner) by taking any other value of x.

At this point it should be mentioned that the data given in Table 1 also reveal that for $x = 0$ the accuracy of the approximation (3) is much reduced relative to the case $x = 1$ (cf. Figs. 3 and 4). This, in turn, shows how the expressions for RE put forward by Wilcox [17] and Swinborne–Sheldrake et al. [18] can be substantially improved. Furthermore, our results suggest that not the Kekulé structure count K, but the hitherto overlooked quantity $\zeta(1)$ is the one that should be used for the rationalization of the stability and aromaticity of benzenoid molecules.

In the subsequent section we point out some properties of $\zeta(1)$.

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4. On properties and interpretation of $\zeta(1)$

Let B be the molecular graph of a benzenoid system, and let e be its edge. Then by $B - e$ we denote the subgraph obtained by deleting from B the edge e, and by $B - [e]$ the subgraph obtained by deleting from B the edge e and its both endvertices.

In what follows, in order to emphasize its analogy to $\zeta(B, 1)$, we write $\zeta(B, 0)$ for the number of Kekulé structures of B. Then, a well known result in the theory of Kekulé structure enumeration reads [6,22]:

$$\zeta(B, 0) = \zeta(B - e, 0) + \zeta(B - [e], 0)$$

where e may be any edge of B. The analogous recurrence relation for $\zeta(1)$ is

$$\zeta(B, 1) = \zeta(B - e, 1) + 2\,\zeta(B - [e], 1) \ .$$

It holds if e belongs to a terminal hexagon of B, and is at greatest distance from the edge shared by this hexagon and its neighbor. (It holds also in some other cases that we will not specify here.)

As special cases of the above relations we have for L_h, the linear polyacene with h hexagons,

$$\zeta(L_h, 0) \ = \ \zeta(L_{h-1}, 0) + 1 \ ; \ \ \zeta(L_1, 0) = 2$$
$$\zeta(L_h, 1) \ = \ \zeta(L_{h-1}, 1) + 2 \ ; \ \ \zeta(L_1, 1) = 3$$

implying $\zeta(L_h, 0) = h + 1$ and $\zeta(L_h, 1) = 2h + 1$. It is known [22] that $\zeta(B, 0) \geq h + 1$ holds for all normal benzenoids with h hexagons. (Recall that a benzenoid hydrocarbon is normal if it is Kekuléan, and has no fixed single or double bonds [6,22]; all catacondensed benzenoids are normal.) It can be shown that, analogously, also $\zeta(B, 1) \geq 2h + 1$ holds for all normal benzenoids with h hexagons.

Let $k_1, k_2, \ldots, k_{\zeta(0)}$ be the Kekulé structures of the benzenoid system B. Consider a particular Kekulé structure k_i. Let α_i be the number of hexagons of B in which the double bonds are arranged as in diagram **I** in Fig. 5. Let β_i be the number of hexagons of B in which the double bonds are arranged as in diagram **II** in Fig. 5. Then

$$\zeta(B, 1) = \sum_{i=1}^{\zeta(0)} 2^{\alpha_i} = \sum_{i=1}^{\zeta(0)} 2^{\beta_i} \ . \tag{4}$$

Fig. 5 comes about here

Formula (4) may serve for a structural interpretation of $\zeta(1)$. Whereas $\zeta(0)$ is the count of Kekulé structures in which each such structure has a unit weight, $\zeta(1)$ is the count of Kekulé structures, weighted in the above specified peculiar manner. According to (4) the weight associated to the Kekulé structure k_i is either 2^{α_i} or 2^{β_i}. Thus $\zeta(1)$ may be understood as a Kekulé structure count in which not all Kekulé structures are given equal importance.

A proof and detailed discussion of Eq. (4) will be given elsewhere.

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h	maximal R	minimal ARE	a	b
4	0.998 (at $x = 0.9$)	0.53% (at $x = 0.7$)	0.167 (at $x = 0.9$)	0.191 (at $x = 0.9$)
5	0.993 (at $x = 0.8$)	0.80% (at $x = 0.7$)	0.168 (at $x = 0.8$)	0.233 (at $x = 0.8$)
6	0.991 (at $x = 0.9$)	0.88% (at $x = 0.8$)	0.159 (at $x = 0.9$)	0.283 (at $x = 0.9$)
7	0.991 (at $x = 1.6$)	1.00% (at $x = 1.6$)	0.128 (at $x = 1.6$)	0.368 (at $x = 1.6$)
	R (at $x = 1.0$)	ARE (at $x = 1.0$)	a (at $x = 1.0$)	b (at $x = 1.0$)
4	0.998	0.54%	0.160	0.199
5	0.993	0.80%	0.154	0.250
6	0.991	0.89%	0.153	0.292
7	0.991	1.03%	0.154	0.322
	R (at $x = 0.0$)	ARE (at $x = 0.0$)	a (at $x = 0.0$)	b (at $x = 0.0$)
4	0.994	0.98%	0.306	0.056
5	0.991	0.90%	0.279	0.118
6	0.988	1.10%	0.271	0.154
7	0.983	1.48%	0.272	0.164

Table 1. Statistical data (obtained by least–squares fitting) for the approximation (3) for the sets of isomeric catacondensed benzenoid hydrocarbons with $h = 4, 5, 6$, and 7 hexagons ($C_{4h+2}H_{2h+4}$). The results for $x = 1$ only slightly differ from the optimal ones. The results for $x = 0$ indicate considerably weaker correlations relative to those for optimal x or $x = 1$.

Fig. 1. The 11 ways in which the vertices of the phenanthrene graph can be covered by mutually disjoint hexagons and/or isolated edges. Diagrams C_1–C_5 correspond to the five Kekulé structures of phenanthrene; diagram C_{11} pertains to its (unique) Clar formula.

Fig. 2. Correlation between TRE and $\ln \zeta(1)$ in the case of isomeric heptacyclic catacondensed benzenoid hydrocarbons ($C_{30}H_{18}$); correlation coefficient: 0.991. The data–point in the lower left corner pertains to heptacene (the linear polyacene).

Fig. 3. Dependence of the correlation coefficient R, pertaining to formula (3), on the variable x, in the case of pentacyclic catacondensed benzenoid hydrocarbons ($C_{22}H_{14}$). Note that $x = 0$ corresponds to formula (1).

Fig. 4. Dependence of the average relative error ARE (in %), pertaining to formula (3), on the variable x, for the same data set as in Fig. 3. Note that $x = 0$ corresponds to formula (1). The apparent ruggedness of the line is not an artifact, but reflects its true shape, and cannot be "smoothened" by increasing the density of the calculated data points.

Fig. 5. Two possible arrangements of three double bonds in a hexagon of a benzenoid molecule, used for stating Eq. (4). Note that these are just the "proper" and "improper" sextets playing an important role in Clar theory [4,23].

Table 1. Statistical data (obtained by least–squares fitting) for the approximation (3) for the sets of isomeric catacondensed benzenoid hydrocarbons with $h = 4, 5, 6$, and 7 hexagons ($C_{4h+2}H_{2h+4}$). The results for $x = 1$ only slightly differ from the optimal ones. The results for $x = 0$ indicate considerably weaker correlations relative to those for optimal x or $x = 1$.