# Relating resonance energy with the Zhang–Zhang polynomial

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*Abstract:* The Zhang–Zhang polynomial $\zeta(x)$ is a recently conceived tool in the mathematical apparatus of theoretical chemistry. It combines (in a quantitative manner) the Kekulé- and Clar-structure-based features of benzenoid molecules. It is shown that the topological resonance energy (*TRE*) can be accurately approximated as $TRE \approx a\sqrt{\zeta(x)} + b$, where $x \approx 0.5$, by which fact a significant insight is gained into the structure-dependence of *TRE* of benzenoid molecules.

*Keywords:* benzenoid hydrocarbons, Kekulé structures, Clar structures, Zhang–Zhang polynomial, resonance energy

## INTRODUCTION

A few years ago, the Chinese mathematicians Heping Zhang and Fuji Zhang introduced a polynomial that is based on the Kekulé and Clar structures of benzenoid molecules.[1–3] Although these authors reported some chemical applications of their polynomial,[4,5] intensive research along these lines started only relatively recently.[6–9]

In what follows, the polynomial conceived by Zhang and Zhang will be referred to as the *Zhang–Zhang polynomial*, and will be denoted by $\zeta(B,x)$ or $\zeta(x)$, with B symbolizing the underlying benzenoid molecule.

The Zhang–Zhang polynomial is defined in the following manner. Let B be a benzenoid system *i.e.*, a graph representing the carbon-atom skeleton of a benzenoid hydrocarbon; for details see the book.[10] It is assumed that B is Kekuléan, *i.e.*, that it has at least one Kekulé structure. Consider the so-called "*Clar covers*" of B, subgraphs in which all vertices are covered by either isolated edges or by disjoint hexagons. Let $z(B,k)$ be the number of Clar covers of B, containing exactly $k$ hexagons. Then

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

An example illustrating this definition is given in Fig. 1. According to it, the Zhang–Zhang polynomial of pyrene is $6+6x+x^2$. More details on the Zhang–Zhang polynomial can be found elsewhere,[1–9] especially in the chemist-friendly review.[8]
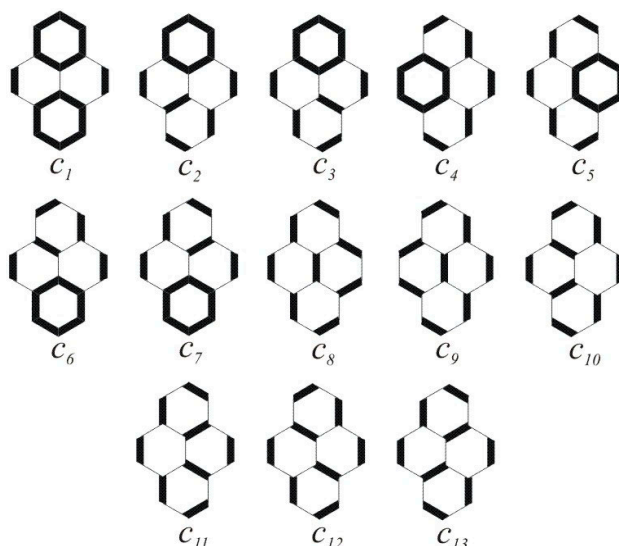


Fig. 1. The Clar covers of pyrene; the chosen edges and hexagons are indicated by heavy lines. One should note that $s_1$ corresponds to the Clar aromatic sextet formula of pyrene, whereas $c_8$–$c_{13}$ correspond to its six Kekulé structures. Only the Clar cover $c_1$ possesses two hexagons; therefore $z(B,2) = 1$. Six Clar covers: $c_2$, $c_3$, $c_4$, $c_5$, $c_6$, $c_7$ possess a single hexagon; therefore $z(B,1) = 6$. Six Clar covers: $c_8$, $c_9$, $c_{10}$, $c_{11}$, $c_{12}$, $c_{13}$ do not possess any hexagon; therefore $z(B,0) = 6$. The Zhang–Zhang polynomial of pyrene is thus $z(B,0) + z(B,1)\, x + z(B,2)\, x^2 = 1 + 6x + 6x^2$.

The Zhang–Zhang polynomial unifies the Kekulé- and Clar-theory-based features of the respective benzenoid hydrocarbon. Therefore, its chemical applications should, first of all, be sought in those parts of the theory of benzenoid hydrocarbons in which Kekulé and Clar formulas play a significant role.[10–12] One possible way in which the Zhang–Zhang polynomial can be applied is the following.

An elementary property of the Zhang–Zhang polynomial is that $\zeta(B,0)$ is equal to the number $K$ of Kekulé structures of the benzenoid molecule B. Suppose now that a certain property $P$ of B can be (at least approximately) calculated from the respective $K$-value:

$$P \approx f(K)$$

which is tantamount to

$$P \approx f(\zeta(0)) \tag{1}$$

Now, if instead of $\zeta(0)$, the Zhang–Zhang polynomial for some other value of $x$ is substituted into formula (1), it may happen that this will result in a better approximation for $P$ than $f(\zeta(0))$.

In this work, the topological resonance energy (*TRE*) and its dependence on the Zhang–Zhang polynomial is examined. Recall,[13,14] that *TRE* is a variant of the Dewar resonance energy[15,16] in which no additional semi-empirical parameters are used for the calculation of the reference energy. More details on *TRE* can be found in the recent reviews[17,18] and in the references cited therein.

### DEPENDENCE OF THE TOPOLOGICAL RESONANCE ENERGY ON THE KEKULÉ STRUCTURE COUNT

Although *TRE* has been known for 30 years, and although numerous of its mathematical properties were established, its dependence on the number of Kekulé structures was never properly analyzed. The dominant factor determining the value of *TRE* (as well as of any other kind of resonance energy) is the number of π–electrons[17,18] which, in the case of conjugated hydrocarbons, is determined by the number of carbon-atoms and carbon–carbon bonds. Therefore, in order to examine the influence of other structural factors on *TRE* it is necessary to restrict the consideration to sets of isomers (in which all members have equal number of carbon atoms and equal number of carbon–carbon bonds).[19]

In this work, the results obtained for six sets of benzenoid isomers, those with formulas $C_{22}H_{14}$ (12 isomers), $C_{24}H_{14}$ (13 isomers), $C_{26}H_{14}$ (9 isomers), $C_{26}H_{16}$ (36 isomers), $C_{28}H_{16}$ (62 isomers), and $C_{30}H_{18}$ (118 isomers), are reported. In each of these sets, all possible isomers were taken into consideration.

In earlier works,[5–7] the dependence of *TRE* on *K* (and, consequently, the dependence of *TRE* on $\zeta(x)$) was postulated to be logarithmic. This assertion is a consequence of non-critically accepting that a logarithmic approximation for the original Dewar resonance energy[20] can be applied also to *TRE*. This turned out to be a mistake, since – as seen from Fig. 2 – the dependence of *TRE* on *K* is essentially linear, and by no means logarithmic.

In order to learn about the dependence of *TRE* of benzenoid molecules on their Kekulé structure count, first a typical plot of *TRE vs. K* is shown in Fig. 2.

From Fig. 2, it can be seen that there is a good linear correlation between *TRE* and *K*. Such results are found for all the examined sets of benzenoid isomers. However, these correlations can be somewhat improved if, instead of *K*, *TRE* is correlated with $K^\lambda$. Surprisingly, the values of the exponent $\lambda$ for which the best correlations are obtained are significantly different from unity. A characteristic example is shown in Fig. 3.

The $\lambda$-values that minimize the average relative error of the approximation

$$TRE \approx a\,K^{\lambda} + b \qquad (2)$$

are given in Table I. The $\lambda$-values for which the correlation coefficients become maximal are close, yet not identical, to those given in Table I. In formula (2) and later in the text *a* and *b* are coefficients calculated by least-squares fitting (differing, of course, for each of the examined six sets). Their values can be obtained from the authors (I.G. & S.R.) upon request.
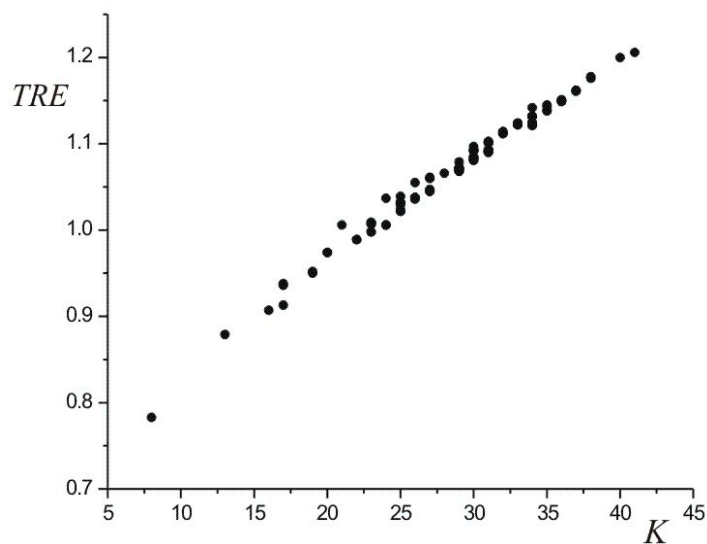
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Fig. 2. The topological resonance energies of the heptacyclic catacondensed benzenoid isomers $C_{30}H_{18}$ plotted versus the Kekulé structure count *K*. The correlation appears to be linear. Indeed, the correlation coefficient is 0.993, and the approximation $aK + b$ (with *a* and *b* determined by least-squares fitting) reproduces the *TRE* with an average relative error of 0.55 %. Yet, a slight curvilinearity in these correlations can be observed, and *TRE* is better reproduced by a linear function of $K^{\lambda}$, $\lambda \neq 1$, see Fig. 3.
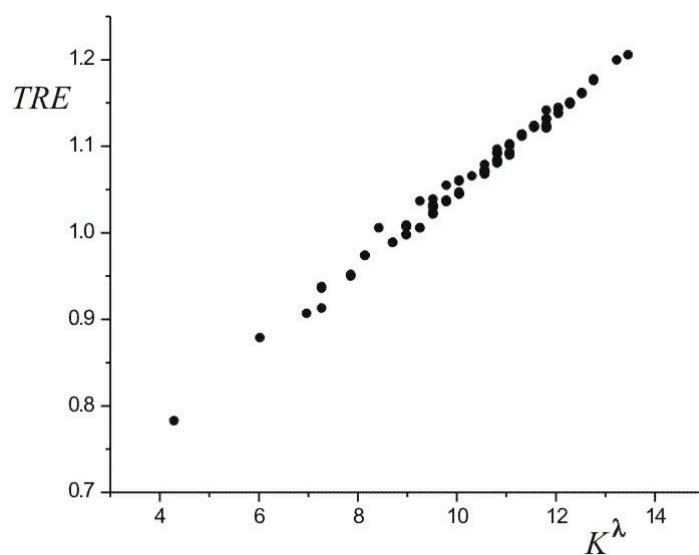


Fig. 3. Same *TRE* values as in Fig. 2 plotted versus $K^{\lambda}$, $\lambda = 0.70$. This value of the exponent lambda minimizes the average relative error (= 0.50 %).

TABLE I. Data on the dependence of the topological resonance energy on the Kekulé structure count, of the form given by Eq. (2), for six sets of benzenoid isomers. *N.I.* = the number of Kekuléan isomers of the benzenoid systems with the given formula; all these isomers were contained in the sets considered; *AERR*($\lambda$) = average relative error for the given (optimal) value of the parameter $\lambda$; *AERR*($\lambda$ = 1) = average relative error of formula (2) for $\lambda$ = 1, *i. e.*, for the linear dependence of *TRE* on *K*

| Formula | *N.I.* | $\lambda$ | *AERR*($\lambda$) / % | *AERR*($\lambda$ = 1) / % |
|---|---|---|---|---|
| $C_{22}H_{14}$ | 12 | 0.89 | 0.37 | 0.39 |
| $C_{24}H_{14}$ | 13 | 1.53 | 0.55 | 0.71 |
| $C_{26}H_{14}$ | 9 | 0.75 | 0.44 | 0.46 |
| $C_{26}H_{16}$ | 36 | 0.77 | 0.46 | 0.50 |
| $C_{28}H_{16}$ | 62 | 1.24 | 0.71 | 0.75 |
| $C_{30}H_{18}$ | 118 | 0.70 | 0.50 | 0.55 |

## DEPENDENCE OF TOPOLOGICAL RESONANCE ENERGY ON THE ZHANG–ZHANG POLYNOMIAL

The findings outlined in the previous section suggest that in the case of topological resonance energy, the approximation of type (1) should be chosen to have the form

$$TRE \approx a\,\zeta(x)^{\lambda} + b \qquad (3)$$

where the parameters $\lambda$ and $x$ should be used for optimization. The optimal values of these parameters (determined so as to minimize the average relative error) are given in Table II.

TABLE II. Data on the dependence of the topological resonance energy on the Zhang–Zhang polynomial, of the form given by Eq. (3), for the same benzenoid isomers as in Table I. *AERR*($\lambda$,$x$) = = average relative error for the given (optimal) values of the parameters $\lambda$ and $x$; *ERR*(max) = = maximal relative error observed

| Formula | $\lambda$ | $x$ | *AERR*($\lambda$,$x$) / % | *ERR*(max) / % |
|---|---|---|---|---|
| $C_{22}H_{14}$ | 0.65 | 0.31 | 0.33 | 0.56 |
| $C_{24}H_{14}$ | 0.33 | 0.69 | 0.41 | 1.16 |
| $C_{26}H_{14}$ | 0.34 | 0.86 | 0.31 | 0.78 |
| $C_{26}H_{16}$ | 0.51 | 0.30 | 0.39 | 1.15 |
| $C_{28}H_{16}$ | 0.64 | 0.54 | 0.71 | 0.75 |
| $C_{30}H_{18}$ | 0.45 | 0.36 | 0.50 | 0.55 |

Both the optimal $\lambda$- and optimal $x$-values given in Table II vary to a great extent from sample to sample. Nevertheless, it appears as if both the $\lambda$- and the $x$-va-

lues "oscillate" around the value 0.5. Indeed, the approximation (3) will not lose much of its precision if one sets $\lambda = 0.5$ and also $x = 0.5$. If so, then one arrives at the expression

$$TRE \approx a\sqrt{\zeta(1/2)} + b \qquad (4)$$

Statistical data pertaining to formula (4) are given in Table III. As seen by comparing the columns *AERR* and *AERR*(min), the accuracies of formula (4) and of the optimized formula (3) are practically the same. One should, nevertheless, bear in mind that the exponent $\lambda = 0.5$, leading to the expression (4) was chosen only because of simplicity. Other values for this exponent could serve as well, but then the form of the resulting approximation would be somewhat more complicated.

TABLE III. Data on the dependence of the topological resonance energy on the Zhang–Zhang polynomial, of the form given by Eq. (4), for the same benzenoid isomers as in Table I. *AERR* = average relative error for $\lambda = x = 0.5$; *ERR*(max) = maximal relative error observed; *AERR*(min) = the (minimal) *AERR*-value, attained for the optimal choices of $\lambda$ and $x$ (same as *AERR*($\lambda$,$x$) in Table II).

| Formula | *AERR* / % | *ERR*(max) / % | *AERR*(min) / % |
|---------|-----------|----------------|-----------------|
| $C_{22}H_{14}$ | 0.35 | 0.67 | 0.33 |
| $C_{24}H_{14}$ | 0.43 | 1.17 | 0.41 |
| $C_{26}H_{14}$ | 0.33 | 0.66 | 0.31 |
| $C_{26}H_{16}$ | 0.42 | 1.10 | 0.39 |
| $C_{28}H_{16}$ | 0.56 | 2.56 | 0.52 |
| $C_{30}H_{18}$ | 0.46 | 2.73 | 0.41 |

## CONCLUSIONS

By means of formula (4), the *TRE*–values may be reproduced with an error that is (on average) around 0.5 % or below, and (in the worst case) less than 2–3 %. This aspect of Eq. (4) may be viewed as something not particularly valuable. In our opinion, *the true value of the formula (4) is* not so much in its ability to estimate *TRE*, but *in the insight that it gives* into the structure–dependence of *TRE* and, consequently,[13–19] *into the structure-dependence of the stability and "aromaticity" of benzenoid molecules*. In particular, formula (4) provides a *quantitative* connection between Clar-theory-based structural features and resonance energy. Recall that in the original Clar aromatic sextet theory,[11] all considerations were non-quantitative, and that until now very few quantitative Clar-theory-based approaches have been put forward.[21]

The fact that in formulas (3) and (4) the parameter $x$ is significantly different from zero indicates that not only the Kekulé structures (*via* $z(B,0)$), but also the cyclic Clar covers (*via* $z(B,1)$, $z(B,2)$, ...) influence the value of the topological resonance energy. As $x \approx 1/2$, it can be seen that the (stabilizing) effect of a Clar

cover with a single hexagon is about 50 % of the effect of a Kekulé structure, the effect of a Clar cover with two hexagons is about 25 % of the effect of a Kekulé structure, etc.

ИЗВОД

ВЕЗА ЕНЕРГИЈЕ РЕЗОНАНЦИЈЕ СА ЖАНГ–ЖАНГОВИМ ПОЛИНОМОМ

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Жанг–Жангов полином $\zeta(x)$ је један недавно предложени објекат који се примењује у математичком формализму теоријске хемије. Он повезује (на квантитативан начин) особине засноване на Кекулеовим и Кларовим структурама бензеноидних молекула. Показано је да се тополошка енергија резонанције (*TRE*) може веома тачно апроксимирати формулом $TRE \approx a\sqrt{\zeta(x)} + b$, где је $x \approx 0,5$.

(Примљено 23. октобра 2006, ревидирано 9. фебруара 2007)

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