

I. Gutman (Ed.)
Mathematical Methods in Chemistry
Prijeopolje Museum, Prijeopolje, 2006, pp. 141-158

ZHANG–ZHANG POLYNOMIAL AND SOME OF ITS APPLICATIONS

Sabina Gojak,^a Sonja Stanković,^b Ivan Gutman^b
and Boris Furtula^b

^a*Faculty of Science, University of Sarajevo, Bosnia and Herzegovina and*

^b*Faculty of Science, University of Kragujevac,
Kragujevac, Serbia and Montenegro*

Abstract

The Chinese mathematicians Heping Zhang and Fuji Zhang conceived a combinatorial polynomial associated with benzenoid molecules. This “Zhang–Zhang polynomial” contains information on both Kekulé– and Clar–structure–based characteristics of the underlying benzenoid molecule. We first explain the definition of the Zhang–Zhang polynomial (and the theoretical concepts on which it is based), and then point out some of its applications to resonance energies. A peculiar discovery made by means of the Zhang–Zhang polynomial is that there are substantial differences between the structure dependence of the Dewar resonance energy and the topological resonance energy.

INTRODUCTION

In the theoretical chemistry of benzenoid hydrocarbons [1] *Kekulé structures* play an outstanding role. For details on this matter see the books [1,2] and the references quoted therein. Another important direction in the theory of benzenoid molecules is the diagrammatic approach put forward by Clar [3], in which so-called *Clar aromatic sextet formulas* are used to describe the dominant modes of cyclic conjugation of π -electrons [1,3,4].

The number of Kekulé structures and Clar formulas of a benzenoid system B will be denoted by $K = K(B)$ and $C = C(B)$, respectively. The number Cl of aromatic sextets in (any of the) Clar formulas of a benzenoid system is said to be its *Clar number*.

Recently, in the mathematical literature a combinatorial polynomial has been proposed [5–7], from which K , C , Cl , C , and many other Kekulé- and Clar-structure-based properties of a benzenoid molecules can be directly deduced. Its inventors are the Chinese mathematicians Heping Zhang and Fuji Zhang and therefore we propose to call it the *Zhang–Zhang polynomial*.

The Zhang–Zhang polynomial (in the variable x), pertaining to the benzenoid system B , will be denoted by $\zeta(B, x)$ or simply by $\zeta(x)$.

In what follows we provide the definition of the Zhang–Zhang polynomial and present its chemically most important properties. In order to do this we, however, need some preparations which we do in the subsequent section. In that section the concepts of Kekulé, Clar, and generalized Clar formulas are clarified. In the next section we state the definition of the Zhang–Zhang polynomial, together with some illustrative examples. In the fourth section we then show how the Zhang–Zhang polynomial can be applied in the theory of resonance energy.

FROM THE THEORY OF BENZENOID HYDROCARBONS

Details on the theory of benzenoid hydrocarbons and, especially, on its Kekulé and Clar structures, can be found in the book [1,2]. In what follows we explain some

of the basic notions of this theory, needed for the definition of the Zhang–Zhang polynomial.

A Kekulé structure of a benzenoid hydrocarbon is an arrangement of double bonds, such that exactly one double bond ends at every carbon atom. The number of Kekulé structures (= the Kekulé structure count) of a benzenoid system B will be denoted by $K = K(B)$. In what follows we consider only Kekulé benzenoids, i. e., benzenoid species for which $K > 0$. In Fig. 1 are depicted all the nine possible Kekulé structures of benzo[a]pyrene (BAP); thus, $K(BAP) = 9$.

In Clar theory a group of six π -electrons (the so-called aromatic sextet) is represented by a circle drawn in a hexagon. The Clar aromatic sextet formulas of a benzenoid molecule are obtained by drawing circles in some hexagons, so that the following three requirements are obeyed:

- 1° Circles must not be drawn in adjacent hexagons.
- 2° The part of the benzenoid system not covered by circles must have a Kekulé structure.
- 3° As many as possible circles are drawn, taking care that conditions 1° and 2° are not violated.

All Clar formulas of B possess an equal number of aromatic sextets, which is just the Clar number $Cl = Cl(B)$.

In Fig. 2 the diagrams c_1 , c_2 , and c_3 are the three Clar formulas of benzo[a]pyrene; thus $C(BAP) = 3$ and $Cl(BAP) = 2$.

Hosoya and Yamaguchi [8] proposed to abandon requirement 3°, which then results in the so-called generalized Clar formulas. The generalized Clar formulas may thus possess Cl or fewer than Cl circles, including the case of the “empty” formula without any circle. In Fig. 2 are depicted all the nine generalized Clar formulas of benzo[a]pyrene, with c_9 being the “empty” formula.

The fact that the number of generalized Clar formulas of benzo[a]pyrene is equal to its Kekulé structure count (cf. Figs. 1 and 2) is the consequence of a deep-lying connection between the two theories. A procedure for achieving a one-to-one corres-

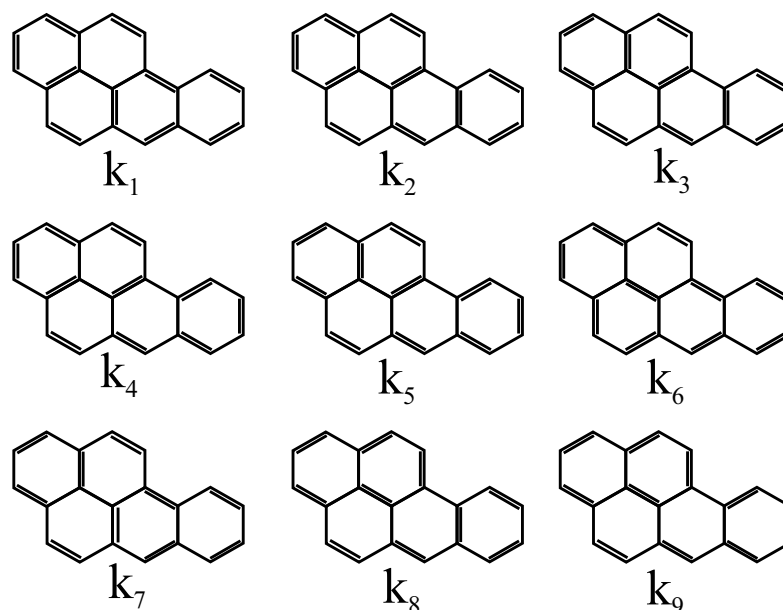


Fig. 1. The nine Kekulé structures of benzo[a]pyrene (*BAP*). These have been drawn in such a manner that the Kekulé structure k_i corresponds to the generalized Clar formula c_i in Fig. 2, $i = 1, 2, \dots, 9$. The correspondence is achieved by drawing circles into the hexagons in which there are three double bonds with the vertical double bond on the left-hand side, and leaving all other hexagons empty. (More details on this correspondence are found in the book [2].)

pendence between the Kekulé and generalized Clar structures is described in the caption of Fig. 1.

THE ZHANG–ZHANG POLYNOMIAL

The idea of the Zhang–Zhang polynomial relies on the observation that whereas in ordinary Clar formulas the arrangement of the remaining double bonds (if any) is uniquely determined, the generalized Clar formulas are compatible with several such arrangements. Zhang and Zhang call these arrangements “*Clar covers*” [5–7].

In Fig. 3 we consider the example of benzo[a]pyrene. In diagrams cc_{11} , cc_{21} , and cc_{31} are indicated the positions of the double bonds in the Clar formulas c_1 , c_2 , and c_3 , respectively (cf. Fig. 2). These arrangements are unique. In the case of generalized Clar formulas with fewer than Cl aromatic sextets, several arrangements

of the double bonds are possible: three for c_4 and c_8 , two for c_5 and c_7 and only one for c_6 , a total of 11 Clar covers with a single aromatic sextet. The “empty” generalized Clar formula c_9 (see Fig. 2) is compatible with all nine Kekulé structures of benzo[a]pyrene, cf. Fig. 1.

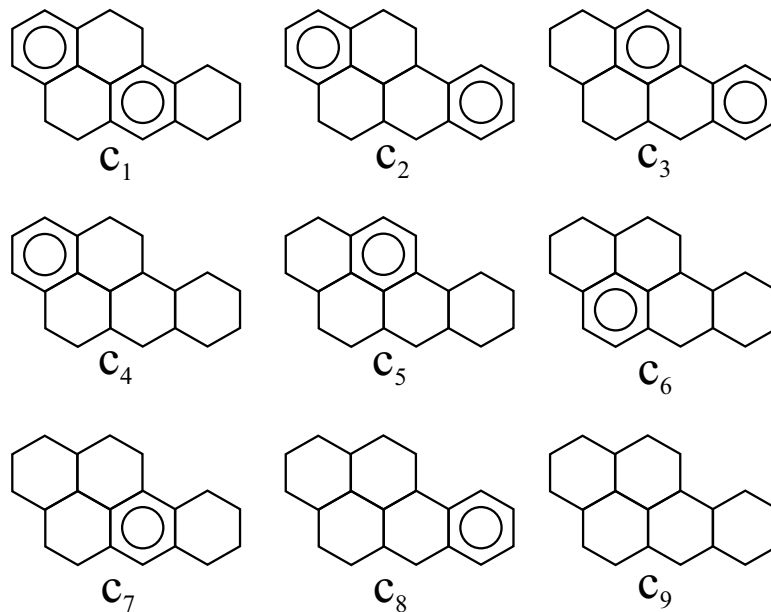


Fig. 2. The nine generalized Clar structures of *BAP*. The three diagrams c_1 , c_2 , and c_3 are the ordinary Clar formulas, each possessing $Cl = 2$ aromatic sextets. There are five diagrams with a single sextet (c_4 – c_8) and a unique “empty” diagram (c_9).

Let $z(B, k)$ be the number of Clar covers of the benzenoid system B , possessing exactly k aromatic sextets. Then the Zhang–Zhang polynomial of B is defined as [5,9]

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

An example illustrating the definition of the Zhang–Zhang polynomial is found in the caption of Fig. 3. More examples can be found in the recent papers [10–12].

In the paper [12] we have shown how the Zhang–Zhang polynomial can easily be calculated in a recursive manner. (The algorithm elaborated in [12] was earlier communicated by Zhang and Zhang [5], but in a style not easy to chemists to understand.) Anyway, if $\zeta(B, x)$ is known, then we immediately know also the following:

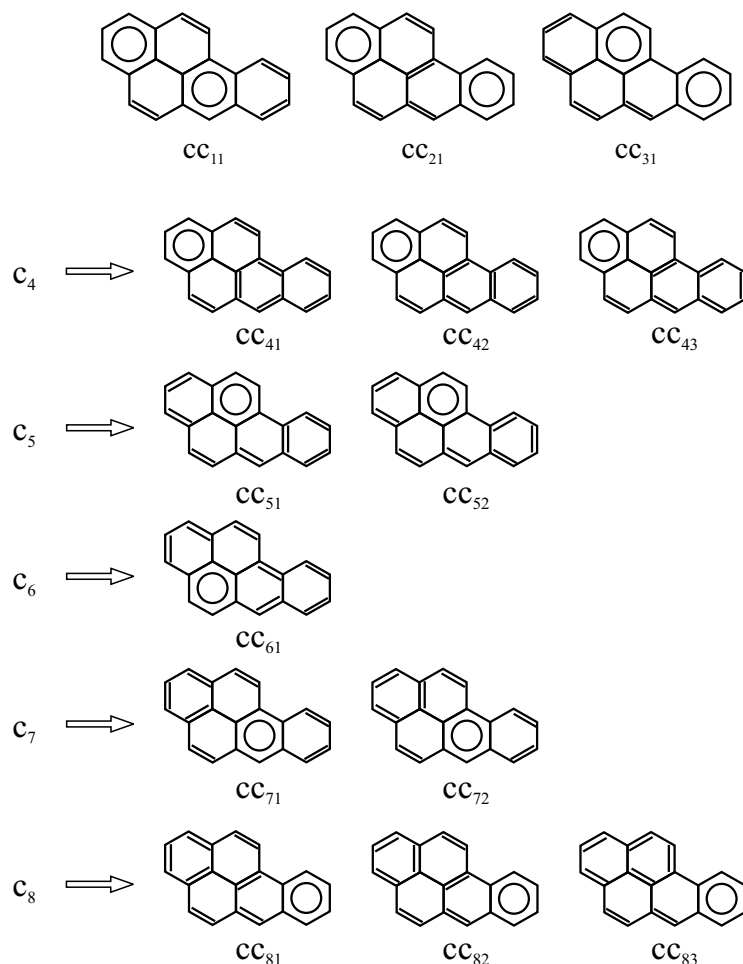


Fig. 3. The Clar covers of *BAP* pertaining to the generalized Clar structures c_1 – c_8 from Fig. 2. The diagrams cc_{11} , cc_{21} , and cc_{31} have two aromatic sextets whereas cc_{41} , cc_{42} , cc_{43} , cc_{51} , cc_{52} , cc_{61} , cc_{71} , cc_{72} , cc_{81} , cc_{82} , and cc_{83} have one sextet. The Clar covers pertaining to the “empty” Clar formula c_9 are just the nine Kekulé structures depicted in Fig. 1, possessing no aromatic sextets. Thus benzo[*a*]pyrene has 9, 11, and 3 Clar covers with, respectively, 0, 1, and 2 aromatic sextets, i. e., $z(BAP, 0) = 9$, $z(BAP, 1) = 11$, and $z(BAP, 2) = 3$, resulting in the Zhang–Zhang polynomial $\zeta(BAP, x) = 9 + 11x + 3x^2$.

- the Kekulé structure count — since $K(B)$ is the first coefficient of $\zeta(B, x)$, i. e., $K(B) = \zeta(B, 0) = z(B, 0)$;
- the Clar number — since $Cl(B)$ is equal to the degree of the polynomial $\zeta(B, x)$;

- the Clar structure count — since $C(B)$ is equal to the coefficient of the greatest-power term of $\zeta(B, x)$, i. e., $C(B) = z(B, Cl)$.

In addition to this, the second coefficient of the Zhang–Zhang polynomial, i. e., $z(B, 1)$, is equal to the number of greatest off-diagonal matrix elements in Herndon’s resonance–theoretical approach [1,13,14]. The sum of all coefficients of the Zhang–Zhang polynomial, i. e., $\zeta(B, 1)$, was recently shown to be related to the resonance energy of the underlying benzenoid molecule [10,11].

ON RESONANCE ENERGY

In the 1970s theoretical chemists were much interested in so-called “resonance energies”, quantities aimed at measuring the “aromaticity” (or “antiaromaticity”) of polycyclic conjugated π -electron systems. The breakthrough in this direction was achieved by Dewar, who recognized that aromaticity/antiaromaticity is a consequence of thermodynamic stabilization/destabilization caused by cyclic conjugation of π -electrons. In order to measure this effect, a new resonance energy was conceived [15] in which the reference was chosen so that the resonance energy of acyclic polyenes is nil. Eventually, this quantity was named “Dewar resonance energy” (*DRE*) [16,17]. The original Dewar–de Llano version of *DRE* [15] was computed by means of a complicated (and at that time advanced) semiempirical SCF-MO method. In 1971 Hess and Schaad showed [18,19] that equally good results are obtained when *DRE* is calculated by the simple Hückel molecular orbital (HMO) model. Somewhat later, using the mathematical apparatus of graph spectral theory, the same idea (again within the HMO scheme) was put in an algebraically more pleasing form, resulting in the “topological resonance energy” (*TRE*). The discovery of *TRE* was made by Gutman, Milun and Trinajstić [20,21] and independently by Aihara [22,23]. For more details on the *DRE* and *TRE* concepts, as well for comparative studies of these and other resonance energies, see the books [24,25], the reviews [4,26], and the references quoted therein.

From the very beginning it was anticipated that *DRE* and *TRE* reflect one and the same physico–chemical feature of polycyclic conjugated molecules. This viewpoint

was believed to be satisfactorily and completely verified by the finding of a (not very good) linear correlation between DRE and TRE [21] and by establishing a simple (yet approximate) mathematical relation between the two resonance energies [27].

In Fig. 4 we illustrate the correlation between DRE and TRE in the case of isomeric benzenoid hydrocarbons. This correlation is linear, having a very small (and statistically insignificant) curvilinearity.

Also in the 1970s, approaching the problem from a different direction, Herndon proposed a resonance–energy–concept, based on Kekulé structures [13,28,29]. As a non-surprising result he could show [30] that in the case of benzenoid hydrocarbons, DRE is proportional to $\ln K$, where K is the Kekulé structure count. It is interesting, however, that neither Herndon nor anybody else ever checked if DRE of benzenoid molecules is really proportional to the logarithm of the Kekulé structure count.

Because DRE strongly depends on the size of a benzenoid molecule, it is purposeful to examine the DRE / K correlation within sets of isomers. In Figs. 5 and 6 we show a characteristic example, corroborating the logarithmic dependence of DRE on K .

Bearing in mind the (now established) logarithmic dependence of DRE on K , and the (almost) linear correlation between DRE and TRE , it was reasonable to expect that also TRE depends on K in a linear manner. However, this conclusion happens to be false, as will be demonstrated later in this paper. The fact is that the structure–dependencies of DRE and TRE are significantly different. These differences can be best envisaged by using the Zhang–Zhang polynomial. Namely, the Zhang–Zhang polynomial makes it possible to shed new light on the structure–dependence of DRE and TRE [10,11], as outlined in due detail in the subsequent section.

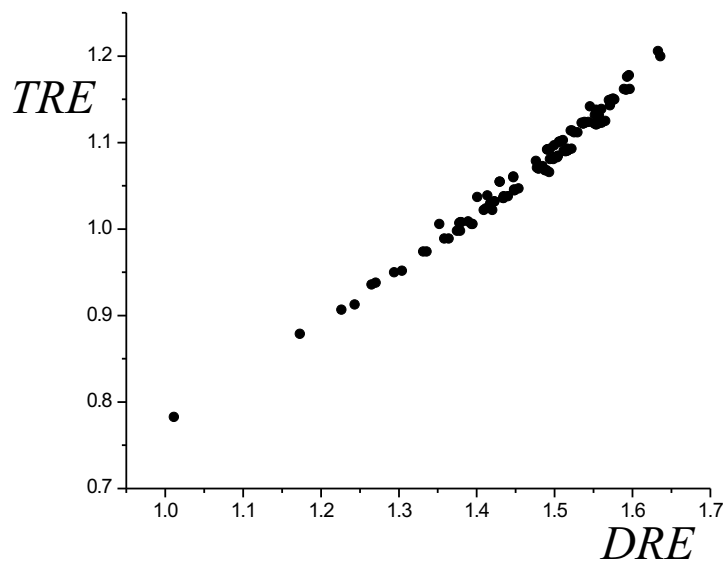


Fig. 4. Correlation between TRE and DRE for the (complete) set of 118 isomeric heptacyclic catacondensed benzenoid hydrocarbons $C_{30}H_{18}$. The correlation is linear. By a careful inspection a slight curvilinearity can be observed. However, by means of F -test, this curvilinearity is found to be statistically not significant at a 90% (or higher) confidence level.

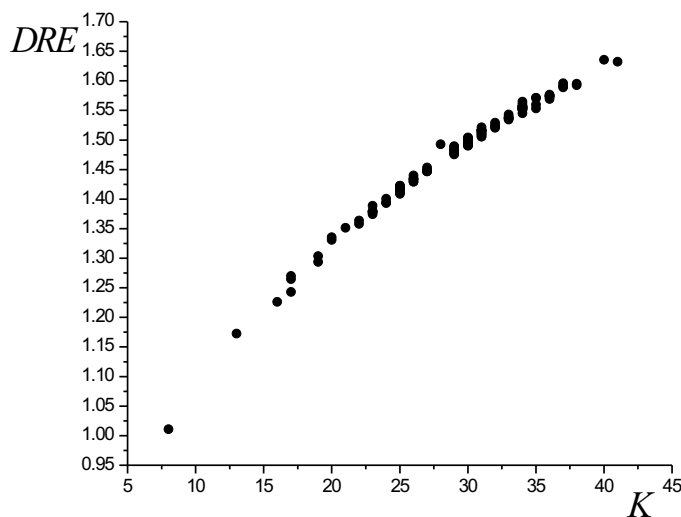


Fig. 5. Correlation between DRE and K for the (complete) set of 118 isomeric heptacyclic catacondensed benzenoid hydrocarbons $C_{30}H_{18}$. The correlation is evidently curvilinear.

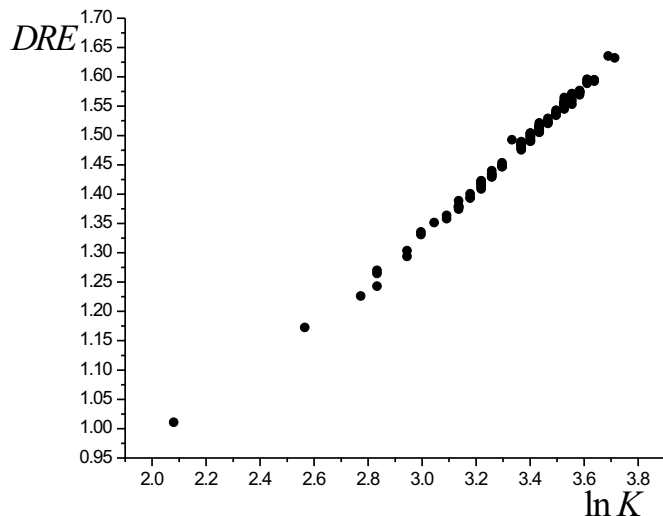


Fig. 6 Correlation between DRE and $\ln K$ for the same benzenoid molecules as in Fig. 5. The correlation is linear; correlation coefficient $R = 0.996$; if any curvilinearity exists at all, it is statistically insignificant (at 99% confidence level, as checked by F -test). This result verifies that the dependence of the Dewar resonance energy on the Kekulé structure count is logarithmic.

ZHANG–ZHANG POLYNOMIAL AND RESONANCE ENERGY

As explained above the logarithm of the Kekulé structure count K was believed to be related to various resonance energies. Bearing in mind that K is equal to the Zhang–Zhang polynomial at $x = 0$, an approximation of the form

$$RE \approx a \ln \zeta(x) + b \quad (1)$$

comes readily to mind [10,31]. In formula (1) the variable x may be viewed as an adjustable parameter, not necessarily equal to zero. On the other hand, it looked reasonable to expect that the optimal value of x in Eq. (1) will be the same (or at least nearly same) for all Dewar-type resonance energies, in particular for DRE and TRE . We, however, found that this is not the case, revealing a concealed, but significant, difference between the structure-dependence of these two variants of Dewar resonance energy. Whereas for DRE , in harmony with earlier studies,

the optimal value of x is near to zero, TRE is found to be best reproduced by the logarithm of $\zeta(1)$.

In this work we report the results of the examination the dependence of the precision of the approximation (1) on the variable x for catacondensed benzenoid isomers.

As well known [1], a catacondensed benzenoid hydrocarbon with h six-membered rings has $4h + 2$ carbon and $2h + 4$ hydrogen atoms, i. e., its formula is $C_{4h+2}H_{2h+4}$. Consequently, all catacondensed benzenoid systems with the same h -value are isomers.

Four sets of catacondensed benzenoid isomers were studied, each consisting of all possible isomers: those with $h = 4$ (5 isomers), $h = 5$ (12 isomers), $h = 6$ (36 isomers), and $h = 7$ (118 isomers). In all examined cases there is some “optimal” value of x at which the correlation coefficient is maximal, and an equal or near-lying value of x at which the average relative error is minimal. However, these optimal values of x significantly differ for DRE and TRE . The respective results are collected in Tables 1 and 2.

In the case of DRE the optimal value of x is remarkably close to zero. In the case of TRE this optimal value is much larger, and does not significantly differ from unity.

Such great differences between the behavior of DRE and TRE call for an explanation. This explanation (found by us by performing numerous – in most cases unsuccessful – computer experiments) is remarkably simple: Whereas DRE is, TRE is not a logarithmic function of the Kekulé structure count K . Indeed, TRE was found to be an almost perfect linear function of K , implying that in the case $RE = TRE$ instead of Eq. (1) one should use

$$RE \approx a\zeta(x) + b. \quad (2)$$

In Figs. 7 and 8 we illustrate the fact that the correlation between TRE is linear (Fig. 7), and by no means logarithmic (Fig. 8). More data on this newly discovered regularity will be communicated elsewhere. Some preliminary result are collected in Table 3.

h	maximal R	minimal ARE
4	0.9996 (at $x = -0.03$)	0.23% (at $x = 0.03$)
5	0.997 (at $x = -0.05$)	0.58% (at $x = -0.16$)
6	0.997 (at $x = 0.14$)	0.49% (at $x = 0.13$)
7	0.996 (at $x = 0.27$)	0.41% (at $x = 0.19$)
	R (at $x = 0.0$)	ARE (at $x = 0.0$)
4	0.9996	0.24%
5	0.997	0.59%
6	0.997	0.49%
7	0.996	0.44%
	R (at $x = 1.0$)	ARE (at $x = 1.0$)
4	0.995	0.88%
5	0.994	0.79%
6	0.994	0.73%
7	0.994	0.59%

Table 1. Statistical data (obtained by least-squares fitting) for the approximation (1) for $RE = DRE$ and for the sets of isomeric catacondensed benzenoid hydrocarbons with $h = 4, 5, 6$, and 7 hexagons. The results for $x = 0$ practically coincide with the optimal ones. The results for $x = 1$ are significantly weaker, relative to those for optimal x or $x = 0$.

h	maximal R	minimal ARE
4	0.998 (at $x = 0.92$)	0.53% (at $x = 0.71$)
5	0.993 (at $x = 0.78$)	0.79% (at $x = 0.71$)
6	0.990 (at $x = 0.81$)	0.78% (at $x = 0.67$)
7	0.989 (at $x = 0.82$)	0.71% (at $x = 0.76$)
	R (at $x = 0.0$)	ARE (at $x = 0.0$)
4	0.994	0.98%
5	0.991	0.90%
6	0.986	0.99%
7	0.984	0.87%
	R (at $x = 1.0$)	ARE (at $x = 1.0$)
4	0.998	0.54%
5	0.993	0.80%
6	0.990	0.80%
7	0.989	0.72%

Table 2. Same data as in Table 1 for $RE = TRE$. In this case the results for $x = 1$ only slightly differ from the optimal ones. For $x = 0$ considerably weaker correlations are obtained.

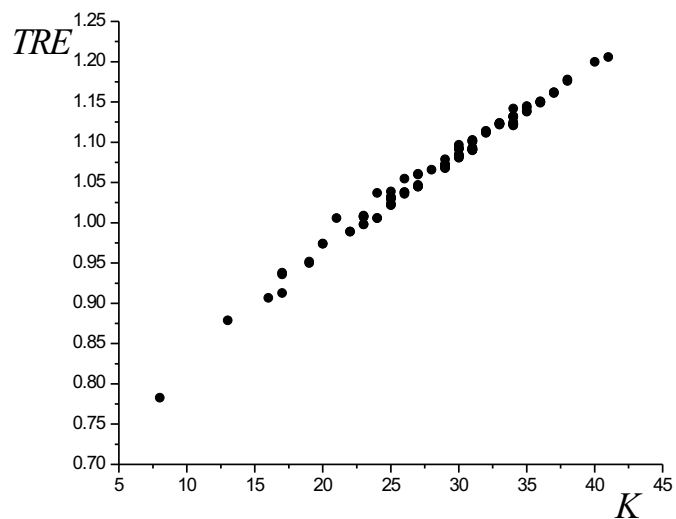


Fig. 7. Correlation between TRE and K for the same benzenoid molecules as in Fig. 5. The correlation appears to be linear; correlation coefficient $R = 0.993$; if any curvilinearity exists at all, it is statistically insignificant (at 99% confidence level, as checked by F -test). This result verifies that the dependence of the topological resonance energy on the Kekulé structure count is essentially linear and by no means logarithmic.

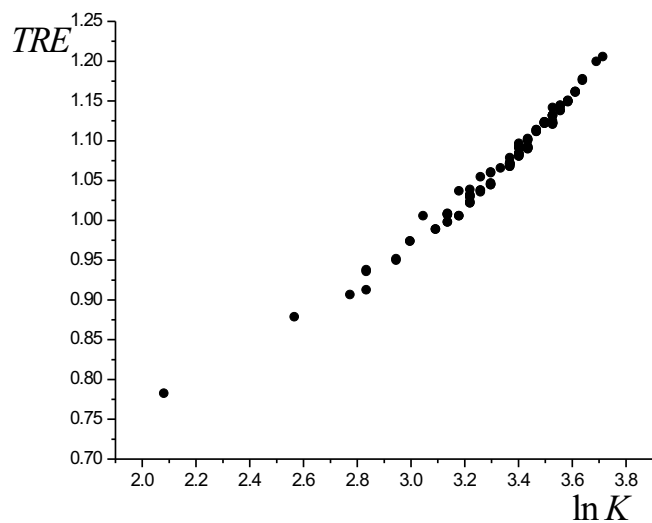


Fig. 8. Correlation between TRE and $\ln K$ for the same benzenoid molecules as in Fig. 5. This correlation is evidently curvilinear.

h	maximal R	minimal ARE
4	0.999985 (at $x = 0.21$)	0.04% (at $x = 0.21$)
5	0.998 (at $x = 0.12$)	0.39% (at $x = -0.03$)
6	0.996 (at $x = -0.03$)	0.49% (at $x = 0.03$)
7	0.993 (at $x = -0.07$)	0.55% (at $x = 0.01$)
	R (at $x = 0.0$)	ARE (at $x = 0.0$)
4	0.9994	0.28%
5	0.998	0.39%
6	0.996	0.50%
7	0.993	0.55%
	R (at $x = 1.0$)	ARE (at $x = 1.0$)
4	0.9992	0.36%
5	0.997	0.47%
6	0.992	0.64%
7	0.988	0.64%

Table 3. Statistical data (obtained by least-squares fitting) for the approximation (2) for $RE = TRE$ and for the sets of isomeric catacondensed benzenoid hydrocarbons with $h = 4, 5, 6,$ and 7 hexagons. The results for $x = 0$ practically coincide with the optimal ones. The results for $x = 1$ are significantly weaker, relative to those for optimal x or $x = 0$.

REFERENCES

- [1] I. Gutman and S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag, Berlin, 1989.
- [2] I. Gutman, *Uvod u hemijsku teoriju grafova*, PMF Kragujevac, Kragujevac, 2003.
- [3] E. Clar, *The Aromatic Sextet*, Wiley, London, 1972.
- [4] M. Randić, Aromaticity of polycyclic conjugated hydrocarbons, *Chem. Rev.* **103** (2003) 3449–3606.
- [5] H. Zhang and F. Zhang, The Clar covering polynomial of hexagonal systems I, *Discr. Appl. Math.* **69** (1996) 147–167.
- [6] H. Zhang, The Clar covering polynomials of hexagonal systems with an application to chromatic polynomial, *Discr. Math.* **172** (1997) 163–173.

- [7] H. Zhang and F. Zhang, The Clar covering polynomial of hexagonal systems III, *Discr. Math.* **212** (2000) 261–269.
- [8] H. Hosoya, T. Yamaguchi, Sextet polynomial. A new enumeration and proof technique for the resonance theory applied to the aromatic hydrocarbons, *Tetrahedron Lett.* (1975) 4659–4662.
- [9] H. Zhang, The Clar covering polynomials of S,T-isomers, *MATCH Commun. Math. Comput. Chem.* **29** (1993) 189–197.
- [10] I. Gutman, S. Gojak, B. Furtula, Clar theory and resonance energy, *Chem. Phys. Lett.* **413** (2005) 396–399.
- [11] I. Gutman, S. Gojak, S. Stanković, B. Furtula, A concealed difference between the structure–dependence of Dewar and topological resonance energy, *J. Mol. Struct. (Theochem)* **757** (2005) 119–123.
- [12] I. Gutman, A. T. Balaban, B. Furtula, Algorithm for simultaneous calculation of Kekulé and Clar structure counts, and Clar number of benzenoid molecules, *Polyc. Arom. Comp.*, in press.
- [13] W. C. Herndon and M. L. Ellzey, Resonance theory. V. Resonance energies of benzenoid and nonbenzenoid π systems, *J. Am. Chem. Soc.* **96** (1974) 6631–6642.
- [14] I. Gutman and W. C. Herndon, On resonance theory, *Chem. Phys. Lett.* **34** (1975) 387–391.
- [15] M. J. S. Dewar, C. de Llano, *J. Am. Chem. Soc.* **91** (1969) 789.
- [16] N. C. Baird, Calculation of ‘Dewar’ resonance energies in conjugated organic molecules, *Canad. J. Chem.* **47** (1969) 3535–3538.
- [17] N. C. Baird, Dewar resonance energy, *J. Chem. Educ.* **48** (1971) 509–514.
- [18] B. A. Hess, L. J. Schaad, Hückel molecular orbital π resonance energies. A new approach, *J. Am. Chem. Soc.* **93** (1971) 305–310.
- [19] B. A. Hess, L. J. Schaad, Hückel molecular orbital π resonance energies. The benzenoid hydrocarbons, *J. Am. Chem. Soc.* **93** (1971) 2413–2416.
- [20] I. Gutman, M. Milun, N. Trinajstić, Topological definition of delocalisation energy, *MATCH Commun. Math. Comput. Chem.* **1** (1975) 171–175.

- [21] I. Gutman, M. Milun, N. Trinajstić, Graph theory and molecular orbitals. 19. Nonparametric resonance energies of arbitrary conjugated systems, *J. Am. Chem. Soc.* **99** (1977) 1692–1704.
- [22] J. Aihara, A new definition of Dewar-type resonance energies, *J. Am. Chem. Soc.* **98** (1976) 2750–2758.
- [23] J. Aihara, Resonance energies of benzenoid hydrocarbons, *J. Am. Chem. Soc.* **99** (1977) 2048–2053.
- [24] A. Graovac, I. Gutman, N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules*, Springer-Verlag, Berlin, 1977.
- [25] I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer-Verlag, Berlin, 1986.
- [26] L. J. Schaad, B. A. Hess, Dewar resonance energy, *Chem. Rev.* **101** (2001) 1465–1476.
- [27] I. Gutman, Some properties of the topological resonance energy, *J. Serb. Chem. Soc.* **43** (1978) 191–197.
- [28] W. C. Herndon, Resonance energies of aromatic hydrocarbons. A quantitative test of resonance theory, *J. Am. Chem. Soc.* **95** (1973) 2404–2406.
- [29] W. C. Herndon, Resonance theory and the enumeration of Kekulé structures, *J. Chem. Educ.* **51** (1974) 10–15.
- [30] R. Swinborne-Sheldrake, W. C. Herndon, I. Gutman, Kekulé structures and resonance energies of benzenoid hydrocarbons, *Tetrahedron Lett.* (1975) 755–758.
- [31] F. Zhang, H. Zhang and Y. Liu, The Clar covering polynomial of hexagonal systems. II. An application to resonance energy of condensed aromatic hydrocarbons, *Chin. J. Chem.* **14** (1996) 321–325.

ZHANG–ZHANGOV POLINOM I NEKE NJEGOVE PRIMENE

Sabina Gojak, Sonja Stanković, Ivan Gutman i Boris Furtula

IZVOD

Zhang–Zhangov polinom je nedavno uvedeni kombinatorni objekt koji u sebi sadrži sve osnovne kvantitativne pokazatelje o Kekuléovim strukturama i Clarovim formu-
lama benzenoidnih jedinjenja. Ovaj polinom koncipirali su kineski matematičari Hep-
ing Zhang i Fuji Zhang i u nizu radova ustanovili njegove osnovne osobine. Ti radovi
su, međutim, objavljeni u matematičkim časopisima i hemičari na njih do sasvim
nedavno nisu obratili potrebnu pažnju.

U članku je navedena definicija Zhang–Zhangovog polinoma, i ilustrovana jednim
detaljno razrađenim primerom (Slike 1, 2 i 3). Pre toga opisani su osnovni pojmovi
teorije benzenoidnih sistema koji su potrebni za definisanje Zhang–Zhangovog poli-
noma.

Za benzenoidni sistem B , Zhang–Zhangov polinom $\zeta(B, x)$ je definisan na sledeći
način:

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

gde $z(B, k)$ predstavlja broj Clarovih prekrivanja sistema B , koji sadrže tačno k
aromatičnih sekteta. (Za primer koji ilustruje ove pojmove videti Sliku 3.)

Jedna od osnovnih osobina Zhang–Zhangovog polinoma jeste da je njena vrednost
za $x = 0$ jednaka broju Kekuléovih struktura K . Na toj osobini zasnivaju se primene
Zhang–Zhangovog polinoma koje su u ovom radu razmatrane.

Naime, broj Kekuléovih struktura K je jedna od najbolje proučenih i najčešće
primenjivanih kvantitativnih strukturnih karakteristika benzenoidnih ugljovodonika.
Ako se neka osobina benzenoidnog sistema B može prikazati (kao više ili manje dobra
aproksimacija) u obliku $f(K(B))$, onda se ta ista osobina može aproksimirati i kao
 $f(\zeta(B, x))$ za neku vrednost promenljive x , koja može ali ne mora biti jednaka nuli.

U radu smo proučavali dve energije rezonancije koje se od sedamdesetih godina prošlog veka mnogo primenjuju u teoriji benzenoidnih jedinjenja, za opisivanje njihove takozvane “aromatičnosti”. To su *Dewarova energija rezonancije DRE* i *topološka energija rezonancije TRE*. Obe su zamišljene da opisuju jednu te istu elektronsku karakteristiku benzenoidnih jedinjenja, i zato ne iznenađuje da među njima postoji veoma dobra (skoro potpuno linearna) korelacija. Ona je, na primeru izomernih heptacikličnih katakondenzovanih ugljovodonika, prikazana na Slici 4.

Budući da je od ranije bila u upotrebi aproksimacija

$$RE \approx a \ln K + b$$

za $RE = DRE$, mi smo ispitili formule

$$RE \approx a \ln \zeta(x) + b$$

kako za $RE = DRE$ tako i za $RE = TRE$. Dobiveni rezultati prikazani su u Tabelama 1 i 2. Iz ovih tabela se vidi da je u slučaju DRE optimalna vrednost za x bliska nuli, dok je u slučaju TRE ova optimalna vrednost znatno veća i bliža je jedinici. Tako velika razlika u zavisnosti ovih energija rezonancije od molekulske strukture ukazuje da u slučaju TRE upotreba logaritamske zavisnosti nije legitimna. Dalja istraživanja su pokazala da DRE zaista ima logaritamsku zavisnost od K (Slike 5 i 6), ali da je zavisnost TRE od K u suštini linearna (Slike 7 i 8). Iz toga sledi da se u slučaju TRE ne smeju primenjivati gore pomenute aproksimacije, nego

$$RE \approx a K + b$$

i

$$RE \approx a \zeta(x) + b .$$

Rezultati nađeni za linearnu zavisnost TRE of $\zeta(x)$ prikazani su u Tabeli 3. Nađene optimalne vrednosti za promenljivu x sada su veoma bliske nuli.